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Synthesiology

English edition

A social system for production and utilization of thermophysical quantity data

National standards of length for high-capacity optical fiber communication systems

Research and development of solar hydrogen production

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Development of lectin microarray, an advanced system for glycan profiling

Development of a household high-definition video transmission system based on ballpoint-pen technology

Synthesiology editorial board

MESSAGES FROM THE EDITORIAL BOARD

There has been a wide gap between science and society. The last three hundred years of the history of modern science indicates to us that many research results disappeared or took a long time to become useful to society. Due to the difficulties of bridging this gap, this stage has been recently called the valley of death or the nightmare stage (Note 1). Rather than passively waiting, therefore, researchers and engineers who understand the potential of the research should actively try to bridge the gap.

To bridge the gap, technology integration (i.e. *Type 2 Basic Research* – Note 2) of scientific findings for utilizing them in society, in addition to analytical research, has been one of the wheels of progress (i.e. *Full Research* – Note 3). Traditional journals, have been collecting much analytical type knowledge that is factual knowledge and establishing many scientific disciplines (i.e. *Type 1 Basic Research* – Note 4). Technology integration research activities, on the other hand, have been kept as personal know-how. They have not been formalized as universal knowledge of what ought to be done.

As there must be common theories, principles, and practices in the methodologies of technology integration, we regard it as basic research. This is the reason why we have decided to publish "*Synthesiology*", a new academic journal. *Synthesiology* is a coined word combining "synthesis" and "ology". Synthesis which has its origin in Greek means integration. Ology is a suffix attached to scientific disciplines.

Each paper in this journal will present scenarios selected for their societal value, identify elemental knowledge and/or technologies to be integrated, and describe the procedures and processes to achieve this goal. Through the publishing of papers in this journal, researchers and engineers can enhance the transformation of scientific outputs into the societal prosperity and make technical contributions to sustainable development. Efforts such as this will serve to increase the significance of research activities to society.

We look forward to your active contributions of papers on technology integration to the journal.

Addendum to Synthesiology-English edition,

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Papers or articles published in "Synthesiology-English edition" appear approximately four months after the publication of the original "Synthesiology". Those published in Japanese are translated into English, so the views expressed in translated versions are exclusively those of the Japanese authors and editors. The Japanese authors are generally consulted regarding the translation of their papers, but are not responsible for the published English version.

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Synthesiology Editorial Board
(written in January, 2008)

Note 1 : The period was named "nightmare stage" by Hiroyuki Yoshikawa, the then President of AIST, and historical scientist Joseph Hatvany. The "valley of death" was used by Vernon Ehlers in 1998 when he was Vice Chairman of US Congress, Science and Technology Committee. Lewis Branscomb, Professor emeritus of Harvard University, called this gap as "Darwinian sea" where natural selection takes place.
Note 2 : *Type 2 Basic Research*
This is a research type where various known and new knowledge is combined and integrated in order to achieve the specific goal that has social value. It also includes research activities that develop common theories or principles in technology integration.
Note 3 : *Full Research*
This is a research type where the theme is placed within the scenario toward the future society, and where framework is developed in which researchers from wide range of research fields can participate in studying actual issues. This research is done continuously and concurrently from *Type 1 Basic Research* (Note 4) to *Product Realization Research* (Note 5), centered by *Type 2 Basic Research* (Note 2).
Note 4 : *Type 1 Basic Research*
This is an analytical research type where unknown phenomena are analyzed, by observation, experimentation, and theoretical calculation, to establish universal principles and theories.
Note 5 : *Product Realization Research*
This is a research where the results and knowledge from *Type 1 Basic Research* and *Type 2 Basic Research* are applied to embody use of a new technology in the society.

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A social system for production and utilization of thermophysical quantity data

— Measurement technology, metrological standard, standardization of measurement method, and database for thermal diffusivity by laser flash method —

Tetsuya BABA * and Megumi AKOSHIMA

[Translation from *Synthesiology*, Vol.7, No.1, p.1-15 (2014)]

The National Metrology Institute of Japan designed a system to supply reliable thermal diffusivity data efficiently and quickly to society. The system was founded on the technology for thermal diffusivity measurement by using a laser flash method, by establishing a metrological standard and reference materials, and by standardization of measurement technology. Uncertainty in measurement of thermal diffusivity with practical apparatus by the laser flash method was reduced using elemental technologies to homogenize the laser beam, a fast response infrared thermometer, and a curve fitting method to analyze temperature response curves. JIS and ISO standards were established or revised based on the developed technologies. In addition, methods to evaluate uncertainty in measurement of thermal diffusivity and calibration procedure by reference materials are described in the latest update of the JIS standard for the laser flash method. A procedure to obtain intrinsic thermal diffusivity is also described. Traceable thermophysical quantity data produced by this social system can be accumulated in a database system developed and operated by the National Metrology Institute of Japan (NMIJ), which is accessible via the Internet.

Keywords : Thermophysical quantity data, thermal diffusivity, laser flash method, metrological standard, reference material, standardization of measurement method, database, traceability, uncertainty, intellectual infrastructure

1 Introduction

In advanced devices, equipment, or structures, it is often pointed out that their thermal properties are bottlenecks to their performance and reliability. For example, in order to have a highly integrated electronic device to function fully, a cooling mechanism that efficiently removes the massive amount of heat produced by multiple elements that are packed in a limited space is necessary. For space vehicles entering the atmosphere to withstand severe aerodynamic heating, a special material that possesses a heat insulation function under ultra high temperature is necessary for its exterior. When analyzing a severe accident at a nuclear power plant, it is necessary to accurately simulate the temperature behavior of the nuclear fuel and the core that surrounds it, all the way to ultra high temperature. It is necessary to improve the efficiency of thermal energy use of the whole society in order to reduce fossil fuel consumption and carbon dioxide gas emissions, and therefore, it is necessary to choose the appropriate materials with excellent insulation, conductance, and heat storage functions.

For a device, instrument, or structure to operate with full function safely and effectively, a highly reliable thermal design should be made in advance. In a thermal design, accurate thermophysical quantity data must be known for all related materials and components. However in reality, one often faces problems when trying to obtain such data from available information.[1]-[3] When there was need for thermophysical quantity data, it was a common practice for the researcher to look through data books or databases for the material that was the subject of interest.[4] However, the required thermophysical quantity data often could not be found. Even if some data was found, it was unclear whether the data could be assigned to the exact material of interest. This situation is not so much a problem if one simply needed the thermophysical quantity data as a rough guideline, but such data were insufficient for realizing the maximum function or guaranteeing safety, and the researcher him/herself had to measure the thermophysical quantities or subcontract such measurement to a specialized lab. If measurement is necessary, the next problem is how to choose the appropriate measurement method and how to evaluate reliability of thermophysical quantity data measured by the method. However, there is no such information or guideline yet based on agreement among the academic and technological community.[1][2]

While various advanced materials are being developed in the fields of electronics, precision optics, environment and energy, aerospace, and nuclear technologies, it is not easy to obtain highly reliable thermophysical quantity data of the materials. In order to solve this situation, the National Institute of Advanced Industrial Science and Technology (AIST) has been conducting research on the thermophysical quantity measurement and reference materials for the past 30 years. In setting the research scenario, the greatest

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focus was placed on how AIST could play a public role in society. In other words, the production of highly precise thermophysical quantity data at AIST that was responsible for metrological standards should not be the endpoint, but the final goal of the research was to envision and construct the technological infrastructure, in which specialists of not only Japan but also of the world could efficiently produce highly reliable thermophysical quantity data, and these data could be effectively utilized in society. This can be called a "social system for efficient production and effective use of thermophysical quantity data."[3]

To achieve this goal, AIST engaged in various research activities on thermophysical quantities. In this paper, we shall focus on the thermal diffusivity of solid materials, and describe the research scenario of precise measurement technology, metrological standards, reference materials, standardization of practical measurement methods, and research results. AIST also conducted R&D for the thermophysical quantity database, but due to limitations of space in this paper, we shall only list them in the references.

2 Measurement and data of thermophysical quantities

2.1 Definition of thermophysical quantities

Thermophysical quantity values are numerical expressions for thermophysical properties of materials and substances. The functions pertaining to the transfer and storage of heat energy such as insulation, thermal conductance, or thermal storage are expressed as thermophysical quantity values such as thermal conductivity, specific heat capacity, thermal diffusivity, and thermal effusivity. These thermophysical quantity values are defined as follows.[4]

Thermal conductivity (λ): The phenomenon in which heat is transferred by conduction in a material is expressed as thermal conductivity, and is defined as the ratio of the heat flow density that passes through the material to the temperature gradient. The unit is $Wm^{-1}K^{-1}$.

Specific heat capacity (c): The amount of heat necessary to raise the temperature of a material 1 K per unit mass. The unit is $Jkg^{-1}K^{-1}$.

Thermal diffusivity (α): This is defined by the following equation based on thermal conductivity λ, specific heat capacity c, and density ρ.

$$\alpha = \lambda / (c\rho) \quad \dots (1)$$

The unit of thermal diffusivity is m^2s^{-1}. When part of a material insulated from the environment is heated in a short time to raise the temperature of that part only, the heat spreads throughout the material in time, and homogenous temperature is attained eventually. The speed at which the temperature converges to the final homogeneous temperature is proportional to the thermal diffusivity.

When it is difficult to directly measure the thermal conductivity λ, thermal conductivity measurement can be substituted by separate measurements of thermal diffusivity α, specific heat capacity c, and density ρ, and the thermal conductivity can be calculated from Equation (1).

Thermal effusivity (b): This is defined by the following equation calculated from thermal conductivity λ, specific heat capacity c, and density ρ.

$$b = \sqrt{\lambda c\rho} \quad \dots (2)$$

The unit of thermal effusivity is $Jm^{-2}s^{-1/2}K^{-1}$. It can be intuitively explained as the capability of the material of a sufficiently thick object to absorb heat when the surface is heated uniformly. Materials such as iron that has large thermal conductivity and density have large thermal effusivity, and the temperature rise of the heated surface is small. Inversely, insulating materials with low thermal conductivity and low density has small thermal effusivity, and therefore the temperature rise of the heated surface is large.

The four values, thermal conductivity λ, volume heat capacity C (= specific heat capacity × density), thermal diffusivity α, and thermal effusivity b are not mutually independent. If the arbitrary two quantities are known, the remaining two quantities are determined. Since these thermophysical quantity values are temperature dependent, they must be expressed as functions of temperature.

While the electric/electronic, mechanical, and optical quantities can be relatively easily measured in accordance with a defined condition, it is not easy to accurately measure thermophysical quantities according to the definitions explained above. The main reason is the difficulty of complete insulation and of accurately controlling heat flow in contrast to the situation of electricity which can be almost perfectly insulated by electrically insulating materials. Even in vacuum, heat energy can be transferred as thermal radiation. That is the reason why measurement methods for thermophysical quantities are still actively developed and improved, incorporating new technologies.

2.2 Traceability of measurement and reference materials

The National Bureau of Standards (NBS) developed reference materials[5] and organized standard data[6] in a wide range of fields including thermophysical quantities, in order to fulfill a national demand for achieving measurement traceability in the 1960s. NBS was reorganized into the National Institute of Standards and Technology (NIST) in 1988. NIST gradually lost its ability to develop new reference materials in the thermophysical quantity field, and is currently unable to replenish the out-of-stock reference materials of thermophysical quantities.

The development of thermophysical quantity reference materials was also done in Europe. For solid materials, the Institute for Reference Materials and Measurements (IRMM) started providing three types of reference materials for thermal conductivity and thermal diffusivity in the 1990s.[7]

In Japan, there is a well-organized traceability system, or a social system in which measurement results taken at any institution are guaranteed within a certain range of uncertainty, as long as the instruments used are traceable to the national standards for basic quantities such as length, mass, time, electricity, or temperature. One example of such a system is the Japan Calibration Service System (JCSS).[8] Although JCSS was established for the thermal conductivity measurement of insulation materials by contribution of the Japan Testing Center for Construction Materials (JTCCM), a traceability system for thermal diffusivity measurement or thermal conductivity measurement of dense materials has been established using the reference materials developed by AIST instead of JCSS.[2][3][9]

Efforts for “a social system for production and utilization of thermophysical quantity data” by the academic community in Japan, Comité International des Poids et Mesures (CIPM), and the former National Research Laboratory of Metrology (NRLM), Agency of Industrial Science and Technology, Ministry of International Trade and Industry are described in the appendices.

2.3 History of accumulation, evaluation and publication of thermophysical quantity data

There is a long history in Europe and the United States for collecting thermophysical quantity data of substances and materials, and then providing them systematically to a wide range of users. Germany has continuously worked on collecting and evaluating physical quantity data including thermophysical quantities since the end of the 19th century, and the results were compiled and published, for example, as the Landolt-Börnstein Data book. Today, the data is available online as Springer Materials (Landolt-Börnstein Database).[10]

In the United States, compilation of the international critical tables was started under the auspices of NBS in the 1920s.[11] The US Congress established the “standard reference data act” in 1968, and the US government decided to start the data evaluation program named the National Standard Reference Data System (NSRDS).[12] As a part of this program, the Thermophysical Property Research Center (TPRC) at Purdue University collected and evaluated a vast amount of thermophysical quantity data, and published a 14-volume thermophysical property data book, the TPRC Data Series.[13]

This data series collected the thermophysical quantity data of a wide range of materials and substances, mainly for practical materials in addition to basic substances such as elements. For some data, the reliability was evaluated and recommended values were provided. However, the collected data included those obtained by measurement methods that were not well established. In some cases, the measurement apparatus were not correctly calibrated and the information to identify the measured substances and materials (characterization information) was limited.

The TPRC was reorganized into and the activities continued at the Center for Information and Numerical Data Analysis and Synthesis (CINDAS) at Purdue University over the 1980s. Currently, the data has been succeeded by the CINDAS Limited Liability Company, and is available online as a database.[14]

In the field of thermophysical quantities for solid materials, the notable accomplishments of NSRDS were the thermophysical quantity reference materials of NBS and the Purdue University TPRC database, but the cooperation between the two activities was not so effective. It was not common practice for apparatus of thermophysical quantity measurements to be calibrated or verified by the reference materials provided by NBS when TPRC data series were published.

Although the demands for thermophysical quantity data for electronics, environment and energy, and life science materials increased in recent decades, there has been no compilation or publication of a comprehensive data book comparable to the TPRC Data Series to the present.

2.4 Reliability of the thermophysical quantity data and the issues of measurement technology

Even for measurement methods that were used popularly to obtain thermophysical quantity data, there were examples in which handling of the measuring apparatus was too complicated, the reliability (precision and accuracy) of the measurement was not enough, or the evaluation of reliability was not easy. There were fairly large variations in the thermophysical quantity data obtained for the same specimen even based on the same measurement method, and the variations increased further when the measurement methods differed.[3][15][16]

It would be useful if thermophysical quantity data became universal information generalized from an individual measurement apparatus or a laboratory. To realize such a situation, the triangle set of tasks was planned, including the establishment of national standards and reference materials, standardization of the measurement methods, procedures of measurement, and specifications of apparatus (JIS and ISO standards), and development of practical measurement apparatus that fits the standard.[17]

3 Scenario setting

In the initial stages of research, we envisioned a social system where engineers and researchers could easily and speedily access thermophysical quantity data with sufficiently small uncertainty. Hence, we set the research scenario as shown in Fig. 1.[3][15]

In the scenario of Fig. 1, first, improvement of precision and accuracy for the measurement technology of corresponding thermophysical quantities and the establishment of national standards and reference materials based on this technology were set. Second, the conditions required for reference materials were specified that they should be homogenous and their properties should not change over a long period of time. Then, the reference values of the reference materials should be determined by the national standard, the uncertainty of reference values should be evaluated, and the related information should be provided to society.

Third, the standardization of measurement technology or the organization of standards was planned. If the measurement methods and procedures for thermophysical quantities were standardized by JIS or ISO, it would be possible to evaluate measurement uncertainty as well as to realize thermophysical quantity measurement traceable to the national standard, by calibrating/validating the measurement apparatus using the aforementioned reference materials according to the document standard such as JIS or ISO.

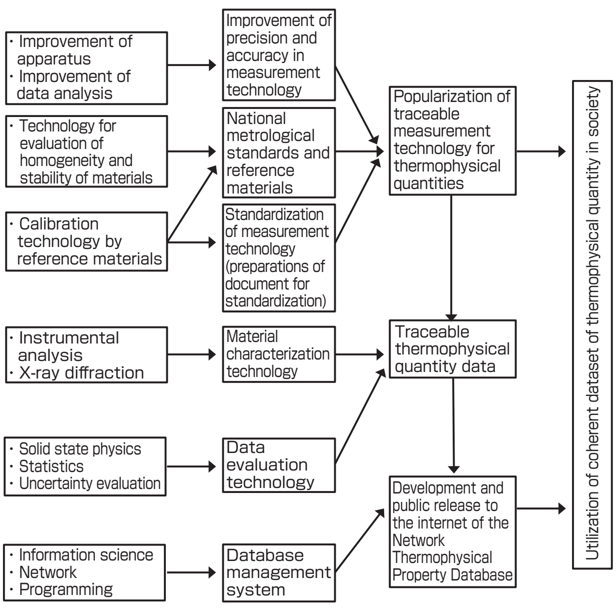

Fig. 1 Scenario for constructing a social system for the production and use of thermophysical quantity data

Fourth, the material characterization technology was addressed. Physical properties of a material are universal information applicable to materials with the same characteristics (composition, structure, etc.) at the same conditions (temperature, pressure, etc.), in contrast to the measurement data for physical variables such as temperature and pressure which are only applicable to each measurement. However, contrary to a physical quantity of a liquid which is uniquely determined by composition, a thermophysical quantity value of a solid may change depending on characters, even if the material has the same composition. Particularly, the transfer quantities such as thermal conductivity and thermal diffusivity are sensitively dependent on the characters such as crystal structures and grain boundaries.

Fifth, if the measured thermophysical quantity data could be successfully assigned to the information of characters such as compositions and structures of materials, the combination of measurement values of thermophysical quantities and material character could be called a "Coherent Dataset." which would be widely useful in society.

Moreover, if data evaluation technology and data management system would be implemented to the database, the thermophysical quantity data with high reliability and universal value would be produced continuously and systematically, according to the scenario shown in Fig. 2.

In the field of physical measurement of basic quantities such as length, mass, time, electricity, and temperature, the common practice is to maintain traceability of the measured value by conducting calibration using a higher-level standard by transporting the standard artifact. In the field of chemical analysis, the traceability of measurement value is maintained by transporting the reference material.

There is a special approach specific to the field of material measurement including thermophysical quantities where traceability can be proved by presenting the set of information for "standard data" and "material character"

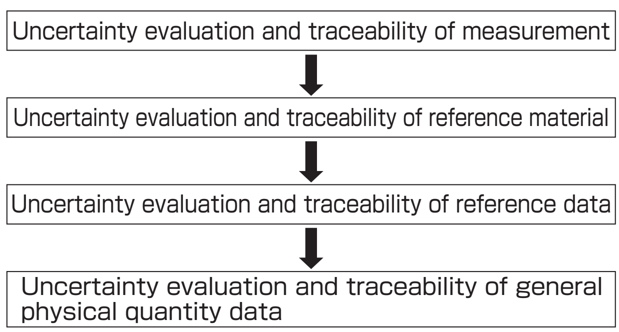

Fig. 2 Process of generalizing concept of uncertainty evaluation and traceability from "measurement of physical quantities" to "physical quantity data"

(that is, it is not necessary to transport any artifact or material), in addition to the conventional traceability system of transporting the standard artifact or reference materials.[16][18]

In this scenario, the concept of uncertainty evaluation and traceability was consecutively expanded from measurement to reference materials, to standard data, and then to general physical quantity data. Eventually, the reliability of the general thermophysical quantity data would be proved. In order to realize this process, new R&D that allows quantitative expression of material character and physical quantity value is necessary as shown in Fig. 2.

4 Measurement of thermal diffusivity by a laser flash method

4.1 Selection of the laser flash method

Since thermal conductivity and thermal diffusivity are proportional to each other as indicated by Equation (1) when specific heat capacity and density are fixed, measurements of thermal conductivity and thermal diffusivity are complementary to each other and each can be chosen to be measured according to the situation.

Thermal conductivity is generally measured by a steady-state method. In the steady method, a certain amount of constant heat flow passes through a specimen, and the thermal conductivity is calculated by measuring the temperature gradient that occurs in the specimen. On the other hand, thermal diffusivity is generally measured by a transient method. In the transient method, the thermal diffusivity is calculated by measuring the relaxation time where the temperature distribution becomes homogenous over time in a specimen in which the temperature was initially inhomogeneous.

In thermal conductivity measurement by a steady-state method, it is necessary to measure the absolute value of the temperature by attaching thermometers to the specimen. Therefore, this method is suitable for materials where a specimen of a large size can be obtained. Since the heat source, heat sink, and thermometers should be in contact with the specimen, various conditions must be considered such as selecting the materials for heat source and heat sink, selection of the thermometers, and correction for radiation heat loss, particularly in conducting the measurement at high temperature.

For measurement technology of thermal diffusivity by a transient method, a laser flash method had already been developed in advance before the start of our research. It was widely used as a standard method for measuring thermal diffusivity of dense solid materials such as metals, alloys, ceramics, semiconductors, and graphite.[19]-[22] Reflecting such wide-spread use, most of the thermal diffusivity values listed in product catalogs and those in the data books and database for dense solid materials have been measured using the laser flash method.

The measurement principle of the laser flash method is shown in Fig. 3. With this method, the front face of a planar specimen that has been maintained at steady temperature is pulsewise heated. Then, the heat diffuses one-dimensionally from the front face of this specimen to the inside of the specimen, and finally, the entire specimen reaches homogeneous temperature.[19]-[22] The thermal diffusivity of the material is calculated from the rate of temperature rise at the rear face of the specimen.

As a measurement method of thermal diffusivity, other than pulse heating, cyclical heating methods and step-function heating methods have been developed. Thermal effusivity can also be calculated from the temperature change at the location where the specimen surface is heated.[4]

Advantages that the laser flash method possesses are as follows :

- Quality of the measurement can be evaluated by fitting the analytically calculated theoretical curve to the temperature response curve at the rear face of the specimen under one-dimensional heat diffusion after pulse heating.
- Typical shape and size of a specimen is a disk of 10 mm in diameter and 1 -2 mm in thickness and one measurement can be completed within a few seconds.
- Impulse heating and measurement can be done without contact by using a pulsed laser and a radiation detector for measuring the temperature changes, respectively.
- Measurement can be made at a wide temperature range from lower than room temperature to higher than 2,000 °C.
- Since the method using a flash lamp was invented in 1961, many researchers have contributed to improving the method, and its validity, reliability and superiority are commonly recognized. As a result, practical measurement apparatus are widely used.

From the above background, we decided to start research of the laser flash method in order to establish the national

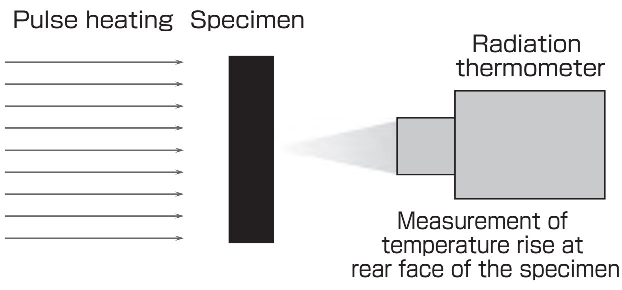

Fig. 3 Measurement principle of the laser flash method

standard for thermal diffusivity measurement since it had potential for achieving precise and accurate thermal diffusivity measurement. On the other hand, we noticed that the laser flash method had not matured enough for the national metrological standard of thermal diffusivity, and the uncertainty evaluation of measurement results had not been done sufficiently when we decided to start the research of the laser flash method in 1983. Therefore, the first priority was set to improve the measurement technology. In order to provide highly reliable thermal diffusivity data to society efficiently and quickly, development of the reference materials and standardization of the measurement technology (organization of the JIS and ISO standards) were also set as research topics.

4.2 Improvement of measurement technology

Figure 4 shows a non-dimensional temperature rise (temperature rise normalized by the maximum temperature rise) at the rear face of a specimen under the ideal initial conditions and boundary conditions. It is expressed as the function of non-dimensional time (time normalized by the characteristic time $\tau = d^2/\alpha$ of heat diffusion across the thickness). The rate of temperature rise at the rear face of the specimen is proportional to the thermal diffusivity α, and is inversely proportional to the square of the specimen thickness. In ideal conditions, the thermal diffusivity can be calculated from the specimen thickness d and the half rise time $t_{1/2}$ required to reach half of the maximum temperature rise $\Delta T/2$, by the following equation.[19][20]

$$\alpha = \frac{0.1388\, d^2}{t_{1/2}} \quad \ldots (3)$$

Figure 5 shows the time change of the temperature at the rear face of the specimen observed for glass like carbon by the laser flash method.

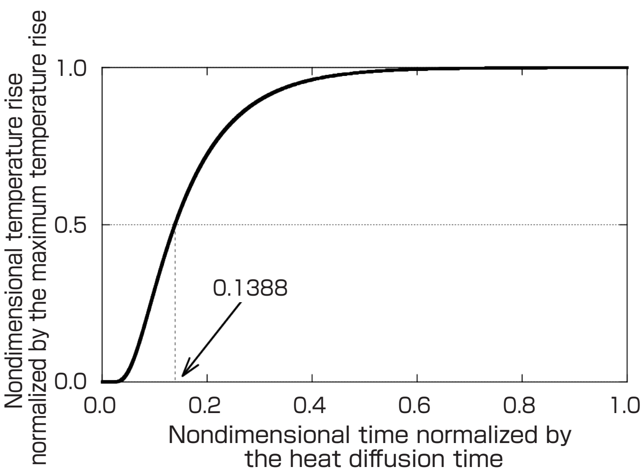

Fig. 4 Temperature response curve at rear face of the specimen by the laser flash method under ideal initial and boundary conditions

AIST developed several new elemental technologies of the laser flash method. First, the spatial energy distribution of the laser beam was homogenized to realize one-dimensional heat flow within the specimen by passing the pulse laser beam through optical fibers.[22][23] Second, the temperature change at the rear face of the specimen was accurately measured by using the high speed infrared radiation thermometer.[22][24] Third, the thermal diffusivity was calculated considering the heat loss from the specimen surface to the environment through radiation.[20][21] Fourth, the intrinsic thermal diffusivity unique to the material was calculated by extrapolation when the heating laser energy was zero (Fig. 6).[22][25]-[27]

Figure 7 shows the photograph of the national standard apparatus of the laser flash method.

4.3 Development of the national standard and reference materials

The National Metrology Institute of Japan (NMIJ), AIST accomplished the development plan of the national

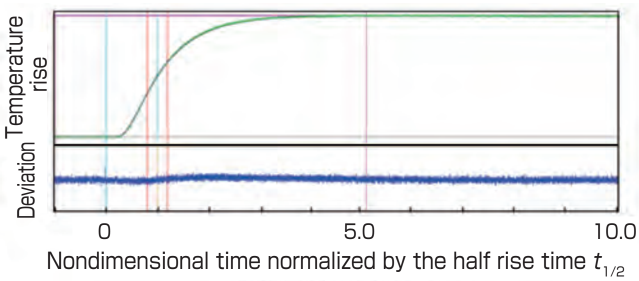

Fig. 5 Temperature response curve (green) at rear face of the specimen of glass like carbon measured by the laser flash method, ideal curve (black), and the deviation between the two curves (shown in blue at bottom part of graph, magnified 10 times)

The measured curve (green) and ideal curve (black) are agree with each other and systematic deviation could not be observed.

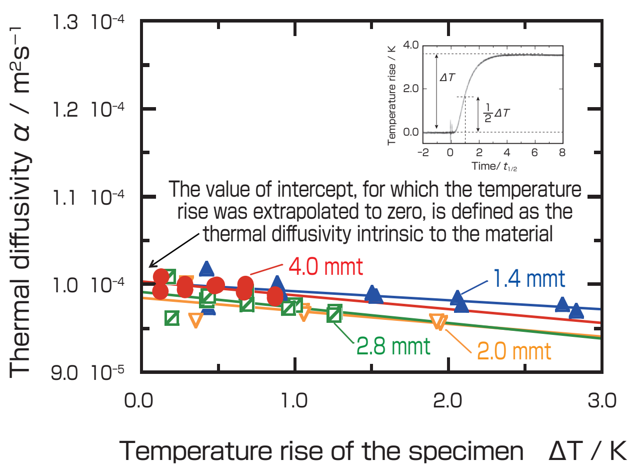

Fig. 6 Data plot to calculate the thermal diffusivity intrinsic to the material (example where the high-density isotropic graphite is measured at room temperature)[26]

Table 1. Items for which standards are provided in the solid thermophysical quantity field based on the national metrological standard development plan (~2010)

Development plan Number	Quantity (item of calibration service)	Range (range of calibration temperature for service)	Extended (relative) uncertainty of coverage factor k=2	Type of service	Remarks
240-00 241-00	Thermal diffusivity	$1\times10^{-6}m^2s^{-1}$～$5\times10^{-4}m^2s^{-1}$ (297 K～1500 K)	< 3.4 %	Calibration service (general)	Calibration specified for isotropic graphite
		(300 K～1500 K)	5 %～7 %	Certified reference material NMIJ CRM5804-a	Isotropic graphite supplied as NMIJ RM 1201-a before 2010
242-00	Thermophysical quantities of thin films (heat diffusion time across thickness of the specimen)	100 ps～6500 ps	4.2 % (Mo thin film of 400 nm thick)	Calibration service	Thin film of from 100 nm to 400 nm thick
242-10		40 ns～1000 ns	3.6 %	Calibration service	Calibration specified for titanium nitride thin film on transparent glass substrate
		150 ns (Room temperature)	4.9 %	Certified reference material NMIJ RM1301-a	Titanium nitride thin film of 700 nm thick on transparent glass substrate
244-00	Thermal conductivity	(300 K～900 K)	7.4 %～9.8 %	Certified reference material NMIJ RM1401-a	Isotropic graphite
245-00	Specific heat capacity	(50 K～350 K)	$1.3\times10^{-3}JK^{-1}g^{-1}$ ～$6.1\times10^{-3}JK^{-1}g^{-1}$	Calibration service	Adiabatic calorimetry
246-00		(300 K～900 K)	$1.9\times10^{-2}JK^{-1}g^{-1}$ ～$3.1\times10^{-2}JK^{-1}g^{-1}$	Calibration service	Differential scanning calorimetry

metrological standards, with the goal of establishing 250 physical metrological standards and 250 chemical metrological standards by 2010.[28] The thermophysical property standard section, physical property statistics division (currently material physical property division), NMIJ AIST was in charge of the solid thermophysical quantity field and has established the metrological standards for thermal diffusivity, thermal conductivity, and specific heat capacity of the bulk materials, as shown in Table 1. Also, reference materials for thermal conductivity, thermal diffusivity, and specific heat capacity have been developed and supplied.[9][29][30] Responding to the needs from advanced industry, AIST has also engaged in the development of metrological standards for thermal diffusivity and heat diffusion time of thin films, and started measurement service and supply of a reference material.[31][32]

Fig. 7 The apparatus of national standard for thermal diffusivity

NMIJ established the SI traceable thermal diffusivity measurements and completed uncertainty evaluation according to GUM. A quality management system based on ISO 17025,[33] the international requirement for calibration laboratories, has been established and is under operation at NMIJ. The calibration service of thermal diffusivity started in 2004. High-density isotropic graphite was selected as the distributed thermal diffusivity reference material because of its homogeneity, stability, and black surface without a coating process.[34][35] Its reference values were determined using the national standard of thermal diffusivity, and distribution was started in 2006.The quality management system of thermophysical quantity reference material is operated in accordance with ISO Guide 34[36] that is an international requirement for manufacturers of reference materials since FY 2010. It has been provided as a certified reference material called NMIJ CRM-5804 since 2010.

As the next step after the establishment of the national standard, it is important to verify whether the Japanese and overseas national standards for thermophysical quantity measurement are equivalent.[37] To do so, the homogenous specimens cut from the same lot are distributed to several national metrology institutes (NMIs), and the measurement values at each NMI are compared to see whether they agree within the range of uncertainty. This is called an international comparison of national metrological standards. The NMIs with which the measurement results agreed mutually recognize their calibration and measurement capabilities (CMCs), and the results are entered into the BIPM Key Comparison Database (KCDB)[38] that can be viewed by everyone.

International comparisons for thermophysical quantities have been conducted by the Working Group 9 (WG9) for thermophysical quantities of the CIPM Consultative Committee for Thermal Metrology (CIPM CCT)[39] and the Technical Committee for Thermometry (TCT) of the Asia Pacific Metrology Programme (APMP).[40][41]

The pilot study of thermal diffusivity measurements of solid materials by the laser flash method was conducted from 2008 to 2011.[42][43] This was the first international comparison of thermal diffusivity measurement by the laser flash method among the NMIs, and the objective was to survey the level of the latest measurement technology, as well as to obtain common understanding of the measurement procedure, data analysis, and the uncertainty evaluation method. One of the authors (Akoshima) was the organizer of this pilot study, and four NMIs participated, including the Laboratoire National de Metrologie et d'Essais (LNE) of France, the National Institute of Metrology (NIM) of China, the NMIJ AIST of Japan, and the National Physical Laboratory (NPL) of the UK.

Armco iron and high-density isotropic graphite were selected because they were readily available on the market, and have been confirmed to be stable based on sufficient evaluations in the past. Each set of disk specimens of Armco iron and high-density isotropic graphite with a diameter of 10 mm and thickness of 1.0, 1.4, 2.0, 2.8, and 4.0 mm were prepared for each participating NMIs. After checking the homogeneity, one set each was sent to the participating NMIs for measurement.[43] For the measurement procedure, a method for obtaining intrinsic thermal diffusivity that was proposed by AIST was used,. The results reported by all NMIs are shown in Fig. 8 and Fig. 9. The figures show a set of data by an NMI systematically deviates from those of the other NMIs. This systematic deviation was attributed to slow response of the detector for the rear face temperature change used by the apparatus. After excluding this set of data, the other data agreed within the uncertainty range, where the standard deviation of variation among the three NMIs were 7 % or less in the temperature range from 300 K to 1200 K. From this international comparison, it was confirmed that the thermal diffusivity measurement by the laser flash method had sufficient equivalency among the NMIs. The result of the comparison has been published already.[42][43] The pilot comparisons of CCT-WG9 were registered as supplementary comparisons of key comparison database of BIPM, KCDB, in 2012.

At the meeting of CCT in 2010, an agreement was reached to incorporate thermal conductivity, thermal diffusivity, specific heat capacity, and thermal expansion of the thermophysical quantity field into the service category of thermal metrology registered in the Key Comparison Database (KCDB). Protocol for reviewing the CMC for thermal diffusivity has been submitted to the Working Group 8 of CCT.

In APMP, the Regional Metrological Organization (RMO) of which members are NMIs in the Asia-Pacific region, a working group for thermophysical properties was established in the Technical Committee covering Thermal Measurement (TCT) in 2010. In conjunction with the activities of CIPM CCT, two supplementary comparisons were organized in the Asia-Pacific region. Specifically, they were thermal diffusivity measurement by the flash method (APMP T.S-9) and thermal conductivity measurement of insulating

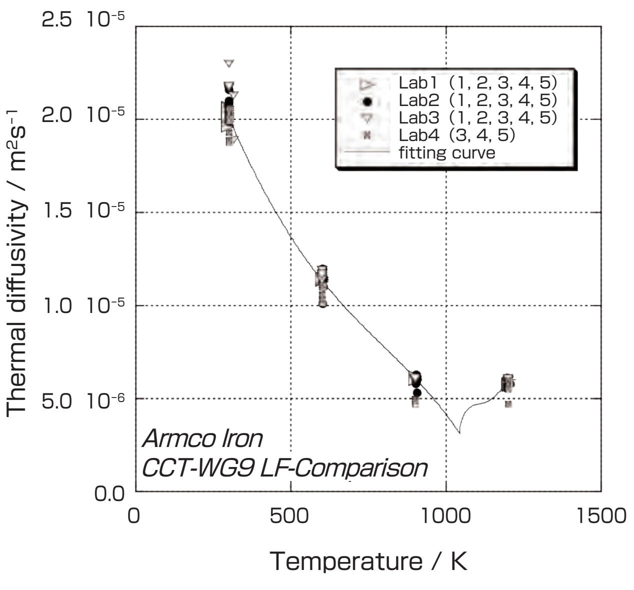

Fig. 8 Result of the pilot study for international comparison of the thermal diffusivity of Armco iron[43]

The numbers in parentheses [e.g. Lab1 (1, 2, 3, 4, 5)] indicate the specimen identification numbers.

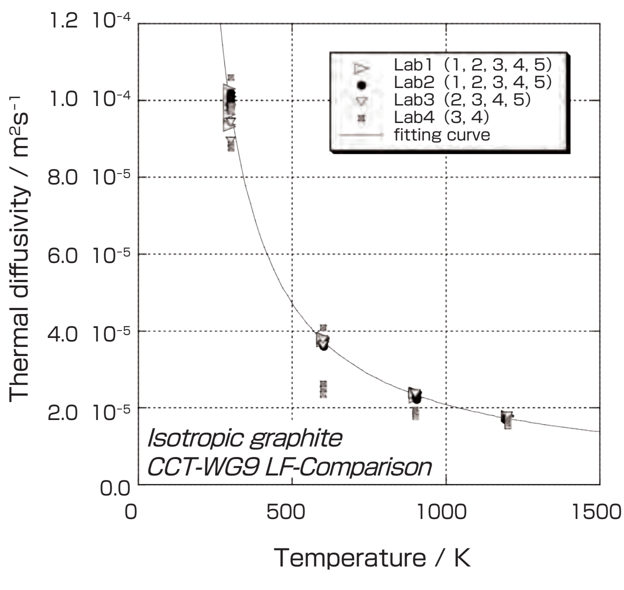

Fig. 9 Result of the pilot study for international comparison of the thermal diffusivity of high-density isotropic graphite[43]

The numbers in parentheses [e.g. Lab1 (1, 2, 3, 4, 5)] indicate the specimen identification numbers.

Table 2. ISO and JIS standards related to the laser flash method to which this study contributed

Category	Standard identification number.	Issued year	Japanese title	English title
ISO	18755	2005	—	Fine ceramics: Determination of thermal diffusivity of monolithic ceramics by laser flash method
JIS	R1611	1991 (Revised 2010)	ファインセラミックスのレーザフラッシュ法による熱拡散率・比熱容量・熱伝導率試験方法	Test methods of thermal diffusivity, specific heat capacity, and thermal conductivity for fine ceramics by flash method
JIS	H7801	2005	金属のレーザフラッシュ法による熱拡散率の測定方法	Method for measuring thermal diffusivity of metals by the laser flash method
JIS	R1667	2005	長繊維強化セラミックス複合材料のレーザフラッシュ法による熱拡散率測定方法	Determination of thermal diffusivity of continuous fiber-reinforced ceramic matrix composites by the laser flash method
JIS	H8453	2010	遮熱コーティングの熱伝導率測定方法	Measurement method for thermal conductivity of thermal barrier coatings

materials by the GHP method (APMP T.S-10). APMP T.S-9 is a joint project of TCT and the Technical Committee for Material Measurement (TCMM).

4.4 Standardization of the measurement technology

For the thermophysical quantity data to be utilized widely for design and performance evaluation of apparatus and instruments, evaluation of energy-saving performance, or guarantee of quality and safety, it is desirable that the measurement procedure and the specifications of the apparatus used to measure thermophysical quantities are standardized and operated by a standard guideline.

The list of the standards documents to which the results of this research and related activities contributed is shown in Table 2. One of the authors (Baba) worked as the chairman or project manager of the Draft Proposal Committee for the two JIS standards (JIS H7801 and R1667).[44][45] He also participated as the Japanese representative to WG15 of ISO/TC206 (Fine Ceramics) and contributed to the establishment of ISO 18755 “Fine Ceramics: Determination of thermal diffusivity of monolithic ceramics by laser flash method.”[46]

The technologies of thermal diffusivity measurement can be roughly classified into the general technologies not specific to measured material, and the individual technologies specific to each material. The former are shared in society as universal technological standards through standardization. In the case of the thermal diffusivity measurement by the laser flash method, as shown in Fig. 10, the general technologies independent of the material can be classified into the specifications of the measurement apparatus (hardware technology) and data analysis (software technology).

The following technical requirements are listed in this standardization:

1) A specimen is maintained stably in a condition where contact thermal conductance with the specimen holder is minimized.
2) Temperature of the specimen is kept constant and is accurately measured.
3) Front face of the specimen is pulsewise heated by spatially uniform beam.
4) Duration of pulse heating should be sufficiently short compared with the heat diffusion time across the specimen.
5) Temperature rise at the rear face of the specimen after pulse heating is observed by a detector with sufficiently fast response.

The developed technologies which satisfy these conditions have been transferred to the manufacturers of the apparatus.

The authors (Akoshima and Baba) contributed to the revision of JIS R1611 in 2010.[47] In this revision, procedure for uncertainty evaluation of measurement data, calibration/

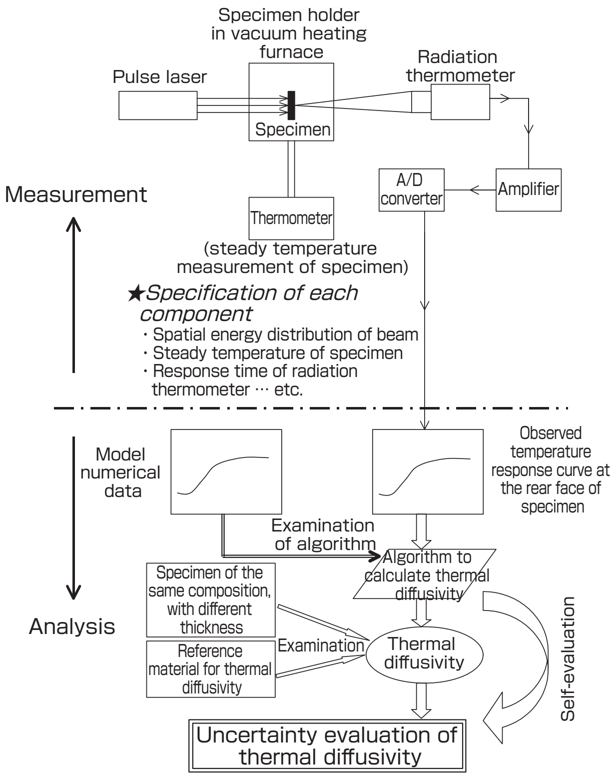

Fig. 10 Specification of the measurement apparatus and the analysis technology for the laser flash method

validation method using thermal diffusivity reference materials, estimation of intrinsic thermal diffusivity as physical properties of material, and quantitative evaluation method of the effect of black coating on surfaces of the specimen were added in the Appendices.

Our efforts in thermophysical quantity measurement were exerted in a triangle set of style as shown in Fig. 11 where the metrological standards, standardization, and practical measurement technologies contributed mutually to the overall improvement. Similar effort was made for the thermal diffusivity measurement of thin film.[17]

5 Current situation of developing a social system of thermophysical quantities

Figure 12 shows categories of technologies related to the thermal diffusivity measurement by the laser flash method and their relationships. As shown in the middle of the figure, thermal diffusivity is calculated by fitting the theoretical curve to the temperature response curve using a data analysis algorithm. In this case, there was a synergetic effect where the progress of data analysis technology was inspired by the improvement of measurement technology, and also the demand for an improved measurement apparatus was induced by the progress of the analysis technology. Therefore, the measurement technology and data analysis technology closely interacted with each other and evolved cyclically.

One specific example is that one-dimensional heat diffusion in a specimen was realized by homogenizing the spatial energy distribution of the pulse laser beam using optical fibers.[22][23] Stimulated by such advances in the measurement technology, universal data analysis technology for one-dimensional thermal diffusivity was developed as an application of a response function method.[48]-[50]

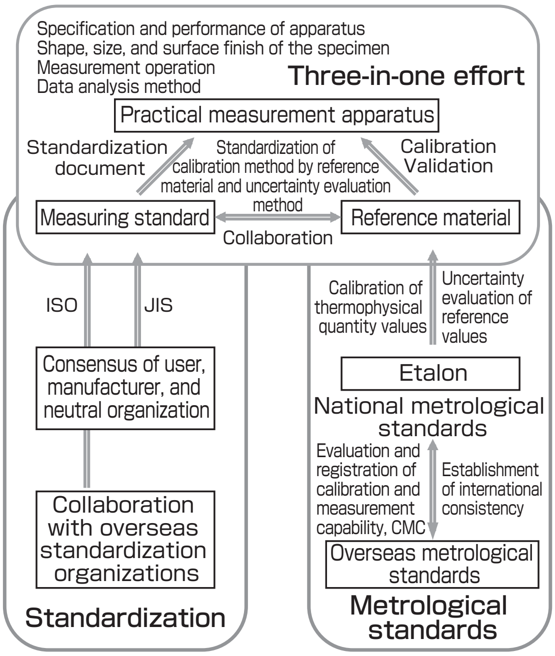

Fig. 11 Standardization of measurement technology and collaboration with metrological standard

6 Summary and future development

A triangle set of measurement technologies, metrological standards, and standardization for thermal diffusivity measurement by the laser flash method was developed synthetically in order to create a social system for efficiently and quickly providing highly reliable thermal diffusivity data. The national standards and reference materials were established based on the measurement and data analysis technologies developed in this research. These technologies have also been transferred to practical measurement apparatus. JIS and ISO standards were revised reflecting these new technologies. A database of thermophysical quantities was developed to accumulate traceable data produced from this social system, and was opened on the Internet.

Current approach for uncertainty evaluation and traceability will be extended to the general thermophysical quantity data, not just to the standard values and standard data of the reference materials. A method for quantitatively expressing the correlation between the material characters and quantity values is expected to be a key technology.

By actively collaborating with the overseas institutions working on the physical quantity data of substances and materials as well as Japanese institutions (such as universities, national laboratories, academic societies, companies, etc.), we aim to develop a system to continuously produce highly reliable thermophysical quantity data which is the basic information for science and technology and accumulate the produced data in the Network thermophysical property database.

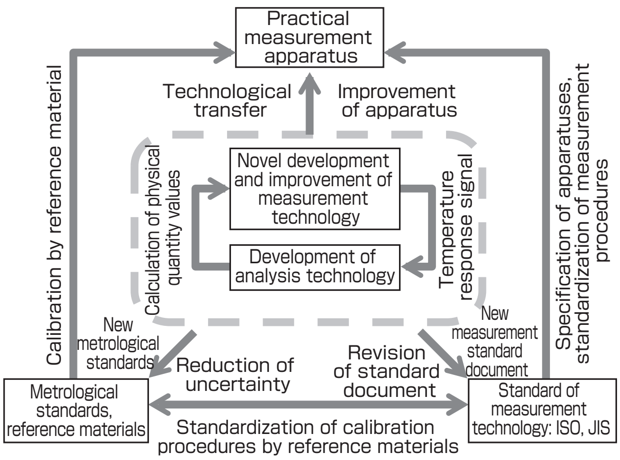

Fig. 12 Systematized techniques for thermal diffusivity measurement by the laser flash method

In the future, we hope to evolve this system into an international framework. The practical measurement apparatus of the laser flash method whose measurement target is bulk materials is commonly used among a wide range of users throughout the world. The international standard is set as ISO/TC206 (Fine Ceramics), and further efforts are in progress for the organization of the metrological standards under the Meter Convention in the CIPM CCT Task Group on thermophysical quantities. We aim to spread the standards to the manufacturers of the measurement apparatus, research institutes, energy related companies, electronic companies, and others that need the thermophysical quantity data, in collaboration with the overseas NMIs.

Appendix A Effort in the academic societies

In Japan, importance of thermophysical quantity data was strongly recognized in the 1970s when science, technology, and industry caught up with the developed countries. In 1980, the Japan Research Meeting for Thermophysical Properties was established, and this was renamed the Japan Society for Thermophysical Properties (JSTP) in 1990.[51]

The JSTP hosts the Japan Symposium on Thermophysical Properties every year and publishes the academic journal *Netsu Bussei (Japan Journal of Thermophysical Properties)*.[52] Also, the Asian Thermophysical Properties Conference (ATPC) was started in 1986, and the World Congress on Thermophysical Properties was formed in collaboration with the research institutions on thermophysical properties of the United States and Europe, and it provides a place for worldwide research exchange.

The JSTP published the *Netsu Bussei Handbook* (Thermophysical Property Handbook) in 1990 that compiled information on thermophysical properties in wide-ranging fields of science and technology.[53] The *Netsu Bussei Handbook* not only collected thermophysical quantity data, but also provided definitions and descriptions of thermophysical quantity values, how to search data, data availability, and measurement methods. It systematically described how to obtain and utilize thermophysical quantity data, including cases in which one must obtain thermophysical quantities through actual measurement by oneself. In 2008, it was revised to reflect the progress in science and technology and the increase in data from the first edition up to that time, and was published as the *Shinpen Netsu Bussei Handbook* (Thermophysical Property Handbook, New Edition).[4]

The importance of the scientific and technical infrastructure was pointed out in the Technology Basic Plan of Japan announced in 1996.[54] Metrological standards, safety management of chemical substances, human life and welfare, biological resource information, and materials were selected as the fields of focus where organization and R&D should be done actively to promote the creation of new industry by the “Special Committee on Measurement Standards and Intellectual Infrastructure” which was organized in 1998 as a joint effort of the Industrial Technology Council and the Japanese Industrial Standards Committee.[55] In linkage with this movement, the JSTP investigated the “Role of Thermophysical Properties in Intellectual infrastructure” in 1997, and this was reported as a proposal of JSTP in 1998.[2]

Appendix B Efforts at CIPM

For over 100 years since the establishment of the Meter Convention, national standards were mainly set for basic quantities such as length, mass, time, electricity, and temperature. However, in recent years, equivalence of analysis results for the content of elements and chemical substances became widely required in the tests for food safety and environmental pollutants, health check, and others. International consistency and traceability were demanded for chemical measurements.[56] In response to such demands, the Consultative Committee for Amount of Substance (CCQM) was established in CIPM within the framework of the Meter Convention in 1995.[57]

While the physical standards are provided through the calibration services with the national standards based on the calibration and measurement capabilities (CMCs) of the NMIs of each country, in general, the material quantity standards are mainly provided by the certified reference materials (CRMs) and thereby the traceability is maintained.

In the field of material measurement evaluation, the Versailles Projects on Advanced Materials and Standards (VAMAS) was organized “to support trade in high technology products, through international collaborative projects aimed at providing the technical basis for drafting codes of practice and specifications for advanced materials” among the participating countries, at the Versailles Summit in 1982.[58]

At the CIPM, considering the importance of the technological role and trade of “materials” that support modern society, it decided to establish the Ad Hoc Working Group of Material Metrology (WGMM) in 2005. This was composed of the NMIs of the world and the specialists from material research institution, with the purpose of studying general material quantities including mechanical and electric quantities of materials as well as thermophysical quantities. Discussions were started in 2006, and the final report was submitted to the CIPM in 2007.[59] The WGMM concluded that instead of establishing a new consultative committee for material measurement, the WG on materials in the existing CC should work in liaison with VAMAS. The details of the activities were published as a special edition of *Metrologia*.[60]

WG9 for Thermophysical Quantity was established in CCT in 2003.[61] One of the authors (Baba) was the chairman of WG9 from 2005 to May, 2014. WG9 decided to start three pilot studies for international comparisons of thermal conductivity of insulation materials by the guarded hot plate (GHP) method, thermal diffusivity of dense solid materials by the laser flash method, and thermal radiation of dense solid materials from 2008. There are comprehensive needs for their metrological standards among a wide range of fields of science and technology.[16] Thermal diffusivity of a dense solid material is intrinsic to the material with which the same value can be obtained independent of the measurement methods as described in chapter 1[27][62]. The measurement results of the participating NMIs were collected at the pilot institution and the final report is currently being drafted. Activities of WG9 were succeeded by the Task Group on thermophysical quantities in May, 2014.

Appendix C Effort of NRLM

The National Research Laboratory of Metrology (NRLM), Agency of Industrial Science and Technology, Ministry of International Trade and Industry was one of the predecessors of the National Metrology Institute of Japan, AIST. It conducted the “Survey Research for Physical Property Measurement” and the results were presented as a report in 1985.[1] The thermophysical property department was established based on this investigation, and the organizational effort for the research on the measurement technology and metrological standard for thermophysical quantities was started.

As part of the effort, within the Promotion System for Intellectual Infrastructure of Research and Development of the Special Coordination Funds for Promoting Science and Technology, the former NRLM acted as a core institution and instigated the five-year plan for “Research on the thermophysical property measurement technology and reference material for functional materials” from FY 1997. In this research topic, the following goals were set for density, thermal conductivity/diffusivity, specific heat capacity, thermal expansion, radiation, acoustic speed, and elasticity. These were conducted as a joint research project by over ten Japanese institutions.[3][15][63]

1) To establish primary standards of Japan by developing precision measurement technology for thermophysical property values.
2) To develop reference specimens and materials, to obtain standard data, and to widely distribute them to sites of research and production.
3) To develop state-of-the-art measurement methods capable of handling advanced functional materials, and to standardize practical measurement methods.
4) To identify material character for certain important materials, to create coherent datasets for thermophysical property values (set of data that includes the character for identifying the materials as well as the thermophysical property values), and to verify the efficacy of the approach of this research.
5) To create prototypes of thermophysical property database and then to verify the efficacy as a data diffusion tool.

A social system for production and utilization of thermophysical quantity data has been developed through the accumulation of projects including this Intellectual infrastructure Organization Promotion Project. The prototypes of thermophysical property database described in 5) has been evolved into the network thermophysical property database opened on the NMIJ website.[64]-[66]

References

[1] National Research Laboratory of Metrology AIST-MITI (ed.): Survey Research Report on Physical Property Measurement Technology, (1985) (in Japanese).
[2] S. Fukusako: What Thermophysical Properties Activities should be as a Technical Infrastructure, *Japan Journal of Thermophysical Properties*, 12 (3), 152-169 (1998) (in Japanese).
[3] A. Ono: Technical Infrastructure and Thermophysical Properties, *Japan Journal of Thermophysical Properties*, 12 (1), 20-30 (1998) (in Japanese).
[4] Japan Society of Thermophysical Properties (ed.): *Thermophysical Properties Handbook, New Edition*, 23-25, Yokendo (2008) (in Japanese).
[5] http://www.nist.gov/srm/
[6] http://www.nist.gov/srd/
[7] http://irmm.jrc.ec.europa.eu/reference_materials_catalogue/Pages/index.aspx
[8] http://www.iajapan.nite.go.jp/jcss/outline/index.html
[9] M. Akoshima: Development of thermal diffusivity standard of solid materials, *Measurement Standards and Metrology Management*, 59 (2), 23-29 (2009) (in Japanese).
[10] http://www.springermaterials.com/navigation/
[11] National Research Council: International Critical Tables of Numerical Data, *Physics, Chemistry and Technology Vol. 1-7*, U.S. (1929).
[12] D. R. Lide Jr.: Critical data for critical needs, Science, 212 (4501), 1343-1349 (1981). DOI:10.1126/science.212.4501.1343
[13] Y. S. Touloukian and C. Y. Ho eds.: *Thermophysical Properties of Matter; TPRC Data Series*, 1970-1972, IFI-Plenum, New York (1970).
[14] https://cindasdata.com/
[15] A. Ono, T. Baba and K. Fujii: Traceable measurements and data of thermophysical properties for solid materials: a review, *Meas. Sci. Technol.*, 12 (12), 2023-2030 (2001).
[16] T. Baba: Measurements and data of thermophysical properties traceable to a metrological standard, *Metrologia*, 47 (2), S143-S155 (2010). DOI:10.1088/0026-1394/47/2/S12
[17] Joint Meeting of the Industrial Structure Council and the Japanese Industrial Standards Committee: *Interim Report Compiled by the Special Committee on Measurement Standards and Intellectual Infrastructure –Promotion of the Program to Develop and Promote the Utilization of Intellectual Infrastructure–*, 49 (2012) (in Japanese). http://www.meti.go.jp/press/2012/08/20120815002/20120815002-3.pdf

[18] T. Baba and Y. Yamashita: Development of a network database system for thermophysical property data, *Measurement Standards and Metrology Management*, 59 (2), 49-57 (2009) (in Japanese).

[19] W. J. Parker, R. J. Jenkins, C. P. Butler and G. L. Abbott: Flash method of determining thermal diffusivity, heat capacity, and thermal conductivity, *J. Appl. Phys*., 32 (9), 1679-1684 (1961).

[20] Y. Nagasaka and T. Baba: Optical measurement technology of solid thermophysical properties, *Progress in Heat Transfer, New Series*, 3, Chap. 3, 163-226, Yokendo, (2000) (in Japanese).

[21] A. Cezairliyan, T. Baba and R. Taylor: A high-temperature laser-pulse thermal diffusivity apparatus, *Int. J. Thermophys*., 15 (2), 317-341 (1994).

[22] T. Baba and A. Ono: Improvement of the laser flash method to reduce uncertainty in thermal diffusivity measurements, *Meas. Sci. Technol*., 12 (12), 2046-2057 (2001). PII: S0957-0233 (01) 27342-1

[23] T. Baba, M. Kobayashi, A. Ono, J. H. Hong and M. M. Suliyanti: Experimental investigation of the nonuniform heating effect in laser flash thermal diffusivity measurements, *Thermochim. Acta*, 218, 329-339 (1993).

[24] M. Kobayashi, T. Baba and A. Ono: Infrared radiation thermometer for laser flash thermal diffusivity measurements, *Japan Journal of Thermophysical Properties*, 8 (3), 143-148 (1994) (in Japanese).

[25] M. Ogawa, K. Mukai, T. Fukui and T. Baba: The development of a thermal diffusivity reference material using alumina, *Meas. Sci. Technol*., 12 (12), 2058-2063 (2001). DOI:10.1088/0957-0233/12/12/305

[26] M. Akoshima and T. Baba: Study on a thermal-diffusivity standard for laser flash method measurements, *Int. J. Thermophys*., 27 (4), 1189-1203 (2006).

[27] M. Akoshima, B. Hay, M. Neda and M. Grelard: Experimental verification to obtain intrinsic thermal diffusivity by laser-flash method, *Int. J. Thermophys*., 34 (5), 778-791 (2013). DOI:10.1007/s10765-013-1470-7

[28] http://www.nmij.jp/service/

[29] T. Baba, K. Ehara, S. Yamada and K. Fujii: Achievement and future of physical property measurement and metrological statistics technology, *Measurement Standards and Metrology Management*, 60 (4), 2-9 (2011) (in Japanese).

[30] T. Baba, N. Yamada, N. Taketoshi, H. Watanabe, M. Akoshima, T. Yagi, H. Abe and Y. Yamashita: Research and development of metrological standards for thermophysical properties of solids in the National Metrology Institute of Japan, *High Temperatures-High Pressures*, 39 (4), 279-306 (2010).

[31] N. Taketoshi, T. Yagi and T. Baba: Current activity of thin film thermal diffusivity standard using pulsed light heating thermoreflectance method, *Measurement Standards and Metrology Management*, 59 (2), 36-41 (2009) (in Japanese).

[32] T. Yagi, N. Taketoshi and T. Baba: Thermophysical property measurement and standard of thin films: Standard thin film for thermal expansion time, *Measurement Standards and Metrology Management*, 59 (2), 42-48 (2009) (in Japanese).

[33] ISO/IEC 17025 1999 General requirements for the competence of testing and calibration laboratories.

[34] M. Akoshima and T. Baba: Thermal diffusivity measurements of candidate reference materials by the laser flash method, *Int. J. Thermophys*., 26 (1), 151-163 (2005).

[35] M. Akoshima and T. Baba: Laser flash thermal diffusivity measurements of isotropic graphite and glass-like carbon, *Thermal conductivity*, 28, 497-506 (2006).

[36] ISO Guide 34:2009 General requirements for the competence of reference material producers.

[37] Mutual recognition of national measurement standards and of calibration and measurement certificates issued by national metrology institutes, BIPM (1999).

[38] http://kcdb.bipm.org/

[39] http://www.bipm.org/en/committees/cc/cct/

[40] http://www.apmpweb.org/

[41] http://www.bipm.org/en/committees/cc/cct/tor_wg9.html

[42] M. Akoshima, B. Hay, J. Zhang, L. Chapman and T. Baba: International comparison on thermal diffusivity measurement using laser flash method - preliminary results, *Thermal Conductivity*, 30, 367-377 (2010).

[43] M. Akoshima, B. Hay, J. Zhang, L. Chapman and T. Baba: International comparison on thermal-diffusivity measurements for iron and isotropic graphite using the laser flash method in CCT-WG9, *Int. J. Thermophys*., 34 (5), 763-777 (2013). DOI:10.1007/s10765-012-1209-x

[44] JIS H7801 Method for measuring thermal diffusivity of metals by the laser flash method (established 2005).

[45] JIS R1667 Determination of thermal diffusivity of continuous fiber-reinforced ceramic matrix composites by the laser flash method (established 2005).

[46] ISO 18755:2005 Fine ceramics (advanced ceramics, advanced technical ceramics) - Determination of thermal diffusivity of monolithic ceramics by laser flash method.

[47] JIS R1611 Measurement methods of thermal diffusivity, specific heat capacity, and thermal conductivity of fine ceramics by flash method (established 1991, modified 2010).

[48] T. Baba: Introduction of a response function method for analysis of functionally gradient materials, *Japan Journal of Thermophysical Properties*, 7 (1), 14-19 (1993) (in Japanese).

[49] T. Baba and N. Taketoshi: Analysis of thermal diffusion in multi-layer thin films by a response function method, *Proc. of Eurotherm*., 57, 285-292 (1999).

[50] T. Baba: Analysis of one-dimensional heat diffusion after light pulse heating by the response function method, *Jpn. J. Appl. Phys*., 48, 05EB04. 1-05EB04.9 (2009).

[51] http://www.netsubussei.jp/

[52] http://www.jstage.jst.go.jp/browse/jjtp/-char/ja

[53] Japan Society of Thermophysical Properties (ed.): *Thermophysical Properties Handbook, First Edition*, Yokendo (1990) (in Japanese).

[54] http://www8.cao.go.jp/cstp/kihonkeikaku/index4.html

[55] http://www.meti.go.jp/report/committee/data/g_commi03_01.html

[56] Evolving Needs for Metrology in Trade, Industry and Society and the Role of BIPM, edited R. Kaarls, (2007) http://www. bipm.org/utils/en/pdf/Kaarls2007.pdf

[57] http://www.bipm.org/en/committees/cc/ccqm/

[58] http://www.vamas.org/index.html

[59] S. Bennett and G. D. Sims: Evolving Needs for Metrology in Material Property Measurements, *Report of the CIPM ad hoc Working Group on Materials Metrology (WGMM)*, (2007).

[60] S. Bennett and J. Valdés: Special issue for materials metrology: *Metrologia*, 47 (2) (2010). DOI:10.1088/0026-1394/47/2/E01

[61] http://www.bipm.org/en/committees/cc/cct/working_groups.html#wg9

[62] R. G. Munro: Data Evaluation Theory and Practice for Materials Properties: *NIST Recommended Practice Guide*, SP 960-11, U.S. Government Printing Office, Washington (2003).

[63] http://www.mext.go.jp/a_menu/kagaku/chousei/data/14/

hyoka030129/2/40.pdf
[64] http://tpds.db.aist.go.jp/
[65] T. Baba, Y. Yamashita and A. Nagashima: Function sharing and systematic collaboration between a networking database system and printed media on thermophysical properties data, *J. Chem. Eng. Data*, 54, 2745-57 (2009).
[66] Y. Yamashita, T. Yagi and T. Baba: Development of network database system for thermophysical property data of thin films, *Jpn. J. Appl. Phys.*, 50 (13) 11RH03 (2011).

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Completed the doctorate course at Graduate School of Science of the University of Tokyo in 1979 (Doctor of Science). Joined the National Research Laboratory of Metrology, Agency of Industrial Science and Technology, Ministry of International Trade and Industry in 1980. Visiting Researcher, National Institute of Standards and Technology, USA from 1986 to 1988. Chief, Thermophysical Property Section, Physical Property Statistics Division, National Metrology Institute of Japan, AIST in 2001. Chairman, Working Group 9, Thermophysical Quantities, Consultative Committee for Thermal Metrology, Comité International des Poids et Mesures (CIPM) from 2005 to 2014. Prime Senior Researcher, National Metrology Institute of Japan, AIST from 2007 to 2012. President of Japan Society of Thermophysical Properties in 2011. Engaged in the research of measurement technology, metrological standards, and reference materials for thermal quantities and the development of thermophysical quantity database. Received the Thermal Conductivity Award in 1999; Ichimura Award for distinguished accomplishment in science in 2000; Commendation for Science and Technology in Research by the Minister of Education, Culture, Sports, Science and Technology in 2005; and Significant Contribution Award of the Asian Thermophysical Properties Conference in 2013. In this paper, led the entire project.

Megumi AKOSHIMA

Completed the doctoral course at the Department of Applied Physics, Graduate School of Engineering, Tohoku University in 2000. Ph.D.(Engineering). Research Fellow (DC) of the Japan Society for the Promotion of Science from January 1999 to March 2001. Joined AIST in 2001. Appointed to the Thermophysical Property Standard Lab, Physical Property Statistics Division (currently Material Physical Property Division), National Metrology Institute of Japan. Since joining AIST, engaged in the research for the thermal diffusivity measurement of solid materials. Established the method for determining the intrinsic thermal diffusivity of materials that are SI traceable using thermal diffusivity measurement using the laser flash method. Receives subcontract testing and provides reference materials. Recently, involved in the CCT WG9 and APMP TCT as the organizer for the international comparisons of thermal diffusivity. In this paper, was in charge of the development and standardization of the measurement technology, metrological standard, and reference materials of thermal diffusivity, as well as the international comparisons.

Discussions with Reviewers

1 Overall evaluation

Comment (Akira Ono, AIST)

This paper is a description of excellent synthetic research with a goal to build a whole system that allows efficient production and effective use of thermophysical properties of solid materials in society. I am impressed with the grand scale of the research goal and the practical scenario to realize such a goal that invites the involvement of multiple stakeholders.

2 Situation of thermophysical property research in the USA

Question (Akira Ono)

In subchapter 3.2, the authors look back at the thermophysical property research in the United States from the 1960s to 70s, and you mention that the collaboration between the thermophysical property reference materials of the National Bureau of Standards (NBS) and the data evaluation of the Thermophysical Property Research Center (TPRC) at Purdue University was not quite sufficient.

At the time, thermophysical property research was very active in the US, and the results contributed to various technological fields. Are the authors saying that even though the reference materials were used widely in society and consequently many good thermophysical property data were produced, there was not enough time for them to be reflected in the Purdue University data book? What were the points that constrained the thermophysical property research in the US?

Also, please give the authors' opinion on what motivation or scenario could have been shared between the NBS and Purdue University to encourage their better collaboration?

Answer (Tetsuya Baba)

The "data evaluation" at Purdue University TPRC was conducted before the concept of measurement traceability and uncertainty prevailed over science and technology. Therefore, rather than evaluating data from the traceability of measurement, the reported data were overviewed as a whole, and evaluation was done individually based on the knowledge of the evaluator on physical properties and the reputation of the institution that conducted the measurement.

Development of thermophysical property reference materials at NBS was started slightly later than the data evaluation at TPRC, and most data in TPRC data series have been published in the latter half of the 1970s. Unfortunately, there has been no comprehensive revision of the thermophysical property data book of TPRC or its succeeding institution CINDAS.

If Purdue University had enough time to recognize the importance of the "uncertainty and traceability of measurement" in its data evaluation, it could have created reference information from the data obtained using a measurement apparatus calibrated by NBS reference materials, and could have developed a general data evaluation method based on measurement uncertainty, by introducing the viewpoint of evaluating the reliability of other general data using the reference information.

3 Maintaining traceability by information

Question & Comment (Akira Ono)

In chapter 4, the authors mention that in the field of material standards, there may be possibility that the traceability can be maintained only by information, without depending on artifacts such as standards or reference materials. This is a flexible idea about traceability unheard of before, and I hope the authors proceed with it.

(1) Specifically, with which materials is it possible to maintain the traceability only by information? Do you think thermophysical property of single crystal silicon is a candidate?

(2) I think the idea of maintaining the traceability only by information is not widely accepted by the metrological community at the moment. Can the authors introduce typical examples, such as how the uncertainty (variation and bias) of measurement results is evaluated when the traceability is maintained only by information. If the authors have any thoughts on how this idea can be widely accepted, please state them.

Answer (Tetsuya Baba)

(1) The thermophysical quantity data of water in liquid and gas phase can be supplied as universal data with evaluated uncertainty as long as the compositions (amount of impurities and isotope composition ratio are considered as needed) are specified and the measurement traceability is maintained. For example, for temperature scale, the triple point of pure water with the isotope composition of Vienna Standard Mean Ocean Water (VSMOW), which is a reference material of the International Atomic Energy Agency (IAEA), can be realized universally without the calibration by a higher level standard. For the viscosity standard, the viscosity of distilled water at 20 °C at atmospheric pressure as designated by ISO/TR3666:1998(E) comprises the primary standard.

For specific heat capacity and thermal expansion, the silicon single crystal of a certain lot is stored at NMIJ, their homogeneities are evaluated, valuation is done using the national standard, and these are provided as reference materials. As the next step, the possibility of providing the standard data for specific heat capacity and thermal expansion of silicon single crystal with better purity than the designated one can be provided as information without depending on artifacts. Also, for silicon single crystal, we think it is possible to provide the standard data for thermal diffusivity without depending on artifacts, as described in this paper.

Complimentary to the abovementioned efforts on the provision of national metrological standards, aluminum oxide can be mentioned as a reference material for specific heat capacity, as the de facto standard born from the demand of the users and instrument manufacturers. As a reference material for enthalpy and specific heat capacity, NIST provides “Enthalpy and Heat-Capacity Standard Reference Material: Synthetic Sapphire” (Alpha-Al_2O_3) which is provided in a thin columnar shape. Since disk shaped specimens are commonly used for differential scanning calorimetry (DSC), this NIST CRM is not appropriate for DSC, and the general practice is to use the commercially available highly pure alumina of a disk shape. There has been no systematic investigation of the information about the variation in specific heat capacity of the alumina from a random lot produced by the same manufacturer or different manufactures yet. This would be of an issue for investigation in the future.

(2) In order for the idea that traceability can be maintained with information only to be accepted by the metrological community, first, it is necessary to prove that the values are consistent with the results of the measurements traceable to the national standard. Second, it is essential to clearly characterize materials and substances that correspond to the information. For gas and liquid, substances can be quantitatively defined by composition, but for solids, the methodology to quantitatively describe the structures of different hierarchy of micro, meso, and macro scales has not been established yet.

Today, a vast amount of digital information is produced, shared on the web, and analyzed and utilized. How to evaluate and guarantee the reliability and credibility of such data is the most basic and most difficult problem. Among various data, the reliability and credibility of the quantitative data of the measurement apparatus including sensors can be expressed as uncertainty, and we believe the realization of “traceability of information” is a promising approach.

4 Standardization of the uncertainty evaluation procedure

Question & Comment (Akira Ono)

In subchapter 5.4, the authors state that the calibration/validation method and uncertainty evaluation method of measurement data using thermal diffusivity reference materials were standardized in JIS R1611. I think this is a wonderful achievement and should be highly evaluated.

Now please explain briefly yet specifically, how the authors standardized the procedure of the uncertainty evaluation method in JIS R1611.

Also, I expect that this movement will spread to the standardization of measurement methods of physical properties other than thermal diffusivity as well as to standardization of general test and evaluation method. What would be the point in enabling this spread in the future?

Answer (Megumi Akoshima)

The explanation of the evaluation procedure for uncertainty was added in the 2010 revision of JIS R1611 “Measurement methods of thermal diffusivity, specific heat capacity, and thermal conductivity for fine ceramics by flash method.”

Specifically, the following appendices were added in this revision.

Appendix E: Reference data and reference materials of thermal diffusivity

Appendix JB: Calibration/validation using reference specimen and correction of the measurement result

Appendix JD: Uncertainty evaluation of thermal diffusivity

Appendix JC: Evaluation method for the effect of coating for thermal diffusivity measurement by flash method

With the measurement of thermal diffusivity by the flash method, there are cases in which calibration or correction is done using the reference specimens shown in Appendix JB, and cases in which absolute measurement is taken for heat diffusion time without the reference specimen, and the method for evaluating the uncertainty in both cases are shown in Appendix JD.

When the specimen is transparent, or in a case where the absorption of flash heating light of the specimen or the radiation at the radiation thermometry wavelength are not sufficiently high, black, opaque thin film is applied on both surfaces of the specimen. The presence of this thin film increases the heat diffusion time more than an untreated specimen. The method for evaluating and correcting the increase is described in Appendix JC.

As an assumption for determining the uncertainty evaluation method for the measurement data and the calibration/validation method in the measurement of physical quantities, I think the physical quantities must be intrinsic quantities of the materials that do not depend on the measurement method.

In a case of quantity dependence on the measurement method (procedural quantity), even if the same material is measured, the measured value may differ depending on the measurement method.

In JIS R1611, the uncertainty evaluation method is much more effective because it explains in the standard the measurement method including the method for verifying whether the measured thermal diffusivity is an intrinsic quantity.

To spread the calibration/validation method and the uncertainty evaluation method of the measured data, I think the points are to systematically work on the development of precise measurement technology indicated in this paper, the organization of metrological standards and reference materials, and the standardization of the measurement methods.

5 Importance of the triangle set of efforts

Question & Comment (Akira Ono)

In subchapter 5.4 and chapter 6, the authors state that the root of the social system for production and utilization of the thermophysical property data is the “organization of the metrological standards and reference materials,” “standardization of the measurement method,” and “development and popularization of practical measurement apparatus.” I expect that such efforts will occur in fields other than thermophysical quantities as well in the future. What were the factors that led to such efforts in the field of thermophysical properties? I think it will be useful for people of other fields if the authors, who were directly involved, provide comments.

Answer (Tetsuya Baba)

In the basic quantities such as length or temperature, there are several digits of differences in precision between the metrological standards and the practical measurements, and the technologies used for metrological standards are usually quite different from the technologies of practical measurements. In this paper, approach of organizing the national standard for thermal diffusivity by the laser flash method was chosen since it was widely used as the practical measurement technology, and therefore, the result of the technological development contributed to both the metrological standard and the practical measurement technology. Moreover, the developed elemental technologies, the achievement of high precision of practical measurement technology through their systemization, and the realization of traceability to the national standard through the developed reference materials were reflected in the standardization of the measurement technology.

Such an approach is employed in the technology for applying the ultra high-speed laser flash method to thin films, and a similar triangle set of a social system is being organized.

I expect similar approaches can be applied to the social system not only for thermophysical quantities, but also to the production and utilization of data for mechanical electrical, magnetic, and optical quantities.

6 Expectations for the stakeholders in the development of a social system

Question & Comment (Akira Ono)

Figure 1 shows the research scenario for developing a social system where the thermophysical property data are efficiently produced and effectively used. Currently, the authors have the skeleton of this social system, and I think the content will be filled in gradually along with the strengthening of the skeleton.

For this system to become established in society, I think there are many roles expected from the various stakeholders of thermophysical properties (such as universities, public research institutions, material manufacturers, material users, and standardization organizations). What activities do the authors expect from the stakeholders?

Answer (Tetsuya Baba)

For the manufacturers of measurement apparatus for thermophysical quantities, I expect them to widely provide to society the thermophysical quantity measurement apparatus for which the uncertainty of measurement has been objectively guaranteed and is traceable through the reference materials and standards.

For the universities and academic societies, I hope they will discover new approaches for evaluating the thermophysical quantity data that continue to increase with the advances in measurement technology, utilizing the advancements in traceability, uncertainty evaluation, and information technologies.

For public research institutions, I expect them to collect and evaluate the thermophysical quantity data of their field of specialty, in a systematic and continuous manner. For example, I expect that AIST will be involved in the thermophysical quantity data for energy or electronics related materials. Likewise I expect that the Japan Atomic Energy Agency will be handling the thermophysical quantity data needed for nuclear industry and research.

The material manufacturers can make measurements of thermophysical quantity values using the measurement technology traceable to the metrological standards, and provide these data along with the uncertainty of measurement. Also, indication of the variation of thermophysical quantity values for all material products that they supply would be useful.

The material users can discover materials with overall properties (including thermophysical quantities) needed to advance products or innovation through our social system. If the existing materials cannot fulfill the overall properties, AIST shall serve as an information hub for passing on the demand for a material that may fulfill the necessary overall properties to the material manufacturers.

National standards of length for high-capacity optical fiber communication systems

— Development of fiber-based optical frequency combs —

Hajime INABA*, Atsushi ONAE and Feng-Lei HONG

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An optical frequency comb is a collection of laser modes with identical frequency intervals in the visible to near-infrared regions that enables direct comparison of optical frequencies with microwave atomic frequency standards. Traditional solid-state laser-based frequency comb systems are large, expensive, and very difficult to operate for long periods of time during experiments. From an early stage of development, we proposed fiber lasers as a feasible means of achieving a reliable frequency comb. After we succeeded in developing an in-house fiber-based frequency comb at the National Institute of Advanced Industrial Science and Technology (AIST), we made further advances, including calibration of the optical telecommunication band, establishment of national standards of length, and development of a narrow-linewidth comb for optical lattice clocks.

Keywords : Optical frequency comb, fiber-based frequency comb, optical frequency measurement, length standard, optical telecommunication band, wavelength-stabilized lasers

1 Introduction

Before the invention of the optical frequency comb, frequency measurement in the optical domain was extremely difficult. Requiring a number of microwave oscillators, special frequency multipliers/mixers, and wavelength or frequency-stabilized lasers (hereinafter referred to as “stabilized lasers”) as measuring devices, the “frequency chain,”[1][2] which linked with frequency in the optical domain after repeatedly multiplying and mixing in sequence, was based on 9 192 631 770 Hz, the microwave frequencies generated from the cesium atomic frequency standard. The extremely extensive measuring equipment required not only development but also enormous costs and human resources. In addition, this equipment could only measure the frequency of a single laser, which meant that lasers with different wavelengths required different frequency chains to be constructed.

Under these circumstances, the International Committee for Weights and Measures (CIPM) prepared a list of frequency-stabilized lasers based on the laser frequencies measured with frequency chains and recommended that they be used as wavelength standards (length standards) for the purpose of a practical metric realization.[3] Frequency-stabilized lasers developed in national metrology institutes of different nations are gathered to validate their equivalence for the international comparison of frequencies (hereafter referred to as “international comparison”). The lasers compared internationally serve as the basis for the reference laser for length measurement in a nation. The most internationally compared laser is the 633 nm iodine-stabilized He-Ne laser. In Japan, the national standard of length had been the iodine-stabilized He-Ne laser kept by the National Institute of Advanced Industrial Science and Technology (AIST) until 2009.[4]

Frequency measurement in the optical domain has a number of applications other than the length standard, among which the most important field in a social context is optical fiber communications. In the 1990s, wavelength-division multiplexing began to increase communication capacity, and many specialists anticipate that precise optical frequency management is required in the near future. It was therefore necessary to add a stabilized laser in the 1.5-μm optical communication band as a frequency standard to the CIPM’s recommendation, and to develop the technology to measure laser frequency in the 1.5-μm band. In Japan, where the 633-nm iodine-stabilized He-Ne laser served as the national measurement standard, the 1.5-μm stabilized lasers needed to be traceable to the 633-nm national measurement standard.

It was in 1999 that the first breakthrough came in overcoming the difficulties in conventional optical frequency measurement using the frequency chain. German and American groups achieved absolute measurement of laser frequency using the “optical frequency comb” with a mode-locked laser,[5][6] which led to enormous technical innovations in this field. The optical frequency comb was a great success and enabled laser frequency to be measured to the accuracy of the cesium atomic frequency standard (11 to 16 digits depending on the mean time or oscillator types). The linkage of optical frequency with microwave frequency by means of the optical frequency comb

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(in a comparatively easy manner) gave great momentum to the study of the "optical clock" as a next-generation frequency standard to replace the cesium atomic clock. J. L. Hall and T. W Hänsch, who had been engaged in the invention of the optical frequency comb, were awarded the Nobel Prize for Physics in 2005 in recognition of their "contributions to the development of laser-based precision spectroscopy, including the optical frequency comb technique".

However, this does not mean that their invention solved all problems. To use the optical frequency comb as a practical tool in various applications, a second breakthrough is required to overcome problems in the photonic crystal fiber or the titanium-sapphire (Ti:S) laser, which was the mode-locked laser used for the optical frequency comb at that time. Large in size, the Ti:S laser requires an expensive and power-consuming pump laser. In addition, the complicated equipment needs an operator with technical knowledge for operation of the optical frequency comb. With difficulties in continuous operation over a long period of time, even in a laboratory environment, it still has a long way to go before it can be commercialized.

This study is related to the second breakthrough noted above and focuses on the development of a reliable optical-fiber frequency comb using an erbium-doped fiber-based mode-locked laser (hereinafter referred to as a "fiber comb") as an alternative to the conventional optical frequency comb using a mode-locked Ti:sapphire laser-based frequency comb (hereinafter referred to as a "Ti:S comb"). This paper begins with a brief explanation of the principles of the optical frequency comb and the problems of the Ti:S comb. It then provides an overview of using the fiber comb to solve these problems, as well as giving background of R&D including the fabrication of the comb. Furthermore, this paper describes frequency measurement of the optical communication band laser, national measurement standards for length including international activities, and a high-speed controllable frequency comb for next-generation optical frequency standards as achievements of this development.

2 Optical frequency comb

To understand the optical frequency comb, it is necessary to consider both waveforms on the time domain and spectra on the frequency domain. As shown in Fig. 1, the optical frequency comb observed in the time domain is the ultrashort optical pulse train, which consists of optical pulses each with durations between several and several hundreds of femtoseconds arranged at regular time intervals. In the frequency domain, in contrast, it is the Fourier transform of the optical frequency comb, and appears as an assembly of line spectra arranged at regular frequency intervals. The broadened spectra and mode spacings in the frequency domain represent the reciprocals of the optical pulse sharpness (duration) and interval time of the optical pulse train in the time domain, respectively. It is also possible to determine that each line spectrum on the frequency domain is continuous light and that their phases are synchronized to form optical pulses as a whole.

The most important characteristic of the optical frequency comb is that the frequency spacing of line spectra is consistent regardless of wavelength. For instance, the vertical modes of optical cavities represented by the Fabry–Perot cavity have spectra very similar to those of the optical frequency comb, although the free spectral range $c/2nL$ (where c stands for light speed, n for phase refractive index, and L for cavity length) varies with atmosphere or cavity dispersion (i.e., n varies by wavelength). In contrast, the mode spacing of the optical frequency comb is consistent regardless of wavelength, as it is produced at regular intervals as a result of mode synchronization. As shown in Fig. 1, the N-th comb mode

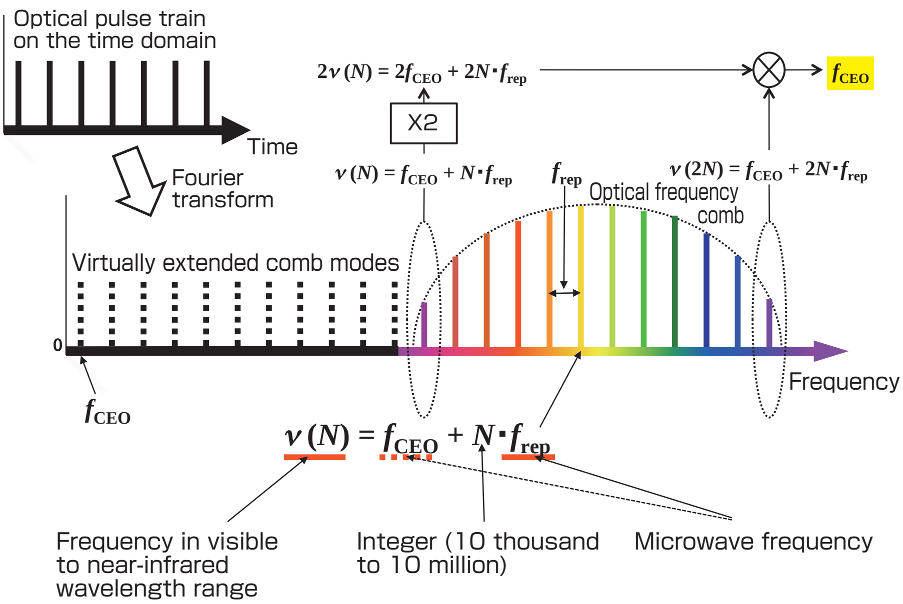

Fig. 1 Conceptual diagram of the optical frequency comb
The ultrashort optical pulse train observed in the time domain is Fourier-transformed and appears as the optical frequency comb in the frequency domain. With consistent mode spacing regardless of wavelength, it is appropriate to virtually extend the comb mode outside the actual comb mode. The radiofrequency f_{rep} is uniquely linked to the optical frequency $\nu(N)$. Furthermore, broadening the frequency comb by more than an octave facilitates detection of the f_{CEO} signal.

frequency $\nu(N)$, regarding f_{CEO} as the zeroth frequency, in the optical domain can thus be described as:

$$\nu(N) = f_{CEO} + N \cdot f_{rep}, \quad (1)$$

where f_{rep} represents the frequency spacing between adjacent comb modes, equal to a repetition frequency of the ultrashort optical pulse train in the time domain; N stands for an integer from several tens of thousands to several millions; and f_{CEO} stands for a uniform offset frequency of the optical frequency comb from $N \cdot f_{rep}$ of each mode. This equation indicates that the unique $\nu(N)$ between 180 and 600 THz (equivalent to the near-infrared to visible wavelength range) is determined by defining f_{CEO} and f_{rep} between several tens and several hundreds of MHz (hereinafter referred to as microwave frequency). In particular, it should be noted that the microwave frequency f_{rep} is multiplied by an integer and reaches a frequency in the optical frequency range. The optical frequency comb could thus be regarded as a frequency multiplier (or divider) that links microwave frequency with optical frequency.

Values for f_{CEO} are extremely small compared to an optical frequency of several hundreds of THz. However, f_{CEO} is an important parameter that links frequencies in the optical range to frequencies from atomic clocks in the microwave range. To detect f_{CEO}, the spectra of the optical frequency comb should be broadened by more than "an octave". Figure 1 shows how to observe f_{CEO}. The "octave-spanning comb" means that the N-th and $2N$-th modes simultaneously exist in the comb. The difference in frequency between the second harmonic of the N-th mode and the $2N$-th mode is equal to f_{CEO}, which is how f_{CEO} is observed in an experimental manner.

The output spectrum of the mode-locked laser is an optical frequency comb, but it is not generally broadened to an octave. In most cases, these optical spectra are broadened using the photonic crystal fiber or the highly nonlinear fiber. In doing so, the original comb mode is broadened by such nonlinear effects as self-phase modulation, four-wave mixing, and Raman amplification while maintaining frequency spacing. The "frequency ruler," with broadening to as much as an octave in the optical frequency range, is used in a number of applications including frequency metrology.

3 Problems of the optical frequency comb using the Ti:S laser and solutions using the fiber comb

The octave-spanning comb used a Ti:S laser as a mode-locked laser, and a photonic crystal fiber for broadening the spectrum in the initial stage. Although the Ti:S laser realized the octave-spanning comb and was a major success, serious problems remained in commercializing them. This section describes some important problems of Ti:S combs that need to be solved and how fiber combs solve these issues.

3.1 Large and expensive pump laser

Figure 2 shows a schematic view of the Ti:S comb. A high-power solid-state laser is used to excite the Ti:S laser. The typical, commercially available laser head and controller are comparatively large in size, as shown in the photo. The main units of the pump laser and Ti:S laser require water coolers. In addition, the 5–10-W pump laser used for the Ti:S laser for the optical frequency comb is expensive, and the consumables that need to be replaced periodically are also

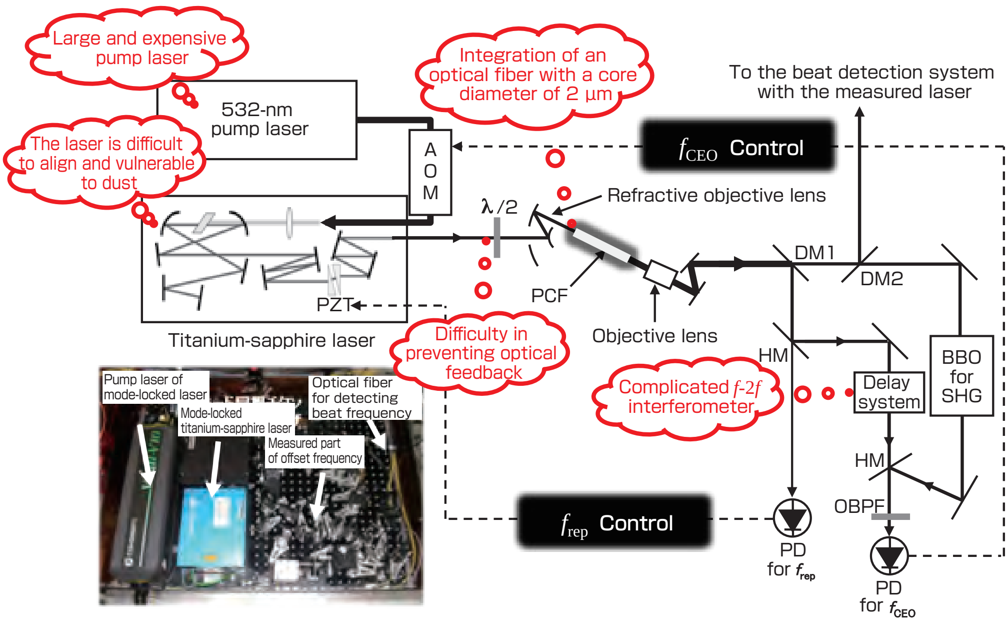

Fig. 2 Schematic view of the optical fiber comb system using the titanium-sapphire laser

The space optical system is hard to operate over a long period of time. The photo shows an example compact system. PZT: piezoelectric transducer; AOM: acousto-optic modulator; $\lambda/2$: 1/2-wavelength plate; PCF: photonic crystal fiber; DM: dichroic mirror; HM: half-transparent mirror; OBPF: optical bandpass filter; BBO: β barium borate crystal; SHG: second-harmonic generation; PD: photo detector.

expensive.

Figure 3 shows a schematic view of the fiber comb system, where the small semiconductor laser, which is incorporated into a butterfly package as shown in the bottom right photo, is used as a pump laser. The controller for the system is markedly smaller than that for the solid-state laser, which means that the entire system could be made much smaller than the Ti:S system. The price is less than a tenth of that for the solid-state laser used for exciting the Ti:S laser. The mode-locked fiber laser does not require water cooling.

3.2 Difficulties in long-term continuous operation

It is difficult to continuously operate the Ti:S comb over a long period of time. One of the reasons is instability of optical coupling to the photonic crystal fiber used for broadening the spectrum of the optical frequency comb. Since the core diameter of the photonic crystal fiber is as small as approximately 2 μm (while the core diameter of the regular single-mode fiber is approximately 10 μm), the relative positions of laser light and the fiber core are likely to fluctuate as a result of temperature changes or other factors. In addition, the beam orientation of a large pump laser and a Ti:S laser tends to be unstable. As a result, the coupling efficiency of laser light to the fiber changes over time, and the S/N ratios of the offset beat signal and beat signal with a continuous wave (CW) laser are reduced, which lead to a loss of control and/or frequency counting. Hardly resistant to dust, the Ti:S laser, acting as a space laser, attracts a very small quantity of dust around the high-optical intensity crystal, resulting in unstable operation. Therefore, optical frequency measurement with the Ti:S comb is unlikely to be feasible over 24 consecutive hours.

In the fiber comb system, the mode-locked fiber laser, the optical amplifier, and the highly nonlinear fiber consist of optical fiber systems, enabling fusion splices between fibers. This eliminates the need for precise alignment that is essential for the space optical system and allows all connections with a single optical fiber, which provides an almost complete solution to the abovementioned drawbacks of the Ti:S comb.

4 Fiber comb development

As mentioned above, the developed fiber comb displayed obvious advantages. We began with the “initial assessment of the fiber combs” to ensure that it was feasible. We then formulated the idea that robust and low-noise fiber combs may be self-fabricated if such fundamental technological goals as “design and fabrication of the mode-locked fiber lasers,” “design and fabrication of amplifiers,” “assessment of the highly nonlinear fibers,” and “development of the high-speed controllable frequency comb” are achieved. Successful self-fabrication can bring about an optical frequency comb that could achieve the aims of “calibration of laser frequency in the optical communication band,” “development of national measurement standards,” “applications to the optical

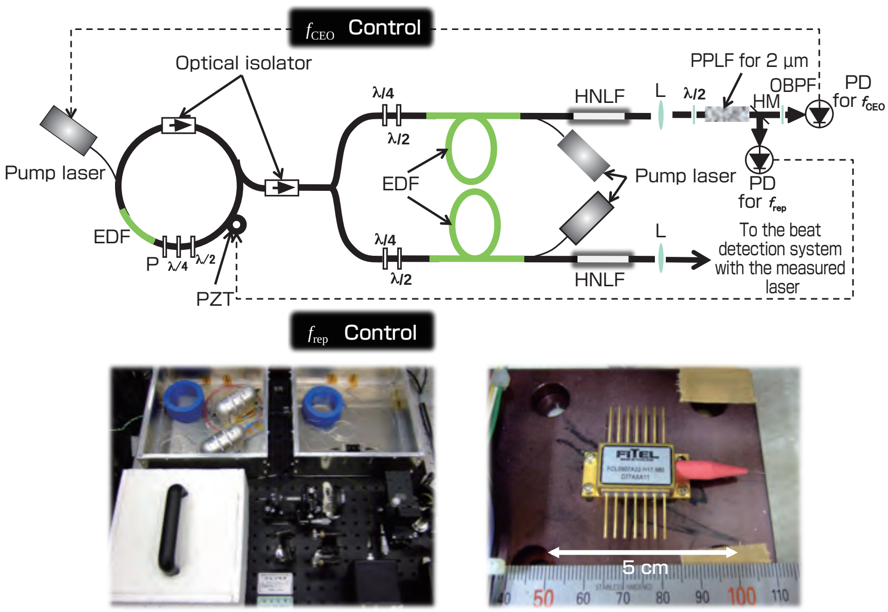

Fig. 3 Schematic view of the optical fiber comb system using the fiber laser

The fiber ring on the left is the mode-locked fiber laser that uses nonlinear polarization rotation as the mode-locking mechanism. The output is branched into two to four, each of which is amplified and/or broadened as required for use. All sections represent the optical fiber systems and enable continuous operation over a long period of time. The photos show the section between the laser and optical amplifier (right) and a pump laser (left) of the optical frequency comb system used as the national measurement standard. EDF: erbium-doped optical fiber; PZT: piezoelectric transducer; P: polarizer; $\lambda/2$: 1/2-wavelength plate; $\lambda/4$: 1/4-wavelength plate; HNLF: highly nonlinear fiber; L: lens; PPLN: periodically poled lithium niobate; HM: half-transparent mirror; OBPF: optical bandpass filter; PD: photo detector.

lattice clocks," and other objectives as well as technologies involved in their development. Furthermore, we want to transfer these research outcomes to companies or universities in order to ultimately contribute to the improved reliability of time-frequency and length standards (Fig. 4).

When we began the development of the fiber comb before 2000, however, we were not certain that the fiber comb could achieve a performance equivalent to that of the Ti:S comb. We in fact needed to undertake some research steps to develop a fiber comb that could replace the Ti:S comb. This section describes the process from joint research with a company in the early stages of development of the optical frequency comb, to the transfer to the framework to fabricate the overall system within AIST, and to the establishment of the fabrication techniques.

4.1 From offset beat detection to absolute frequency measurement — joint research with companies

The mode-locked Ti:S laser and mode-locked fiber laser oscillate in the 800-nm band and in the 1550-nm band (the optical communication band), respectively. The power and optical pulse duration of the Ti:S laser are 300–800 mW and 10–30 fs, respectively, while those of the fiber laser are around 1–10 mW and 100 fs. It is necessary to find the conditions for broadening the spectra of those pulses with significantly different properties. The Ti:S laser uses a photonic crystal fiber with zero-dispersion wavelength around an 800-nm band for broadening, which cannot be directly applied to the fiber laser oscillating in the 1.5-μm band. The company that engaged in joint research (1999–2004) provided AIST with a state-of-the-art and reliable mode-locked fiber lasers, winning the world's leading market share. We achieved the world's first frequency measurement using a mode-locked fiber laser, including a frequency link[9] between the 778-nm and 1556-nm bands.

We further aimed to detect the f_{CEO} signal by broadening the second harmonic of this laser by means of the photonic crystal fiber. Although the use of a photonic crystal fiber does not even broaden the spectrum of the comb to less than an octave, we use a longer fiber for the Ti:S laser. We successfully observed the f_{CEO} signal of the fiber comb for the first time in the world by using a new self-referencing method,[10] in which the optical frequency comb components broadened by the photonic crystal fiber interfered with the third harmonic of the laser in the 520-nm band. Shortly after, the octave-spanning optical frequency comb was achieved by the highly nonlinear fiber with a zero-dispersion wavelength in the 1.5-μm band. We also developed the control and other systems in collaboration with the company and successfully performed an absolute frequency measurement of the stabilized laser using the fiber comb for the first time in the world.[11]

4.2 From transfer to self-fabrication to long-term continuous operation

Once absolute frequency measurement became feasible by means of the fiber comb, the consequent requirement was the ability to "customize specifications according to purposes or applications" or "provide multiple sets of equipment for different applications." To this end, we reached the conclusion that it would be quicker and easier to assemble parts on our own rather than receiving laser systems from a company. Fortunately being used in the major industrial area of optical communication, fiber and optical parts for the 1550-nm band are often both affordable and outstanding. Prior to our commitment to research into combs, we engaged

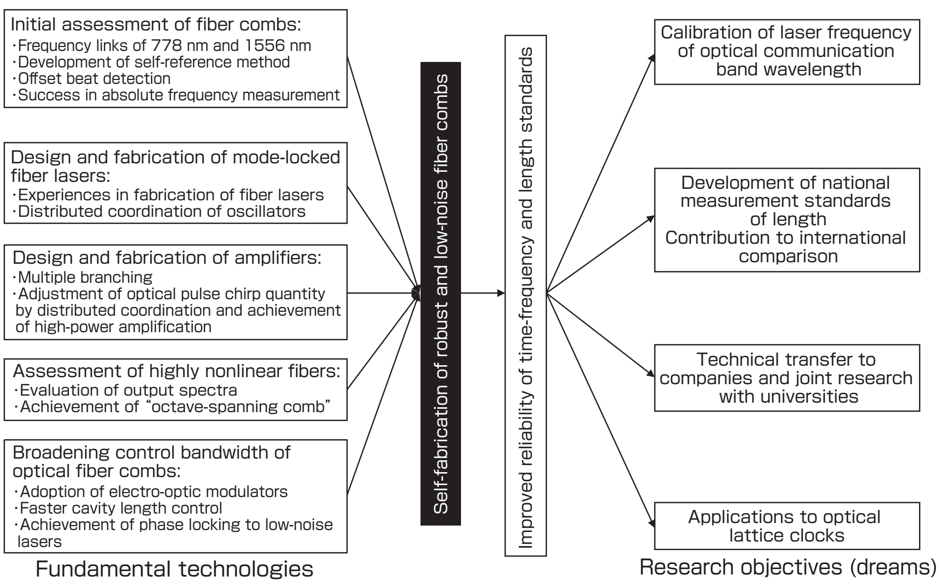

Fig. 4 Scenarios from fundamental technologies for self-fabrication of fiber combs to research objectives

in R&D of a CW fiber laser, during which we obtained technical findings on the fiber optical system. This led us to the next objective of fabricating the fiber comb system in-house (hereinafter referred to as self-fabrication).

Around the end of 2004 when we launched the self-fabrication effort, we aimed to establish a simple and robust structure, eliminating any mechanisms unnecessary for the purposes or applications and facilitating fabrication, based on the abovementioned demands. For instance, the use of saturable absorbers or other special devices that were hardly available was avoided and the mode-locking mechanism was changed to a nonlinear polarization rotation to make up the structure, eliminating the space optical system to the maximum possible extent and focusing on fibers. However, the first attempt to fabricate a mode-locked laser on our own did not go well. During the same period, the highly nonlinear fiber with the best possible performance (even to this date) functioning in the 1–2 μm range was available as a key to broaden the comb.

With this basis, we successfully designed and fabricated a mode-locked fiber laser and an ultrashort optical pulse amplifier, broadened the optical frequency comb by means of the highly nonlinear fiber, detected the offset frequency signal, arranged and fixed the fiber system to ensure robustness, and finally constructed the control system for phase lock or temperature control, as early as about a year from the beginning of the self-fabrication effort. In the beginning of 2006, we achieved optical frequency measurement[12] for a full consecutive week, a long-term measurement that had never previously been reported with the Ti:S comb or even with the fiber comb. This robustness has been accounted for using our unique laser systems, including the replacement of all components of the mode-locked fiber laser by fibers, the branching structure (Fig. 3) of the optical amplifier section used to gain the S/N ratio of a high beat signal, and the selection of the highly nonlinear fiber optimal for generating the optical frequency comb of the intended wavelength. These are the achievements of the self-fabrication effort.

Long-term continuous measurement soon brought about some practical findings. We have developed iodine-stabilized Nd:YAG lasers in the 532-nm band with high frequency stability and outstanding robustness.[13] A gradual decrease in the frequency of one of the several lasers we kept was observed through long-term measurement (Fig. 5, top). The long-term continuous measurement using the fiber comb observed a reduction in frequency at the same pace (about −20 Hz per week) (Fig. 5, bottom) and revealed that the frequency changes were not intermittent but continuous.[12] This method of long-term continuous measurement allows us to observe phenomena we could not previously see. In the application to optical frequency standards that will be put to practical use, continuously measurable robustness is also one of the vitally required features.

4.3 Importance of dispersion adjustment — establishing fabrication techniques

Although the first self-fabricated fiber comb system was completed and was successful in continuous measurement, there were problems in the poor reproducibility of power or spectra from the ultrashort optical pulse amplifiers or in broadening by the highly nonlinear fiber in the subsequent processes of fabricating several mode-locked fiber lasers (oscillators) and ultrashort optical pulse amplifiers. Examining the polarization dependency or the mean and peak powers entering the optical pulse amplifier revealed that these problems were caused by a difference in the chirp quantities of optical pulses arising from dispersion of optical fibers linking the oscillators with the amplifiers.

While it was well known that dispersion adjustments of the oscillator, and of the optical path between the amplifier and highly nonlinear fiber were necessary, the importance of the dispersion adjustment of the optical path between the oscillator and amplifier was not well known. The results of past experiments only reported the chirped pulse amplification method,[14] in which optical pulses were significantly chirped on either the positive or negative side before the amplifier in order to reduce their peak power for amplification, followed by chirping on the other side in order to compress the pulses. We determined the ideal length of optical fiber between the oscillator and amplifier required to maximize the mean power from the amplifier and to change the chirp quantity of optical pulses entering the amplifier (Figure 6).[15] Under these conditions, optical pulses are amplified while being compressed by chirp compensation in order to obtain high optical pulse peak power, narrow

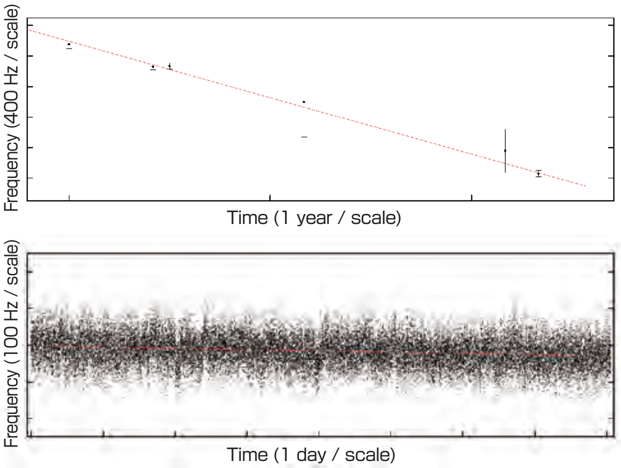

Fig. 5 Frequency changes of our iodine-stabilized Nd:YAG laser in the 532-nm band

Results of intermittent measurements with the Ti:S comb for 2.5 years (top) and a consecutive week of measurement with the fiber comb (bottom). Both results show a rate of change of about −20 Hz per week.

optical pulse duration, wide spectrum, and high average power. These are consistent with the conditions described as “adiabatic compression” in a report on broadened spectra in 1990;[16] however, it was not known that they were associated with an increase in average power. The reason for this increased power remains unknown but it could be that a number of erbium ions with inhomogeneous broadening of gains can contribute to the optical pulse amplification, because the pulse spectrum is broadened, and thus resulting in high average power.

This study also revealed that the optical pulse amplified under these conditions is optimal for broadening the spectra by means of the highly nonlinear fiber and that they broaden more easily than optical pulses amplified under other conditions. This discovery significantly contributed to the improved reproducibility of power and spectra and established an important foundation for the subsequent “mass production” of fiber combs in laboratories. Furthermore, we applied for a patent on this method and equipment, which was then registered in January 2013 (Registration No.: 5182867).

4.4 Development of a high-speed controllable frequency comb — evolution to a sophisticated and practical optical frequency comb

The fiber comb was said to be practical and robust but had greater phase noise than the Ti:S comb, and an f_{CEO} signal with a relatively broad linewidth unique to the fiber comb has been observed.[10] While the spectral linewidth of f_{CEO} is 100 kHz or less for the Ti:S laser in free operation, it could be as large as several megahertz for the fiber comb, which was for a while discussed as the most remarkable defect of the fiber comb. It has been revealed that phase noise derives not from the optical pulse amplifier or the highly nonlinear fiber but from the mode-locked fiber laser (oscillator). The subsequent accumulation of knowledge regarding oscillator fabrication, including total dispersion of the cavity,[17] has elevated the fiber comb to an equivalent level to the Ti:S comb in terms of phase noise.

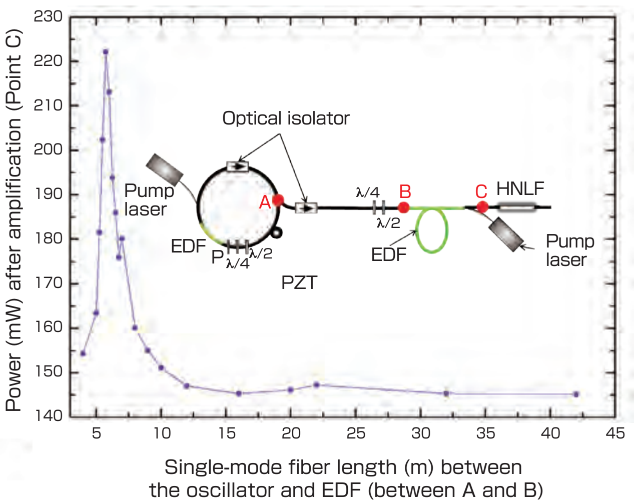

Fig. 6 Variation in average optical power at the optical amplifier section (Point C) when varying the length of the single-mode fiber (SMF) between the oscillator output (Point A) and optical amplifier input sections (Point B)
The length of SMF needed to maximize average power is the optimum value for generating the octave-spanning optical frequency comb.

The most important aspect that not only completely solves the problems of phase noise but also makes the fiber comb exceed the capability of the Ti:S comb is high-speed controllability. The frequency values of the optical frequency comb have two degrees of freedom. For example, an optical frequency measurement needs to control f_{rep} and f_{CEO} independently. In most cases, f_{CEO} is controlled by changing the pump power for the mode-locked laser while f_{rep} is controlled by changing the cavity length. While pump power is controllable at a relatively high speed with the Ti:S or fiber laser, cavity length is hard to control at a high speed. These lasers generally change their cavity length by moving the mirror or fiber with the piezoelectric transducer. However, the servo bandwidth in this case is limited to several hundred to several tens of kilohertz. When f_{rep} is phase-locked to the microwave frequency standard, the narrow servo bandwidth would be mostly unproblematic owing to the low carrier frequency and the small absolute quantity of the phase noise. Nevertheless, if one of the modes of the optical frequency comb is phase-locked to the optical frequency standard (a stabilized laser) by controlling cavity length, then the high carrier frequency results in a large absolute quantity of the phase noise, despite the same frequency stability, causing a shortage in gains and servo bandwidth of the cavity length control and difficulties in reducing phase noise. The relative spectral linewidth of the optical frequency comb will not be improved if much phase noise remains. The improvement of the relative spectral linewidth requires two parameters to be controlled at a high speed. We developed a high-speed controllable frequency comb with the electro-optic modulator (EOM) inserted into the cavity of the mode-locked fiber laser,[18] with which we achieved control to around the 1-MHz band for both lasers.[19] The mode-locked laser with the intra-cavity EOM has only been possible for fiber laser, which has been an advantage of the fiber comb.

4.5 Comparison with the conventional Ti:S comb or the fiber comb using Yb-added optical fibers

By employing the mode-locked fiber laser as the light source of the optical frequency comb, a number of defects in the conventional, mainstream Ti:S comb have been overcome through the developments stated in this section. The fiber comb that we have developed uses erbium (Er)-doped optical fiber with gains in the 1.5-µm band as the laser medium, while some other groups have developed fiber combs using ytterbium (Yb)-doped optical fiber with gains in the 1-µm band. Table 1 shows a list of features of the Ti:S comb, Er fiber comb, and Yb fiber comb.

Table 1. Characteristics of optical fiber combs depending on the types of mode-locked lasers

	Ti:S comb	Er fiber comb	Yb fiber comb
Output (mean power)	Up to 1 W	Up to 200 mW (after amplification)	Up to 10 W (after amplification)
Optical pulse width (typical value after chirp compensation)	Several femtoseconds	Several tens of femtoseconds	Several tens of femtoseconds
Wavelength (typical central wavelength of an oscillator)	780 nm	1550 nm	1030 nm
Wavelength range (typical value after broadening)	400–1200 nm	900–2500 nm	900–2500 nm or 700–1400 nm
Spectral linewidth of the CEO signal in free operation	Several tens of kHz to several MHz	Several tens of kHz to several MHz	Several tens of kHz to several MHz
Bandwidth control (cavity length)	Up to several tens of KHz	Up to several MHz	Up to several MHz
Pump laser	Mainly solid-state laser	Mainly semiconductor laser	Mainly semiconductor laser
Difficulty of long-term operation	Difficult (instability of free space optical system and pump laser)	Easy	Easy but free-space optical system is required for the cavity-dispersion compensation

A comparison of these three types of optical frequency comb shows that our Er fiber comb has advantages not for the performances of optical pulses in the time domain, including power and pulse width, but for the performances of the optical frequency comb in the frequency domain, like low noise (narrow spectral linewidth), reliability, and high-speed control.

As the Ti:S comb and Yb fiber comb have such advantages as high power, short wavelength, or narrow optical pulse width, these optical frequency combs would be the only solution to a number of applications in the ultraviolet region or those requiring high resolution in the time domain. However, as far as frequency metrology with a wavelength longer than the visible region is concerned, the Er fiber comb is the most sophisticated and practical.

5 Expanded fiber comb applications

The self-fabrication of fiber combs enabled us to select robust, easy-to-use, and sophisticated optical frequency comb systems according to the intended purposes. As was expected in the beginning, it was an inevitable result of developing optical frequency combs in research or business applications. Our group has already completed more than fifteen fiber comb systems. This section provides particularly important explanations of several topics, including the “calibration of the optical communication band wavelength laser,” “national measurement standards,” and “development of the high-speed controllable frequency comb.”

5.1 Frequency calibration of lasers in the optical communication band

The demand for increased transmission capacity in optical communication has been steady growing. Multiplexing the communication bandwidth and increasing the number of channels is effective for a greater transmission capacity. However, frequency management is required to set the communication channels, owing to the limited power to transmit through the single-mode fibers and to the limited range of wavelengths that are low in transmission loss. As a platform for this wavelength division multiplexing, the frequency grid (ITU-T G694.1) is available at 12.5 GHz, 25 GHz, 50 GHz, and 100 GHz intervals from 193.1 THz, which is the carrier frequency of the communication band C. The recent rapid development of digital coherence techniques (digital signal processing that has been used in the field of radio, applied to optical communication) has led to wavelength multiplexing up to near the theoretical limit of the transmission capacity of a single-mode fiber. For an application to the flexible grid (a channel at 6.25-GHz intervals), a reduction of uncertainty in the frequency management technology, including frequency measurement, would be increasingly important.

When manufacturers of optical measuring instruments or optical devices require 7 to 8-digit precision for optical spectrum analyzers or wavemeters, a laser stabilized to an absorption line of a molecule is used, which provides around 9-digit precision. We began developing the wavelength standards in the 1.5-μm band, foreseeing these needs before the optical frequency comb had become available. Our acetylene-stabilized laser with a 1542-nm wavelength[20] has been recommended as the only wavelength standard in the 1.5-μm band by the CIPM. Furthermore, laser frequency calibration in the 1510–1570-mm band became feasible by broadening the power of this laser by means of the side-band optical frequency comb.[21] Problems, however, still remained. First, calibrations by the stabilized laser and the side-band optical frequency comb required the international comparison of the stabilized laser itself as the reference frequency or calibration with the optical frequency comb. The national measurement standards for wavelength were the iodine-stabilized He-Ne laser with a wavelength of 633 nm, which could fall into a double standard. On the other hand, the optical frequency comb measures frequency (wavelength) based on the frequency standards and allows the wavelength in both the 633-nm and 1.5-μm bands to directly connect to the International System of Units (SI) without the use of the stabilized laser. It also facilitates the actions to be taken when traceability needs to be secured with different wavelengths in the future. Having said that, the initial Ti:S comb could broaden the spectral range by only 500–1100 nm and is not very applicable to the optical communication band wavelength. This is because the measured laser with CW light is less efficient in generating the second harmonic.

The fiber comb operates in the 1–2-μm band and covers all optical communication band wavelengths. Manufacturing such components as light sources or optical filters to cover further downsized and complicated communication grids requires wavemeters or optical spectrum analyzers of higher precision and, as the reference standards of these measuring instruments, stabilized lasers with different wavelengths in the optical communication band will be required. This bandwidth range contains a number of transitions preferred as wavelength standards for acetylene molecules or hydrogen cyanide molecules, which seems to indicate that the fiber comb is optimal for calibrating stabilized lasers of those transitions. In addition, the optical frequency comb uses optical pulses that are highly efficient in second-harmonic generation and is also applicable to the visible wavelength range. It is thus expected to replace the Ti:S comb.

5.2 National measurement standards of length

The traceability system for both wavelengths (633 nm and 1.5 μm) can be simplified if we set the atomic clock (frequency standard) and an optical frequency comb as the national measurement standards of length (Fig. 7), which can also achieve length standards faithful to the definition of the meter. The iodine-stabilized He-Ne laser with a 633-nm wavelength, which had been the conventional national measurement standard, is compact, has an uncertainty as low as 2.5×10^{-11}, and is complete as a length standard. However, some issues remain in using it as the national measurement standard. One is that, as a stabilized laser, it requires periodic calibration using the optical frequency comb or international comparison. Considering the possible fluctuations of frequency values after cavity alignment, group management of several equivalent units must also be carried out to ensure that each unit runs properly.

The secondary standards (i.e., devices directly calibrated by the national measurement standards) owned by accredited calibration laboratories are also iodine-stabilized He-Ne lasers with no difference in performance from the national measurement standards, which means that calibration results are not necessarily successful in properly evaluating the performances of the measured object. If the national measurement standards have the same uncertainty as the secondary standards, then the uncertainty of calibration results will be $\sqrt{2}$ times as much as each uncertainty. This means the uncertainty assumed to be equal to that of the national measurement standards would be underestimated.

To avoid such degradation, the uncertainty was regarded as being the same as that of the national measurement standards, assuming the secondary standards to be equivalent to the national measurement standards if the compared frequencies were found to be within the normal range. A comparison between iodine-stabilized He-Ne lasers employed a method of estimating the original frequency difference by measurement of a total of six differential frequencies by locking each laser at four absorption lines (a matrix method) as no measurement could be made where there was too small a difference in frequency. Calibration therefore required a great deal of time and effort. Furthermore, the iodine-stabilized He-Ne laser is sensitive to vibration and noise. The unit at AIST is reinforced against such vibration or noise but is still somewhat sensitive.

Our fiber comb solves all these problems. The reference frequency of the optical frequency comb represents the frequency standard in synchronization with the International Atomic Time (TAI), requiring no periodic calibration. Essentially, a defect in microwave frequency synthesis (included in the “f_{rep} control” in Fig. 3) would be the only possible cause for values to deviate, but this can also be detected during measurement, and therefore requires no group management. With an uncertainty 1/300th of the secondary standards, the calibration results almost completely show the performances of the device under test (DUT). This enables the frequency and uncertainty of calibration to be clearly provided in the calibration certificate. Also robust when locking, our fiber comb can facilitate operation for around one consecutive week, and calibration of the DUT only requires measurement of the frequency of the

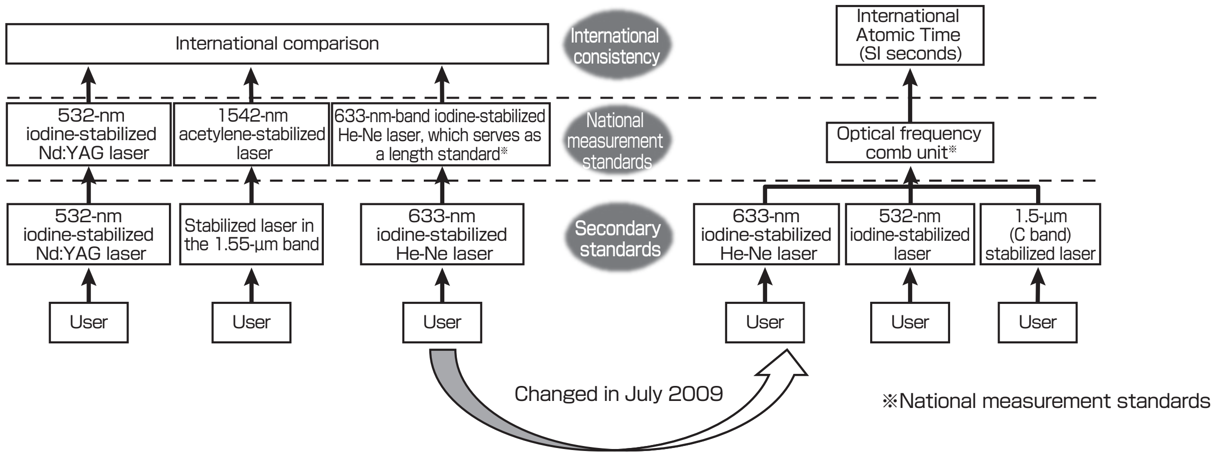

Fig. 7 Old and new traceability systems for length measurement (SI to secondary standards)
A simple traceability system has been achieved in all wavelength regions by setting the optical frequency comb as the national measurement standard.

laser locked at the appropriate absorption line, resulting in a significant reduction in time and effort. The calibration work that once took a few days is expected to be completed in half a day to a day since the change in the national measurement standards in July 2009.

5.3 International comparison of the frequency-stabilized laser

It is also important to verify international equivalence. National metrology institutes from different nations must gather their stabilized lasers for international comparison in order to verify their equivalence. In the 20th century, researchers from the International Bureau of Weights and Measures brought their portable iodine-stabilized He-Ne laser with them to different regions, where the frequency of their laser was compared with iodine-stabilized He-Ne lasers from other regions or nations. This is how the equivalence of iodine-stabilized He-Ne lasers around the world had formerly been verified.

However, a review of works by the International Bureau of Weights and Measures led to the launch of a new international comparison system (CCL-K11) for the stabilized laser in 2004, under which an international comparison came to be carried out by each grouping of national metrology institutes in each region. With a pilot laboratory to begin with, a “node laboratory” that leads the relevant region is set up for nine large or small groupings of national metrology institutes in different regions, including the Asia Pacific Metrology Programme (APMP). The node laboratory measures the frequency of the frequency-stabilized laser using the optical frequency comb on a periodic basis. The national metrology institutes from different nations bring their lasers to the node laboratory of the region to measure frequency and verify equivalence. The equivalence of frequency measurements between different node laboratories is ensured by the Coordinated Universal Time (UTC) maintained by node laboratories and Calibration and Measurement Capability (CMC) registration of optical frequency combs.

Of the nations in the APMP, Japan, China, Korea, Singapore, and Australia owned their own optical frequency combs, some nations of which also owned fiber combs as of 2010. However, while those nations, except Japan, purchased units that were commercially available, AIST of Japan engaged in self-fabrication. AIST has been recognized for their related technologies and has been designated as the node laboratory in the APMP region. The international comparison of the iodine-stabilized He-Ne laser that was carried out at AIST in April 2010 was a symbolic event that demonstrated the superiority of our fiber comb. The national metrology institutes of eight nations in the Asian and Oceanian regions brought their 633-nm iodine-stabilized He-Ne lasers to AIST, the node laboratory, to compare frequencies of the lasers using the fiber comb we have developed.

Using our robust and accurate fiber comb to simplify measurements as described above, the measurement went extremely well and was fully completed in around a day. Moreover, a time-consuming long-term frequency stability measurement was successfully made upon request from the institutes. This helped evaluate the performances of all stabilized lasers, with no anxiety of unmanned operation of fiber combs even at midnight. The results of laser measurements from the eight nations were within the uncertainty range in a list of recommended values of standard frequencies by the General Conference on Weights and Measures, indicating the equivalence of the stabilized lasers.[22] These lasers now play a role as the national measurement standards in their nations. This means that traceability of the SI length in these eight nations always passes through AIST fiber comb.

5.4 Application of the high-speed controllable frequency comb to the optical lattice clock

Our group has developed the “optical lattice clock”[23] to be the next-generation frequency standard. The “optical clock” represented by the optical lattice clock, based on the clock transition on the optical frequency domain, requires a narrow spectral linewidth at the hertz level of the laser for observing clock transitions, owing to the extremely narrow spectral linewidth of the transition and the low probability of transition. The method employed to achieve such a laser regulates the temperature of a cavity that has high finesse and a low rate of thermal expansion in vacuum for high stabilization, and stabilizes the laser to a longitudinal mode of the cavity. We have developed Yb and Sr optical lattice clocks, with clock transition wavelengths of 578 nm and 698 nm, respectively. While ultrastable cavities are generally used for each clock transition wavelength, we use an ultrastable cavity for 1064 nm, different from the clock transition wavelengths. This is in order to achieve “linewidth transfer” (Fig. 8), where the frequency stability and spectral linewidth of the 1064-nm cavity are transferred to the 578-nm and 698-nm cavities using the high-speed controllable optical frequency comb.[24]

The advantages of this method include the following points. (1) A reliable and stable laser system can be realized because a cavity can be used for wavelengths available with a robust and sophisticated laser (e.g., 1064 nm), and only a single ultrastable cavity is required. (2) Frequency variations in the reference-stabilized laser can be compensated by measuring the frequency ratio of the two optical lattice clocks, which consequently offers a high frequency stability that no other method can achieve. (3) The mode spacing of the optical frequency (40–200 MHz) is smaller than the free spectral range of the ultrastable cavity (around 2 GHz in general), thus increasing the range of options in selecting an acousto-optic modulator to be used as a bridge to the clock transition frequency. This method will be an important technology in operating several optical clock systems.

6 Conclusion

How far a unit should be disassembled for self-fabrication or whether it is simpler to purchase a commercially available item is a difficult issue. Fortunately, however, our attempt to self-fabricate a mode-locked fiber laser and ultrashort optical pulse amplifier was more successful than anticipated. It enabled optimization of lasers and amplifiers for design and fabrication and enabled quick changes in specifications to help take advantage of the design and development of optical systems, laser control, frequency measurement, and other technologies that we have proved capable of, which dramatically accelerates the development speed. As a result, the optical frequency measuring instrument once available for use only for a short period of time, and the optical frequency comb formerly only a tool for demonstration, have been adapted to calibration of optical communication band wavelengths. They have not only successfully replaced national measurement standards for length but have also been successfully applied to the laser systems of optical lattice clocks and in other practical contexts. One may argue that this is the second breakthrough required to put the optical frequency comb in practical use.

With respect to the national measurement standards, we have long realized the importance of calibration services in the optical communication band and have always taken initiative in the establishment of traceability systems and calibration works. The recent steady increase in the number of tests requested demonstrates the strategic significance of performing optical measurement in the optical communication band. The completion of a large-scale international comparison with as many as eight nations within a short time was something we did not anticipate but it served as a symbolic example demonstrating the superiority of the fiber comb.

Although it has high reliability and a relatively simple configuration, the fiber comb needs improved reliability at a higher level and an even simpler configuration when taking into account commercialization or applications to other fields. To this end, we need to collaborate with companies. We have experience in technical transfer through joint research or technical training with several companies taking advantage of programs, including the “Grant for Industrial Technology Research” program of the New Energy and Industrial Technology Development Organization. We also aim to commercialize sophisticated fiber combs by dividing fiber optical systems and control systems for modularization. If the fiber comb is downsized, commercialized, and offered at lower prices, then it could possibly be used not only for calibration but also as communication technology itself, including direct generation of signal light strictly conforming to the grid wavelength in the area of optical communication. Furthermore, in the area of length standards, accredited calibration laboratories will own their own optical frequency combs, ultimately eliminating the necessity of transporting iodine-stabilized He-Ne lasers. Optical communication technologies, traceability systems in Japan, and the CCL-K11 international comparison system for stabilized lasers are expected to evolve into more reasonable dimensions as time goes on, and we expect our fiber comb to be of some help in this evolution.

Terminologies

Term 1. Mode-locked laser: If loss or modulation of the index of refraction is applied to a cavity at a frequency close to the free spectral range, then the free spectral range will be drawn into and

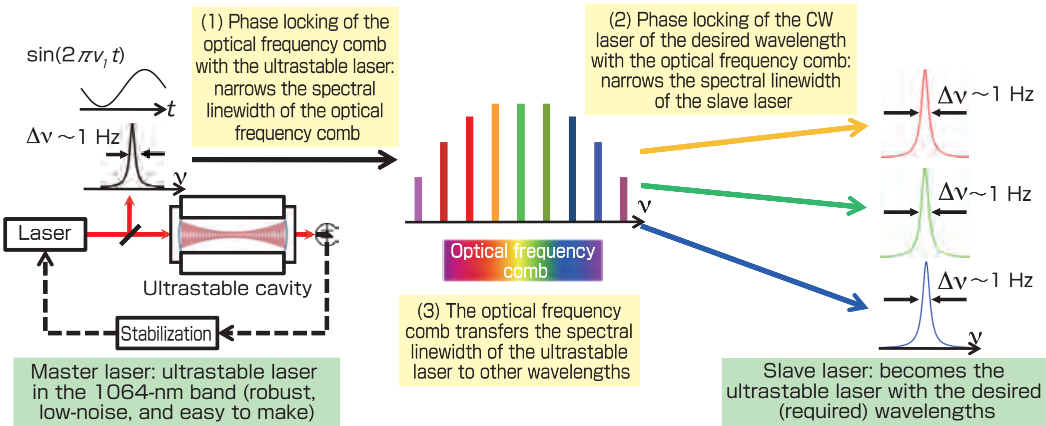

Fig. 8 “Linewidth transfer” using the optical frequency comb

The spectral linewidths of all modes for the octave-spanning optical frequency comb are narrowed down by phase-locking one of the modes for the optical frequency comb with a master laser for narrowing the spectral linewidth of a given wavelength, and at the same time by narrowing down the spectral linewidth of f_{CEO} by phase-locking with a broad servo bandwidth. This method provides the spectral linewidth and frequency stability of the master laser to the slave lasers in desired wavelengths. It also requires the “high-speed controllable frequency comb” that enables step (1) “Phase locking of the optical frequency comb with the ultrastable laser.”

equal to the modulation frequency. This is called mode locking. Mode locking by externally adding modulation is called active mode locking, while synchronization by fluctuations in light power in the cavity without adding external modulation is called passive mode locking.

Term 2. Highly nonlinear fiber: An optical fiber with a high nonlinear coefficient used for broadening the output spectrum of the mode-locked laser to an octave or more. It generally refers to a fiber with a zero-dispersion wavelength in the 1.5-μm band, though a photonic crystal fiber with a zero-dispersion wavelength around the 800-nm band is also a highly nonlinear fiber.

Term 3. Side-band optical frequency comb: A type of optical frequency comb used before the optical frequency comb with the mode-locked laser was invented. It can acquire a number of relatively broadened side bands entered into the CW laser by inserting the electro-optic modulator into a cavity and applying a modulation frequency close to the free spectral range frequency. Although it yields an extremely high mode spacing frequency and high power per mode, no report has yet been made that obtained the CEO signal. The side-band optical frequency comb has been little used for frequency measurement after it was replaced by the optical frequency comb using the mode-locked laser.

Term 4. Asia Pacific Metrology Programme (APMP): Launched in 1980, the APMP conducts international comparisons of standards from different nations and technical cooperation as a grouping of national metrology institutes engaged in metrology activities based on the Metre Convention under the umbrella of Asia-Pacific Economic Cooperation (APEC). Apart from APMP, the SIM in North America, the EUROMET mainly located in the European continent, and six other large and small groupings of national metrology institutes around the world are in mutual cooperation.

Term 5. Calibration and Measurement Capability (CMC): Uncertainty of measurement of national measurement standards internationally accepted by examinations under the Metre Convention.

Term 6. Optical lattice clock: Compared to other "optical clocks" with the clock transition frequency in the optical region, the optical lattice clock can achieve both high accuracy and frequency stability. It is thought to be the best candidate for a next-generation frequency standard. Proposed by Dr. Katori, a professor at the University of Tokyo, this standard has been subject to research and development at leading national metrology institutes around the world over 10 years.

References

[1] H. Schnatz, B. Lipphardt, J. Helmcke, F. Riehle and G. Zinner: First phase-coherent frequency measurement of visible radiation, *Phys. Rev. Lett.*, 76 (1), 18-21 (1996).

[2] Y. Miki, A. Onae, T. Kurosawa, Y. Akimoto and E. Sakuma: Frequency chain to 3.39-μm CH_4-stabilized He-Ne-laser using Josephson point-contact as harmonic mixer, *Jpn. J. Appl. Phys. Part 1*, 33, 1655-1658 (1994).

[3] T. J. Quinn: Practical realization of the definition of the metre, including recommended radiations of other optical frequency standards (2001), *Metrologia*, 40 (2), 103-133 (2003).

[4] J. Ishikawa: Portable national length standards designed and constructed using commercially available parts, *Synthesiology*, 2 (4), 276-287 (2009) (in Japanese) [*Synthesiology English edition*, 2 (4), 246-257 (2010)].

[5] T. Udem, J. Reichert, R. Holzwarth and T. W. Hänsch: Absolute optical frequency measurement of the cesium D_1 line with a mode-locked laser, *Phys. Rev. Lett.*, 82, 3568-3571 (1999).

[6] D. J. Jones, S. A. Diddams, J. K. Ranka, A. Stentz, R. S. Windeler, J. L. Hall and S. T. Cundiff: Carrier-envelope phase control of femtosecond mode-locked lasers and direct optical frequency synthesis, *Science*, 288 (5466), 635-639 (2000).

[7] T. Okuno, M. Onishi, T. Kashiwada, S. Ishikawa and M. Nishimura: Silica-based functional fibers with enhanced nonlinearity and their applications, *IEEE J. Sel. Top. Quant. Electron.*, 5, 1385-1391 (1999).

[8] J. K. Ranka, R. S. Windeler and A. J. Stentz: Optical properties of high-delta air silica microstructure optical fibers, *Opt. Lett.*, 25, 796-798 (2000).

[9] A. Onae, T. Ikegami, K. Sugiyama, FL. Hong, K. Minoshima, H. Matsumoto, K. Nakagawa, M. Yoshida and S. Harada: Optical frequency link between an acetylene stabilized laser at 1542 nm and an Rb stabilized laser at 778 nm using a two-color mode-locked fiber laser, *Opt. Commun.*, 183, 181-187 (2000).

[10] FL. Hong, K. Minoshima, A. Onae, H. Inaba, H. Takada, A. Hirai, H. Matsumoto, T. Sugiura and M. Yoshida: Broad-spectrum frequency comb generation and carrier-envelope offset frequency measurement by second-harmonic generation of a mode-locked fiber laser, *Opt. Lett.*, 28 (17), 1516-1518 (2003).

[11] T. R. Schibli, K. Minoshima, FL. Hong, H. Inaba, A. Onae, H. Matsumoto, I. Hartl and M. E. Fermann: Frequency metrology with a turnkey all-fiber system, *Opt. Lett.*, 29 (21), 2467-2469 (2004).

[12] H. Inaba, Y. Daimon, FL. Hong, A. Onae, K. Minoshima, T. R. Schibli, H. Matsumoto, M. Hirano, T. Okuno, M. Onishi and M. Nakazawa: Long-term measurement of optical frequencies using a simple, robust and low-noise fiber based frequency comb, *Opt. Express*, 14 (12), 5223-5231 (2006).

[13] FL. Hong, J. Ishikawa, ZY. Bi, J. Zhang, K. Seta, A. Onae, J. Yoda and H. Matsumoto: Portable I2-stabilized Nd : YAG laser for international comparisons, *IEEE T. Instrum. Meas.*, 50 (1), 486-489 (2001).

[14] D. Strickland and G. Mourou: Compression of amplified chirped optical pulses, *Opt. Commun.*, 56 (3), 219-221 (1985).

[15] Y. Nakajima, H. Inaba, FL. Hong, A. Onae, K. Minoshima, T. Kobayashi, M. Nakazawa and H. Matsumoto: Optimized amplification of femtosecond optical pulses by dispersion management for octave-spanning optical frequency comb generation, *Opt. Commun.*, 281 (17), 4484-4487 (2008).

[16] M. Nakazawa, K. Kurokawa, H. Kubota, K. Suzuki and Y. Kimura: Femtosecond erbium-doped optical fiber amplifier, *Appl. Phys. Lett.*, 57, 653-655 (1990).

[17] L. Nugent-Glandorf, T. A. Johnson, Y. Kobayashi and S. A. Diddams: Impact of dispersion on amplitude and frequency noise in a Yb-fiber laser comb, *Opt. Lett.*, 36 (9), 1578-1580 (2011).

[18] Y. Nakajima, H. Inaba, K. Hosaka, K. Minoshima, A. Onae, M. Yasuda, T. Kohno, S. Kawato, T. Kobayashi, T. Katsuyama and FL. Hong: A multi-branch, fiber-based frequency comb with millihertz-level relative linewidths using an intra-cavity electro-optic modulator, *Opt. Express*, 18 (2), 1667-1676 (2010).

[19] K. Iwakuni, H. Inaba, Y. Nakajima, T. Kobayashi, K. Hosaka, A. Onae and FL. Hong: Narrow linewidth comb realized with a mode-locked fiber laser using an intra-cavity waveguide electro-optic modulator for high-speed control, *Opt. Express*, 20 (13), 13769-13776 (2012).

[20] A. Onae, K. Minoshima, J. Yoda, K. Nakagawa, A. Yamaguchi, M. Kourogi, K. Imai and B. Widiyatomoko: Toward an accurate frequency standard at 1.5 μm based on the acetylene overtone band transition, *IEEE T. Instrum. Meas.*, 48, 563-566 (1999).

[21] M. Kourogi, K. Nakagawa and M. Ohtsu: Wide-span optical frequency comb generator for accurate optical frequency difference measurement, *IEEE J. Quant.Electron.*, 29, 2693-2701 (1993).

[22] M. Matus, P. Balling, P. Kren, P. Mašika, FL. Hong, J. Ishikawa, H. Inaba, K. Hosaka, M. Yasuda, D. Akamatsu, A. Onae, RH. Shi, JL. Peng, E. Howick, J. Qian, XY. Liu, M. Ranusawud, A. Tonmueanwai, S. L. Tan, ZX. Chao, KH. Yeoh, N. Mat Daud, T. K. Chan, R. Fira, O. Stalder, K. Tomanyiczka and L. Robertsson: The CCL-K11 ongoing key comparison: final report for the year 2010, *Metrologia*, 48 (2011).

[23] M. Yasuda, H. Inaba, T. Kohno, T. Tanabe, Y. Nakajima, K. Hosaka, D. Akamatsu, A. Onae, T. Suzuyama, M. Amemiya and FL. Hong: Improved absolute frequency measurement of the 171Yb optical lattice clock towards a candidate for the redefinition of the second, *Appl. Phys. Express*, 5 (2012).

[24] H. Inaba, K. Hosaka, M. Yasuda, Y. Nakajima, K. Iwakuni, D. Akamatsu, S. Okubo, T. Kohno, A. Onae and FL. Hong: Spectroscopy of 171Yb in an optical lattice based on laser linewidth transfer using a narrow linewidth frequency comb, *Opt. Express*, 21 (7), 7891-7896 (2013).

Authors

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Earned a Master's degree in applied physics, Graduate School of Engineering, Hokkaido University, in 1993. Joined the National Research Laboratory of Metrology the same year. Engaged in the development of continuous wave (CW) fiber lasers. Chief scientist, National Metrology Institute of Japan, National Institute of Advanced Industrial Science and Technology since 2001. Doctor of engineering at Hokkaido University in 2004. Engages in research into generation and control of the optical frequency comb and applications to technologies related to frequency standards. Received the Award of the Minister of Education, Culture, Sports, Science and Technology in 2008, and the Ichimura Academic Award in 2012. In this study, he played a leading role in the self-fabrication of fiber combs, establishing national measurement standards, and achieving a narrower spectral linewidth.

Atsushi ONAE

Dropped out of the doctoral program in Physics, Graduate School of Science, the University of Tokyo in 1988. Joined the National Research Laboratory of Metrology the same year. Doctor of Science at the University of Tokyo in 1990. Engaged in the development of wavelength standards in the optical communication band using acetylene molecules and research into optical frequency measurement technology to evaluate the standards. Currently the senior chief scientist of the National Metrology Institute of Japan, National Institute of Advanced Industrial Science and Technology. Received the Japan Society of Applied Physics Outstanding Achievement Award in Optics and Quantum Electronics in 2003, and the Award of the Minister of Education, Culture, Sports, Science and Technology in 2008. In this study, he played a leading role in technical development in the optical communication band wavelength (the development of stabilized lasers and frequency measurement using the optical frequency comb).

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Discussions with Reviewers

1 Overall

Comment (Naoto Kobayashi: Center of Research Strategy, Waseda University)

I would say that this paper on optical frequency comb generation is an excellent work suitable for *Synthesiology* in the sense that it overcame a number of drawbacks of conventional comb generation with the solid-state laser by means of the fiber comb, and demonstrated outstanding performance in relation to standards in the optical communication frequency domain.

Comment (Hidemi Tsuchida: AIST)

This paper is regarded as research and development for establishing an optical frequency comb apparatus for practical purpose, based on the invention of the fundamentals by Hall and Hänsch. Regarding the development of the fiber-based optical comb, the paper clearly describes the target and the approach leading to the goal.

2 Title

Question and comment (Hidemi Tsuchida)

While you have entitled the paper as "National standards of length for high-capacity optical fiber communication systems," the requirement of the optical communication systems is not "length" but "optical frequency" standards. Is it possible to change the title so as to fit the intention of the paper, for example, into "National standards of optical frequency for high-capacity optical fiber communication systems"?

Answer (Hajime Inaba, Atsushi Onae, and Feng-Lei Hong)

Support for the communication band is obviously an important mission, and we have constantly taken initiatives in establishing calibration technology. On the other hand, however, developing the technology to realize length standards is also one of our most important missions, on which we have long operated the national measurement standards to achieve the SI meter. From a historical perspective, researchers have traditionally attempted to realize length standards, while optical frequency standards only came to be required at the beginning of the 21st century. Taking this history into consideration, we would like to mention length standards to begin with, followed by optical frequency standards. Therefore, it would be appreciated if you could allow us to keep the title unchanged.

3 Application fields of optical fiber combs

Comment (Hidemi Tsuchida)

I understand from the title that the paper focuses on optical communication as the main application field of optical fiber combs. However, chapter 5 concerns diverse topics such as optical communication, length standards, international comparisons, and high-speed control. It may be reasonable to pick up a topic on length standards, but I recommend enriching the discussions on optical communication. For the purpose of helping the readers' understanding, it will be necessary to include descriptions on the frequency grid standardized in optical communication, the demands for frequency measurement technology, and how fiber combs are utilized in the industry.

Answer (Hajime Inaba, Atsushi Onae, and Feng-Lei Hong)

We believed that in discussing the achievements of the fiber comb in this paper, the various applications would also be an important point. Nevertheless, we have added further descriptions of optical communication at the beginning of chapter 5 to prevent readers from feeling that the topic of the paper is spread out as has been pointed out.

4 Motivation and predictions of fiber comb development

Question and comment (Naoto Kobayashi)

This paper argues that the use of the fiber combs overcame almost all drawbacks of the solid-state laser comb and that it successfully created an optical frequency comb of extremely high precision. Now, I have two questions. (1) While the paper describes that the motivation for developing fiber combs was a sophisticated fiber laser provided by a joint research company, did you begin by anticipating that the development of the fiber comb could result in a more sophisticated comb? (2) In relation to the description that self-fabrication of fiber combs was the major development factor on this occasion, did you anticipate from the beginning that this would cause the development process to proceed well?

Answer (Hajime Inaba, Atsushi Onae, and Feng-Lei Hong)

We conducted joint research with a company as part of the 2002–2004 Project of the Special Coordination Funds for Promoting Science and Technology called "Broadband Optical Synthesizer". The mode-locked fiber laser from that company was reliable and superior in the sense that the incorporated nonlinear crystal was able to generate an optical frequency comb in the 800-nm band. Furthermore, in 2004, we achieved absolute optical frequency measurement in combination with the highly nonlinear fiber, when development of the fiber comb slowed.

However, as the laser system was a product developed by the company, we could not alter the component that generated the comb but instead had to ask the company for alterations, for instance, when the S/N ratio of the beat signal was low or when we were dissatisfied with the control or other systems. We also had a number of studies we wanted to engage in using the optical frequency comb, which meant that we needed a large quantity of them. Under these circumstances, we realized the importance of self-fabrication of all systems, including selection of mode-locked fiber lasers, amplifier systems, and highly nonlinear fibers in order to perform the subsequent development and use it as a tool to advance the study.

With experience in fabricating Ti:S combs and vendor fiber combs and in fabricating CW fiber lasers, we were at least certain we could self-fabricate a system for frequency measurement. However, we were aware of a number of challenges to overcome. We were not confident enough to produce the most sophisticated and easy-to-use self-fabricated systems, however.

We still have some opportunities to examine commercially available comb systems, which are often designed to make it harder for us to alter on our own, even if they contain unwanted functions. We would not be willing to use those troublesome systems.

5 Realization of high performance optical frequency comb

Question and comment (Hidemi Tsuchida)

At the beginning of section 4.1 there is a description on performance comparison (power and pulse width) between the Ti:S laser and fiber laser, but it does not clearly state how the difference in the performances were overcome in order to meet the specification as an optical frequency comb. Please describe the method used (e.g., optical amplification, pulse compression) and to what extent the difference reduced.

Answer (Hajime Inaba)

In broadening the optical frequency comb, not only was it effective to improve the laser performances like power or pulse width, but it was also necessary to optimize components other than the laser by selecting the highly nonlinear fiber or elaborating the CEO signal detection system. On this occasion, for instance, we successfully detected the CEO signal by detecting the CEO signal of a comb with a wavelength band less than an octave, by means of a 2f–3f interferometer or by finding and applying the optimal highly nonlinear fiber. As added in section 4.5, the differences in the laser performances like power or pulse width in the time domain were no smaller than those of the Ti:S comb, owing to the self-fabrication of the laser. What we intend to develop is a fiber comb that is robust and has low noise, and is sophisticated and practical in the frequency domain.

6 Realization of high performance optical frequency comb

Question and comment (Hidemi Tsuchida)

Section 4.3 describes the necessity of dispersion control, which seems to be common knowledge for researchers in optical fiber communication or ultrashort optical pulses. The difference between the mean and peak powers is not clear and their relationship with spectral broadening is not clarified.. Please revise the corresponding descriptions intelligibly including the cause of the accompanying power enhancement.

Answer (Hajime Inaba)

We have differentiated the mean power from the peak power as pointed out. We also added a possible cause for the power boost although this is a hypothesis. The phenomenon discussed in section 4.3 regarding distributed control—in that the mean power of radiation increases by properly adjusting the chirp quantity of optical pulses entering the optical amplifier—is our original result supported by academic papers and patents. It would be appreciated if you could kindly examine this.

Research and development of solar hydrogen production

— Toward the realization of ingenious photocatalysis-electrolysis hybrid system —

Kazuhiro SAYAMA * and Yugo MISEKI

[Translation from *Synthesiology*, Vol.7, No.2, p.81-92 (2014)]

It is important to carry out research strategically and in a step-by-step manner in order to put new solar energy conversion technologies into practical use and to realize a society based on renewable energy. In this paper, we clarified the meaning of “solar hydrogen,” compared various solar hydrogen production technologies, and discussed their feasibilities. Specifically, we showed the effectiveness of the “photocatalysis-electrolysis hybrid system,” which was invented by AIST, as a promising candidate technology for low cost solar hydrogen production, based on preliminary cost estimations. The scenario toward the realization of the hybrid system is also discussed.

Keywords : Solar hydrogen production, photocatalysis-electrolysis hybrid system, artificial photosynthesis, redox mediator

1 Introduction: Significance of solar energy use technology and its issues

Recently, the issues of depletion of fossil resources and global warming due to carbon gas emitted by their consumption have become apparent, and it is necessary to reduce the dependence on fossil resources as quickly as possible to respond to such issues. For the humankind to build a sustainable society and to continue growth, the early development of an innovative technology for utilizing renewable energy is essential. Among the renewable energies, solar energy is most abundant, and is the source of wind, wave, tide, and biomass power. It is possible to cover one year’s worth of the entire global energy consumption with one hour’s worth of solar energy that shines on earth, and its total amount is about 500, 5,000, and 50,000 times greater than wind, geothermal, and hydro power, respectively. However, there are two major disadvantages to solar energy: the energy density is low and it is greatly influenced by weather. Therefore, the technologies that can be used effectively are limited. While photovoltaic generation, use of solar heat, and fuel manufacturing using biomass are already put to practical use, it cannot be foreseen that extending these technologies may replace fossil resources to solve the global energy problem.

To further make use of the solar energy with low energy density, an innovative technological development which is much lower in cost and is simpler than photovoltaic generation is essential. Options of solar energy use includes “artificial photosynthesis” where the photons are directly converted to chemical energy, just as in photosynthesis in plants. While the term artificial photosynthesis sounds extremely attractive, it may lead to misunderstandings since the definition is vague. In a wide sense, it means to wholly or partially simulate the photosynthetic mechanism of plants, and the research is done not necessarily to solve the energy problem. In a situation where energy has become an outstanding issue, it is necessary to rethink the meaning of the terms for artificial photosynthesis and its R&D scenario to quickly realize the practical use of new solar energy conversion technologies.

2 What is solar hydrogen production?

In the artificial photosynthesis technology, the term “solar hydrogen production” using photocatalysts and photoelectrodes is becoming popular. In FY 2012, research on hydrogen production from water using photocatalysts and photoelectrodes using the term “solar hydrogen” started in the Future Pioneering Project of the Ministry of Economy, Trade and Industry (METI). The solar hydrogen production focuses on the water decomposition using solar energy to achieve a clean and sustainable hydrogen society (Fig. 1). While the ultimate goal expected from the research of artificial photosynthesis and solar hydrogen production technology is solving the energy problem on a global scale, it is important to note that the latter is used with strong goal orientation. The photosynthesis mechanism is divided into the light and dark reactions. The light reaction, which is the first stage where the reductant of a high-energy state is produced as oxygen is pulled out of water, directly pushes the energy-storing chemical reaction through photons, and the decomposition of water is the basic reaction of photosynthesis. If hydrogen energy derived from solar energy using water as the source material can be manufactured in a large amount, several existing technologies can be applied to CO_2 fixing reaction that corresponds to the dark reaction.

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While there is much artificial photosynthesis research that focuses only on the organic synthesis of the dark reaction, unless it is combined with the energy-storing chemical reaction of the light reaction, it does not lead to the solution of the energy problem. The objective and direction arising from the term “artificial photosynthesis” is unclear, and much is in the realm of *Type 1 Basic Research*. To quickly move to *Type 2 Basic Research*, it is necessary to consciously use an objective-oriented term. From the above thinking process, in this paper, among the artificial photosynthesis technologies, the technology to produce hydrogen and oxygen by decomposing water, with the objective of building a sustainable society through solar energy, will be called “solar hydrogen production,” and this will be positioned as *Type 2 Basic Research*. (The system in which the two technologies for photovoltaic generation and electrolysis are simply combined may be called the solar hydrogen production in a wide sense, but it does not belong in the realm of artificial photosynthesis because it does not directly use photons for chemical reaction. Also, power generation methods using high temperature produced by gathering sunlight as well as water decomposition by thermochemical cycle are not addressed in this paper.)

Figure 2 is a technological map in which the vertical axis shows the solar energy conversion efficiency and the horizontal axis the cost or system complexity for the various solar energy conversion technologies. Photovoltaic generation, use of solar heat, and fuel production using biomass lie on the line representing practical use. While the current solar hydrogen production technologies that use photocatalysts and photoelectrodes are still far from being practically applied, it is necessary to present their future potential for practical efficiency that is overwhelmingly simpler and lower in cost compared to the system that combines photovoltaic generation and electrolysis. The application and diffusion of solar hydrogen production technology as well as the realization of future renewable energy society that does not depend on fossil resources are not easy and are likely to take time. Therefore, it is desirable to surely and strategically engage in research while looking over the direction we must take from this point. It is necessary to discern which technology will surpass the line of practical use and arrive first at the final goal.

This paper compares various solar hydrogen production technologies and discusses their future prospects. Particularly, the main objectives are to present a scenario for practical use, efficiency, and cost performance of the “photocatalysis-electrolysis hybrid system”[1][2] that the authors developed, and to compare this with other technologies to discuss whether it can stand at the starting line of *Type 2 Basic Research*.

3 Importance of the research scenario for practical use of solar hydrogen production and the cost target

3.1 Setting the long-term scenario and the appropriate interim goal

The research of artificial photosynthesis and solar hydrogen production has been influenced greatly by the price of fossil resources. The first boom occurred around the 1973 Oil Shock, but as the oil prices decreased after 1986, the research stalled rapidly. In the 1990s, the global warming issues came into focus with the accompanying increase in oil prices, and the research is attracting attention again. In the United States, the Solar Innovation Hub, a major solar hydrogen production project of the Department of Energy (DOE), started in 2010, but the interest in solar energy is falling slightly after the sharp decrease in natural gas prices due to the shale gas revolution. Although the ebb and flow of research cannot be avoided, such a situation is not desirable for the R&D of solar energy conversion that requires a long time to reach practical use. To continue long-term research, it is extremely important to set the research scenario and roadmap for

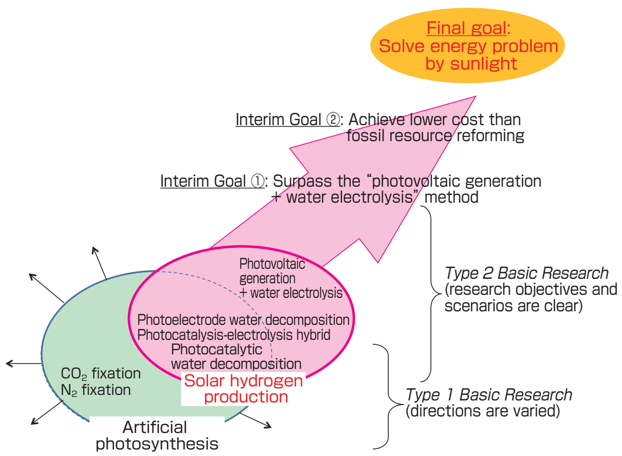


Fig. 1 Positioning of the solar hydrogen production and its interim and final goals

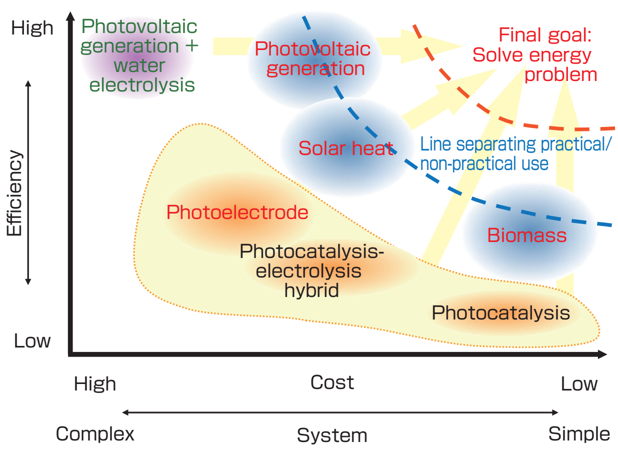


Fig. 2 Technological map of various solar energy conversion uses

practical use, the interim goals, and long-term prospects, not just the clarification of the research significance as the final goal. Also, to have as many people understand the points of this paper is the most effective way to achieve the goal and will lead to stable and continuous R&D. Since the Great East Japan Earthquake, interest in renewable energy has increased in Japan. Because the expectations are high, the achievability and speed to practical use are demanded, not simply idealistic theory.

Up to this point, the roadmaps for energy have been created by the Cool Earth Promotion Programme of the government, Science Council of Japan, Japan Society of Applied Physics, Chemical Society of Japan, and others. For example, the Dream Roadmap[3] of the Science Council of Japan that was written after the Great East Japan Earthquake contains several keywords such as artificial photosynthesis and solar hydrogen production, and practical use is set between 2030~2040. However, when the keywords are set in too distant future, though the research significance may be recognized, it will not help promote the short to mid-term research and may even work negatively. For now, it is important to set the short to mid-term strategic scenario and the interim goals that are highly achievable. We offer the following discussion, and set two clear interim goals as shown in Fig. 1: ① to reduce the cost to lower than the hydrogen obtained by simply combining photovoltaic generation and electrolysis, and ② to reduce the cost to lower than the hydrogen from reforming of fossil resources.

3.2 Specific interim goals for the hydrogen production cost

The roadmap (2010) for hydrogen production in the fuel cell and hydrogen technology development[4] of the New Energy and Industrial Technology Development Organization (NEDO) describes the interim goal for cost. For the cost of off-site hydrogen production, low carbon is achieved using renewable energy in 2020 at the same cost (30 yen/Nm^3) as the steam reforming of natural gas, and aims for lower cost in 2030. On the other hand, for the cost of large-scale photovoltaic generation, the prospect for 2030 in the Report of the Committee for Investigation of Cost and Others[5] of the Energy and Environment Council of the government is 9.9~26.4 yen/kWh. In the NEDO roadmap for photovoltaic generation (PV2030+, 2009),[6] the power generation cost goal for 2020 is 14 yen/kWh and for 2030 is 7 yen/kWh. Calculating the cost of combining the photovoltaic generation and large-scale solid polymer electrolytic device based on the report of the Central Research Institute of Electric Power Industry,[7] the cost of hydrogen production will be over 35 yen/Nm^3 even if the power generation goal of 7 yen/kWh is achieved.

The two interim goals that we presented are greatly affected by the costs of photovoltaic generation and fossil resources, but the cost of hydrogen production is calculated to be less than 35~65 yen/Nm^3 in the Interim Goal ① and 30 yen/Nm^3 in the Interim Goal ②. In the future, to achieve these cost goals and to achieve a clean hydrogen society using renewable energy, early development of an innovative technology unseen before is mandatory. Even if something is an ideal technology, if there are a number of very difficult issues to overcome, it is necessary to consider that time is needed for realization.

4 Comparison of various solar hydrogen production technologies using semiconductors

4.1 Principle of water decomposition by semiconductors

The first process in using sunlight is the absorption of photons by photoabsorptive materials. In the research for solar hydrogen production in artificial photosynthesis, the photoabsorptive materials are roughly divided into semiconductors and dyes. Currently, the former is much more advanced than the latter. The researches for solar hydrogen production technology using semiconductors have been conducted throughout the world and can be historically divided into two streams: photocatalysts and photoelectrodes. The principles of the two methods are shown in Fig. 3. The water decomposition by TiO_2 photoelectrode was invented in Japan,[8] and the concept of the photocatalytic water decomposition was established later. When the light is absorbed by a semiconductor, electrons are generated in the conduction band and holes in the valence band, and these are used in the reduction and oxidation reaction of water, respectively. While the principle of light absorption and charge separation are the same as in the solar cell, the overall concept is closer to fuel production using biomass in the point that the solar energy is directly converted to chemical energy or hydrogen for long-term storage.

Figure 4 shows the various water decomposition technologies by photocatalysts and electrolysis, and their potential map. In the water decomposition of photocatalysts, the potential of the conduction band is limited to being more negative than the redox potential of hydrogen ($E°(H^+/H_2) = 0$ V), and the valence band potential is more positive than the potential when oxygen is produced from water ($E°(O_2/H_2O) = +1.23$ V). Also, in the case of photoelectrodes, they use external bias (external power), as shown in Fig. 3. By using external bias, there are advantages that there will be loose limitation to the level of semiconductors used in photoelectrodes, charge separation is promoted, and hydrogen and oxygen can be separately produced. In the example of the n-type semiconductor in Fig. 3, the potential of the necessary external bias is the difference between the minimum potential of the conduction band and H^+/H_2 potential in theory, and the voltage can be lower than the ordinary electrolysis of water. On the other hand, there are advantages of having a short charge transfer distance and simplification, since the reaction is completed for each semiconductor particle in the photocatalyst.

4.1.1 Diversification and progress of the photocatalyst system

Currently, the photocatalyst and photoelectrode systems are diversified and progressing in various forms as shown in Table 1. The photocatalyst system can be roughly categorized into conventional photocatalyst (single-step photoexcitation type), double-step photoexcited photocatalyst using the redox mediator (Z-scheme type), and the photocatalysis-electrolysis hybrid system. A redox mediator is a substance that transfers the electron while undergoing the cycle of oxidation and reduction. The reaction of double-step photoexcitation is similar to photosynthesis in plants, and is called the Z-scheme reaction that describes the zigzag processes where the electrons are photoexcited twice using the redox mediators. In the photocatalysis-electrolysis hybrid system, external bias is used as in Fig. 4, but since the needed bias is equal to the potential difference between redox potential of the redox mediator and the hydrogen in theory, the voltage can be lower than the ordinary electrolysis of water. The Japanese research is advanced in all areas of the photocatalyst system. Under certain conditions (such as 10 % solar energy conversion efficiency), the conventional and Z-scheme photocatalysts are estimated to achieve hydrogen production costs at 30 yen/Nm^3 or less,[9] but there are several issues that must be overcome for practical use, as shown in Table 1 and chapter 5.

4.1.2 Diversification and progress of the photoelectrode system

The photoelectrode system is categorized into n-type semiconductors, p-type semiconductors, p+n type semiconductors, and pn bonding films. The combination of the n- and p-type semiconductors can conduct water decomposition without external bias. However, when hydrogen is generated by the p-type semiconductor, cocatalyst for the hydrogen production with low overvoltage such as Pt

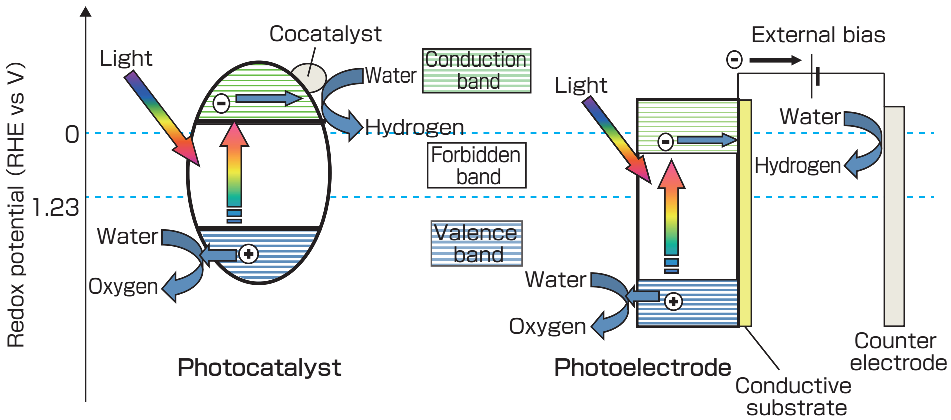


Fig. 3 Principle of water electrolysis by photoelectrode and photocatalyst using semiconductor

When light is absorbed by the semiconductor, electrons are produced in the conduction band and holes in the valence band, and these products are used in the reduction and oxidation reactions of water, respectively. The diagram of a photoelectrode is an example of an n-type semiconductor. The electrons from the conduction band move to the counter electrode and are used for hydrogen production.

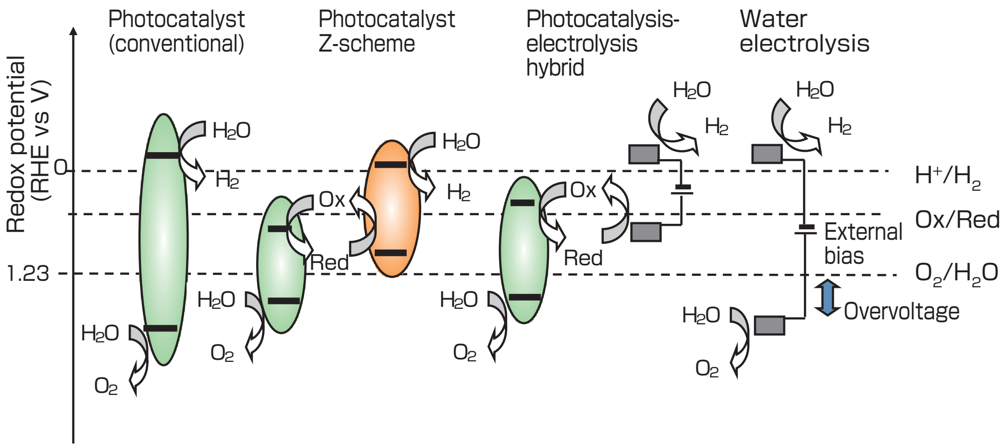


Fig. 4 Various hydrogen production technologies from water and their potential map

Ox and Red are the oxidants and reductants of the redox mediator.

Table 1. Comparison of various solar hydrogen production technologies using semiconductor

		Advantage	Disadvantage
Photocatalyst system	Conventional photocatalyst (single-step photoexcitation)	· Simplest · External bias not necessary	· Efficiency is currently low · Mixed production of hydrogen and oxygen · Hydrogen production cocatalyst needed for large area · Potential limitation of semiconductor is strict · Hydrogen accumulation at large area
	Double-step photoexcitation photocatalyst (Z-scheme type)	· More variety compared to single-step photoexcitation · External bias not necessary · In theory, gas separation and production are possible	· Efficiency is currently low · Activity declines when gas separation · Hydrogen production cocatalyst needed for large area · Hydrogen accumulation at large area
	Photocatalysis-electrolysis hybrid system	· Few potential limitation of semiconductor · Hydrogen accumulation is easy · Efficiency is currently high	· External bias necessary
Photoelectrode system	n-type semiconductor	· Hydrogen accumulation at counter electrode is easy · Many oxidants, preparation is easy	· External bias necessary
	p-type semiconductor	· Efficiency is high at current state	· External bias necessary · Hydrogen production cocatalyst needed for large area · Hydrogen accumulation at large area · Same material as solar cell, high cost
	p-type + n-type semiconductor	· External bias not necessary	· Hydrogen production cocatalyst needed for large area · Hydrogen accumulation at large area
	pn bonded film (without bias)	· External bias or wire not necessary · Diffusion length of charge is short	· Hydrogen production cocatalyst needed for large area · Hydrogen accumulation at large area

is necessary over a large area, and the development of a non-precious metal for hydrogen production cocatalyst becomes extremely important. Also, a hydrogen-accumulating hood is necessary for a large area. The p-type semiconductor photoelectrode has higher efficiency at the moment compared to the n-type, but with the condition of film-forming using the same material and method as the solar cell, the cost becomes extremely high, and it is difficult to achieve the hydrogen production cost of 40 yen/Nm^3 or less with the extension of this technology[9] (in the DOE calculation, the multiple bonding film of the SIGS compound semiconductor is used). For the n-type semiconductor electrode, while the clear cost estimate is not published, it can be assumed that lower cost can be achieved compared to the p-type semiconductor photoelectrode since the method and hydrogen accumulation are simple and the precious metal is used only at the counter electrode. It is therefore studied throughout the world, mainly in Europe. The authors have reported the solar energy conversion efficiency of 1.35 % [external bias considered; applied bias photon-to-current efficiency (ABPE)] which was the highest value achieved in the n-type oxidant semiconductor photoelectrode.[10]

4.2 Which method should be prioritized?

If there is infinite time for R&D, hydrogen production using the simplest conventional photocatalyst will probably have the lowest cost. However, considering the practical use in the near future, for example, 2030, the speed and the scale of barriers to realization must be considered, not just the future cost of hydrogen production. As shown in Fig. 2, current solar energy conversion efficiency, system cost, and complexity are in trade-off relationships with most of the technologies. Similar trends can be seen for the solar hydrogen production technology in Table 1. Although it is difficult to compare technologies with differing advantages and disadvantages, a certain level of research concentration is necessary to accelerate the practical use. The authors considered both the hydrogen production cost and barriers to realization, and have engaged in research thinking that the originally developed photocatalysis-electrolysis hybrid system may emerge as one of the priority methods. In the following chapters, we explain the principle, background of development, current progress, reasons for prioritization considering the advantages and disadvantages, cost estimate, and research scenario toward practical use for the photocatalysis-electrolysis hybrid system.

5 Principles and advantages of the photocatalysis-electrolysis hybrid system

5.1 Limitation of photocatalytic water decomposition using visible light

The authors have engaged in the research of photocatalytic water decomposition by single-step photoexcitation for over 25 years. The complete decomposition of water by ultraviolet light (steady production of H_2 and O_2 in stoichiometric proportion) has been realized in much photocatalysis, but was difficult using visible light. Since we were studying dye-sensitized solar cells using redox mediators at the same time, we shifted our viewpoint and attempted the complete decomposition of water using two types of photocatalysts and redox mediators by simulating the Z-scheme reaction as in the double-step photoexcitation seen in plant photosynthesis. As a result, we succeeded in the complete decomposition reaction of the Z-scheme type by combining the Fe^{3+}/Fe^{2+} redox, photocatalyst, and ion photoreaction with use of ultraviolet light in 1997.[11] Moreover, in 2001, we succeeded in the photocatalytic water decomposition with visible light only, for the first time in the world.[12]

This was a system that used the Pt-$SrTiO_3$ (Cr-doped) photocatalyst in the hydrogen production side, Pt-WO_3 photocatalyst in the oxygen production side, and IO_3^-/I^- as the redox mediator. This system was interesting academically as an artificial photosynthesis model, and later there were reports from a few groups on improved photocatalysts. However, the apparent quantum efficiency (QE)[Term 1] was about 6 % and the solar energy conversion efficiency ($\eta_{\text{ sun}}$)[Term 2] remained at around 0.1 %. Particularly, as shown in Fig. 4, the suitable semiconductor materials were extremely limited due to the problem of potential limitation of the conducting band, and it was difficult to raise the efficiency of the photocatalyst on the hydrogen production side.

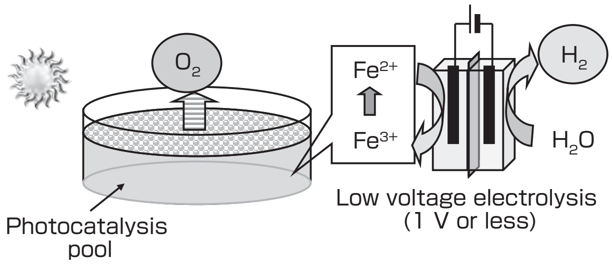
5.2 Invention of the photocatalysis-electrolysis hybrid system

In the water decomposition reaction by photocatalyst, there are several major hurdles toward practical use, not just the low efficiency. They include the fact that hydrogen and oxygen are produced as detonating gas, a transparent hydrogen accumulating cover that has large area without gas leaks is necessary, a large amount of precious metal cocatalyst is necessary to enhance the performance of hydrogen production rate, and others. Unless these issues are resolved, practical use is difficult even if a high performing photocatalyst is discovered. Therefore, the authors considered a future image of a system that was highly practical.

We came across a paper for a pilot plant for low-voltage electrolytic hydrogen production by Fe^{2+} ion.[13] In this paper, the objective was to recover energy from H_2S as hydrogen rather than incinerating the H_2S gas emitted from the petrochemical plant. When the H_2S is bubbled through the pool containing Fe^{3+} ions, sulfur and Fe^{2+} are produced, and sulfur is removed by filtration. Since the redox potential (E°) of Fe^{3+}/Fe^{2+} is +0.77 V, the electrolytic voltage can be kept at 1 V or less when the hydrogen is produced by oxidizing the Fe^{2+} to Fe^{3+} (Fig. 4). In ordinary water electrolysis, a total of about 1.6~2.0 V is necessary because the overvoltage of oxygen production is large, in addition to the theoretical electrolytic voltage (1.23 V). The majority of the hydrogen production cost by general electrolysis is the electricity cost, and if a large amount of Fe^{2+} is present, the hydrogen production cost can be reduced greatly by reducing the electrolytic voltage.

The authors took some ideas as clues from the above, and devised a "photocatalysis-electrolysis hybrid system" that produces Fe^{2+} from Fe^{3+} while producing oxygen by oxidizing water by photocatalysts, as seen in Fig. 5, and then combining it with hydrogen-producing low-voltage electrolysis.[1][2] In electrolysis, the Fe^{2+} is regenerated to Fe^{3+} to produce hydrogen. The overall reaction equations are shown at the bottom of Fig. 5. In the conventional photocatalysis, there are limitations of the conduction band potential and valence band potential as described earlier, but in this hybrid system, the potential restriction of the semiconductor is loosened, and several visible light responsive materials can be used. Moreover, since hydrogen is not produced at the surface of the photocatalyst, there is no need to depend on a precious metal cocatalyst, and hydrogen trapping is very simple. Various ion pairs can be used for the redox mediator. If the redox mediator with redox potential close to 0 V (RHE) can be used, the electrolytic voltage becomes close to zero, and the theoretical marginal efficiency of the photocatalyst of this redox reaction becomes equivalent to the conventional, single-step photoexcitation photocatalyst. The reaction of the redox mediator itself has the same function as the storage battery. As it can be seen, the "photocatalysis-electrolysis hybrid system" is a breakthrough system that solves almost all the issues of conventional photocatalysis reaction by replacing the photocatalysis reaction on the hydrogen production side of the Z-scheme reaction with electrolysis.

Although the concept of external bias used in the photocatalysis-electrolysis hybrid system may be difficult to understand, we would like to emphasize that it is not mere energy loss. Most of the energy supplied by external bias is converted into hydrogen. If the ordinary water electrolysis is done at 1.23 V, the conversion of energy from electric power to hydrogen is 100 % efficient, that is, the energy loss is of overvoltage only. Since the overvoltage of Fe^{3+}/Fe^{2+} is smaller than O_2/H_2O, it becomes small as energy loss. It is an important point that to keep the external bias at 1.23 V or less means that the apparent electrolytic efficiency can be 100 % or higher using light energy.



Photocatalysis : $2H_2O + 4Fe^{3+} \rightarrow O_2 + 4Fe^{2+} + 4H^+$
Electrolysis : $4Fe^{2+} + 4H^+ \rightarrow 4Fe^{3+} + 2H_2$
Total : $2H_2O \rightarrow O_2 + 2H_2$

Fig. 5 Photocatalysis-electrolysis hybrid system using redox mediator
The photocatalysis pool is made of plastic bag. It consists of film formed with photocatalyst powder and electrolytic aqueous solution containing the redox mediator.

6 Technological issues in the photocatalysis-electrolysis hybrid system

6.1 Improvement of redox reactions

The elemental technologies needed for the practical use of photocatalysis-electrolysis hybrid system are shown in Fig. 6. The elemental technology development is wide ranging from the design of electrolysis device to the overall system, besides the development of the photocatalyst and the redox mediator. For the realization of the photocatalysis-electrolysis hybrid system, particularly the development of the photocatalyst with high performance redox reactions is the most important and the most difficult elemental technology development. The present status of development of this photocatalyst for redox reaction will be explained.

In the iron redox reaction, because the Fe^{3+} ion must preferentially adhere to the photocatalyst surface and receive the electron smoothly for the Fe^{3+} reduction reaction to progress with high efficiency, the reaction activity is likely to be greatly affected by the condition of the Fe^{3+} ion. Therefore, the authors studied the oxygen production reaction from various iron salt aqueous solutions using the TiO_2 powder that is a representative oxygen producing photocatalyst.[14] As a result, it was found that the oxygen production activity of perchlorate was more than 10 times higher than conventionally used sulfates. The apparent QE of TiO_2 photocatalyst at optimal conditions was 55 % (365 nm). This is the highest value for QE at ultraviolet wavelength within sunlight in the reversible redox reaction. To be able to achieve such high QE with a simple photocatalyst is highly significant in considering the future possibility of the reaction.

Next, the visible light responsive WO_3 photocatalysts was investigated for the counter anion effect of the iron salt, and the result showed that the oxygen production activity was highest when perchlorate was used. In the perchlorate iron solution, water preferentially coordinates with iron ion while perchlorate ion is difficult to coordinate, but the sulfate ion strongly coordinates with the iron ion. The difference of coordination of water and anion against the iron ion is thought to affect the activity. Also, when surface treatment was done against the WO_3 powder using aqueous solution containing various metal salts, it was shown that the WO_3 photocatalyst that was surface treated with cesium salt solution showed extremely high oxygen production activity.[2] The QE at 420 nm reached 27 %, and this was the highest value in the visible light range. It is thought that there is a mechanism by which ion exchange sites are newly formed on the WO_3 surface by cesium treatment and that the adherence and reaction of Fe^{3+} and H_3O^+ are facilitated. When the solar energy conversion efficiency (η sun) is calculated whereby the energy of sunlight is converted to the chemical energy of Fe^{2+} ion, it reaches 0.35 %. This value surpasses the value for switchgrass (0.2 %), a plant known as the hopeful source of biofuel. $BiVO_4$ is another semiconductor that can absorb longer wavelengths than WO_3, and light up to 520 nm can be used.

The research of redox mediators other than iron ion is extremely important, and several redox mediators have been developed recently. They include IO_3^-/I^- (E° = +1.086 V), VO_2^+/VO^{2+} (E° = +1.00 V),[15] and I_3^-/I^- (E° = +0.545 V).[16] There is an advantage that the voltage necessary for electrolysis decreases as the E° approaches zero. At this moment, however, the iron redox mediator is considered optimal from the perspectives of photocatalytic activity, cost, stability, nontoxicity, and others.

6.2 Evaluation of the theoretical limit of solar energy conversion efficiency

To discuss the possibility of the practical use of the photocatalysis-electrolysis hybrid system, we conducted the estimation of the theoretical limit of solar energy conversion efficiency (η_{sun}^m). Figure 7 shows the photoabsorption

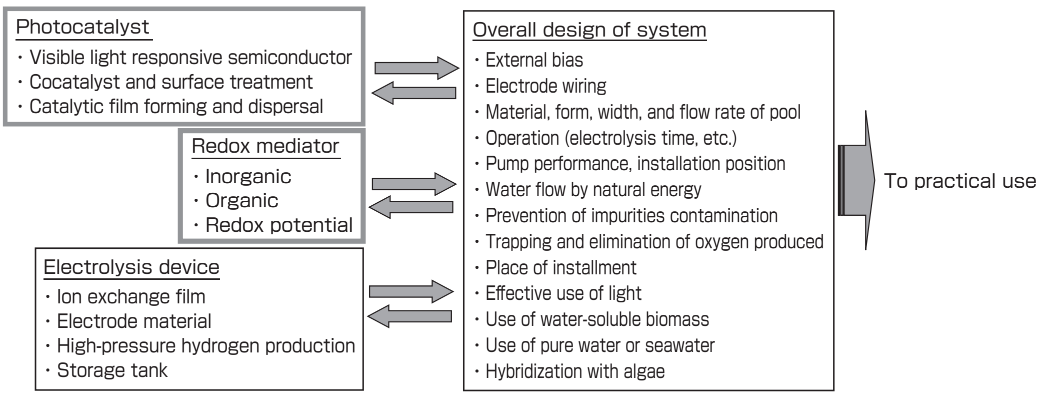


Fig. 6 Elemental technology development and scenario for achieving practical use of the photocatalysis-electrolysis hybrid system

The photocatalyst and redox mediators in the thick-lined boxes are issues that must be studied predominantly for major breakthroughs.

wavelength threshold (L_{max}, nm) of the semiconductor and η_{sun}^{m} when QE is assumed to be 100 %, based on the solar spectrum data for AM-1.5 total solar irradiation as designated by JIS-C-8911. For photoabsorption rate, light with shorter wavelength than L_{max} is assumed to have 100 % absorption (no loss by light reflection or permeation). The energy (eV) of one photon necessary for the potential difference (V) of a reaction is calculated by "1240/L_{max}." The values for V and eV can be considered equivalent. As examples, the theoretical limits η_{sun}^{m} of photocatalysis reactions when the iron redox is used and when an ideal redox mediator where the redox level is 0 V are shown. Theoretically, the long wavelength light of up to 2,700 nm and 1,000 nm, respectively, can be used, but it is not realistic to set the loss (U_{loss}) from reaction overvoltage to zero. For the estimate of U_{loss}, the electrolytic voltage of 1.6 V or less (corresponds to 0.37 V or less in U_{loss}) has been achieved in the hydrolysis method so far. In photosynthesis, it is notable that the potential difference of individual redox mediators in various electron transfer processes is about 0.2 V. If iron and ideal redox mediators are used with minimum U_{loss} value (0.4 V as for two electron transfer processes), the photocatalytic reactions can be used up to 1,440 nm and 760 nm, respectively, and their η_{sun}^{m} will be maximum 24 % and 30 %, respectively. As such η_{sun}^{m} is much larger in theory than the actual η_{sun} obtained, the experimental values are likely to increase in the future.

For the current semiconductor material, η_{sun}^{m} is about 2.4 % when the reduction of the iron redox mediator is conducted at QE = 100 % as all light up to 480 nm are entirely absorbed as in the WO_3 photocatalyst. If all light from 520 nm to 600 nm can be used for this reaction as in $BiVO_4$ or Fe_2O_3, it can be seen that the values from 3.6 % to 6.2 % can be achieved. The relationship of L_{max} and η_{sun}^{m} when QE is used as the variable using the iron redox mediator is shown in Fig. 8. It can be seen that η_{sun}^{m} of 3 % can be achieved if the QE is set at about 80 % using light up to 520 nm. The major characteristic of photocatalysis is that the reaction is complete with one particle, so that mixing and layering of several photocatalysts are easy. In cases where different semiconductors are layered in the photoelectrode, matching of the conduction band and the valence band is necessary, but this does not have to be considered in photocatalysts. This means, the whole performance can be increased by concurrently conducting the research to improve the QE in each photocatalyst and then combining them.

6.3 Practical evaluation of the solar energy conversion efficiency

Next, the solar energy conversion efficiency (η_{sun}) that was actually obtained will be discussed. The result up to now is that the η_{sun} of the powder photocatalysis reached about 0.35 %, as mentioned earlier. While this value seems to be very small compared to photovoltaic generation, it is at the level surpassing the efficiency of plants such as the switchgrass. For example, in the case of bioethanol production using biomass energy, the η_{sun} is about 0.8 % and algae that has the highest performance is about 3 %. Although these values are one digit less than the values for photovoltaic generation, it is important to note that it has been put to practical use in some countries and regions. Bioethanol has the major advantage unavailable in photovoltaic generation that the energy can be stored. As it can be seen, economic feasibility can be maintained sufficiently depending on the conditions and cost even if the η_{sun} is small. The concept of photocatalytic water

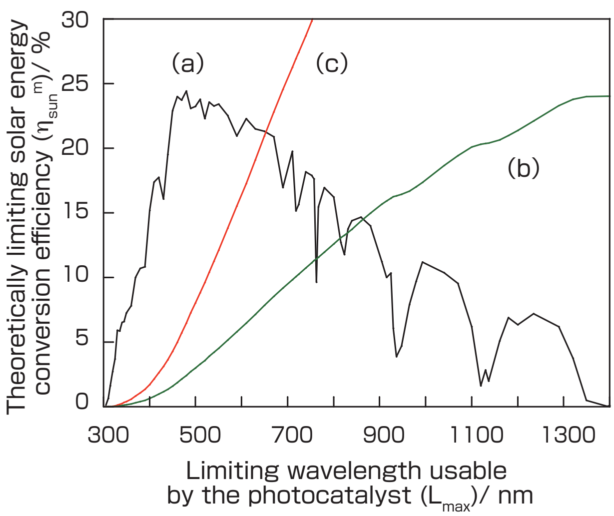


Fig. 7 Theoretically limiting solar energy conversion efficiency (η_{sun}^{m}) for the redox reaction of photocatalyst
In the case where the quantum efficiency and photoabsorption efficiency up to the limiting wavelength that can be used by photocatalyst is 100 %; (a) Sunlight spectrum, (b) iron ion redox reaction, and (c) E° = 0 redox reaction.

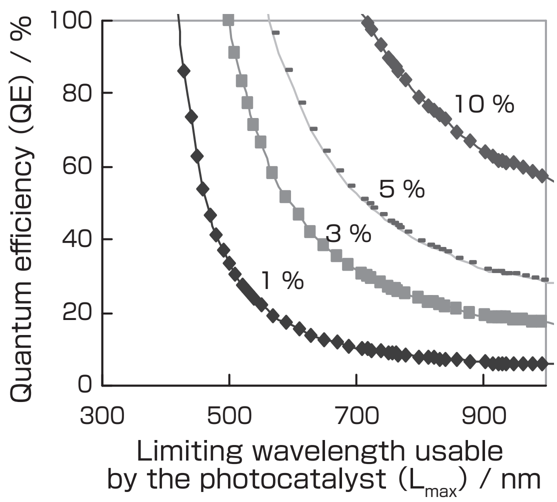


Fig. 8 Quantum efficiency (QE) of the iron ion redox reaction of photocatalyst (E° = +0.77 V) and the theoretically limiting solar energy conversion efficiency (η_{sun}^{m})
In the case where the photoabsorption efficiency up to the limiting wavelength that can be used by the photocatalyst is 100 %

electrolysis is closer to biomass energy than photovoltaic generation in the sense that the solar energy can be stored directly as chemical energy, and to surpass the η_{sun} of biomass use is a major milestone.

The solar energy conversion efficiency by current photocatalysts is much lower than that of algae, but the increase of efficiency of the light reaction of biomass must be achieved by genetic recombination, and there is a limit to how much artificial manipulation can be done. On the other hand, the efficiency of photocatalysts can be increased dramatically by finding the materials and devising preparation methods. Moreover, unlike biomass ethanol, the photocatalytic energy conversion storage does not require the processes of harvesting, grinding, glycosylation, or fermentation. It also has the advantage that it will not wither, does not require care of cultivation, and can be used in deserts or on the sea. The photocatalytic reaction using redox is an ultimate artificial photosynthesis system that can take place in a simple, uncovered pool. By comparison with biomass use, if it can achieve 3 % or more as its η_{sun} goal, it can sufficiently compete with photovoltaic generation.

7 Cost estimation of the photocatalysis-electrolysis hybrid system and the possibility of its practical use

Ultimately, in the discussion of practical use, it is necessary to estimate the cost of the whole system and compare the costs of hydrogen production. For the photocatalysis-electrolysis hybrid system, we must see whether the hydrogen production is possible at lower cost than the system that combines photovoltaic generation and water electrolysis in the Interim Goal ①, and whether the cost will be 30 yen/Nm^3 or less that is the goal of the Interim Goal ② and NEDO. For the solid polymer film electrolysis used in the cost estimation, the report of the Central Research Institute of Electric Power Industry was used as a reference.[7] For the photocatalysis pool and land price, the DOE report was used.[9]

As the water electrolysis device to be compared, a large-scale solid polymer hydrolysis device (32,000 Nm^3/h) is assumed. For the electricity cost, the least expensive power during the time zone is selected, and 8 yen/kWh (corresponds to night-time electricity rate) at 40 % operation is assumed. For the photocatalysis-electrolysis hybrid system, iron ion redox is used with solar energy conversion efficiency (η_{sun}) of the photocatalyst at 3 %. Other assumptions are: the photocatalyst cost is twice that of WO_3, the photocatalyst pool is made of polyethylene, depreciation of 10 years, Fe^{2+} is produced during the day and electrolysis is done during the night (10 h). The results and the example of the assumptions are shown in Fig. 9. The area of the photocatalyst pool needed for the above production of hydrogen is 3 km^2. The photocatalysts pool cost is 268 yen/m^2, and it is the same level as the DOE report (about 300 yen/m^2). The premium price over the costs related to the photocatalysts pool (facility, pump, cost of labor, land cost, management fee, interest, etc.) is about 3 yen/Nm^3. If the electrolysis voltage of the electrolyte solution containing Fe^{2+} is set at 0.8 V, the cost of electric power can be reduced to half, and the cost merit of this part is extremely high compared to the usual electrolysis. From the above assumption, the hydrogen production cost of the photocatalysis-electrolysis hybrid system was estimated to be about 25 yen/Nm^3. Under the same conditions, the hydrogen production cost by the usual large-scale water electrolysis using power at 8 yen/kWh would be about 41 yen/Nm^3. As mentioned in chapter 3, the power cost by photovoltaic generation is currently around 40 yen/kWh, and even if 7 yen/kWh (the development goal for 2030) is achieved, the hydrogen production cost will be over 35 yen/Nm^3. As a result of the above calculation, it was shown that for the Interim Goal ①, the photocatalysis-electrolysis hybrid

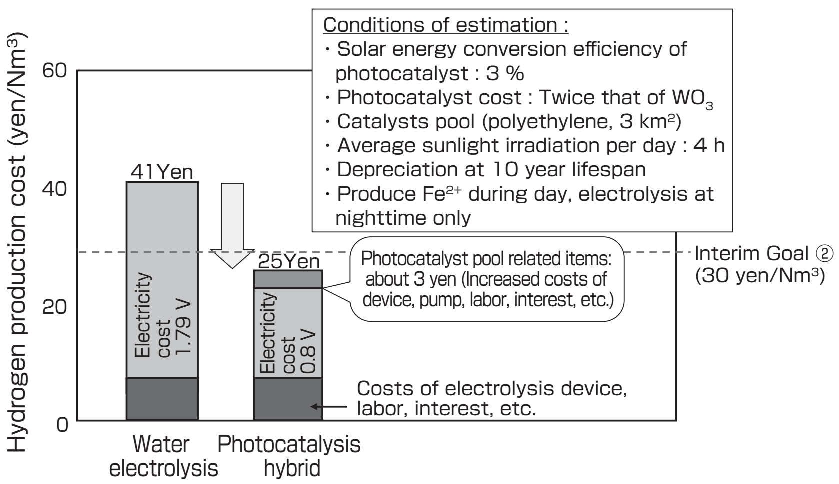


Fig. 9 Detailed cost estimation of the photocatalysis-electrolysis hybrid system

Common conditions: solid polymer type electrolysis (32,000 Nm^3/h), electricity cost 8 yen/kWh, and 40 % operation rate system is capable of producing hydrogen at lower cost than the system that simply combines the photovoltaic generation and water electrolysis. Moreover, possibilities were shown of lowering the cost of hydrogen production through the photocatalysis-electrolysis hybrid system using any kind of electric power including photovoltaic generation. Also, it can be said that 30 yen/Nm^3 or less of the Interim Goal ② can be achieved depending on the conditions. This is the basic data of the cost estimation.

In practice, it is necessary to additionally consider the factors of cost increase and decrease based on this calculation. The cost increase factors include, for example, electricity charges, land cost, and cost of measures against natural disasters such as typhoons. If the electricity charges are set at 1.5 times higher or 12 yen/kWh with the aforementioned assumption, the electrolysis system hybridized with photocatalysts and the usual electrolysis without hybridization will be 33 yen/Nm^3 and 58 yen/Nm^3 respectively. The cost decrease factors include the development of an excellent redox mediator with redox potential closer to zero than iron ion as well as improved solar energy conversion efficiency of the photocatalyst. Since the theoretical limit is about 24 % and 30 % for the iron ion and an ideal redox mediator as explained above, the increase in performance of the photocatalyst in the future is possible, and the area of the photocatalyst pool can be reduced. Also, if the electrolyte power can be brought close to zero using the ideal redox mediator, the hydrogen production cost will be nearly 14 yen/Nm^3. Considering both the cost estimation results and the low barrier to realization (possibility of realization and time), it can be concluded that there is significance in concentrating on this system.

8 Scenario toward practical use

8.1 Social roadmap

In the photocatalyst research of the Future Pioneering Project of METI, the goal values for the efficiency of solar energy contributing to hydrogen production were set as 1 %, 3 %, 7 %, and 10 % for FY 2014, 2016, 2019, and 2021, respectively. Recently, in the Innovation Plan for Environmental Energy Technology that includes the schedule of technological development up to 2050 as measures against global warming issued by the Council for Science, Technology and Innovation, the addition of artificial photosynthesis and solar hydrogen is being deliberated, and the above goal values are followed. While there is vagueness in the definition of the numerical goals, they should serve as an approximate time frame for the scenario toward practical use of solar energy conversion efficiency. Following the NEDO's hydrogen production roadmap for the hydrogen production cost, the Interim Goal ① is to be achieved before 2020, and 30 yen/Nm^3 or less of the Interim Goal ② will be pursued by 2030.

8.2 Future research prospect of solar hydrogen production

The hydrogen production by sunlight using the photocatalyst (and photoelectrode) was developed mainly in the chemistry field, and was studied as part of artificial photosynthesis. However, in the future, the authors think that the term "solar hydrogen production" should be used preferentially as a keyword to allow hybridization of different fields to accelerate the practical use. As mentioned in chapter 2, solar hydrogen production is a term that clearly indicates the objective-oriented *Type 2 Basic Research*. Also, there is a school of thought which considers that external bias should not be used in artificial photosynthesis, but in solar hydrogen production, it is thought that it should be actively employed. Whether the photocatalysis-electrolysis hybrid system can be put to practical use depends heavily on the total system design including the external bias as shown in Fig. 6, as well as the improvement of the performance of photocatalytic reaction. There are very few researchers in this field, and the application to practical use is expected to accelerate if the hybridization of different fields (new participation from different fields and developments within different fields) progresses. The "photovoltaic generation + water electrolysis " in the Interim Goal ① is not a rival, but should be considered one of the partners with whom we should hybridize.

The photocatalysis-electrolysis hybrid system is similar to the concept of the hybrid automobile. It is natural that the vehicle price increases if the gasoline engine, motor, and batteries are simply all installed in an automobile, and it may not necessarily improve the actual fuel consumption. The fuel consumption is reduced only when all elemental technologies are optimized and work complementarily. The hydrogen production cost of the photocatalysis-electrolysis hybrid system corresponds to fuel consumption. Even if the initial investment of the whole system is high, we may see the prospect for practical use by decreasing the hydrogen production cost or by increasing the additional value. In the initial phase of this research, new development in photocatalyst materials such as semiconductors and cocatalysts is extremely important. The authors are working on a high-speed automatic screening technology for material development.[17] There are countless numbers of metal compositions for semiconductors and combinations of cocatalysts and redox mediators, and searching by human hand is limited. By using a high-speed automatic screening technology, it may be possible to quickly find some unexpected, novel material candidates. As a ripple effect of this research, the research for photocatalytic reaction in the redox mediator can be directly applied to the research of oxygen-producing photocatalyst of Z-scheme reaction. Also, research for fuel cells using Fe^{2+} ion and redox flow batteries is being done, and if it becomes possible to produce large amounts of redox mediators with high reductive capacity using solar energy, it will be possible to convert the stored energy into electric power rather than hydrogen.

8.3 Practical introductory scenario

Concurrently with the search for materials in the early phase of this research, it is necessary to conduct small verification tests for the whole system to extract and solve problems. The material development for photocatalysts will progress mainly at universities and research institutes, and the companies can utilize their potentials for designing the device and electrolysis. Therefore, collaboration of industry-academia-government is important. The authors plan to conduct small-scale verification experiments for an integrated system in the future.

Since the photocatalytic pool functions as a large storage battery, the important characteristics is that it is highly compatible with renewable energies with high fluctuation such as wind generation as well as photovoltaic generation. Accompanying the wide introduction of renewable energy, the storage of its output variation is necessary. As the technology to store a large amount of electric power at lower cost than ordinary batteries, the hydrogen production by electrolysis is being studied for the excess power of renewable energy such as wind and photovoltaic generation. Depending on the location, this electrolysis device can be combined with photocatalysts and redox reactions. If the daytime and nighttime electrolysis can be combined, the facility operation rate will increase and the hydrogen production cost can be reduced further. Large-scale smoothing of power load at short and long cycles can be achieved. The hurdle in using the excess power is low for the initial introductory verification, and the full verification research of the hybrid system for such excess power electrolysis and photocatalysts will be the first step toward practical use.

Terminologies

Term 1. Apparent quantum efficiency (QE): percentage of the number of photons used in a reaction against the number of incident photons at a certain wavelength.

Term 2. Solar energy conversion efficiency (η_{sun}): percentage of energy extracted against the incident solar energy. In case of iron ion, it is the percentage of energy stored in the reaction in which Fe^{3+} is reduced to Fe^{2+} by decomposing water into oxygen. In the case of agricultural crops, it is the percentage of stored energy calculated from the annual amount of dried cop harvested against the annual total solar energy. Since η_{sun} is determined by several factors such as photoabsorption wavelength range, photoabsorption efficiency, QE, and percentage of photon energy stored in a substance, it becomes smaller than the value of QE.

References

[1] K. Sayama, H. Arakawa, K. Okabe and H. Kusama: Jpn. Patent 3198298 (2001); U.S. Patent 09/028495 (1998).

[2] Y. Miseki, H. Kusama, H. Sugihara and K. Sayama: Cs-modified WO_3 photocatalyst showing efficient solar energy conversion for O_2 production and Fe (III) ion reduction under visible light, *J. Phys. Chem. Lett.*, 1 (8), 1196-1200 (2010).

[3] Science Council of Japan: Science-Dream Roadmaps in the Fields of Science and Engineering, (2011) (in Japanese). http://www.scj.go.jp/ja/info/kohyo/kohyo-21-h132.html

[4] NEDO: Nenryo Denchi Suiso Gijutsu Kaihatsu Rodomappu 2010 (Development Roadmap for Fuel Cells and Hydrogen Technology 2010), (2010) (in Japanese). http://www.nedo.go.jp/news/other/FF_00059.html

[5] Energy and Environment Council: KosutoTo Kensho Iinkai Hokokusho (Report of the Committee for Investigation of Cost and Others), (2011) (in Japanese). http://www.aec.go.jp/jicst/NC/tyoki/sakutei/siryo/sakutei10/siryo2-2-3.pdf

[6] NEDO: Taiyoko Hatsuden Rodomappu (PV2030+) (Roadmap PV2030+), (2009) (in Japanese). http://www.nedo.go.jp/library/pv2030_index.html

[7] Y. Asaoka and M. Uotani: Feasibility study on hydrogen production with off-peak electricity -evaluation of the effects of availability and electric power transmission, *CRIEPI Research Report*, T02039, 1-16 (2003).

[8] A. Fujishima and K. Honda: Electrochemical photolysis of water at a semiconductor electrode, *Nature*, 238, 37-38 (1972).

[9] B. D. James, G. N. Baum, J. Perez and K. N. Baum: Technoeconomic analysis of photoelectrochemical (PEC) hydrogen production, *DOE Report (2009)*, Contract No. GS-10F-009J (2009).

[10] R. Saito, Y. Miseki and K. Sayama: Highly efficient photoelectrochemical water splitting using a thin film photoanode of $BiVO_4/SnO_2/WO_3$ multi-composite in a carbonate electrolyte, *Chem. Commun.*, 48, 3833-3835 (2012).

[11] K. Sayama, R. Yoshida, H. Kusama, K. Okabe, Y. Abe and H. Arakawa: Photocatalytic decomposition of water into H_2 and O_2 by a two-step photoexcitation reaction using a WO_3 suspension catalyst and an Fe^{3+}/Fe^{2+} redox system, *Chem. Phys. Lett.*, 277 (4), 387-391 (1997).

[12] K. Sayama, K. Mukasa, R. Abe, Y. Abe and H. Arakawa: Stoichiometric water splitting into H_2 and O_2 using a mixture of two different photocatalysts and an IO_3^-/I^- shuttle redox mediator under visible light irradiation, *Chem. Commun.*, 2416-17 (2001).

[13] S. Mizuta, W. Kondo, K. Fujii, H. Iida, S. Isshiki, H. Noguchi, T. Kikuchi, H. Sue and K. Sakai: Hydrogen production from hydrogen sulfide by the Fe-Cl hybrid process, *Ind. Eng. Chem. Res.*, 30, 1601-1608 (1991).

[14] Y. Miseki, H. Kusama, H. Sugihara and K. Sayama: Significant effects of anion in aqueous reactant solution on photocatalytic O_2 evolution and Fe(III) reduction, *Chem. Lett.*, 39 (8), 846-847 (2010).

[15] Y. Miseki, H. Kusama and K. Sayama: Photocatalytic energy storage over surface-modified WO_3 using V^{5+}/V^{4+} redox mediator, *Chem. Lett*, 41 (11), 1489-1491 (2012).

[16] Y. Miseki, S. Fujiyoshi, T. Gunji and K. Sayama: Photocatalytic water splitting under visible light utilizing I_3^-/I^- and IO_3^-/I^- redox mediators by Z-scheme system using surface treated PtO_x/WO_3 as O_2 evolution photocatalyst, *Catal. Sci. Technol.*, 3, 1750-1756 (2013).

[17] H. Kusama, N. Wang, Y. Miseki and K. Sayama: Combinatorial search for iron/titanium-based ternary oxides with a visible-light response, *J. Comb. Chem.*, 12 (3), 356-362 (2010).

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Completed the doctorate courses at the Department of Chemistry, Graduate School of Science, Tokyo University of Science in March 2009. Joined AIST in April 2009. Currently, Senior Researcher, Solar Light Energy Conversion Group, Energy Technology Research Institute. Since dissertation, has engaged in the development of new materials for water decomposition using photocatalysts. In this paper, was mainly in charge of the cost estimate of the photocatalysis-electrolysis hybrid system.

Discussions with Reviewers

1 Overall

Question and comment (Yasuo Hasegawa, AIST; Hiroshi Yanagishita, Research Institute for Innovation in Sustainable Chemistry, AIST; Hiroshi Tateishi, AIST)

This paper sets as its main topics the R&D goal and scenario that are important in promoting the long-term R&D for the practical use of solar hydrogen production. It also describes the process by which the results of the basic research are expanded into various projects, and therefore, we believe it is appropriate as a paper to be published in *Synthesiology*. In general, the flow of R&D takes the course in which the scenario for practical use can be drawn only after what is considered to be *Type 2 Basic Research* is achieved. However, in this particular research, the scenario for practical use is drawn at the basic research phase. Please emphasize the necessity and importance of doing so.

Answer (Kazuhiro Sayama)

The point that you indicate is certainly the point that I wish to convey the most in this paper. There is a long history of solar hydrogen production technology development, and while this applies generally to the development of energy technology that requires a long time before it is put to practical use, the progression and direction of basic research is greatly affected by the fluctuations in energy prices and changes in energy policies, and I think those are the major barriers in promoting the R&D. To effectively promote the practical use of R&D that requires a long period of time, I think a long-term R&D plan that clearly states the development goal, milestones, and the scenario toward practical use is particularly important. These points were explained in detail in chapters 1 and 2.

2 Scenario and time axis

Question and comment (Hiroshi Tateishi)

In general, the usual course to promote the introduction of new energy technology and to achieve practical use is to start the verification research at introduction even at high cost, by combining the subject with large added value and other R&Ds, and to attempt cost reduction through concurrent basic research. In the scenario of chapter 7, can you describe this development clearly considering a time axis if possible?

Answer (Kazuhiro Sayama)

As you indicated, the overall flow along a time axis of the research for solar hydrogen production toward practical use was added in the first paragraph of chapter 7. In the photocatalyst research of the Future Pioneering Project of METI, the goal value of 10 % by FY 2021 was set as the efficiency with which solar energy should contribute to hydrogen production. This goal is followed in the Innovation Plan for Environmental Energy Technology of the Council for Science, Technology and Innovation. For the hydrogen production cost, if the NEDO's hydrogen production roadmap is followed, the Interim Goal ① should be achieved before 2020, and 30 yen/Nm^3 or less of the Interim Goal ② will be sought by 2030.

3 Goal setting, scenario, and the synthesis and integration of elemental technologies

Question and comment (Hiroshi Tateishi)

Please describe more clearly the "specific scenario, research procedure, and process of synthesis and integration of the elemental technologies including the goal setting and social value" that is part of the purposes of publishing *Synthesiology*. Also, please make sure that researchers of different research fields can easily understand how *Type 1 Basic Research* conducted by you leads to *Type 2 Basic Research* and *Product Realization Research*.

Answer (Kazuhiro Sayama)

To ensure that the researchers of other fields, not just those of this field, would understand, I explained the process from *Type 1 Basic Research* to *Type 2 Basic Research*, and to the final goal of solving the energy problem.

4 "Artificial photosynthesis"

Question and comment (Hiroshi Yanagishita)

This paper mainly discusses the technological development for efficiently producing solar hydrogen. On the other hand, the term "artificial photosynthesis" is used in general, including the solar hydrogen production technology as described in this paper, and there are government R&D projects with this name. Is "artificial photosynthesis" a process for producing organic material using sunlight as in the photosynthesis in plants?

Answer (Kazuhiro Sayama)

"Artificial photosynthesis" that the general public thinks of is the process of synthesizing organic material from CO_2, and it may be unnatural to include the technology of producing hydrogen by water decomposition using sunlight as “artificial photosynthesis.” On the other hand, in the roadmap of the Innovation Plan for Environmental Energy Technology of the Council for Science, Technology and Innovation, artificial photosynthesis and hydrogen production by sunlight are included in the category for “recovery, storage, and use of carbon dioxide,” and it has always been discussed as part of CO_2 use.

The photosynthesis mechanism is divided into the light reaction where water is decomposed and the dark reaction where CO_2 is fixed. To solve the energy problem it is necessary to simulate the former, but in general, attention is paid to the latter. There is no term that clearly expresses the importance of the reaction that simulates the former light reaction, and we needed a new term. Therefore, in this paper, we decided to use the term “solar hydrogen production,” which is now being recognized little by little, and provided detailed explanation.

Considering the background of the historical progress of the field and the principles, I think “solar hydrogen production” should be positioned within “artificial photosynthesis” (Fig. 1). In the wide-ranging field of artificial photosynthesis, the research of hydrogen production by sunlight has been rapidly progressing, and the author believes that it can eventually achieve practical use. In this paper, we defined “solar hydrogen production” as a term that expresses the objective-oriented *Type 2 Basic Research* to realize a sustainable society by creating hydrogen from solar energy and water.

On the other hand, in the future, I think there may be problems if we continue to position “solar hydrogen production” within “artificial photosynthesis.” For example, the term “artificial photosynthesis” is strongly linked to the chemistry field and *Type 1 Basic Research*, and this may be a hurdle for the development in diverse fields (particularly physics, engineering, and corporate participation) that are essential in achieving the practical use of the “solar hydrogen production” technology. I think we should widely use the term “solar hydrogen production” as a keyword to express the shift from *Type 1 Basic Research* to *Type 2 Basic Research*.

5 Time frame for achieving practical use

Question and comment (Hiroshi Yanagishita)

There are still several issues that must be cleared before achieving the practical use of technology for solar hydrogen, and I think it is often considered as a technology for the distant future. What perspective do you have on the time frame for achieving practical use?

Answer (Kazuhiro Sayama)

As it could not have been imagined 20 years ago that photovoltaic generation would rapidly spread to homes as today, I think “solar hydrogen” will also diffuse dramatically through some technological breakthrough, as long as the principles and assumptions are appropriate and the scenario is clear. As explained in chapter 7, I think the verification research using excess electric power is the first step.

6 Future strategic development and system of the R&D

Question and comment (Hiroshi Tateishi)

I think this paper assumes a hydrogen society centering on fuel cells. For use of fuel cells, the stationary type and automobile type are assumed, and the current mainstream is fossil fuel reformulation for the former and pure hydrogen for the latter. On the other hand, the powerful sales point in the current society for photovoltaic power generation is that electric output can be obtained directly. To store solar energy by converting it into an energy mediator such as hydrogen is effective in stabilizing output temporally and spatially, but new issues are generated at the same time. How can hydrogen be stored – in high pressure, in hydrogen storing substance, or as liquefied hydrogen? How will it be transported?

Also, when actually constructing a system proposed in this paper, are you going to put it in cities or some desert or field? I think there may be different technological issues depending on the location.

It is necessary to concurrently engage in the energy system design, and I think you should discuss this with the researchers of systems in the course of future strategic development of R&D.

Answer (Kazuhiro Sayama)

The primary motivation of our research up to this point is to realize conversion and storage for solar energy. If we can produce a large amount of hydrogen from sun and water, we will be very happy just with that, and since there are many researchers who will think about how to use hydrogen, I think the research will progress rapidly.

On the other hand, I recognize that for practical use, energy system design is another side of the coin. In the future, I would like to get the systems researchers involved in the discussion to achieve the practical use of solar hydrogen production.

Methodology for designing cryptographic systems with advanced functionality based on a modular approach

— Towards reducing the barrier to introducing newly-designed cryptographic schemes into real-world systems —

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In this article, we point out that in general, newly-designed highly functional cryptographic schemes have significantly complicated structures that hinder user understanding. Furthermore, this fact may prevent these new technologies from being introduced into real world systems. We propose a new methodology for overcoming this barrier. We take proxy re-encryption as an example, and discuss how the barrier to user understanding is reduced by our proposed methodology.

Keywords : Public-key cryptosystems, digital signature, proxy re-encryption, provable security, standardization

1 Introduction

1.1 Background and Motivation

Background

With the advancement of the network society, new advanced or highly functional cryptographic schemes are being designed to provide secure information services that are becoming ever complex, as exemplified by cloud storage. One representative example of such highly functional cryptographic schemes is proxy re-encryption.[1]

In proxy re-encryption, the sender designates a receiver and conducts encryption. Then the server called "proxy" can re-designate a different receiver without conducting decryption. By using this technology, data access is allowed to an indefinite number of authorized users, while viewing by any unauthorized user can be prevented. For example, one may wish to encrypt and protect the electronic charts used at hospitals because they contain private information, but the information must be shared when the patient is transferred to another residence or hospital, and proxy re-encryption will be significantly useful in such a situation.

However, although such highly functional cryptographic schemes including proxy re-encryption are expected to provide high security and convenience, it is not easy to intuitively understand the security and functionalities due to their complex construction. For example, four papers on highly functional cryptographic schemes were published at the CRYPTO 2012, which is the most authoritative international conference on cryptology, and the papers were on average 34 pages long of which on average 24 pages were devoted to security definitions and security proofs. The contents are lists of difficult-to-understand mathematical formulas, and it is not easy to understand the correlation between these formulas and actual security. This is thought to be the major barrier in introducing highly functional cryptographic schemes to the real world. Particularly, even specialized researchers find it difficult to be convinced of the security, and a general user cannot be expected to use these schemes with full confidence. In fact, error in proof is often discovered later, even with cryptographic schemes that the designers have claimed that their security has been mathematically proven. Hereinafter, this problem will be called *the security verification problem* in cryptographic schemes.

Motivation

In light of the above situation, this paper addresses the methodology to promote the introduction of a new highly functional cryptographic scheme with complex functions to the real world. Particularly, we propose a design principle to simplify the understanding of the security of the cryptographic schemes where the security verification tends to be complex and difficult for the researchers and engineers who are not specialists of the field. Specifically, we indicate the importance of breaking down the needed functionalities before engaging in design and describing them by the combination of simple functionalities as much as possible, rather than conducting scratch development[Term] for highly functional cryptographic schemes with complex functionalities. In this case, it is desirable to breakdown

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the functionalities into basic cryptographic schemes where the individual functionalities are already widely in use. By achieving the complex functionalities only through the combination of existing schemes without scratch development, the security can be based on the reliability of the existing schemes that comprise the elemental technologies. Moreover, since the existing technologies are already widely used in the real world, their reliability can be considered sufficiently high.

The modularization where the complex problem is reduced to smaller, easier-to-understand elements is a common practice in the field of programming, but it was not commonly done in cryptographic research. One of the reasons is that compared to the usual information technology where "appropriate things are done," the cryptographic schemes differ greatly in characteristic because it is necessary to ensure that "inappropriate things cannot be done." This is a point that necessitates a new set of arguments to justify the modularization method. Since previously, in the field of highly functional cryptographic scheme field, system design for specialists was mainstream, and the work of "making things understandable" like modularization was taken lightly. However, it has come to the point that recent highly functional cryptographic schemes have become increasingly complex, and even the specialists cannot correctly understand the newly proposed schemes. There are cases where errors in security proofs are pointed out in the schemes that were peer-reviewed and accepted by the international conferences that are supposed authorities. Currently, as highly functional cryptographic schemes are put to practical use, it is important to explain the technology to those who are not specialists, and we believe the necessity and importance of incorporating the modularization method into cryptographic research are increasing.

Note that the objective of the proposed methodology is not to strengthen the security of the cryptographic schemes, but the main objective is to achieve equivalent security in a form that is understandable to a third party (potential user). This research is to point out that there is a significant difference between the cryptographic schemes where just the theoretical verification for security has been done (to some degree), and the cryptographic schemes where the security verification result is easy to understand for the user, in terms of ease of introduction to the real world, and this difference is the barrier to the practical use of new highly functional cryptographic schemes. This research attempts to promote the wide use of highly functional cryptographic schemes in the real world by removing such barriers.

In the next section, we discuss the case of proxy re-encryption as a specific case study to observe the barrier due to the security verification problem.

1.2 Outline and current status of the proxy re-encryption

Outline of the proxy re-encryption

Proxy re-encryption is a technology that allows conversion of encrypted data addressed to a different receiver without decrypting the encrypted data that is addressed to a certain receiver (Fig. 1). It was proposed for the first time by Blaze *et al.*[1] in 1998. In a normal situation, the proxy re-encryption works similarly to public key encryption, and the receiver can designate a certain user, other than oneself, to the server called the "proxy," and can deposit a "re-encryption key." The proxy can convert the ciphertext addressed to each user to the ciphertext addressed to a different designated user by activating the re-encryption key. By using this cryptographic scheme, multiple users can be adaptively designated instead of one certain user. We note that some proxy re-encryption schemes allow multiple re-encryptions, but in this paper, proxy re-encryption schemes that allow re-encryption only once will be discussed.

Proxy re-encryption is significantly useful in achieving secure access control in an environment where there is indefinite number of users such as in cloud storage, and R&Ds have been done actively and globally since 2006. While the discussions for security had been insufficient back in 1998, focus was placed on designing a system with powerful, mathematically provable security in a series of research since 2006. Such powerful mathematical proof for security arose not merely from theoretical interest, but due to practical necessity. In the work of standardization, for example, in the selection of CRYPTREC e-Government Recommended Ciphers,[2] which is considered as the standard cryptographic schemes in Japan, the presence of mathematical security proof is an important selection criterion.

Necessity of proxy re-encryption

In the cloud storage such as Dropbox[3] and Google Drive[4] that are widely used, the reading and writing of the files can be done only by multiple users with valid authorization, and such authorization can be set flexibly.

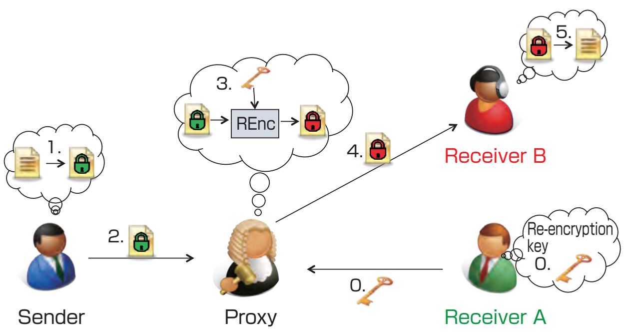

Fig. 1 Overview of proxy re-encryption

However, since the data stored in these storages are assumed to be shared by multiple users, they are either not encrypted or are encrypted in a manner in which the data storage server can decrypt them, and the data can be accessed by the server manager. Therefore, even if the user takes extra caution to manage the data, there is danger of data leakage due to the server manager with malicious intentions or negligence. Recently, the whistleblowing by the employee of the Central Intelligence Agency (CIA) and National Security Agency (NSA) of the United States had international repercussions. There are also reports of possibility that mail addresses and phone numbers of 6 million Facebook users were released due to a fault on the server side. Such events are examples of the limitations of the system design that places unconditional confidence in the server.

One of the methods to prevent spying and leakage of data through the server as mentioned above is to store the data that have been encrypted by the user in the storage. The server that does not have the decryption key cannot read the data, and the plaintext will not leak from the server. However, it should not be assumed that the decryption key needed to access the data is safely distributed only to users with valid authorization. This is because if there is a mechanism where the decryption key can be safely distributed to authorized users only, the data can be distributed only to authorized users using that mechanism.

When proxy re-encryption is used in such a situation, each user can not only store the data in storage in encrypted form, but other authorized users are allowed flexible access control by depositing the re-encryption key to the proxy. The cloud storage using proxy re-encryption is being used commercially.[5] Since the problems that occurred in Facebook and others were due to complex factors, not all problems can be immediately solved by introducing proxy re-encryption. However, it will be significantly effective as it can eliminate the assumption of the existence of a highly reliable server.

Barriers in introducing the proxy re-encryption

As mentioned above, while proxy re-encryption is useful in achieving the cloud storage with flexible access control that is secure against spying and leakage of data through the server, there are still barriers in introducing this technology to the real system. The barrier is not directly related to the functionality of proxy re-encryption, and actually there will be absolutely no problem if the given proxy re-encryption scheme can be confirmed to work as intended. Here, detailed explanation will be given on the barriers to introducing proxy re-encryption.

There are security verification problems as mentioned at the beginning of this section in most of the highly functional cryptographic schemes, and this is particularly significant in proxy re-encryption. The proxy re-encryption scheme proposed at PKC 2009, an international conference that is the authority on public key cryptography, had excellent efficiency,[6] but it was pointed out in PKC 2010 of the following year that the security proof was wrong and it could be attacked.[7] In that paper, a new proxy re-encryption scheme was proposed, but the error in the security proof was pointed out and attacked at the following PKC 2011.[8]

Therefore, there seems to be no method in which the functionality and security are reliable as claimed by the designer for the various proxy re-encryption schemes that had been proposed so far, and this is a major barrier to practical use. For the proxy re-encryption scheme[5] that has been commercialized recently, it should be noted that the service is provided by the company to which the designer belongs, and the practical use has not necessarily been promoted after wide recognition of the technological adequacy.

Other highly functional cryptographic schemes

As mentioned earlier, this paper proposes the guideline for solving the common problems in the practical use of various highly functional cryptographic schemes that have recently been proposed, and proxy re-encryption is just one example. The examples of highly functional cryptographic schemes other than proxy re-encryption include attribute-based encryption, keyword-searchable encryption, homomorphic encryption, group signature, and others. In all these highly functional cryptographic schemes, the structure and security definition become complex as in proxy re-encryption, and this again is a major barrier to their practical use.

2 Functionalities and security definitions of proxy re-encryption

In this chapter, we explain the functionalities and security definitions of proxy re-encryption, and discuss how the construction and its security proofs become complex when a proxy re-encryption scheme that satisfies them is designed by conventional approaches.

2.1 Formal model of proxy re-encryption

First, we explain the algorithms that constitute proxy re-encryption. These are listed as follows:

[Algorithm 1] Key generation for each user
As in an ordinary public key encryption scheme, a proxy re-encryption scheme has the algorithm with which each user generates a pair of a public encryption key and a secret decryption key.

[Algorithm 2] Re-encryption key generation
A proxy re-encryption scheme has the algorithm for

generating a re-encryption key that can be used to transform a ciphertext for User A into a ciphertext for User B. User A generates a re-encryption key by using User A's secret key and User B's public key, and gives it to a proxy.

[Algorithm 3] Encryption
As in an ordinary public key encryption scheme, a proxy re-encryption scheme has the algorithm with which a user can generate a ciphertext that can be decrypted by a legitimate receiver who possesses a secret key. In the encryption algorithm, a ciphertext is generated from a plaintext to be encrypted and the receiver's public key. Moreover, as mentioned above, a ciphertext generated by this algorithm must be transformable to a ciphertext that can be decrypted by a different receiver by using a re-encryption key.

[Algorithm 4] Re-encryption
A proxy re-encryption scheme has the algorithm that enables a proxy who holds a re-encryption key to transform a ciphertext that was originally designated to some receiver into a ciphertext that can be decrypted by another receiver who is different from the original receiver. In this re-encryption algorithm, a re-encrypted ciphertext is generated from a ciphertext (that has not been re-encrypted) and a re-encryption key.

[Algorithm 5] Decryption of ciphertexts that are not re-encrypted
A proxy re-encryption scheme has the algorithm that enables us to decrypt ciphertexts that are generated by the encryption algorithm (Algorithm 3). In this decryption algorithm, a plaintext is recovered from a ciphertext (generated under a legitimate receiver's encryption key) and the receiver's decryption key.

[Algorithm 6] Decryption of re-encrypted ciphertexts.
Similarly to the above, a proxy re-encryption scheme has the algorithm that enables us to decrypt re-encrypted ciphertexts that are generated by the re-encryption algorithm (Algorithm 4). In this decryption algorithm, a plaintext is recovered from a re-encrypted ciphertext and a legitimate receiver's decryption key.

As can be seen from Algorithms 1 to 6, there are six algorithms that constitute a proxy re-encryption scheme, and all of them have complex functionalities. Therefore, even if a designer of a proxy re-encryption scheme claims that the proposed scheme satisfies the functionalities, it is not always easy to verify the correctness.

2.2 Security Definitions of proxy re-encryption

As mentioned in subchapter 2.1, the formal model of proxy re-encryption is already quite complex, and the security definitions are even more complicated and hard-to-understand for non-specialists. In this section, we provide the security requirements of proxy re-encryption. For details, refer to reference [9], for example.

The security notion usually required by ordinary public key encryption (without the re-encryption functionality) is called "security against chosen ciphertext attacks." This security notion ensures that no attacker can obtain even one bit of information of the plaintext from a target ciphertext, even if the attacker is allowed to observe decryption results of arbitrary ciphertexts other than the target ciphertext. It is known that this security not only ensures that the information does not leak from the ciphertext, but also ensures security against "active" attacks such as modification of ciphertexts, and is nowadays considered as a desirable security notion for public key encryption used in practice.

Basically, the aforementioned security is also required for proxy re-encryption. However, as already seen in subchapter 2.1, there are two types of ciphertexts in proxy re-encryption, namely "ciphertexts that are not re-encrypted" and "re-encrypted ciphertexts," and an attacker who wishes to obtain the information of a plaintext may attack either type of ciphertexts. Moreover, since proxy re-encryption has the re-encryption functionality as well as the functionality to generate re-encryption keys, the attacker may try to extract useful information for its attack from these functionalities. Therefore, the security definition of proxy re-encryption must take into account such situations. Particularly important is that the security definition must ensure that the information of a plaintext does not leak from a ciphertext to a proxy that performs re-encryption. Moreover, considering the real use situation, the information of communications to a legitimate user must be protected even when multiple users and proxies collude. Based on the above explanation, the security requirements of proxy re-encryption are organized as follows. (Below, for notational convenience, the user who is under attack will be called A.)

[Security of ciphertexts that are not re-encrypted]
This security notion requires that even if there is any kind of collusion among users and proxies except the "collusion for which attack cannot be prevented in principle," even one bit of plaintext information will not be leaked from a ciphertext (that is not re-encrypted) designated to A. This security notion also requires that a ciphertext cannot be converted to a different, meaningful ciphertext other than a "re-encrypted ciphertext designated to another user." Note that due to the definition of the functionalities of proxy re-encryption, when "User B" and the "proxy that can re-encrypt a ciphertext designated to A to a ciphertext designated to B" form a collusion, all ciphertexts (that have not been re-encrypted) designated to A can be decrypted. Thus, this security notion takes care of all attack situations except the collusion that cannot be prevented in principle.

[Security of re-encrypted ciphertexts]

This security notion requires that in the situation where a ciphertext that has not been re-encrypted is designated to a user different from A (we call the user B), even if all users including B and proxies collude, even one bit of plaintext information will not be leaked from a re-encrypted ciphertext designated to A. This security notion also requires that a re-encrypted ciphertext cannot be transformed to any different, meaningful ciphertext.

The above are the security notions required of proxy re-encryption, and it would be easily seen that there arises the security verification problem in which understanding and verifying the security definitions and security proofs are difficult.

2.3 Example of an existing proxy re-encryption scheme

Figure 2 shows part of the construction of the proxy re-encryption scheme proposed by Libert and Vergnaud.[10] This scheme was designed and implemented from scratch, using a cyclic group with a special kind of mapping (function e in the figure) that has bilinearity. (This mapping is called "pairing" in cryptography.) By assuming the hardness of solving some mathematical problem on the cyclic group, the authors of this paper provided the security proofs which show that this proxy re-encryption scheme satisfies the security notions explained in subchapter 2.2. This proxy re-encryption scheme is known as one of the representative schemes that achieve both security and practical efficiency.

However, as can be seen from the figure, the description of the scheme is quite complex. The components of a ciphertext and various keys cannot be clearly parsed into the component that plays the role of hiding the information, a plaintext, the component that enables re-encryption, or the component that contributes to security, and the components are complexly intertwined. The structure of the parameters and the order of calculations are combined in a "craftsman-like" manner, and it is even difficult for us, the researchers in cryptography, to clearly explain the individual roles. For example, as shown

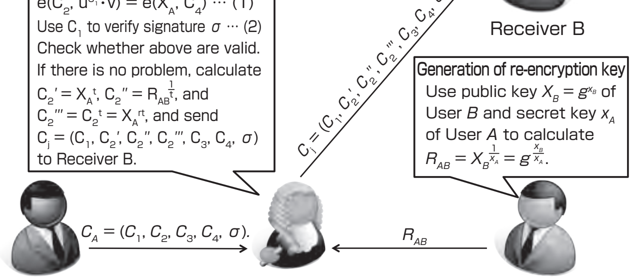

Fig. 2 Re-encryption functionality in an existing scheme[10]

in Fig. 2, the components C_2', C_2'', C_2''' in a re-encrypted ciphertext are not independent, but are correlated via the common internal randomness t. Also, although not explicitly described in the figure, the components C_2''', C_3, C_4 in a re-encrypted are also correlated via the common internal randomness r, and the component σ is generated depending on C_1, C_3, C_4. Thus, it can be seen that all the components in the ciphertext are mutually correlated, and therefore are involved in the various functionalities of proxy re-encryption in one way or the other. Furthermore, the cyclic group with "pairing" described above must use a special cryptographic software library that is difficult to be appropriately used by anyone other than engineers with a certain level of knowledge of cryptography using elliptic curves, and it is also poor in modularity and transplantability.

3 Proposed method: Methodology and example of application to proxy re-encryption

In order to resolve the security verification problem, in this section we discuss our methodology to make highly functional cryptographic schemes (including proxy re-encryption) that have complex algorithm and security definitions easily understandable by a third party who may be a potential user, and to smoothly introduce them to the real world. Also, we describe the proxy re-encryption scheme that was actually designed based on our methodology, and explain the design philosophy behind the construction.

3.1 Overview of the proposed methodology

So far, highly functional cryptographic schemes with complex functionality requirements have very often been designed from scratch to satisfy their functionalities and security definitions. Since a system designed from scratch tries to achieve required functionalities and security simultaneously in an inseparable manner by voluminous and complex mathematical equations, it is extremely difficult for a third party to verify the correctness of them.

Here, we consider such a conventional approach of designing from scratch to be the major inhibiting factor in introducing highly functional cryptographic schemes to the real world. As the methodology for solving the problem, we propose to "insert the steps of modularizing the required functionalities and security as much as possible before the phase of starting the actual design" and emphasize its importance (See Fig. 3). In particular, considering the security verification problem, we pursue "modularization" as much as possible so that the modularized functionalities and security notions can be achieved by directly using existing basic cryptographic schemes that have already been well-known and well-studied. While expertise in existing basic cryptographic schemes is still required, these basic primitives have already been sufficiently studied and analyzed, and there are many more researchers and engineers who are capable of verifying and understanding them, compared to highly functional cryptographic schemes such as proxy re-encryption.

By designing a highly functional cryptographic scheme after the step of modularizing the requirements of functionalities and security, it becomes possible to facilitate a third party to understand the functionalities and security provided by a designed system. More specifically, the following positive effects can be expected.

- It becomes easier to understand what roles individual modularized functionalities and security play in the designed system.
- Since the functionalities and security of the basic cryptographic schemes used as building blocks have already been well-understood, it becomes easier to understand and to verify the correctness of functionalities and security of the designed system.
- For each modularized functionality and security, it becomes possible to select a suitable building block that works in the most effective way, depending on applications. Furthermore, once any problems are found in the building blocks, we can easily and quickly replace them with some other building blocks.

Due to these positive effects, the barriers in introducing a newly designed highly functional cryptographic scheme into a real world system will be significantly reduced.

In the next section, we will explain a concrete proxy re-encryption scheme that was designed based on our proposed methodology. Before doing so, in order to confirm that the above positive effects are indeed achieved by the proposed methodology, we exemplify a simpler case of public key encryption that allows variable length of plaintexts.

Generic construction of public key encryption that allows plaintexts with variable length

In most of the existing public key encryption schemes, for example, references [11] and [12], the size of plaintexts that can be encrypted is strictly limited due to the algebraic structure on which the schemes are based. In practice, however, it is often the case that we need to be able to encrypt data of various sizes. On the other hand, in the research on symmetric key encryption, it is usual to design schemes that can encrypt messages of variable length by default. In the beginning of the 2000s, the methodologies for constructing a public key encryption scheme that allows plaintexts of variable length were systematized, and the following generic construction was proposed: (1) First, a session-key K with a fixed length is selected, and a plaintext is encrypted by a symmetric key encryption scheme using the session-key K. (2) Next, the session-key K is encrypted using a public key encryption scheme (that allows only fixed length plaintexts). Finally, the set of two ciphertexts obtained in the above steps (1) and (2) are used as a ciphertext of this construction.

This construction can be seen as a specific example of the design methodology of highly functional cryptographic schemes proposed in this paper. Specifically, the basic functionality of public key encryption and the functionality to encrypt variable length plaintexts are separated into an (ordinary) public key encryption scheme and a symmetric key encryption scheme , respectively. This construction has been further refined and sophisticated, and currently, the above functionalities (1) and (2) are standardized individually in the standardization activities, such as ISO[13], of public key cryptographic schemes. From this simple example, the effectiveness of the design methodology proposed in this paper can be appreciated.

3.2 Application to proxy re-encryption

Here, we introduce the proxy re-encryption scheme that was designed by Hanaoka et al.[9] based on the methodology proposed in the previous section. This scheme is constructed by combining a public key encryption scheme,[11][12] a digital signature scheme,[11][14] and a threshold public key encryption scheme[15] as building blocks, and it is easy to understand the correspondence of how and by which building blocks the required individual functionalities and security are achieved.

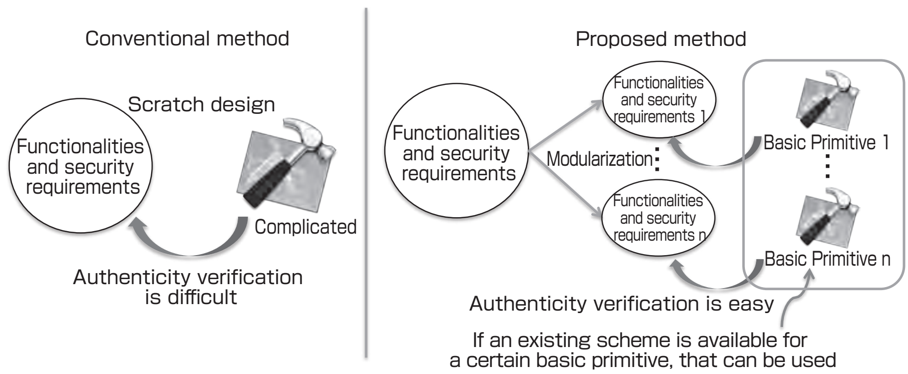

Fig. 3 Difference between the conventional and proposed methodologies

Building blocks

In the following, we will first briefly explain public key encryption, digital signature, and threshold public key encryption. We will explain how to construct a proxy re-encryption scheme from these building blocks in subchapter 3.2. We note that each of the building blocks has multiple functionalities (algorithms), and the six algorithms of proxy re-encryption can be achieved by combining them appropriately.

· Public key encryption
A pair of secret and public keys are generated by a receiver of a message, and the public key is publicized. A sender of a message uses the receiver's public key to encrypt the message and sends the ciphertext to the receiver. The receiver can decrypt the ciphertext using the secret key. By using public key encryption, we can communicate privately with others without sharing any information in advance , and this is one of the most basic cryptographic primitives used widely, such as in SSL and TLS.[Note)]

· Digital signature
A signer of a message generates a signing key and a verification key, and publicizes the verification key. The signer signs on a message using the signing key. A verifier who obtains the pair of the message and the generated signature can verify them by using the verification key. Digital signature is an analogue of a seal in the real world, and is the most important cryptographic primitive that supports authentication infrastructures in the network society. It is already widely used in PKI and in many other applications.

· Threshold public key encryption
This is an extension of public key encryption, in which a secret key, which is normally a single element, is divided into multiple "partial secret keys." In threshold public key encryption, a plaintext is encrypted by a (single) public key as in ordinary pubic key encryption, and using one of the partial secret keys, the ciphertext can be "decrypted" into a partial decryption result called a "decryption share". One can recover the original plaintext hidden in the ciphertext by collecting more decryption shares than the "threshold." In the proxy re-encryption scheme described in this section, we use a threshold public key encryption scheme in which a secret key is divided into two partial secret keys and a ciphertext can be decrypted by collecting the two decryption shares of the ciphertext.

Threshold public key encryption is an important cryptographic scheme in the construction of electronic voting (e-voting) systems, and research on it has been active since the 1990s. It has already been introduced to some practical systems, and its functionalities and security have been well-studied and deeply understood.

The proposed construction of proxy re-encryption

In the construction of proxy re-encryption explained here, the threshold public key encryption scheme plays a central role. As shown in Fig. 4, in this construction, a sender encrypts a message using the Receiver A's public key of the threshold public key encryption scheme, and sends the ciphertext. This ciphertext can be decrypted by Receiver A who possesses the secret key of the threshold public key encryption scheme. This functionality corresponds to that of ordinary public key encryption.

As shown in Fig. 5, when generating a re-encryption key, User A encrypts one of the two partial secret keys using User B's public key, where User B is the designated receiver of re-encrypted ciphertexts, and gives this to the proxy. Here,

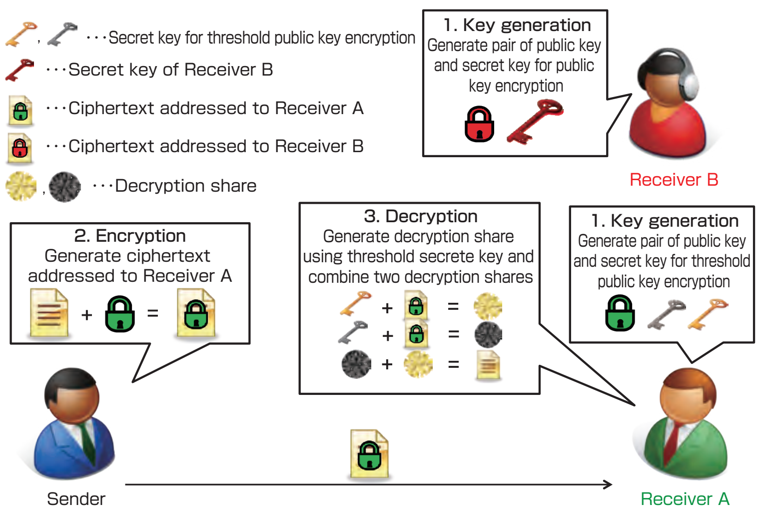

Fig. 4 Construction by the proposed method (key generation, encryption, decryption by Receiver A)

the authenticity of the re-encryption key is ensured by using the digital signature scheme. When re-encrypting, the proxy partially decrypts the ciphertext using the partial secret key that is not encrypted, calculates the decryption share, and sends this to User B along with the encrypted partial secret key.

As shown in Fig. 6, User B who receives the re-encrypted ciphertext decrypts the encrypted partial secret key, and then recovers the original plaintext by obtaining the other decryption share using the partial secret key, and combining both of the decryption shares.

4 Evaluation of the proposed method

To gain confidence in the security of highly functional cryptographic schemes, as mentioned above, it is important to break things down into basic elemental schemes that are already widely used. Here, using the example of the proxy re-encryption scheme described in the previous section, we explain in detail into which basic scheme it was broken down, and why the breakdown into those basic schemes were done.

Specifically, the proxy re-encryption scheme of the previous section is broken down into basic schemes such as public key encryption, digital signature, and threshold public key encryption, and these are not only basic compared to proxy re-encryption scheme, but are also already used widely. The breakdown was not accidental, but was intentional since highly secure and reliable implementations have been done for these schemes. For public key encryption, the RSA-OAEP method is widely used, as well as the RSASSA-PKCS1-v1_5 method for the digital signature in SSL/TLS. In fact, although there are over 800 thousand SSL server certificates issued and installed by the Symantec Corporation of the USA,[16] there have been no security problems despite such wide use (however, not all implementation of the RSASSA-PKCS1-v1_5 method is secure, and it is necessary to carefully select the implementation with highly reliable performance). Threshold public key encryption is not widely used compared to the above two schemes, but it is used in e-voting, and can be considered sufficiently reliable. From the above, one can understand what policy is employed in the functionality breakdown in the proxy re-encryption scheme as presented in the previous section.

There are the following five advantages when the functionalities are broken down as above.

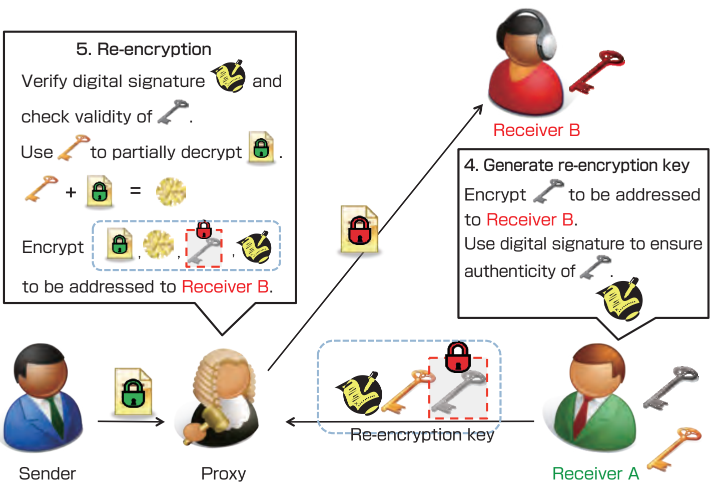

Fig. 5 Construction by the proposed method (generation of re-encryption key, re-encryption)

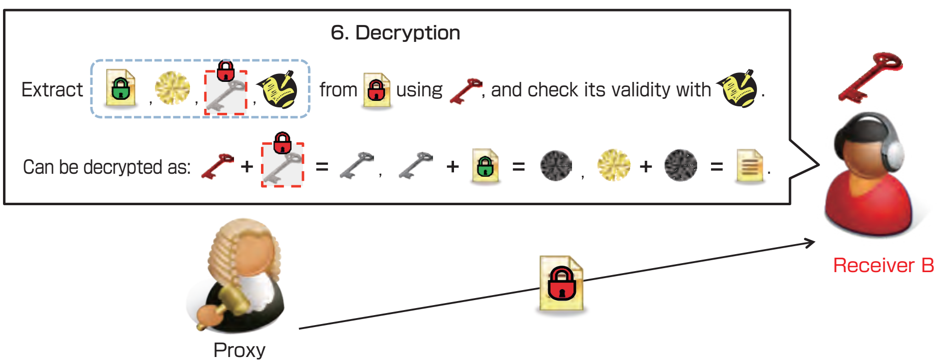

Fig. 6 Construction by the proposed method (decryption by Receiver B)

[Advantage 1] Compared to scratch construction, it can be readily understood that a highly functional scheme called proxy re-encryption has been achieved. Considering how the functionalities described in subchapter 2.1 are achieved, the following points can be intuitively understood without following the difficult mathematical equations.

- The key generation of Algorithm 1 is achieved as Receiver A generates a pair of threshold public and secret keys, and Receiver B generates a pair of the usual public and secret keys (Fig. 4).
- The re-encryption key generation of Algorithm 2 is achieved as one of the two threshold secret keys is encrypted by Receiver B's (usual) public key, and then combined with the remaining threshold secret key, is used as the re-encryption key (Fig. 5).
- The encryption and decryption of Algorithms 3 and 5 are achieved by the encryption and the decryption of the threshold public key encryption scheme (Fig. 4).
- The re-encryption of Algorithm 4 is achieved as the proxy partially decrypts the ciphertext using the obtained threshold secret key, and then encrypts and sends the bundle of obtained decryption share, ciphertext addressed to A, and encrypted threshold secret key to Receiver B (Fig. 5).
- In the decryption of the re-encrypted ciphertext of Algorithm 6, Receiver B decrypts the sent ciphertext using its own secret key, and then decrypts the encrypted threshold secret key in the sent material. The obtained threshold secret key is used to partially decrypt the ciphertext addressed to A, whereby the second decryption share is obtained and the message can be decrypted, and Algorithm 6 is achieved (Fig. 6).

[Advantage 2] In relation to Advantage 1, the understanding of the achieved security as a whole is facilitated, by clarifying the role division of the component for each functionality of proxy re-encryption. Also, if error is found in the security proof, the proof can be corrected readily since it is clear which part of the error corresponds to which component scheme.

[Advantage 3] Even when replacing a component cryptographic scheme of the above proxy re-encryption scheme with another scheme with equivalent functionalities, the performance and customization of the resulting proxy re-encryption scheme can be done readily. In the case of scratch construction, the burden is great because one must check whether the change does not interfere with the functionalities or security by returning to the whole construction each time a part is changed, for example, for increasing the execution speed. On the other hand, with this methodology, the local characteristics need only to be checked to see whether the function of a component is maintained when the construction of a component is changed, and the work is facilitated.

[Advantage 4] In relation to Advantage 3, even when the update of the encryption method will be needed due to increased cryptographic attacks in the future, using this methodology, only the component scheme whose security is compromised can be replaced, and the operation cost necessary for updating can be reduced. Similarly, in case one wishes to construct a proxy re-encryption scheme that cannot be cracked with a quantum computer (i.e. quantum resistant) that is expected to be available in the future, the above mentioned three components can each be made quantum resistant. This is much easier compared to developing a quantum-resistant proxy re-encryption scheme from scratch.

[Advantage 5] In relation to Advantage 4, in the case of this methodology, for example, by developing a superior scheme compared to the conventional digital signature schemes, the digital signature scheme itself and the proxy re-encryption scheme that uses digital signature schemes as its components can be simultaneously improved. Such a characteristic of this methodology will contribute to increased efficiency of the research resource allotment for the R&Ds of the entire field of cryptography.

5 Application to other highly functional cryptographic scheme

In this chapter, we discuss the applicability of the design policy of highly functional cryptographic schemes proposed in this paper to other cryptographic schemes other than proxy re-encryption, particularly to group signature. The interference of the components that may occur when the proposed method is used and the ways to avoid such interference will also be discussed.

5.1 On application to group signatures

A group signature scheme is a digital signature scheme in which the privacy of the signer is ensured. Since its concept was first proposed by Chaum *et al*.[17] in 1991, several specific constructions have been proposed. Other than the functionalities of the conventional digital signatures, the group signature has the confidentiality for identity of the signature issuer. It is a digital signature with enhanced privacy protection functionality that is significantly effective for electronic bulletin boards, electronic auction sites, and others.

However, since the functionalities are significantly complex compared to the conventional digital signatures, a concrete construction with sufficiently high level of security was hardly in existence. In response, in 2003, Bellare *et al*.[18] indicated that the group signature could be achieved by combining the functionalities of digital signature, public key encryption, and zero-knowledge proof. Since this accomplishment, there was a paradigm shift where the designers of group signatures started to consider the appropriate selection of a digital signature scheme, public key encryption scheme, and zero-knowledge proof system, in the mode of the breakdown of functionalities as mentioned above. As a result, compared to the conventional schemes by scratch design, the functionalities and security of the newly proposed scheme can be thoroughly understood by a third party, and this is affecting the progress of commercialization and standardization.[19]

There are already widely used, highly reliable schemes of digital signature and public key encryption as mentioned above. Zero-knowledge proofs are widely used in user authentication schemes, and are sufficiently reliable scheme.

The importance of functionality breakdown in designing the highly functional cryptographic scheme as proposed in this paper has been implied by Bellare *et al.* in some sense, and the main result of this paper is to explicitly discuss this point and indicate that it is a universal design concept not just for group signatures. For group signatures where the proposed method was implicitly used in this paper, the effectiveness of the proposed method can be understood since the standardization of this scheme has progressed.

5.2 On the interference of the components to security

This paper claims the effectiveness of achieving the functionalities of a highly functional cryptographic scheme to be designed through the combination of basic cryptographic schemes. However, there are cases where the basic cryptographic schemes used interfere with each other, and the total security cannot be ensured even if the security is ensured for individual schemes. Here, we discuss the method for investigating whether such a problem is occurring in the designed system.

In a case where the targeted highly functional cryptographic scheme can be generically constructed using only the basic component schemes in a strict sense, the security proof of the individual scheme that is a special case will not be necessary, if the security proof of this generic construction has been done. That is, if the underlying basic schemes fulfill certain conditions required for this generic construction, the security of the total scheme that is constructed using the above basic schemes is automatically ensured regardless of which basic component schemes are used. The construction of the proxy re-encryption scheme discussed in this paper is generic in this strict sense.

There is a concept called universal composability that is the concept of security that ensures that the elemental schemes do not interfere with each other. The interference among the elemental schemes can be prevented by using the component schemes that fulfill this security concept.

5.3 Basic schemes to which the breakdown is done

In breaking down the functionalities of highly functional cryptographic schemes, it is necessary to keep in mind that the basic scheme to which the breakdown is done shall be the ones for which security is considered highly reliable. In that case, as the criteria for determining whether it is evaluated highly for its security, it should have usage performance in a wide range and that there has been no essential problem in security over a long-term. From such perspectives, there is no doubt that public key encryption, digital signature, symmetric key encryption, and message authentication code are reliable schemes. For public key encryption and digital signature, as mentioned earlier, implementations with high use performance are known. There are also schemes that are already widely diffused with no security problem found as in the AES (95.4 % deployment in commercial products) for symmetric key encryption, and the HMAC (82.1 % deployment in commercial products) for message authentication code.[20] Other than the aforementioned threshold public key encryption and zero-knowledge proof, broadcast encryption is widely used in the protection of copyrights for Blue Ray discs, and it can be considered a sufficiently reliable scheme.

6 Summary

While highly functional cryptographic schemes are useful in recent highly sophisticated networks, the introduction into society is not progressing well. In this paper, we indicated that to promote the use of highly functional cryptographic schemes, not only do the functionality and security have to be advanced, but also they must be readily understandable. Then, we proposed the design concept to achieve such understandability.

In response to the expected advancement of the network technology in the future, highly functional cryptographic schemes with even more advanced functions and security will be required. Considering practical use, they must not just satisfy the required functionality and security but also must be readily understandable to the third party, and we think it is possible to promote the practical use by using the method proposed in this paper. Since the proposed method is to improve the “ease of understanding,” the establishment of the quantitative evaluation method for “ease of understanding” is necessary to widely communicate the effectiveness of this method to society. As one method, it may be possible to evaluate it by estimating the input size for the automatic security verification tool. This shall be a future research topic.

Notes

Note) SSL and TLS are communication protocols that require security, and provide the functionalities of authentication, encryption, and forgery detection. We can choose some algorithms for these protocols, and selection are made among the algorithms which allowed by both parties as the start of communication.

Terminologies

Term. Scratch development: Development where the (cryptographic) system is constructed from zero (or scratch) without utilizing the already existing technologies.

References

[1] M. Blaze, G. Bleumer and M. Strauss: Divertible protocols and atomic proxy cryptography, *EUROCRYPT '98*, 1403, 127-144 (1998).
[2] CRYPTREC Ciphers List, http://www.cryptrec.go.jp/english/list.html
[3] Dropbox https://www.dropbox.com/
[4] Google Drive https://drive.google.com/
[5] Digital Kashi Kinko (Digital Rental Safe) http://tosafebox.com/
[6] J. Shao and Z. Cao: CCA-secure proxy re-encryption without pairings, *PKC 2009*, 5443, 357-376 (2009).
[7] T. Matsuda, R. Nishimaki and K. Tanaka: CCA proxy re-encryption without bilinear maps in the standard model, *PKC 2010*, 6056, 261-278 (2010).
[8] J. Weng, Y. Zhao and G. Hanaoka: On the security of a bidirectional proxy re-encryption scheme from PKC 2010, *PKC 2011*, 6571, 284-295 (2011).
[9] G. Hanaoka, Y. Kawai, N. Kunihiro, T. Matsuda, J. Weng, R. Zhang and Y. Zhao: Generic construction of chosen ciphertext secure proxy re-encryption, *CT-RSA*, 7178, 349-364 (2012).
[10] B. Libert and D. Vergnaud: Unidirectional chosen-ciphertext secure proxy re-encryption, *PKC 2008*, 4939, 360-379 (2008).
[11] R. Rivest, A. Shamir and L. Adleman: A method for obtaining digital signatures and public-key cryptosystems, *Commun. ACM*, 21 (2), 120-126 (1978).
[12] R. Cramer and V. Shoup: A practical public key cryptosystem provably secure against adaptive chosen ciphertext attack, *CRYPTO '98*, 1462, 13-25 (1998).
[13] V. Shoup: A proposal for an ISO standard for public key encryption (version 2.1), http://www.shoup.net/papers/iso-2_1.pdf (2001).
[14] Digital Signature Standard, http://csrc.nist.gov/publications/fips/fips186-3/fips_186-3.pdf
[15] Y. Desmedt and Y. Frankel: Threshold cryptosystems, *CRYPTO '89*, 435, 307-315 (1989).
[16] VeriSign, Inc.: (Press Release) Symantec achieves highest number of SSL certificates issued globally, https://www.verisign.co.jp/press/2012/pr_20120427.html (2012).
[17] D. Chaum and E. Heyst: Group signatures, *EUROCRYPT '91*, 547, 257-265 (1991).
[18] M. Bellare, D. Micciancio and B. Warinschi: Foundations of group signatures: Formal definitions, simplified requirements, and a construction based on general assumptions, *EUROCRYPT 2003*, 2656, 614-629 (2003).
[19] NEC Corporation: (Press Release) NEC develops technology for anonymous authentication to achieve both security and privacy in a cloud environment, http://www.nec.co.jp/press/ja/1106/0703.html (2011).
[20] CRYPTREC Report 2012, http://www.cryptrec.go.jp/report/c12_opr_web.pdf (2013).

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Discussions with Reviewers

1 Definition of the problem in question

Question and comment (Toshihiro Matsui, Research Institute for Secure Systems, AIST)

You state repeatedly that the verification and proof of security for the highly functional cryptosystem is difficult. Since the main subject of this paper is how to overcome this difficulty, we recommend giving an appropriate name to this matter, so you can refer to the problem by name.

Though you express the difficulty using the phrase “craftsman-like,” it should be discussed in a more scientific manner, since it relates to the definition of the problem. If you understand the content of the difficulty, you can derive a solution. Difficulty overlaps with complexity. Complexity is dissolved to the types of elements, the types of links (relationships), and the numbers of these elements and links. Clues to the solution might be found in a task to unravel the complexity.

Answer (Goichiro Hanaoka)

I shall name the difficulty in having a third party understand the security of highly functional cryptographic scheme, the “security verification problem.” To see the difficulty of the security verification problem, we exemplified the papers on highly functional cryptographic schemes from the major international conferences in the area of cryptography, and pointed out that the security definition, description of the systems, and security proofs dominate a large portion of the papers. We can consider the usage of formal method to solve the security verification problem, and it may possible to evaluate the complexity of problem based on the input data size for verification tools. However, as of now, the application of formal method to the security proof in highly functional cryptographic schemes as addressed in this paper is still very difficult, and we shall leave this as a future research topic.

2 Solution by modularization

Question and comment (Toshihiro Matsui)

In this paper, the solution of the problem is sought through the modularization by breaking down the problem into elements. Since reductionism is an orthodox approach in science, this paper might be regarded as another example of general reductionism. Can you compare your modularization with other contrasting problem-solving methods? Or, giving a more precise modularization guideline, particularly for functional cryptosystems among other modularization principles is useful.

Question and comment (Hideyuki Nakashima, Future University Hakodate)

Since this is a difficult problem (or unfamiliar to the general public), I think you need some more explanations in various places. Particularly, the description of the intention of “why I did it this way” is important for *Synthesiology*, not just “how I did it.”

Answer (Goichiro Hanaoka)

Since the above two comments that I received from the two reviewers are closely related to each other, I would like to answer them both in a single reply.

As you indicated, the proposed method can be seen as following the orthodox approach that should be considered. However, the modular approach was not taken in the research for cryptosystems up to now. There are probably two reasons. First reason is that in cryptosystems, one must prove not only the “correctness” where the functionality one wishes to achieve is completed, but also the “security” where nothing other than the functionality to be achieved can be carried out. Therefore, the modularization of security technology is much more complex than other technologies. Second reason is that the cryptography researchers did not have sufficient motivation to engage in such complex modularization. In the previous technology, the user side could somehow understand the technology, and I don’t think the cryptography researchers ever thought of spending so much effort in modularization. In contrast, the series of highly functional cryptosystems that are being proposed recently seem to exceed the range. In such a situation, I think it is extremely useful for our related field to explicitly indicate the importance of the orthodox general theory called decomposition.

As the policy for modularization, from the perspective of pursuing highly reliable security, we shall adopt modularized individual primitives which have already been widely used in practice.

Including the above, I added the descriptions throughout the paper to clarify the intent of the authors.

3 Problem of module interference

Question and comment (Toshihiro Matsui)

The interference between the components you mention in subchapter 5.2 is the wall to complete reductionism. The optimization of the entire system cannot be achieved by a simple sum of the elemental technologies. For the proxy re-encryption, can you add the findings to see whether such interferences are happening or not, how such interferences can be avoided if any are present, and how this experience can be generalized (in what case do you regard the interferences to be minor)?

Answer (Goichiro Hanaoka)

The removal of interferences among the building blocks is, as you indicate, the part that requires careful consideration in our proposed method. As measures, rather than intuitive and rough decomposition, we must conduct generic construction in the strict sense including the mathematical security proof. The proxy re-encryption scheme addressed in this paper is such a generic construction, and as long as the individual building blocks are secure, the security of the whole system is automatically ensured. As a more general discussion, universal composability is known as the concept for security to ensure that mutual interferences do not occur when the building blocks for cryptosystems are combined. This is also briefly addressed in this paper.

4 Effect of modularization

Question and comment (Toshihiro Matsui)

I think the argument will become more convincing if there is a comparison of the proposed method with the total optimization that is a contrasting approach to this problem. For example, an energy-saving system is not only about increasing efficiency of the component machines such as the boiler, generator, or condenser, but the energy-saving becomes more effective by increasing the linkage of the elements, such as warming the bath using the excess heat from the boiler or returning the heat from the condenser to the boiler. Although decomposition is powerful approach, when ultimate efficiency is pursued, the option of attempting total optimization or building from scratch is attractive. Compared to such total optimization, I think one way is to discuss why modularization is so important in the cryptosystems development.

Answer (Goichiro Hanaoka)

As you indicate, it is better to aim for total optimization by building from scratch from the perspective of good efficiency (length of the ciphertext, computational cost, etc.). On the other hand, the maintenance of sufficient security is of top priority in cryptosystems, and I think the advantage is on the modularization side, considering the security verification problem. Whether the security is formally proved or not is very important from the perspective of standardization, and I think this way of thinking should be prioritized in diffusing highly functional cryptographic schemes in the future. Furthermore, it is also the attractiveness of modularization that, after conducting construction and security proof by modularization, we can construct various instantiations by choosing different underlying primitives. Particularly, it is expected that efficiency can be improved by changing the individual primitives to more efficient ones, and actual researches on this have been done in the past.

Development of lectin microarray, an advanced system for glycan profiling

— From frontal affinity chromatography to evanescent wave excitation fluorescence detection method —

Jun HIRABAYASHI

[Translation from *Synthesiology*, Vol.7, No.2, p.105-117 (2014)]

Glycans are called the third class of biopolymers, after nucleic acids (first class) and proteins (second class). Elucidation of glycan functions has long been hampered by the difficulty in analyzing their structure. However, recent progress in proteomics technology has also accelerated progress in glycomics, which is the systematic study of glycans. As a result, glycan profiling has increasingly attracted attention as a method that enables rapid analysis of complex features of glycans. Lectin microarray provides a novel platform with a simplified experimental procedure, because it does not require glycan liberation and separation prior to the analysis. It is now being applied to tumor marker investigation, stem cell qualification, and biologics development. The author reviews the last 10 years of lectin microarray development, a period that began as a national project in which he has been actively involved.

Keywords : Glycan profiling, frontal affinity chromatography, lectin microarray, evanescent wave, GLIT (Glyco-innovation and Industrial Technology)

1 Introduction

1) Why glycomics is difficult

Glycans or sugar chains are biological information molecules with complex structures and varied forms of existence. Unlike nucleic acids and proteins, they have diverse bonding forms and branch structures, and therefore the structures cannot be predicted from genetic information. These make both the analysis and understanding of glycans very difficult. One of the structural characteristics of glycans is the existence of multiple isomers. Since these isomers usually have similar properties, it is generally very difficult to completely isolate them from each other. On the other hand, glycans are present in milk or urine in free form, but most are covalently bound to proteins or lipids, and are present in the cells or are secreted in the bodily fluids such as blood. In glycoproteins, it is known that profuse amount of glycosylation occurs in the biosynthetic process. Figure 1 shows a model of a typical glycoprotein. The glycan structure has basic common properties such as the monosaccharide composition, but this complicates the preparation of antibodies for glycans, and makes the tissue distribution determination and isomer detection difficult. On the other hand, glycan structures often differ significantly by organisms. Recently, the mainstream method is to use animal cells to produce hormones and antibodies needed for biopharmaceuticals, and many of the biopharmaceuticals are actually glycoproteins. Therefore, even if the amino acid sequence of a protein is the same as humans, the glycan structure may be heterologous depending on the production host. The technology to attain complete human glycan structures has not been perfected, and the dangers of allergies and acute rejections have been indicated in the biopharmaceuticals prepared from animal cells such as CHO (Chinese hamster ovary) cells.

Although it is extremely difficult to analyze glycans, fortunately, glycan research has been active in Japan, and many analysis technologies and glycosidase essential for glycomic research were created in Japan.[Note 1)] On the other hand, at the beginning of the 21st century, it was thought that structural glycomics would be done well by “mass spectrometry.” While mass spectrometry is highly effective for detailed structural analysis, the disadvantage is that it is very difficult to handle biological samples with this technique. On this point, the glycan profiling technology, which is the subject of this paper, has the possibility of overcoming some of the disadvantages of mass spectrometry. Described in a few words, glycan profiling is to obtain structural characteristics of glycans quickly and easily, and although precise structural identification may not be possible, major characteristics (type of glycan, presence of epitope,[Note 2)] degree of branching, degree of glycosylation, etc.), as well as differences or similarities between the compared samples can be shown.

2) Looking back at year 2002 (year before the launch of the Structural Glycomics Project)

To introduce myself, the author joined the National Institute of Advanced Industrial Science and Technology (AIST) in

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November 2002, as a member participating in the Project for the Development of Glycomics Technology of the New Energy and Industrial Technology Development Organization (NEDO) that started in 2003. Invited by Hisashi Narimatsu, Deputy Director (at the time) of the Research Center for Glycoscience and the person who would become the Project Leader, I resigned from a private university where I taught for 21 years. This was the start of the Structural Glycomics (SG) Project. Narimatsu had moved from a university to AIST a few years back to lead the "Project for the Development of Glyco-gene (GG) Library" of the Ministry of Economy, Trade and Industry (FY 2001~2003) and contributed to the development of the glycogene library in Japan.[2] After this success, the development of the analysis technology for glycan structures was considered a priority issue. The matrix-assisted laser desorption/ionization (MALDI) method created by Koichi Tanaka, particularly the AXIMA-QIT-MALDI device, was expected to be the most useful method for analyzing complex glycan structures.

The actual SG Project progressed in two part development of structural analysis and synthesis technology. The details of the framework of structural analysis technology development and the research subjects in which the author was directly involved are shown in Table 1.

3) Objective and demand

Since the glycans exist as mixtures of heterogeneous structures within the protein, it is almost impossible to accurately determine their chemical structures and existing amounts. However, if the minute differences in structure

Table 1. SG Project (supplementary budget in FY 2002 ~ FY 2005): Topics for the development of glycoproteomics technology and the organizations involved

1. Development of the glycoproteomics technology
1-1. Glycoproteomics (AIST, Tokyo Metropolitan U, Kinki U, Shimadzu Corp, GL Sciences, etc.)
  - Proteome strategy (identification of large glycoproteins by proteomics method)
  - Glycome strategy (development of methodology to obtain both protein identification and glycomic information)
  - Glycoform analysis (analysis of methods to excise glycans from glycoproteins and to analyze glycans)
1-2. Glycomics using mass spectrometry (AIST, Shimadzu Corp, Cyber Laser, Mitsui Knowledge, Tokyo U of Science, etc.)
  - Glycomics by MALDI-QIT-TOF mass spectrometry, exploration of high-throughput soft ionization method suitable for glycopeptides, and exploration of fragmentation method suitable for structural analysis of glycopeptides
1-3. Glycan profiling technology (AIST, Shimadzu Corp, J-Oil Mills, U of Tokyo, etc.)
  - FAC: Comprehensive interaction analysis between lectins and standard glycans
  - Development of glycan profiler: Development of lectin microarrays based on evanescent wave excitation method
2. Construction of glycomic identification database (AIST, Mitsui Knowledge, Fujitsu)
  - Construction of glycoprotein database
  - Construction of oligosaccharide database
  - Analysis of lectin profiles
  - Development of glycomic software by mass spectrometry
  - Development of glycan fragmentation prediction software based on molecular calculation

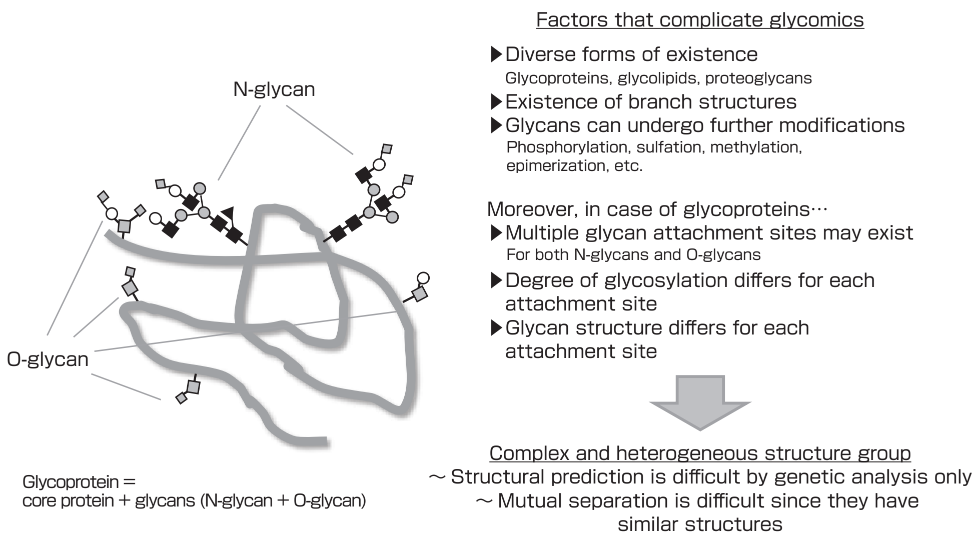

Fig. 1 Schematic diagram of a glycoprotein and factors that complicate glycomics

The peptide chain that forms the core protein is shown as the thick stringy line. Glycosylation of most of the secreted and membrane-bound proteins occurs during or after the translation process. There may be one or multiple glycan attachment sites. The glycan types are roughly divided into the N-glycans that attach to the asparagine residue (-NH_2) side chain and the O-glycans that attach to the serine-threonine residue (-OH) side chain. The rate of glycosylation at every attachment site is not necessarily 100 %, and normally 10 or more structural variations may coexist. When these factors are combined, the structural diversity of glycoproteins is enormous. The glycan structures differ as the types of cells differ. The various glycan biomarkers utilize this characteristic. This is the reason why glycans are called the "cell signatures" and proportion of glycans can be detected quickly and easily, the extracted information will be very useful in detailed structural analyses and search for biomarkers later. In cases such as the comparison of cell-surface glycans of microorganisms for which no analysis has ever been done,[3][4] glycan profiling may provide sufficiently meaningful results. Yet, this technology focuses on its use in the introductory part of the analysis strategy in biomarker development. The main difference from the analysis methods such as mass spectrometry or LC mapping is that glycans are fluorescent labeled and analyzed in their original form, without excising them from the protein. The LC mapping method[5] is a reference identification method[Note 3)] for glycan structures developed in Japan. In general, glycans are excised by glycosidase or hydrazine, and the reducing terminals of the glycans that were bonded to the protein are labeled by a fluorescent agent to facilitate mutual separation and detection.[6] However, it is not easy to separate and identify glycans of a glycoprotein all at once, since there may be several tens to several hundred types. Therefore, in most cases, the structural analysis alone becomes the research objective and the real objective beyond this cannot be reached. If the necessary information can be obtained using the shortest route by eliminating the procedures of excision and mutual separation of glycans, the speed and quality of glycan analysis can be increased dramatically. The role of glycan profiling is to shorten this time to move on quickly to the study of glycan functions (Fig. 2). It can be said that the reason glycan research did not progress, although many researchers have realized that it was important, was because there was no efficient glycan profiling technology.

Yoshitaka Nagai, Director (at the time) of the Mitsubishi Kagaku Institute of Life Sciences and the pioneer of glycan research, stated the significance of device development when starting the SG Project in the *Nikkan Kogyo Shimbun* dated July 4th, 2003: “If there is no automated device, the research can be taken up only by specialists. If sequences can be known and the necessary glycans be produced using an automated device without spending time listening to specialists and getting their permission, anyone can do it. This will increase the number of researchers and progress will occur explosively.” Glycan profiling was certainly a subject that matched this objective and demand.

2 Elemental technology and the new concept, “glycan profiling”

The author focused on lectins, proteins that specifically bind to certain moieties within the glycan structure, and devised an analyzing platform where multiple types of lectins are arranged on a slide glass (Fig. 3). Although the thought was like “wishful thinking,” I remember it was accepted at various academic societies, forums, and study sessions because of its “novelty.” Many people might have felt that a new image would eventually materialize from where there

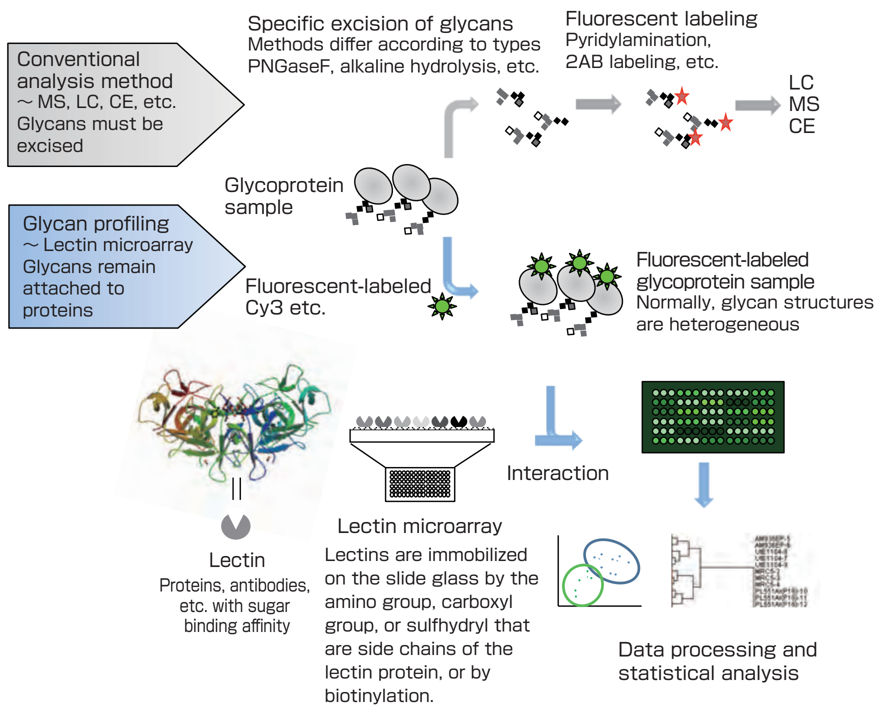

Fig. 2 Differences in the conventional glycomic methods (LC, MS, CE) and the glycan profiling by lectin microarray method
In the former, it is necessary to excise glycans from glycoproteins to compare with the standard products with known structures (memory verification method). In the MS, it is necessary to mutually separate isomers and to refine them by LC prior to analysis. In contrast, with the lectin microarray, the glycoprotein sample can be directly fluorescent-labeled, and the interaction with the lectin series can be analyzed all at once. Since the results of the interaction with lectins are reflected in the output, the analysis patterns may change due to the types or concentration of the core protein even if the glycan structures are the same.

was nothing.[7][8]

I mentioned that the objective of glycan profiling is not the strict determination of the chemical structure, but is to discern the “differences” in the structure among several samples. However, this idea and principle did not descend on me suddenly, but a prior technology provided an important clue. I shall describe the two elemental technologies that were essential in achieving the glycan profiling technology.

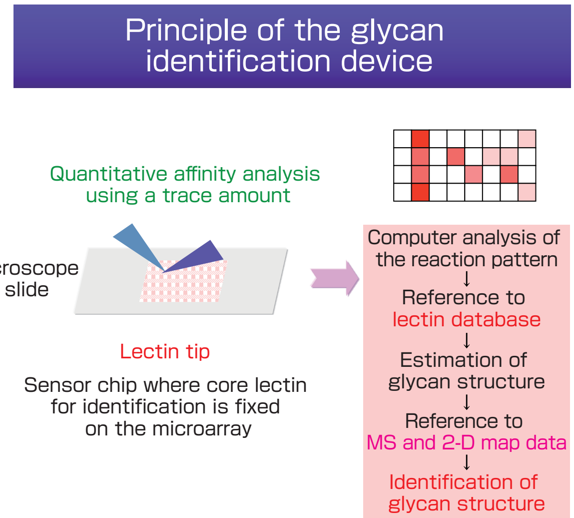

Fig. 3 Diagram showing the principle of the glycan profiler

Tens of lectin types (proteins that bind to sugars) are immobilized on the glass substrate such as the slide glass. The idea is to make glycans and glycoproteins that are glycosylated with suitable labeling groups react, and trace detection is attempted using a special detection principle. (From the author’s presentation slide used at the study session organized by the Research Association for Biotechnology held in July 30, 2002).

1) Prior technologies: investigation of the principle by FAC and the Hect-by-Hect Project

By analyzing the interactions of 100 (hecto) lectins and 100 glycans by the quantitative analysis FAC, the database for interaction information was created. It was also found experimentally that each individual glycan had a unique “fingerprint” (that was left there by lectins).

It was readily predicted that the lectin microarray was appropriate for glycan profiling. However, no one had investigated whether there was really unique information like fingerprints for individual glycans, or how many lectins should be used to identify the glycan structure. Therefore, the author conducted a comprehensive analysis by FAC, a prior technology, to determine the affinity among multiple lectins and multiple glycans.

Frontal affinity chromatography (FAC), also called the frontal analysis, is a quantitative interaction analysis method developed by Ken-ichi Kasai *et al.* of the Hokkaido University (at the time) in 1975.[9] The principle was published the year before by B. M. Dunn and I. M. Chaiken, and it was essentially the same as the method that would be later called the zonal analysis method.[10] The procedures and principles of FAC are shown in Fig. 4. This technology was devised to analyze the interaction of proteases such as trypsin and substrates (inhibitors). When David Schriemer *et al.* of the University of Alberta succeeded in linking this technology to MS detection at the end of the 20th century, the road to high throughput was opened.[11] The author participated in the International Carbohydrate Symposium (San Diego) in 1998, and dropped in on a lecture for the reception of the Whistler Award by Ole Hindsgaul (currently, Carlsberg Research Center), who was

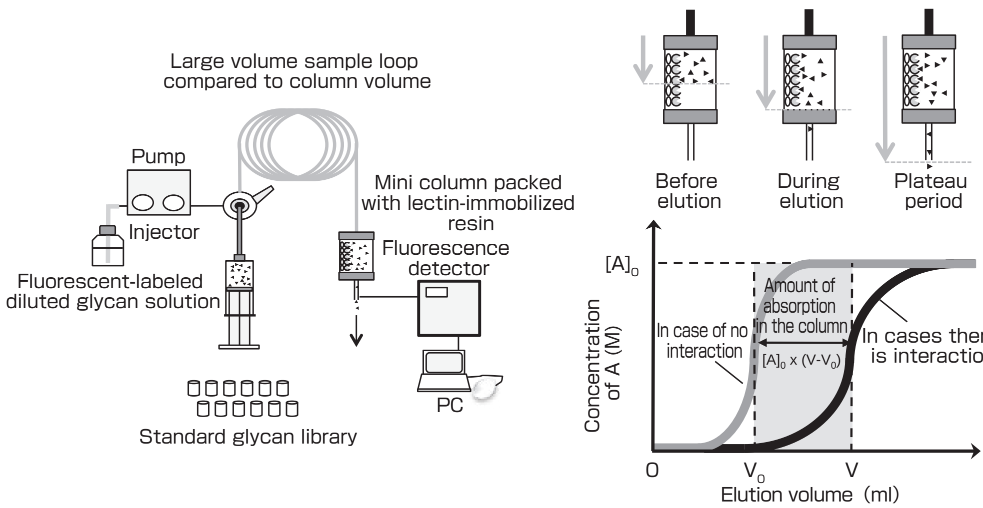

Fig. 4 Principle of FAC (right) and its procedure (left)

When glycans interact with the ligands (lectins) immobilized in the column, the elution front volume (V) that overflows from the column becomes greater compared to the control substance with no interaction (V_0). The difference ($V-V_0$) has the relationship $K_d = B_t/(V-V_0)-[A]_0$ (where B_t is the effective ligand content for the column used, and $[A]_0$ is the initial concentration of the glycan) with the dissociation constant (K_d) that is the scale that expresses the affinity between the glycan and lectin. In general, the dissociation constant of lectin against the glycan is large (dissociates easily), and since the fluorescent-labeled glycan is sufficiently diluted, K_d>>$[A]_0$ holds. Therefore, the above equation becomes $K_d = B_t/(V-V_0)$ that is not dependent on the concentration of the glycan used. This is the reason FAC is considered to be a method suitable for analyzing weak interaction.

Schriemer's superior. At the end of the lecture, Hindsgaul said, "There's wonderful news." He said he applied FAC, which Kasai developed 20 years ago, to the screening of compounds synthesized by combinatorial chemistry. They filled a PEEK tube about 10 cm long with beads to which lectins were immobilized, and cleverly linked this "column" to the ESI-MS device via an ingenious handmade device. I was amazed that my boss' name suddenly came up in an award reception lecture, but more than that, their achievement was way beyond what conventional FAC was thought to be able to do.

I was stimulated, of course. At that time, my colleagues were conducting analysis using the open glass columns and fraction collectors. I abandoned this preconception or the norm and sought the road to quick, highly sensitive, and high throughput by a method different from Schriemer. Although MS devices were not available in regional universities at that time, the laboratory had an isocratic liquid chromatography (LC) pump and a fluorescence detector that a joint research company left behind. Conveniently, we also had some standard fluorescent-labeled glycans called pyridylamino (PA) glycans that had just recently become commercially available. Thinking about what could be done with these items, one day, an "idea from a different angle" emerged. With FAC, the break-through of affinity capacity is observed as the emergence of "elution front" when excess diluted analyte floods the relatively small column. Maintaining the relationship of these two "volumes" (i.e., those of analyte and column) is essential for the analysis, and I thought, "Can't we keep the column size as small as possible, but flood the column with analyte using a relatively long sample loop with 20 times or more capacity than the column?" With usual LC, a sample loop with small capacity is used to maintain the resolution, and thus making the loop longer was unthinkable. It was found that volume ratio of 20:1 could be easily maintained if a PEEK tube with appropriate internal diameter was used.

After trial and error, we used the commercially available guard column (inner diameter of 4 mm, length of 10 mm, volume of 126 μl). A solution of PA glycans was poured into this column at a constant flow rate via the 2-ml sample loop. The fluorescence of the eluting PA glycans was tracked using an integrator connected to a fluorescence detector. First, the column was packed with agarose resin to which commercially available plant lectins were immobilized. Then the PA glycans that were thought to be interacting eluted with delay, while the glycans with no interaction eluted through (Fig. 5, refer to the chromatogram on the left).[12] One day, my colleague Yoichiro Arata (currently, Josai University), who was impressed by the beauty of the elution curve, PC-converted the digital data read by the fluorescence detector, and developed an algorithm to automatically calculate the elution frontal volume (V value in Fig. 4).[13] This was the birth of the original high-performance fluorescence detector FAC.

After that, improvements were made to FAC, and the product

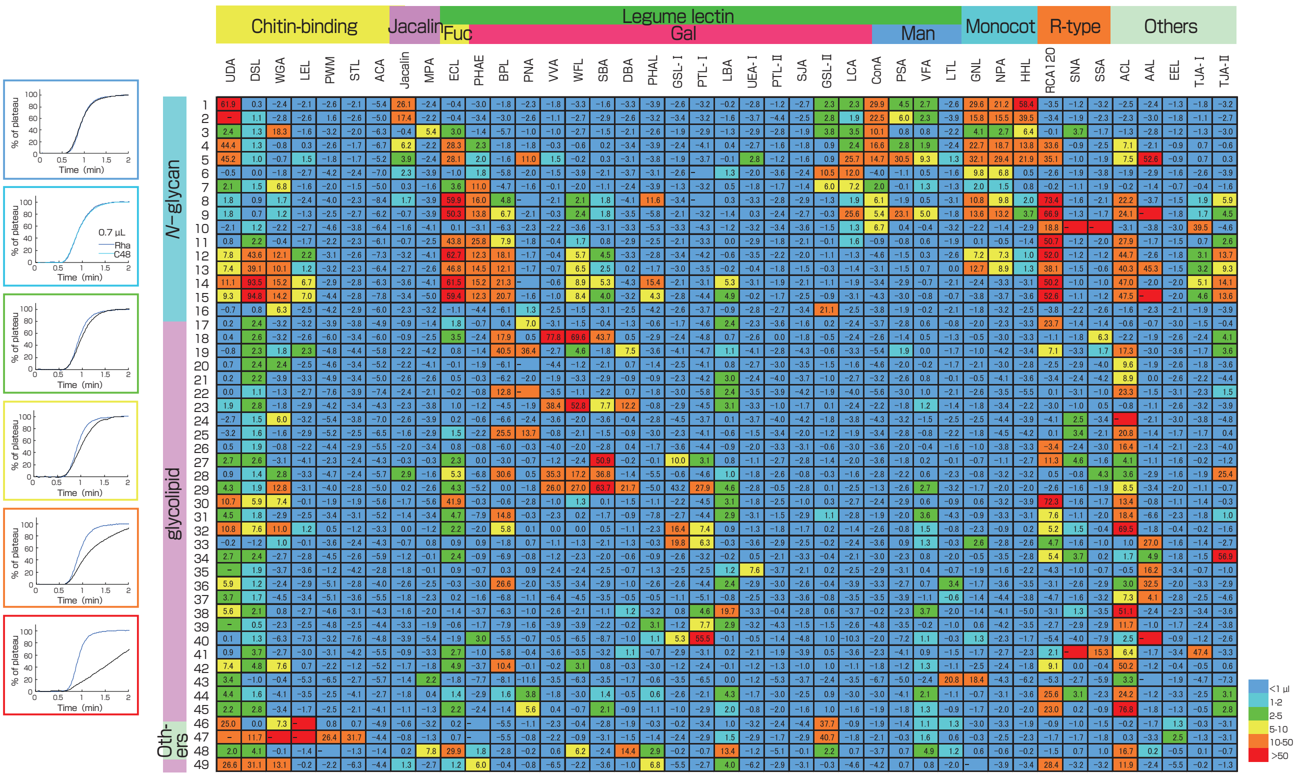

Fig. 5 Lectin-glycan interaction data (partial) produced in the Hect-by-Hect Project

The degree of interaction is observed as the delay in the elution front (V-V_0). The matrix shows the strongest interaction in red, and cases without interaction in blue.

was commissioned for manufacture and sales from Shimadzu Corporation as Automatic FAC.[Note 4)] The FAC using the fluorescence detector developed by the author *et al.* operated and was used differently from Schriemer's FAC directly connected to MS, and it has been positioned as an almost different technology.[14][15] The high-performance FAC played a leading role in the Hect-by-Hect Project[Note 5)] in NEDO's SG Project mentioned earlier. Here, the specificities of the several known and new lectins were clarified at a speed unseen before. However, the most important point that the high-performance FAC showed was that there was a unique pattern to each glycan in terms of reactivity with various lectins. I had suspected this when I was working on a manual device at the university, but the voluminous data from the Hect-by-Hect Project (Fig. 5) proved that this was correct. The matrix in Fig. 5 is composed of the vertical axis (type of glycans) and horizontal axis (type of lectins), and the grid shows the strength of the interaction. Red is the strongest and blue shows no interaction. When this matrix is cut in the "vertical direction" and taken apart, one sees that the pattern of each strip is different. This shows that there are differences in the glycan specificity of each lectin, and merely confirms the conventional way of seeing the issue. Then what about cutting the strips in the "horizontal direction"? One can see that the affinity pattern for each lectin of each glycan shown in each strip is also different. This shows that when the lectin affinity is weighed, each glycan leaves a different "fingerprint."

If the high-performance FAC had not been achieved, the voluminous data resulting from increased throughput could not have been viewed. Remember that FAC is a particularly excellent method for measuring the weak interactions (see explanation in Fig. 4). Although many methods for measuring interactions are suitable for seeking strong bindings, they do not focus on measuring the weak interactions. Since FAC could accurately calculate the affinity (expressed as the reciprocal of dissociation constant $1/K_d$) for weak interactions, this added some rich interaction information to the matrix of Fig. 5, and therefore, the fingerprints unique to glycans could be found easily. As the proof-of-principle was accomplished, the rest was how to construct the actual glycan profiler.

2) Evanescent wave excitation fluorescence detection method

This is a method to selectively detect the bound molecules in the liquid phase without the washing procedure, after interacting the fluorescent-labeled glycoprotein to the lectin array. This method is useful for glycans with weak interaction.

New ideas for research are often conceived by different groups at about the same time. In fact, when the authors succeeded in developing lectin microarrays by the principle of evanescent wave excitation fluorescence detection and published the paper in 2005, three other research groups published papers on the principle of the lectin microarray.[16]-[19] Although the paper was published later, Procognia Ltd., an Israeli venture company, was working earlier on the development of the lectin array platform (http://www.procognia.com/). Although there were several other papers on the development of the principle of lectin microarrays,[20][21] the prior technology called the serial lectin affinity chromatography was the major influence rather than FAC. In this method, several types of lectin columns are prepared, glycans that are radioactive-labeled by tritium or others are poured in order, and the degree of absorption (strong, weak, or absent) is studied to estimate the glycan structure.[22]-[24] While it made sense, many researchers must have been secretly thinking about shifting to an easier method because it took so much time and effort. On the other hand, although FAC had become higher performing, simultaneous analysis of multiple samples could not be done because it was LC, and the subject of analysis was limited to refined glycans. What was in demand at the site of R&D was the technology to directly and freely handle cellular extracts and blood serums.

Here, the author *et al.* focused on the detection principle. The technology to use the evanescent wave[Note 6)] as the excitation wave of fluorescence was known for a long time, and had been applied to evanescent microscopes. To use this on the slide glass of a lectin microarray, it was necessary to apply the wave to a wide field of view rather than to the small microscope field. Before joining AIST, the author checked a venture company called the Nihon Laser Electronics (NLE) K.K. that engaged in the development of DNA microarrays using a method of illuminating the exciting incident light from the edge of the slide glass. Based on the explanation diagram for the evanescent waves shown on the company's website, I have drawn the concept for lectin microarrays using the evanescent wave excitation fluorescence detector (Fig. 6).

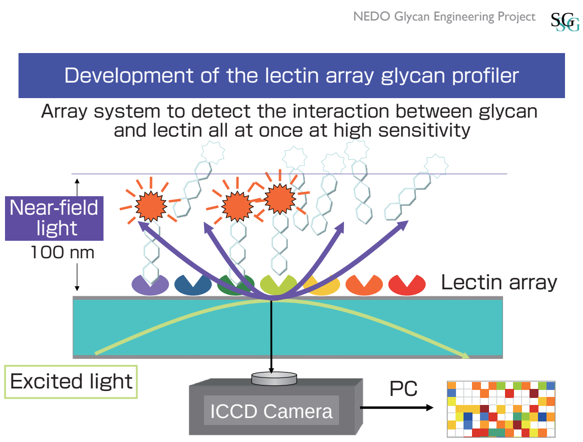

Fig. 6 Diagram showing the principle of the lectin microarray by evanescent wave excited fluorescence detection method

Created based on the slide used in the first meeting of the Japan Consortium for Glycobiology and Glycotechnology that was also the kick-off of the SG Project (Tokyo, November 3, 2003). Things have progressed remarkably compared to Fig. 3.

One of the characteristics of this technology was to excite fluorescence by illuminating evanescent waves from the edge of the glass. Since evanescent waves are light that soaks through from the glass surface to proximal range (<100 nm), the fluorescent-labeled glycans (actually glycoproteins) trapped at the surface of the slide glass to which the lectins are immobilized are selectively excited. I mentioned that the affinity between lectin-glycan is generally weaker compared to those between DNA-DNA (RNA) and antibody-antigen. That is, the glycoproteins bound weakly to lectins are easily torn off in the washing procedure after the reaction, and this binding is missed by the confocal fluorescence scanner that is normally used. The dissociation constant (K_d) between the glycan-lectin observed by FAC is at most only about 10^{-6} M (1 μM), where most are around 10^{-4} M (100 μM), and this is 100 times weaker than the antigen-antibody interactions. The most important advantage of illumination from the glass edge is that the entire surface of the glass is excited by the evanescent waves. The high-throughput analysis on the microarray platform rather than the small range of microscopes is made possible by this edge illumination. In fact, this became an important point in the later patent evaluation. There are secondary advantages in using the evanescent wave excitation method. Since the washing procedure is not necessary, the operation is facilitated, and this may lead to reduced analysis time and improved reproducibility.

To the present, only the author's group has used the evanescent wave excitation scanner, and all others use the confocal methods (washing procedure is necessary). However, they somehow function as lectin arrays because in many cases, the glycoproteins are in the multivalent state, and the affinity to the lectins that assume the oligomer structure is actually sufficiently high.[25] Measurement of the binding of excised glycans has been accomplished only by our evanescent wave excitation method.[26] However, the actual advantage of using our system, above all others, is the high detection sensitivity. In a sense, this might be expected as the washing procedure is not required, but in reality, it is not that simple. The employment of a high-output halogen lamp was essential for achieving high sensitivity, but the reduction of background was even more important. Specifically, various know-how was needed in the optically optimum filter, the selection of the slide glass, the fixation method in the biochemical procedure, the optimization of blocking method, and the image processing. While strict performance comparison with other devices is difficult, judging from the amount of samples used and users' comments reported in papers, the detection sensitivity of the evanescent wave excitation fluorescence scanner is at the top of all glycan analyzing devices. The official detection limit of this system is as follows: 100 pg/ml for the asialofetuin (the terminal sialic acid has been removed by acid treatment from the fetuin, a representative blood serum glycoprotein) against RCA120 lectin, and 100 pM for the asialo biantennary complex N-glycan against RCA120 lectin (amount used was about 0.1 ml).[26] The evanescent wave excitation fluorescent scanner (GlycoStation™ Reader 1200) was manufactured and sold by Moritex Corporation (at the time) in October 2006 along with the lectin microarray (LecChip™).

3 Up to the development of a device: corporate collaboration and IP strategy ~ the reality of bioventures

The NEDO Project for Structural Glycomics started under the supplementary budget of FY 2002, but Nihon Laser Electronics (NLE) K.K. that was the partner for the lectin array development suffered a managerial setback and went bankrupt the following year. However, AIST succeeded in the principle development of lectin arrays on its own. With the efforts of Atsushi Kuno and Noboru Uchiyama who were in charge of the development, the basic patents for the glycan profiling principle and the lectin array analysis were filed on December 25, 2003. The lectin array group was carried over by the NLE Project Group of Moritex Corporation, and with the management and technological foundations of a large corporation, the first commercial device was completed, totally refreshed from the first prototype that was reminiscent of the days of Nihon Laser Electropnics. This accomplishment received acclaim as a success case by NEDO (http://www.meti.go.jp/committee/summary/0002220/024_02_12b.pdf). However, the Lehman Shock rocked the world in 2008, and business declined rapidly and the bio section was cut off. With twists and turns of events, about a dozen members of the glycan group established the GP Biosciences Ltd. This company gained attention as a bioventure, and was taken up in NEDO's "Following up the R&D Series 1" (http://www.nedo.go.jp/hyoukabu/jyoushi_2008/gp/index.html). However, business was not easy, and the company filed for bankruptcy in April 2013.

4 Development

1) Research Center for Medical Glycoscience and GLIT

In December 2003, basic patent application was filed for the glycan profiling technology, a paper was published in December 2005, and the new NEDO project "Development of Technology for Medical Glycomics (MG: Medical Glycomics)" was started in April 2006. In December 2006, the Research Center for Medical Glycoscience (RCMG) was established for utilizing the glycans in the medical field, with Hisashi Narimatsu as the Director. One of the objectives of the new RCMG was to spread the results of the glycan research that have been accumulated over the years. At the time, basic and core research was in a noncompetitive state. To accomplish the above objective, it was thought necessary to create a place where excellent results could be handed over quickly to the industrial world. The forum for Glyco-innovation and Industrial Technology (GLIT; http://www.glit.jp/wp/) was established with various industrial associations and interested parties by holding discussions with people inside and outside of AIST. The GLIT contributed in spreading the advanced glycan technology to industry and in promoting the exchange of human resources through various research sessions and symposiums, as a part of the joint effort with the Japan Bioindustry Association (JBA). Since these were new activities for AIST, they attracted attention from both inside and outside the institute. While it was essentially an engine for the promotion of industry-academia collaboration, it was a one-stop organization to promote such collaboration rather than a merit-based organization, and we constantly had to discuss what should be done next. Yoichi Shinma, a leader of the Collaboration Strategy Group that was newly established in the RCMG, contributed greatly to the management of GLIT.

The issues that stood before GLIT are more or less reflected in the following points taken from slides for the panel discussion at Bio Japan 2008. Although the conference was held six years ago, it serves as a reference in predicting the future of bioresearches including glycoscience.

- The positioning of the Japanese glycoscience is at the top level in the world as we possess outstanding technologies and core resources.
- However, the long time required for R&D due to various factors is making funding difficult.
- As a result, companies and universities need a “nudge” before employing the new glycan technology, and there are many issues in the use and diffusion of the advanced technology.
- It is important to clear these issues strategically to attain a breakthrough.
- In this discussion, we wish to share our thoughts by discussing the future strategy (for technology, human resources, mechanism) through the analysis of the current situation and understanding of the issues.

With the support from GLIT, 15 GlycoStation™ Reader 1200, the evanescent scanner manufactured by GP Biosciences, were sold (as of July 2013). The bio companies are realizing the importance of glycans and many businesses are interested in glycans. One company is starting to develop biopharmaceuticals, regenerative medicine, as well as biomarker diagnosis systems such as tumor markers. The GlycoStation™ Reader 1200 is gaining attention overseas as support for the development of biopharmaceuticals (particularly biosimilars).[27]

When it was first launched, the author’s lab dominated the reports and papers on the usage of this system, but now the situation is reversing. It is also a fact that there are academic conflicts as a result of promoting the sales channels for the product. In that sense, perhaps GLIT has finished its role. However, the GLIT activities and the lectin microarrays were always linked, and produced many new technologies. Recently, the author and the members of the development group (Masao Yamada, Atsushi Kuno, and Hiroaki Tateno) wrote a grand review of the lectin microarray, so please refer to it for details.[28]

The following are examples of the research topics where the lectin microarray and its application went well.

2) Examples of use in the bio fields

In the aforementioned MG project, focus was placed on chronic diseases such as cancer, and excellent results were obtained for hepatic fibrosis markers and refractory intrahepatic bile duct cancer. In both cases, lectin microarrays played important roles (refer to Reference [2] by Narimatsu for details). The microarrays were partially responsible for the success of the MG Project, the main focus of the RCMG. There is no greater joy for the developer.

The application of lectin microarrays progressed first in stem cells. In the cooperative relationship between Akihiro Umezawa, Division Chief (currently Deputy Director) of the National Center for Child Health and Development (NCCHD), analyses were done for the mesenchymal stem cell lineup using the bioresources owned by the NCCHD, as well as the mouse embryonic stem (ES) cells and embryonic carcinoma (EC) cells.[29]-[32] The strategy for analysis was mostly completed in 2006, and to accomplish the technological transfer of the analysis platform to NCCHD the following year, the author *et al.* participated in the NEDO project for bridging technology and R&D (Development of Technology for Translational Research to Clinical Research / Development of Translational Research Technology / Quality Evaluation of Stem Cell Population by Glycan Profiling, R&D of Safety Evaluation System; period October 2007 to March 2009). Just when the research started, we heard the news of the “successful production of human iPS cells” by Professor Shinya Yamanaka. The world was surprised by the reality of genetic reprogramming.

Unfortunately, there were hardly any researchers studying the glycan structure of stem cells at the time. However, the SSEA-1/3/4 and Tra1-60/81 that are known as the surface markers of undifferentiated cells are certainly glycan markers. If various cells can be prepared homogenously including the undifferentiated cells, it can be shown that there are clear differences in their glycan profiles. Since the mesenchymal stem cells are heterogeneous, we thought the iPS and ES cells should be the subjects of comparative glycan profiling.

Therefore, following the above translation research project, we joined the new NEDO project (Development for the Core Technology for Applying Stem Cells such as iPS Cells to Industry, April 2009~) to fully promote glycan profiling for stem cells in collaboration with Makoto Asashima, Director (at the time) of the Organ Development Research Laboratory and his group. This project ended in two years due to various reasons, but we worked eagerly on the analysis of diverse undifferentiated cells.

Hiroaki Tateno who joined the Lectin Application Development Team from 2006 refined the system, and newly developed high-density lectin arrays composed of 96 types of lectins including recombinant lectins. The 100 ES/iPS cells were excellent subjects to try the "sharpness" of this new array. The author *et al.* collaborated with Team Leader Yuzuru Ito and Senior Researcher Yasuko Onuma of the Research Center for Stem Cell Engineering, and powerfully promoted glycan profiling for the series of stem cells. Since the results were published through press releases, many people may already know what followed. Nevertheless, the development of the research in chronological order will be explained below.

(1) Reality of glycan reprogramming
Over 100 types of human undifferentiated cells (ES/iPS) were analyzed using the newly developed high-density lectin array with 96 lectins. As a result, characteristic glycan structures common in undifferentiated cells but not present in somatic cells were extracted. In consequence, it was observed for the first time that the glycan structure is reprogrammed through the introduction of Yamanaka's four factors.[33] Particularly, the recombinant lectin called rBC2LCN that reacted commonly with all undifferentiated cells did not react with the parent cell (somatic cell) that was the base of the iPS cell production, and it was shown that rBC2LCN could be a new probe for the detection of undifferentiated markers.[Note 7)]

(2) Quantitative comparative analysis of the glycan structure of iPS and somatic cells
Representative iPS cell 201B7 and dermal fibroblasts that are its source were prepared in large amounts, and overall analysis for glycoprotein glycans (both N- and O-glycans) were conducted by the LC mapping method that combined MS and glycosidase digestion. The observation of the lectin microarray in (1) was actually confirmed, and the dramatic shift of the sialic acid linkage from α2-3 to α2-6 types in the N-glycan was confirmed.[34] There was interest in what was the undifferentiated glycan marker that could be recognized by the aforementioned rBC2LCN, but the H type 3 structure (Fuc α 1-2Gal β 1-3GalNAc α) was found specifically in the O-glycan.

(3) rBC2LCN can be used to stain undifferentiated cells alive
Usually, in flow cytometry and histological staining, antibody is used as the probe. The surface markers SSEA-1/3/4 or Tra1-60/81 are also detected by antibodies, but in general, the cells must be fixed. However, such cells die since the membranes are treated with formalin or glutaldehyde, however, rBC2LCN is known to possess sufficient ability to bind in the live cell condition. Moreover, when the undifferentiated cell is induced to differentiate using an agent, the staining property of rBC2LCN disappears promptly.[35] It should be noted that there are many advantages considering the future practical use, such as the lower development cost compared to antibodies.[Note 8)]

(4) The ligand of rBC2LCN is H type 3 structure seen in podocalyxin
Podocalyxin is a glycoprotein with large molecular weight that is expressed in kidneys or certain types of carcinoma cells. It is expected to be a sialomucin where most of the extracellular domain is heavily covered with sialylated O-glycans. The important issue in clarifying the undifferentiation mechanism is to see which glycoproteins on the undifferentiated cell are recognized by rBC2LCN that recognizes the aforementioned undifferentiation markers. By seeking out this molecule from the characteristic of the molecular structure and genetic expression, the target was identified using the antibody against podocalyxin.[36] The observations so far, including the facts that podocalyxin contains abundant O-glycans, to which rBC2LCN is specifically bound, and O-glycan with H type 3 structure has been identified from the iPS cell (201B7), now all come together in one piece.[Note 8)]

5 Future prospects

Other than the biomarker exploration and stem cell evaluation technology, lectin microarrays are utilized in various places. About 60 reports of the use of GlycoStation™ Reader 1200 have been published as papers, and about one-third of them are by external research institutes unrelated to the author *et al.* There are about 10 papers from overseas research institutes. While it is not addressed in this paper, the demand for this device is expected to increase rapidly in the development of biopharmaceuticals (particularly for biosimilars).

Recently, the National Academy of Science of the USA reported that the study of glycans is the core science that stretches across a wide range of life sciences. The report titled *Transforming Glycoscience* indicates that glycans are important in three major topics of "health," "materials," and "energy," and the dramatic progress in glycoscience is likely to occur at a global level.[37] The glycans are about to be released from the realm of specialists to leap into globalization.

There are many books that collect data and technology of glycans. In contrast, the book which will be published soon from Springer Japan intends to introduce the “topics that are in the news in the periphery of glycans” for the researchers who are not glycan specialists.[38] In bioresearch, one must be facing glycan issues regardless of whether one is aware of it or not. The reason we study glycans is because it is important, universal, and difficult.[39] It must not be forgotten that glycans are widely existent. This is the other side of the fact that the origin of sugar is old. Though it may sound paradoxical, the author believes, “glycans do not exist because they are important, but became important because they have existed.”[40]

There are major issues left in the synthesis technology. The creation of biopharmaceuticals by homogenous glycans is a major goal of biologics.[41] While the lectin array is evaluated highly as a tool for that purpose, lectins themselves may eventually turn out to be something major.

6 Summary: Components of the technology and the opportunities for integration

Finally, we shall investigate how the lectin microarray technology was synthesized, how the core technological components were integrated, and what were the opportunities for breakthroughs (Fig. 7). First, there was a demand for the development of glycan analysis technology. The opportunity to develop such technology came to the author in 2002. At the time, a high performance of FAC was achieved by the author at a university, and this brought about the change of thinking that it was possible to profile glycans using lectins. I joined AIST almost immediately afterwards, and was assigned to the glycomics project. The concept of glycan profiling that was merely a pie in the sky became a solid project after collaboration with companies and verifying the principle. The patent application was in 2003, the publication of the academic paper was in 2005, and the launch of the glycan profiling device was in 2006. The blooming of this technology continued. It was utilized in the biomarker development in the subsequent glycomics project, and a wider approach to its use was created through the organizational efforts of GLIT to promote the results. This strongly pushed the bridging of glycans to industry. One of the new applications was the discovery of the new undifferentiated marker detection probe called rBC2LCN in the stem cell evaluation technology. This was the impetus to new development including the detection and elimination of the undifferentiated cells in regenerative medicine, as well as the shift to recombinant lectins. Perhaps it might have opened the door to a new discipline called lectin engineering.

Looking back at the series of events, what was the most important point? The author believes it was the thorough technological pursuit of the “weak interactions” as exemplified by the glycan-lectin binding. The FAC achieved this pursuit in principle, but the achievement of high throughput was necessary before arriving at the idea of glycan profiling. However, since FAC could not handle crude extracts derived from living tissues, it was necessary to shift to a totally different platform called the lectin array. Then focus was placed on the evanescent wave excitation method that allowed capturing weak interactions. At the same time, there were many groups that proposed the lectin array, but only the author’s group reached product development that produced satisfactory results. The reason the author took up, without hesitation, the evanescent wave excitation

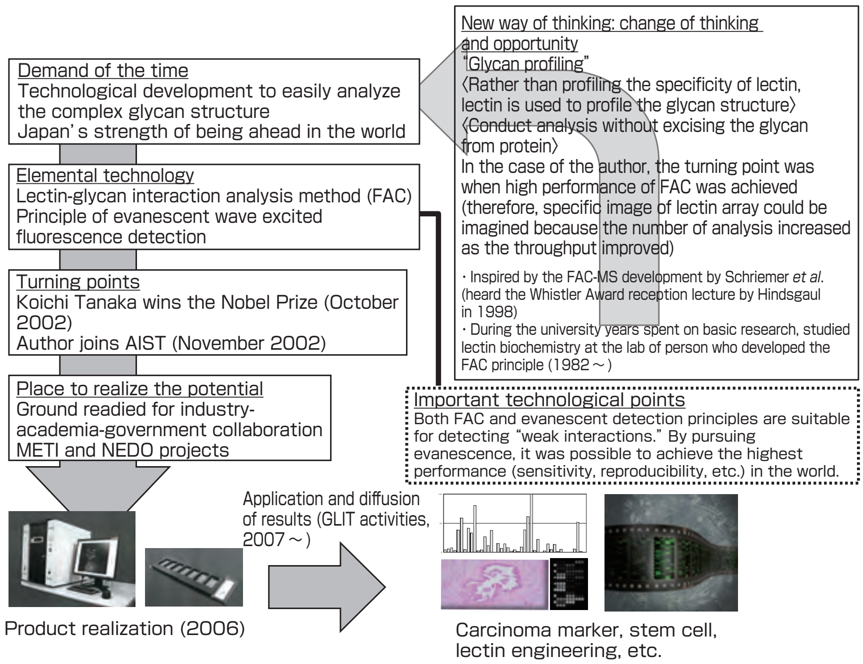

Fig. 7 Summary of the synthesis of the lectin microarray technology

fluorescence detection principle that allowed detection of weak interactions was perhaps because he was a newcomer to the optics field, and did not look aside for other technical options. In fact, theoretically "evanescence is not necessarily highly sensitive," but as of now, no device that surpasses the precision and sensitivity of the evanescent wave excitation scanner that we developed has emerged.

Notes

Note 1) Because glycans have complex structures with unknown functions, the USA and the European countries were reluctant to invest a large amount of research funds. In contrast, there was an understanding for the importance of sugars and sugar research as a national policy in Japan, and the government supported the development of glycomics technology and enzyme exploration such as glycosidase that the Japanese researchers probably started from half curiosity and half determination. Moreover, high achievement of the biochemical refinement technology strengthened the accumulation of glycan resources and know-how, and Japan was way ahead of the race for patents and papers on glycans. On the other hand, there were people overseas who focused on glycans before, and there was an interesting background in the start-up of a new discipline called glycobiology.[1]

Note 2) Antigen determinant recognized by antibodies. In a wider sense, it includes the structures involved in the recognition.

Note 3) A method to identify structures by referencing to standard products with known structures. It is also called the memory verification method. It is distinguished from the method that directly determines structures such as the methylation analysis in NMR and MS.

Note 4) I asked Koichi Tanaka of Shimadzu Corporation whom I met at a study session before the project start-up to act as the mediator for the LC section. Later, Tanaka declined participation to our project as he received the Nobel Prize.

Note 5) The project to comprehensively analyze the interactions between 100 lectins and 100 glycans (standard products with known structures) using FAC. Masugu Kamei of Honen Corporation (currently, J-Oil Mills, Inc.) traveled throughout Japan to collect lectins, and Norihiro Kikuchi and Junko Takahashi of the Mitsui Knowledge Industry Co., Ltd. was in charge of the data analysis (see Table 1). Shoko Nakamura (née), Postdoctoral Fellow (at the time), led the project at AIST.

Note 6) The meaning of this word is "light of the fleeting moment," and it is also called the evanescent field or nearoptic light. In the reflection phenomenon of the magnetic wave (light), it is the permeating magnetic wave that occurs in the reflecting medium under certain conditions. Excellent explanation is provided in the following Nikon site. http://www.nikon.co.jp/profile/technology/rd/core/optical/evanescent/index.htm

Note 7) April 2, 2012, AIST Press Release: Facile diagnosis of iPS cells using glycan profiling technology –Identification of a novel pluripotency marker by high-density lectin microarray

Note 8) May 16, 2013, AIST Press Release: A novel probe for live human iPS cell imaging–iPS cells can be cultured with monitoring of their quality

References

[1] A. Varki and N. Sharon: *Essentials of Glycobiology, 2nd edition* (edited by. A. Varki, R. D. Cummings, J. D. Esko, H. H. Freeze, P. Stanley, C. R. Bertozzi, G. W. Hart and M. E. Etzler), Cold Spring Harbor Laboratory Press (2009).

[2] H. Narimatsu: Development of basic tools for glycoscience and their application to cancer diagnosis - A 10-year strategy of the Research Center for Medical Glycoscience of AIST, *Synthesiology*, 5 (3), 190-203 (2012) (in Japanese) [*Synthesiology English edition*, 5 (3), 201-215 (2012)].

[3] E. Yasuda, H. Tateno, J. Hirabayashi, T. Iino and T. Sako: Lectin microarray reveals binding profiles of Lactobacillus casei strains in a comprehensive analysis of bacterial cell wall polysaccharides, *Appl. Environ, Microbiol*, 77 (13), 4539-4546 (2011).

[4] A. Shibazaki, H. Tateno, A. Ando, J. Hirabayashi and T. Gonoi: Profiling the cell surface glycome of five fungi using lectin microarray, *J. Carb. Chem*., 30 (3), 147-164 (2011).

[5] N. Takahashi: Three-dimensional mapping of N-linked oligosaccharides using anion-exchange, hydrophobic and hydrophilic interaction modes of high-performance liquid chromatography, *J. Chromatogr. A*, 720 (1-2), 217-225 (1996).

[6] S. Hase, S. Hara and Y. Matsushima: Tagging of sugars with a fluorescent compound, 2-aminopyridine, *J. Biochem*., 85 (1), 217-220 (1979).

[7] J. Hirabayashi and K. Kasai: Glycomics, coming of age! *Trends Glycosci. Glycotechnol*., 12 (63), 1-5 (2000).

[8] T. Feizi: Progress in deciphering the information content of the 'glycome' - a crescendo in the closing years of the millennium, *Glycoconj. J*., 17 (7-9), 553-565 (2000).

[9] J. Hirabayashi: Furontaru afiniti kuromato-bunsekiho (Frontal affinity chromatography), *Seibutsu Kogaku Kaishi*, 89 (7), 394-397 (2011) (in Japanese).

[10] K. Kasai, Y. Oda, M. Nishikata and S. Ishii: Frontal affinity chromatography: theory for its application to studies on specific interactions of biomolecules, *J. Chromatogr. B*, 376, 33-47 (1986).

[11] D. C. Schriemer, D. R. Bundle, L. Li and O. Hindsgaul: Micro-scale frontal affinity chromatography with mass spectrometric detection: a new method for the screening of compound libraries, *Angew. Chem. Int. Ed*., 37, 3383-3387 (1998).

[12] J. Hirabayashi, Y. Arata and K. Kasai: Reinforcement of frontal affinity chromatography for effective analysis of lectin-oligosaccharide interactions, *J. Chromatogr. A*, 890 (2), 261-271 (2000).

[13] Y. Arata, J. Hirabayashi and K. Kasai: Application of reinforced frontal affinity chromatography and advanced processing procedure to the study of the binding property of a Caenorhabditis elegans galectin, *J. Chromatogr. A,* 905 (1-2), 337-343 (2001).

[14] E. S. Ng, N. W. Chan, D. F. Lewis, O. Hindsgaul and D. C. Schriemer: Frontal affinity chromatography-mass spectrometry, *Nat. Protoc*., 2 (8), 1907-1917 (2007).

[15] H. Tateno, S. Nakamura-Tsuruta and J. Hirabayashi: Frontal affinity chromatography: sugar-protein interactions, *Nat. Protoc*., 2 (10), 2529-2537 (2007).

[16] S. Angeloni, J. L. Ridet, N. Kusy, H. Gao, F. Crevoisier, S. Guinchard, S. Kochhar, H. Sigrist and N. Sprenger: Glycoprofiling with micro-arrays of glycoconjugates and lectins, *Glycobiology*, 15 (1), 31-41 (2005).

[17] K. T. Pilobello, L. Krishnamoorthy, D. Slawek and L. K. Mahal: Development of a lectin microarray for the rapid analysis of protein glycopatterns, *ChemBioChem*, 6 (6), 985-989 (2005).

[18] T. Zheng, D. Peelen and L. M. Smith: Lectin arrays for profiling cell surface carbohydrate expression, *J. Am. Chem.* Soc., 127 (28), 9982-9983 (2005).

[19] A. Kuno, N. Uchiyama, S. Koseki-Kuno, Y. Ebe, S. Takashima, M. Yamada and J. Hirabayashi: Evanescent-field fluorescence-assisted lectin microarray: A new strategy for glycan profiling, *Nat. Methods*, 2 (11), 851-856 (2005).

[20] R. Rosenfeld, H. Bangio, G. J. Gerwig, R. Rosenberg, R. Aloni, Y. Cohen, Y. Amor, I. Plaschkes, J. P. Kamerling and R. B. Maya: A lectin array-based methodology for the analysis of protein glycosylation, *J. Biochem. Biophys. Methods*, 70 (3), 415-426 (2007).

[21] S. C. Tao, Y. Li, J. Zhou, J. Qian, R. L. Schnaar, Y. Zhang, I. J. Goldstein, H. Zhu and J. P. Schneck: Lectin microarrays identify cell-specific and functionally significant cell surface glycan markers, *Glycobiology*, 18 (10), 761-769 (2008).

[22] K. Kornfeld, M. L. Reitman and R. Kornfeld: The carbohydrate-binding specificity of pea and lentil lectins, *J. Biol.Chem.*, 256 (13), 6633-6640 (1981).

[23] K. Yamamoto, T. Tsuji, I. Matsumoto and T. Osawa: Structural requirements for the binding of oligosaccharides and glycopeptides to immobilized wheat germ agglutinin, *Biochemistry*, 20, 5894-5899 (1981).

[24] R. D. Cummings and S. Kornfeld: Fractionation of asparagine-linked oligosaccharides by serial lectin-Agarose affinity chromatography, *J. Biol. Chem.*, 257 (19), 11235-11240 (1982).

[25] C. D. Rillahan and J. C. Paulson: Glycan microarrays for decoding the glycome, *Annu. Rev. Biochem.*, 80, 797-823 (2011).

[26] N. Uchiyama, A. Kuno, H. Tateno, Y. Kubo, M. Mizuno, M. Noguchi and J. Hirabayashi: Optimization of evanescent-field fluorescence-assisted lectin microarray for high-sensitivity detection of monovalent oligosaccharides and glycoproteins, *Proteomics*, 8 (15), 3042-3050 (2008).

[27] A. Kuno, S. Takeishi and J. Hirabayashi: Rekuchin maikuro arei no tanpakushitu iyakuhin seisan purosesu kaihatsu eno oyo (Application of lectin microarray to the development of protein pharmaceutical production process), *Bio Iyakuhin Kaihatsu Ni Okeru Tosa Gijutsu* (Glycotechnology for Development of Biotechnology Protein Products) (T. Hayakawa, K. Kakehi, J. Hirabayashi eds.), CMC Publishing, 230-241 (2011) (in Japanese).

[28] J. Hirabayashi, M. Yamada, A. Kuno and H. Tateno: Lectin microarrays: concept, principle and applications, *Chem. Soc. Rev.*, 42 (10), 4443-4458 (2013).

[29] A. Kuno, Y. Itakura, M. Toyoda, Y. Takahashi, M. Yamada, A. Umezawa and J. Hirabayashi: Development of a data-mining system for differential profiling of cell glycoproteins based on lectin microarray, *J. Proteomics Bioinformatics*, 1 (2), 68-72 (2008).

[30] M. Toyoda, M. Yamazaki-Inoue, Y. Itakura, A. Kuno, T. Ogawa, M. Yamada, H. Akutsu, Y. Takahashi, S. Kanzaki, H. Narimatsu, J. Hirabayashi and A. Umezawa: Lectin microarray analysis of pluripotent and multipotent stem cells, *Genes Cells*., 16 (1), 1-11 (2011).

[31] Y. Itakura, A. Kuno, M. Toyoda, A. Umezawa and J. Hirabayashi: Podocalyxin-targeting comparative glycan profiling reveals difference between human embryonic stem cells and embryonal carcinoma cells, *J. Glycom. Lipidom.*, S5-004 (2013).

[32] S. Saito, Y. Onuma, Y. Ito, H. Tateno, M. Toyoda, A. Hidenori, K. Nishino, E. Chikazawa, Y. Fukawatase, Y. Miyagawa, H. Okita, N. Kiyokawa, Y. Shimma, A. Umezawa, J. Hirabayashi, K. Horimoto and M. Asashima: Possible linkages between the inner and outer cellular states of human induced pluripotent stem cells, *BMC Syst. Biol.*, 5 Suppl 1, S17 (2011).

[33] H. Tateno, M. Toyoda, S. Saito, Y. Onuma, Y. Ito, K. Hiemori, M. Fukumura, A. Matsushima, M. Nakanishi, K. Ohnuma, H. Akutsu, A. Umezawa, K. Horimoto, J. Hirabayashi and M. Asashima: Glycome diagnosis of human induced pluripotent stem cells using lectin microarray, *J. Biol. Chem.*, 286 (23), 20345-20353 (2011).

[34] K. Hasehira, H. Tateno, Y. Onuma, Y. Ito, M. Asashima and J. Hirabayashi: Structural and quantitative evidence for dynamic glycome shift on production of induced pluripotent stem cells, *Mol. Cell. Proteomics*, 11 (12), 1913-1923 (2012).

[35] Y. Onuma, H. Tateno, J. Hirabayashi, Y. Ito and M. Asashima: rBC2LCN, a new probe for live cell imaging of human pluripotent stem cells, *Biochem. Biophys. Res. Commun.*, 431 (3), 524-529 (2013).

[36] H. Tateno, A. Matsushima, K. Hiemori, Y. Onuma, Y. Ito, K. Hasehira, K. Nishimura, M. Ohtaka, S. Takayasu, M. Nakanishi, Y. Ikehara, M. Nakanishi, K. Ohnuma, T. Chan, M. Toyoda, H. Akutsu, A. Umezawa, M. Asashima and J. Hirabayashi: Podocalyxin is a glycoprotein ligand of the human pluripotent stem cell-specific probe rBC2LCN, *Stem Cells Transl. Med.*, 2 (4), 265-273 (2013).

[37] National Research Council: *Transforming Glycoscience*, The National Academies Press (US), (2012).

[38] N. Taniguchi, T. Suzuki and K. Ohtsubo (eds.): *Sugar Chains*, Springer, Tokyo (2014) (in press).

[39] J. Hirabayashi, A. Kuno and H. Tateno: Lectin-based structural glycomics: a practical approach to complex glycans, *Electrophoresis*, 32 (10), 1118-1128 (2011).

[40] J. Hirabayashi: *Tosa no Hanashi* (Story about Sugar Chains), Nikkan Kogyo Shimbun (2008) (in Japanese).

[41] J. Hirabayashi: Tenkanki o mukaeta baio iyakuhin – Seihi no kagi wa opun inobeshon to tosa seigyo (Biopharmaceuticals at a turning point - Key to success are open innovation and glycan control), *MEDCHEM NEWS*, 23 (2), 16-21 (2013) (in Japanese).

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Discussions with Reviewers

1 Overall comment

Comment (Kanji Ueda, Hyogo Prefectural Institute of Technology)

I see that there were several important leaps in the progress of this research. The research is narrated in a story form, the epochs are emphasized and the content is easy to understand. However, the leaps must have been based on some hypotheses rather than being mere coincidences. Did you hypothesize some new elemental technology, or did you set up a hypothesis to synthesize the existing technologies? Please explain clearly. I think such explanation will make the paper even more appropriate for *Synthesiology*.

Also, to enhance the readers' understanding, I think you should add an explanatory flow chart that goes along with the structure of this paper. The reader will be able to logically understand the paper along with the storytelling.

Comment (Noboru Yumoto, AIST)

The objective of this research is the "development of glycan profiling technology," and with the major breakthrough of the "proof of concept by FAC," the elemental technologies such as "lectin arrays" and "evanescent wave excitation fluorescence detection" were integrated to develop the lectin microarrays. However, the scenario is not easy to understand by people outside of the bio field. The main reason is because the description is provided in chronological order. Therefore, I think you should insert a conceptual diagram for the lectin microarray and glycan profiling, and explain why you needed the proof of concept, and how you integrated the elemental technologies for the microarray.

Answer (Jun Hirabayashi)

Except for the "application development" of the latter half, I made revisions by clarifying the technological scenario and the hypothesis, considering the point that you indicated. I added Fig. 7 that shows the correspondence between the story and the structure and reasoning of this technology, and also added a summary for the technology-centered scenario.

However, if I break the chronological (the storytelling) style, I think the characteristics will be lost (though it may depend on my writing ability) and I will end up having to rewrite the whole text. After much consideration, I left the chronological description as is. I implanted the image of how difficult glycomics is in the beginning of the paper (presentation of the issue). Then I clarified the difference between the conventional method and the lectin microarray procedure (Fig. 2), explained the flow from the principle of the lectin array (Fig. 3) to the improvement of FAC that provided the breakthrough (Fig. 4), and presented the data obtained in the Project (Fig. 5 is the image of the lectin array). Moreover, I added a summary in the end for a technology-centered scenario that can be reviewed by the readers.

2 Clarification of the difficulty of the structural analysis of glycans

Comment (Kanji Ueda)

You emphasize the facts that glycans have much structural diversity, temporary instability, and complexity, and those were the starting points of the research. I think the readers will be able to understand better if you give a numerical example of how different glycans are compared to nucleic acids and proteins.

Comment (Noboru Yumoto)

Can you describe why glycan profiling is important at the beginning for the readers outside of your field? I think you should let people know how complex it is by adding the chemical structure of a representative glycan, and by stating that there are multitudes of lectins that recognize various glycans.

Answer (Jun Hirabayashi)

I newly created Fig. 1 to explain why the structural analysis of glycans is difficult compared to other polymers, with added schematic diagram of a glycoprotein and the factors that make it complicated from the viewpoint of hierarchy. I think this makes Fig. 2 that shows the difference between the conventional method where the glycans are excised and mutually separated and the approach using lectin arrays easier to understand compared to the former text.

3 Superiority of the developed system

Comment (Noboru Yumoto)

In the section of "evanescent wave excitation fluorescence detection method," it is rather difficult to understand the superiority of the system developed by the author *et al*. You mention the superiority of "high detection sensitivity," but I cannot see from where this characteristic arises. At the end of the text, you write "theoretically 'evanescence is not necessarily highly sensitive.'" Perhaps it is not clear why high sensitivity could be achieved, but can you add some explanation?

Answer Answer (Jun Hirabayashi)

I added the point that to achieve high sensitivity, not only the employment of the principle of the evanescent wave excitation, but various measures for reducing the background including optical, biochemical, and software measures contributed.

Development of a household high-definition video transmission system based on ballpoint-pen technology

— A low cost, easily deployed optical connection using a ballpoint-pen type interconnect —

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Higher quality video formats beyond HDTV are being developed, but these formats require data communication rates greater than 10 Gbps, which are not easily adaptable to household applications. Moreover, household usage requires ease of handling, robustness against poor connectivity, and affordable cost. Conventional silica optical fibers are not suitable for applications that involve high-speed, short-range communication, because of their fragility, and difficulty in achieving precise connectivity with a low cost connecting method. We proposed a novel expanded-beam interconnect using a graded-index plastic optical fiber (GI POF) with a glass spherical collimator lens uniquely fabricated by low cost ballpoint-pen technologies at both ends. Our power budget evaluation verified its suitability for consumer applications. Successful validation was then conducted by transmitting 4K-3D uncompressed video content.

Keywords : Optical communications, collimator lens, optical system design, ballpoint pen, plastic optical fiber

1 Introduction

The uncompressed image transmission at home requires quite high bandwidth. Although the current high-definition (HD) television format (1920 × 1080 pixels/60 fps/interlace) provides high quality video for consumers, more advanced video technologies that deliver even higher quality than HDTV are becoming more and more important, because of increased display size of television sets in consumer living rooms. To keep the equal resolution, a television set having twice the size of its display needs double the number of pixels in both the horizontal and vertical directions (four times more pixels in total) compared to that of the HD format and an optional double frame rate for fast moving picture smoothness. The 4K format (3840 × 2160 pixels/60 fps/progressive) requires eight times faster data communication than full high definition video format or over 10Gbps bandwidth. In addition to this, if stereo 3D viewing also becomes popular, the data size would have to be doubled in order to maintain the same image resolution for each viewing.

To achieve the target transmission speed for such higher definition digital video formats, the existing copper wire communications, such as DVI (Digital Visual Interface) or HDMI (High-Definition Multimedia Interface) are insufficient and optical communications are required. Conventional silica multimode optical fibers (Silica MMFs) can be applied, which are widely used for professional data communication. However, being fragile, they are not appropriate for consumer short-reach applications at home or offices.[1][2] Users may step on them or may wire, bundle, or use them carelessly, that increase risk of fiber breaking. Broken fibers can hurt users and should not be discarded as normal garbage. Moreover, a user has to wipe dust or stains on a fiber end with alcohol or to blow them with clean air spray to ensure its connectivity.

To solve the connecting problem, lens termination of the fiber end improves the ease of use of optical fibers, since it expands and collimates output beam. A ball lens connector is a good practical solution and is called the "expanded-beam connector."[3] Figure 1 compares (a) a conventional butt-coupling connection with (b) a ball lens connection. The expanded-beam output from the ball lens increases the tolerance of both gap distance and axial alignment. The lens also protects the fiber end making it more robust and less sensitive to dust and contaminations and has often been used for heavy duty applications, such as that in vehicles or military circumstances, where ease of connection under rugged conditions is required.[4] In order to attach a ball lens well aligned to the center of the optical fiber core, designing its connector housing needs high preciseness which results in expensive manufacturing cost. Because of this, it has only been applied to special applications. Moreover, its housing becomes bulky and difficult to be made small. To overcome silica fiber fragility against bending, an improved product is available, but its cable is too thick for consumer application with its thick cover material.

Considering these backgrounds, we propose a safe, easy to handle, reliable, and low cost high speed optical communication

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system in this study, which enables transmitting uncompressed high resolution video. Specifically, an ultra small optical interconnect having a small ball lens on an end of the plastic optical fiber was developed. A novel connector combining multiple interconnects was then developed and its verification test was run successfully.

2 Target and Scenario

Concerning the issues which must be examined in introducing the optical fiber communications system for consumer homes, one should consider not only technical requirements to meet specific transmission speed (bandwidth), but also requirements of safety, ease of handling, simple and reliable connection, and its low cost availability from the consumers' points of view.

Instead of silica optical fibers which are difficult to meet these requirements, plastic optical fibers (POFs) are the most promising candidates as they have better flexibility, physical durability, and can be mass produced at low cost.

POF is strong enough against stamping on or bending tightly so that fiber breakage does not occur, compared with silica optical fibers. A step-index (SI) type POF generally diffused in the market is thought to be appropriate for in-door wiring use, as it does not require special care against axial misalignment or dust and scratches on a fiber end at its connection because of its large core diameter. Considering uncompressed high resolution video transmission of this study, however, since it has narrow transmission band, access speed is insufficient in the zone of several 100 Mbps.

On the other hand, perfluorinated graded-index plastic optical fibers (PF GI POF) (Fig. 2) invented by Y. Koike, *et al.* at Keio University have been commercialized for high speed communication. PF GI POF has better flexibility than silica optical fiber, and the world's fastest GI POF transmits approximately 40 Gbps, with POF flexibility advantage. Koike, *et al.* has proposed "Face-to-Face Communication System" between remote places using a large size high resolution display with the perfluorinated GI POF.[5]

Since PF GI POF has similarly wide bandwidth and rather better physical material characteristics than silica optical fibers, Ralph, *et al.* of Georgia Institute of Technology evaluated it highly.[6] Because it is a plastic material, it is possible to mass produce it with extrusion-molding

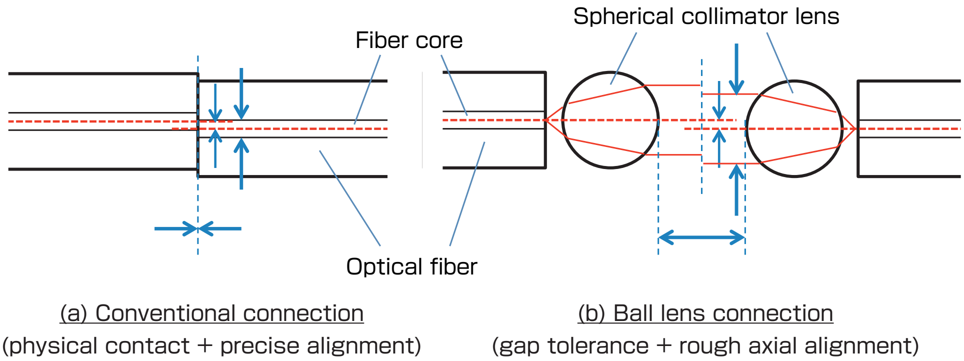
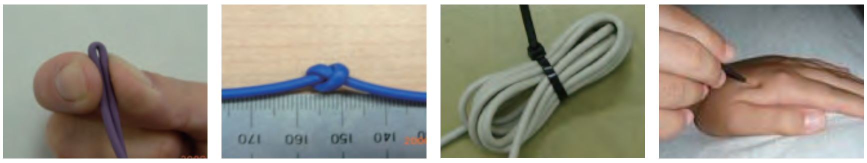


Fig. 1 Schematic image of ball lens benefits
Conventionally optical fibers should be connected with physical contact and precise axial alignment. A ball lens on the end of optical fiber collimates output light with expanded beam which makes it easier to connect without precise alignment or physical contact.



《Strength》
○ High speed communication ○ Safe (no dangerous broken piece)
○ Flexibility (bending resistance) ○ Low cost, continuous mass production
《Weakness》
× Softness (weak scratch resistance) × Not suitable for small volume
× Electrostatic (attracts dust) × Few adoption results yet

Fig. 2 Strength and weakness of GI POF
Perfluorinated GI POF (graded index plastic optical fiber) is physically flexible compared with silica optical fibers, and shows excellent bending resistance and is safe against breakage. Thus it is easy for consumers to handle it. However, one has to be careful not to scratch the ends or use it in a dusty environment.

technology at low cost. However, in order to make high-speed communication possible, the diameter of the fiber core should be designed small and it loses the advantage of ease of connection of POF. The high speed POF requires precise connection with accurate axial alignment and special care for dust and scratches on the fiber ends similar to silica MMF. To keep the ends clean, it should have an end cap for dust prevention and one needs to clean the ends in advance to the connection. As a plastic tends to attract more dust with static electricity and is softer or has lower scratch resistance, such care should be taken even more than silica.

Although it is known that above-mentioned ball lens protects the fiber ends and can improve such failure problems, conventional process of attaching a ball lens is costly and minimizes POF benefits of low-cost short-reach communication business. Since GI POF was invented 20 years ago, even though it has been said to be an ideal solution for home network systems, the application of GI POF has been limited because of these trade-offs. Our study can be an innovative integration technology to breakthrough this fact.

Figure 3 explains the scenario of the development. As already mentioned, an expanded-beam connector having a ball lens on its end has been known to improve connectivity and to prevent dust and scratches on fiber ends. However, if it is used with POF, it is costly; if it is used with silica MMF, it does not meet consumer needs of flexibility. In other words, although the function of the ball lens is excellent, the conventional ball attaching technology cannot be a solution to improve the trade-offs.

Torikai (one of the authors of this paper, worked for Japan Aviation Electronics Industry at that time), on the other hand, was struggling to develop a small optical interconnect for electronics on-board application that can connect the narrow spaces within the equipment as a jumper wire. Although connection became easy when there was a ball lens, he remembered difficulty in using micro form required for a jumper wire. One day in 2009, he had an opportunity to discuss it with an engineer from Mitsubishi Pencil who produces ballpoint pens in a cross-industrial networking meeting. He realized the similarity of the structural concept of ball attachment on a tip of a thin tube or fiber, although the material of the ball was different; one was glass and the other, metal.

A joint research project between the two companies was initiated right after the meeting. A silica glass optical fiber was first inserted instead of the ink tube of the needle tip ball-point pen. However, the silica fiber broke easily in the metal sleeves, when it was crimped by a regular punching process to anchor the fiber. In 2010, when the team was almost giving up the development, they met Koike by chance who had just been assigned as a technical advisor to Mitsubishi Pencil. Koike was consulted about the development and suggested to replace silica fiber with GI POF, Koike's invention. He thought that the plastic material similar to the ink tube was flexible and should work.

Furthermore, when using the ballpoint pen technology, attaching a ball lens could realize the low cost solution. It was expected that such a low cost connector with a ball lens could be introduced not only into the electronics field but also into households. As a result of an experiment, GI POF was successfully attached to the needle tip metal sleeve without breakage which made the team re-start the project.

To summarize the scenario, the purpose of the study was to develop basic technology and to verify if it could optically transmit high resolution video for consumer use. We conducted the study with the scenario that the ballpoint pen component technology enables GI POF to be used at low cost with an expanded-beam connector at its end.

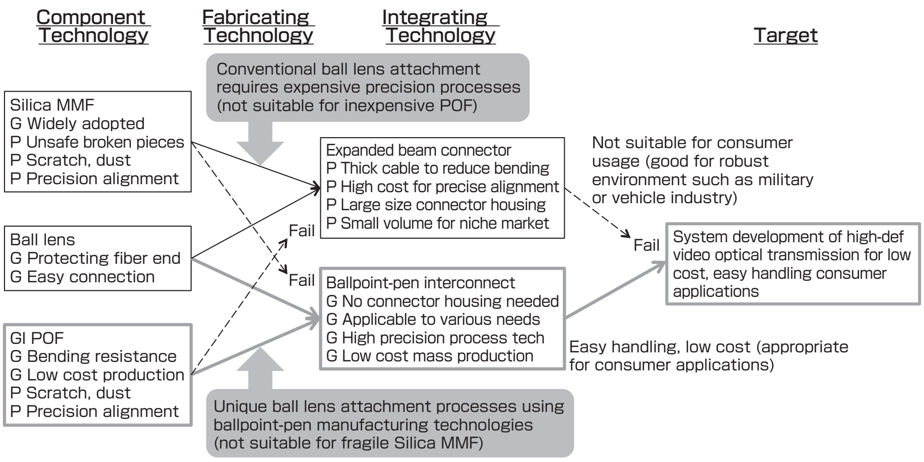


Fig. 3 Scenario of technology development for consumer optical connection

Benefits of ball lens have been well known, but its fabrication requires high, expensive precision processes which means limited usage in robust, special applications. This study enabled low cost, precision ball lens attachment using ballpoint-pen manufacturing technologies.

3 Development of ballpoint pen type optical interconnect

To attach a ball lens on an end tip of the plastic optical fiber, we introduced for the first time in the world a unique manufacturing method—ballpoint pen production processes that considerably reduce process cost.[7] The construction of the unique, novel ball lens attachment concept is shown in Fig. 4.

The tip of the needle-tip type ballpoint pen comprises three components: needle shape metal sleeve (inside diameter 0.5 mm, length 7.8 mm), metal ball inserted in the tip (precisely polished to a perfect sphere of 0.55 mm diameter), and a capillary that helps ink to flow. We kept the metal sleeve as-is and replaced the metal ball with a highly transparent glass sphere (material #BK7, 0.55 mm diameter, polished precisely to a perfect sphere), then inserted PF GI POF from AGC “FONTEX®” instead of the ink capillary. The metal sleeve is punch processed so that an optical fiber and a glass ball can keep the distance between them precisely. After that, the fiber was fixed by crimping it from the outside of the sleeve so that it could not be removed.

Axial alignment of POF and the ball should be good enough. From this point of view, the ballpoint pen production technology is able to satisfy the need of precise alignment for optical communication, since alignment of these pen components has to be precise in design and manufacturing to minimize writing failure for the ballpoint pen. In addition to this, the precision polishing of the ball to produce ballpoint pens is also the right technology appropriately fit for high quality optical characteristics which require the ball lens to be a perfect sphere with a smooth surface.

Crimping process is also done with the existing technology for ballpoint pen production to prevent inserted optical fiber from removal failure. Flexibility of POF fit quite well with the process technology. The locations and pressure of crimping were adjusted by trial and error within the regular production parameters for ballpoint pens.

These processes were difficult to accomplish for a silica optical fiber. This is the most unique, essential discovery in this study to make use of POF characteristics. In other words, conventional ballpoint pen production technologies, which need precision component alignment, ball polishing and tube crimping, just perfectly fit the needs of the tiny optical interconnection and made it possible to realize it at extremely low cost in manufacturing.

4 Experimental setup and results

Experimental procedures and the results to evaluate performance of the newly developed optical interconnect are discussed in this section.

4.1 Evaluation of connecting loss from misalignment

Optical power meter “Photom 205A” from Graytechnos was used to read optical power transmitted for each condition. We set a pair of optical cables on an apparatus that can precisely control distance and angle of x, y, and z axes between the two cable ends. Wavelength of the light source was 850nm. Dust particles on the ends were carefully removed in advance of the measurement by an air cleaner. The best condition was sought by adjusting the x, y, and z axes where the power was maximized and this condition was considered as the base point (the x, y, and z locations were zero at this condition). From this point, we measured the optical power in dBm unit at each different misalignment location. The data was normalized using the maximum power condition.

Connecting loss simulation was run by a ray tracing method using ZEMAX™. The number of ray tracing trials was 200,000 in order to predict coupling loss distribution by introducing Gaussian distributed misalignment tolerance. In the simulation, GI POF of 0.49 mm diameter with 55 μm core (n = 1.350, NA = 0.245) and a glass ball lens of 0.55 mm diameter (n = 1.51) were used. The distance between the fiber end and the ball was set at the optimized length and was based on our other simulation results (to be reported elsewhere).

Four types of losses can be considered to evaluate total

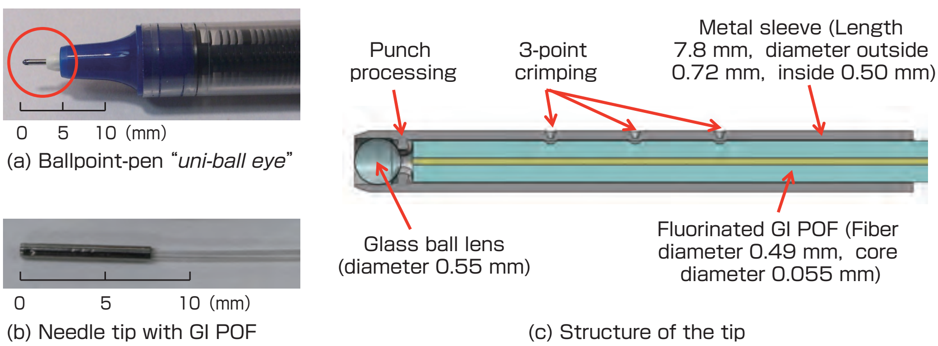


Fig. 4 Structure of the ballpoint-pen interconnect
Applying needle-tip ballpoint-pen technologies enables low cost and precise attachment of ball lens. The ball lens is attached not into the connector housing, but directly onto a fiber tip. This invention gives high freedom to connector designing.

connecting loss: collimation loss, axial misalignment loss, gap tolerance loss, and bending loss. The results of these evaluations are as follows.

(1) Collimation loss

We made 40 ball-lens-terminated GI POF samples and evaluated the connection loss using one of them as a master. Figure 5 is a histogram of the connection loss data from 39 samples. The average loss was -1.36 dB. From this result, the coupling loss number we used for power budget estimation (chapter 5) was 2.72 dB (1.36 dB × 2 for both ends of the fiber).

(2) Axial misalignment loss

Axial misalignment loss was also evaluated, which occurs when a couple of cables were misaligned perpendicular to the axis, comparing with and without ball lens.

Figure 6 shows loss data from axial misalignment. Data was normalized in dB by setting the coupling loss at the best aligned condition to zero. As shown in Fig. 6, the ball lens works quite well to increase the tolerance margin of the axial misalignment.

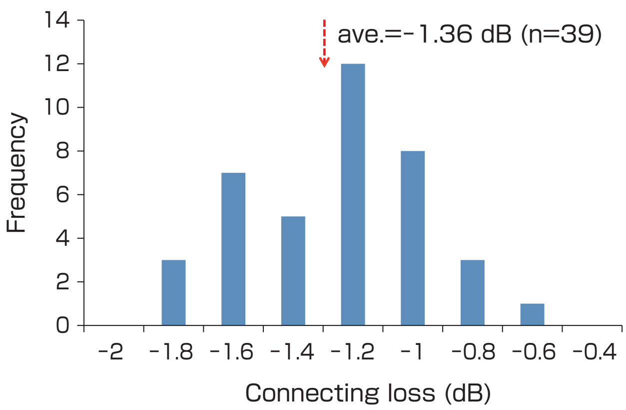


Fig. 5 Connection loss histogram of 39 samples

Shows evaluation results of connecting loss using prototype samples. The average loss is 1.36 dB.

Without the ball, very precise alignment within 10 μm is required to minimize loss below 1 dB, while the ball lens connector can misalign up to 60 μm, providing six times wider window of tolerance. This feature improves design flexibility for all surrounding parts and devices that will likely decrease manufacturing cost and labor cost for fabrication.

(3) Gap tolerance loss

Figure 7 shows the gap tolerance loss data. The gap tolerance is typically within 0.05 mm to keep the power loss below 1 dB. However, once the ball lens is applied to the fiber end, the tolerance becomes much bigger, there is almost no loss up to 0.5 mm, and is still good at 0.8 mm. Collimated beam output from the ball lens provides this significant advantage.

(4) Bending loss

Bending loss evaluation was conducted comparing GI POF with two commercially available silica multimode optical fibers: “OM2” and “OM3” from Furukawa Electric as representing commercial silica MMFs. As a typical perfluorinated GI POF, FONTEX® from AGC was used. As shown in Fig. 8, bending loss of GI POF was considerably lower than MMFs from Furukawa Electric and this result is promising for home or office network applications. No loss was observed down to R=3.5 mm which simulated tying the cable tightly.

4.2 Characteristic analysis by light power measurement

To understand characteristics of the optical interconnect we invented, attenuation was evaluated using an optical power meter.

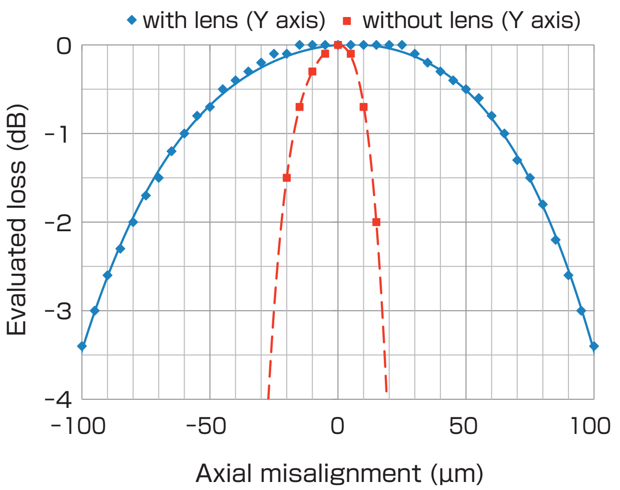


Fig. 6 Connecting loss against axial misalignment

Loss data against axial misalignment perpendicular to the axis. The use of ball lens increases the tolerance margin against axial misalignment.

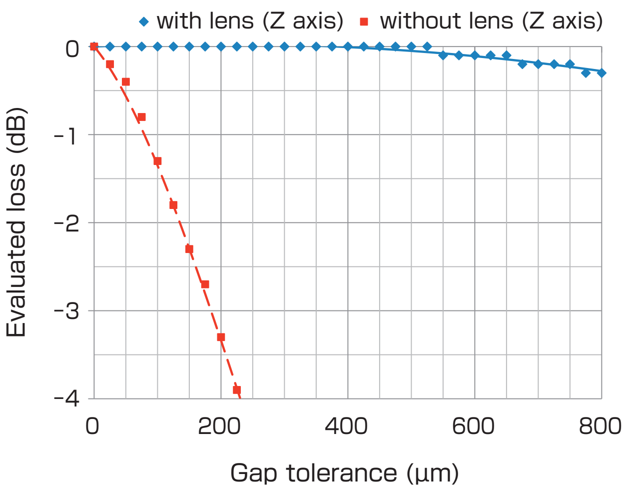


Fig. 7 Coupling loss of gap tolerance

Gap tolerance loss data. With the ball lens, the tolerance becomes much bigger, there is little loss up to 0.8 mm.

(1) Bit error rate test (BERT) for power penalty

Bit error rate (BER) was measured using BER and EYE/pulse scope "BERTWave MP2100A" from Anritsu, and optical power was adjusted using optical attenuator "N7766A" from Agilent Technologies. Power penalty (required power increase to make up for a loss in the transmission channel) was calculated as the difference in power value at BER 1E-12 between the sample and back-to-back reference (a standard condition at the lowest loss by directly connecting the transmitter and the receiver).

Power penalty at the low bit error rate (BER) by cable length was also evaluated. Figure 9 (a) shows the loss caused by the cable itself as a function of cable length. It shows almost a linear relationship between the length and the loss. The power penalty loss number for a 100-m-long cable is 1.12 dB, 50-m is 0.66 dB, 20-m is 0.29 dB, and 10-m is 0.11 dB. These data are used for power budget calculation in chapter 5.

(2) Cable loss evaluation

PNA-X Network Analyzer "N5242A" and Lightwave Component Analyzer "N4376B" from Agilent Technologies were used for measuring frequency characteristics of the optical fibers, and the DC mode value (zero frequency) was considered as a loss from the cable itself, as a function of its length.

Cable losses as functions of its length were then measured. Figure 9 (b) shows plotted data of cable losses at different cable lengths. From these results, cable loss for a 100-m-long cable is 3.76 dB, 50-m is 1.87 dB, 20-m is 0.75 dB, and 10-m is 0.38dB. These values are also used in chapter 5.

(3) Eye Safety of laser

Considering light leakage that occurs at cable breakage, eye safety evaluation was conducted using optical power meter "8250A/82311" from ADCMT. As the light source, we used NEC's optical transmitter with 850 nm light source and their receiver. We evaluated the light power based on the accessible emission limit (AEL) standard for eye safety, considering an emergency case of cable breakage. The AEL value per fiber was calculated as -1.57 dBm, which met the Class 1 eye safety standard (Class 1 is the safest standard value for consumer electronics applications).

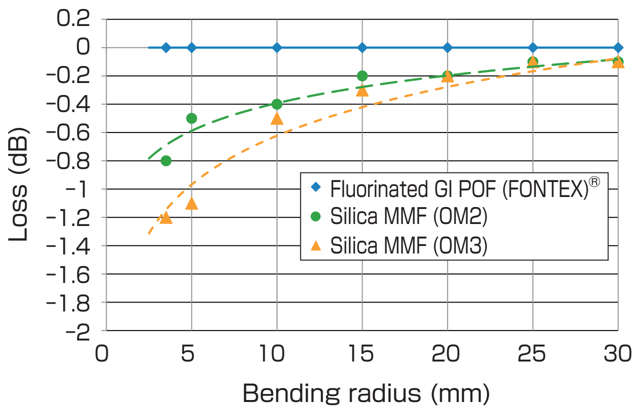


Fig. 8 Bending loss data

Bending loss comparing perfluorinated GI POF with two commercially available silica multimode optical fibers. bending loss of GI POF was considerable lower than MMFs.

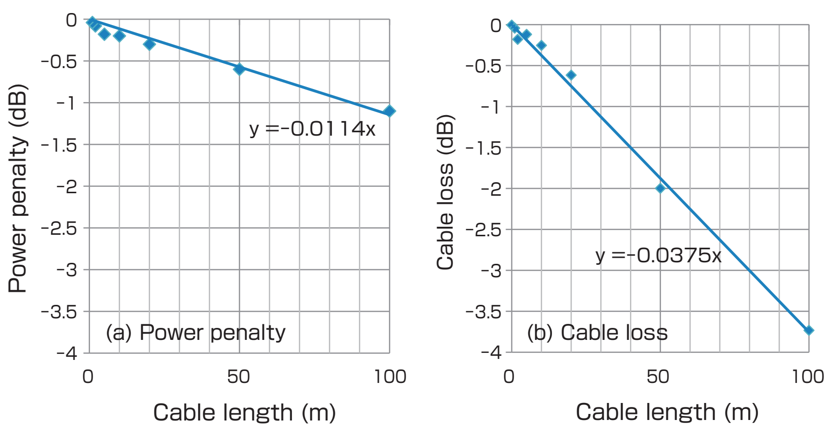


Fig. 9 Power penalty and cable loss by its length

Left (a): Power penalty data and its trend line evaluated by cable length.
Right (b): Cable loss data and its trend line evaluated by cable length.

5 Power budget evaluations

To see if the proposed system is suitable for proper communication, we combined these loss data into the power budget estimation shown in Fig. 10. The graph shows total loss at the cable lengths of 10m, 20m and 50m from four possible loss factors: collimation loss, alignment loss, power penalty, and cable loss. The target power budget value 7.43 dB was taken from Stressed Receiver Sensitivity (SRS) of IEEE802.3ae, which is -9 dBm, minus Launch Power considering eye safety, which is -1.57 dBm (9 dB – 1.57 dB = 7.43 dB).

Collimation loss (2.72 dB) was calculated by doubling the average of individual collimation loss shown in Fig. 5 (1.36 dB), as the loss occurs at each end of the fiber cable. Alignment loss (2.04 dB) was calculated from the total loss of the assembled connector having 8-channel GI POF fibers to be discussed in chapter 6, minus connecting loss of each channel from Fig. 5 (4.76 dB – 2.72 dB = 2.04 dB). In other words, the total of collimation loss and alignment loss is the insertion loss of the connector. The cable loss data were calculated by using the coefficient of the trend line obtained in Fig. 9 (b). The power penalty data were similarly calculated using Fig. 9 (a).

The combined power budget for the 10-m-long GI POF was 5.25 dB, including insertion loss of 4.76 dB, which is independent of cable length, and power penalty (0.11 dB at 10-m-length) plus cable loss (0.38 dB at 10-m-length), which are dependant on cable length. There was enough margin of 2.18 dB against the target budget (7.43 dB). The length of 10 meters is enough for in-room wiring of most consumer electronics. It is also the length between the devices of our system test prototype described in section 6.2.

Other losses coming from axial misalignment, gap tolerance, and bending shown in Figs. 6–8 were not included in Fig. 10, assuming the cables were connected at the optimal conditions. In other words, if there is enough margin against the budget, these alignments do not have to be strictly precise.

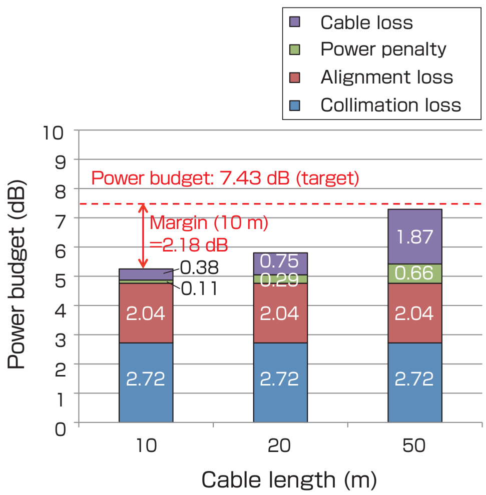


Fig. 10 Accumulated loss and power budget
Evaluated power budget margin by accumulating measured losses. The margin of 10-m-long cable is over 2 dB. 50-m-long cable still has slight margin which is promising for future home network applications.

As we discussed in chapter 4, ball lens attachment proposed in this study improved optical connectivity to that with little optical loss even if a consumer connects the cable roughly. This fact enables designing optical connection easily with enough margin of power budget. It also influences tolerance of other components and quality control processes which results in possible cost reduction. In contrast, with the conventional butt-coupling optical connection, it is quite difficult to achieve low optical loss under power budget without very precise connection, and it has a high risk of disconnection which makes it not recommendable for consumer home use. Improving connectivity by increasing preciseness is costly and makes it difficult to be handled by a consumer. Therefore, it is thought that this suggested system has enough performance and saves cost to tolerate the home optical network use and it has high flexibility for designing home wiring applications.

As the data in Fig. 10 show, power budget becomes tighter when the cable becomes longer. When a 20-m-long cable is considered, doubling the length makes it possible to connect electronics between rooms at home. The 20 m GI POF power budget was 5.80 dB; it still has more than 1 dB margin to the target (1.63 dB).

Our target is to apply the new cable to home network. Up to a length of 50 m, the novel GI POF interconnects can be used under target budget. Since the margin of the length is tight (0.14 dB), it has a high risk of implementation. However, as we discussed, our proposed ball lens system has very low connecting loss. Prospect for a home network using the cables up to 50-m-length is optimistic. These results were encouraging when considering the new interconnect to be used in the home network market. To extend the cable for longer applications in the future, we need to think about reducing alignment loss of 2.04 dB that comes from multichannel connector variables.

6 Verification of uncompressed video data transmission

6.1 Optical / HDMI-like hybrid interface

In this chapter, results of verification experiments are reported of transmitting high-definition video through a prototype of optical cable connector using the ballpoint-pen technology.

The use of optical interconnections is still limited in consumer electronics applications. Considering a practical use, it is not easy to replace all of video transmission connectors with optical ones. As a transition period, it might be better to develop a connector which can be used for both electric and optical input/output.

An active optical cable (AOC) has also been developed in the market which receives signals electrically, transmits them optically by E/O (electrical to optical) conversion, and delivers them electrically by O/E (optical to electrical) conversion. However, we instead developed a prototype of an advanced optical/electrical hybrid connector, to maintain backward compatibility with existing electrical lines for lower speed control signals and existing power supply.

Our newly developed hybrid connector that combines HDMI-like interface with our new optical interface is shown in Fig. 11. As an existing electrical line, we adopted an extension of the HDMI format, because of its reliability for consumer electronics having secured copyright protection. Compatibility with the current HDMI interface is one of the most important requirements to design the interface, which

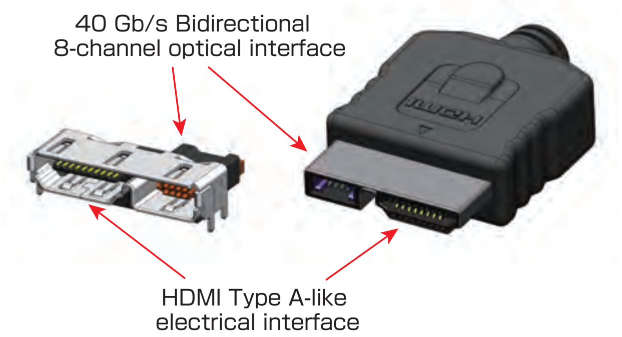


Fig. 11 Prototype of optical/electrical hybrid connector
Having a conventional HDMI-like interface, the connector also has 8-channel ballpoint pen interconnects for high speed optical communication to transmit uncompressed ultra high definition video.

enables consumers and device makers to transit the system smoothly. To achieve 40 Gbps, we chose a four-channel system having four optical cables of 10 Gbps quality for each direction (eight channels for both directions), which enables us to develop a product cheaper and faster using existing technologies, compared with using one cable of 40 Gbps which would be the ideal solution for the future.

The prototype is a pair of receptacle and plug as shown in Figure 11. The left side of the receptacle or the right side of the plug is an HDMI-like electric connector for normal HD content transmission. The other side is the newly developed optical connection for 40 Gbps bidirectional transmission having eight channel ball lens connectors.

6.2 System testing by transmitting 4K3D uncompressed video

Using the prototype developed in this study, we successfully verified the system performance at Keio University by communicating between two remote locations interactively using 4K-3D 60i uncompressed, synchronized video (3840 × 2160 pixels/60 fps/interlace, 3D dual stream) for one direction and Full HD 60p uncompressed video (1920 × 1080 pixels/60 fps/progressive) for the other direction. No interruption or pauses occurred during the test.

The 4K-3D video used is an approximately 10-minute duration film which was shot and edited by Keio University in collaboration with NHK Media Technology Inc. in 2010 using two 4K cameras from Red.com Inc. with a 3D rig. The video was stored and played by UDR-20S from Keisoku Giken Co. Ltd.

Figure 12 shows the system structure describing devices and their connections used in the verification test. The experimental run was conducted in May 2012 at the Concurrent Design Facility (CDF) at Hiyoshi Campus, Keio

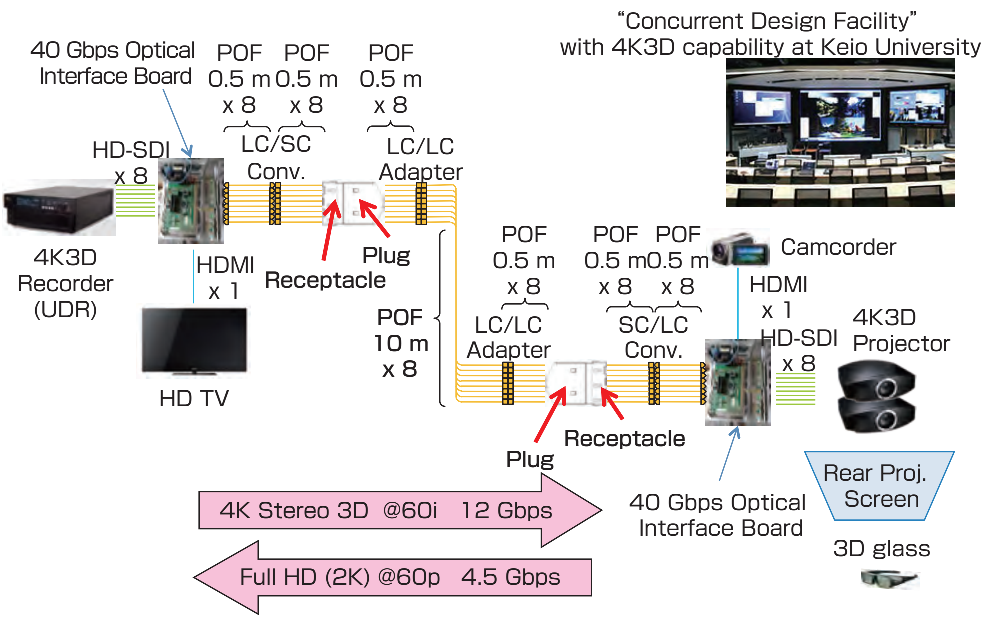


Fig. 12 System structure of 4K3D video transmission
Using the prototype of hybrid connector with ballpoint pen optical interconnects, successful verification test was conducted by communicating uncompressed 4K-3D video in one direction and full HD video in the other direction.

University and proved that the uncompressed 4K-3D video transmission was promising using the connector.

7 Conclusions

In this study, we have proposed an uncompressed high-definition video transmission system for future consumer electronics using ballpoint pen manufacturing technologies, which enables safe, easy and reliable optical connections through high speed optical communication. Specifically, we developed an extremely small interconnect using perfluorinated GI POF with a glass spherical collimator lens on its each end, and an optical/electrical hybrid connector which includes eight optical interconnects in one cable. Successful verification of the hybrid connector was then conducted by transmitting high definition uncompressed video contents.

The feature of our newly proposed ballpoint pen type optical interconnect is its small size connection without a bulky housing attaching a ball lens directly on the fiber tip, compared with conventional bulky, costly housing design combining a ball lens with an optical fiber precisely. The novel optical interconnect can be used as a jumper wire without a connector or a connecting adaptor. By bundling multiple fibers into one connector, it can conveniently be used for ultra high speed communication for consumer applications.

Moreover, because the ballpoint pen production processes are applied, the ball lens attachment can be mass produced at extremely low cost and is highly practical and almost a complete method to achieve high precision alignment. Not just showing its optical performances, ease of connectivity was practically proved in this paper as well. Optical loss was minimized, even when the axial alignment and gap tolerance were not perfect.

The power budget evaluation results suggested further improvements are required for longer than 50-m length application, such as in home optical network. However, the results showed promisingly that short reach applications between devices up to 10-meter length are highly practical.

Acknowledgements

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References

[1] P. Polishuk: Plastic optical fibers branch out, *IEEE Commun. Mag.*, 44 (9), 140-148 (2006).
[2] I. Mollers, D. Jager, R. Gaudino, A. Nocivelli, H. Kragl, O. Ziemann, N. Weber, T. Koonen, C. Lezzi, A. Bluschke and S. Randel: Plastic optical fiber technology for reliable home networking: overview and results of the EU project POF-ALL, *IEEE Commun. Mag.*, 47 (8), 58-68 (2009).
[3] J. C. Baker and D. N. Payne: Expanded-beam connector design study, *Applied Optics*, 20, 2861-2867 (1981).
[4] R. J. Pimpinella: A new type of fiber optic connector designed for military optics backplanes, *IEEE Trans. Comp. Hybrids Manufact. Technol.*, 15, 992-997 (1992).
[5] Y. Koike and T. Ishigure: High-bandwidth plastic optical fiber for fiber to the display, *J. Lightwave Technol.*, 24 (12), 4541-4553 (2006).
[6] P. Decker, A. Polley, J. Kim and S. Ralph: Statistical study of graded-index perfluorinated plastic optical fiber, *J. Lightwave Technol.*, 29 (3), 305-315 (2011).
[7] T. Torikai, T. Yamauchi, S. Mine, N. Moriya, A. Mitsui, H. Suzuki, Y. Watanabe, T. Toma and Y. Koike: Optical I/O connectors employing ball-point pen type optical collimator lenses suitable for plastic optical fiber communications, *Proceedings of 21th International Conference on Plastic Optical Fibers (POF2012)*, (Atlanta, USA, 2012).

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After obtaining a master’s degree in Applied Chemistry from Keio University in 1988, joined Sumitomo 3M. Moved to 3M Company in USA in 2001 and worked as an advanced product development specialist until 2007. After serving for 20 years in 3M, he joined Keio University in 2008 and is researching communication systems. Received Ph.D. in System Design and Management in 2014. Lead a sub-team to develop optical home network system on the FIRST Program of the Cabinet Office of Japan since 2010. Contributed as a team leader of this project and wrote this paper.

Hiroshi TAKIZUKA

Completed M.S. degree in Electrical Engineering at Keio University and joined Sony Corporation in 1978. Developed technologies for home network and introduced variety of products into the market; such as OP i.Link, xvYCC color and HDMI standard,s for example. Became a researcher of Keio Photonics Research Institute in 2013, after finishing work at Sony. For this study, designed the optical interconnect system and optimized it by evaluating its characteristcs.

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Tetsuro OGI

Obtained a master's degree in Mechanical Engineering from the University of Tokyo, and joined Mitsubishi Research Institute in 1986. Earned a Ph.D. in Mechanical Engineering from the University of Tokyo in 1994 and was named associate professor in 1996. In 2004, he moved to the Graduate School of Systems and Information Engineering, University of Tsukuba as an associate professor. In 2008, he moved to the Graduate School of System Design and Management, Keio University. His research field includes systems engineering, virtual reality, human interface, etc. Served as an advisor of this project from the network technology standpoint.

Yasuhiro KOIKE

Earned his B.S. at Keio University in 1977, M.S., in 1979 and Ph.D. in 1982 in applied chemistry at the Graduate School of Engineering of Keio University. Has been Professor at Keio University since 1997. Specializes in "photonics polymer" such as graded-index polymer optical fiber (GI POF), highly scattered optical transmission (HSOT) polymer, zero birefringence polymer, etc. He has been pursuing an R&D project of Face-to-Face Communication system on the FIRST Program of the Cabinet Office of Japan since 2010. He is a recipient of International Engineering and Technology Award of the Society of Plastics Engineers, the Fujiwara Award, and Medal with Purple Ribbon from the government, etc. Councilor, Keio University. The material and the basic concept of this study were his original inventions.

Discussions with Reviewers

1 Overall evaluation

Comment (Naoto Kobayashi, Center for Research Strategy, Waseda University)

This paper shows successful development of an optical interconnect that combines a ball lens and a plastic optical fiber by using ballpoint-pen production technology, and the actual verification test results using the optical interconnect to realize a high-definition video optical transmission system for home use which has to meet extremely severe demands such as high-performance, simplicity and easiness of use, inexpensiveness, safety and security. The paper is valuable not just because it describes the unique component technology, but also because it shows demonstration results using an actual system in which the unique technology is integrated. Thus, the paper is appropriate for *Synthesiology*.

Comment (Hiroshi Ishikawa, AIST)

I highly evaluate the low-cost optical coupling using the ballpoint-pen technology as an important development for the wide application of POF. In addition, it is an interesting fact that an opportunity for cross-industrial networking led to this technology development.

2 Scenario

Comment (Motoyuki Akamatsu, AIST)

The key point of this technology is realizing the combination of ballpoint-pen type interconnects with fluorinated GI POF, and the scenario is written in chapter 2. Merits of GI POF are written in several paragraphs in the first half of chapter 2, but it says in the sixth paragraph that "the ball lens attachment was impossible using POF." The ball connector is mentioned from the seventh paragraph, and in the ninth paragraph, it says that you "came across GI POF by chance." It seems the paper is saying that the research was based on the thought that POF exists in the first half, but, on the other hand, in the second half, it says that POF was found after trials to solve fragility problems of silica optical fiber when it was put into the metal sleeve of the ballpoint-pen tip to make a ball lens connector cheaply. There seem to be two different scenarios of opposite directions which confuse readers: one goes from POF to ball connector and the other goes from ball connector to POF. You have to write clearly which scenario was close to the real fact or whether both ran concurrently.

Answer (Tetsuya Toma)

There were two groups who had developed an optical connection independently. One day they met by chance and noticed each other's common points which then led to this joint study. I rewrote the description on this part to make it clearer.

3 Wave length and bandwidth of plastic fiber

Comment (Hiroshi Ishikawa)

You should write the wavelength of the light source somewhere in the paper, though I believe that POF is used in the 0.8 μm area. In addition, you should better explain briefly the reason why a bandwidth of SI POF is limited differently from the one of GI POF, as I think that the majority of readers do not know the causing factor. I am familiar with the dispersion of silica fiber, but I not familiar with that of POF.

Answer (Tetsuya Toma)

Because absorption of carbon-hydrogen bonding exists in the infrared region for regular acrylic polymers, one should use the visible light region for communication. However, if you use the perfluorinated polymer instead, absorption of the infrared region falls. We used 850 nm this time (described in chapter 4), but the perfluorinated polymer actually works similarly to silica fiber using wavelengths between 700 and 1300 nm, or rather it allows faster transmission speed because of its lower material dispersion. In addition, a pulse spreads broadly for SI type fiber, because a light ray that travels through the center of the core and another that travels with many total reflections at an interface of the core and clad have different path lengths within the fiber. On the other hand with the GI type fiber, all the light rays travel without a reflection in the core where refractive index distribution profile has been designed properly, and propagate at the same speed to the end of the fiber by drawing a sine curve. This results in the GI fiber being able to transmit more pulses per second at a wider bandwidth than SI fiber.

4 Ballpoint pen technology

Comment (Naoto Kobayashi)

I think that the important key technology in this study was the combination of lens system adoption using ballpoint-pen production technology with a plastic optical fiber. The experimental results were excellent, but I want to know if there were any particular difficult points in achieving the technology.

Answer (Tetsuya Toma)

As I wrote in the paper, crimping a plastic optical fiber was physically easy to fix to the metal sleeve without breakage, but it was not so easy to optimize the crimping condition in fixing without loss.

5 Cross-industrial networking

Comment (Naoto Kobayashi)

About developing the optical interconnect using the ballpoint-pen production technology which is the critical point of this study, there was an indication that the cross-industrial networking was important to make this invention happen. Please tell us if you have any thoughts on an active, conscious method to bring about innovation through such a cross-industrial cooperation in the future.

Answer (Tetsuya Toma)

At an opportunity of cross-industrial networking, I believe that it is important to find a common point by conceptually regarding each other’s technology from a higher level of abstraction. I think that a new idea is born by abstracting system elements from both physical and functional viewpoints.

6 Competition with wireless technology

Comment (Naoto Kobayashi)

Considering Tokyo Olympic and Paralympic Games in 2020, the need of the high-definition video transmission for home use will be increasing in the future. However, on the other hand, wireless technology such as LTE has been and will also be rapidly progressing. As a result, it can be said that optical fiber communication only needs to transmit data to the home except in some special cases such as ultra high-definition video, and it is reasonable to use wireless communication in the home. Please tell us about the competition and segregation between optical fiber communication and wireless communication for home use in the future.

Answer (Tetsuya Toma)

Because transmission speed of wireless is slower than wired and the quality of communication of wireless varies by environment conditions, the transmission of more than 10 Gbps needed to transmit uncompressed SHV of 4K and 8K is difficult. In addition, the higher the frequency increases (tens of GHz or more), wireless becomes easily affected by the environment conditions; the transmission may fail when a person walks by, or it may not be easy to pass beyond a wall. I don’t think that there is a merit of wireless for the high-speed transmission over 10 Gbps. In addition, additional care has to be taken for security management of wireless compared with wired communication.

Editorial Policy

Synthesiology Editorial Board

Objective of the journal

The objective of *Synthesiology* is to publish papers that address the integration of scientific knowledge or how to combine individual elemental technologies and scientific findings to enable the utilization in society of research and development efforts. The authors of the papers are researchers and engineers, and the papers are documents that describe, using “scientific words”, the process and the product of research which tries to introduce the results of research to society. In conventional academic journals, papers describe scientific findings and technological results as facts (i.e. factual knowledge), but in *Synthesiology*, papers are the description of “the knowledge of what ought to be done” to make use of the findings and results for society. Our aim is to establish methodology for utilizing scientific research result and to seek general principles for this activity by accumulating this knowledge in a journal form. Also, we hope that the readers of *Synthesiology* will obtain ways and directions to transfer their research results to society.

Content of paper

The content of the research paper should be the description of the result and the process of research and development aimed to be delivered to society. The paper should state the goal of research, and what values the goal will create for society (Items 1 and 2, described in the Table). Then, the process (the scenario) of how to select the elemental technologies, necessary to achieve the goal, how to integrate them, should be described. There should also be a description of what new elemental technologies are required to solve a certain social issue, and how these technologies are selected and integrated (Item 3). We expect that the contents will reveal specific knowledge only available to researchers actually involved in the research. That is, rather than describing the combination of elemental technologies as consequences, the description should include the reasons why the elemental technologies are selected, and the reasons why new methods are introduced (Item 4). For example, the reasons may be: because the manufacturing method in the laboratory was insufficient for industrial application; applicability was not broad enough to stimulate sufficient user demand rather than improved accuracy; or because there are limits due to current regulations. The academic details of the individual elemental technology should be provided by citing published papers, and only the important points can be described. There should be description of how these elemental technologies are related to each other, what are the problems that must be resolved in the integration process, and how they are solved (Item 5). Finally, there should be descriptions of how closely the goals are achieved by the products and the results obtained in research and development, and what subjects are left to be accomplished in the future (Item 6).

Subject of research and development

Since the journal aims to seek methodology for utilizing the products of research and development, there are no limitations on the field of research and development. Rather, the aim is to discover general principles regardless of field, by gathering papers on wide-ranging fields of science and technology. Therefore, it is necessary for authors to offer description that can be understood by researchers who are not specialists, but the content should be of sufficient quality that is acceptable to fellow researchers.

Research and development are not limited to those areas for which the products have already been introduced into society, but research and development conducted for the purpose of future delivery to society should also be included.

For innovations that have been introduced to society, commercial success is not a requirement. Notwithstanding there should be descriptions of the process of how the technologies are integrated taking into account the introduction to society, rather than describing merely the practical realization process.

Peer review

There shall be a peer review process for *Synthesiology*, as in other conventional academic journals. However, peer review process of *Synthesiology* is different from other journals. While conventional academic journals emphasize evidential matters such as correctness of proof or the reproducibility of results, this journal emphasizes the rationality of integration of elemental technologies, the clarity of criteria for selecting elemental technologies, and overall efficacy and adequacy (peer review criteria is described in the Table).

In general, the quality of papers published in academic journals is determined by a peer review process. The peer review of this journal evaluates whether the process and rationale necessary for introducing the product of research and development to society are described sufficiently well.

In other words, the role of the peer reviewers is to see whether the facts necessary to be known to understand the process of introducing the research finding to society are written out; peer reviewers will judge the adequacy of the description of what readers want to know as reader representatives.

In ordinary academic journals, peer reviewers are anonymous for reasons of fairness and the process is kept secret. That is because fairness is considered important in maintaining the quality in established academic journals that describe factual knowledge. On the other hand, the format, content, manner of text, and criteria have not been established for papers that describe the knowledge of "what ought to be done." Therefore, the peer review process for this journal will not be kept secret but will be open. Important discussions pertaining to the content of a paper, may arise in the process of exchanges with the peer reviewers and they will also be published. Moreover, the vision or desires of the author that cannot be included in the main text will be presented in the exchanges. The quality of the journal will be guaranteed by making the peer review process transparent and by disclosing the review process that leads to publication.

Disclosure of the peer review process is expected to indicate what points authors should focus upon when they contribute to this journal. The names of peer reviewers will be published since the papers are completed by the joint effort of the authors and reviewers in the establishment of the new paper format for *Synthesiology*.

References

As mentioned before, the description of individual elemental technology should be presented as citation of papers published in other academic journals. Also, for elemental technologies that are comprehensively combined, papers that describe advantages and disadvantages of each elemental technology can be used as references. After many papers are accumulated through this journal, authors are recommended to cite papers published in this journal that present similar procedure about the selection of elemental technologies and the introduction to society. This will contribute in establishing a general principle of methodology.

Types of articles published

Synthesiology should be composed of general overviews such as opening statements, research papers, and editorials. The Editorial Board, in principle, should commission overviews. Research papers are description of content and the process of research and development conducted by the researchers themselves, and will be published after the peer review process is complete. Editorials are expository articles for science and technology that aim to increase utilization by society, and can be any content that will be useful to readers of *Synthesiology*. Overviews and editorials will be examined by the Editorial Board as to whether their content is suitable for the journal. Entries of research papers and editorials are accepted from Japan and overseas. Manuscripts may be written in Japanese or English.

Required items and peer review criteria (January 2008)

	Item	Requirement	Peer Review Criteria
1	Research goal	Describe research goal ("product" or researcher's vision).	Research goal is described clearly.
2	Relationship of research goal and the society	Describe relationship of research goal and the society, or its value for the society.	Relationship of research goal and the society is rationally described.
3	Scenario	Describe the scenario or hypothesis to achieve research goal with "scientific words".	Scenario or hypothesis is rationally described.
4	Selection of elemental technology(ies)	Describe the elemental technology(ies) selected to achieve the research goal. Also describe why the particular elemental technology(ies) was/were selected.	Elemental technology(ies) is/are clearly described. Reason for selecting the elemental technology(ies) is rationally described.
5	Relationship and integration of elemental technologies	Describe how the selected elemental technologies are related to each other, and how the research goal was achieved by composing and integrating the elements, with "scientific words".	Mutual relationship and integration of elemental technologies are rationally described with "scientific words".
6	Evaluation of result and future development	Provide self-evaluation on the degree of achievement of research goal. Indicate future research development based on the presented research.	Degree of achievement of research goal and future research direction are objectively and rationally described.
7	Originality	Do not describe the same content published previously in other research papers.	There is no description of the same content published in other research papers.

Instructions for Authors

"Synthesiology" Editorial Board
Established December 26, 2007
Revised June 18, 2008
Revised October 24, 2008
Revised March 23, 2009
Revised August 5, 2010
Revised February 16, 2012
Revised April 17, 2013
Revised May 9, 2014

1 Types of articles submitted and their explanations

The articles of *Synthesiology* include the following types:
• Research papers, commentaries, roundtable talks, and readers' forums
Of these, the submitted manuscripts of research papers and commentaries undergo review processes before publication. The roundtable talks are organized, prepared, and published by the Editorial Board. The readers' forums carry writings submitted by the readers, and the articles are published after the Editorial Board reviews and approves. All articles must be written so they can be readily understood by the readers from diverse research fields and technological backgrounds. The explanations of the article types are as follows.

① Research papers
A research paper rationally describes the concept and the design of R&D (this is called the scenario), whose objective is to utilize the research results in society, as well as the processes and the research results, based on the author's experiences and analyses of the R&D that was actually conducted. Although the paper requires the author's originality for its scenario and the selection and integration of elemental technologies, whether the research result has been (or is being) already implemented in society at that time is not a requirement for the submission. The submitted manuscript is reviewed by several reviewers, and the author completes the final draft based on the discussions with the reviewers. Views may be exchanged between the reviewers and authors through direct contact (including telephone conversations, e-mails, and others), if the Editorial Board considers such exchange necessary.

② Commentaries
Commentaries describe the thoughts, statements, or trends and analyses on how to utilize or spread the results of R&D to society. Although the originality of the statements is not required, the commentaries should not be the same or similar to any articles published in the past. The submitted manuscripts will be reviewed by the Editorial Board. The authors will be contacted if corrections or revisions are necessary, and the authors complete the final draft based on the Board members' comments.

③ Roundtable talks
Roundtable talks are articles of the discussions or interviews that are organized by the Editorial Board. The manuscripts are written from the transcripts of statements and discussions of the roundtable participants. Supplementary comments may be added after the roundtable talks, if necessary.

④ Readers' forums
The readers' forums include the readers' comments or thoughts on the articles published in *Synthesiology*, or articles containing information useful to the readers in line with the intent of the journal. The forum articles may be in free format, with 1,200 Japanese characters or less. The Editorial Board will decide whether the articles will be published.

2 Qualification of contributors

There are no limitations regarding author affiliation or discipline as long as the content of the submitted article meets the editorial policy of *Synthesiology*, except authorship should be clearly stated. (It should be clearly stated that all authors have made essential contributions to the paper.)

3 Manuscripts

3.1 General

3.1.1 Articles may be submitted in Japanese or English.
Accepted articles will be published in *Synthesiology* (ISSN 1882-6229) in the language they were submitted. All articles will also be published in *Synthesiology - English edition* (ISSN 1883-0978). The English edition will be distributed throughout the world approximately four months after the original *Synthesiology* issue is published. Articles written in English will be published in English in both the original *Synthesiology* as well as the English edition. Authors who write articles for *Synthesiology* in Japanese will be asked to provide English translations for the English edition of the journal within 2 months after the original edition is published.
3.1.2 Research papers should comply with the structure and format stated below, and editorials should also comply with the same structure and format except subtitles and abstracts are unnecessary.

3.1.3 Research papers should only be original papers (new literary work).
3.1.4 Research papers should comply with various guidelines of research ethics

3.2 Structure

3.2.1 The manuscript should include a title (including subtitle), abstract, the name(s) of author(s), institution/contact, main text, and keywords (about 5 words).
3.2.2 Title, abstract, name of author(s), keywords, and institution/contact shall be provided in Japanese and English.
3.2.3 The manuscript shall be prepared using word processors or similar devices, and printed on A4-size portrait (vertical) sheets of paper. The length of the manuscript shall be, about 6 printed pages including figures, tables, and photographs.
3.2.4 Research papers and editorials shall have front covers and the category of the articles (research paper or editorial) shall be stated clearly on the cover sheets.
3.2.5 The title should be about 10-20 Japanese characters (5-10 English words), and readily understandable for a diverse readership background. Research papers shall have subtitles of about 15-25 Japanese characters (7-15 English words) to help recognition by specialists.
3.2.6 The abstract should include the thoughts behind the integration of technological elements and the reason for their selection as well as the scenario for utilizing the research results in society.
3.2.7 The abstract should be 300 Japanese characters or less (125 English words). The Japanese abstract may be omitted in the English edition.
3.2.8 The main text should be about 9,000 Japanese characters (3,400 English words).
3.2.9 The article submitted should be accompanied by profiles of all authors, of about 200 Japanese characters (75 English words) for each author. The essential contribution of each author to the paper should also be included. Confirm that all persons who have made essential contributions to the paper are included.
3.2.10 Discussion with reviewers regarding the research paper content shall be done openly with names of reviewers disclosed, and the Editorial Board will edit the highlights of the review process to about 3,000 Japanese characters (1,200 English words) or a maximum of 2 pages. The edited discussion will be attached to the main body of the paper as part of the article.
3.2.11 If there are reprinted figures, graphs or citations from other papers, prior permission for citation must be obtained and should be clearly stated in the paper, and the sources should be listed in the reference list. A copy of the permission should be sent to the Publishing Secretariat. All verbatim quotations should be placed in quotation marks or marked clearly within the paper.

3.3 Format

3.3.1 The headings for chapters should be 1, 2, 3…, for subchapters, 1.1, 1.2, 1.3…, for sections, 1.1.1, 1.1.2, 1.1.3, for subsections, 1.1.1.1, 1.1.1.2, 1.1.1.3.
3.3.2 The chapters, subchapters, and sections should be enumerated. There should be one line space before each paragraph.
3.3.3 Figures, tables, and photographs should be enumerated. They should each have a title and an explanation (about 20-40 Japanese characters or 10-20 English words), and their positions in the text should be clearly indicated.
3.3.4 For figures, image files (resolution 350 dpi or higher) should be submitted. In principle, the final print will be in black and white.
3.3.5 For photographs, image files (resolution 350 dpi or higher) should be submitted. In principle, the final print will be in black and white.
3.3.6 References should be listed in order of citation in the main text.

Journal – [No.] Author(s): Title of article, *Title of journal* (italic), Volume(Issue), Starting page-Ending page (Year of publication).

Book – [No.] Author(s): *Title of book* (italic), Starting page-Ending page, Publisher, Place of Publication (Year of publication).

4 Submission

One printed copy or electronic file (Word file) of manuscript with a checklist attached should be submitted to the following address:

Synthesiology Editorial Board
c/o Website and Publication Office, Public Relations Department, National Institute of Advanced Industrial Science and Technology(AIST)
Tsukuba Central 2 , 1-1-1 Umezono, Tsukuba 305-8568
E-mail: synthesiology-ml@aist.go.jp
The submitted article will not be returned.

5 Proofreading

Proofreading by author(s) of articles after typesetting is complete will be done once. In principle, only correction of printing errors are allowed in the proofreading stage.

6 Responsibility

The author(s) will be solely responsible for the content of the contributed article.

7 Copyright

The copyright of the articles published in “*Synthesiology*” and “*Synthesiology English edition*” shall belong to the National Institute of Advanced Industrial Science and Technology(AIST).

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Letter from the editor

It is now the seventh year since the launch of Synthesiology. As written in the objective of the editorial policy, unlike conventional academic journals, this journal was launched as an academic journal "for the purpose of accumulating knowledge of what ought to be done to get the research results utilized in society," and continues to this date. The requirements of the paper are also quite different as they include the description of the relationship between research objectives and society, as well as the process (scenario) to realize the research goals.

When the journal was first launched, editing was done mainly by the people of AIST. Starting in the summer of last year, we asked people from external institutions to act as senior editors, and discussed various reforms to further diffuse the journal. From these discussions, we decided to set up a page to highlight the Synthesiology-like aspects of the published papers, and we shall do a trial in this issue. They are as follows.

National length standard supporting high-capacity optical fiber communication systems
The subject of this paper is R&D for the optical frequency comb that leads to the international standard of "length" and next-generation optical frequency standards. It describes the evolutionary process from the optical comb using pumped laser, which is a cumbersome device with large power consumption, to the optical fiber frequency comb that is highly reliable and allows continuous operation over a long period of time. The paper has a Synthesiology style structure including a scenario and a process that describes how researchers resorted to a homemade device in the course of R&D.

Research and development of solar hydrogen production
This paper introduces R&D of solar hydrogen production technology that is one of the ways for using solar energy, an important resource of renewable energy. This subject requires a long time to realize, and the interim goals are set from the aspect of cost in two steps toward the final R&D goal. Various hydrogen production technologies are compared and studied, the theoretical limit of the conversion efficiency for the originally developed "photocatalysis-electrolysis hybrid system" is determined, the cost estimate of the hybrid system is conducted, and a scenario for the future deployment of the technology is presented.

Methodology for designing the cryptographic systems with advanced functionality based on a modular approach
Cryptosystems that support information security are often breached, and improvements must be made constantly. Every time they are upgraded, cryptosystems become complex, and it has become difficult even for specialists to prove their security. Moreover proofs may occasionally turn out wrong. In this paper, an interesting high-function cryptosystem called the proxy re-encryption is taken as an example to propose a method for simplifying proofs by breaking down the cryptosystem into modules. It is an effective method to safely diffuse advanced IT technology to society.

Development of lectin microarray, an advanced system for glycan profiling
Glycans or sugar chains are called the third chain of life after genes and proteins, but the clarification of the functions lags behind due to the lack of a method that allows simple analysis of their complex structures. This paper focuses on a protein, lectin, which binds specifically to a certain glycan structure, and describes the process that leads to the creation of "glycan profiling," a new concept that quickly and easily clarifies the structural characteristics of glycans. The reader can feel the author's passion for a "breakthrough toward a new discipline called glycoengineering."

Development of a household high-definition video transmission system based on ballpoint-pen technology
This paper introduces R&D for the connection of optical fibers to transmit high definition images for high-vision TVs that have become household items. Safe, simple, highly reliable, and low cost are set as research goals, other than the technological requirement for communication speed performance. The scenario for the development and integration of the elemental technologies such as a new optical connection method combining plastic fiber and ball lens is presented, as well as the results of the demonstration experiment.

The journal has carried over 130 papers, but the majority was written by researchers at AIST. Submissions from researchers and engineers of universities and corporations are increasing, but the number is still small. There are many projects where the researchers and engineers of industry, academia, and government collaborate in society. I hope that by publishing the results of such R&D and then publishing the research processes that actually took place, we wish to establish "methodologies to effectively and efficiently execute research that will be useful for society" and to have such results shared as knowledge in society.

The papers published in the journal can be viewed in the electronic journal on the AIST website as well as on J-Stage (the integrated electronic journal platform of the Japan Science and Technology Agency). Please take advantage of this system.

(Mitsuru TANAKA, Senior Editor)

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Messages from the editorial board

Research papers

A social system for production and utilization of thermophysical quantity data
―*Measurement technology, metrological standard, standardization of measurement method, and database for thermal diffusivity by laser flash method*―
T.Baba and M.Akoshima

National standards of length for high-capacity optical fiber communication systems
―*Development of fiber-based optical frequency combs*―
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Research and development of solar hydrogen production
―*Toward the realization of ingenious photocatalysis-electrolysis hybrid system*―
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Methodology for designing cryptographic systems with advanced functionality based on a modular approach
―*Towards reducing the barrier to introducing newly-designed cryptographic schemes into real-world systems*―
G.Hanaoka, S.Ohata, T.Matsuda, K.Nuida and N.Attrapadung

Development of lectin microarray, an advanced system for glycan profiling
―*From frontal affinity chromatography to evanescent wave excitation fluorescence detection method*―
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Development of a household high-definition video transmission system based on ballpoint-pen technology
―*A low cost, easily deployed optical connection using a ballpoint-pen type interconnect*―
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Editorial policy
Instructions for authors

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