Synthesiology
English edition

Development of human-friendly polymeric actuators based on nano-carbon electrodes

High quality and large-area graphene synthesis with a high growth rate using plasma-enhanced CVD

Radioactive cesium decontamination technology for ash

Development of HASClay® as a high-performance adsorption material

A super-growth method for single-walled carbon nanotube synthesis

Special Issue of Nanomaterials

Synthesiology editorial board

2016

3

Highlights of the Papers in *Synthesiology* Volume 9 Issue 3 (Japanese version Oct. 2016)

Synthesiology is a journal that describes the objectives and social value of research activities that attempt to utilize the results in society, the specific scenarios and research procedures, and the process of synthesis and integration of elemental technologies. To allow the readers to see the value of the papers in a glance, the highlights of the papers characteristic to *Synthesiology* are extracted and presented by the Editorial Board.

Synthesiology **Editorial Board**

Development of human-friendly polymeric actuators based on nano-carbon electrodes
— Toward the practical realization of artificial muscles —
Kinji Asaka

Asaka (AIST) realized soft actuators that employ ion conductive polymers as base materials using carbon nanotubes as electrode materials. The elemental technologies and research scenario are introduced by looking at ways to utilize the properties of large deformation at low-voltage and in thin film form with excellent processability. The prototype was made and evaluation tests of the thin and light film braille displays were conducted by joint research with a company, and it is an excellent example by which the social value of the product has been increased.

High quality large-area graphene synthesis with high growth rate using plasma-enhanced CVD
— Toward a high throughput process —
Masataka Hasegawa *et al.*

Hasegawa (AIST) *et al.* aimed for the use of transparent conductive films and demonstrated the superiority of a synthesis method using a plasma-enhanced chemical vapor deposition (CVD) process as a graphene manufacturing technology for large area, high quality, and high throughput. Through the discussions including the differences with a thermal CVD process and the comparison to competing technologies, we are able to understand the R&D scenario that led to successful development of large-area graphene transparent conductive films. Particularly impressive is the detailed data analyses that are the basis of the solutions of each elemental technology.

Radioactive cesium decontamination technology for ash
— Utilization and application of nanoparticles as an adsorbent —
Tohru Kawamoto *et al.*

In response to urgent governmental demands to decontaminate the radioactive material that leaked from the TEPCO Fukushima Daiichi Nuclear Power Plant, Kawamoto (AIST) *et al.* developed in an extremely short time the decontamination technology for ash contaminated by radioactive cesium using Prussian blue nanoparticle materials. This synthesiological paper draws our attention because it is a summary of the technologies and overall scenario that enabled achievement of results in an extremely abnormal environment and condition, including the overview of the whole problem to original research strategies, the exchange with researchers of different fields, and the collaboration with stakeholders of companies, the government, local governments, and local residents.

Development of HASClay® as a high-performance adsorption material
— Developing adsorbents for energy conservation systems from a kind of clay nanoparticle —
Masaya Suzuki *et al.*

Suzuki (AIST) *et al.* developed synthetic clay mineral HASClay® under a clearly set scenario aiming for application as desiccant air conditioning adsorbents, starting from the basic research on the structures and functions of allophene and imogolite that are natural clay minerals. It is interesting to see the course by which they felt the limitation of natural materials from the perspectives of low cost, synthesis cost, mass production, and adsorption functions, and embarked on creating a synthesized product that met all conditions through joint research with companies, while oscillating between basics and application.

A super-growth method for single-walled carbon nanotube synthesis
— Development of a mass production technique for industrial application —
Kenji Hata

Hata (AIST) developed and realized the industrial mass production technology that was composed of totally different elemental technologies from the lab-scale innovative synthesis method for single-walled carbon nanotubes that he originally developed. This is truly world-leading nanotechnology where the passion of the author and the company contributed to its realization. This paper is worth reading as the diverse elemental technologies that were determined essential, their advancement, and the scenario for integration through corporate collaboration are presented concisely, under a research policy conceived by the author.

Synthesiology - English edition Vol.9 No.3 (Feb. 2017)
Special Issue of Geological Surveys
Contents

Development of human-friendly polymeric actuators based on nano-carbon electrodes

— Toward the practical realization of artificial muscles —

Kinji Asaka

Human-friendly machines are expected to increase in demand. To meet this demand, we have developed electrically driven soft actuators based on ionic polymers. This paper describes the development process, design guidelines, current state of R&D, and future prospects for low-voltage, polymeric actuators based on nano-carbon electrodes.

Keywords : Polymeric actuator, soft actuator, nano-carbon, ionic liquid, gel

1 Background—Research of muscles and soft actuators

Japan has become an unprecedented aging society where 22.5 % of the population are 65 years old or older. The use of welfare devices and services that enhance the quality of life (QOL) of the disabled and the elderly and support their social participation are expected to increase. Requirements for such devices are safety, increased operability, downsizing, weight reduction, cost reduction, and others to enable adaptation to unfamiliar environments. The development of soft actuators has been conducted worldwide as a key technology for such devices. The development is being done for various human-friendly medical devices that can be directly worn by people for the purpose of home rehabilitation or care, as well as for communication devices for physically challenged people that allows the transfer of information by tactile or auditory senses while worn on the body.

The goal of soft actuator development is to create an actuator that functions like muscles of organisms, and this is the aim of the researchers around the world. The motive power of movement of living organisms is the muscle, and it is well known that muscles have excellent characteristics as actuators. While excellent actuators with excellent individual specs have been developed, an actuator that is light, soft, and powerful and is capable of working in groups like muscles has not been developed.

Setting the simulation of muscles as a guideline, the research of soft actuators using polymers as basic materials are being conducted around the world.[1] Particularly, the development of an electric-power-driven expanding/contracting actuator using various electroactive polymers is nearing practical use, and there are high expectations. At AIST, since the time of the Government Industrial Research Institute, Osaka, the Agency of Industrial Science and Technology, we have engaged in the research of low-voltage-driven soft actuators with ion conductive polymers. Such a polymeric actuator is light weight, excellent in flexibility, and workability, and major deformation can be obtained at low voltage of 1 V order. Therefore, it is an essential device in advancing the technical development of the aforementioned human-friendly devices.

In this paper, we describe the scenario, the current status, and the future prospect for conducting the development of electrically driven polymeric actuators using nanocarbon electrodes, as the soft actuator technology essential for developing human-friendly devices.

2 Basic soft actuator technology and the guideline for materials of new soft actuator development

At AIST Kansai, the development of ion conductive polymeric actuators was started when the organization was called the Government Industrial Research Institute, Osaka, the Agency of Industrial Science and Technology. This involved a conjugate of fluorine ion exchange resin used in polymer electrolyte fuel cells treated by electroless deposition of precious metals such as platinum and gold. When low voltage of about 1 V is applied between the electrodes, deformation occurs as the counter ions or cations move to the negative electrode (Fig. 1).[2] This technology was developed for the first time in the world for polymeric actuators in 1991, and various application research was conducted based on

Inorganic Functional Material Research Institute, AIST   1-8-31 Midorigaoka, Ikeda 563-8577, Japan
E-mail: asaka-kinji@aist.go.jp

this technology for active catheters, tactile displays, aquatic micro-robots, and others.[3] Although this actuator was an excellent device, there were many problems that hampered practical use in devices. The main problems were as follows: 1) material costs as precious metals such as gold or platinum had to be used as electrodes; 2) manufacturing costs because the method of electroless deposition took time; 3) surface area was too small to achieve high electrode performance (i.e. capacitance or ability to store ion was small); and 4) since the fluorine ion exchange resin must contain water to maintain ion conductivity, it was difficult to operate in air, and practical use was limited. To solve these problems, we started reviewing the development of a low-voltage-driven soft actuator around 2000 with the following characteristics: a) use of low cost materials; b) manufacturable by a simple process; c) use of electrode materials with large capacitance; and d) use of ion conductive polymers that can be operated in air.

3 Research scenario for the polymeric actuators using nanocarbon and ionic liquids

In 1999, a famous paper on carbon nanotube (CNT) actuators was published in *Science*.[4] This paper reports that when paper-like electrodes are made from single-layered CNTs and voltage is applied to the counter electrode in the aqueous electrolyte solution such as sodium chloride, the CNT electrodes expand and contract. The paper explains that when the voltage is applied, the ions with different charge adhere to the surface of CNTs that compose the electrodes, the electric double layer is created and the CNTs become charged, the state of the graphene bond that comprises the CNTs changes due to a quantum effect, and the CNTs expand and contract. The paper also predicts computationally that an actuator with extremely high energy and power densities can be created considering the large Young's modulus
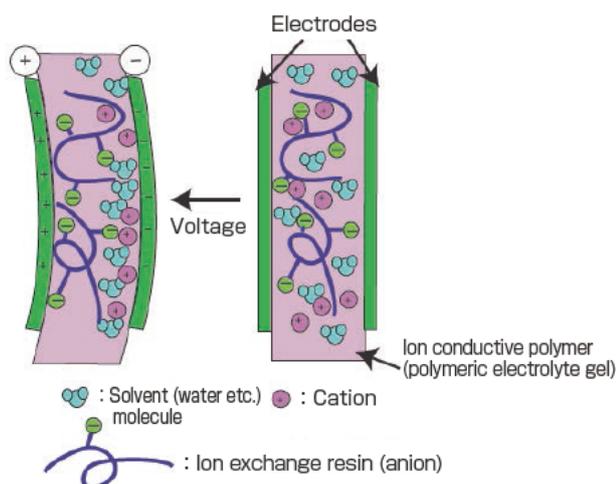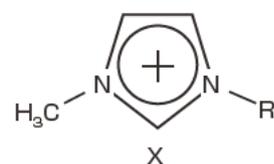
and electroconductivity of CNTs. Moreover, other papers found that CNTs have high electroconductivity,[5] strong mechanical strength,[6] and large specific surface area i.e. large capacitance,[7] and may be ideal as actuator electrodes. Therefore, we decided to use nanocarbons such as CNTs for our electrode material.

For in-air operability that is another issue, we attempted coating the aqueous element surface or impregnating the ion exchange resin with a solvent with a high boiling point instead of water. However, we were unable to obtain any practical element due to various problems. On the other hand, the research of ionic liquids, which is salt that maintains a liquid form at room temperature (Fig. 2), became active around 2000, and this became available for use in device research. This is an organic substance as shown in Fig. 2, and has the characteristics of being liquid at room temperature, of refractory, high conductivity, and stability. That is, it became possible to use this substance like water at room temperature without concern about evaporation.

Based on the above findings, we started reviewing the use of CNTs as the electrodes of ion conductive polymeric actuators, and the use of the ionic liquid system as the electrolytes. At the time, single-layered CNTs available were extremely expensive, but we expected that the price would decrease if they were mass produced in the future. Therefore, we decided the following: to use nanocarbon electrodes such as CNTs to solve problems 1) and 3) described above; to form using a process of printing dispersed CNT electrodes for problem 2); and to use an ionic liquid gel for problem 4).

4 Polymeric actuator research using the bucky gel

At first, we engaged in research starting from improvement of ion conductive polymeric actuators, pasted the aforementioned CNT paper electrodes to the fluorine ion exchange membrane,

Fig. 1 Schematic diagram of the structure of an ion conductive polymeric actuator and the bending response principle

EMIBF$_4$: R=C$_2$H$_5$, X=BF$_4$
EMITFSI: R=C$_2$H$_5$, X(CF$_3$SO$_2$)$_2$N
EMITFS: R=C$_2$H$_5$, X=CF$_3$SO$_3$
BMIBF$_4$: R=C$_4$H$_9$, X=BF$_4$
BMIPF$_6$: R=C$_4$H$_9$, X=PF$_6$
BMITFSI: R=C$_4$H$_9$, X=(CF$_3$SO$_2$)$_2$N

Fig. 2 Structural formula of the ionic liquids used in polymeric gel actuators

soaked them with ionic liquids, and fabricated the actuator element. Yet, we could not obtain good results. During this time, we were introduced to bucky gel research by Researcher Takanori Fukushima (currently, Professor, Tokyo Institute of Technology) of the JST ERATO Aida Project in 2003, and we commenced joint research for its application to actuators. Fukushima et al. discovered the phenomenon in which a gel was formed when CNTs and ionic liquids are ground together in a mortar, and this gel was named bucky gel.[8] Fukushima et al. also found that this phenomenon occurred as the imidazolium cation of the ionic liquids bonds with the π electron of CNTs, bridges the CNTs, and forms the gel.[8] We started the joint research for using the gel as the actuator electrode.

While the CNTs have various excellent properties as actuator electrodes as mentioned earlier, the problem was how to form them into an electrode. In forming the electrode from the CNT materials, the electrode must be made by dispersing the individual molecules of CNTs so they may come into contact with the electrolytes, or the characteristic large specific surface area cannot be utilized, and the electrode will not store the ions. We thought the reason we failed with the paper electrode described earlier was because of this point.

The technology of the CNT bucky gel using ionic liquids was considered ideal as a manufacturing method of actuator electrodes because it solved the problem of CNT dispersal, and the ionic liquids themselves would become the electrolytes. Moreover, this electrode forming method would be applicable to a low-cost mass production method such as printing and casting. However, A bucky gel of CNTs and ionic liquids only was too soft as an actuator electrode. Therefore, poly(vinylidene fluoride-co-hexafluoropropene) [PVdF (HFP)] that has good compatibility with ionic liquids was added as a mechanical support polymer to form the electrode. Using the ion gel of PVdF (HFP) and ionic liquids as the ion conductive polymer, we succeeded in developing the actuator element with three layers as shown in Fig. 3.[9][10] As described in the initial scenario, this element is a low-voltage-driven soft actuator with the following characteristics: 1) uses materials whose costs can be reduced; 2) can be fabricated by a simple process; 3) uses electrode materials with large capacitance; and 4) uses ion conductive polymers that can be operated in air.

5 Characteristics of the bucky gel actuator and the scenario for its application

The characteristics of the developed bucky gel actuator will be summarized. The manufacture method is extremely simple. The solution, in which the components of the CNT electrode layer and the ion gel layer are well dispersed, is prepared, the solvent is evaporated by casting, electrode films and an ion gel film are manufactured, and the ion gel film is

sandwiched with the electrode films and hot pressed together. It is possible to apply this to mass production methods such as printing.

The principle of deformation response is as shown in Fig. 4, and the deformation occurs as the ions move to the respective electrodes upon application of voltage, and the electrode layers expand or contract. A thin actuator film with large deformation at voltage of 3 V or less can be obtained, as shown in Fig. 5. The characteristics of the bucky gel actuator are as follows: 2) it is a thin film, 3) has large deformation, 3) is low-voltage driven, and 4) has good workability. Utilizing these characteristics, developments of basic materials through joint research with the JST Aida Project, and by AIST alone
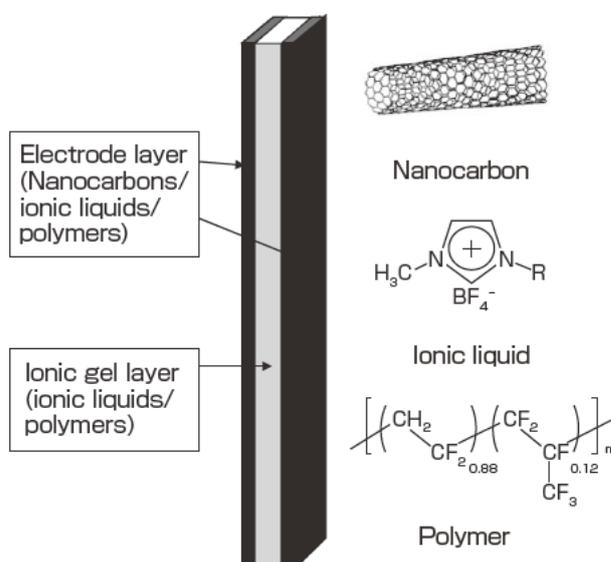

Fig. 3 Schematic diagram of the structure of the bucky gel actuator
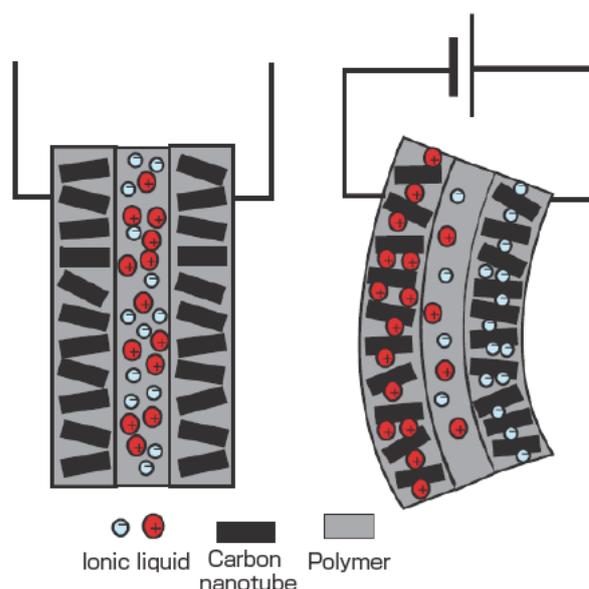

Fig. 4 Deformation response principle of the bucky gel actuator

were conducted. Then, from 2006–2007, the development to achieve a high performance actuator for human-friendly devices was conducted through joint development with a private company.

The human-friendly devices in which the polymeric actuators are needed include the devices worn on the body that require polymeric actuators that are soft, light, and low-voltage driven. The size of the devices can be divided into large human-sized devices such as Power Assist, and thin and light devices such as wearable micro-pumps and portable information display devices. The former was positioned as a future issue that necessitates upsizing technology through polymeric actuator stacking. For the latter, development of materials was continued to realize the application of polymeric actuators to thin and light devices by improving the bending strength, responsiveness, and bending displacement of the actuators.

6 Improvement of the performance of bucky gel actuators

Here, the points in improving the performance of bucky gel actuators are summarized from the perspective of materials development. Since the driving principle of this actuator is the polarization of ions to electrodes, the keys are the development of a material that increases polarization to improve the generative force and displacement, and the development of a material that increases the polarization speed to improve the response rate. Based on this basic way of thinking, the following materials development was started in 2007 jointly with corporations, toward application to thin and light human-friendly devices. Refer to Reference [11] for details of the materials development.

6.1 Improvement of nanocarbon dispersibility
As mentioned earlier, the dispersal of nanocarbons in the electrode layer is closely related to the conductivity, capacitance, and Young's modulus of the electrode layer. By increasing the nanocarbon content with good dispersibility, it is possible to manufacture electrodes with high conductivity

Fig. 5 Deformation of the bucky gel actuator at 3 V applied voltage

and capacitance, and the actuator performance is expected to increase.

The single-layered CNTs have excellent performance but have poor dispersibility, and it was conventionally considered difficult to bring out the individual performance when forming them into electrodes or other products. We used the ionic liquids as dispersants, used various dispersing methods such as ultrasound, ball mill, or jet mill, developed the process for dispersing the single-layered CNTs and manufactured the electrode in which the CNTs were dispersed in high concentration. Also, we found that the actuator performance increased dramatically by adding carbon black (CB) and carbon nanohorn (CNH) to the CNT electrode layer. Therefore, we succeeded in manufacturing an excellent actuator electrode by seeking the optimal dispersing condition of such mixed electrodes.

From the above, it can be inferred that the properties required for electrode nanocarbons are not simply mechanical properties of single elements such as conductivity, initiation stress, expansion/contraction ratio, specific surface area, or Young's modulus, but also involve geometric factors such as aforementioned dispersibility or aspect ratio that appear as the properties of an assembly of elements. The improvements of actuator performance by the addition of CB and CNH are thought to be achieved through the contribution not only of the conductivity and capacitance of CB or CNH, but the contribution of their geometric factors such as enhanced dispersability of CNTs or increased density of the electrode structure.

We have sought the optimal electrode composition and its dispersal conditions through experience, but in the future, we wish to engage in research for quantitative evaluation of the dispersability in relation to actuator performance, to develop a nanocarbon polymeric actuator with higher performance.

6.2 Ionic liquids
The factor that determines the performance of this actuator along with the nanocarbon electrode is the ionic liquids used. Based on the deformation model shown in Fig. 4, we looked at the size difference of the cation and anion in terms of displacement, and looked at the ion conductivity for the displacement rate. Using five types of imidazole ionic liquids and two types of quaternary ammonium ionic liquids that were used frequently in electrochemical devices, we manufactured the actuator films, compared their performances, and sought the optimal ionic liquids. As a result, we obtained guidelines for the selection of the ionic liquids based on the deformation model of Fig. 4 as follows: 1) the rate of response of the actuator is determined by the ion conductivity and electrode conductivity, and 2) the degree of displacement response is dependent on the size difference of the cation and anion.
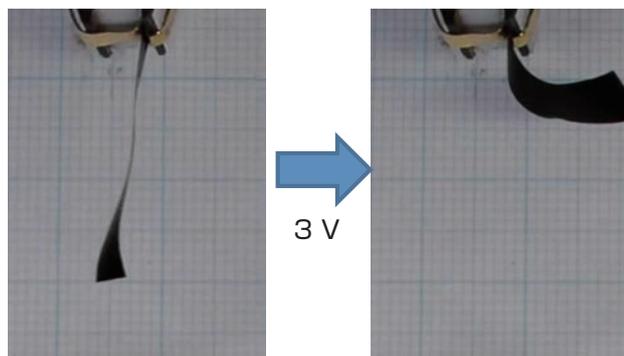
Table 1. Comparison of the performances of bucky gel and piezoelectric ceramics actuators

Actuator	Workability	Driving voltage	Displacement	Response	Generating force
Piezoelectric ceramics	×	100 V or more	2 μm	1 ms	100 gf
Bucky gel	○	3 V or less	1 mm	1s	3 gf

Note: The performance values are representative values of a 5 mm × 5 mm size actuator. The values for a piezoelectric ceramic actuator are literature values of the bimorph type.

6.3 Comparison of the performances of a bucky gel actuator and a piezoelectric ceramics actuator

The bimorph-type actuator made of piezoelectric ceramics is known as the commercially available actuator that undergoes voltage-driven bending deformity. Here, we shall compare the actual values for a piezoelectric ceramics actuator and a bucky gel actuator (Table 1).

For workability, compared to piezoelectric ceramics that requires complex processes such as sintering and polling, the bucky gel can be mass produced by printing and other methods, and it is clear it has excellent workability. Looking at the actuator property, the bucky gel is low-voltage driven and has large deformation, while the piezoelectric ceramics excels in high response rate and large generative power. The bucky gel actuator can be used for products that require low-voltage-drive and large deformation that cannot be handled by piezoelectric ceramic actuators. We believe the issue of low generative power can be overcome in the future by developing the stacking technologies taking advantage of bucky gel's workability.

7 Application of the bucky gel actuator to light and thin braille displays

We worked on several applications in thin and light devices. Here, we shall describe the braille display development that reached the stages of prototype development and user evaluation.

The braille system where the letters are represented by six dots is the only writing system that can be used by the visually impaired. Currently, there are about 300 thousand visually impaired people in Japan, and there are 30 thousand braille users. Due to the advancement of digital information technology in recent years, braille displays have become commercially available as information terminals for the visually impaired. These use the piezoelectric system or solenoid actuators, and in principle, the size of the element becomes large. Therefore, such information terminal devices cannot be carried around conveniently. Moreover, only one line can be displayed. The users have requested for a device that is portable and can display multiple lines that allows easy reading.

Against the above background, under the FY 2009 R&D Project for Service and Support for Persons with Disabilities[12] and FY 2010 R&D Project for Service and Support for Persons with Disabilities[13] of the Ministry of Health, Labour and Welfare, we engaged in joint research for applying the bucky gel polymeric actuator to light and thin braille displays with the following organizations: the Sendai R&D Center, Alps Electric Co., Ltd.; Research and Education Center for Natural Sciences, Keio University; and School of Engineering, the University of Tokyo. If the braille can be presented by arranging the actuator filmstrips in planar configuration and by controlling each element independently with electric signals, it is possible to create a light and thin multi-line braille display. We continued the prototype development for braille displays and created a demo prototype for an ultra-thin light braille display that can display six letters (Fig. 6).

Through evaluation experiments by users using this demo prototype, high expectations were raised for various uses of such thin and light multi-line braille displays. For example, it may be used to replace the liquid display control panels of various home appliances and bank ATMs, or used for page displays through multi-line display. There are also expectations for displaying figures and tables. We also received inquiries from overseas such as Europe and Canada as well as throughout Japan.

In the evaluation experiment, several problems such as durability and reliability of the device as well as fluctuation in properties became apparent. We continued improvement of the actuator and the mechanical structure of the braille display, and saw a clear way for realizing thin and light braille display.
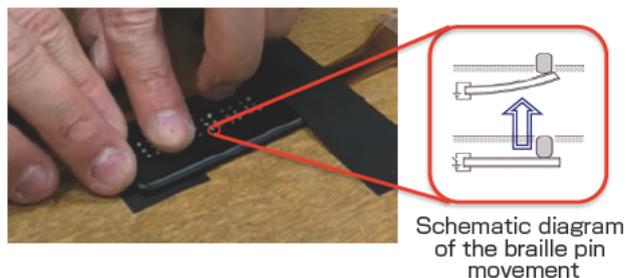

Schematic diagram of the braille pin movement

Fig. 6 Braille display using the bucky gel actuator

8 Current status of the polymeric actuator technology using nanocarbons and future prospects

For the practical issues of durability and reliability of the actuator that became apparent through the braille display project, many issues were solved through the NEDO grant and corporate joint research after the completion of the MHLW project. As a result, we succeeded in developing polymeric actuators using nanocarbons that are applicable to various kinds of utilization.[14]

In the future, we wish to realize the application to thin and light devices using this actuator element, as well as the development of a robot actuator such as Power Assist by upscaling through the development of stacking technology.

References

[1] K. Asaka and H. Okuzaki (eds.): *Soft Actuators: Materials, Modeling, Applications and Future Perspectives*, Springer, Tokyo (2014).

[2] K. Asaka and K. Oguro: Chap. 5 IPMC actuator: fundamentals, *Biomedical Applications of Electroactive Polymer Actuators* [F. Carpi and E. Smela (eds.)], Wiley (2009).

[3] K. Asaka and K. Oguro: Chap. 6 Active microcatheter and biomedical soft devices based on IPMC actuators, *Biomedical Applications of Electroactive Polymer Actuators* [F. Carpi and E. Smela (eds.)], Wiley (2009).

[4] R. H. Baughman, C. Cui, A. A. Zakhidov, Z. Iqbal, J. N. Barisci, G. M. Spinks, G. G. Wallace, A. Mazzoldi, D. De Rossi, A. G. Rinzler, O. Jaschinski. S. Roth and M. Kertesz: Carbon nanotube actuators, *Science*, 284 (5418), 1340–1344 (1999).

[5] T.W. Ebbesen, H. J. Lezec, H. Hiura, J. W. Bennett, H. F. Ghaemi and T. Thio: Electrical conductivity of individual carbon nanotubes, *Nature*, 382, 54–56 (1996).

[6] M. R. Falvo, G. J. Clary, R. M. Taylor II, V. Chi, F. P. Brooks Jr, S. Washburn and R. Superfine: Bending and buckling of carbon nanotubes under large strain, *Nature*, 389, 582–584 (1997).

[7] S. Shiraishi, H. Kurihara, K. Okabe, D. Hulicova and A. Oya: Electric double layer capacitance of highly pure single-walled carbon nanotubes (HiPcoTM BuckytubesTM) in propylene carbonate electrolytes, *Electrochem. Commun.*, 4 (7), 593–598 (2002).

[8] T. Fukushima, A. Kosaka, Y. Ishimura, T. Yamamoto, T. Takigawa, N. Ishii and T. Aida: Molecular ordering of organic molten salts triggered by single-walled carbon nanotubes, *Science*, 300 (5628), 2072–2074 (2003).

[9] K. Asaka, T. Fukushima, T. Aida and A. Ogawa: Patent No. 4038685 Actuator soshi (actuator element), patent application Dec 8, 2003; registration Nov 16, 2007 (in Japanese).

[10] T. Fukushima, K. Asaka, A. Kosaka and T. Aida: Fully plastic actuator through layer-by-layer casting with ionic-liquid-based bucky gel, *Angew. Chem. Int. Ed.*, 44 (16), 2410–2413 (2005).

[11] K. Asaka, K. Mukai, T. Sugino and K. Kiyohara: Ionic electroactive polymer actuators based on nano-carbon electrodes, *Polym. Int.*, 62 (9), 1263–1270 (2013).

[12] Ministry of Health, Labour and Welfare: Heisei 21 Nendo Shogaisha Jiritsu Shien Kiki to Kenkyu Kaihatsu Project —Keitai denwa no ryomen nimo sochaku kano na keiryo de usui (ususa 1 mm) tenji device no kaihatsu hokokusho ["Development of light and thin (1 mm thickness) braille device that can be installed on both sides of cell phones," Report of FY 2009 R&D Project for Service and Support for Persons with Disabilities] (2010), http://www.mhlw.go.jp/bunya/shougaihoken/cyousajigyou/jiritsushien_project/seika/S04Report/Report_Mokuji04 htm, accessed 2010-04-01 (in Japanese).

[13] Ministry of Health, Labour and Welfare: Heisei 22 Nendo Shogaisha Jiritsu Shien Kiki To Kenkyu Kaihatsu Sokushin Jigyo—"Denshi tenji tosho hakujo (B5 teido) no tenji display" ni kansuru kaihatsu ["Development of braille display for thin (about B5 size) electronic braille book," Report of FY 2010 R&D Project for Service and Support for Persons with Disabilities] (2011), http://www.mhlw.go.jp/bunya/shougaihoken/cyousajigyou/jiritsushienkiki/H22/S03/H22_seika-03 htm, accessed 2011-06-01 (in Japanese).

[14] AIST (2013-08-23): Keiryo de shohi denryoku no sukunai nanocarbon kobunshi actuator o kaihatsu—Carbon nanotube o mochiite kotaikyusei kohojisei o jitsugen (Press Release: Development of nanocarbon polymer actuator that is light and has low power consumption—Realization of high durability and high retention using carbon nanotubes), https://www.aist.go.jp/aist_j/press_release/pr2013/pr20130823/pr20130823 html, accessed 2013-08-23 (in Japanese).

Author

Kinji ASAKA

Completed the master's program at the Graduate School of Science, Kyoto University in March 1986 (Chemistry). Obtained doctor's degree at Kyoto University in 1990. Faculty staff at the Institute for Chemical Research, Kyoto University from 1986 to 1993. Joined the Government Industrial Research Institute, Osaka, Agency of Industrial Science and Technology (currently, AIST) in 1993. Currently Group Leader, Hybrid Actuator Group, Inorganic Functional Materials Research Institute, AIST. Visiting Professor at Shinshu University and Wakayama University. Specialties are interfacial electrochemistry and development of polymeric actuators.

Discussions with Reviewers

1 Overall
Comment (Hiroaki Tao, AIST)

This paper presents the realization of a soft actuator that is also called an artificial muscle, by using carbon nanotubes, ionic liquids, and other advanced materials. The background of development, the working principle, and points of materials development are described appropriately. As an example of practical use, the application to braille displays is considered, manufacturing and evaluation are done through corporate joint research, and future points of improvement are reviewed. The flow of the R&D from the development of new technology, product realization, and future prospects are explained, and I think this paper will be particularly useful to the researchers in the field of materials development.

2 Meaning of "human-friendly"
Comment (Noboru Yumoto, AIST)

I think the term "human-friendly" in the title seems to be rather broad. The required characteristics of an actuator differ according to use, and the restrictions of materials and other factors greatly change depending on whether it is used outside or inside the body. Therefore, I think it is necessary to clarify what use you have in mind for the actuator developed in this paper.

Answer (Kinji Asaka)

Compared to other actuators, the nanocarbon polymeric actuator described in this paper has characteristics of being low-voltage driven and operable in air. We did not intend it to be "used inside the body," and I corrected the meaning of "human-friendly" as limited to "wearable on the human body."

3 Superiority of the developed actuator
Comment (Hiroaki Tao)

There is no quantitative description on the performances of the actuator developed in this paper, particularly in comparison with the conventional materials or the materials that serve as world benchmarks. I think this prevents communicating the superiority of your technology to the readers.

Answer (Kinji Asaka)

In Table 1, I added the comparison with the piezoelectric ceramics bimorph actuator that is widely used and commercially available. I also added an explanation of our actuator in the text.

4 Process of improving the performance
Question (Hiroaki Tao)

For improving the performance of the bucky gel actuator, you conducted various experiments and succeeded in developing useful materials and setting the guideline. Did you obtain these through experience of repeated trial-and-error, or did you set up a hypothesis that ion conductivity and molecular size are relevant, and then conduct experiments by selecting ionic liquids with different physical properties to prove your hypothesis?

Answer (Kinji Asaka)

For the optimal ionic liquids, we did a search by setting up a hypothesis based on the deformation model in Fig. 4. Specifically, we looked at the size difference of cation and anion for the degree of displacement, and we looked at the ion conductivity for the displacement rate. I added this process of investigation to the text.

5 Reason for improved performance
Question (Hiroaki Tao)

Why does the performance improve dramatically when you add carbon black or carbon nanohorn?

Answer (Kinji Asaka)

The properties required of electrode nanocarbons are not simply mechanical properties of single elements such as conductivity, initiation stress, expansion/contraction ratio, specific surface area, or Young's modulus, but the geometric factors such as dispersibility and aspect ratio become important as the properties of an assembly of elements. It is inferred that the improvement of actuator performance by the addition of carbon black or carbon nanohorn is due to the contribution of their geometric factors such as improved CNT dispersibility and increased density of the electrode structure, as well as their contribution to conductivity and capacitance. I added this inference to the text.

High quality and large-area graphene synthesis with a high growth rate using plasma-enhanced CVD

― Toward a high throughput process ―

Masataka Hasegawa[1,2]*, **Kazuo Tsugawa[2]**, **Ryuichi Kato[2]**, **Yoshinori Koga[2]**, **Masatou Ishihara[1,2]**, **Takatoshi Yamada[1,2]** and **Yuki Okigawa[1,2]**

The current trend in graphene synthesis is to use thermal chemical vapor deposition(CVD) at the temperature of 1000 °C or higher. For industrial use of graphene as transparent conductive films, higher throughput of graphene synthesis is necessary. We were among the first to adopt the plasma-enhanced CVD method, and have developed a process of high-speed large-area deposition for transparent conductive film applications. The development and a method to remove impurities from the process are presented in this paper. We report improvement in graphene film quality and other properties by decreasing the nucleus density using plasma-enhanced CVD.

Keywords : Graphene, plasma CVD, large area synthesis, high growth rate, high throughput, transparent electrode

1 Introduction

Graphene[1] is a single atomic sheet in which carbon atoms are arranged in a hexagonal honeycomb lattice. Graphene has a very unique band structure (zero bandgap, linear dispersion), and thereby it shows brilliant electronic and optical characteristics such as extremely high carrier mobility and light absorption which does not depend on wavelength. (2.3 % absorption per layer.) Moreover graphene has the property of flexibility which indium tin oxide (ITO)[2] does not possess, and an attempt has been made to use a few layers of graphene(FLG) as transparent electrodes in such devices as flexible organic light-emitting diode (OLED), solar batteries, and displays.

For transparent electrode application of graphene, it is necessary to establish production technology of high quality and high throughput for large area graphene. Among the various methods of graphene production such as mechanical exfoliation of bulk graphite,[1][3] exfoliation of graphene oxide in liquid phase,[4] thermal decomposition of SiC,[5] etc., chemical vapor deposition (CVD) on catalytic transition metal surfaces, in particular on a copper surface, has great promise as a production method for transparent electrode application. Recently, high conductivity graphene has been synthesized on copper substrates by energetic development of the thermal CVD method.[6][7] On the other hand, since throughput of the thermal CVD method is insufficient, synthesis time needs to be significantly shortened for transparent electrode application. In this paper, we report an attempt to develop high throughput plasma-enhanced CVD for high quality graphene.[8]-[16]

2 Preparation of a substrate for graphene synthesis and suppression of impurity incorporation.

In the case of CVD of graphene using a copper foil substrate, surface cleaning technique of copper foil before CVD is especially important. Also in the case of plasma-assisted CVD (plasma CVD), it is necessary to prevent contamination such as impurities released from the reaction chamber by plasma exposure, particularly silicon, which originate from the quartz of antenna units for exciting plasma.

Commercially available copper foil surfaces are subjected to anticorrosive treatment in order to prevent oxidation. Moreover, even foil with anticorrosive treatment has a surface that is still covered with a thin copper oxide layer. For high-quality graphene synthesis, it is necessary to remove these copper oxide and anticorrosive treatment carefully. In thermal CVD of graphene, electrolytic cleaning and successive high-temperature treatment at about 1000 °C of the copper foil substrate in the reaction chamber are effective for removing copper oxide and the anticorrosive treatment layer. Furthermore, in order to flatten the copper foil surface, chemical polishing (CMP) before electrolytic cleaning and annealing treatment is effective.[17][18] On the other hand, electrolytic cleaning is a wet process and thus there is a possibility of recontamination before CVD. Therefore, cleaning methods consistent with CVD are desirable.

1. Nanomaterials Research Institute, AIST Tsukuba Central 5, 1-1-1 Higashi, Tsukuba 305-8565, Japan ∗E-mail: hasegawa. masataka@aist.go.jp, 2. Technology Research Association for Single Wall Carbon Nanotubes, Graphene Division Tsukuba Central 5, 1-1-1 Higashi, Tsukuba 305-8565, Japan

In this study, plasma is used, and by establishing plasma cleaning of the surface of the copper substrate, cleaning and synthesis can be carried out continuously in situ. For this reason, it is possible to prevent the recontamination of the substrate.

In many processes using plasma, an inert gas is added to the discharge gas in order to illuminate stably, and argon is commonly used as an inexpensive inert gas. On the other hand, from the point of view of sputtering that causes release of impurities from the reaction chamber, it is desirable to use lighter inert gas.[19]–[21] Thus, we attempted plasma CVD synthesis of graphene using helium, which is expected to be effective for preventing impurity incorporation because of it being the lightest inert gas.

Figure 1 shows a schematic illustration of the surface-wave microwave plasma CVD equipment.[13] The waveguide for microwave propagation is connected to the reaction chamber. The waveguide is equipped with a slot antenna that emits the microwaves into the reaction chamber through a quartz window. In the case of surface-wave microwave plasma, high-density plasma is excited along the surface of the quartz window. High-density plasma which exceeds the cutoff density of 7.4×10^{10} cm^{-3} is excited along the surface of the quartz window by 2.45 GHz microwaves.[22]–[27] Microwaves cannot penetrate through the high density plasma, and the copper foil substrate is not exposed to the microwaves directly. Therefore, temperature control of the substrate is easy over a wide range from low-temperature to high-temperature.[10][11][14]

A tough-pitch copper foil (purity: 99.7 %) with a thickness of 33 μm was used for graphene synthesis. We compared plasma pretreatment of copper foil using two kinds of gas mixtures,
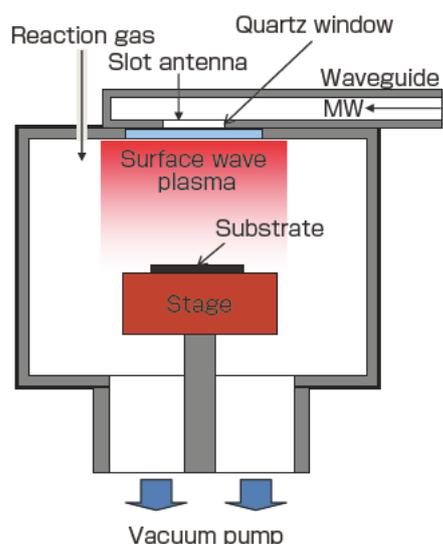
Ar/H$_2$ and He/H$_2$. The copper foil substrate was placed 50 mm away from the quartz window and the substrate temperature was kept in the range of 350−400 °C. The duration of pretreatment was 1 min. The cleaning effect for the copper foil surface by the plasma pretreatment was confirmed by X-ray photoelectron spectroscopy (XPS) (ULVAC Phi ESCA 5800X, AlKα). XPS measurement was performed ex situ after the cleaning. Quantitative evaluation was considered difficult owing to the oxidation of the copper foil surface by air exposure after cleaning. Therefore, we conducted XPS measurement under the same ex situ condition for all samples and compared the results in terms of the changes in the spectra.

Subsequent to the plasma pretreatment of the copper foil substrate in the reaction chamber, synthesis of graphene by plasma CVD was performed using two kinds of gas mixtures, He/H$_2$/CH$_4$ and Ar/H$_2$/CH$_4$. The synthesis time was 20 min. The synthesized graphene films were evaluated by Raman scattering spectroscopy (HORIBA XploRa, spot size 1 μm and wavelength 638 nm), energy-dispersive X-ray spectroscopy (EDS) (JEOL-2100F with EDS detector JED-2300F; acceleration voltage, 200 kV), and XPS. For cross-sectional transmission electron microscope (TEM) observation, an amorphous carbon thin film was deposited on an as-deposited graphene surface in order to make the sample structure robust for gallium focus ion beam etching. TEM observation was performed at an acceleration voltage of 300 keV.

Figure 2 shows the XPS survey spectrum of the as-received tough-pitch copper foil substrate. In this spectrum, the peaks corresponding to Cu 3*d*, 3*p*, 3*s*, 2*p*, and 2*s* and Cu Auger were observed.[28] The peaks of C 1*s* and O 1*s* were also observed together with the low-intensity peaks of Si 2*p* and N 1*s*. It was suggested that these were because organic silicon and hydrocarbon compounds containing nitrogen were coated on the surface of the as-received tough-pitch rolled copper foil. In this study, we examined the removal of these impurities from the copper foil substrate surface by the plasma pretreatment.

In Fig. 3, we compared the XPS high-resolution spectra from the copper foil substrate before and after the plasma pretreatment. First, the removal of copper oxide on the copper foil surface by plasma pretreatment was examined using O 1*s* signals. O 1*s* binding energy spectra are shown in Fig. 3(a). In the case of Ar/H$_2$ plasma pretreatment, the O 1*s* peak was still observed, which indicates that oxygen was not removed efficiently by this plasma treatment. Moreover, the peaks were separated more clearly, which suggests that a certain amount of oxygen was newly formed during the Ar/H$_2$ plasma treatment. In contrast, the O 1*s* peak disappeared with the He/H$_2$ plasma pretreatment, which indicates that the oxygen on the surface was removed efficiently by this plasma

Fig. 1 Schematic illustration of the surface-wave microwave plasma CVD equipment[13]
Copyright (2014) The Japan Society of Applied Physics

treatment.

Next, we examined the spectrum of Cu 2*p* binding energy shown in Fig. 3(b). For the as-received copper foil substrate, satellite peaks (942.5 eV and 963 eV) attributed to bivalent

copper oxides were observed, as well as peaks from Cu 2*p* by orbit-spin coupling and the 2*p*$^{3/2}$ (933 eV) and 2*p*$^{1/2}$ (953 eV) peaks.[29]–[33] The high-energy side of the Cu 2*p*$^{3/2}$ peak of the as-received Cu foil is broad, which is caused by bivalent copper compounds such as Cu(OH)$_2$ and CuO.[29]–[33] In the
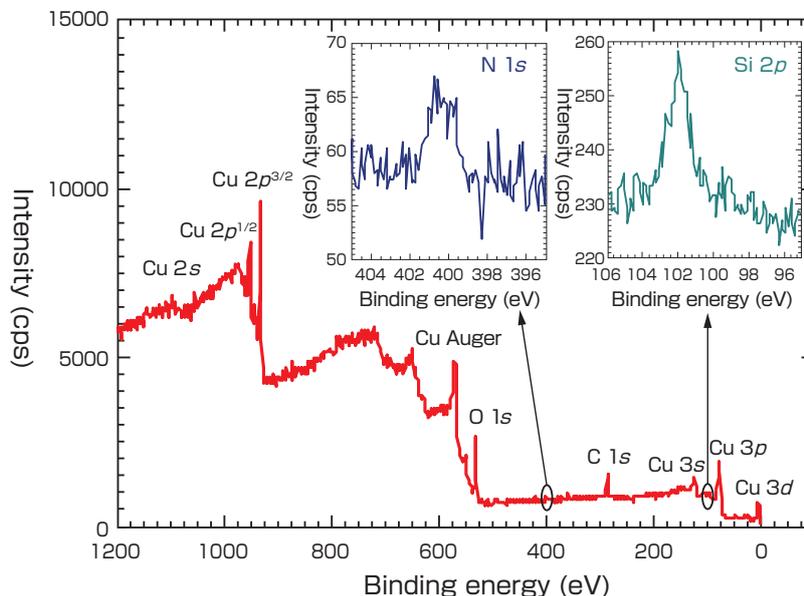

Fig. 2 XPS survey spectrum of the as-received copper foil[13]
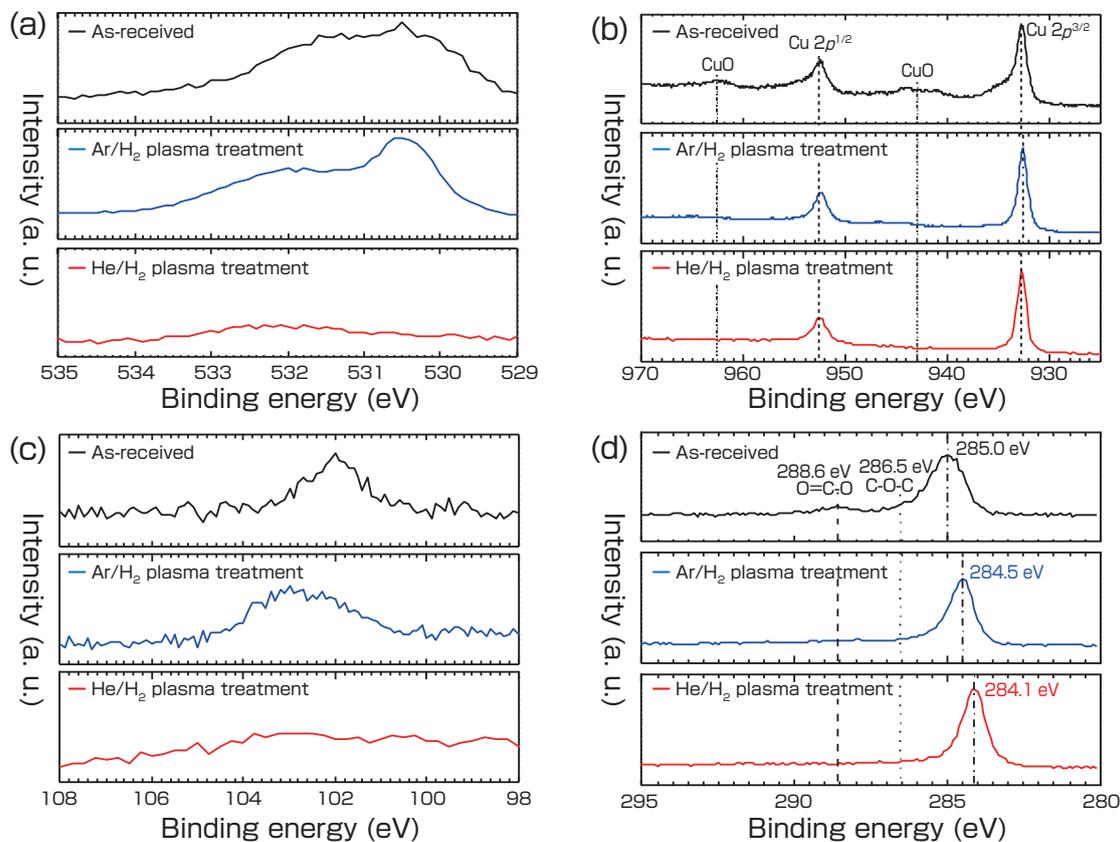Copyright (2014) The Japan Society of Applied Physics

Fig. 3 XPS spectrum of the copper foil with plasma pretreatment and without plasma pretreatment[13]
(a) O 1*s* binding energy, (b) Cu 2*p* binding energy, (c) Si 2*p* binding energy, (d) C 1*s* binding energy
Copyright (2014) The Japan Society of Applied Physics

case of Ar/H$_2$ plasma pretreatment, the broad peaks (934.5 eV and 942.5 eV) of Cu $2p^{3/2}$ of the bivalent copper oxide compounds disappeared. The peaks due to the monovalent copper oxide Cu$_2$O still remained in the vicinity of 932.5 eV and 952.5 eV.[29]–[33] From these results, we confirmed that the surface of the as-received copper foil substrate is covered with the bivalent copper oxide on Cu$_2$O/Cu. The bivalent copper oxide was completely eliminated from the substrate and the monovalent copper oxide was not removed by the Ar/H$_2$ plasma pretreatment. On the other hand, in the spectrum obtained after the He/H$_2$ plasma pretreatment, the peaks attributed to monovalent copper oxide, Cu$_2$O, and the bivalent compounds Cu(OH)$_2$ and CuO were not observed, only the peaks attributed to Cu $2p^{1/2}$ and Cu $2p^{3/2}$ of pure copper were observed. This is consistent with there being no O $1s$ signals related to any oxides on the copper foil substrate after the He/H$_2$ plasma pretreatment, as shown in Fig. 3(a). This indicates that the He/H$_2$ plasma pretreatment is very effective for removing copper oxide on the surface of copper foil substrates.

Then, we examined the removal of silicon impurities on the copper foil substrate from the XPS spectrum of the Si $2p$ binding energy shown in Fig 3(c). A peak with Si $2p$ binding energy of 102 eV was observed on the surface of the as-received copper foil substrate. We surmise that siloxane compounds containing Si, such as silicone were applied as protective coating for copper foil surfaces before shipment from the factory. The Si $2p$ binding energy of Si compounds depends on the oxidization state of siloxy units[34][35] and silicon oxides.[36] If the number of oxygen atoms binding to Si atoms increases, the Si $2p$ binding energy will shift from 101 eV to 103 eV. The observed binding energy of 102 eV of Si $2p$ corresponds to that of poly(dimethylsiloxane) (PDMS),[34][35] as shown in Fig. 3(c). In the case of Ar/H$_2$ pretreatment, a new peak at 103.0 eV due to Si $2p$ appeared, although the peak intensity of Si $2p$ at 102.0 eV of the as-received copper foil substrate decreased slightly. The appearance of the peak of Si $2p$ at 103.0 eV following the Ar/H$_2$ plasma pretreatment occurs for two reasons. First is the oxidation of PDMS, indicating the formation of a CH$_3$SiO$_3$ siloxy unit by the oxidization of the CH$_3$SiO$_2$ (PDMS), as shown in Fig. 3(c). Second is the formation of SiO$_2$ from etching of the quartz window by the Ar/H$_2$ plasma. In contrast, the peak due to Si $2p$ disappeared completely after the He/H$_2$ plasma pretreatment. Hence, it is found that the He/H$_2$ plasma pretreatment effectively eliminates silicon impurities including silicon oxides on the copper foil surface and suppresses the extreme over-plasma etching of the quartz window.

Furthermore, we investigated the XPS spectrum of the C $1s$ region in order to clarify the protective coating material on the as-received copper foil substrate, as shown in Fig. 3(d). There are three peaks at 285.0 eV, 286.5 eV, and 288.6 eV observed for the as-received copper foil. The strongest peak observed at 285.0 eV is mainly due to the C-C and C-H

bonded groups in a sp^3-hybridized state.[37] The shoulder peak observed at 286.5 eV is due to C-O-C bonding of the ether/phenolic components, and the highest binding energy observed at 288.5 eV is due to O=C-O bonding of the ester/carboxylic components.[37] Furthermore, we observed nitrogen atoms at 400.2 eV in the inset of the survey spectrum in Fig. 2. Again, we surmise that this is due to a corrosion inhibitor for copper foil that contains O=C-O, C-O-C, C-C, and C-H groups and N. It is well known that benzotriazole (BTAH) is used as an effective corrosion inhibitor for copper.[38][39] Although, BTAH (C$_6$H$_5$N$_3$) has none of the functional groups of O=C-O and C-O-C, Finšgar *et al.* have observed the XPS C $1s$ spectrum with these groups on the surface of copper after of 1 h treatment with 3 % NaCl solution containing 10 mM BTAH.[38] They suggested that either the oxidation of carbonaceous species occurred or oxidized carbon compounds were adsorbed on the topmost surface of copper. Their spectrum closely resembles that of the as-received copper foil in Fig. 3(d). They have also observed signals of the Cu Auger L$_3$M$_{4,5}$M$_{4,5}$ region of the Cu-BTAH complex at 572.6 eV at uppermost part of the copper substrate using angle resolved XPS measurement. The signal of the Cu-BTAH complex in the region of Cu Auger was not detected in our experiment, because it was not an angle-resolved measurement.

After the Ar/H$_2$ plasma pretreatment, the peak of C $1s$ at 285 eV observed for the non-plasma-treated substrate became sharper and the peaks at 288.6 eV and 286.5 eV disappeared. This means that BTAH is easily decomposed by the Ar/H$_2$ plasma pretreatment. The peak of C $1s$ at 285.0 eV shifted to 284.5 eV after the Ar/H$_2$ plasma pretreatment. The binding energy of 284.5 eV corresponds exactly to that of PDMS.[35] Hence, PDMS was mostly left on the copper foil substrate after the Ar/H$_2$ plasma pretreatment. This is consistent with the existence of PDMS of O $1s$ (532.0 eV) in Fig. 3(a) and Si $2p$ (102.0 eV) in Fig. 3(c) after the Ar/H$_2$ plasma pretreatment. After the He/H$_2$ plasma pretreatment, the binding energy observed at 284.1 eV corresponds to that of HOPG which is composed of sp^2 bonding.[40][41] These were confirmed as amorphous sp^2 carbon films from the Raman spectrum.

The difference between the effect of He/H$_2$ and Ar/H$_2$ plasma pretreatment methods can be attributed to the difference between the sputtering yields of SiO$_2$ for helium and argon. In the case of surface-wave plasma CVD, high-density plasma is excited in the vicinity of the quartz window, and the mixing of silicon and oxygen with the plasma by the sputtering of the quartz window is a major issue. That is, it is necessary to suppress the deposition of such impurities onto the substrate. According to the basic theory of sputtering by Sigmund, sputtering yield depends on the atomic weight and atomic number of the target and ions.[20] When the ion energy is 100–600 eV, the yield of quartz (SiO$_2$) sputtering with argon ions is 2.5–3.8 times greater than that of helium ions.

Furthermore, the molecular dynamics simulation of energetic ion bombardment of He^+, Ne^+, Ar^+, Kr^+ and Xe^+ for SiO_2 have also been reported.[21] The sputtering yield for SiO_2 substrates increased along with the atomic number of impact ions. The lightest He^+ among these ions could not efficiently transfer its energy to surface atoms on the SiO_2 substrate even at ion energy of 100 eV, and the sputtering yield by He^+ was almost zero. On the other hand, Ar^+ effectively showed sputtering of SiO_2.[21] Therefore, it was shown that it was possible to suppress the deposition of silicon and oxygen from the quartz window onto the copper foil substrate by the He/H_2 plasma pretreatment, and the cleaning of the copper foil surface could be performed effectively.

The syntheses of graphene by $Ar/H_2/CH_4$ and $He/H_2/CH_4$ plasma CVD on a copper foil substrate pretreated with Ar/H_2 and He/H_2 plasma was examined and compared with that without such pretreatment. The Raman spectra of the synthesized graphene by plasma CVD are shown in Fig. 4. The G-band (1520 cm^{-1}) overlapping with the D'-band and the D-band (1320 cm^{-1}) were observed for the as-received copper foil substrate prepared by $He/H_2/CH_4$ plasma

CVD. However, the 2D-band was not observed on the as-received substrate prepared without plasma pretreatment. In the case of $Ar/H_2/CH_4$ plasma CVD subsequent to the Ar/H_2 plasma pretreatment, the 2D-band (2650 cm^{-1}) was observed with half the intensity of the G-band. In the case of $He/H_2/CH_4$ plasma CVD subsequent to the He/H_2 plasma pretreatment, the 2D-band (2650 cm^{-1}) was observed with the same intensity as the G-band. This result, combined with the result of the cross-sectional TEM image, indicates that the crystalline of graphene synthesized using $He/H_2/CH_4$ plasma CVD at low-temperature (350–400 °C) on a He/H_2 plasma pretreated copper foil substrate is better than that synthesized on an Ar/H_2 plasma pretreated substrate, as will be described later. That is, it suggests that the He/H_2 plasma pretreatment successfully removes copper oxide and impurities on the substrate surface and recovers the catalytic effect of the copper surface for graphene synthesis. In plasma CVD of graphene, the synthesis is completed within several tens of seconds, and has the potential to synthesize graphene in a short time. In order to realize the continuous synthesis of high-quality graphene of high-throughput, it is necessary to sufficiently remove the oxide and contaminations prior to the synthesis.

Figure 5 shows a comparison of the details of the spectra at around Si 2p binding energy for graphene films synthesized using $He/H_2/CH_4$ and $Ar/H_2/CH_4$ plasma CVD. The Si 2p (103.0 eV) was observed clearly in the spectrum of the graphene film synthesized by $Ar/H_2/CH_4$ plasma CVD, but not in the spectrum of that synthesized by $He/H_2/CH_4$ plasma CVD. In order to obtain more detailed information with respect to the impurities contained in the graphene film, an elemental analysis of very thin (one or two layers) films was conducted by EDS (Fig. 6). In the case of the synthesized graphene film using $Ar/H_2/CH_4$ plasma CVD, about 2 % silicon was detected, whereas less than 0.8 % silicon including the background signals was detected in the graphene film synthesized using $He/H_2/CH_4$ plasma CVD. Therefore, from the results of impurity analysis of XPS and EDS, it is concluded that the incorporation of silicon from
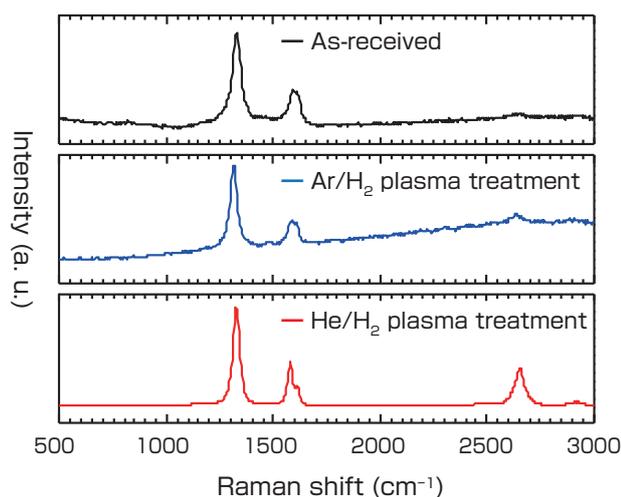
Fig. 4 Raman spectrum of graphene synthesized on the copper foil substrate[13]
Copyright (2014) The Japan Society of Applied Physics

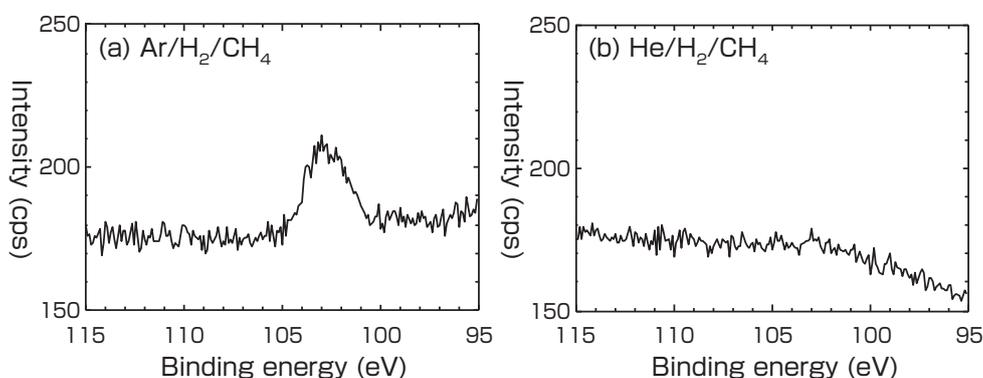**Fig. 5 XPS spectrum of Si 2p binding energy for synthesized graphene using (a) the Ar/H$_2$/CH$_4$ gas mixture and (b) the He/H$_2$/CH$_4$ gas mixture[13]**
Copyright (2014) The Japan Society of Applied Physics

the quartz window onto the synthesized graphene film is suppressed more effectively by He/H$_2$/CH$_4$ than Ar/H$_2$/CH$_4$.

As in the pretreatment of the substrate, mixed gas using helium or argon for plasma CVD results in a significant difference between the synthesized graphene films. Figure 7 shows the comparison between the cross-sectional TEM images of graphene films synthesized using (a) He/H$_2$/CH$_4$ and (b) Ar/H$_2$/CH$_4$ mixed gases. In the case of mixed gas of helium, a multilayer graphene film consisting of 20 layers was synthesized directly on the copper foil substrate by CVD for 20 min. The layer spacing was 0.34 nm, which is slightly larger than 0.335 nm of graphite. In the thermal CVD on the copper foil substrate, the growth of graphene is limited to two or three layers.[6] In contrast, in the case of plasma CVD of graphene, a much thicker film is grown on the copper foil substrate as shown in this example. This is one of the remarkable features of this method. In the case of mixed gas of argon, on the other hand, the diagonal layered structure in the cross-sectional TEM image was confirmed on the copper foil substrate. A layer spacing of 0.27–0.28 nm, which corresponds to that of CuO(110), indicates the formation of

the copper oxide layer during Ar/H$_2$/CH$_4$ plasma CVD. Along the surface of the copper oxide layer, a weak contrast of the layered structure was also confirmed. The layer spacing of 0.34–0.37 nm, however, is much larger than that of graphite, which suggests that the synthesized graphene layer was partly oxidized like the copper foil substrate.

In this research we developed a plasma pretreatment method for copper foil substrates, and a plasma CVD method for high-quality graphene by suppressing the impurity incorporation onto the graphene surface. It is found that the plasma pretreatment using He/H$_2$ removes copper oxide on the surface more effectively than using Ar/H$_2$, and is also effective for preventing the substrate from being contaminated by silicon impurities attributed to the sputtering of the quartz window. The plasma pretreatment of the copper foil substrate using He/H$_2$ is found to improve the crystalline of synthesized graphene. The incorporation of silicon impurities from the quartz window onto synthesized graphene films is suppressed using He/H$_2$/CH$_4$ more effectively than using Ar/H$_2$/CH$_4$.

Fig. 6 EDX spectrum of Monolayer and/or bilayer graphene synthesized using (a) the Ar/H$_2$/CH$_4$ gas mixture and (b) the He/H$_2$/CH$_4$ gas mixture[13]
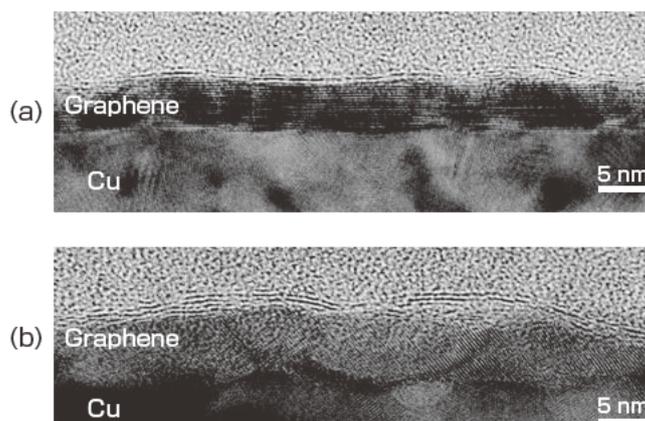
Copyright (2014) The Japan Society of Applied Physics

Fig. 7 Cross-sectional TEM images of synthesized graphene by surface-wave plasma using (a) the He/H$_2$/CH$_4$ gas mixture and (b) the Ar/H$_2$/CH$_4$ gas mixture[13]

Copyright (2014) The Japan Society of Applied Physics

3 A development of plasma CVD using ultralow carbon source

For the industrial application of graphene transparent conductive films, establishment of a synthesis method of high-quality and high-throughput is required. As described previously, the synthesis of graphene by CVD on transitional metal substrates (in particular on copper) is the most promising at the moment.[6] Currently, transmittance of 90 % (four-layers stacking) in the region of visible wavelength and sheet resistance of 30 Ω are indicators of high-performance graphene synthesized by thermal CVD.[7] A demonstration of an organic light-emitting diode (OLED) with graphene anodes which has higher luminous efficiency than by using ITO has been reported.[42] Since visible light transmittance of 90–93 % is required for the transparent electrode application of graphene, three or four layers of graphene are necessary. Hence, it is important to improve the controllability of the graphene synthesis for multilayers as well as a single layer.

For the realization of the mass production of graphene by a roll-to-roll method, it is required to reduce the thermal load on the apparatus and to attain a significant reduction of synthesis time. An attempt was made to reduce the thermal load on the apparatus by direct joule heating of the copper foil substrate and to demonstrate roll-to-roll thermal CVD synthesis of graphene at 950 °C by the Sony group.[43] In this example, winding speed of the copper foil substrate was 1.5 mm/sec, and further increase of speed is desired for high-throughput production. Also in order to suppress the microcracks due to thermal expansion and thermal contraction of the copper foil to improve the quality of the graphene, further reduction of the temperature is required.

We have developed plasma CVD of graphene to reduce the process temperature and the process time at the same time. By combining low temperature surface-wave plasma CVD with roll-to-roll transfer of copper foil substrate, high-throughput synthesis of graphene with winding speed of 5–10 mm/s was demonstrated by the AIST group.[9][10] The problem of plasma CVD of graphene is the crystal size (domain size) of 10 nm or smaller, which inhibits electrical conductivity. By the large growth rate and high nucleation density of plasma CVD, graphene growth in the two-dimensional direction is prevented, which causes stacking of small flakes in multiple layers and deterioration of the controllability of the number of layers.

In this study, we attempted to expand the size of graphene crystals and to improve the controllability of the number of layers by reducing the concentration of the carbon source used for graphene synthesis which is expected to suppress the nucleation density. Without supplying carbon-containing gas such as methane, as an ultralow concentration of carbon source, we utilized trace amount of carbon contained in

the copper foil and/or supplied from the environment in the reaction chamber. We attempted to expand the crystal size of graphene and improve the electrical conductivity by developing this method. Moreover, we attempted to synthesize AB-stacked bilayer graphene with good controllability in a high yield. This method combines joule heating and hydrogen plasma treatment for the copper foil substrate and it is aimed at the establishment of an industrially advantageous method at lower temperature and requiring shorter time as compared to the conventional thermal CVD method.

First of all, we performed only heat treatment at each temperature of 300, 400, 600, 800, and 1000 °C of the copper foil by using direct joule heating in 20 Pa hydrogen for 15 min in the reaction chamber and the foil was cooled down to room temperature. The size of the heat treated sample was 6×6 mm^2. A copper foil heated at each temperature was examined by Raman spectroscopy (Model: HORIBA XploRa, beam spot of 1 μm in diameter, excitation laser of 632 nm wavelength). It was tested whether graphene was synthesized by only the joule heat treatment in a hydrogen atmosphere as shown in Fig.8.

Hydrogen plasma treatment was performed in 30 sccm flow and 5 Pa for 30 s. The surface-wave microwave plasma with low electron temperature which was expected to reduce the ion bombardment was utilized for plasma treatment.

The synthesized graphene was transferred to a transparent polymer substrate to measure the electrical conductivity and the optical transmittance. The slightly-adhesive resin film was used as the transparent polymer substrate. The thickness of the resin film was 41–42 μm. After bonding the resin film and copper foil with graphene onto the surface of the copper foil substrate, the copper foil was removed by etching using an aqueous solution of ammonium persulfate (0.50 mol/ℓ).

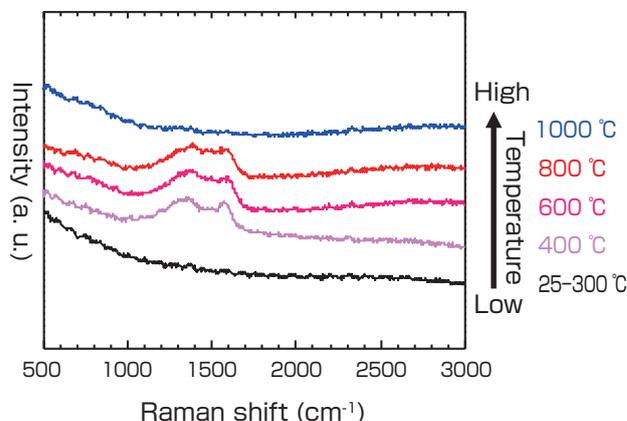The electrical characteristic of the synthesized graphene

Fig. 8 Raman spectrum of the copper foil heated from room temperature up to 1000 °C at hydrogen atmosphere[14]
Copyright (2014), with permission from Elsevier

was measured at 36 points by a four probe method for sheet resistance using gold alloy probes at 1 mm mesh over the sample area of 6×6 mm^2. The carrier mobility was estimated by Hall effect measurement in Van der Pauw geometry.[44]

Next, the transferred graphene on the polymer substrate was immersed in an isopropyl alcohol solution of gold chloride (20 mol/ℓ), and dried.

Figure 8 shows the Raman spectra of copper foil observed at room temperature after only the joule heating treatment in a hydrogen atmosphere. Although carbon-related signals in the Raman spectrum were not observed within the detection limit for the heat treatments lower than 300 °C, the spectra of copper foil subjected to the heat treatment at 400, 600, and 800 °C indicated the formation of amorphous carbon films[45] on the surface. Since carbon-containing gas such as methane was not introduced, there should be alternative carbon sources such as one dissolved in the copper foil and/or one supplied from the environment inside the reaction chamber.

The concentration of impurity carbon in the copper foil was examined by a combustion method, which has been estimated to be 5–31 ppm. The areal density of carbon atoms in graphene is 3.8×10^{15}/cm^2. If a graphene sheet with the highest impurity carbon concentration of 31 ppm is used, copper foil of 15 μm thickness is at least necessary to supply the carbon atoms to synthesize single layer graphene. Because the thickness of the copper foil in the present study was 6.3 μm, carbon atoms supplied from the environment in the reaction chamber must have been from an additional or main source of carbon atoms. The base pressure of the reaction chamber, which was evacuated by using oil-free turbo molecular pump system, was lower than 1.0×10^{-4} Pa. It was not clarified which was the main supplier of carbon, the copper foil or the environment in the reaction camber. In this paper, the discussion is based on both having the possibility.

The copper foil substrate was treated by the joule heating treatment of temperatures up to 1000 °C in hydrogen atmosphere without supplying any carbon gas sources. Raman spectra were measured at room temperature after the cooling of the copper foil substrate in a hydrogen atmosphere. As shown in Fig. 8, however, we could not observe the Raman peaks which indicate the graphene formation on the copper surface. The peaks from amorphous carbon at 1350 cm^{-1} and 1580 cm^{-1} were lost by the heating at 1000 °C. It was considered that it was because heat treatment was conducted at temperature close to the melting point of copper (1085 °C) under low pressure, and the precipitated carbon atoms decomposed or were lost with the evaporation of the copper foil surface.

Therefore, although amorphous carbon precipitation was observed at 400, 600, and 800 °C, there were no Raman

signals on the copper substrate pretreated at the temperature between 25 °C and 300 °C, and 1000 °C.

A Raman spectrum for only hydrogen plasma treatment for 30 s without heat treatment of copper foil is shown in Fig. 9(a). In this case, no peaks attributed to carbon related materials such as graphene and amorphous carbon were observed. Figure 9(c) shows a Raman spectrum from copper foil subjected to hydrogen plasma treatment for 30 s subsequent to the treatment by joule heating at 1000 °C. Although, the very weak G-band (1580cm^{-1}) and the D-band (1350 cm^{-1}) were observed, the 2D-band in the range of 2641–2681 cm^{-1} was not observed. This indicated that graphene was not formed at this temperature because an extremely small amount of carbon supply disappeared along with the evaporation of the copper foil substrate. Figure 9(b) shows Raman spectra from the copper foil substrate subjected to hydrogen plasma treatment for 30 s at 850 °C subsequent to the treatment by joule heating at 850 °C. Distinct G-band and 2D-band were observed with very low intensity of the D-band which indicated low defect.

Then, since in Fig. 9(b) it was shown that the 2D-band has different line width and intensity distribution, we analyzed it in more detail. As shown in Fig. 10, two kinds of graphene which have different full width at half maximum (FWHM) of the 2D-band were observed. We analyzed the 2D-band at 46 points in 12 samples which were synthesized under the same conditions using the curve fitting by a single Lorentzian peak and the sum of four single Lorentzian peaks as shown in Fig. 10(a) and (b), respectively, according to the fitting

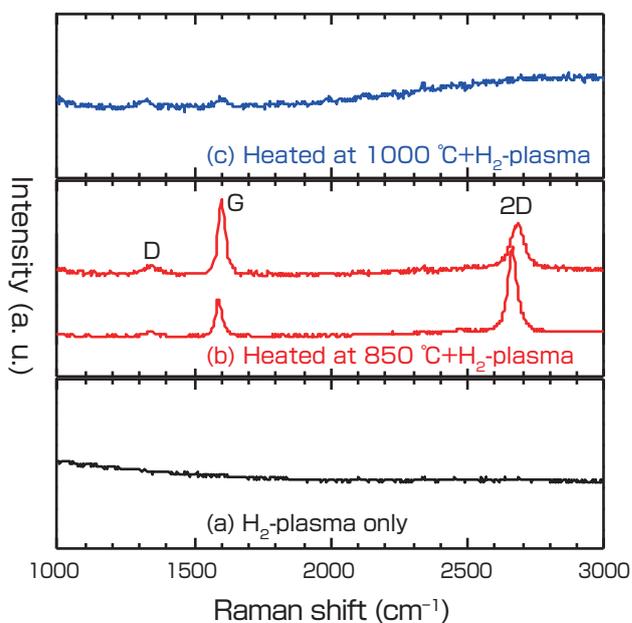
Fig. 9 Raman spectrum of the copper foil after hydrogen plasma treatment[14]
(a) only hydrogen plasma, (b) hydrogen plasma while heating at 850 C, and (c) hydrogen plasma while heating at 1000 C
Copyright (2014), with permission from Elsevier

method cited in References [46] and [47]. AB-stacked bilayer graphene is fitted by the sum of four Lorentzian peaks of the 2D-band with FWHM from 41.0–59.5 cm⁻¹ (Fig. 10(a)). On the other hand, a disoriented stacked bilayer graphene is fitted by a symmetric single Lorentzian peak with FWHM of 36.0–40.5 cm⁻¹ (Fig. 10(b)).

To examine the yield of AB-stacked bilayer and disoriented bilayer graphene, histograms of FWHM values of the 2D-band and Raman intensity of the 2D-band/G-band ratio are shown in Fig. 11. In the case of Raman intensity ratio (2D-band/G-band), the range of 0.7–2.7 is for AB-stacked bilayer graphene and 2.8–5.1 is for disoriented bilayer graphene. These results indicate a graphene yield of 60 % of AB-stacked bilayer graphene and 40 % of disoriented bilayer graphene on the copper foil substrate synthesized by hydrogen plasma treatment during heat treatment by joule heating. The D-band (1338cm⁻¹) due to the defects in graphene crystal was observed with very weak intensity.

With the identification of the number of layers and the stacked structure by Raman spectroscopy, single layer graphene and trilayer graphene were not observed in all samples synthesized by this plasma treatment condition. The crystal size of graphene was about 100 nm by estimated Raman intensity D-band/G-band ratio. (Described later) While the crystal size of synthesized graphene by using carbon source gas of the previous method was less than 10 nm, it is possible to definitely improve the crystal size by plasma CVD using a carbon source of ultralow concentration of the present method. In addition, it is suggested that this method is quite suitable for industrial continuous production such as the high-throughput roll-to-roll method from the point of view of very short process time and high growth rate.

Then, the synthesized graphene in this study was transferred to a slightly-adhesive resin film in order to measure the optical transmittance. Fig. 12 shows the optical transmittance

Fig. 10 Raman spectrum fitting analysis of 2D-band[14]
(a) AB-stacked bilayer graphene which fits sum of four Lorentzian peaks, and (b) disorder-stacked bilayer graphene which fits the symmetric peak
Copyright (2014), with permission from Elsevier

Fig. 11 The histograms of FWHM values of 2D-band and intensity ration of 2D-band/G-band[14]
Red bar is AB-stacked bilayer graphene and blue bar is disorder-stacked bilayer graphene.
Copyright (2014), with permission from Elsevier

Table 1. Mobility, FWHM of 2D-band, yield of AB-stacked bilayer graphene[14]
Copyright (2014), with permission from Elsevier

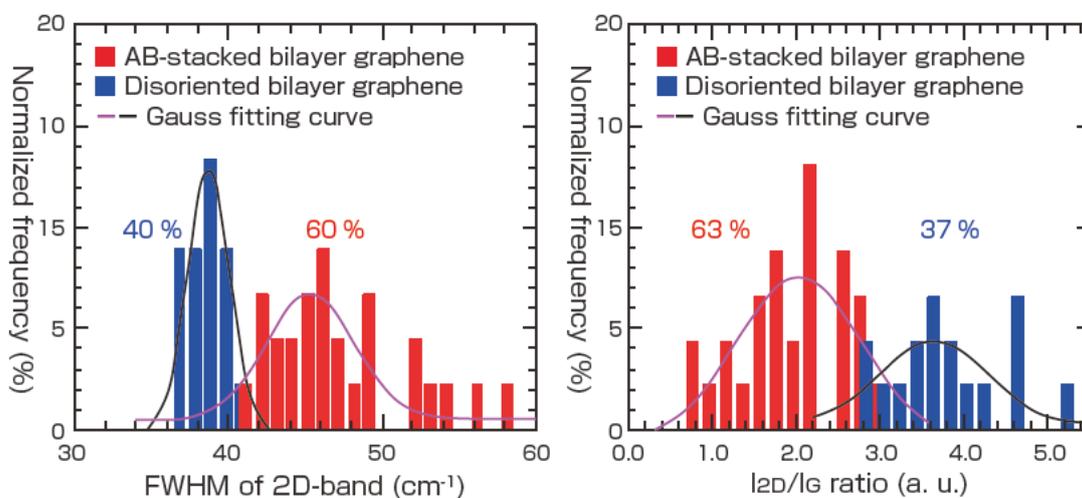| Growth process (Substrate & temperature)	Mobility (cm²/Vs)	FWHM of 2D-band for AB-stacked (cm⁻¹)	Yield of AB-stacked (%) [Yield of disoriented (%)]	Reference
Cu(25 μm), 1050 ℃	1500-4400	47.4-62.0	90[10]	L.Liu et al.,ACS Nano.6, 8241(2012)
Cu(25 μm), 1000 ℃	350-400	—	67*1	K. Yan et al.,Nano Lett.11,6(2011)
Cu(25 μm), 1000 ℃	580	45.0-53.0	99*2	S. Lee et al.,Nano Lett.10,4702(2010)
Cu(1.2 μm)-Ni(0.4 μm), 920 ℃	3485	38.0-50.0	98*3	W.Liu et al.,Chem. Mater.26,907(2014)
Cu(25 μm), 980 ℃	—	—	70[30]	L.Brown et al.,Nano. Lett.12,1609(2012)
Cu(6.3 μm), 850 ℃	1000	41-59.5	60[40]	This study

∗1   Small amount of trilayer graphene was also observed.
∗2   The rest of AB-stacked bilayer graphene was 32 % of single layer graphene.
∗3   The amount of trilayer graphene was 1 %.

of a slightly-adhesive resin film (a), a graphene/slightly-adhesive resin film (b) and the ratio spectrum of only graphene (c) which is calculated by dividing (a) by (b). The optical transmittance of the slightly-adhesive resin film was 91.5 % and the graphene/slightly adhesive resin film was 86.4 % at wavelength of 550 nm. The only graphene film transmittance was 94.5 % at wavelength of 550 nm. It was found that the layer number corresponded to 2 layers estimated from 2.3 % transmittance loss of single layer graphene.[49]

The reported values of the mobility of bilayer graphene are listed together with the yield, synthesis temperature, and FWHM of AB-stacked bilayer graphene in Table 1.
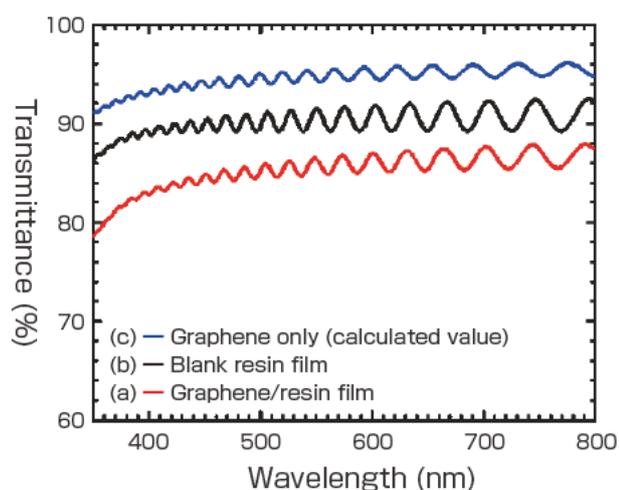
In this study, the synthesis temperature is lower and the synthesis time is shorter compared to past reported values. However, the carrier mobility of 1000 cm^2/Vs obtained at room temperature showed significant improvement from the one around 100 cm^2/Vs[13] for previous plasma CVD. Higher mobility values than ours have been reported by Liu *et al*. of 1500−4400 cm^2/Vs[48] and Liu et al. of 3845 cm^2/Vs.[50] It is considered that the quality of bilayer graphene synthesized by plasma CVD can be improved further.

The sheet resistance of synthesized graphene was 951 Ω on average in this study. This sample was doped by gold chloride. Figure 13 shows the sheet resistance map after being doped by gold chloride. As shown in Fig. 13, the average sheet resistance of a 6×6 mm^2 sheet was 130 Ω and the lowest sheet resistance was less than 100 Ω.

By the development of plasma CVD using ultralow carbon

Fig. 12 Optical transmittance of base resin film and graphene/resin films[14]
Transmittance of graphene only (c) is calculated by dividing graphene/resin film (a) by blank resin film (b). Interference fringes of (a) and (b) are due to a very thin resin film.
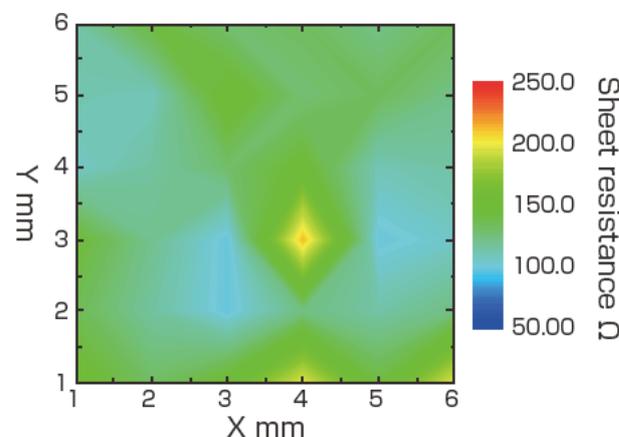Copyright (2014), with permission from Elsevier

Fig. 13 The sheet resistance map of graphene after wet doping with gold chloride[14]
Copyright (2014), with permission from Elsevier

source, the crystalline quality of synthesized graphene was significantly improved, and the controllability of the number of layers was also improved. As carbon sources for graphene synthesis, we utilized trace amount of carbon contained in the copper foil and carbon supplied from the environment in the reaction chamber. Graphene of 60 % AB-stacked bilayer graphene and 40 % of disoriented bilayer graphene was synthesized. The sheet resistance of bilayer graphene was 951 Ω on average, and the carrier mobility was 1000 cm^2/Vs at room temperature. The sheet resistance of 130 Ω was attained after doping with a gold chloride solution.

4 The development of large area graphene synthesis technology

We attempted to synthesize A4 size large area graphene by combining plasma treatment and joule heating using ultralow carbon sources developed in this study. Figure 14 shows an A4 size large area graphene transparent conductive film which was synthesized on a copper foil substrate using the above method and then transferred onto a PET film. The optical transmittance of only graphene was 92 % (3.6 layers) and the sheet resistance was less than 500 Ω without doping. In this way, we succeeded in fabricating a A4 size large area graphene transparent conductive film using plasma treatment of ultralow carbon sources developed in this study.

5 The relationship between Hall mobility and crystalline quality

We examined the correspondence between Hall mobility and crystalline quality by Raman spectroscopy measurements of van der Pauw devices which measured the Hall mobility. Here, the Raman intensity ratio of the D-band and the
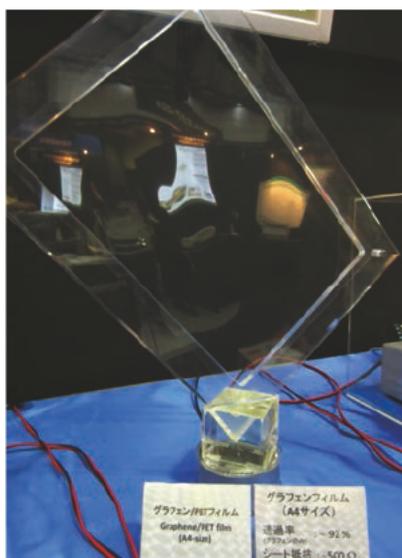
G-band was an index for graphene crystalline quality. The relationship between the Hall mobility and the intensity ratio of the D-band/G-band is shown in Fig. 15. In this study, we prepared two graphene films. One was synthesized by plasma CVD using methane and hydrogen gas, the other was synthesized by combining plasma treatment and the joule heating method without using methane gas carried out in this study. In the case of plasma CVD of the previous method, the intensity ratio of the D-band/G-band was higher and mobility was 10–100 cm^2/Vs. On the other hand, in the case of the novel method, the intensity of the D-band/G-band was lower and mobility was 100–1000 cm^2/Vs, and we succeeded in achieving 10 times larger electric conductivity than the previous method. From the intensity ratio of Raman signals of the D-band and the G-band, it was possible to estimate the graphene domain size.[51] In the case of plasma CVD of the previous method, the estimated graphene domain size was 17 nm. On the other hand, in the case of the novel method which combined hydrogen plasma treatment and joule heating, it was 170 nm. Also from this result, we confirmed that the domain size had expanded to 10 times larger than the previous method.

6 Estimation of domain size by dark-field TEM

To directly estimate the domain size of the synthesized graphene film by plasma treatment of this study, we measured the graphene film by dark-field TEM. Graphene samples transferred to a TEM grid using polymethyl methacrylate (PMMA) were prepared. Figure 16(a) shows a bright-field TEM image, and Fig. 16(b) shows the selected area electron diffraction pattern (SAED). The graphene film seemed to be relatively uniform in the bright-field TEM image, but many family spots were observed in the SAED. The results suggest that several domains with different orientations exist. The

Fig. 14 A4 size large area graphene transparent conductive film
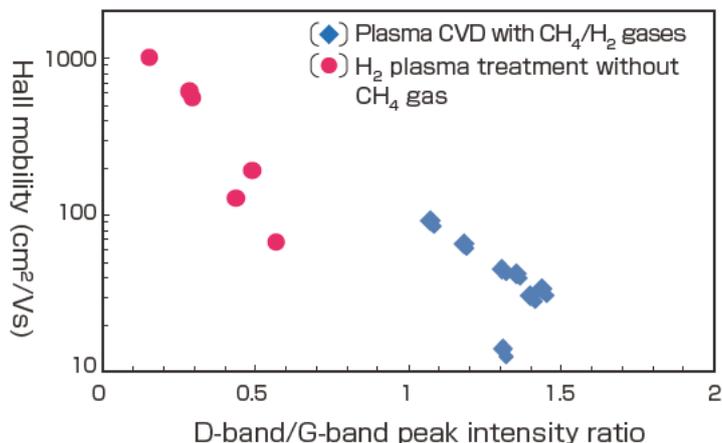Transmittance : 92 % and sheet resistance : less than 500 Ω

Fig. 15 The relationship between the Hall mobility and Raman intensity D-band/G-band ratio[15]
◆ Plasma CVD using CH$_4$/H$_2$ gas mixture, ● Hydrogen plasma treatment without CH$_4$ gas
Copyright (2015), with permission from Elsevier

Table 2. Comparison table of graphene synthesis by plasma CVD and thermal CVD

Plasma CVD	Thermal CVD

· Low temperature process
· Large area deposition
  (Deposition area increases by antenna)
· Wide layer control range
· High growth rate and continuous deposition
· High throughput
  (Integration of pretreatment and synthesis process)
· Low cost
	· High temperature process
	· Deposition area is limited by CVD furnace size
	· Narrow layer control range
	· Low growth rate
	· Low throughput
	  (Pretreatment and synthesis process are not integrated)
	· High cost

dark-field TEM images of each spot are shown in Fig. 16(c) and (d). Both figures suggest that the domain size is about 100 nm, which is consistent with the domain size estimated from the Raman measurement.

7 Comparison of graphene synthesis by plasma CVD and thermal CVD

Finally, based on results obtained in this study, comparison of graphene synthesis by plasma CVD and thermal CVD methods is shown in Table 2.

8 Summary and Future Perspectives

In this paper, we reported the attempt of the establishment of high-throughput plasma-enhanced CVD for high-quality graphene. By using plasma CVD methods, we elucidated the mechanism of attaining high purity of the copper foil surface by He/H$_2$ plasma pretreatment and the suppression of silicon impurities from the quartz window. Furthermore, we developed a plasma CVD method using ultralow carbon

sources for reduction of nucleation density, and the selective bilayer graphene synthesis was attained combining plasma CVD and joule heating. The grain size of graphene was expanded to 10 times and the Hall mobility was improved to 1000 cm^2/Vs.

Though we did not mention in detail the difference between plasma CVD and thermal CVD in this paper, we have recently clarified the advantages of plasma CVD from the view point of reduction of process time and process temperature.[16]

In the near future, we want to push forward the establishment of a high-throughput plasma CVD method for high-quality and large-area graphene which exceeds the graphene quality synthesized by the main current high-temperature thermal CVD methods.

Acknowledgements

References

[1] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva and A. A. Firsov: Electric field effect in atomically thin carbon films, *Science*, 306, 666–669 (2004).

[2] A. Kumar and C. Zhou: The race to replace tin-doped indium oxide: Which material will win?, *ACS Nano*, 4 (1), 11–14 (2010).

[3] A. K. Geim: Graphene: Status and prospects, *Science*, 324, 1530–1534 (2009).

[4] K.H. Liao, A. Mittal, S. Bose, C. Leighton, K. A. Mkhoyan and C. W. Macosko: Aqueous only route toward graphene from graphite oxide, *ACS Nano*, 5 (2), 1253–1258 (2011).

[5] C. Virojanadara, M. Syväjarvi, R. Yakimova, L. I. Johansson, A. A. Zakharov and T. Balasubramanian: Homogeneous large-area graphene layer growth on 6H-SiC(0001), *Phys. Rev.*, B 78, 245403-1–245403-6 (2008).

[6] X. Li, W. Cai, J. An, S. Kim, J. Nah, D. Yang, R. Piner, A. Velamakanni, I. Jung, E. Tutuc, S. K. Banerjee, L. Colombo and R. S. Ruoff: Large-area synthesis of high-quality and uniform graphene films on copper foils, *Science*, 324, 1312–1314 (2009).
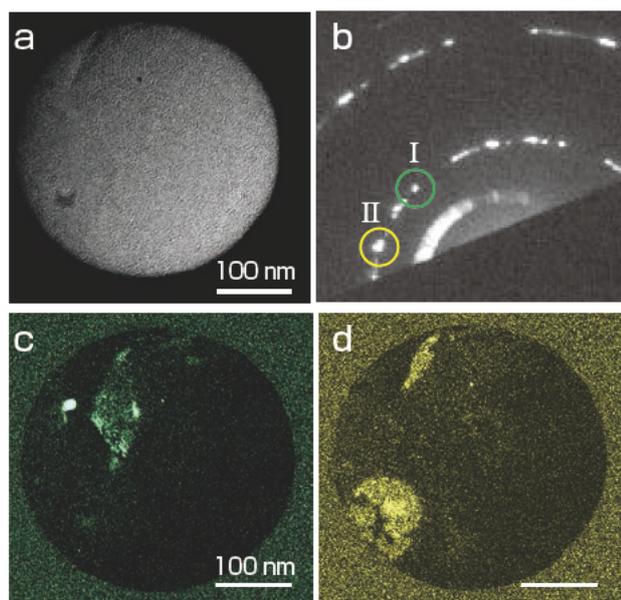

Fig. 16 (a) TEM image, (b) the selected area electron diffraction pattern, and (c) (d) The dark-field TEM images[15]
Copyright (2015), with permission from Elsevier

[7] S. Bae, H. Kim, Y. Lee, X. Xu, J. S. Park, Y. Zheng, J. Balakrishnan, T. Lei, H. R. Kim, Y. I. Song, Y.J. Kim, K. S. Kim, B. Özyilmaz, J.H. Ahn, B. H. Hong and S. Iijima: Roll-to-roll production of 30-inch graphene films for transparent electrodes, *Nature Nanotechnology*, 5, 574–578 (2010).

[8] J. Kim, M. Ishihara, Y. Koga, K. Tsugawa, M. Hasegawa and S. Iijima: Low-temperature synthesis of large-area graphene-based transparent conductive films using surface wave plasma chemical vapor deposition, *Appl. Phys. Lett.*, 98, 091502-1–091502-3 (2011).

[9] T. Yamada, M. Ishihara, J. Kim, M. Hasegawa and S. Iijima: A roll-to-roll microwave plasma chemical vapor deposition process for the production of 294 mm width graphene films at low temperature, *Carbon*, 50, 2615–2619 (2012).

[10] T. Yamada, J. Kim, M. Ishihara and M. Hasegawa: Low-temperature graphene synthesis using microwave plasma CVD, *J. Phys. D: Appl. Phys.*, 46, 063001–063008 (2013).

[11] T. Yamada, M. Ishihara and M. Hasegawa: Low temperature graphene synthesis from poly(methyl methacrylate) using microwave plasma treatment, *Appl. Phys. Express*, 6, 115102-1–115102-3 (2013).

[12] Y. Okigawa, K. Tsugawa, T. Yamada, M. Ishihara and M. Hasegawa: Electrical characterization of graphene films synthesized by low-temperature microwave plasma chemical vapor deposition, *Appl. Phys. Lett.*, 103, 153106-1–153106-4 (2013).

[13] R. Kato, K. Tsugawa, T. Yamada, M. Ishihara and M. Hasegawa: Improvement of multilayer graphene synthesis on copper substrate by microwave plasma process using helium at low temperatures, *Jpn. J. Appl. Phys.*, 53, 015505-1–015505-6 (2014).

[14] R. Kato, K. Tsugawa, Y. Okigawa, M. Ishihara, T. Yamada and M. Hasegawa: Bilayer graphene synthesis by plasma treatment of copper foils without using a carbon-containing gas, *Carbon*, 77, 823–828 (2014).

[15] Y. Okigawa, R. Kato, T. Yamada, M. Ishihara and M. Hasegawa: Electrical properties and domain sizes of graphene films synhesized by microwave plasma treatment under a low carbon concentration, *Carbon*, 82, 60–66 (2015).

[16] R. Kato, S. Minami, Y. Koga and M. Hasegawa: High growth rate chemical vapor deposition of graphene under low pressure by RF plasma assistance, *Carbon*, 96, 1008–1013 (2016).

[17] Z. Luo, Y. Lu, D. W. Singer, M. E. Berck, L. A. Somers, B. R. Goldsmith and A. T. C. Johnson: Effect of substrate roughness and feedstock concentration on growth of wafer-scale graphene at atmospheric pressure, *Chem. Mater.*, 23, 1441–1447 (2011).

[18] G. H. Han, F. Günes, J. J. Bae, E. S. Kim, S. J. Chae, H. -J. Shin, J. Y. Choi, D. Pribat and Y. H. Lee: Influence of copper morphology in forming nucleation seeds for graphene growth, *Nano Lett.*, 11, 4144–4148 (2011).

[19] M. L. Hartenstein, S. J. Christopher and R. K. Marcus: Evaluation of helium-argon mixed gas plasmas for bulk and depth-resolved analyses by radiofrequency glow discharge atomic emission spectroscopy, *J. Anal. At. Spectrom.*, 14, 1039–1048 (1999).

[20] P. Sigmund: Theory of sputtering. I. Sputtering yield of amorphous and polycrystalline targets, *Phys. Rev.*, 184, 383–416 (1969).

[21] D-H. Kim, G-H. Lee, S. Y. Lee and D. H. Kim: Atomic scale simulation of physical sputtering of silicon oxide and silicon nitride thin films, *J. Cryst. Growth*, 286, 71–77 (2006).

[22] H. Sugai, I Ghanashev and M. Nagatsu: High-density flat

[23] H. Sugai, I. Ghanashev and K. Mizuno: Transition of electron heating mode in a planar microwave discharge at low pressures, *Appl. Phys. Lett.*, 77 (22), 3523–3525 (2000).

[24] K. Tsugawa, M. Ishihara, J. Kim, M. Hasegawa and Y. Koga: Large-area and low-temperature nanodiamond coating by microwave plasma chemical vapor deposition, *New Diamond Front. Carbon Technol.*, 16 (6), 337–346 (2006).

[25] K. Tsugawa, M. Ishihara, J. Kim, Y. Koga and M. Hasegawa: Nanocrystalline diamond film growth on plastic substrates at temperatures below 100 °C from low-temperature plasma, *Phys. Rev.*, B82, 125460-1–125460-8 (2010).

[26] J. Kim, K. Tsugawa, M. Ishihara, Y. Koga and M. Hasegawa: Large-area surface wave plasmas using microwave multi-slot antennas for nanocrystalline diamond film deposition, *Plasma Sources Sci. Technol.*, 19, 015003-1–015003-5 (2010).

[27] K. Tsugawa, S. Kawaki, M. Ishihara, J. Kim, Y. Koga, H. Sakakita, H. Koguchi and M. Hasegawa: Nanocrystalline diamond growth in surface-wave plasma, *Diamond & Related Materials*, 20, 833–838 (2011).

[28] Z. H. Gan, G. Q. Yu, B. K. Tay, C. M. Tan, Z. W. Zhao and Y. Q. Fu: Preparation and characterization of copper oxide thin films deposited by filtered cathodic vacuum arc, *J. Phys. D: Appl. Phys.*, 37 (1), 81–85, (2004).

[29] J. Ghijsen, L. H. Tjeng, J. van Elp, H. Eskes, J. Westerink, G. A. Sawatzky and M. T. Czyzyk: Electronic structure of Cu_2O and CuO, *Phys. Rev.*, B 38, 11322–11330 (1988).

[30] C. C. Chusuei, M. A. Brookshier and D. W. Goodman: Correlation of relative X-ray photoelectron spectrscopy shake-up intensity with CuO particle size, *Langmuir*, 15, 2806–2808 (1999).

[31] B. Balamurugan, B. R. Mehta and S. M. Shivaprasad: Surface-modified CuO layer in size-stabilized single-phase Cu_2O nanoparticles, *Appl. Phys. Lett.*, 79 (19), 3176–3178 (2001).

[32] M. Yin, C-K. Wu, Y. Lou, C. Burda, J. T. Koberstein, Y. Zhu and S. O'Brien: Copper oxide nanocrystals, *J. Am. Chem. Soc.*, 127, 9506–9511 (2005).

[33] S. K. Chawla, N. Sankarraman and J. H. Payer: Diagnostic spectra for XPS analysis of Cu-O-S-H compounds, *J. Electr. Spectrosc. Relat. Phenom.*, 61, 1–18 (1992).

[34] B. Schnyder, T. Lippert, R. Kötz, A. Wokaun, V-M. Graubner and O. Nuyken: UV-irradiation induced modification of PDMS films investigated by XPS and spectroscopic ellipsometry, *Surf. Sci.*, 532–535, 1067–1071 (2003).

[35] L-A. O'Hare, A. Hynes and M. R. Alexander: A methodology for curve-fitting of the XPS Si 2*p* core level from thin siloxane coatings, *Surf. Inter. Analy.*, 39, 926–936 (2007).

[36] J-H. Lin, H-C. Chiu, Y-R. Lin, T-K. Wen, R. A. Patil, R. S. Devan, C-H. Chen, H-W. Shiu, Y. Liou and Y-R. Ma: Electrical and chemical chracteristics of probe-induced two-dimensional SiO_X protrusion layers, *Appl. Phys. Lett.*, 102, 031603-1–031603-5 (2013).

[37] M. J. Webb, P. Palmgren, P. Pal, O. Karis and H. Grennberg: A simple method to produce almost perfect graphene on highly oriented pyrolytic graphite, *Carbon*, 49, 3242–3249 (2011).

[38] M. Finšgar, J. Kovač and I. Milošev: Surface analysis of 1-hydroxybenzotriazole and benzotriazole adsorbed on Cu by X-ray photoelectron spectroscopy, *J. Electrochem. Soc.*,

157, C52–C60 (2010).

[39] R. M. Souto, V. Fox, M. M. Laz, M. Pérez and S. González: Some experiments regarding the corrosion inhibition of copper by benzotriazole and potassium ethyl xanthate, *J. Electroanaly. Chem.*, 411, 161–165 (1996).

[40] H. Kinoshita, M. Umeno, M. Tagawa and N. Ohmae: Hyperthermal atomic oxygen beam-induced etching of HOPG (0001) studied by X-ray photoelectron spectroscopy and scanning tunneling microscopy, *Surf. Sci.*, 440, 49–59 (1999).

[41] T. Terasawa and K. Saiki: Growth of graphene on Cu by plasma enhanced chemical vapor deposition, *Carbon*, 50, 869–874 (2012).

[42] T-H. Han, Y. Lee, M-R. Choi, S-H. Woo, S-H. Bae, B. H. Hong, J-H. Ahn and T-W. Lee: Extremely efficient flexible organic light-emitting diodes with modified graphene anode, *Nat. Photon.*, 6, 105–110 (2012).

[43] T. Kobayashi, M. Bando, N, Kimura, K. Shimizu, K. Kadono, N. Umezu, K. Miyahara, S. Hayazaki, S. Nagai, Y. Mizuguchi, Y. Murakami and D. Hobara: Production of a 100-m-long high-quality graphene transparent conductive film by roll-to-roll chemical vapor deposition and transfer process, *Appl. Phys. Lett.*, 102, 023112-1–023112-4 (2013).

[44] L. J. van der Pauw: A method of measuring specific resistivity and Hall effect of discs of arbitrary shape, *Philips Res. Repts.*, 13, 1–9 (1958).

[45] J. Robertson: Diamond-like amorphous carbon, *Mater. Sci. Eng.*, R37, 129–281 (2002).

[46] L. G. Cançado, A. Reina, J. Kong and M. S. Dresselhaus: Geometrical approach for the study of *G'* band in the Raman spectrum of monolayer graphene, bilayer graphene, and bulk graphite, *Physical Review*, B77, 245408-1–245408-9 (2008).

[47] A. C. Ferrari, J. C. Meyer, V. Scardaci, C. Casiraghi, M. Lazzeri, F. Mauri, S. Piscanec, D. Jiang, K. S. Novoselov, S. Roth and A. K. Geim: Raman spectrum of graphene and graphene layers, *Phys Rev Lett.*, 97, 187401-1–187401-4 (2006).

[48] L. Liu, H. Zhou, R. Cheng, W. J. Yu, Y. Liu, Y. Chen, J. Shaw, X. Zhong, Y. Huang and X. Duan: High-yield chemical vapor deposition growth of high-quality large-area AB-stacked bilayer graphene, *ACS Nano.*, 6, 8241–8249 (2012).

[49] R. R. Nair, P. Blake, A. N. Grigorenko, K. S. Novoselov, T. J. Booth, T. Stauber, N. M. R. Peres and A. K. Geim: Fine structure constant defines visual transparency of graphene, *Science*, 320, 1308 (2008).

[50] W. Liu, S. Kraemer, D. Sarker, H. Li, P. M. Ajayan and K. Banerjee: Controllable and rapid synthesis of high-quality and large-area Bernal stacked bilayer graphene using chemical vapor deposition, *Chem. Mater.*, 26, 907–915 (2014).

[51] L. G. Cançado, K. Takai, T. Enoki, M. Endo, Y. A. Kim, H. Mizusaki, A. Jorio, L. N. Coelho, R. M.-Paniago and M. A. Pimenta: General equation for the determination of the crystallite size L_a of nanographite by Raman spectroscopy, *Appl. Phys. Lett.*, 88, 163106-1–163106-3 (2006).

Authors

Masataka Hasegawa
Completed the doctor's program at the Graduate School of Engineering, Kyoto University in 1990. Joined the Electrotechnical Laboratory, Agency of Industrial Science and Technology in 1990. Currently, Group Leader, Carbon-Based Thin Film Materials Group, Nanomaterials Research Institute, AIST. General Manager, Graphene Division Project Headquarters, Technology Research Association for Single Wall Carbon Nanotubes (TASC) from 2011 to present. Engages in the R&D for electroconductivity control of diamond semiconductor, CVD growth on monocrystal diamond, CVD synthesis of nanocrystal diamond thin film, and CVD synthesis for graphene. In this paper, was in charge of overseeing the overall research topics and the development of plasma CVD device for graphene and its synthesis method.

Kazuo Tsugawa
Graduated from the Department of Electronics and Communication Engineering, School of Science and Engineering, Waseda University in 1992. Withdrew from the doctor's program at the Department of Electronics, Information and Communication Engineering, Graduate School of Science and Engineering, Waseda University in 1998. Assistant, School of Science and Engineering, Waseda University from 1998 to 2000. Researcher, Japan Fine Ceramics Center from 2000 to 2003; Postdoctoral Fellow and Technical Staff at the Research Center for Advanced Carbon Materials, Nanocarbon Research Center, and CNT Application Research Center, AIST from 2003 to 2011; and Researcher, Graphene Division, Technology Research Association for Single Wall Carbon Nanotubes from 2010 to 2013. Part-time Lecturer, Faculty of Science and Engineering, Waseda University from 2010 to 2013. Application Manager, Seki Diamond Systems, Cornes Technologies Ltd. from 2013 to present. Doctor (Engineering). In this paper, was in charge of the CVD synthesis of graphene and its evaluation.

Ryuichi Kato
Graduated from the College of Engineering Sciences, University of Tsukuba in 2008. Withdrew from the master's course at the Department of Materials Science, Graduate School of Pure and Applied Sciences, University of Tsukuba in 2011. Currently enrolled in the doctor's program at the Department of Materials Science, Graduate School of Pure and Applied Sciences, University of Tsukuba. Researcher, Graphene Division, Technology Research Association for Single Wall Carbon Nanotubes (TASC) from 2011 to present. In this paper, was in charge of the development of plasma pretreatment technology for graphene copper substrate using helium, and the synthesis and analysis of double-layered graphene using low-concentration carbon source.

Yoshinori Koga
Graduated from the Department of Applied Chemistry, Faculty of Science and Engineering, Waseda University in 1969. Withdrew from the doctor's program at the Department of Applied Chemistry, Graduate School of Science and Engineering, Waseda University in 1974. Joined the Government Chemical Industrial Research Institute, Tokyo, Agency of Industrial Science and Technology in 1974. Doctor (Science) in 1974. Deputy Manager, Planning Office and Section Chief, Polymer Analysis Section, National Chemical Laboratory for Industry. Manager of Molecular Measurement Laboratory and Manager of Laser Reaction Lab, National Institute of Materials and Chemical Research in 1993. Deputy Director, Research Center for Advanced Carbon Materials, AIST from 2001 to 2008. Part-time Lecturer, Graduate School of Science and Technology, Nihon University from 2010 to 2014; and Part-time Lecturer, Graduate School of Engineering, Mie University from 2015 to present. Researcher, Graphene Division, Technology Research Association for Single Wall

Carbon Nanotubes (TASC) from 2011 to present. In this paper, was in charge of the plasma analysis and double-layered graphene analysis.

Masatou ISHIHARA
Graduated from the Department of Industrial Chemistry (currently Pure and Applied Chemistry), Faculty of Science and Technology, Tokyo University of Science in 1991. Researcher, Research Department, Kurami Works, Nippon Mining and Metals Co., Ltd. (currently JX Nippon Mining and Metals Corporation). Completed the doctor's program at the Department of Materials Science and Technology, Graduate School of Industrial Science and Technology, Tokyo University of Science in 1997. Doctor (Engineering). Postdoctoral Fellow, Japan Science and Technology Agency in 1997. Joined the National Institute of Materials and Chemical Research, Agency of Industrial Science and Technology in 2000. Researcher, Research Center for Advanced Carbon Materials, AIST in 2001. Senior Researcher, Carbon-Based Thin Film Materials Group, Nanomaterials Research Institute, AIST from 2015 to present. In this paper, was in charge of the substrate pretreatment by wet method, the transfer of graphene to transparent substrate, the development of use of transparent conductive films, and others.

Takatoshi YAMATAKA
Graduated from the Department of Electronics, School of Engineering, Tokai University in 1996. Completed the master's program at the Department of Electronics, Graduate School of Engineering, Tokai University in 1998. Assistant, College of Science and Engineering, Aoyama Gakuin University in 1998. Assistant, Institute of Multidisciplinary Research for Advanced Materials, Tohoku University in 2003. Joined AIST in 2004. Currently, Senior Researcher, Carbon-Based Thin Film Materials Group, Nanomaterials Research Institute. In this paper, was in charge of the impurity analysis for plasma CVD graphene and the evaluation of electrical characteristics.

Yuki OKIGAWA
Graduated from the Department of Electrical Electronic Engineering and Information Engineering, School of Engineering, Nagoya University in 2007. Completed the doctor's program at the Department of Quantum Science and Energy Engineering, Graduate School of Engineering, Nagoya University in 2012. Doctor (Engineering). Joined the CNT Application Research Center, AIST in 2012. Currently, Researcher, Carbon-Based Thin Film Materials Group, Nanomaterials Research Institute. In this paper, was in charge of the fabrication of device using graphene and the evaluations of electroconductivity characteristic and crystallization property of the device.

Discussions with Reviewers

1 Overall
Comment (Shuji Abe, Musashino University)
This paper is very convincing as it experimentally investigates details of plasma CVD synthesis technology for graphene developed by the authors employing various original ideas, and then it empirically describes high quality graphene synthesis that has become possible through such efforts.

Comment (Hiroaki Hatori, AIST)
The technology that enables high-quality, high-speed, and large-area synthesis of graphene is the key in the realization of long-awaited transparent electrodes, and I think it is very interesting to see a discussion of such a technological development process in a synthesiological light. This paper is significant in that it shows the course of R&D for the establishment of high-quality high-throughput synthesis technology for graphene transparent conductive films using plasma CVD.

2 Prospects for industrial production
Question and Comment (Shuji Abe)
The "ultralow carbon concentration plasma CVD" does not use carbon-containing gas at all, and the materials for graphene are the carbon supplied from the impurities in copper foil and environment inside the reaction chamber, but these are factors that cannot be controlled by engineering. Certainly, we see that the crystal size is improved and the plasma treatment time is shortened in the laboratory, but do you have prospect toward industrial production?

Answer (Masataka Hasegawa)
Since it has become clear that the improvement of crystal size is due to the reduction of nucleus formation site in ultralow carbon concentration, monitoring the impurities in the production process is important, and forming good quality graphene films by reducing the number of nucleus formation sites is extremely important in future industrial processes. Therefore, the supply of excessive carbon reduces the quality of graphene, and impurity monitoring from the reaction chambers and others will be necessary in the industrial production. Currently, we are conducting an A4-size bench scale experiment, and continuous supply of carbon sources at optimal concentration will become necessary for large-scale continuous film forming.

3 Technological selection for achieving the goal
Question and Comment (Hiroaki Hatori)
In this paper, the background of development, the scenario, and the results based on this scenario are summarized for each elemental technology including the solution for impurity incorporation, the improvement of quality by reduction of graphene nucleus formation density, and the development of selective synthesis of double-layered graphene. Ultimately, you succeeded in the synthesis of a large-area transparent graphene conductive film. On the other hand, from the perspective of technological selection toward the final goal of realizing the transparent graphene electrode, I think the readers will better understand the overall scenario by which the authors achieved success in developing the large-area transparent graphene conductive film if you discuss the differences of your technology against the thermal CVD method that you mention partially in this paper, and make contrasts with other competing technologies.

Answer (Masataka Hasegawa)
We created and inserted a table comparing the plasma CVD and the conventional thermal CVD in Chapter 7, to allow easy understanding of the superiority of the high-throughput plasma CVD method.

Radioactive cesium decontamination technology for ash

— Utilization and application of nanoparticles as an adsorbent —

Tohru Kawamoto[1*], **Hisashi Tanaka**[1], **Yukiya Hakuta**[1], **Akira Takahashi**[1], **Durga Parajuli**[1], **Kimitaka Minami**[1], **Tetsuo Yasutaka**[2] and **Tatsuya Uchida**[1]

The accident at the Fukushima Daiichi Nuclear Power Station in 2011 spurred rapid research and development at AIST for radioactive cesium decontamination systems. In this paper, we introduce the development of an ash-decontamination technology that uses Prussian blue (PB) nanoparticles. We developed all aspects of the system using a combination of fundamental technologies, which included optimization of the PB nanoparticle structure for use as a cesium adsorbent, composite fabrication as granules for use as an adsorbent, and extraction of radioactive cesium from contaminated ash. All aspects of development were achieved rapidly through close collaboration among materials science, computational science, and geology researchers. Collaboration with private companies was also effective.

Keywords : Prussian blue, nanoparticle, radioactive cesium, decontamination, ash

1 Background: Radiation leakage accident and AIST efforts

As a consequence of the great earthquake which occurred on March 11, 2011, a giant tsunami struck the Fukushima Daiichi Nuclear Power Plant operated by Tokyo Electric Power Company. In the aftermath, the nuclear reactors, which could not be cooled, leaked radioactive materials. Most of those leaked materials had a low boiling point, which exacerbated their release: an estimated 1.6×10^{17} Bq of iodine−131 and 1.5×10^{17} Bq of cesium−137 were ejected into the environment.[1] Because iodine and cesium exist as salt compounds at room temperature, they fell on the ground to contaminate the soil, or dissolved in river and sea waters. The respective half-lives of cesium−134 and cesium−137 are approximately two years and 30 years. Therefore, their effects are expected to persist for a long time. The Japanese government has held the decontamination of radioactive cesium from the environment as an urgent task, and has concentrated on research and development to achieve that objective.

Great efforts for decontamination have been undertaken at AIST for various developments, such as those of decontamination technology for contaminated water, soil, and incinerated ash using Prussian blue (PB) nanoparticles,[2]–[6] of a concentrator for analyzing ultra-trace radioactive materials in environmental water,[7][8] of reference materials to evaluate brown rice contamination,[9] of dynamic evaluation methods for radioactive cesium in the environment,[10][11] and of decontamination cost estimation.[12] We specifically examined the development of decontamination and measurement technologies using PB nanoparticles having high adsorption capacities for radioactive cesium.

Decontamination technology is an extremely urgent topic. Therefore, R&D has been conducted more rapidly than a regular schedule might allow. Our core material is PB nanoparticles. Although R&D activities are mainly conducted from the standpoint of materials science, for the practical application of decontamination technology, it has also been necessary to combine diverse specialties such as chemical engineering, geo-engineering, and agriculture. Because AIST is a research institute, it cannot engage in final commercial projects. Therefore, the developed technologies must be transferred to a company to carry out commercial tasks. It is also necessary to pursue coordination with the national government and local governments, particularly with efforts of coordination with the local area in which the pilot plant tests would be done.

As described in this paper, we address the example of the decontamination technology of incinerated ash using PB nanoparticles. Details of the R&D are presented in Chapter 2. The strategy and management for conducting this technological development are presented in Chapter 3.

2 Development of incinerated ash decontamination technology

2.1 Technological background

The radioactive cesium adsorbent, our core technology,

consists of metal hexacyanoferrate (MHCF or Prussian blue type complex) nanoparticles. Actually, MHCF is a porous coordination polymer with chemical composition of $A_yM[Fe(CN)_6]_{1-x} \cdot zH_2O$, where A stands for a cation such as an alkali metal, and M denotes a transition metal cation. When M = Fe, it is Prussian blue (PB), an artificial pigment synthesized in the early 18th century, used by van Gogh and Hokusai in their paintings, and even used in present days. The metal species (A, M) and composition (x, y, z) can be controlled over a wide range. The crystal structure, presented in Fig. 1, has a jungle-gym structure in which the cyano group crosslinks the metal atoms. The crystal includes a hollow network in which cation A adsorbs and desorbs. It is known for its highly selective adsorption of cesium ions.[13]
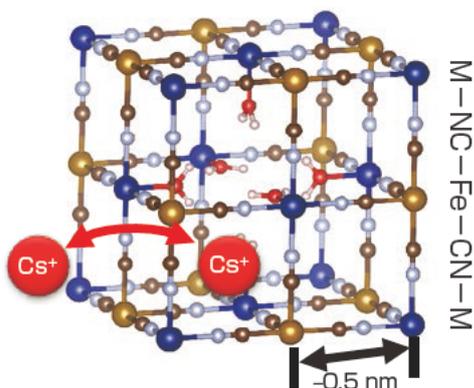

Fig. 1 The crystal structure of hexacyanoferrate $A_yM[Fe(CN)_6]_{1-x} \cdot zH_2O$, where A and M indicate the cations and the transition metal ions of Fe, Cu, Co, or others
The red atoms around the vacancy show the oxygen in the H_2O molecule.

The first report of the radioactive cesium adsorption capacity of PB was published around 1950.[14] Since then, radioactive cesium adsorption by various MHCFs, not only PB, has been investigated and used.[13][15]–[17] For example, various MHCFs were used for removing radioactive cesium from contaminated water at Hanford, where nuclear development was conducted in the United States in the 1960s.[18] Recently, nickel hexacyanoferrate (NiHCF) was used in the Areva device for decontamination of contaminated water from the nuclear plant accident in 2011.[19][20]

An outline of PB research at AIST is presented in Fig. 2. At AIST, the development of a PB type complex has been conducted jointly with Yamagata University from 2005,[21][22] with particular emphasis on the development of electrochromic devices.[23]–[26] Before the accident at Fukushima, we had been involved in R&D of a system for electrochemically adsorbing/desorbing and concentrating radioactive cesium.[27]–[29] The accident at Fukushima occurred as we were accumulating related technological knowledge. In its aftermath, we immediately shifted the main focus of our R&D to decontamination. We conducted R&D of two main areas: the development of an adsorbent based on PB nanoparticles,[30]–[34] and the development of decontamination technology using this adsorbent.[35]–[38]

2.2 Outline of incinerated ash decontamination technology

One specifically examined technological development topic is the volume reduction of vegetal contaminants.[3][5][6] Actually, incinerated ash decontamination includes this technology. An
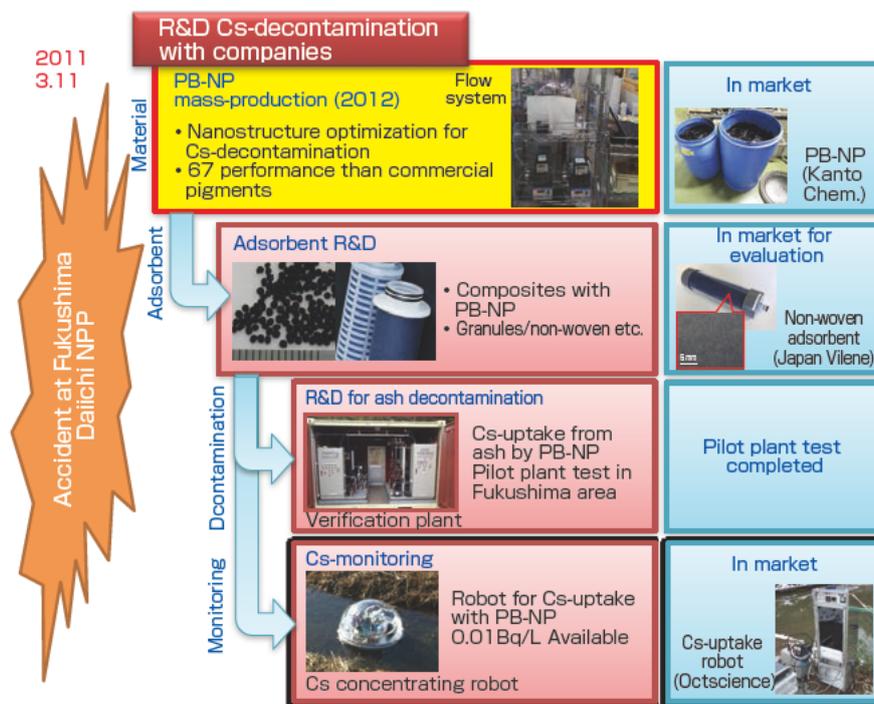

Fig. 2 History of the development of radioactive cesium decontamination technology using PB nanoparticles at AIST, where PB and PB-NP represent Prussian blue and PB nanoparticles, respectively

outline of the technology is depicted in Fig. 3. The vegetal materials contaminated by radioactive cesium would be produced in large amounts because of forest contamination. If such combustible contaminants are not treated appropriately, then they might be heated by fermentation or other processes and then ignite. Therefore, appropriate incineration is necessary. However, because radioactive cesium elutes from the incinerated ash through contact with water,[39][40] such ash cannot be processed as regular industrial waste. Our approach is washing after incineration of the contaminants, followed by radioactive uptake by the adsorbent, resulting in volume reduction to 1/500–1/3,000 of the ash, or 1/25,000–1/300,000 of the material before incineration.

Although similar decontamination technology has been investigated by many organizations,[41]–[44] the advantage of our technology is the high radioactive cesium adsorption capacity of the PB nanoparticles. Nevertheless, it is unrealistic to apply powder or dispersion liquid of the nanoparticles to the decontamination site. R&D is required for various stages of fabrication of the adsorbent and design of the plant facility. The technology flow is portrayed in Fig. 4 for materials, development of the adsorbent, plant design, and demonstration. By developing the whole process from materials to the plant facility based on the PB nanoparticles, we aimed at making the most of the nanomaterial function for contribution to cesium decontamination. During progress from this material to the plant facility, our development involves different scales from atomic size, nanometer, micrometer to meter scales. For example, control of the chemical composition is necessary in materials development, whereas plant design is development of a metric scale. Such integrated development from materials to plant facilities necessitates the development of technologies on various scales.
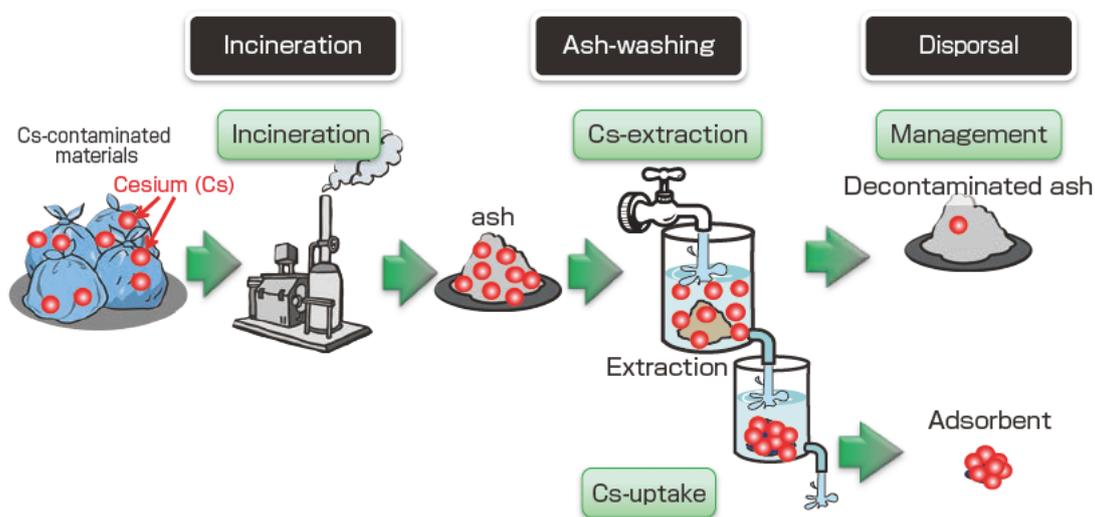

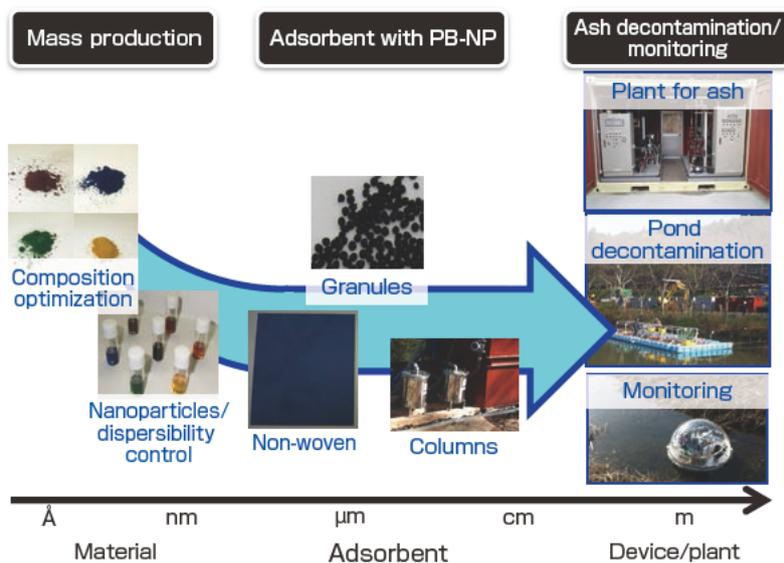Fig. 3 Outline of volume reduction of vegetal contaminants and incinerated ash using PB nanoparticles[6]

Fig. 4 Technology development for each scale of the decontamination technology development using PB nanoparticles at AIST

– 141 –

Table 1. Outline of Prussian blue nanoparticle[30]

Name	Nanoparticle (11 μm)	Nanoparticle (60 μm)	Commercially available PB
Composition	$Fe[Fe(CN)_6]_{0.75}$		$(NH_4)_{0.64}Fe[Fe(CN)_6]_{0.91}$
Primary particle diameter	8.8 nm		36 nm
Secondary particle diameter	11 μm	60 μm	9 μm

2.2.1 Development of PB nanoparticles for use as radioactive cesium adsorbents

The benefits of the PB nanoparticles, the material of our technology for use with radioactive cesium, is its high selectivity and efficient adsorption. Although PB tends to form fine particles, the cesium adsorption performance can be increased through optimization of the chemical composition as well as its particle size.[30][32] The particle size and composition of the PB nanoparticles is shown in Table 1 in comparison with "konjo" (905; Dainichiseika Color & Chemicals Manufacturing Co., Ltd.), a commercially available form of Prussian blue.[30] The points are the optimization of the composition and the control of the particle size. In general, the Prussian blue composition is expressed as $A_yFe[Fe(CN)_6]_{1-x}$, implying the vacancies of $[Fe(CN)_6]$'s or alkali cations insertion in its structure. The x and y in the chemical composition respectively represent the amount of the $[Fe(CN)_6]$ vacancies, and the amount of cation introduced. Prussian blue is obtainable by mixing the $Fe^{\alpha+}$ ion water solution and $[Fe(CN)_6]^{\beta-}$ ion solution. It is possible to control the composition by appropriate choice of the mixing ratio, types of counter ion, and valence numbers of the ions. Results show that the adsorption capacity changed greatly according to the composition.[45]

To increase the adsorption performance, we reduced the material to nanoparticles. The size of our nanoparticles was about 8–20 nm (Fig. 5(a)). The primary particle size of nanoparticles is dependent on the synthesis method. For example, it is possible to reduce the particle size by rapid mixing. In the case of copper hexacyanoferrate, a Prussian blue analog, we achieved improvement of 7.7 times in adsorption speed compared with the case of conventional synthesis by the reduction of the particle size by micro-mixer synthesis.[33] The particle size can also be controlled to a certain degree by controlling the ionic valence number or temperature during mixing.

Powder size, the secondary particle size, also affects the adsorption performance. The diffusion coefficient of radioactive cesium in a powder is low compared to that in liquid, implying that a higher adsorption rate is possible by reducing the secondary particle diameter. For example, for powder synthesis by drying of the PB nanoparticle suspension, an appropriate choice of the drying method is necessary to achieve the small secondary particle size.

Figure 5(b) presents the dependence of the cesium adsorption rate on the liquid–solid ratio when various adsorbent powders were added to water for washing the incinerated ash. When our PB nanoparticles were used, almost 100 % adsorption was observed with a liquid–solid ratio of 5,000 or 200 ppm contents. However, the adsorption rate of commercial PB was approximately 80 %, and for zeolite, it was used frequently as a cesium adsorbent: it was 20 % or less. The reasons for the difference of the adsorption rate against the commercial PB are its different particle size and different chemical composition. The poor adsorption of zeolite derives from its
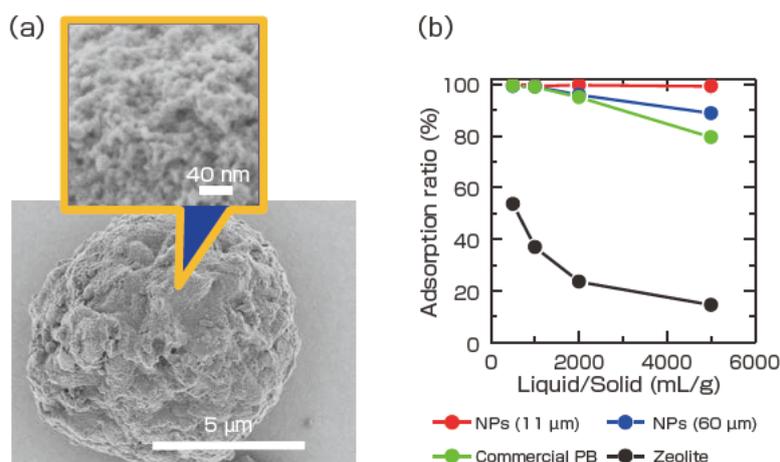

Fig. 5 (a) Electron microscope image of PB nanoparticle powder. (b) Liquid–solid ratio dependency of adsorption performance when various cesium adsorbents are added to the water after washing the incinerated ash[3][30]

poor selectivity for cesium uptake and the high concentration of other ions in the ash washing water.

2.2.2 Mass production of the PB nanoparticles and adsorbent development

Mass production of the PB nanoparticles was conducted through joint research with Kanto Chemical Co., Inc. Our fundamental strategy was the following: AIST determined the appropriate composition and crystal structure for the radioactive adsorbent. The manufacturing method was also investigated among the methods available for mass-production. Finally, this technology was transferred to the company, and Kanto Chemical improved the manufacturing method for mass production.

We were successful at developing the PB nanoparticles exhibiting high cesium adsorption capacity, but this material was normally obtained in the form of powder or slurry. For radioactive cesium removal from ash washing water, solid–liquid separation with powder or slurry must be done after adding the powder to washing water.[46] However, safety concerns were often raised for the powder addition method for the concentration of radioactive materials. Especially, the risk of system trouble exists because an engineer must handle the adsorbent powder with high concentrations of radioactive cesium. To avoid such a risk, with cooperation from companies, we started the development of another system with the adsorbent sealed in a container such as a column. If the adsorbent is enclosed in a column, even if clogging occurs, it would only be necessary to exchange the column. There would be no need to handle the adsorbent directly.

First, we originally developed the adsorbent supported by cotton cloth, and confirmed its sufficient adsorbent properties.[47] Next, through collaboration with Kanto Chemical and Japan Vilene Co., Ltd., we developed adsorbents of two types: a granular one[34][36] and an adsorbent-immobilized nonwoven one[38][48] (Fig. 6). The granules contain 80 % PB nanoparticles with high adsorption capacity. The nonwoven adsorbent has a large surface area that supports high-speed adsorption. These adsorbents are used for another purpose: concentration of radioactive material in environmental water for pretreatment of the trace analysis and pond water decontamination. For this development, computational approaches such as a simulation of adsorption performance were also used.[49]

2.2.3 System development of volume reduction of incinerated ash

We sought to create an ash washing system using the adsorbents. Our goal was to reduce the volume of contaminants generated in environmental decontamination work by the government. The government planned that the contaminated materials would be collected and incinerated in a newly built temporary incinerator.[50] Therefore, all facilities including the

washing device and the storage will be newly constructed. Considering this situation, we designed the most efficient method for volume reduction of waste. We integrated the components from incineration, ash washing, recovery of radioactive cesium by adsorbents, and a storage of used adsorbents.

For the pilot plant for demonstration at a realistic scale, we designed each component as follows: as an incinerator, a biomass boiler was used. To remove radioactive cesium completely from the exhaust gas and to study the contaminant behavior, a three-step treatment device was installed for the exhaust gas, a cyclone, a bag filter, and a HEPA filter. We also confirmed that the addition of calcium chloride during incineration improves the extraction rate of radioactive cesium by washing at a later stage. Particularly, the "main ash" recovered from the bottom of the incinerator presents difficulties for extraction of radioactive cesium by washing. Those difficulties are different from those related to the "fly ash" recovered from the chimney. Nevertheless, we were able to achieve a high extraction rate of 60 % by adding calcium chloride.[6]

Regarding the washing process, we tried to reduce the water demand. For decontamination activities, great concern has arisen in relation to contaminated water processing because the handling of contaminated water storage at the Fukushima Daiichi Nuclear Power Plant is a serious matter, and because drinking water and agricultural water might be directly affected if environmental water is contaminated. Therefore, it is important to reduce the amount of water used to the greatest degree possible. For cases in which water discharge is not permitted even if it is properly treated, water treatment without discharge is necessary. By reduction of the water amount, it is possible to avoid discharge, e.g. by evaporation. A schematic diagram of the plant for ash washing and recovery by adsorbents is portrayed in Fig. 7. Our design has three important points: (1) use of a vibrating granulator to mix the ash with as little water as possible, (2) avoiding clogging by increasing the
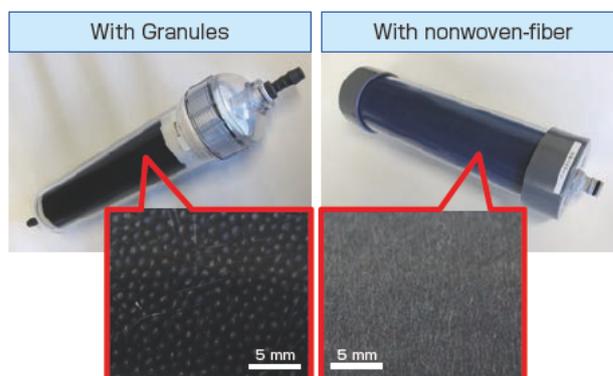

| With Granules | With nonwoven-fiber |

Fig. 6 Radioactive cesium adsorbents that contain PB nanoparticles
Left: Granular adsorbent made by Kanto Chemical. Right: Nonwoven fabric supported adsorbent made by Japan Vilene.

– 143 –

solid–liquid ratio at the dehydration of ash, and (3) reuse of water used for washing. Because ash often exhibits extreme hydrophobicity, water and ash cannot be mixed by simple stirring. The cesium extraction is difficult. Point (1) is effective to resolve the problem. A vibrating granulator is normally used at incineration plants as a device to create granules when transporting incinerated ash to the final disposal site. Water and ash are mixed to form granules by adding only a small amount of water. Using this device, it was possible to mix water and ash effectively. In addition, because block-like ash can be ground by the device, the washing was done smoothly. With point (2), the filter press method was used as an inexpensive solid–liquid separation device. By setting up a circulating route, the solid–liquid ratio in the dehydration area was increased to avoid clogging. For point (3), water reuse became possible by installing a coagulation–sedimentation basin to remove harmful substances other than radioactive cesium.

For the recovery of radioactive cesium that is dissolved in water, the granular adsorbent or the nonwoven type with the PB nanoparticles was used. Results verified that the expected adsorption was generally achieved. Results clarified that the adsorption behavior was estimated by the dosage monitor set on the column.

Figure 8 presents the effect on volume reduction of waste using this technology. For example, when one ton of combustible waste contaminated by 1,800 Bq/kg of radioactive cesium was processed, the waste materials that can be treated as regular waste, those that must be disposed in managed disposal sites, and those that must be stored at interim storage facilities were 7.8 kg, 6.0 kg, and 4.4 g, respectively. Thereby, extremely high volume reduction was achieved.[6]
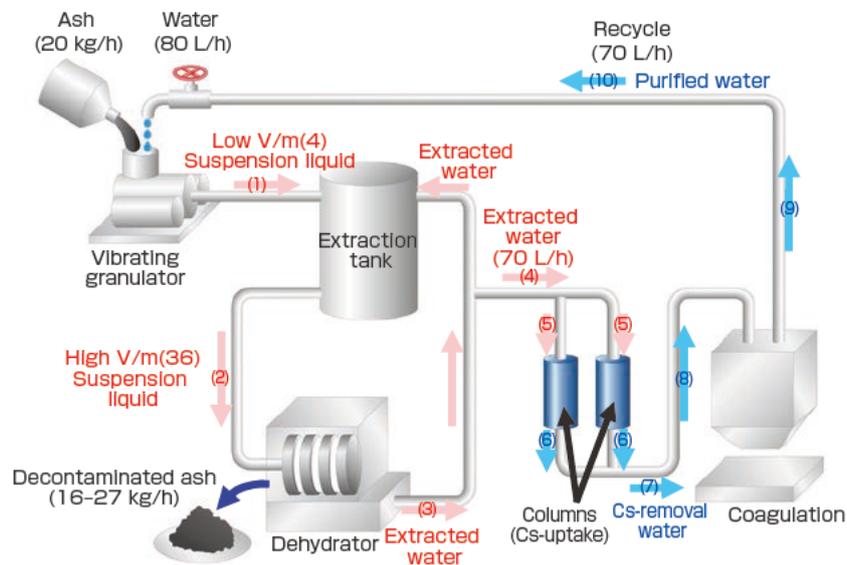

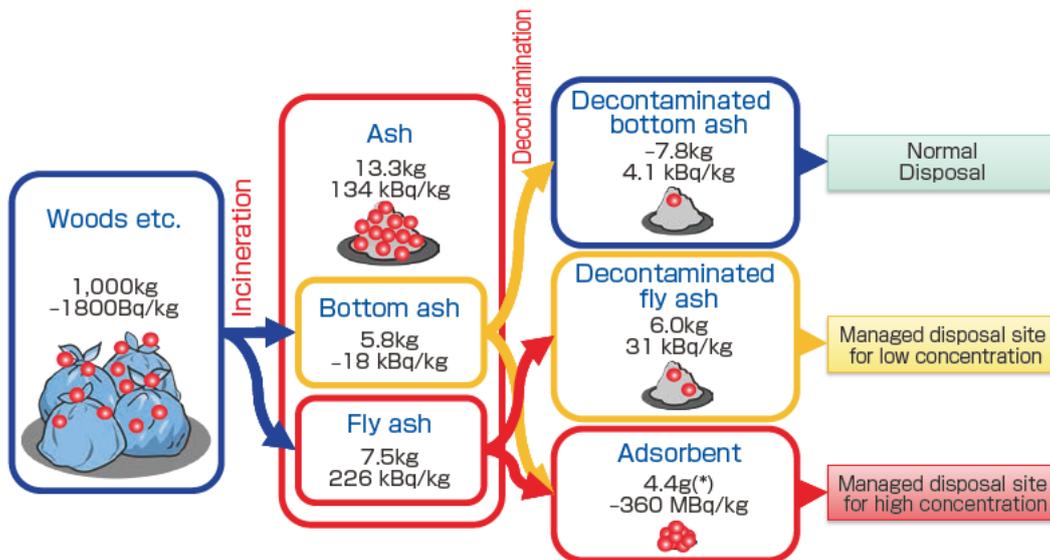**Fig. 7 Schematic view of the ash washing and recovery plant[6]**

Fig. 8 Example of volume reduction when the incinerated ash processing technology is used[6]

Table 2. Research for the development of ash decontamination technology and the policies for technological development
The transferring strategies are: (1) patent + technological transfer, (2) technology disclosure, (3) research by companies, and (4) utilization of conventional technology

Components of technology		Method for R&D	Technology transfer				Laboratory	Pilot plant
			(1)	(2)	(3)	(4)		
Incineration		Purchase		○		○	Convectional technology	20kg/h biomass boiler
Cs-extraction		Internal collaboration + Invited researchers		○		○	Conventional/ condition optimization	Ash crushing/decrease of water amount
Cs-uptake	Material	Original + universities	○				Optimization of PB-NP composition	Mass-production
	Granulation /immobilization	With companies			○		Granule/non-woven	Mass production
	Adsorbent management	Original + with companies		○			Elution management	Scale up
Plant-site management		With companies + support by AIST			○		–	Local agreemen t/on-site management
Waste management	Ash/liquid	Conventional technology		○		○	–	Law-compliance
	Adsorbent	Original+ With companies	○	○			Method development	

2.2.4 Storage and disposal of post-treatment waste

Regarding the practical application of our technology, the remaining issue is storage of the waste materials generated by the treatment. The main waste materials are washed incinerated ash, wastewater used for washing, and the adsorbents after adsorption. With regard to washed ash, waste standards are 8,000 Bq/kg and 100,000 Bq/kg of radioactive cesium concentration, the criteria for the storage level by regulation of the Japanese government. The washed ash could be stored or disposed of to maintain the standards. Regarding wastewater, because radioactive cesium can be removed sufficiently by the adsorbent, the water can be released after conducting regular wastewater processing. Even in cases where release is difficult because of the concerns of local governments, treatment is possible by minimization of the amount of water use by reuse, followed by evaporation.

The used adsorbent would pose no problem for regular storage because it is sufficiently stable. However, in this case, extremely long-term storage might be necessary because it includes radioactive materials. In this case, safer storage methods will be requested. To convert the used adsorbents into oxides is an approach for storage in a stable condition. However, oxidation reaction of PB entails large amounts of oxidative heat, implying the evaporation of the adsorbed radioactive cesium at temperatures higher than 600 °C. For stable oxidation at temperatures lower than 500 °C, we established an oxidation method under mild conditions using superheated steam. Using this method, we converted the adsorbents into oxides while maintaining evaporation of cesium at an extremely low level.[51]

3 Team formation for the ash decontamination technology development

As described above, we proceeded with the integration of technologies using the incineration method, the extraction of radioactive cesium from ash, recovery by adsorbents, and the safe storage of waste products. We also conducted tests at a pilot plant on site after laboratory tests. Using these approaches, it was possible to establish technologies for practical use in a short period. At the initial stage of this research, the researchers in materials science played a central role, followed by participation of chemical engineering and geo-engineering researchers at AIST. However, it was impossible for the AIST researchers to construct everything. For example, incineration technology, plant design, operation, and the design of adsorbents that could be set for mass production in a short time could not be accomplished by AIST, a research institute, alone. For these missions, corporate collaboration is necessary.

We first produced a ground design for commercialization, extracted elemental technologies to achieve such commercialization from the design, and formulated a strategy for the realization of the elemental technologies. What is important is that the strategy must include "who" will conduct the process, "when" the R&D for each technology will be done, "who" will do it, and "when" the commercialization will be done. As described above, because AIST is a research institute that cannot engage in commercial projects, commercialization is conducted by companies. Therefore, it is necessary to produce an R&D plan with consideration of the technology transfer to companies at a certain time. For the specific R&D contents, the theme in the pilot plant must be determined with tests to realize the technology transfer strategy. Moreover, the theme at the laboratory must be determined to find a means of deciding the parameters used in the pilot plant test. The strategy established in this manner is presented in Table 2, which shows the experiment contents and the R&D method, which are presented in a bottom-up fashion from the initial stage or a small-scale stage. It

is noteworthy that the actual thinking process functions in reverse. In the following section, the procedures for setting the strategy will be described according to the order in which they were formulated.

3.1 Strategy for technology transfer

As a strategy for transfering technology to companies, we decided to use four methods so that the appropriate person might work for each mission. These are (1) retaining the intellectual property by AIST + technology transfer, (2) publication of our technology with appropriate retention of intellectual property, (3) research by companies, and (4) utilization of conventional technology. In a usual case of technology transfer by a research institute, it is considered that the institute obtains intellectual property rights. Then this technology is transferred to a company, as incase (1). However, when conducting R&D for the total integration of issues as in this case, the development rate will be slowed if all the intellectual property is retained, which is unrealistic for companies to derive some benefits. Therefore, the R&D strategy should be determined through comparison of technology maps of AIST and those of the companies.

A requirement for pursuing our strategy is to enable collaboration simultaneously with various companies. For this R&D, coherent development is necessary for materials, plant design, and waste storage, as described earlier. It is unrealistic to address such a wide scope of issues through collaboration with only one company. Even if there were a company that could accommodate all the technologies, much time would be necessary to find such a partner company: the plan might become deadlocked. Therefore, we chose to conduct simultaneous collaborations with various companies to increase the R&D speed and raise the technology to a practical level. This was the main reason to choose a method for each issue in our technology transfer from (1)–(4), as shown below.

The following is a description of the outline of methods of technology transfer.

(1) Retaining intellectual property + technology transfer

This is the main method of technology transfer by R&D institutes. The invention is patented or transformed into know-how. Then the technology is transferred to a company under an appropriate contract. The contract includes joint research agreements, information disclosure agreements, licensing, and other matters. We use this scheme for a technology in which the core technology is held by AIST, and for which AIST would have an advantage in competition against other companies. The technology of PB nanoparticles fits the scheme. The PB nanoparticles have been studied by AIST for a long time, giving AIST advantages in potential R&D development over other companies. Additionally, we also have

unreleased technologies. Under such circumstances, if the technology is disclosed without patenting, then some companies might monopolize the technology by patenting the peripheral technology. If such a limitation of access occurs, then it will be difficult to conduct simultaneous collaboration with multiple companies.

Given such circumstances, we chose to patent the intellectual property for PB nanoparticles to manage through licensing by AIST. We also chose to preserve intellectual property for basic methods for ash decontamination and post-treatment processes for adsorbents after use.

(2) Technology disclosure

Although it is ideal for AIST to manage all related intellectual properties, it is unrealistic because AIST has no superior standing against companies in all technological fields and because time and different costs must be incurred to retain and maintain intellectual property rights. If there is a low risk of exclusion by a company through patenting peripheral technologies, then we were willing to disclose the technology to accelerate the technology transfer.

For example, we distributed knowledge related to the properties of ash obtained from each part of the incineration furnace, the washing method to extract radioactive cesium from the ash, and the technology for the treatment of clumped ash, through press releases or other means.[6] A wastewater management method for cyanide was also distributed through publication of papers because PB nanoparticles contain the cyano group in their structures. Therefore, the elution of cyanide should be a concern.[34][52]

(3) Research by companies

Any technology must be passed to companies for commercialization. Therefore, it is preferred that the companies engage in R&D for technologies if they have some advantage for the technologies. As examples, the method of fabricating adsorbents, methods of preparing compounds with the adsorbent into a usable form, obtaining local agreement to pilot plant construction, on-site plant construction, and plant operation and management have proceeded with this scheme.

For the compound preparation, granulation and immobilization onto nonwoven fabric were considered. In fact, AIST conducted joint research with about 10 companies, including Kanto Chemical, Japan Vilene, and Unitika Trading Co., Ltd. In many cases, the preparation technology was established by the companies, although AIST was in charge of evaluating the performance of the developed adsorbents.

The important point is intellectual property management. In simultaneous collaboration with multiple companies to achieve a mutual goal, it is difficult to manage information while dividing the results into collaboration with each company. To do so, we chose the following policy to manage the knowledge and included it in the joint research agreement: (1) results disclosed to AIST can be disclosed to other joint researchers as necessary; (2) profit of a company that produces an invention will be ensured through patent licensing; and (3) for patents generated through joint research, the percentage of rights will be determined by the degree of contribution to the invention by the parties involved. In addition, even if an invention is patented by a single company, the patent generated via joint research will be licensed to other joint researchers as necessary. The policy means the following.

- Contents that a company wishes to use as know-how should not be discussed with AIST.
- Contents discussed with AIST will be disclosed to other collaborating companies: a company will be able to use other companies' technologies to accelerate development.

This scheme is effective if one needs to share basic technologies among the companies. In the case of the evaluation method of the adsorbents, it is better to follow this scheme. Many companies collaborating for the adsorbent fabrication had no specialization in radioactive materials evaluation. Although the companies have their own core technology for adsorbent fabrication, the performance evaluation should be done with established and unified methods for appropriate comparison, and should be highly rated. Many companies started the joint research with AIST with the agreement of this scheme.

This scheme is expected to be quite effective when development for commercial applications is based on the core technology of public institutes. If a public institute owns the core technology, then a company aiming at practical application must collaborate with the institute. Collaboration with the institute would support future standardization of the technology. It is also important to collaborate with other companies having different core technologies. In this case, our collaboration network included various companies such as an adsorbent manufacturer and plant engineering companies using the adsorbent in their plants, indicating that construction of a supply chain from the material to the plant comes easily. To maintain the scheme, the research institute must have the capacity to manage the supply chain and standardization. This capacity is requested of the research institute in the near future.

(4) Utilization of conventional technology

Using conventional technology to the greatest extent possible is desirable to accelerate research and development. The conventional technology can be expected to provide operational stability, thereby reducing the risks. For this research, we actively used conventional technologies especially those related to incineration technology, ash washing technology, wastewater treatment, and on-site management. For conventional technologies, the companies would have vast knowledge of their business field. Even if they have insufficient knowledge, knowledge acquisition can be done rather easily from public documents.

The most important aspect of technology transfer is how to promote (3) corporate research. The technology should be transferred to companies because an R&D institute cannot accomplish commercialization, and has no knowledge related to commercialization. Construction of the collaboration network is also effective for the company to produce a business plan with a concrete supply chain. The intellectual property should be managed appropriately with appropriate agreement of joint research to encourage understanding of the companies.

3.2 Technology management for R&D

When the strategy for technology transfer is fixed, partners and the approach of the technological development are decided mechanically. In the case of "(3) corporate research," AIST need not introduce the entire technology. For example, for adsorbent fabrication, a company developed the adsorbent fabrication, whereas AIST mainly concentrated on the improvement of the method for evaluating the adsorbent. However, for on-site management of plant engineering, AIST had to provide major support; even though the technology transfer would be done under "(3) corporate research." This was because our theme was the decontamination of radioactive cesium. Even the national government had not investigated cesium decontamination before the accident. Therefore, the technological development was conducted simultaneously with the organization of various legislation. To adjust to the unusual conditions, we were requested to understand the legal policies appropriately, and were asked for requests from the technology side to the government organizations. Especially, AIST participated in the Fly Ash Washing Technology Workshop, conducted by the National Institute of Environmental Studies, to contribute to the publication of "Technical material on fly ash washing technology (Guidelines for performance and design of plants)."[53] The pilot plant tests were conducted in accordance with guidelines to reduce the risk that our technology would not be able to meet legal requests.

In the case of (1) patent + technological transfer and (2) technological disclosure, the R&D must be conducted by AIST. To achieve this, AIST set research teams for the project with a Vice-President as the leader, and with various

– 147 –

specialists, e.g. a researcher for chemical engineering who participated in the plant and column designs, and a computational scientist devoted to the establishment of radioactive Cs amount estimation methods in the column from the dosage of the column surface. When designing the plant close to commercialization, an engineer with experience at chemical manufacturers was invited to design the pilot plant.

Related to scheme (4) utilization of conventional technology, the outside partner mainly worked on the problem with researchers of the collaborating companies and invited researchers from external organizations. The required equipment was purchased without our own development. We devoted particular attention to usability as a general method in commercialization to avoid company specialization only in implementing the technology. Our objective was the development of ash decontamination technologies using the PB nanoparticles. The strategy was that the companies would use the PB nanoparticles without trouble using conventional technologies for other tasks.

3.3 Determination of R&D contents
After the strategy was fixed, the remaining issue was exact determination of who would do it and what would be done. The appropriate R&D content and the schedule were determined mechanically from available resources, budgets, human resources, time, and existing equipment.

We especially devoted attention to choosing the adsorbent for the pilot plant test so that it could be applicable for mass production, i.e. only adsorbents manufactured by companies were used for the pilot plant test. We did not use adsorbents for which technology transfer was not completed. Regarding plant design, the plant would be constructed only by clarifying the technology using the commercially available components. Regarding the adsorbents, manufacturing equipment necessary for laboratory tests and for mass production are completely different. It is important that even if mass production was not achieved at the time, mass production was possible for the company; and at least cost calculation for mass production had been achieved. To achieve the requirement, technologies for which the technology transfer was not completed were avoided.

Collaboration with universities and other research institutes was fundamentally important. Optimization of the materials for PB nanoparticles was conducted with the cooperation of universities and research institutes. At the materials development level, they have powerful foundations. The research institutes for agriculture and environment held abundant knowledge for various applications. An issue related to collaboration with the universities and the institutes is the management of intellectual property. In our research, collaboration with universities and research institutes was

kept to a fundamental level of materials development.

3.4 Flow of corporate collaboration and collaboration with the government and local governments
For commercialization, a time schedule and a strategy for each stage was fundamentally important. An unusual point of the research is that the demand rose suddenly because of the accident at the nuclear power plant. Consequently, many projects were led by the national government and the local government. This situation led researchers to follow the direction of the national government. The local governments frequently speculated on future markets. We participated in the project funded by the Strategic Funds for the Promotion of Science and Technology, led by the Ministry of Agriculture, Forestry and Fisheries from June 2011, where we engaged in R&D for farmland decontamination. In this project, to develop the contamination technology using adsorbents, we organized a research team including AIST, a university, another research institute, and two companies. Therefore, AIST played a leading role in coordination of efforts by the national government, a research institute, and companies.

The R&D of ash decontamination started in autumn 2011. Initially, efforts emphasized the plant design, with some work on the development of adsorbents with the materials manufacturer. The most pressing problem at this stage was to find a place for pilot plant tests. Conventionally, radioactive materials could only be handled in a strictly managed environment according to Japanese law. After the accident, for similar reasons, it was difficult to manage radioactive materials that had been released into the environment. To resolve this difficulty, the technological development was conducted along with legal adjustments, simultaneously. In finding a place for the pilot plant tests, we were requested to watch the action of the Ministry of Environment, to consider appropriate management to maintain safety, and to present it to the local government and area residents to obtain permission. A reliable relation between the project operator and the local governments and residents is especially important. We conducted pilot plant tests for incinerated ash treatment in two places in Fukushima Prefecture: Koriyama city and Kawauchi village. For the former, we provided technological support for the tests conducted at the plant location of the Koriyama Chip Industry Co., Ltd. Because Koriyama Chip Industry had been operating their business at this location since long before the accident, agreement of the surrounding residents to conduct tests was obtained. The latter was done by AIST in collaboration with the Tokyo Electric Power Environmental Engineering Co., Inc. (TEPCO Environmental Engineering; currently, Tokyo Power Technology Ltd.). TEPCO Environmental Engineering had already been working on the decontamination of Kawauchi village when the pilot plant tests started. At Kawauchi village, the union of the local company conducted

decontamination work, and TEPCO Environmental Engineering provided technical support to the union. They gained the confidence of the local government through this activity. Therefore, the local governments also agreed to pilot plant tests.

Although it was a special case because of this unexpected accident, there are many cases in which the laws would not be adjusted, even in regular R&D. It is necessary to set the direction while understanding the laws appropriately, checking the discussions of the committees and other authorities before the enforcement of laws, and setting the R&D strategy based on them.

We shall discuss the stage of corporate collaboration. R&D is often handled as "step by step," starting from "upstream" activities such as raw materials development, and assumed to go "downstream," with development of adsorbents or decontamination methods. However, two problems can hinder such an approach. One is that R&D is time-consuming. Another is that the supply chain is not clear at the start of research: for that reason, one cannot establish a business model. To resolve those difficulties, the R&D of each stage should be conducted "concurrently". This is generally called "concurrent engineering." For the approach, it is necessary to clarify the whole picture of the R&D from the research level to elucidate the picture for all people involved, and to elicit frequent feedback.

3.5 Current status of commercialization

The achievement of the development of ash washing technology is presented in Fig. 2. For example, Kanto Chemical and Japan Vilene conducted the development of the adsorbents. Some of them have become commercially available. Kanto Chemical sells PB nanoparticle materials to other companies. It has developed and sells granular adsorbents.

These technologies are used for various purposes other than ash decontamination. For example, the nonwoven adsorbent of Japan Vilene is also used in the pilot plant tests for preventing radioactive cesium leakage from ponds, and is described in the MAFF manual.[54] Similar nonwoven material is used as a measurement technology for radioactive cesium in environmental waters.[8][55]

4 Conclusion

We developed the technology to remove radioactive cesium from the environment after the leakage of radioactive materials from the Fukushima Daiichi Nuclear Power Plant of the Tokyo Electric Power Company using the PB nanoparticles. As presented in this paper, we described our ash decontamination technology to reduce the volume of combustible contaminants. Because this issue is related to

an urgent matter for Japanese national security, rapid R&D efforts were pursued in preference to those used for regular R&D. Therefore, it was important to clarify the final goal and to build collaboration to reach the goal as quickly as possible. Especially important was the concurrent promotion of both the expansion of collaboration and the management of intellectual property. To achieve such a requirement, we chose the following policy: we retained the intellectual property for the core technology to ourselves to the greatest extent possible, and left R&D for peripheral technology to the companies. We also decided that the know-how disclosed by the companies to AIST would be disclosed to other collaborating companies as necessary, and we decided that licensing to other collaborating companies would be possible even if the technology was patented by a single company.

Through these policies, it was possible to conduct R&D swiftly. This method is expected to be an effective mode of conducting other R&D. However, it is necessary that the research institute possesses the core technology and holds superiority in knowledge and intellectual property. It is also necessary to estimate the supply chain and cost structure in anticipation of commercialization. These are generally not regarded as important for research institutes. However, if a research institute aims to become the nucleus of open innovation in Japan, then these capabilities become necessary. We hope this will be a model of R&D with one research institute at the core. We sincerely wish to contribute to decontamination efforts that are underway in Japan.

Acknowledgements

References

[1] Ministry of Economy, Trade and Industry: Genshiryoku anzen ni kansuru IAEA kakuryo kaigi ni taisuru nihon koku seifu no hokokusho ni tsuite (On the report of the Japanese Government for the IAEA Ministerial Conference on Nuclear Safety), http://www.meti.go.jp/earthquake/nuclear/backdrop/20110607001 html, accessed 2016-01-17 (in Japanese).

[2] National Institute of Advanced Industrial Science and Technology: Prussian blue o riyo shite tayona keitai no cesium kyuchakuzai o kaihatsu (Cesium adsorbent of various forms developed using Prussian blue), http://www.aist.go.jp/aist_j/press_release/pr2011/pr20110824/pr20110824 html, accessed 2015-12-19 (in Japanese).

[3] National Institute of Advanced Industrial Science and Technology: Nano ryushika shita Prussian blue de cesium kyuchakuno ga kojo (Cesium adsorption capacity improved by nanoparticulization of Prussian blue), http://www.aist.go.jp/aist_j/press_release/pr2012/pr20120208/pr20120208.html, accessed 2015-12-19 (in Japanese).

[4] National Institute of Advanced Industrial Science and Technology: Dojochu no cesium o teinodo no san de chushutsu suru koto ni seiko (Succeeded in extracting cesium in soil using low-concentration acid), http://www.aist.go.jp/aist_j/press_release/pr2011/pr20110831/pr20110831 html, accessed 2015-12-19 (in Japanese).

[5] National Institute of Advanced Industrial Science and Technology: Shokubutsukei hoshasei cesium osenbutsu o josen gen'yo suru tame no jissho shiken plant (Verification test plant for decontamination and volume reduction of vegetal radioactive cesium contaminants), http://www.aist.go.jp/aist_j/press_release/pr2012/pr20121112/pr20121112.html, accessed 2015-12-19 (in Japanese).

[6] T. Kawamoto, Y. Hakuta, H. Tanaka, H. Ogawa, K. Minami, A. Kitajima and D. Parajuli: Shokubutsukei hoshasei cesium osenbutsu no shokyakubai o josen suru gijutsu o jissho (Technology for decontaminating incinerated ash of vegetal radioactive cesium contaminants verified), http://www.aist.go.jp/aist_j/press_release/pr2013/pr20131120/pr20131120.html, accessed 2016-06-06 (in Japanese).

[7] National Institute of Advanced Industrial Science and Technology: Suichu no teinodo no yozontai hoshasei cesium o kan'i jinsoku ni sokutei (Quick and simple measurement of low-concentration radioactive cesium dissolved in water), http://www.aist.go.jp/aist_j/new_research/2012/nr20120905/nr20120905 html, accessed 2015-12-19 (in Japanese).

[8] National Institute of Advanced Industrial Science and Technology: Suichu no hoshasei cesium wo subayaku monitoring (Quick monitoring of radioactive cesium in water), http://www.aist.go.jp/aist_j/press_release/pr2014/pr20140407/pr20140407.html, accessed 2015-12-19 (in Japanese).

[9] National Institute of Advanced Industrial Science and Technology: Hoshasei cesium wo fukumu genmai no ninsho hyojun busshitsu o kaihatsu (Certified reference material for brown rice containing radioactive cesium developed), http://www.aist.go.jp/aist_j/press_release/pr2012/pr20120830/pr20120830 html, accessed 2015-12-19 (in Japanese).

[10] National Institute of Advanced Industrial Science and Technology: Abukuma-gawa no suichu hoshasei cesium nodo wa hikui level de aru koto o kakunin (Confirmed that aquatic radioactive cesium concentration in Abukuma River is low), http://www.aist.go.jp/aist_j/new_research/2013/nr20130204/nr20130204.html, accessed 2015-12-19 (in Japanese).

[11] National Institute of Advanced Industrial Science and Technology: Kaze ni notte nagai kyori o hakobareru hoshasei cesium no sonzai keitai (Form of radioactive cesium that is carried over long distance by wind), http://www.aist.go.jp/aist_j/new_research/2012/nr20120731/nr20120731 html, accessed 2015-12-19 (in Japanese).

[12] National Institute of Advanced Industrial Science and Technology: Hoshasen busshitsu josen no koka to hiyo o hyoka (Cost and effect of decontamination of radioactive materials evaluated), http://www.aist.go.jp/aist_j/new_research/2013/nr20130604/nr20130604 html, accessed 2015-12-19 (in Japanese).

[13] P. A. Haas: A review of information on ferrocyanide solids for removal of cesium from solutions, *Sep. Sci. Technol.*, 28 (17/18), 2479–2506 (1993).

[14] Oak Ridge National Laboratory: Quarterly report for liquid waste disposal research (1950).

[15] G. B. Barton, J. L. Hepworth, E. D. McClanahan, R. L. Moore and H. H. Van Tuyl: Chemical processing wastes —Recovering fission products, *Ind. Eng. Chem.*, 50 (2), 212–216 (1958).

[16] H. H. Van Tuyl and R. L. Moore: Recovery of fission product cesium from acidic wastes, *Ind. Eng. Chem.*, 51 (6), 741–744 (1959).

[17] R. Harjula, J. Lehto, A. Paajanen, E. Tusa and P. Yarnell: Use inorganic ion exchange materials as precoat filters for nuclear waste effluent treatment, *React. Funct. Polym.*, 60 (1), 85–95 (2004).

[18] L. L. Burger, D. M. Strachan, D. A. Reynolds and W. W. Schulz: *A Summary of Available Information on Ferrocyanide Tank Wastes*, INIS, (1991).

[19] T. Prevost, M. Blase, H. Paillard and H. Mizuno: Areva's Actriflo-rad water treatment system for the Fukushima Nuclear Power Plant, *Int. J. Nucl. Power*, 308 (2012).

[20] A. Gay, P. Gillet, B. Ytournel, T. Varet, L. David, T. Prevost, C. Redonnet, G. Piot, S. Jouaville and G. Pagis: Multi-phased, post-accident support of the Fukushima Dai-Ichi Nuclear Power Plant, *WM2012*, 12246 (2012).

[21] A. Gotoh, H. Uchida, M. Ishizaki, T. Satoh, S. Kaga, S. Okamoto, M. Ohta, M. Sakamoto, T. Kawamoto, H. Tanaka, M. Tokumoto, S. Hara, H. Shiozaki, M. Yamada, M. Miyake and M. Kurihara: Simple synthesis of three primary colour

nanoparticle inks of Prussian blue and its analogues, *Nanotechnology*, 18 (34), 345609 (2007).

[22] M. Ishizaki, K. Kanaizuka, M. Abe, Y. Hoshi, M. Sakamoto, T. Kawamoto, H. Tanaka, and M. Kurihara: Preparation of electrochromic Prussian blue nanoparticles dispersible into various solvents for realisation of printed electronics, *Green Chem.*, 14 (5), 1537–1544 (2012).

[23] S. Hara, H. Shiozaki, A. Omura, H. Tanaka, T. Kawamoto, M. Tokumoto, M. Yamada, A. Gotoh, M. Kurihara and M. Sakamoto: Color-switchable glass and display devices fabricated by liquid processes with electrochromic nanoparticle "ink", *Appl. Phys. Express*, 1 (10), 1040021–1040023 (2008).

[24] S. Hara, H. Tanaka, T. Kawamoto, M. Tokumoto, M. Yamada, A. Gotoh, H. Uchida, M. Kurihara and M. Sakamoto: Electrochromic thin film of Prussian blue nanoparticles fabricated using wet process, *Jpn. J. Appl. Physics*, 46, 945–947 (2007).

[25] H. Shiozaki, T. Kawamoto, H. Tanaka, S. Hara, M. Tokumoto, A. Gotoh, T. Satoh, M. Ishizaki, M. Kurihara and M. Sakamoto: Electrochromic thin film fabricated using a water-dispersible ink of Prussian blue nanoparticles, *Jpn. J. Appl. Phys.*, 47 (2), 1242–1244 (2008).

[26] KM. Lee, H. Tanaka, A. Takahashi, K. H. Kim, M. Kawamura, Y. Abe and T. Kawamoto: Accelerated coloration of electrochromic device with the counter electrode of nanoparticulate Prussian blue-type complexes, *Electrochim. Acta*, 163, 288–295 (2015).

[27] R. Chen, H. Tanaka, T. Kawamoto, M. Asai, C. Fukushima, M. Kurihara, M. Watanabe, M. Arisaka, and T. Nankawa: Preparation of a film of copper hexacyanoferrate nanoparticles for electrochemical removal of cesium from radioactive wastewater, *Electrochem. Commun.*, 25 (1), 23–25 (2012).

[28] R. Chen, H. Tanaka, T. Kawamoto, M. Asai, C. Fukushima, H. Na, M. Kurihara, M. Watanabe, M. Arisaka and T. Nankawa: Selective removal of cesium ions from wastewater using copper hexacyanoferrate nanofilms in an electrochemical system, *Electrochem. Acta*, 87, 119–125 (2013).

[29] R. Chen, M. Asai, C. Fukushima, M. Ishizaki, M. Kurihara, M. Arisaka, T. Nankawa, M. Watanabe, T. Kawamoto and H. Tanaka: Column study on electrochemical separation of cesium ions from wastewater using copper hexacyanoferrate film, *J. Radioanal. Nucl. Chem.*, 303 (2), 1491–1495 (2015).

[30] D. Parajuli, A. Kitajima, A. Takahashi, H. Tanaka, H. Ogawa, Y. Hakuta, K. Yoshino, T. Funahashi, M. Yamaguchi, M. Osada and T. Kawamoto: Application of Prussian blue nanoparticles for the radioactive Cs decontamination in Fukushima region, *J. Environ. Radioact.*, 151 (P1), 233–237 (2016).

[31] A. Takahashi, H. Tanaka, N. Minami, M. Kurihara and T. Kawamoto: Simultaneous enhancement of Cs-adsorption and magnetic properties of Prussian blue by thermal partial oxidation, *Bull. Chem. Soc. Jpn.*, 88 (1), 69–73 (2015).

[32] M. Ishizaki, S. Akiba, A. Ohtani, Y. Hoshi, K. Ono, M. Matsuba, T. Togashi, K. Kananizuka, M. Sakamoto, A. Takahashi, T. Kawamoto, H. Tanaka, M. Watanabe, M. Arisaka, T. Nankawa and M. Kurihara: Proton-exchange mechanism of specific Cs$^+$ adsorption via lattice defect sites of Prussian blue filled with coordination and crystallization water molecules, *Dalton Trans.*, 42 (45), 16049–16055 (2013).

[33] A. Takahashi, N. Minami, H. Tanaka, K. Sue, K. Minami, D. Parajuli, KM. Lee, S. Ohkoshi, M. Kurihara and T. Kawamoto: Efficient synthesis of size-controlled open-framework nanoparticles fabricated with a micro-mixer - Route to the improvement of Cs adsorption performance, *Green Chem.*, 17 (8), 4228–4233 (2015).

[34] D. Parajuli, A. Takahashi, H. Noguchi, A. Kitajima, H. Tanaka, M. Takasaki, K. Yoshino and T. Kawamoto: Comparative study of the factors associated with the application of metal hexacyanoferrates for environmental Cs decontamination, *Chem. Eng. J.*, 283, 1322–1328 (2016).

[35] D. Parajuli, A. Takahashi, H. Tanaka, M. Sato, S. Fukuda, R. Kamimura and T. Kawamoto: Variation in available cesium concentration with parameters during temperature induced extraction of cesium from soil, *J. Environ. Radioact.*, 140, 78–83 (2015).

[36] GR. Chen, YR. Chang, X. Liu, T. Kawamoto, H. Tanaka, A. Kitajima, D. Parajuli, M. Takasaki, K. Yoshino, ML. Chen, YK. Lo, Z. Lei and DJ. Lee: Prussian blue (PB) granules for cesium (Cs) removal from drinking water, *Sep. Purif. Technol.*, 143, 146–151 (2015).

[37] D. Parajuli, Y. Suzuki, M. Sato, A. Takahashi, H. Tanaka and T. Kawamoto: Assessment of the measures for the extraction or fixation of radiocesium in soil, *Geoderma*, 267, 169–173 (2016).

[38] GR. Chen, YR. Chang, X. Liu, T. Kawamoto, H. Tanaka, D. Parajuli, ML. Chen, YK. Lo, Z. Lei and DJ. Lee: Prussian blue non-woven filter for cesium removal from drinking water, *Sep. Purif. Technol.*, 153, 37–42 (2015).

[39] D. Parajuli, H. Tanaka, Y. Hakuta, K. Minami, S. Fukuda, K. Umeoka, R. Kamimura, Y. Hayashi, M. Ouchi and T. Kawamoto: Dealing with the aftermath of Fukushima Daiichi nuclear accident: Decontamination of radioactive cesium enriched ash, *Environ. Sci. Technol.*, 47 (8), 3800–3806 (2013).

[40] [40] Ministry of Environment: Isezaki-shi Seiso Recycle Center 21—Ippan haikibutsu saishu shobunjo (dai sanki) shinshutsusui shori shisetsu horyusui ni okeru hoshasei cesium ryushutsu taisaku ni tsuite [Isezaki City Cleaning Recycling Center 21—On the measures against leachate of radioactive cesium in the effluent of the water processing plant of the general final disposal site (phase III)], https://www.env.go.jp/jishin/attach/haikihyouka_kentokai/08-ext_1.pdf, accessed 2015-12-20 (in Japanese).

[41] National Institute for Environmental Studies: Shokyaku hibai no mizusenjo ni yoru hoshasei cesium no jokyo (Removal of radioactive cesium by washing incinerated fly ash with water), http://www.nies.go.jp/shinsai/techrepo_r4_140414_8-10.pdf, accessed 2015-05-18 (in Japanese).

[42] Y. Namiki, T. Ueyama, T. Yoshida, R. Watanabe, S. Koido and T. Namiki: Hybrid micro-particles as a magnetically-guidable decontaminant for cesium-eluted ash slurry, *Sci. Rep.*, 4, 6294 (2014).

[43] Y. Nishizaki, H. Miyamae, S. Ichikawa, K. Izumiya, K. Takano, N. Kumagai and K. Hashimoto: New technologies for decontamination of radioactive substances scattered by nuclear accident, *Metall. Mater.*, 58 (1), 283–290 (2013).

[44] Mitsubishi Paper Mills Ltd.: Jisei kyuchakuzai o mochiita hoshasei cesium josen system ni tsuite (On the radioactive cesium decontamination system using magnetic adsorbents), http://www.mpm.co.jp/company/news/pdf/2012/20120517.pdf, accessed 2016-05-15 (in Japanese).

[45] M. Ishizaki, S. Akiba, A. Ohtani, Y. Hoshi, K. Ono, M. Matsuba, T. Togashi, K. Kananizuka, M. Sakamoto, A. Takahashi, T. Kawamoto, H. Tanaka, M. Watanabe, M. Arisaka, T. Nankawa and M. Kurihara: Proton-exchange mechanism of specific Cs$^+$ adsorption via lattice defect sites of Prussian blue filled with coordination and crystallization

water molecules, *Dalton Trans.*, 42 (45), 16049–16055 (2013).

[46] J. Munezawa and K. Nishi: Development of the radioactive cesium recovery system for effective safekeeping at the final disposal site "Adsorption separation-combustion oxidation -concentration", *Journal of the Society for Remediation of Radioactive Contamination in the Environment*, 2 (2), 101–110 (2014) (in Japanese).

[47] A. Kitajima, H. Tanaka, N. Minami, K. Yoshino and T. Kawamoto: Efficient cesium adsorbent using Prussian blue nanoparticles immobilized on cotton matrices, *Chem. Lett.*, 41 (11), 1473–1474 (2012).

[48] A. Kitajima, H. Ogawa, T. Kobayashi, T. Kawasaki, Y. Kawatsu, T. Kawamoto and H. Tanaka: Monitoring low-radioactivity caesium in Fukushima waters, *Environ. Sci. Process. Impacts*, 16 (1), 28–32 (2014).

[49] H. Ogawa, A. Kitajima, H. Tanaka and T. Kawamoto: Numerical evaluation of Cs adsorption in PB column by extended Langmuir formula and one-dimensional adsorption model, *J. Radioanal. Nucl. Chem.*, 303 (2), 1287–1290 (2014).

[50] Ministry of Health, Labour and Welfare: *Jiko Yurai Haikibutsu To Shobun Gyomu Tokubetsu Kyoiku Text* (Textbook on special instruction for disposal of waste material arising from the accident), (2013) (in Japanese).

[51] KM. Lee, M. Asai, T. Uchida, T. Kawamoto, K. Minami, A. Takahashi, D. Parajuli, G. Kido, M. Takasaki, K. Yoshino and H. Tanaka: Decomposition of iron hexacyanoferrate microcapsule beads using superheated steam, *Chem. Lett.*, (2016) (in press).

[52] D. Parajuli, H. Noguchi, H. Tanaka, T. Kawasaki, Y. Kawatsu, T. Kobayashi and T. Kawamoto: Effective removal of hexacyanoferrate anions using quaternary amine type ion exchange resin, *J. Environ. Chem. Eng.*, 3 (4), 2448–2452 (2015).

[53] National Institute for Environmental Studies: Hibai senjo gijutsu ni kansuru gijutsu shiryo (Shisetsu seino sekkei ni kakaru shishin) [Technical reference material on fly ash washing technology (Guidelines for performance and design of plants)], (2014) (in Japanese).

[54] Ministry of Agriculture, Forestry and Fisheries: Tameike no hoshasei busshitsu taisaku gijutsu manual (Manual for measures against radioactive materials in small reservoirs), http://www.maff.go.jp/j/press/nousin/saigai/150327.html, accessed 2016-02-28 (in Japanese).

[55] National Institute of Advanced Industrial Science and Technology: Kaisuichu no teinodo hoshasei cesium o jinsoku ni monitoring (Quick monitoring of low-concentration radioactive cesium in seawater), http://www.aist.go.jp/aist_j/press_release/pr2016/pr20160205/pr20160205 html, accessed 2016-02-28 (in Japanese).

Authors

Tohru KAWAMOTO

Graduated from the Department of Material Physics, School of Engineering Science, Osaka University in 1992. Completed the doctor's program at the Department of Materials Engineering Science, Graduate School of Engineering Science, Osaka University in 1997. Joined the Electrotechnical Laboratory, Agency of Industrial Science and Technology, Ministry of International Trade and Industry in 1997. Engaged in the theoretical research of external responsive materials. Researcher, Nanotechnology Research Institute, AIST in 2001; Senior Researcher in 2006; Group Leader, Molecular Nanophysics Group, Nanosystem Research Institute in 2010; Group Leader, Green Technology Research Group; and Group Leader, Nanoparticle Functional Design Group, Nanomaterials Research Institute in 2015. Visiting Researcher, Graduate School of Science and Engineering, Yamagata University from 2016. In this paper, was in charge of the supervision of the R&D.

Hisashi TANAKA

Graduated from the Department of Chemistry, School of Science, the University of Tokyo in 1994. Completed the doctor's course at the Department of Chemistry, Graduate School of Science, the University of Tokyo in 1999. Doctor (Science). Engaged in the research of molecular superconductor at the Institute for Molecular Science, as Postdoctoral Fellow, Japan Society for the Promotion of Science in 1999. Joined AIST in 2002. Researcher, Nanotechnology Research Institute; Senior Researcher in 2007; Senior Researcher, Nanosystem Research Institute in 2010; and Senior Researcher, Nanomaterials Research Institute in 2015. In this paper, was in charge of the development and evaluation of the adsorbents.

Yukiya HAKUTA

Graduated from the Department of Chemistry, School of Engineering, Tohoku University in 1988. Withdrew from the Department of Chemistry, Graduate School of Engineering, Tohoku University in 1993. Assistant, School of Engineering, Tohoku University in 1993. Joined AIST in 2001. Researcher, Supercritical Fluid Research Center. R&D Staff, Chemicals Division, Manufacturing Industry Bureau, Ministry of Economy, Trade and Industry in 2007. Senior Researcher, Research Center for Compact Chemical Process, AIST in 2008; Senior Researcher, Nanosystem Research Institute in 2010; and currently, Group Leader, Nanoparticle Structure Design Group, Nanomaterials Research Institute in 2015. In this paper, was in charge of the demonstration at the pilot plant for incinerated ash decontamination.

Akira TAKAHASHI

Graduated from the Faculty of Engineering, Kyoto University in 2009. Completed the master's course at the Department of Materials Science and Engineering, Graduate School of Engineering, Kyoto University in 2011. Joined AIST in 2011. Researcher, Green Technology Research Group, Nanosystems Research Institute in 2011. Started the doctor's course at the Department of Chemistry, Graduate School of Science, the University of Tokyo in 2013 while maintaining position at AIST. Researcher, Nanoparticle Functional Design Group, Nanomaterials Research Institute, AIST in 2015. In this paper, was in charge of the synthesis of adsorbents and study of its physical properties.

Durga PARAJULI

Obtained the Masters of Science and Technology in Physical Chemistry at the Tribhuvan University (Nepal) in 2002. Completed the doctor's course at the Saga University in 2006. Doctor (Engineering). Postdoctoral Researcher, Graduate School of Science and Engineering, Saga University in 2006. Postdoctoral Researcher, Quantum Beam Science Center, Japan Atomic Energy Agency from 2008 to 2011. Researcher, Nanosystem Research Institute, AIST in 2011; Researcher, Green Technology Research Group, Nanosystem Research Institute in 2014; and Researcher, Nanoparticle Functional Design Group, Nanomaterials Research Institute in 2015. In this paper, was in charge of the development of cesium elution method from incinerated ash and the development of adsorbents.

Kimitaka MINAMI

Completed the doctor's program at the Department of Chemical Engineering, Graduate School of Engineering, Tohoku University in 2005. Research Center for Compact Chemical Process, AIST in 2005; Institute of Multidisciplinary Research for Advanced Materials, Tohoku University in 2006; Advanced Institute for Materials Research, Tohoku University in Nov 2007; and Assistant, New Industry Creation Hatchery Center, Tohoku University in 2010. Engaged in researches on supercritical fluid and nanoparticle synthesis. Joined the Nanosystem Research Institute, AIST in March 2012; and Senior Researcher from Oct 2013. In this paper, was in charge of the design of the pilot plant.

Tetsuo YASUTAKA

Graduated from the Department of Agricultural and Environmental Engineering, Faculty of Agriculture, Kyoto University in 2000. Completed the master's program at the Graduate School of Agriculture, Kyoto University in 2002. Joined the Kokusai Kogyo Co., Ltd. in 2002. Completed the doctor's program at the Graduate School of Environment and Information Sciences, Yokohama National University in 2007. Researcher, Research Institute for Geo-Resources and Environment in 2011; and Senior Researcher in 2013. In this paper, was in charge of the development of monitoring technology and on-site application.

Tatsuya UCHIDA

Graduated from the Department of Fermentation Technology, Faculty of Engineering, Yamanashi University in 1970. Joined Hitachi Chemical Co., Ltd. in 1970. Worked on the environmental restoration integrated with the production facilities, R&D for Waste Material Recycling Division, and helped export overseas plants. Manager of Design, Household Equipment Division in 1995; Managing Plant Director; and Director, CSR Department and Quality Assurance General Manager, Environmental Safety Department, Cooperate Business Strategy Headquarters in 2004. Member, Recycling Committee, Japan Nuclear Fuel Ltd. from 2005. Established the Uchida Professional Engineer Office in 2008. Technical Support Advisor, AIST in 2011; and Visiting Researcher from 2015. In this paper, was in charge of the design of the pilot plant.

Discussion with Reviewers

1 Overall
Comment (Toshimi Shimizu, AIST)

This paper discusses the decontamination technology for incinerated ashes by using the Prussian blue nanoparticles, in response to the urgent demand against the radioactive material leakage accident at the Fukushima Daiichi Nuclear Power Plant of the Tokyo Electric Power Company. It presents typical nanotechnology in which wide-ranging scales are linked seamlessly from nanoparticles, adsorbents, adsorption systems, to plant construction. Of particular interest is the description of the related technologies that were built under specific environments and conditions, from overviewing the total issue, creating the original research strategy, to collaborating and making adjustments with various stakeholders including the researchers of different fields, Japanese government, local governments, and local residents. I think this paper is suitable for publication in *Synthesiology*.

Comment (Naoto Kobayashi, Waseda University)

This paper describes the results of R&D that has provided solutions in an extremely short period of time using PB nanoparticles, for the urgent issue of decontaminating the leaked radioactive materials from the Fukushima Daiichi Nuclear Power Plant of the Tokyo Electric Power Company due to the Great East Japan Earthquake. It is a significantly useful paper that presents the attainment of the final goal of verification and practical use through collaboration with companies. I believe it is suitable for publication in *Synthesiology*. On the other hand, there seems to be a lack of scientific explanation on the effectiveness of decontamination by PB nanoparticles, which is the essential technology, and additional explanation is recommended.

2 Figure to present the R&D organization
Comment (Toshimi Shimizu)

The explanations of elemental technologies and the integration scenario for synthesiological discussion are presented in Figs. 2 and 4, Table 2, and others. On the other hand, in this research, the stakeholders are the central government, local governments of prefectures, cities, towns, or villages, and local residents, as well as technology users and product manufacturers. It can be positioned as a specific R&D in which the urgent problems had to be solved in a situation where related laws were still lacking. The research was conducted in the restriction of compliance and involved diverse and complex collaboration and interrelationships, but I feel such complexity and difficulty are not sufficiently expressed in the present figures.

For example, I remember that the industry-academia-government collaboration framework was formerly categorized into three forms in AIST, one-to-one collaboration such as regular joint research or subcontracted research, one-to-many such as research consortiums and platforms, and many-to-many such as research associations and research bases. I think the general readers will find it interesting to know how the one-to-one or one-to-many collaboration framework that started from the development of adsorbents and PB nanoparticle mass production through corporate joint research had shifted to some other

collaborative structure, and whether there was a new collaborative framework different from the above three categories. If possible, could you create a schematic illustration to show how the environment surrounding this R&D (including the stakeholders) changed over time? If this is not possible, could you present a schematic illustration that shows the R&D framework (including the stakeholders) at the final stage?

Answer (Tohru Kawamoto)

We decided it was difficult to represent this in a figure, so we added the new subchapter, "3.4 Flow of corporate collaboration and collaboration with the government and local government," in the manuscript.

3 Ways of collaborating with the companies

Question & Comment (Naoto Kobayashi)

In this paper, "3.1 Transferring strategy" was very well written and it is very important. I think it is useful for researchers who will be involved in the "bridging research" or translational research in the future, including those at universities. However, in reality, industry-academia collaboration often does not work very well. If you know any "secrets" in transferring to companies based on your experience, please tell us.

Answer (Tohru Kawamoto)

Thank you for your encouraging comments. For the practical utilization based on the technology originated in the research institute, the important points are described below. Please note that the situation would be different in the case where the research demand is raised by companies. Basically, It would be necessary to establish Table 2 as formal knowledge. Specifically, it is as follows:

(1) Visualization of the business image is the most important, even if it is just an expectational diagram. In general, the researcher in the research institute thinks that the companies should create their business models. However, if we think so, the project will fail regardless of whether the technology is good or bad when the companies cannot achieve their business model. Of course, the companies are responsible for their final business models. However, at the start of the R&D, when the companies know no details, construction of the draft of the model by the institute-side would be important for discussion.

(2) The design of the supply chain is also important. If the partner company is large, it would cover all of the supply chain on its own. But a small and medium-sized company often cannot do that. When a small and medium-sized company establishes the business model, the research institute needs to suggest some material supplier, for example.

(3) Consideration for handling of intellectual properties are also important. At least, when you aim for commercialization involving multiple companies as in this case, AIST is required to keep the basic intellectual property to make the companies follow our vision.

Although I focused on topics other than research, specialty of the technology is the most important, as described in Subchapter

3.4.

Note that we have not yet reached our research goal, unfortunately. I think we are out of the "valley of death" because the companies succeeded in commercializing the adsorbents and the products has been recommended in the government agency manuals. On the other hand, for true contribution to society, we must overcome the "Darwinian sea". Currently, we have not achieved industrialization, one of the reason being that the progress of the cesium decontamination by the government has gone slightly differently from our initial plan. Although this is totally the role of the companies, "what the research institution can do in this stage?" is an issue to be considered.

4 Storage of the adsorbents

Question & Comment (Naoto Kobayashi)

In "2.2.4 Investigation of the storage and disposal of the waste material," you describe the establishment of a mild oxidation method using heated steam. Since this is an extremely important technology in your R&D, it is recommended to show the reference for published papers, if any. If this is the first description, you should provide more explanation including figures about the "large amount of oxidative heat."

Answer (Tohru Kawamoto)

It is cited as Reference [51] as a paper on it has been published on March 25, 2016.

5 Science of hexacyanoferrate

Question (Toshimi Shimizu)

In the cesium adsorption using hexacyanoferrates, are there any scientific experiments on what kinds of structural factors affect the adsorption performance? For example, do different metals such as iron, cobalt, nickel, copper, zinc, or others, or the different composition of iron/cyanoferrate group/ water have great effect on that? In practical application, the adsorbent needs to be used under various and complex aqueous conditions (temperature, coexistence of various ions, presence of other molecular compounds, pH, concentration, etc.). From the perspective of analytical chemistry, are the optimal metal species and compositions for each adsorption under various conditions clear? Or, is it necessary to conduct an adsorption test for each adsorbent on site? Please explain from the scientific view of analytical chemistry.

Answer (Tohru Kawamoto)

I think the optimal solution at the academic paper level is mostly known, e.g. concerning the capacity of the cesium adsorption or high-pH resistance by changing the metal species. However, there isn't a lot of work for the detailed dependence on the composition ratio of each metal species. We have determined the chemical composition with intensive investigation such as the elution properties after adsorption. However, Prussian blue has different properties compared to other analogues. Its mechanism of cesium adsorption is not completely understood. This issue will be discussed elsewhere, since this discussion is beyond the scope of this paper.

Development of HASClay® as a high-performance adsorption material

— Developing adsorbents for energy conservation systems from a kind of clay nanoparticle —

Masaya Suzuki[1]*, Masaki Maeda[2] and Keiichi Inukai[2]

Given the need to reduce greenhouse gases, we have developed an inorganic porous material, HASClay, which possesses excellent water vapor adsorptive efficiency, and the ability to dehydrate using a low grade heat source. In this paper, we explain how the synthetic process of HASClay was developed from a study of naturally existing clay and nanomaterials, and the requirements for widespread use as an adsorption material for energy conservation.

Keywords : HASClay, energy conservation, desiccant air conditioning, moisture conditioning material, synthesis method

1 Objective of the research

In the 21st Conference of the Parties (COP21) of the United Nations Framework Convention on Climate Change (UNFCCC) that was held in Paris in December 2015, the Paris Agreement was adopted as the new framework following the Kyoto Protocol. Further energy savings will be necessary for Japan to reduce greenhouse gases to prevent global warming. The energy-saving technology in Japan has seen innovative development since the 1990s when the reduction of greenhouse gases became a serious social issue. The use of waste heat has also advanced, and currently, waste heat of 100 °C or higher is utilized efficiently, but the technology to use low-temperature waste heat of less than 100 °C is being researched.

There are two types of energy-saving systems using low-temperature waste heat: the adsorption heat pump (adsorption refrigerator) that uses heat generation and absorption that occur when water vapor or ammonia is adsorbed/desorbed by the adsorbent, and the desiccant air conditioning system by which energy saving efficiency can be increased through effective water vapor removal. Desiccant air conditioning uses desiccant rotors including adsorbents to dehumidify and then lowers the temperature to the target temperature. Figure 1 shows the outline diagram of the desiccant air conditioning system. The dehumidification part is separated into the dehumidification zone and reuse zone. In the dehumidification zone, the air taken in from the outside is dehumidified and then supplied to the room, while in the reuse zone, the room air is warmed with a heater to recover the air by releasing the water vapor adsorbed in the dehumidification zone. The adsorption heat pump and the desiccant air conditioning

system have been in existence since the 1990s, but zeolite and silica gel were used as adsorbents. There was a demand for adsorbents that were capable of adsorption/desorption at low temperature of 100 °C or less.

Against such a background, in Japan, the development of adsorbents that can be reused at low temperatures of 40–80 °C was conducted from the late 1990s to early 2000s. The development of adsorbents such as AFI- or CHA-type low-temperature reusable zeolite (AQSOA®), mesoporous silica (TMPS), or polymer adsorbents (TAFTIC®) was conducted. Allophane and imogolite were candidates of clay nanomaterials at the time, and their water vapor adsorption isothermal curves are shown in Fig. 2.[1]-[4] As can be seen,
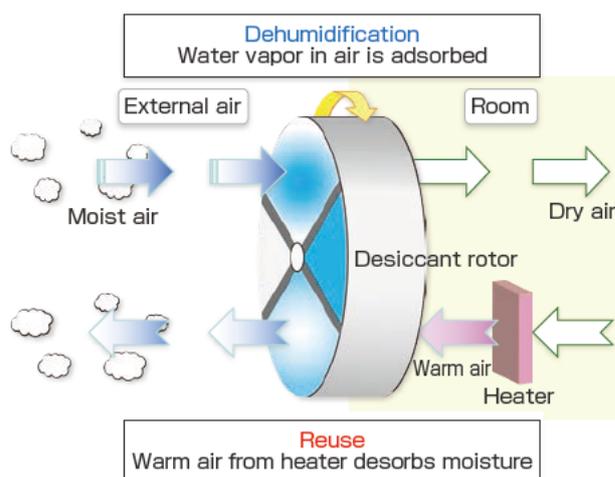

Fig. 1 Outline of the desiccant air conditioner that uses water vapor adsorbent

1. The Research Institute for Geo-Resources and Environment, AIST   Tsukuba Central 7, 1-1-1 Higashi, Tsukuba 305-8567, Japan   * E-mail: masaya-suzuki@aist.go.jp, 2. Structural Materials Research Institute, AIST   2266-98 Anagahora, Shimoshidami, Moriyama-ku, Nagoya 463- 8560, Japan

the adsorption isothermal curves can be roughly divided into two. One is the S-shaped curve that shows rapid start-up in a certain relative humidity range as in the low-temperature reused zeolite and mesoporous silica, and the linear type in which the relative humidity and water vapor adsorption volume show a linear relationship without rapid start, as in the polymer adsorbents and allophane. With adsorption heat pump, the operating environment temperature, waste heat temperature, and cold water temperature in the system are controlled, and because the operating humidity range is determined by these three temperatures, an adsorbent with an S-shape with rapid start-up in the operating humidity range is suitable. On the other hand, because the desiccant air conditioning takes in air with varying humidity, an adsorbent with a linear property where adsorption is possible at a wide humidity range is more suitable.

In this context, (1) no merit was seen in developing adsorption heat pump because the device size would be twice as large as the absorption heat pump that was already widely used, and (2) the adsorption isothermal curves of allophane and imogolite that we had been studying showed a linear characteristic in the medium humidity range. Therefore, we decided to target desiccant air conditioning, and develop a linear inorganic water vapor adsorbent that has performance equivalent to polymer adsorbents.
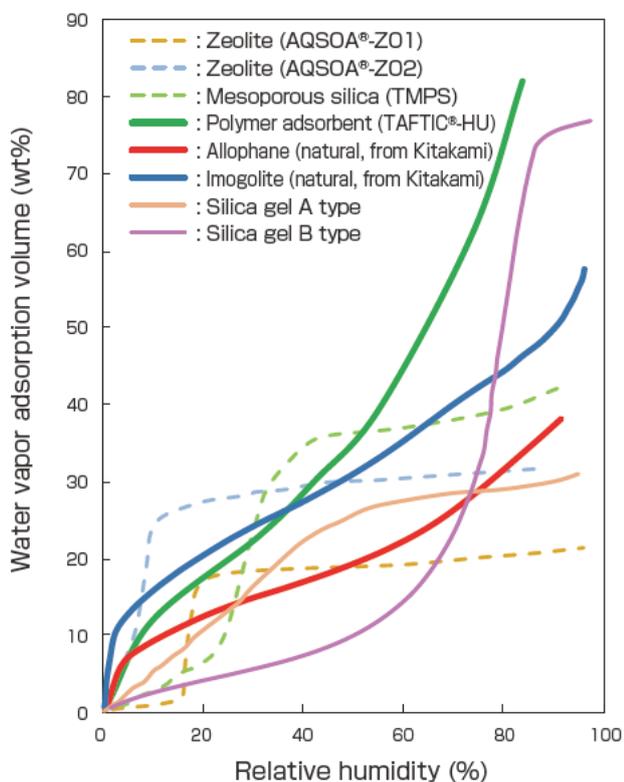

Fig. 2 Water vapor adsorption isothermal curve of the adsorbents that can be reused by low-temperature treatment
(AQSOA®-Z01[2], AQSOA®-Z02[2], TMPS[3], TAFTIC®-HU[4])

2 History of the development (1990s–2005)

2.1 Nanoparticles that exist in the soil
The National Industrial Research Institute of Nagoya (NIRIN), Agency of Industrial Science and Technology to which the authors belonged had been researching ceramics and metals in the Chubu region since its inception in 1952. The work of the Imperial Ceramic Experimental Institute, which was one of the institutes integrated when NIRIN was established, was carried over to Unit 6 (later, Department of Ceramic Technology), and the ceramics research was continued there. The authors were at the Raw Materials Technology Laboratory, Department of Ceramic Technology, and engaged in the research on clay, the raw material of ceramics, as well as utilization of pore that was a major clay characteristics. Allophane and imogolite were clays that had interesting forms.

When one hears of nano-capsules and nanotubes, one immediately thinks of C_{60} fullerene or carbon nanotubes, but nano-capsules and nanotubes exist in the weathered soil derived from volcanic ash. These are substances known as allophane and imogolite. Allophane has the shape of nano-capsules with a diameter of 3.5–5.0 nm, while imogolite is in the shape of nanotubes with an exterior diameter of 1.8–2.2 nm and length of several ten nm–several μm. The schematic diagrams of allophane and imogolite structures are shown in Fig. 3,[5][6] and the transmission electron microscope (TEM) photographs are shown in Fig. 4.[7] The basic structure of allophane and imogolite is the SiO_4 tetrahedron in which the pinnacle is the hydroxyl group bond, and the bottom three oxygen atoms are shared with aluminum, inside the gibbsite sheet composed of aluminum hydroxide. This structure does not include the Si-O-Si bond, and the distance between oxygen atoms of the gibbsite sheet that is bonded to the silicone is quite short. The gibbsite sheet is curved due to this misfit, and this gives the characteristic structure to allophane and imogolite.

Since allophane and imogolite can be seen occasionally in the soil derived from volcanic products such as pumice or volcanic ash, they were mainly studied in the field of soil science until about 1990, but later, they were investigated for their functions as catalysts or gas storage materials. They not only have special nano-size shapes and high specific surface areas, but also have excellent hydrophilicity and adsorption capacity. Therefore, they are studied for application to adsorbents of hazardous pollutants, humidity controlling agents that autonomously control the humidity in the living area, polymer nano-composites, and for application in medical fields.[8]

2.2 Development of humidity controlling building materials using allophane
Japanese buildings were traditionally constructed with wood and mud, and therefore, had good humidity control,

condensation prevention properties, and fungicidal properties, but problems of condensation began to develop as highly airtight buildings were constructed. Corresponding air conditioning facilities became necessary, but from the perspective of energy savings and facility management, humidity controlling building materials were developed to give humidity control functions to the materials themselves.

Allophane was used as such a humidity controlling building material. Allophane dehumidifies when the humidity increases, and humidifies when the humidity decreases, and is capable of maintaining the humidity range in which people can live comfortably. The successful development of humidity controlling tiles using allophane was conducted jointly with a company.[9] These humidity controlling tiles with allophane are used in the building of AIST Chubu.

2.3 Development of imogolite

Imogolite is composed of naturally existing nanotubes. Since the amount existing in nature is extremely small, it was necessary to synthesize it. The synthesis was already done by Farmer et al. in 1977, but it was conducted in dilute concentration. We succeeded in synthesizing at higher concentration of about 10 times the conventional method, by adding a desalination procedure to the processes.[10] Even using this method, only a few grams could be recovered by dehydrating 1 L of the solution, and it was one digit less compared to general clay synthetic products in terms of

production efficiency. On the other hand, when imogolite was evaluated as a heat exchange adsorbent for adsorption heat pump using hydration heat measurement, it was found that it had excellent capacity even by reuse at 40 °C,[11] but we were unable to conduct a practical evaluation.

3 History of the development of new adsorbents (2005–present)

3.1 Breakaway from imogolite

After completing the synthesis and evaluation of imogolite as a heat storage agent by 2003, we looked at various applications for use as nanotubes, and started activities for realizing practical use and pioneering new usages.

The first foothold was a research commission from the Shingijutsu Kyokai (New Technology Association) that was subcontracted by the Japan Science and Technology Agency (JST) in 2004. The "Imogolite Synthesis and Application Technology Workshop" was set up, and investigations were done in the fields of environmental technologies, energy savings, and living environment. We also set up the "Imogolite Workshop" at AIST Chubu in 2006, and obtained opportunities to participate in exhibitions and others at the International Nanotechnology Exhibition and Conference (Nano Tech), and were able to hear voices from companies.

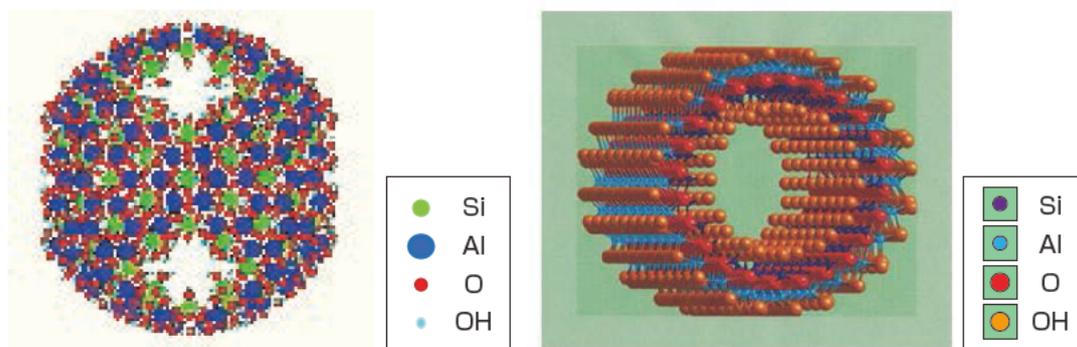We found that the fields of application of imogolite included

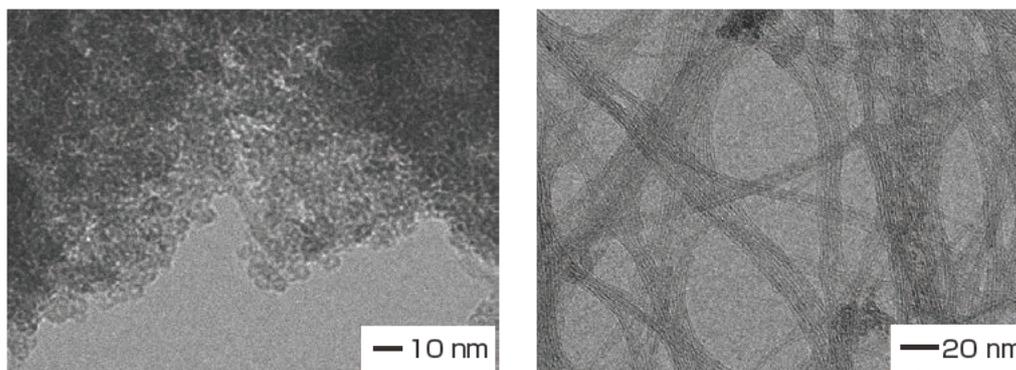Fig. 3 Structural models of allophane and imogolite (Left: allophane[5], right: imogolite[6])

Fig. 4 TEM photographs of allophane and imogolite (Left: allophane[7], right: imogolite[7])

not only the desiccant air conditioning and humidity controlling building materials that we had been studying, but also many domains that the authors never imagined, including compositing with fibers, compositing with rubber, cell immobilizers, release control of aroma, and others (Fig. 5). Since imogolite is composed of nanotubes, we conducted joint research with Hokkaido University to evaluate safety in organisms.

As a result of talking to and conducting joint research with various companies, the following points can be raised as important.

- No matter how good the performance, if its synthesis remains at a laboratory level and there is no prospect for being handled by some company in the future, it is difficult for the company which will be using this material to evaluate in terms of sales and marketing.
- No matter how well it can be synthesized at a laboratory level, unless the method can be used for synthesis at an industrial level, the manufacturers cannot engage in production in tons.
- No matter how well the performance, the range of use will be narrowed if it is expensive, wide diffusion to society cannot be expected, and initial performance may not be attainable since it will be mixed with other substances to cut costs (the only field where it can be used despite high costs is the medical field).
- As can be seen with the case of asbestos, there is concern for the safety of nanotubes, even if we explain the

imogolite properties or its form after dehydration.

Considering the above points, we reached the conclusion that it was meaningless if we were stuck at the research level at AIST, even though the materials had interesting performance and were worthy of obtaining national development grants. It was necessary to conduct materials development that led to future practical use and was cost effective. Therefore, we decided to terminate the research of imogolite except for the medical field.

3.2 Development of a new adsorbent by setting target conditions

Learning from the research on imogolite described above, we conducted investigation on the possibility of forming composites of a HO-Si(-OAl)$_3$ structure, which is the basic structure of allophane and imogolite, and a single layer of layered clay. The schematic diagram of the structure of this new adsorbent is shown in Fig. 6. As the background of this idea, the HO-Si(-OAl)$_3$ structure, which is the basic structure of allophane and imogolite, is formed when the silicate aqueous solution in which the Si/Al molar ratio is prepared to 0.5 is mixed with an aluminum aqueous solution.[12] We thought it was possible to form a 1:1 layer of layered clay where the molar ratio is 1.0 by increasing the Si/Al molar ratio, and to create a composite that contained the structures of the two substances.

On the other hand, we set the target values for the yield that enabled reasonable cost and mass production. For sales price, we targeted the price somewhere between that of silica gel (about 100 yen/kg) and zeolite (1,000 yen/kg) that were being used widely as adsorbents. We set the minimum necessary conditions needed for the synthesis at the beginning, and then started the development. The conditions are shown below (Fig. 7).

(1) From the perspective of synthesis cost, it should be synthesized using raw materials of liquid glass, aluminum sulfate, and sodium hydroxide, to enable synthesis using substances with low raw material cost.

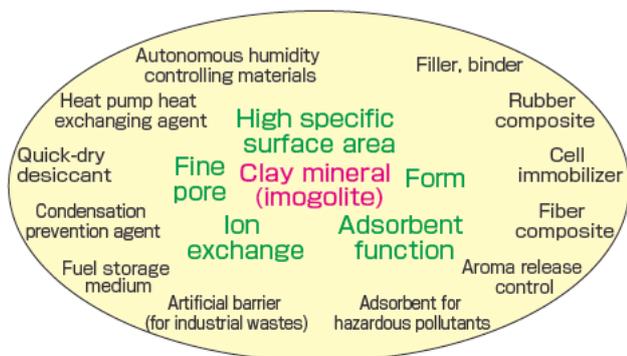(2) To enable industrial synthesis in tons, it should be synthesized using the method for zeolite which is widely
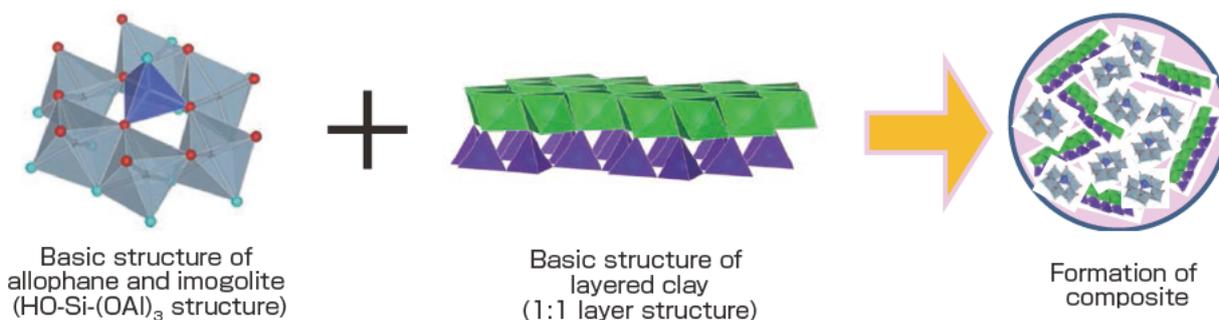

Fig. 5 Fields in which imogolite is used

Fig. 6 Schematic diagram of the formation of new adsorbent structure

used where the heating temperature is less than 100 °C.

(3) The method shall be one where synthesis can be accomplished at one cycle per day.

(4) The synthesis efficiency (yield) shall be adjusted so the concentration at heating will produce 100 g or more of solid weight after dehydration of 1L of the solution.

The number of parameters to be investigated decreased by setting the binding condition as in (1)–(4), and we set the most important parameter as Si/Al molar ratio.

After setting such conditions, we attempted the synthesis of materials that showed adsorption volume of more than 30 wt% at relative humidity of 60 %, and had a linear adsorption isothermal curve. As a result, we succeeded in synthesizing an excellent water vapor adsorbent called HASClay®.[13]

The name HASClay® is derived from the fact that in its x-ray diffraction pattern, although there was no peak or layer structure of amorphous hydroxyl aluminum silicate (HAS), there was a peak for clay sheet. Also, the product was not a mixture of two substances but was one substance, and this was deemed the composite of HAS and clay, hence the name HASClay. The performance of HASClay was about 45 wt%, which greatly surpassed the initial target value of 30 wt% at relative humidity of 60 %. Considering the prospect of this future adsorbent we trademarked the product.

3.3 Study of the structure of HASClay and categorization by performance

Along period of two years was required for us to reach HASClay®. First, we were able to synthesize the material that was the primary substance of HASClay® (HASClay grade III or HASClay GIII). However, in ordinary analysis such as powder X-ray diffraction, we were unable to determine the difference between allophane and a Si/Al amorphous substance, and the difference could be seen only by solid NMR.

To clarify the structure of this substance, we temporarily suspended the conditions we set in Subchapter 3.2, and shifted to the identification of the substances. In the synthesis
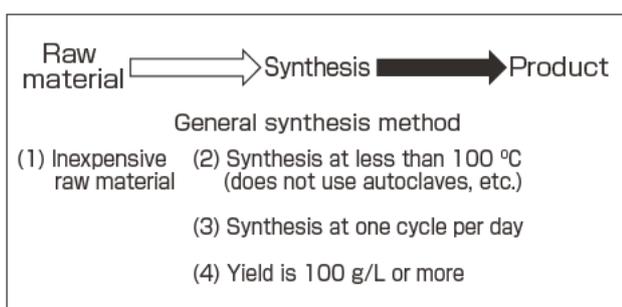
procedure, we conducted the removal of salts such as sodium chloride and sodium sulfate by centrifugation that was mandatory in high-concentration synthesis of imogolite, and the synthesis temperature of 98 °C or less was raised to 110 °C or more. As a result, by desalination, the water vapor adsorption capacity increased (HASClay grade II or HASClay GII). By further removing the salts and heating for 4 h at 200 °C, we discovered a substance that could be clearly identified by X-ray powder diffraction, and this was called the highest performing HASClay® (HASClay grade I or HASClay GI) that was the composite of amorphous aluminum silicate and low-crystalline clay. The HASClay GII and GIII became HASClay GI when it was heated for 40 days at 98 °C, and they were called HASClay precursors.

The X-ray powder diffraction patterns for HASClay GI and HASClay GIII are shown in Fig. 8,[13] the ^{29}Si-NMR spectra in Fig. 9,[14][15] and their TEM photographs are shown in Fig. 10.[14][16]

In X-ray powder diffraction, HASClay GI had two types of peaks: one was a broad peak corresponding to the reflection of layered clay minerals (*hk0*) at around $2\theta = 21°$ and $35°$, and the other was a broad peak characteristic to amorphous aluminum silicate at around $2\theta = 26°$ and $40°$. In contrast, HASClay GIII had only one broad peak that was characteristic to amorphous aluminum silicate at around $2\theta = 26°$ and $40°$.

In the ^{29}Si-NMR spectrum, HASClay GI had a sharp peak at −78 ppm and a broad peak at −86 ppm and −110 ppm. The sharp peak of −78 ppm was caused by the structure similar to allophane and imogolite, and the remaining −86 ppm peak corresponded to the structure of layered aluminum silicate such as vermiculite, while the −110 ppm peak appeared in the area of peaks caused by a structure where all sides of Si tetrahedron had the Si-O-Si bonds. HASClay GIII showed a sharp peak at −78 ppm that arose from the structure similar to allophane and imogolite in the ^{29}Si-NMR spectrum, and

Raw material ⟹ Synthesis ⟹ Product

General synthesis method

(1) Inexpensive raw material

(2) Synthesis at less than 100 °C (does not use autoclaves, etc.)

(3) Synthesis at one cycle per day

(4) Yield is 100 g/L or more

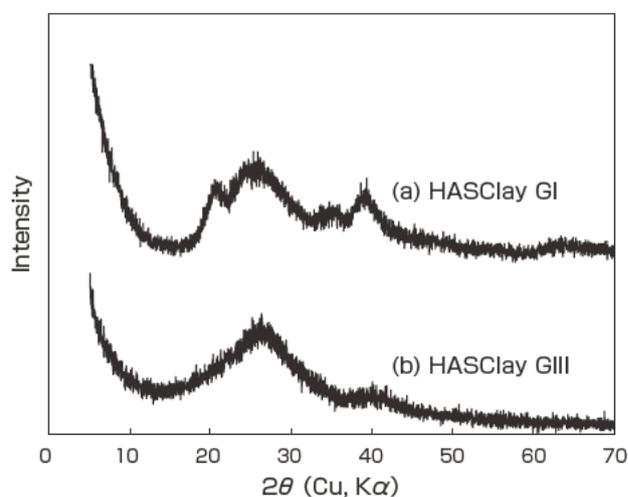**Fig. 7 Conditions necessary for the synthesis of new adsorbents**

Fig. 8 Powder x-ray diffraction pattern of HASClay

Table 1. Category and comparison of HASClay

Name	Synthesis temperature	Desalination before heating	Manufacturing cost	Specific surface area
HASClay®-GI	150～200 ℃	Yes	High	750～850 m²/g
HASClay®-GII	80～100 ℃	Yes	Somewhat low	550～650 m²/g
HASClay®-GIII	80～100 ℃	No	Low	450～550 m²/g

another −86 ppm peak that corresponded to the structure of layered aluminum silicate such as vermiculite.

In TEM observation, HASClay GI was composed of particles of a size about 10 nm,[14] while HASClay GIII was composed of particles of 2–10 nm sizes and hollow spherical particles of 2–3 nm sizes like allophane .[16]

The x-ray powder diffraction pattern of HASClay GIII showed the diffraction pattern of amorphous aluminum silicate, and it could not be differentiated from other amorphous aluminum silicates in the TEM observation. The differentiation of the amorphous aluminum silicate was made possible by the solid ^{29}Si-NMR spectrum that showed two peaks of one derived from the allophane and imogolite

structure and the other derived from the clay structure.

The category and comparison of the three types of synthesized HASClay are shown in Table 1, and their water vapor adsorption isothermal curves are shown in Fig. 11. In HASClay performance, it is estimated that the reason the performance increases by desalination before heating is related to the formation of imogolite. In the synthesis of imogolite, it is known that the growth of nanotubes is inhibited in the presence of anions of chloride ions.[10] Therefore, it is necessary to remove the anions for the development of structures like imogolite to a certain degree.

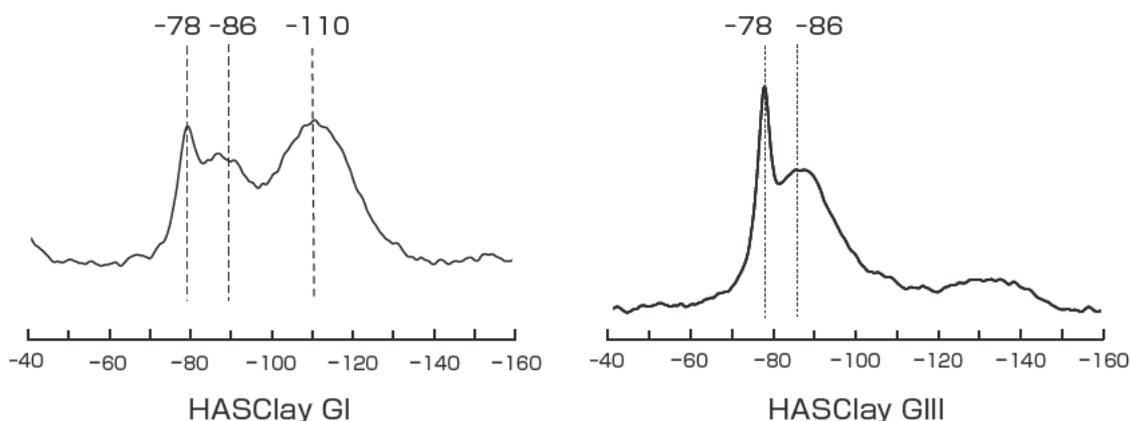By the way, heating at 200 ℃ was a taboo for those who had been studying imogolite. This was because we knew that
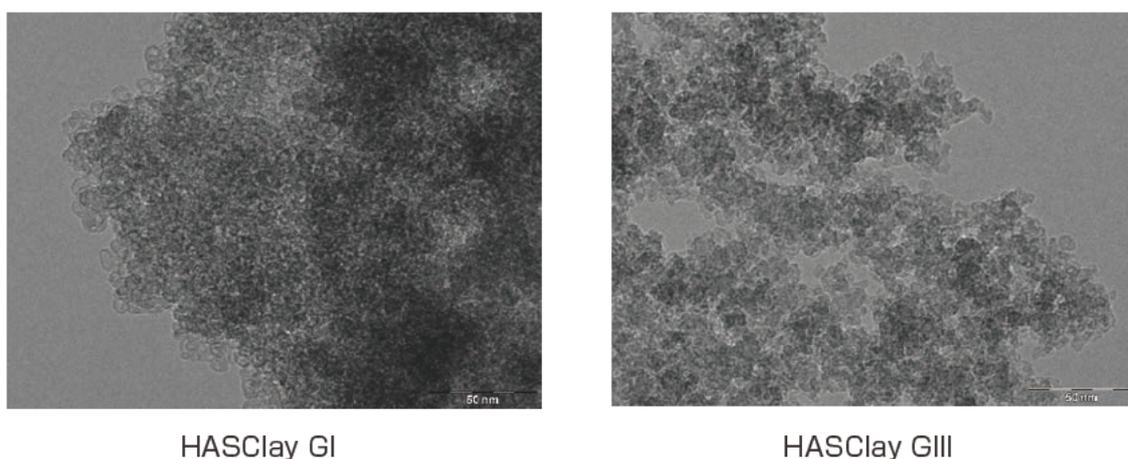

Fig. 9 ^{29}Si-NMR spectra of HASClay

Fig. 10 TEM photographs of HASClay (Left: HASClay GI[16], right: HASClay GIII[14])

phase separation occurred when heating was done at 120 °C or higher, and imogolite would not be produced.[17] This taboo was broken by one question from an assistant staff who said, "What happens when HASClay GIII is heated at high temperature?" At that time, the project was almost over and we had time on our hands, so we went ahead to actually see the phase separation phenomenon, but this led to the discovery of a new substance. We thought it was important not to blindly accept what we had experienced thus far, and to listen to and not reject the ideas of novices. However, over one year passed after the discovery of HASClay GIII before we discovered HASClay GI.

4 Scenario after the development of adsorbents

4.1 Role of AIST in the initial product realization

Although it became possible to develop excellent adsorbents, for industrial mass synthesis, we decided to go ahead with the commercialization of HASClay GIII product since its synthesis method was simple.

The investigation of desiccant rotors that was our primary objective was done using the new material HASClay GIII through joint research with a company that wished to fabricate a desiccant rotor using imogolite. About 1 kg of powder was synthesized without any problem, and good results were obtained in the papermaking test. In the next stage, we shifted to the fabrication of the rotor by actual

Fig. 11 Water vapor adsorption isothermal curves of HASClay

full papermaking, and the amount necessary was 40 kg of powder. In addition to the fact that we were not sure that the synthesizing company would accept this request, we expected that about half a year was necessary, and therefore, the synthesis was conducted at AIST. Although it was already confirmed that the synthesis of 1 kg per batch was possible, the time needed for washing after heating synthesis was a hurdle. This was solved by the suihi method (washing method where the HASClay and a large amount of water are mixed and then left to stand, and the water is separated from HASClay that settles at the bottom of the container by gravity). Our great gain was that we learned the necessary tricks for HASClay synthesis by repeating the procedure for large-volume synthesis. Ultimately, we synthesized 40 kg of materials three times in about eight months. As a result, it seemed that good performance of a desiccant rotor could be obtained, and when we asked the company that had handled imogolite synthesis before, it willingly agreed to synthesize HASClay. This was before the press release, but it was important that the company which would conduct the synthesis and the company which would use the product were starting to take action.

The fact that a company was at a preparatory stage of synthesizing and supplying HASClay was an extremely important factor in doing the press release later.

The development of the desiccant rotor was conducted in the following framework: AIST developed the synthesis method of the material with excellent adsorbent/desorbent capacities; the synthesis company developed the mass synthesis method that enabled synthesis in tons and adjusted particle grinding to create suitable particle distribution for fabricating the desiccant rotor; and the desiccant rotor manufacturing company fabricated the high-performance rotor using the HASClay precursor that was supplied by the synthesis company.

4.2 Development for the expansion of usage

Initially, the development of HASClay was conducted as development of adsorbents for desiccant air conditioning, but other uses were considered since it showed excellent adsorption of water vapor.

In the evaluation for humidity controlling building material, it was demonstrated that when the interior finishing material containing HASClay and gypsum was used, the power consumption of air conditioning was reduced.[18] The demonstration test at the Experimental Building for Environment-Friendly Building Materials of AIST Chubu is shown in Fig. 12. In the evaluation of this humidity controlling building material, there were very few cases where the evaluation of the humidity controlling performance was done for the entire room instead of a test piece at a research lab level. It is important that the evaluation be done in the form close to actual use, and we had great advantage
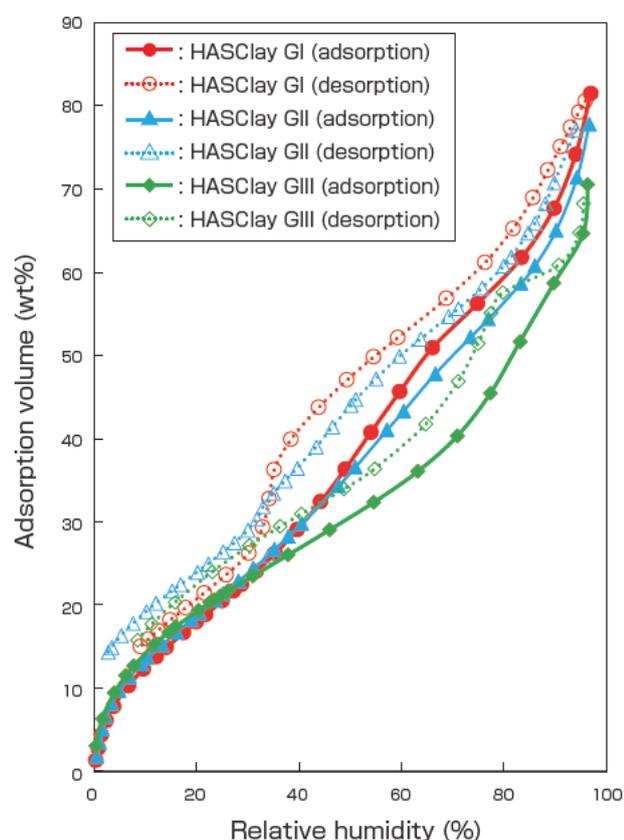
since we had experience in studying the humidity controlling material using allophane as shown in Subchapter 2.2.

The research of the humidity controlling building materials was conducted in a framework where the synthesis company supplied the synthesized HASClay precursor, this HASClay precursor was used at the Experimental Building for Environment-Friendly Building Materials of AIST Chubu, and AIST conducted the performance evaluation.

For the adsorption evaluation of carbon dioxide, it was shown that the adsorption volume was higher at atmospheric pressure or higher, compared to the generally used zeolite.[19] For the adsorption of carbon dioxide, we had the experience of conducting subcontracted development of a substance using imogolite that could store carbon dioxide under a high-pressure condition.

4.3 Development for expanding the market

As explained above, we were able to show the adsorption capacity of water vapor and carbon dioxide, and since we had prospect for companies to produce HASClay and to fabricate desiccant rotors, we did a press release to widen the market. For water vapor, we conducted a press release in October 2008 using the data for HASClay GI, and for carbon dioxide, we did one using the data for HASClay GIII in December 2008.

The reaction after the press releases was great. There was much interest in vapor adsorption, and we received numerous inquiries. On the other hand, for carbon dioxide, although we had inquiries from companies that had high carbon dioxide emission like iron making and cement, the majority of inquiries were from educational science magazines.

Concerning the demands from outside AIST, there were many that were quite unimaginable for us within the institute, and we filed patents jointly following joint research. Although it is possible to imagine one application for one material, we felt the importance of collaborating with outside

organizations for variation. Figure 13 shows the development of HASClay usage one year after the press release. The fields in which imogolite is used as shown in Fig. 5 and the fields for HASClay shown in Fig. 13 are basically the same. When imogolite and HASClay are compared carefully, in the adsorption of water vapor, imogolite has high adsorption/desorption in the low-humidity range and high-humidity range, while HASClay has high adsorption/desorption in the medium-humidity range, and therefore it is more suitable as a desiccant air conditioning material. On the other hand, the form of imogolite is tubular, while the form of HASClay is granular, and the use as a filler that was considered for imogolite cannot be covered by HASClay.

The promotion of photosynthesis in greenhouse cultivation using carbon dioxide was a rather shocking research. In general, the recovery and use of carbon dioxide are mostly conducted for the reduction of carbon dioxide emission to prevent global warming, while the use of carbon dioxide in the agricultural field is not for preventing global warming, but is purely for improving productivity and quality. Fortunately, we were able to work with the people from the Nara Prefecture Agricultural Research and Development Center who were experts in strawberry species development and cultivation, and we obtained public funds to develop a carbon dioxide recovery and delivery system unseen before.[20] At the time of application to the public funds, we stated that carbon dioxide could be stored using HASClay, but the project was ultimately successful because we made the decision to switch to zeolite in the middle of the R&D due to efficiency consideration.

The research for the recovery and use of carbon dioxide involved the following framework: AIST worked on the selection of suitable materials for the recovery of carbon dioxide; the Nara Prefecture Agricultural Research and Development Center and Tohoku Agricultural Research Center, National Agriculture and Food Research Organization investigated the effect of carbon dioxide on strawberries, roses, and Eustomas; and the companies fabricated the whole heat exchange system that decreased the temperature of exhaust
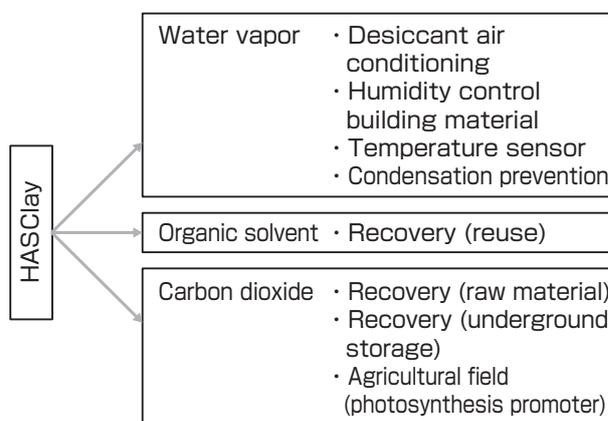

Fig. 12 Application of interior finishing material that contains HASClay
(At AIST Chubu)

Fig. 13 Fields in which HASClay is used

gas and the CO_2 storage layer as well as the construction of the NOx and SOx removal device and dehumidifying systems.

5 Future issues

We discussed the development of HASClay and its application to the present, and the whole flow is shown in Fig. 14. Looking back, we feel that if we started from the sudden discovery of HASClay, it would have been difficult to set up a solid framework that we have now. We were able to achieve what we have now through the experiences with research of clay minerals, research of humidity controlling materials and nanomaterials in natural soil, and synthesis and use development of imogolite.

However, HASClay has not yet made major social contribution. For HASClay to be used more widely, the issue at this point is to change it from powder to a readily usable form. The manufacture of granules is essential, and it is also necessary for the desiccant rotor to be able to meet various requirements.

There are two major points that can be given for future development. As a material, it is necessary to find an adsorbent that has the same performance as HASClay GI, which was the target of the initial new material development, and that can be mass synthesized using inexpensive material at low temperature of 100 °C or less. To increase the production volume of HASClay, it is necessary to develop a new system and build a new industry. A professor of a university said to me, "The person who developed the material knows most about that material. That's why the person who developed the material is the most likely person to develop a good system."

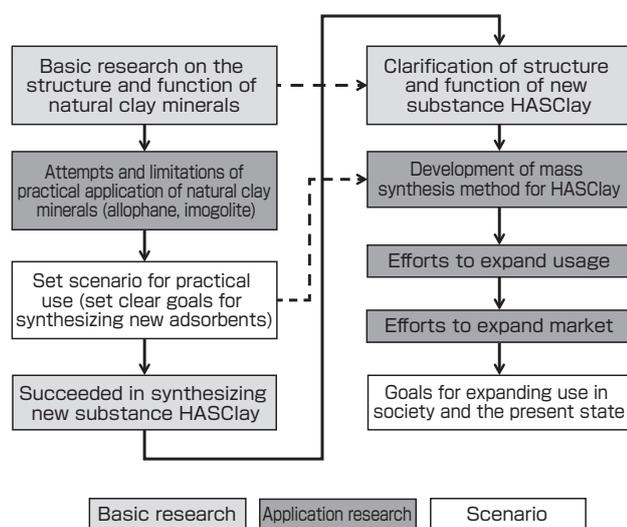We shall continue to develop materials to achieve the initial objective, and we shall also work on the design and construction of a new system to spread the use of this material.

References

[1] M. Suzuki: Development of low temperature regenerated heat exchange materials in adsorptive heat energy system and present state, *J. Society Inorganic Materials, Japan*, 14, 383–389 (2007) (in Japanese).

[2] Mitsubishi Plastics, Inc.: Zeolite kei suijoki kyuchakuzai (Zeolite water vapor adsorbent), https://www.mpi.co.jp/products/industrial_materials/im010 html, accessed 2016-03-25 (in Japanese).

[3] Taiyo Kagaku Co., Ltd.: Kinzoku nanoryushi tanji mesoporous silica (metal nanoparticle supported mesoporus silica), http://taiyo-chem.com/2008/10/14/tmpsfunc, accessed 2016-03-25 (in Japanese).

[4] Japan Exlan Co., Ltd.: Kinosei biryushi (Functional fine particles), http://exlan.co.jp/products/beads/index.html, accessed 2016-03-25 (in Japanese).

[5] Z. Abidin, N. Matsue and T. Henmi: Dissolution mechanism of nano-ballallophane with dilute alkali solution, *Clay Sci.*, 12 (4), 213–222 (2004).

[6] AIST Today: Nanotube-jo aluminum keisan'en no konodo goseiho (High concentration synthesis method for nanotubular aluminum silicate), *AIST Today*, 3 (11), 36 (2003) (in Japanese).

[7] Clay Science Society of Japan: Allophane and imogolite, *Nendo Handbook Dai 3 Han* (Handbook of Clays and Clay Minerals, Third Edition), Gihodo Shuppan, 88–92 (2009) (in Japanese).

[8] M. Suzuki: Synthesis and applications of allophane and imogolite, *Nendo Kagaku*, 50 (2), 81–87 (2011) (in Japanese).

[9] H. Fukumizu and S. Yokoyama: Study on a new humidity controlling material using porous soil "allophane"—Evaluation of humidity controlling performance in test houses, *Architectural Institute of Japan Journal of Technology and Design*, 10, 21–24 (2000) (in Japanese).

[10] M. Suzuki, F. Ohashi, K. Inukai, M. Maeda and S. Tomura: Synthesis of allophane and imogolite from inorganic solution—Influence of co-existing ion concentration and titration rate on forming precursor, *Nendo Kagaku*, 40, 1–14 (2000) (in Japanese).

[11] M. Suzuki, F. Ohashi, K. Inukai, M. Maeda, S. Tomura and T. Mizota: Hydration enthalphy measurement and evaluation as heat exchangers of allophane and imogolite, *Nippon Ceramics Kyokai Gakujutsu Ronbunshi*, 109, 681–685 (2001) (in Japanese).

[12] M. Suzuki and S. Hiradate: Imogolite no gosei katei ni okeru keiso to aluminum no kagaku jotai henka (Changes in the chemical state of silicon and aluminum in the imogolite synthesis process), *Proceedings of 50th Meeting of Clay Science Society of Japan*, 162–163 (2006) (in Japanese).

[13] M. Suzuki and M. Maeda: Nendokei muki takoshitsu zairyo ni yoru desiccant kuchoyo kyuchakuzai no kaihatsu (Development of desiccant air conditioning adsorbent using inorganic porous clay material), *Transactions of the Japan Society of Refrigerating and Air Conditioning Engineers*, 29 (1), 89–96 (2012) (in Japanese).

[14] M. Suzuki, R Nakanishi, K. Inukai, M. Maeda, S. Hiradate and K. Tsukimura: A new amorphous aluminum-silicate: High performance adsorbent for water vapor and carbon dioxide, *Trans Mat. Res. Soc. Japan*, 34 (2), 367–370 (2009).

[15] M. Suzuki: HAS-Clay, *Desiccant Kucho System No Kiso*

Fig. 14 Development of HASClay and flow up to present

Riron To Saishin Gijutsu (Basic Principles and Latest Technologies of the Desiccant Air-Conditioning System), S&T Publishing, 92–100 (2015) (in Japanese).

[16] AIST: Anka na koseino mukikei kyuhoshutsuzai wo kaihatsu (Development of inexpensive, high-performance inorganic moisture adsorbent/desorbent), press release, released 2008/10/08 (in Japanese).

[17] M. Suzuki: Temperature range and rate on formation of Imogolite, *Abstracts of the Japan Association of Mineralogical Sciences*, 163 (2001) (in Japanese).

[18] M. Maeda, K. Inukai and M. Suzuki: Kesshosei nendo to hishoshitsu aluminum keisan'en fukugotai no jitsuyoka ni kansuru kenkyu—Naisokenzai heno oyo (Research on the practical use of composite of crystalline clay and amorphous aluminum silicate—Application in interior building materials), *Proceedings of 57th Meeting of Clay Science Society of Japan*, 174–175 (2013) (in Japanese).

[19] M. Suzuki, C. Ikeda, K. Tajiri, K. Inukai and M. Maeda: Kiatsu ijo no atsuryoku ni izon shite kyuchaku ridatsu kano na nisanka tanso kyuchakuzai (Carbon dioxide adsorbent that can adsorb and desorb according to atmospheric pressure or higher), Patent No. 5229916 (2013) (in Japanese).

[20] M. Suzuki: Kashitsuki haikichu no nisanka-tanso kaishu seisei sairiyo system no kaihatsu (Development of recovery, refinement, and reuse system for carbon dioxide in exhaust gas of humidifiers), *Nisanka Tanso No Chokusetsu Riyo Saishin Gijutsu* (Latest Technologies for Direct Use of Carbon Dioxide), NTS, 55–63 (2013) (in Japanese).

Authors

Masaya SUZUKI

Completed the course at the Graduate School of Science (Department of Mineralogy), University of Tokyo in 1996. Joined the Department of Ceramic Technology, National Industrial Research Institute of Nagoya, Agency of Industrial Science and Technology in 1996. Moved to Research Institute for Geo-Resources and Environment (GREEN), AIST in 2001; and currently, Group Leader, Resource Geochemistry Research Group, GREEN, AIST. Since Nagoya, has engaged in the research for growth, synthesis, and adsorption of amorphous materials and for low-crystalline clay (imogolite). Engaged in application research based on natural phenomena, such as the transition of colloid in high level radioactive waste material disposal and the use of heat for energy saving. In this paper, was in charge of research for synthesis and carbon dioxide adsorption.

Masaki MAEDA

Graduated from the Aichi University of Education in 1984, and worked at the Radioisotope Research Center, Nagoya University in 1984. Joined the National Industrial Research Institute of Nagoya in 1988, and engaged in research on ceramic raw material and humidity controlling building materials. Obtained Doctor (Engineering), Tokyo Institute of Technology in 2002. Chief Senior Researcher, Cycling Material Group, Structural Materials Research Institute, AIST from 2015. In this paper, was in charge of research

for humidity controlling building materials and water vapor adsorption.

Kei'ichi INUKAI

Completed the master's program at the Department of Chemistry, Graduate School of Science, Nagoya University in 1990. Joined the Department of Ceramic Technology, National Industrial Research Institute of Nagoya, Agency of Industrial Science and Technology in 1990. Obtained Doctor (Science), Hokkaido University in 2001. Currently, Senior Researcher, Material Surface Group, Structural Materials Research Institute, AIST. Studied inorganic biochemistry at Nagoya University; after joining NIRIN, studied the effective use of artificial clay (kaolinite) and sepiolite; and then researched the fabrication of clay LB film in the doctor's program. At AIST, engages in the research of imogolite and HASClay for energy saving measures. In this paper, was in charge of research for adsorptions of nitrogen and organic solvents, and was also in charge of the Imogolite Workshop.

Discussions with Reviewers

1 Overall
Comment (Shigeko Togashi, AIST)

With the results of basic research on the structure and function of natural clay as its base, you present the course of synthesizing clay mineral HASClay and achieving its practical use through joint research with companies, through a scenario where clear goals have been set, to realize new use of clay minerals in society.

After you became aware of the limitations of the use of natural clay materials, you shifted to synthesis, and then went back to basic research to clarify the structure and function of the newly synthesized substance HASClay. This led to the improvement of the synthesis method for HASClay and the expansion of its use.

The scenario is developed as you go back and forth between the basic and application research after setting up a scenario with clear goals, and the range of use is expanded through joint research with the private sector. This paper can be evaluated highly as a *Synthesiology* paper.

Comment (Toshimi Shimizu, AIST)

This paper describes the details for the development of the inorganic porous material HASClay® that is a composite of amorphous aluminum silicate and low-crystalline clay, and its application as adsorbents in desiccant air conditioning. After becoming aware of the limitations of natural adsorbents such as allophane and imogolite, you leave them to develop a new adsorbent. You present a scenario in which various requirements are overcome in chronological order. The R&D scenario described is interesting because the issues are solved to obtain the required functions for energy-saving dehumidifier/humidifier by considering inexpensive raw materials, synthesis costs, mass production, and adsorption performance. I think this paper is suitable for publication in *Synthesiology*.

2 Development of the scenario
Comment (Shigeko Togashi)

For development of the overall scenario described herein, please add a flow diagram. Please include the topics of this paper in that diagram, and refer to other *Synthesiology* papers on how to create the diagram.

Answer (Masaya Suzuki)

Based on your comment on the development of the overall scenario, I categorized the items into three categories—basic research, application research, and scenario—and added Fig. 14 in "5. Future issues."

3 Composition of the elemental technologies
Comment (Toshimi Shimizu)

The structure of the first draft is merely a chronological presentation of a usual R&D story, and I feel there is a lack of synthesiological analysis expected for a *Synthesiology* paper. When you set the final target of the adsorbent as use in desiccant air conditioning, the issues to be solved seem to be the drastic improvement of synthesis yield, mass production in tons, reduction of raw material and adsorbent costs, safety of the nanotube substance, and the improvement of adsorption performance as indicated by the linear adsorption isothermal curve. You describe as the elemental technologies the concentration, reaction temperature, desalination, heating, and other conditions during synthesis. However, the correlations between the issues and elemental technologies are not clear. From the perspective of what kind of R&D scenario the authors wrote and how the issues were overcome, I think you need to add a slightly more technological description (especially Subchapters 3.2 and 3.3 of the first draft). To do so, it is important to first draw the correlation diagram of elemental technologies. Although there is no example that's exactly the same, there are *Synthesiology* papers on adsorbents and others that may serve as reference for creating the diagrams that show the elemental technologies and development framework. For elemental technologies, you may be able to refer to "Development of massive synthesis method of organic nanotube toward practical use—Integration of molecular design, molecular synthesis and safety assessment for materials having market competitiveness" [*Synthesiology–English edition*, 1, 169–176 (2008)] and "Novel functional gels and their commercial distribution as chemical reagents—New development of functional soft-materials" [*Synthesiology–English edition*, 5, 181–189 (2012)]. For the development framework and relationship with companies, please refer to "A novel technology for production of drinking water in emergencies—Specific material for selective nitrate adsorption" [*Synthesiology–English edition*, 4, 156–161 (2012)].

Answer (Masaya Suzuki)

Thank you for your advice on the necessity for drawing the diagram of elemental technologies in conducting synthesiological analysis. I felt it was difficult to present a composition diagram of elemental technologies for inorganic substances, unlike the organic nanotubes and polymer gels, but I added the findings so far to Subchapter 3.2. For technological details, I made additions to Subchapter 3.3. For development organization, I added a text to Chapter 4.

4 Definition, birth, and naming of HASClay
Comment (Toshimi Shimizu)

In the first draft, it is unclear what exactly HASClay is. In the paper, it says that you looked at the Si/Al molar ratio as a strategy to solve the issues on raw material costs, synthesis costs, production volume, synthesis yield, and others. Obtaining a hint from the fact that natural imogolite has constant composition ratio, while natural allophane is amorphous with unstable molar ratio between 0.5–1.0, you investigated the adsorption property of the individual products for water vapor, which were obtained by changing the molar ratio. However, the criteria that determine the final grade of HASClay are not the Si/Al molar ratio or the adsorption property, but they seem to be synthesis conditions, particularly temperature conditions and the manufacturing methods involving desalination treatment.

Is HASClay a product with well-defined structures that can only be manufactured under rational synthesis conditions, or is it a product obtained in the course of a reaction process? The readers who specialize in chemistry will be greatly interested in the essence and nature of HASClay. Please describe the structural, morphological, and analytical properties and definitions of HASClay as much as you know or are allowed to disclose. I think you also need to discuss how you differentiate from similar adsorbents whose main ingredients are aluminum silicate, from the viewpoint of intellectual property strategy.

In relation to this, please describe further the need to grade HASClay, and the definitive factor in the birth of HASClay that required two years for its development. Also, HASClay seems to be a trademark, but can you give additional discussion on how you came up with the name and why you decided to trademark this product?

Answer (Masaya Suzuki)

Since I did not provide explanation on the substances and attributes of HASClay, I made additions to Subchapter 3.3. The origin of the name is due to the fact that in x-ray diffraction, although there was no peak or layer structure of amorphous hydroxyl aluminum silicate (HAS), the peak for clay sheet could be seen. Also the product is not a mixture of two substances but consists of one substance that is deemed the composite of HAS and clay, hence the name HASClay. Along with the trademarking, I described this in Subchapter 3.2.

5 Structure of nano-adsorbent
Comment (Toshimi Shimizu)

Allophane and imogolite have well-defined sizes and dimensions as independent structures of nanometer scale. On the other hand, HASClay seems to be a composite of low-crystalline clay and amorphous aluminum silicate that contains imogolite of low-purity. To deepen the understanding of general readers for HASClay, I recommend you provide the structural figures of allophane and imogolite that are already known, as well as a photograph that depicts the powder form of HASClay.

Answer (Masaya Suzuki)

As you indicated, the structural diagrams of allophane and imogolite and the TEM photograph of HASClay are essential in showing the composition of elemental technologies of HASClay and the HASClay structure. The structural diagrams of allophane and imogolite were placed in Subchapter 2.1, while the TEM photograph of HASClay was added to Subchapter 3.3.

6 Development organization and role division
Comment (Toshimi Shimizu)

In conducting joint research with companies specializing in the adsorbents for desiccant air conditioning, materials for room humidity control, carbon dioxide recovery/use systems, and others, please provide additional discussion on the respective elemental technologies to solve the problems for public research institutions and companies, and the division of roles.

Answer (Masaya Suzuki)

Problem solving by public institutions and companies in desiccant air conditioning, room humidity control materials, and carbon dioxide recovery/use systems, and division of roles were explained in Chapter 4.

7 Fields in which HASClay is used
Question (Shigeko Togashi)

For the fields in which imogolite is used as shown in the diagram in the first draft, what are the differences with the fields

in which HASClay is used, other than the possibility of practical realization?

Answer (Masaya Suzuki)

The fields in which imogolite is used and ones in which HASClay is used as shown in Fig. 5 of the final draft are basically the same. For the adsorption of water vapor, imogolite has high adsorption/desorption volume in the low humidity and high humidity ranges, while HASClay has high adsorption/desorption volume in the medium humidity range. Therefore, HASClay is a more suitable material for desiccant air conditioning than imogolite. On the other hand, imogolite has a tubular form while HASClay has a granular form, and therefore, HASClay cannot be used as a filler that was the usage expected for imogolite. These points were added to "4.3 Development for expanding the market."

A super-growth method for single-walled carbon nanotube synthesis

— Development of a mass production technique for industrial application —

Kenji Hata

More than 20 years have passed since Dr Sumio Iijima discovered single-walled carbon nanotubes (CNTs). Development of this material is still an active area of research, world-wide, because the expected high electric and heat conductivity and mechanical strength properties are difficult to obtain with other existing materials. However, low growth efficiency of single-walled CNTs has made the cost of production high compared to that of multi-walled CNTs. Consequently, commercialization of single-walled CNTs has taken longer to develop than multi-walled CNTs. To address this problem, a super-growth process was developed at the National Institute of Advanced Industrial Science and Technology (AIST) that uses an innovative chemical vapor deposition (CVD) method. The super-growth method opens the door to a range of industrial applications widely. This report describes the development of this process for industrial scale, mass production of high quality single-walled CNTs, with commercialization in mind, from the perspective of business-academia collaboration.

Keywords : Super-growth CVD, single-walled CNT, element technology integration, industrial application, business-academia collaboration

1 Background of research

1.1 Introduction of the single-walled CNT

A single-walled carbon nanotube (single-walled CNT, Fig. 1) is composed of a structure in which graphene, which is composed of carbon atoms aligned in a planar honeycomb structure, is rolled into a one-walled cylinder. Ever since the discovery of single-walled CNTs was reported by Dr. Sumio Iijima[1] and the IBM group[2] in 1993, it was experimentally shown to possess electroconductivity, thermal conductivity, and mechanical strength that could not be achieved by conventional materials, and much R&D was conducted with fervor. The application of single-walled CNTs spreads widely over chemical, electrical, and mechanical fields, and as a prime nanotechnology material, researchers around the world have been engaging in fierce competition since its discovery 20 years ago. Figure 2 shows the change in the number of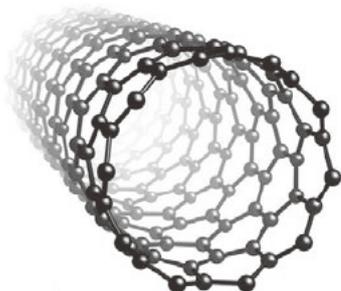 papers on CNTs. Since its discovery 20 years ago, the number of CNT papers has been on the rise. The number of CNT researchers is gradually decreasing since the research boom for CNTs has somewhat settled, but the number of papers is increasing, and this shows that CNTs have spread widely as research material and the number of CNT users has increased. CNT is used for research that generates over 8,000 papers annually, and this is a testament to the fact that CNTs have multiple characteristics that can be applied to various uses.

While academic research of CNTs is enthusiastically conducted, single-walled CNTs are used in a limited manner despite the competitive R&D around the world since its discovery 20 years
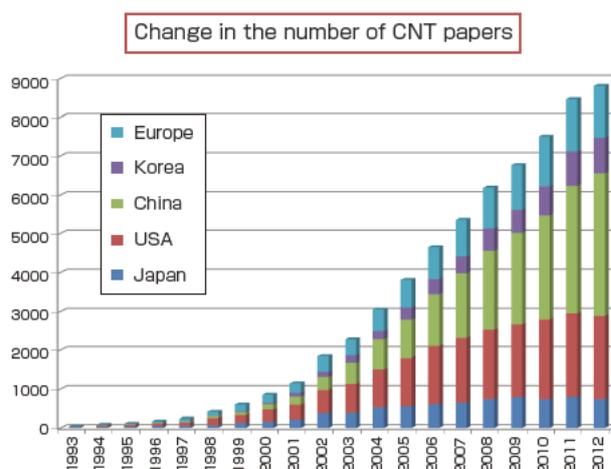

Fig. 1 Single-walled CNT

Fig. 2 Change in the number of CNT papers

CNT-Application Research Center, AIST   Tsukuba Central 5, 1-1-1 Higashi, Tsukuba 305-8565, Japan   ✳ E-mail: kenji-hata@aist.go.jp

ago, and one cannot say that it has been industrialized. The reason is the low growth efficiency of the synthesis of single-walled CNTs. Since the production efficiency is extremely low, the cost is extremely high. The price of the most common commercial single-walled CNT is several tens of thousands of yen per gram, and this price range puts it outside the scope of industrial material. Compared to single-walled CNTs, the multi-walled CNTs have high growth efficiency, are commercially produced, are sold for about five thousand to ten thousand yen per kilogram, and are distributed widely around the world.

1.2 Conventional synthesis methods of CNTs and their issues

Some of the synthesis methods of single-walled CNTs include the laser abrasion method,[3] the electric arc method,[4] and the chemical vapor deposition (CVD) method[5] (Fig. 3). Among these methods, only the CVD method was applied to industrial mass production. For the CVD method, industrial mass production was realized for multi-walled CNTs using the conventional mass production processes that use rotary kilns and fluid bed furnaces, and several commercial plants around the world with production capacity of several hundred tons per year are in operation. However, compared to multi-walled CNTs, single-walled CNTs had narrower diameter and necessitated precise catalyst control. Moreover, the catalyst tended to become deactivated extremely easily, and it was difficult to synthesize at a high yield. When single-walled CNTs were synthesized with the conventional CVD method, the catalyst lifespan was a few minutes, the catalyst activity was several percent, and the growth efficiency was extremely low. As a result, the major problem was the large amount of catalyst metal particles that remained in the CNTs as impurities. Therefore, before actually using the single-walled CNTs, they had to undergo refinement to remove catalyst impurities. This refinement method consisted of several steps of complicated chemical processes such as oxidation at high temperature and acid treatment, and not only were they expensive, but they also would damage the single-walled CNTs.

	Yield	Cost	Purity	Quality
Electric arc	Poor	Poor	Poor	Excellent
Laser ablation	Poor	Poor	Poor	Excellent
Supported catalyst CVD fluid bed furnace	Excellent (3D)	Excellent	Poor	Poor
Vapor fluid method Short Growth Time (e.g. HiPco)	Good(2D)	Moderate	Poor	Good
Vapor fluid method Low Density (e.g. eDips)	Moderate (2D)	Moderate	Good	Excellent
Super-growth	Good(2D)	Moderate	Excellent	Moderate

Super-growth is a synthesis method that fulfills the demands of yield, cost, purity, and quality

Fig. 3 Comparison of the synthesis methods for single-walled CNTs

2 Core technology of the research

2.1 Super-growth method

An innovative CVD method that solved all the technological issues of single-walled CNTs was developed at the National Institute of Advanced Industrial Science and Technology (AIST) in 2004. This was the super-growth method[6] (Fig. 4).

The super-growth method is a method where the activity and lifespan of the catalyst are greatly improved by adding trace amount of water to a regular vapor synthesis atmosphere, and thereby greatly increasing the growth efficiency. By adding trace amount of water, the catalyst activity that was normally a few percent increased to over 84 %[7] and the catalyst lifespan of several minutes extended to over several tens of minutes to an hour.

In the super-growth method, the CNTs can be synthesized most efficiently from iron catalysts on the substrate coated with alumina catalyst supports. It enables the synthesis of "forests" or the long CNT structures aligned vertically on the substrate.

With this super-growth method, the improvement of growth efficiency of several hundred times was achieved compared to the conventional CNT synthesis methods such as laser ablation, electric arc, HiPCo process, alcohol CVD, or vapor fluid methods.

For example, the catalyst efficiency of the super-growth method reached 50,000 % by product/catalyst weight ratio, and this was an improvement of several hundred times compared to the conventional CNT synthesis methods (laser ablation 500 %, HiPCo 300 %, alcohol CVD 800 %, and vapor fluid 100 %). The dramatic decrease of the amount of catalysts used indicated large manufacturing cost reduction in the future using this growth method.
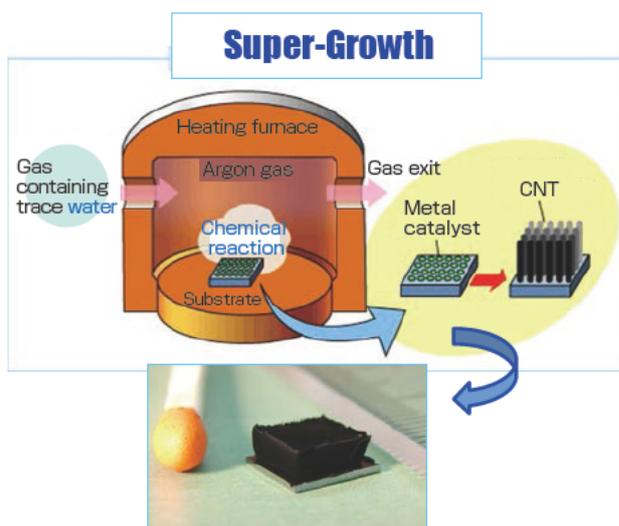
Fig. 4 Super-growth method

As of 2004 when the method was published, the vertically aligned single-wall CNT structure grew to 1.5 mm length in 10 min. This was an improvement of 500 times in length and 3,000 times in time efficiency compared to the world record at the time. The high-speed growth by the super-growth method showed that large amount of CNTs could be synthesized in a short time, and the road to full commercial production of single-walled CNTs was paved.

Moreover, the single-walled CNT forests could be easily sliced off from the substrate using a blade, just like harvesting rice. The catalyst was firmly attached to the substrate, and breakage occurred at the interface of the catalyst and CNTs, and as a result, the CNTs and the catalyst could be separated. Therefore, the amount of catalysts that was mixed in the CNT products was minute, and the CNTs with carbon purity 99.98 % or more could be manufactured on the spot. This purity was 1/2,000 of the impurity concentration in the single-walled CNTs manufactured by the HiPCo method that is most widely used today. The ability to synthesize CNT products with high purity and without need of a refinement process was a major advantage compared to the conventional synthesis method in using the single-walled CNTs as industrial material.

2.2 Research policy that set the direction and my thoughts

Since the super-growth method was published in November 2004, I questioned myself which research to do next. I thought that ideas and what could be done were limitless, including clarification of the mechanism of water addition or the creation of some bizarre CNT structures. In fact, most of the research topics that I conceived at the time or were brewing in the laboratory were published in illustrious academic journals a few years later. The super-growth method opened the possibilities to various new kinds of research.

Although I was surrounded by much exciting research potential, I did not choose my research topics at whim. That was because I gave myself some policies in selecting the research that I should engage in the future. The policies were:
- to engage in research that would be useful to the world,
- to engage in research that would become industrial technology that may support Japan in 10 or 20 years from now, although it may be dull at the moment,
- to engage in research of which I can appreciate the results at the end of my life.

Why did I give myself such research policies? This was because I had a bitter experience when I was working on surface science research. Around 2000, I was conducting research on atomic structure analysis of semiconductor surfaces using the scanning tunneling microscope at Tsukuba University, and I went to the American Vacuum Society (the largest and most authoritative society in the field of surface science) to give a lecture presentation of my greatest finding during the preceding few years (this was later published in *Physical Review Letter*).[8] In a lecture hall having seating capacity of 300 that was normally filled with several hundred people, there were only ten people. Most of them were Japanese. Right before this event, the National Science Foundation (NSF) that was the research funding agency in the United States suddenly decided to cut funds to the surface science field, and researchers left this field like an ebbing tide. Until that moment I thought science was the pursuit of absolute truths to clarify nature's mechanism and therefore it had absolute value. My experience in the US taught me that in the real world there is research that goes in and out of trend, and research is not evaluated based on absolute value.

From this experience in the US, I began to think about engaging in research that was not affected by trend, and wished to do research where the results are ultimately returned and become useful in society, rather than engaging in research to clarify the ways of nature. The aforementioned three research policies were the expression of my thoughts in a somewhat abstract form.

This abstract wish became a specific goal in a slide (Fig. 5) that was used for presentation for visitors from the Ministry of Economy, Trade and Industry (METI) that I was in charge of in March 2005, right after the press release of the super-growth method. Someday, when I go home, my elderly mother will be using a product that contains the super-growth CNTs, and I want to tell her, "Oh, mom. This product has CNTs in it that we developed at Tsukuba." To say this sentence became my personal goal as a researcher. This is because when I say these words, there should be a giant CNT industry in Japan, and our research will be contributing considerably in society. I used this slide repeatedly on visits and in lectures, and I must have re-used it several hundred times, as it represents my research philosophy and goal. In retrospect, this thought and wish were the source of my power to overcome all difficulties that came one after the other, and allowed me to realize the commercial production of the super-growth method.
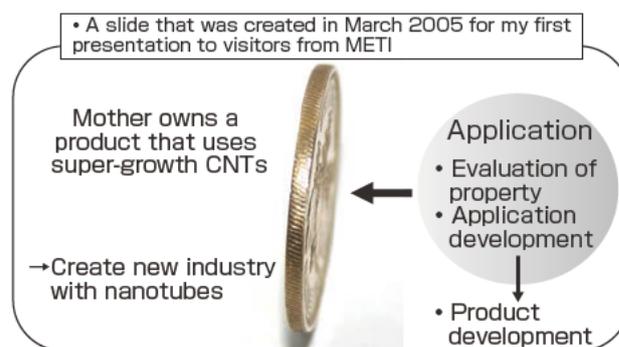

Fig. 5 Personal goal

In my research policy, the final research topic was "to develop mass production technology by the super-growth method and to make available single-walled CNTs as industrial material." Assuming a synthesis furnace of a length of 20 m and a width of 1 m to continuously manufacture single-walled CNTs by the super-growth method, the production volume was calculated at 10 tons per year. Ten tons is not that high in industrial level, but at the time, the production volume of single-walled CNTs in the world was estimated to be 6 tons.[9] If there was one super-growth synthesis furnace, it would be possible to manufacture more single-walled CNTs than the rest of the world. I thought this would be a breakthrough in terms of production volume and price.

If the super-growth method had 1,000 times the growth efficiency of the conventional method, the sales cost of single-walled CNTs that was several tens of thousands of yen per gram would become 1/1,000, or the sale price would be several tens of thousands of yen per kilogram. This would enable the use of single-walled CNTs as industrial material. I was certain that this would generate major innovation. This was the research topic that fulfilled my research policy.

3 Objective of the research

3.1 Development of mass production technology for single-walled CNTs

3.1.1 Industrial mass production method and technical concept

How do we realize industrial mass production based on the super-growth method?

When the article was published in *Science*, the sample size was about 1 cm square, the catalyst was formed by an expensive sputtering method, the substrate was a silicon wafer, and the synthesis was done one batch at a time. Industrial mass production was far away in the distance.

However, the super-growth method had several important characteristics in realizing the industrial mass production process, and we did not mention any of them in the *Science* paper. First, the super-growth method had the world's best synthesis yield of single-walled CNTs per volume and time of a reaction furnace. This meant that if we achieved mass production, we would be superior in terms of productivity and cost against other competing methods. Second, since super-growth involved adding water to the synthesis atmosphere of regular CNTs, we believed the process was scalable. Third, the super-growth method is a reaction process under atmospheric pressure without using vacuum, plasma, or high pressure. Due to these characteristics, we could construct an open system synthesis furnace. This was a great advantage in continuous synthesis. Finally, the optimal growth temperature of the super-growth method was 800 °C.

This indicated that a metal synthesis furnace could be used instead of quartz or ceramic. From these characteristics, we imagined a manufacturing process for continuous synthesis of single-walled CNTs using a large metal synthesis furnace in an open system.

Figure 6 shows the process that we conceived as the mass production process of the super-growth method for single-walled CNTs at low cost while maximizing these characteristics. This was a process in which a metal film is used as substrate material, a catalyst is coated onto the film, continuous synthesis is done on a belt conveyor, and the substrate material can be reused.

What I find interesting is that the lab-scale synthesis process shown in the top part of Fig. 6 and the industrial mass production process shown in the bottom part of Fig. 6 are both super-growth methods, but the elemental technologies are totally different. The top is an academic process while the bottom is an industrial process. I think this figure clearly points out the large difference between academia and industry, and the difficulty of transferring technology developed in the academia to industry.

The manufacturing process where single-walled CNTs are continuously synthesized on flat substrate material was research that no one had ever attempted in the history of mankind, and it was necessary to conduct enormous amount of technological development. We expected it would kick off innovative effects, and we could build a network of intellectual properties that prevented entry of third parties. The innovative effect was the cost reduction to 1/1000 of the conventional method. However, there were many technologies that had to be developed and we could not fail in any area. If we failed in developing just one elemental technology, mass production would not be possible even if we achieved everything else. Therefore, it was obvious that this technological development would be extremely high risk and high return. Also, we could not utilize the existing manufacturing facilities for commercial production. Large facility investment was necessary for product realization.
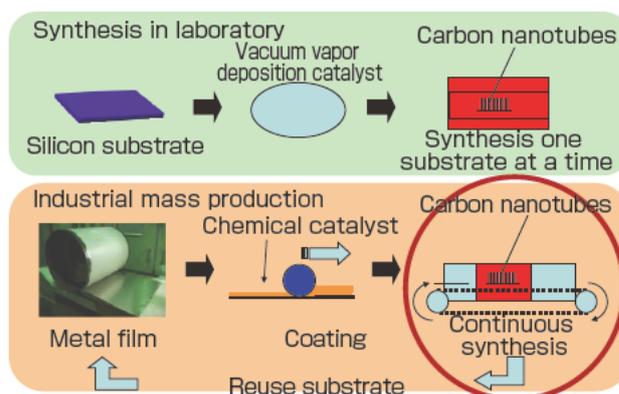

Fig. 6 Lab-scale vs. mass production process

There were mountains of difficulties and issues in realizing the mass production of single-walled CNTs by the super-growth method, but I was looking only at the possibilities of the super-growth method, not the difficulties.

3.1.2 Development of mass production technology in the NEDO "Carbon Nanotube Capacitor Development Project"

Fortunately, AIST obtained an opportunity to develop a mass production process by the super-growth method jointly with Zeon Corporation, in the "Carbon Nanotube Capacitor Development Project (FY 2000~2010)," a nanotechnology program of the New Energy and Industrial Technology Development Organization (NEDO) from 2006 (Fig. 7). It is presently known as a prime example of a successful national project, but it was fraught with hardship in the beginning.

First, one of the absolute conditions in starting the project was to find a partner company with whom we would develop the mass production technology by the super-growth method. Mr. Motoo Yumura who was my superior at the time contacted eight companies that were engaging in CNT R&D and interviewed some of the companies. All companies said, "The super-growth method is wonderful. But we have been conducting R&D for CNTs using our original technology. It is difficult to abandon this technology and switch over to the super-growth method." We were unable to meet a partner that would truly work on the mass production process by the super-growth method. Through an introduction, we met Mr. Kohei Arakawa who was the managing director of the Zeon Corporation.

Mr. Arakawa had experience in CNT research (at the time, it was called simply carbon, not CNT) when he was working at Nikkiso Co., Ltd. He listened to our story with zeal and keenness. He immediately calculated the cost of mass production, determined that it would be viable as business,

and obtained permission from the president to go forward on the R&D. I intuitively felt that super-growth would not be realized unless we teamed up with Mr. Arakawa.

Immediately afterward, the asbestos issue arose. In June 2005, it was reported that workers and families of two companies that were manufacturing asbestos died of malignant mesothelioma. Since CNT had a similar form as asbestos, there was concern that it might cause a similar health problem, and we were flooded with inquiries every day. The permission of CNT R&D was withdrawn, and it seemed we could no longer work with Mr. Arakawa. However, we did not give up. First, Mr. Arakawa asked us to evaluate the amount of CNTs that adhered to the HEPA filter in the laboratory. As a result, it was found that the concentration of CNTs floating in the air in the lab environment was lower than the concentration of asbestos in regular air. Mr. Arakawa directly requested the president for CNT R&D one day before the deadline for application to the NEDO Project, and obtained the president's permission for R&D.

While it felt like treading on thin ice, we were able to start the project with wonderful members who worked hard to realize the single-walled CNTs by the super-growth method.

4 Research scenario for achieving the goal

When the project started, we extracted the technical issues that had to be tackled. The main technical issues listed were as follows: the development of a substrate that was low cost and could be easily upscaled to a large surface area, to replace the silicon wafer; the development of a coating type catalyst to replace the iron thin film catalyst formed by the sputtering method; the development of synthesis technology for synthesizing uniform, vertical arrays by controlling and adding water to a large surface area at PPM level; the development of continuous synthesis technology to continuously transport the substrate material; and others (Fig. 8). Diverse technical issues also included the development of a metal synthesis furnace to replace the quartz furnace, cleaning technology of the furnace, reuse technology of the substrate material, generation of a low-cost gas atmosphere, and others.

Since it was necessary to solve all the issues in five years, we took an approach that we named the "black box strategy." First, we weighed all issues. The issues with absolutely no solution were labeled "black," the issues that could be solved with abundant human and monetary resources were "grey," and the issues that had been solved were "white." Next, the limited research resources were prioritized to turn the black issues grey. Also, to complete the whole picture in a short time, individual elemental technologies were developed concurrently as much as possible, and the elemental technologies were integrated later to complete
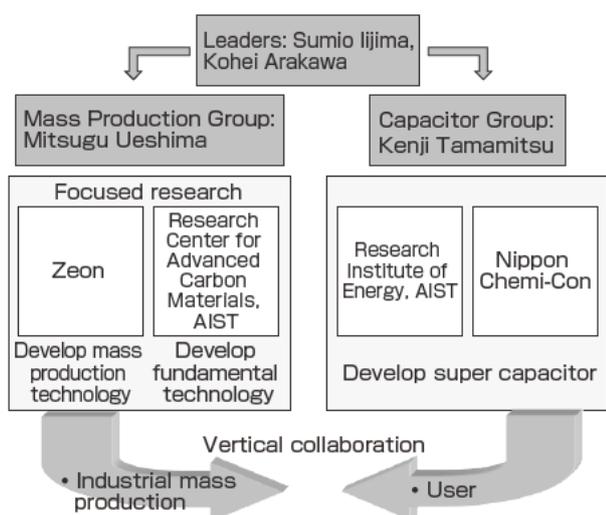

Fig. 7 Organization of Carbon Nanotube Capacitor Project

the mass production process. For the roles of AIST and Zeon, AIST developed methods for solving the issues, and Zeon developed ways to upscale the methods, continuous synthesis, and production technologies.

The greatest black issue was "how to realize continuous synthesis." When we succeeded in continuous synthesis and this issue became grey, Mr. Arakawa would embark on building the commercial plant. At this point, the mass production process was not established at all. I thought Mr. Arakawa was the embodiment of an excellent business manager. Unfortunately, the bankruptcy of Lehman Brothers occurred and it became extremely difficult for the company to make facility investment, and the commercial plant ceased to be.

I shall explain the main elemental technologies including the development of substrate material, a coating type catalyst, large-area synthesis technology, and continuous synthesis technology. Then, I shall describe the course of the research where the elemental technologies were integrated to complete the mass production process.

4.1 Elemental technologies of the mass production process

4.1.1 Technological development of the substrate material

The production process at the time when the article was published in *Science* used a silicon wafer as the substrate, but for mass production, it was necessary to have a substrate that

was low cost as much possible, was capable of synthesizing excellent quality single-walled CNTs at high efficiency, and could be reused repeatedly. Such a substrate must show high durability at synthesis temperature of nearly 800 °C, be highly resistant to hydrogen reduction and oxidation atmospheres due to water addition, and must not inhibit CNT synthesis. As a result of searching for a substrate that fulfilled such strict demands, it was found that single-walled CNTs could be synthesized at similar growth efficiency and quality as silicon wafers when a Ni-Fe-Cr alloy was used as substrate material.[10] Among dozens of materials investigated, only the Ni-Fe-Cr alloy satisfied all the necessary requirements (Fig. 9). We were lucky because the Ni-Fe-Cr alloy was also excellent from the perspective of continuous production and safety. The Ni-Fe-Cr alloy is called stainless or Inconel®, and it is the most widely used economic thermal resistant metal. In fact, the material of metal muffle furnaces used at temperature of 800 °C is usually Inconel®.

There was the problem of carburization, that is, metal was carbonized and weakened when exposed to carbon at high temperature. The raw material of CNTs is hydrocarbon. Moreover, the CNTs are synthesized at high volume continuously in the synthesis furnace, and that inevitably creates a highly concentrated hydrocarbon atmosphere. The effect of carburization was extremely powerful in such synthesizing atmosphere, and for example, the metal screw that joined the metal parts of the sample holder expanded due to carburization after several hundred syntheses and destroyed the sample holder. The Ni-Fe-Cr alloy was least affected by carburization or had a high carburizing resistant property.
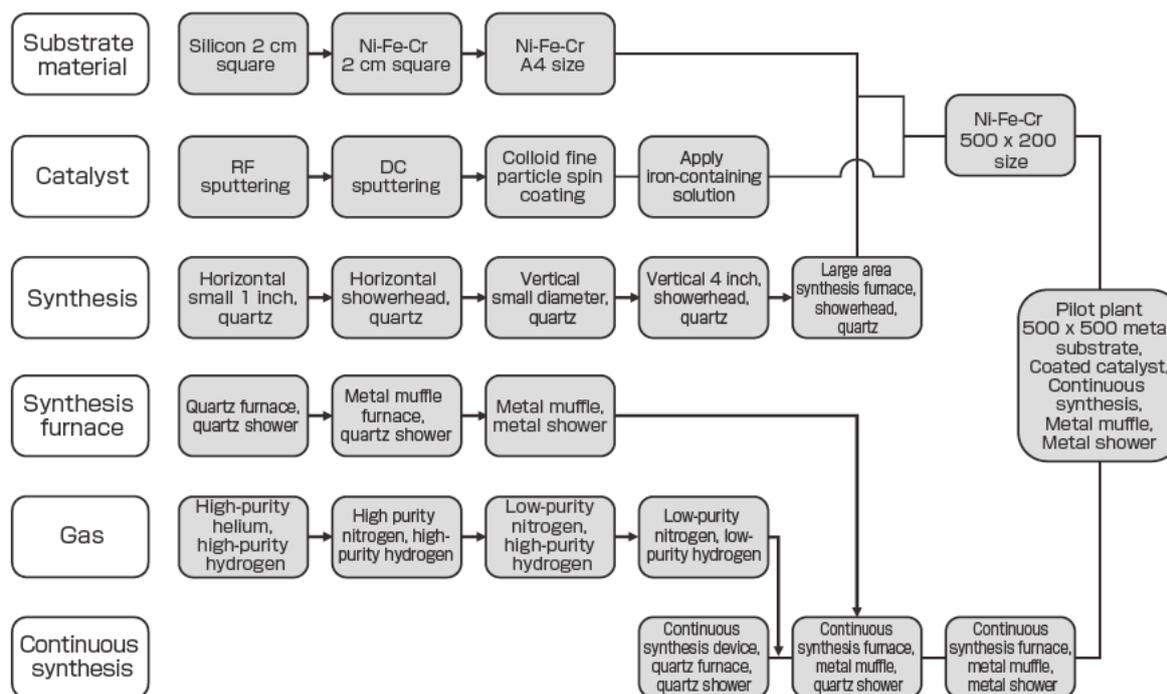

Fig. 8 Development of mass production technology

The excellent thermal resistance and carburizing resistant properties of the Ni-Fe-Cr alloy enabled the reuse of substrate material. Regular metals underwent plastic strain and deformation when they were repeatedly exposed to a highly concentrated hydrocarbon atmosphere at 800 °C and then cooled to room temperature, but these were minimal in the Ni-Fe-Cr alloy. This was one of the extremely important points in establishing the industrial mass production method by the super-growth method.

4.1.2 Technological development of the catalyst

In order to achieve high-speed synthesis of single-walled CNTs that are vertically aligned on the substrate material using the super-growth method, it is necessary for the catalyst to meet strict conditions. In later research, it was clarified that for the single-walled CNTs to grow vertically at millimeter-scale height, there was a sweet spot for the size and spacing of the catalyst[11] (Fig. 10). The sweet spot exists because the region is surrounded by multiple boundaries. That is, multi-walled CNTs are synthesized from large

catalysts (multi-walled CNT boundary), while the growth rate of single-walled CNTs that grow from small catalysts are slow (low yield boundary), and CNTs grow laterally from the catalyst with large spacing. The typical catalyst size of the sweet spot is 3 nm, and the catalyst spacing is 15 nm. This catalyst array has to be stably present for at least 10 min in the synthesis temperature of 800 °C. To the present, the capable catalyst system is only obtainable when the iron thin film on the alumina catalyst support is subject to hydrogen reduction at high temperature of 800 °C.

The control factor that was crucial to place the catalyst in the sweet spot was the thickness of the alumina catalyst support and the iron catalyst, particularly the thickness of the iron catalyst. As a result of research, a single-walled CNT array could be synthesized only when the thickness of the iron catalyst was between 0.8 nm to 1.3 nm.[12] Therefore, the catalyst film was initially formed using the sputtering method that had excellent control of film thickness.
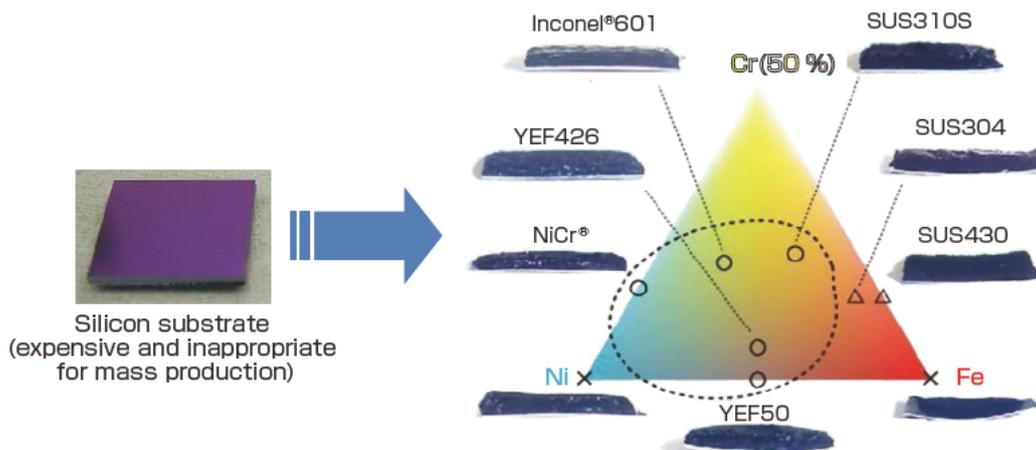

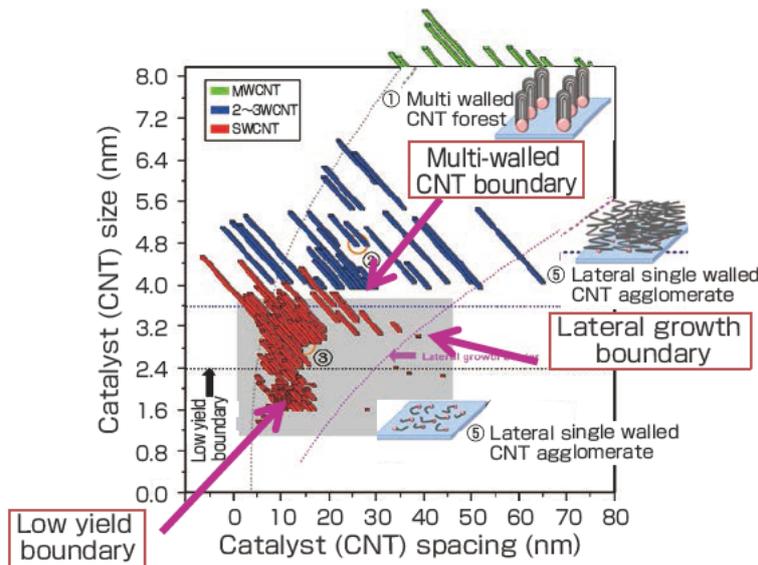**Fig. 9 Development of metal substrate**

Fig. 10 Sweet spot for catalysts[11]

However, from the perspective of industrial mass production, the sputtering method had low productivity and high facility costs, and that meant high overall costs. Therefore, it was necessary to shift to wet catalysts that were low cost, needed small facility investment, and had high productivity. In the sputtering process when the article was published in *Science*, the iron catalyst was sputtered immediately after sputtering the alumina catalyst support with RF. However the RF sputtering of alumina had extremely slow film forming rate, and the productivity of the catalyst was significantly low. Therefore, we developed the technology in which the aluminum was DC sputtered in an atmosphere containing oxygen thereby oxidizing the aluminum on the spot to form the alumina. Through the series of research on catalyst development using sputtering, it was found that various factors such as the composition of alumina catalyst support and surface smoothness greatly affected the growth of single-walled CNTs.

Thinking that the thickness restriction for the iron catalyst was too strict and that it was difficult to apply the iron thin film evenly within the allowed range, we developed iron colloid nanoparticles as wet catalysts synthesized in the iron carboxyl solution (Fig. 11).[13] By thinly coating the iron colloid nanoparticles onto the silicon substrate using spin coating, we were able to grow single-walled CNTs similar to the ones by sputtering thin films. However, when it was investigated closely, the single-walled CNTs did not grow from individual iron colloid nanoparticles. It was found that the iron colloid nanoparticles fused when the catalyst was reduced by hydrogen before synthesis, and then turned back into fine particles again. Therefore, when wet catalysts were used, application of a thin coat to the iron catalyst film was also sufficient.

We first looked at the method called capillary coating as a method of coating the ultra-thin iron film. This was a method for coating the substrate material with a solution containing iron salt that was sucked into the ultra-fine tubes by the capillary effect, and then used for evenly coating substances
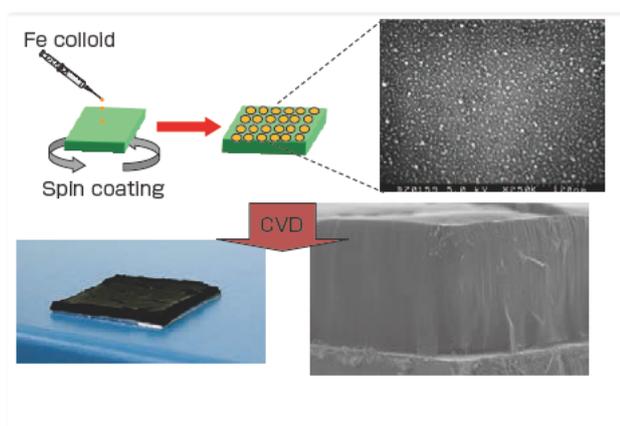

Fig. 11 Development of coated wet catalyst[13]

such as liquid crystals. Using this method, we succeeded in coating ultra-thin iron catalysts onto a flat substrate material, but due to its principle, we were unable to apply the solution evenly to a substrate with distortion or deformation. From the experiments for large-area synthesis, we found that the distortion and deformation of substrates increased as the substrate material increased in surface area and as the substrate material was reused repeatedly. Therefore, we were forced to develop a totally different method. After many twists and turns, we finally succeeded in coating the ultra-thin iron film onto large-area deformed substrate material by the wet method, and this was a very inexpensive and highly productive method for growing single-walled CNTs.

Next, like the iron catalyst, we conducted technological development for coating with alumina catalyst supports. Since alumina had extremely high carburizing resistant property, the substrate material consisting of Ni-Fe-Cr alloys coated with alumina catalyst supports showed excellent durability in the highly concentrated hydrocarbon environment used in the super-growth method. The catalyst we developed became a system that powerfully inhibited the deformation and carburization that were problems in reusing the large-area substrate material.

4.1.3 Development of the synthesis technology optimal for mass production
It was necessary to conduct much technological development for the mass production process in synthesis technology. When the article was published in *Science*, the CNT was synthesized by placing the substrate horizontally in a horizontal synthesis furnace of 1 inch diameter and supplying ethylene and water vapor gas from the side. This small, horizontal synthesis furnace had an optimal structure for creating a laminar flow and preventing gas turbulence. Any gas turbulence significantly decreased the synthesis efficiency of CNTs, and such equipment configuration was optimal in lab scale synthesis. However, this lab scale synthesis furnace or substrate material could not be upscaled to an industrial scale. There was a major problem that most of the supplied gas did not hit the substrate, passed over the catalyst without reaction, and only about 1 % of the supplied ethylene gas was converted to CNTs.

It was necessary to supply the gas from the top to enable upscaling of the synthesis furnace and substrate material, and to greatly improve the conversion rate of the carbon source to CNTs. Therefore, we developed a showerhead (Fig. 12).[14] Various changes were made to the showerhead to evenly supply extremely minute amount of water to the catalysts on the substrate material. Next, the synthesis furnace was made vertical and the diameter was increased from 1 inch, to 2 inches, and then 4 inches. When the furnace was turned vertical and the diameter increased, turbulence occurred immediately. We conducted fluid simulation and

created several prototypes of the gas supply system and the showerhead that allowed even supply of trace water to the substrate material without turbulence.

4.1.4 Technological development of the scalable metal synthesis furnace

The development of the synthesis furnace itself was a major element in technological development. At the time of publication in *Science*, we used a quartz furnace. There was a size limitation to a manufacturable quartz furnace, and it was expensive. It was necessary to make a metal furnace. However, in continuous synthesis, the furnace would be exposed continuously to high temperature and highly concentrated hydrocarbon. The specs required for the synthesis furnace were more severe than those for the substrate material.

Therefore, a dedicated device was introduced to study the materials that were resistant to the synthesis atmosphere with long-term stability. Using this device, deterioration, carbon adhesion, and carburization of the materials were investigated by exposing several candidate materials for a long time to high temperature and to highly concentrated hydrocarbon. The carbon gases and the reaction of trace water and metals greatly affect the synthesis. The material of the furnace was selected considering the effect on CNT synthesis and the long-term durability in the synthesis environment, and the selected materials were used in the actual small synthesis furnace. The metal showerhead was developed after the synthesis furnace, and we finally succeeded in developing a synthesis furnace that did not use quartz.

When the synthesis of CNTs was repeated many times, carbon impurities built up in the synthesis furnace. These carbon impurities had major effects on CNT synthesis by absorbing the water added to the synthesis atmosphere. The furnace had to be cleaned after a certain amount of impurities adhered. Carbon that adhered under high temperature was
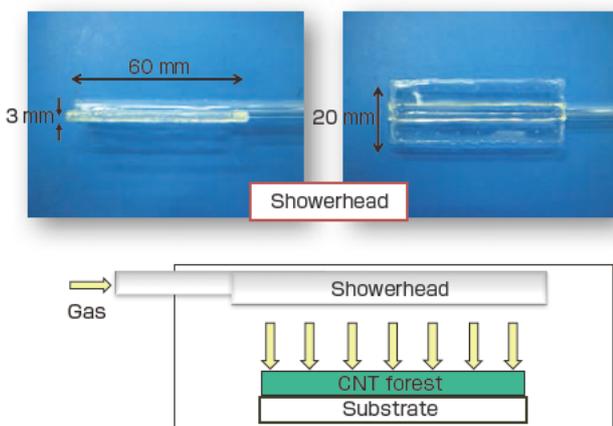
crystallized and removal was difficult. The easiest method was combustion by introducing oxygen at high temperature, but if that was done, the metal furnace would be damaged by oxidation and its lifespan would decrease. Therefore, we developed a cleaning technology to remove the carbon impurities without damaging the metal synthesis furnace.

4.1.5 Large-area synthesis technology

The technologies were taken further to develop a large-area synthesis furnace that could synthesize on large-area substrate material (A4 size or more) (Fig. 13). When the furnace was upscaled by a batch method, about one hour or more was necessary to heat the furnace to synthesis temperature. However, in continuous synthesis, it was necessary to raise the temperature of the substrate material to synthesis temperature in about 10 min. To alleviate this difference, we developed an extremely special large-area synthesis furnace. In this synthesis device, the large-area substrate material was stored inside the quartz horizontal furnace of 300 φ, and the gas was replaced. A large muffle furnace was placed next to it, and this was maintained at synthesis temperature. The high-temperature muffle furnace moved on rails to envelope the quartz furnace to quickly raise the temperature and heat the substrate material. This format was employed to conduct large-area synthesis at thermal history close to the future continuous synthesis as much as possible. After such technological development, we succeeded in large-area synthesis of A4 size and A3 size.

4.1.6 Continuous synthesis technology

The final, most crucial technological development was the development of continuous synthesis technology. Several continuous syntheses and quasi-continuous methods were considered, and finally, a method in which large substrate material was placed on a belt conveyor and transported continuously to the synthesis furnace was employed (Fig. 14). The characteristic of this method was that there were no shutters or partitions on the synthesis furnace, and it was designed as a complete open system. The substrate that entered the continuous synthesis furnace was transported to different areas. First, it was heated in the heating section,

Fig. 12 Development of the showerhead[14]

Fig. 13 Technological development of large-area synthesis

exposed to hydrogen atmosphere in the catalyst formation section, and the iron film was reduced to fine catalyst particles. The CNTs were synthesized in the synthesis section, and the temperature of the substrate material was decreased in the cooling section. The substrate material transported on the belt conveyor in the synthesis furnace underwent several processes continuously. To realize this in the synthesis furnace without shutters or partitions, gas showers were set between each section, to establish sections where the gases were separated although they were connected spatially. The continuous synthesis furnace introduced showed growth of CNTs from the very first substrate, and I was thoroughly impressed by the engineering capability of the company.

4.1.7 Integration of the elemental technologies

While developing the elemental technologies such as substrate material, a catalyst, large-area synthesis technology, and continuous synthesis technology, these technologies were integrated at the same time. Ultimately, unless all elemental technologies were integrated, we would not have a mass production process. However, when the elemental technologies were integrated, the complexity of the technology increased and new technical issues arose.

For example, silicon substrate material was used at first, and the technological development was conducted to replace it with a metal substrate. The size considered was 2 cm square. Several substrate materials were tried to see which 2 cm square was optimal for CNT synthesis. As a result, it was found that Inconel® was optimal. However, since Inconel® contained high amount of nickel, the nickel content had to be reduced to a minimum to reduce the cost. Next, the metal was upscaled to A4 size and growth took place in the large-area synthesis furnace. It was then found that heat distortion occurred when thermal history was added to the large-area metal substrate material, although this was not a problem

Fig. 14 Technological development of continuous synthesis

in small size material. Of course, thermal distortion could be prevented if thicker substrate material was used, but this became costly. Also, the added weight of large-area material made the handling more difficult. Moreover, time was required for heating and cooling, and it could not be used in the continuous synthesis furnace. Therefore, we had to seek a solution that simultaneously fulfilled these conflicting factors.

The integration of technology continued. In fact, sputtered catalysts were used in all the research described above. Therefore, we shifted to wet catalysts and the same considerations were repeated. The density and evenness of the wet catalysts were inferior to the sputtered catalysts, and thermal distortion occurred. When thermal distortion occurred in large-area substrate material, the coating with catalysts became difficult.

Next, we had to reuse the substrate material. It had to be reusable many times or else the cost of the substrate would be added to the cost of the final product. However, if the substrate material was reused, the material would have double, triple, and quadruple thermal history, thermal distortion would accumulate and increase, and it would become more difficult to fulfill all other technological elements at the same time. We had to strike a balance among such diverse factors, and at the same time develop technology to inhibit the negative factors such as thermal distortion. Each elemental technology was integrated to complete the mass production process.

5 Current status of the research and its future

5.1 Commercialization by Zeon Corporation and future prospect

When we succeeded in continuous synthesis, Mr. Arakawa started to consider practical use. In terms of the "black box strategy," we had no more technical issues that could not be solved, and the mass production technology would be completed if sufficient money and manpower were invested. However, the bankruptcy of Lehman Brothers occurred, and the economic situation turned difficult for companies to invest in facilities, and the move toward realization stopped. At that time, the director of METI came for a visit, and advised us to go for product realization using the supplementary budget.

Through such course of events, the pilot plant was built on AIST grounds using the facility funds of the supplementary budget. This plant was managed jointly by AIST and Zeon. The pilot plant was 12 m in length, the muffle furnace was an open system on both ends, the gas sections were created using multiple gas showers, and the super-growth single-walled CNTs were manufactured continuously on a substrate of 50 cm square transported on a belt conveyor.
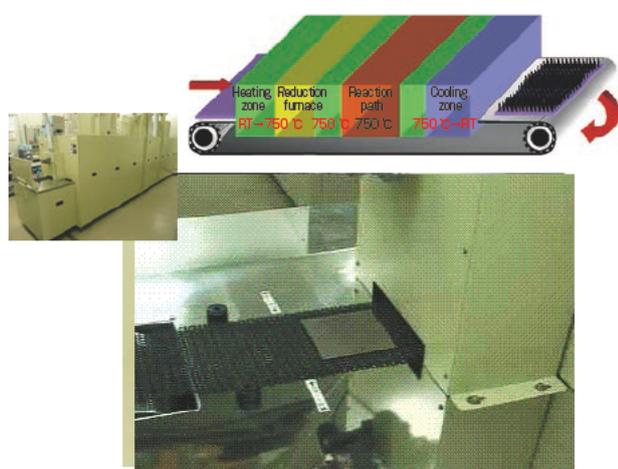
It was designed by integrating the technologies nurtured in the development of continuous synthesis technology and large-area synthesis technology. Other than the continuous synthesis furnace, the continuous sputtering device, wet catalyst coating device, CNT harvesting device, substrate washing device, and others were added. The mass production process developed in the "Carbon Nanotube Capacitor Development Project" was realized, though at a small scale, and this enabled manufacture of super-growth single-walled CNTs at production volume of 100 gram/hour.

The manufactured super-growth single-walled CNTs were supplied to a wide range of domestic companies as sample supplies from AIST. Over 200 agreements have been signed to the present.

From FY 2013, the pilot plant was loaned to Zeon, and the super-growth single-walled CNTs were sold by Zeon utilizing the Result Diffusion Project. We approached the B2B format one step at a time.

Many prospective uses were developed from the super-growth single-walled CNTs that were supplied throughout Japan from the pilot plant, and this spurred actual realization. In the Technology Research Association for Single Wall Carbon Nanotubes (TASC), the technologies to utilize the super-growth single-walled CNTs were developed one after the other, including dispersion, coating, evaluation, forming, and compositing. This led to the development of various parts with excellent properties such as CNT rubber composite material with high thermal resistance, CNT carbon fiber rubber composite material with high heat conductivity, and CNT copper composite material that can pass 100 times the electric current while possessing the same electro-conductivity as copper,[15] and thus the development by companies was accelerated.

The market demand for super-growth single-walled CNTs, development of peripheral technologies such as dispersion and composition, and development of marketable application moved Zeon Corporation to start operation of a commercial plant in 2014. The ceremony for the start of the plant construction was held in Tokuyama in November 2015. I was able to snap a photograph in front of the plant with Dr. Sumio Iijima (former Director, Nanotube Research Center, AIST), Dr. Yumura, Mr. Arakawa, Dr. Mitsugu Ueshima (Zeon), and Dr. Norimitsu Murayama (Director, Department of Materials and Chemistry, AIST) (Fig. 15), and this was when I felt we reached a milestone. Plant construction and the commercial production of super-growth single-walled CNTs are only the starting line in the business world. To grow this business, there are mountains of difficulties and issues that must be overcome. However, since the super-growth single-walled CNTs have overwhelming superiority in purity, length, and specific surface area compared to other CNTs, I believe it will become a major business.

Finally, I believe that it is possible to see the prospect of CNTs in the future by looking at the periodic table of elements. Carbon is the sixth element in the periodic table. The first and second elements, hydrogen and helium, are gas, third element, lithium, is water prohibitive, and fourth, beryllium, is highly toxic. Carbon is the topmost element of the periodic table that can be used safely by humankind in a solid state. This means that carbon has a small nucleus and therefore is the lightest and has the strongest shared bond. CNTs that combine carbon in ideal structures are materials that can bring out the performance of carbon to the maximum. The periodic table tells us that we cannot create any material that is stronger or lighter than CNTs on the earth. If CNTs are fully commercialized, I believe that they will continue to be used as long as human society exists.

CNTs that were found in Japan will grow into a CNT industry that originated in Japan. They will be used in all corners of society making it a place where "carbon nanotubes are here, there, and everywhere," and will benefit human society. My goal is to create such a future.

6 Acknowledgements

Fig. 15 Photograph in front of the carbon nanotube manufacturing plant (Tokuyama Plant, Zeon Corporation)

References

[1]　S. Iijima: Helical microtubules of graphitic carbon, *Nature*, 354, 56–58 (1991).

[2]　D. S. Bethune, C. H. Kiang, M. S. DeVries, G. Gorman, R. Savoy, J. Vazquez and R. Beyers: Cobalt-catalysed growth of carbon nanotubes with single-atomic-layer walls, *Nature*, 363, 605–607 (1993).

[3]　A. Thess, R. Lee, P. Nikolaev, H. Dai, P. Petit, J. Robert, C. Xu, Y. H. Lee, S. G. Kim, A. G. Rinzler, D. T. Colbert, G. E. Scuseria, D. Tomanek, J. E. Fischer and R. E. Smalley: Crystalline ropes of metallic carbon nanotubes, *Science*, 273 (5274), 483–487 (1996).

[4]　C. Journet, W. K. Maser, P. Bernier, A. Loiseau, M. Lamy de La Chapelle, S. Lefrant, P. Deniard, R. Lee and J. E. Fischer: Large-scale production of single-walled carbon nanotubes by the electric-arc technique, *Nature*, 388 (6644), 756–758 (1997).

[5]　H. Dai, A. G. Rinzler, P. Nikolaev, A. Thess, D. T. Colbert and R. E. Smalley: Single-wall nanotubes produced by metal-catalyzed disproportionation of carbon monoxide, *Chem. Phys. Lett.*, 260 (3), 471–475 (1996).

[6]　K. Hata, D. N. Futaba, K. Mizuno, T. Namai, M. Yumura and S. Iijima: Water-assisted highly efficient synthesis of impurity-free single-walled carbon nanotubes, *Science*, 306 (5700), 1362–1364 (2004).

[7]　D. N. Futaba, K. Hata, T. Namai, T. Yamada, K. Mizuno, Y. Hayamizu, M. Yumura and S. Iijima: 84% catalyst activity of water-assisted growth of single walled carbon nanotube forest characterization by a statistical and macroscopic approach, *J. Phys. Chem. B*, 110 (15), 8035–8038 (2006).

[8]　K. Hata, and Y. Sainoo and H. Shigekawa: Atomically resolved local variation of the barrier height of the flip-flop motion of single buckled dimers of Si(100), *Phys. Rev. Lett.*, 86 (14), 3084–3087 (2001).

[9]　P. Eklund, P. Ajayan, R. Blackmon, A. J. Hart, J. Kong, B. Pradhan, A. Rao and A. Rinzler: WTEC Panel report on International Assessment of Carbon Nanotube Manufacturing and Applications, WTEC, (2007).

[10]　T. Hiraoka, T. Yamada, K. Hata, D. N. Futaba, H. Kurachi, S. Uemura, M. Yumura and S. Iijima: Synthesis of single- and double-walled carbon nanotube forests on conducting metal foils, *J. Am. Chem. Soc.*, 128 (41), 13338–13339 (2006).

[11]　G. Chen, R. C. Davis, H. Kimura, S. Sakurai, M. Yumura, D. N. Futaba and K. Hata: The relationship between the growth rate and the lifetime in carbon nanotube synthesis, *Nanoscale*, 7, 8873–8878 (2015).

[12]　T. Yamada, T. Namai, K. Hata, D. N. Futaba, K. Mizuno, J. Fan, M. Yudasaka, M. Yumura and S. Iijima: Size-selective growth of double-walled carbon nanotube forests from engineered iron catalysts, *Nature Nanotechnology*, 1, 131–136 (2006).

[13]　H. Nishino, S. Yasuda, T. Namai, D. N. Futaba, T. Yamada, M. Yumura, S. Iijima and K. Hata: Water-assisted and highly efficient synthesis of single-walled carbon nanotubes forests from colloidal nanoparticle catalysts, *J. Phys. Chem. C*, 111 (48), 17961–17965 (2007).

[14]　S. Yasuda, D. N. Futaba, T. Yamada, J. Satou, A. Shibuya, H. Takai, K. Arakawa, M. Yumura and K. Hata: Improved and large area single-walled carbon nanotube forest growth by controlling the gas flow direction, *ACN Nano*, 3 (12), 4164–4170 (2009).

[15]　C. Subramaniam, T. Yamada, K. Kobashi, A. Sekiguchi, D. N. Futaba, M. Yumura and K. Hata: One hundred fold increase in current carrying capacity in a carbon nanotube copper composite, *Nature Communications*, 4, 2202 (2013).

Author

Kenji HATA

Graduated from the Department of Applied Physics, School of Engineering, the University of Tokyo in 1996. Joined AIST in 2003. Currently, Director, CNT-Application Research Center, AIST. For the development of mass production technology for single-walled carbon nanotubes by super-growth method, received: the 21st Century Invention Encouragement Award, 2016 National Invention Award (Japan Institute of Invention and Innovation); Commendation for Science and Technology (Development) by the Minister of Education, Culture, Sports, Science and Technology; and Special Jury's Prize of the 45th Japan Industry and Technology Prize (Nikkan Kogyo Shimbun).

Discussions with Reviewers

1 Overall
Comment (Toshimi Shimizu, AIST)

This paper presents the course of research in which the innovative synthesis method for single-walled carbon nanotubes developed by the author was advanced from laboratory scale to industrial mass production scale, and the commencement of operation of the world's first mass production plant by a company. The diverse elemental technologies that were determined essential according to the research policy conceived by the author and the scenario for the integration of elemental technologies through corporate collaboration are briefly summarized. The passion of the author and the company propelled the realization of the manufacturing process design for nanomaterials for which there was very little previous experience, and this is world-class nanotechnology that is certainly appropriate for publication in *Synthesiology*.

Comment (Shuji Abe, Musashino University)

This paper offers a clear overview of the development of production technology for single-walled CNTs by the super-growth method developed by the author, from the motivation of development, the efforts spent on the project, the elemental technologies for a mass production process, and the current commercial production. In the first draft, there were many places where the author's "strong thoughts" were presented in literary expression like in a memoire or an essay. While these make the paper very unique, they can also make the paper awkward as an academic article. *Synthesiology* is, in principle, a public academic journal, and the editorial policy is "to publish papers that explain the research process and the results aiming for the introduction of research results into society in the words of science and technology." Overall, this paper is written in the words of science and technology, and although I think some literary expressions are permissible, I also feel that they should not be excessive.

2 Comparison of the methods for single-walled CNT synthesis
Comment & Question (Toshimi Shimizu)

The author cites Fig. 3 to compare the yield, cost, purity, and quality of the various methods of single-walled CNT synthesis. On the other hand, the paper discusses the superiority of the super-growth method against other innovative synthesis methods for single-walled CNTs, from the perspectives of synthesis yield

per volume and time of the reaction furnace, reaction environment (vacuum system, open system, etc.), and reaction temperature. In Fig. 3, for example, if you weigh each score like excellent 4 points, good 3, moderate 2, and poor 1, the supported catalyst CVD method and fluid bed furnace method have a total of 10 points, while the super-growth method has 11 points, and there is not much difference. I think the general readers will intuitively understand the superiority of the super-growth method if you add, as items of comparison, the three items discussed in this paper: synthesis yield, reaction environment, and reaction temperature. Or, is the author's weighing of the scores for the four items of comparison in Fig. 3 different from each point mentioned above?

Answer (Kenji Hata)

The four items shown in Fig. 3 show the characteristics of carbon nanotubes, and they show that the super-growth method is viable as business compared to the conventional synthesis methods. As you indicated, items such as synthesis yield per volume and time of the reaction furnace, reaction environment (vacuum system, open system, etc.), and reaction temperature are discussions about the synthesis condition. Since there are diverse synthesizing formats for each synthesis method, it is difficult to discuss the superiority or inferiority in simple terms. Also, considering practical application, I don't think it is very meaningful to score the items of Fig. 3 as poor 1 point, moderate 2, good 3, and excellent 4.

3 Safety of the single-walled CNTs
Comment (Toshimi Shimizu)

In the first draft, there was an expression that the researchers involved in development might quietly disregard the matter of safety of the single-walled CNTs. For the safety of single-walled CNTs, as a result of the NEDO Project, the safety test manual and guidelines for the work environment and measurements for carbon nanotubes have been published for the workers who handle the CNT materials. I recommend that you add or cite appropriate explanations and results of the concurrent R&D for the ELSI (ethical, legal, and social issues) and EHS (environmental, health, and safety) concerns that are essential in the development of nanomaterials.

Answer (Kenji Hata)

I corrected the text so the explanation centers on the activities conducted primarily by AIST and Zeon. At the time, the NEDO Project that led to the drafting of the safety test manual and work environment guidelines for carbon nanotubes manufactured by the super-growth method had not been implemented. Since this departs from the main topic of this paper, I did not discuss the details of the various kinds of EHS research that were conducted concurrently.

Comment (Shuji Abe)

In the first draft, though it may not be representative of the author's thinking, there was a text that the readers might mistake that you are scientifically negating the health damage of asbestos. I recommend you correct the text appropriately.

Answer (Kenji Hata)

As you indicated, I corrected the expression that may give the readers the impression that I am negating the health effect of asbestos that has been scientifically proven.

4 Mass production of single-walled CNTs
Question (Shuji Abe)

What specific degree of production volume do you mean when you say "mass production" in "3.1 Development of mass production technology for single-walled CNTs"? There was a description in Subchapter 2.2, that you set a personal goal of "10 tons annually," but can I assume that the Zeon's CNT production plant that started operation in 2015 surpassed this goal?

Answer (Kenji Hata)

Zeon has not released the actual figures. Therefore, I shall not publish the figures in this paper.

5 Grade and quality assurance of single-walled CNTs
Question (Toshimi Shimizu)

In the case of multi-walled CNTs, I think the diameter, length, purity, metal oxide amount, specific surface area, and others are noted as their qualities. What are the parameters to assign the grade and to assure quality of the single-walled CNTs that were massively produced here? Do you conduct the quality control by using Raman spectroscopy, optical absorption spectroscopy, or thermogravimetry?

Answer (Kenji Hata)

In general, the carbon nanotubes synthesized by the super-growth method have the characteristics of high specific surface area, high purity, and long length, and actual quality control is done based mainly on purity and specific surface area.

6 Elemental technologies of the mass production process
Comment (Toshimi Shimizu)

You present the division of roles where AIST develops the method for solving the issues, and Zeon Corporation develops the ways to upscale the methods, continuous technology, and production technology. In "4.1 Elemental technologies of the mass production process", can you color-categorize each elemental technology (currently grey) in Fig. 8 into those achieved by AIST, Zeon Corporation, or AIST + Zeon Corporation. In this paper, there are no names of the people in charge of the development of individual elemental technologies described in Subchapter 4.1. I think the reader's understanding will deepen if people or organizations in charge are clarified.

Answer (Kenji Hata)

Since this paper was written by AIST alone, I described the parts in which AIST was primarily in charge. However, to help understanding of the whole flow, I explained the parts where Zeon was in charge as much as they were disclosed. For the division of research topics between AIST and Zeon, AIST developed the fundamental technology while Zeon developed the mass production method. The research for large-area synthesis and continuous synthesis was mainly conducted by Zeon.

Comment (Shuji Abe)

In "4.1 Elemental technologies of the mass production process," you describe the development of various elemental technologies, and I think you should discuss the contributions of teams and joint researchers for particularly important technologies. If it is difficult to mention them individually, it can be placed at the end in a form of acknowledgement.

Answer (Kenji Hata)

Since it is difficult to mention them individually, I added the acknowledgement of the people involved.

7 Integration of the elemental technologies
Comment (Toshimi Shimizu)

The section of "4.1.7 Integration of the elemental technologies" is an overlap of the contents in 4.1.1 to 4.1.6. Here, why don't you give us the final summary of the results of integration and the conclusion of results as much as you are allowed to disclose. I think the readers can readily understand if you refer to Fig. 8.

Answer (Kenji Hata)

The integration of elemental technologies is what we spent most effort on, and there are many parts that cannot be disclosed at this point, and it is very difficult to comprehensively describe the whole picture. However, it was the part on which we spent most effort, and I decided to give some details using case studies. Please understand that this paper was written under such restrictions.

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

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).

Website—[No.] Author(s) name (updating year): Title of a web page, Name of a website (The name of a website is possible to be omitted when it is the same as an author name), URL, Access date.

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 Public Relations Information Office, Planning Headquarters, National Institute of Advanced Industrial Science and Technology(AIST)
Tsukuba Central 1, 1-1-1 Umezono, Tsukuba 305-8560
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).

Inquiries:
Synthesiology Editorial Board
c/o Public Relations Information Office, Planning Headquarters, National Institute of Advanced Industrial Science and Technology(AIST)
Tel: +81-29-862-6217 Fax: +81-29-862-6212
E-mail: synthesiology-ml@aist.go.jp

Letter from the editor

We deliver you *Synthesiology* Volume 9 Issue 3 that is our second special issue. This time, it features five research papers on "nanomaterials." The final goal or the mission of nanotechnology is to fully utilize the "functions" and "structures" in the size range of one-billionth meter (nanometer) in engineering, and to implement this technology in industry and society. This is the reason why nanotechnology is considered the core of common fundamental technology in the forefront. About ten years ago, in the Third Science and Technology Basic Plan that was established in FY 2008, the field of nanotechnology materials was positioned as one of the areas of priority. The roots of nanomaterial research that is presented in this issue go back to a period before this Basic Plan. In nanotechnology, the collaboration and fusion of different fields and different businesses are essential, because in order to socially implement the nanometer-size materials, various technologies must be linked in a configurational manner, surpassing the barrier of nine-digit size differences all the way to meter size. Therefore, the story of how the individual elemental technologies and scientific findings are integrated and synthesized by what scenario toward the research goals and strategies to create values that would be accepted in society is an excellent topic of synthesiology.

For example, the nanomaterials represented by carbon nanotubes hold the potential to revolutionize the world through their electronic, magnetic, and engineering properties. However, due to their minute size, before such materials can become usable in society, a novel and innovative production process, for which we have no past experience, is necessary in order to enable macroscopic expressions while maintaining their microscopic properties. In the paper on the super-growth method, please take note of the research scenario that took the production technology for single-walled carbon nanotubes from lab scale to plant scale for which the elemental technologies were completely different. Moreover, it is important to pioneer technologies to composite and disperse the nanomaterials into the matrices. In the paper on the development of human-friendly polymeric actuators, the major point is the attainment of portability, film formation, and weight reduction of the braille displays that can be used by visually impaired people by using the carbon nanotubes as electrodes. In the paper on the development of the high-performance adsorbent HASClay®, the main attraction is the research story where an artificial product was ultimately developed after dropping the attempt to find nanomaterials from natural minerals, in developing the adsorbent for an energy-saving system.

It is also essential to achieve diverse hierarchization such as the achievement of a large surface area, thin films, and systems for the products, as well as their production and process technologies. In the paper for high-quality high-speed large-area CVD synthesis of graphene, the detailed scenario for the development of a plasma-assisted film-forming process towards the use of flexible transparent conductive films is introduced along with detailed data analysis. In the paper on technology for decontaminating ash contaminated by radioactive cesium, it is fascinating to see the technology that uses as raw material Prussian blue, a pigment known since ancient times, advance to a decontamination system for contaminated ash. I hope you enjoy this special issue that contains plenty of synthesiological case studies in which the social values of nanomaterials that have nanometer pores and cavities are enhanced as actuators, transparent conductive films, decontamination material, humidity control material, electronic material, and others.

(Toshimi SHIMIZU, Executive Editor)

Aim of *Synthesiology*
— Utilizing the fruits of research for social prosperity —

There is a wide gap between scientific achievement and its utilization by society. The history of modern science is replete with results that have taken life-times to reach fruition. This disparity has been called the *valley of death*, or the *nightmare stage*. Bridging this difference requires scientists and engineers who understand the potential value to society of their achievements. Despite many previous attempts, a systematic dissemination of the links between scientific achievement and social wealth has not yet been realized.

The unique aim of the journal *Synthesiology* is its focus on the utilization of knowledge for the creation of social wealth, as distinct from the accumulated facts on which that wealth is engendered. Each published paper identifies and integrates component technologies that create value to society. The methods employed and the steps taken toward implementation are also presented.

Highlights of the Papers in *Synthesiology*

Research papers

Editorial policy
Instructions for authors
Letter from the editor
Aim of *Synthesiology*