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# Revolutionizing Japanese-Originated Mesoporous Materials


Grazing Incidence Small Angle X-ray Scattering

# Revolutionizing Japanese-Originated Mesoporous Materials

## Discovery and Development of Japanese-Originated Mesoporous Materials

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Mesoporous materials have an intermediate pore diameter between that of micropores (less than 2 nm) and macropores (more than 50 nm). Distinctive features include a uniform pore size and regular arrangement of pores. To date, many mesoporous materials have been prepared under various synthetic conditions. The mesoporous materials have nano-sized pores that break the pore size barrier of zeolites, which are typical microporous crystals, and thus are key materials for current nanotechnology.

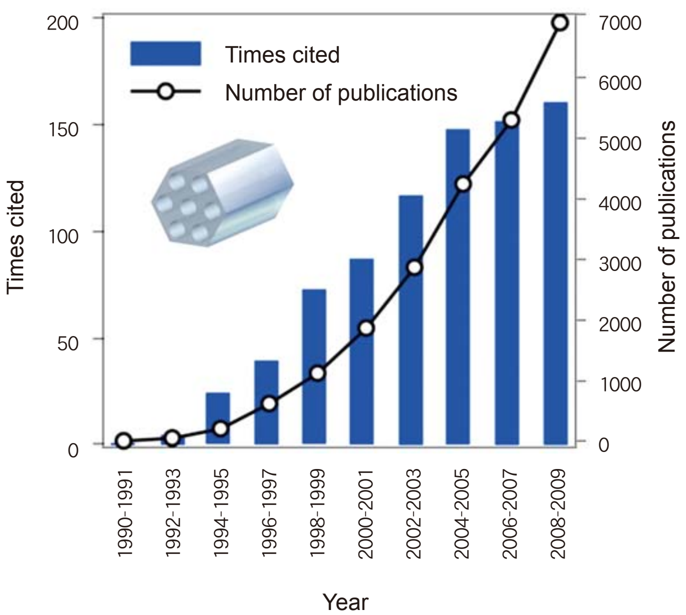
In the 1980s, in the process of research on intercalation compounds, we realized that the reaction product of layered silicate kanemite and a cationic surfactant (alkyltrimethylammonium ion) maintained uniform interlayer spacing after calcination. Measurements by solid-state NMR (nuclear magnetic resonance) revealed that the silicate framework became 3-dimensionalized, producing porous materials with very high surface area. This is an example of serendipity, in which research on organic derivatives of layered silicate led to the discovery of new mesoporous silica (KSW-1).

We presented this result orally at the Spring Meeting of the Chemical Society of Japan in 1988, and published a paper on the subject in the Bulletin of the Chemical Society of Japan (BCSJ) in 1990. From the annual trend in citations of this paper, it can be understood that the synthesis of this new material was gradually recognized as a Japanese achievement. In 1992, Mobil published papers on mesoporous silica (MCM-41, etc.) in Nature and the Journal of the American Chemical Society (JACS). This created a sensation and led to intense research on mesoporous materials.

Great progress has been made in the 20 years since this discovery, and the number of papers listing "mesoporous" as a keyword has increased steadily. Research spans a diverse range of topics, from synthesis and structural analysis to research on applications such as catalyst supports, adsorbents, optical materials, and biomedical applications, among others. Progress is also being achieved in precisely morphological controls, including thin films, monoliths, nanoparticles, fibers, etc. The composition of pore walls has become more diverse, and development has extended to various metal oxides, carbons, organic-inorganic hybrids, and metals. Design of the pore environment by organic modification in the mesopores is also progressing. In the future, the research on mesoporous material is expected to shift toward more applied research.

Mass production of mesoporous silica has become possible, at last opening the way to practical applications. At the present applications, however, the orientation of the mesopores and their regular arrangement at the mesoscale still are not fully utilized. A higher level of activity in applied research, with substantial involvement by industry, is necessary in order to achieve further breakthroughs.

I am extremely pleased by the role that NIMS is playing in this field, which includes the publication of a series of high impact results ranging from the creation of new mesoporous materials such as metal-based and nitride-based compositions, to application to sensing, catalysts, electrochemical batteries, etc. I hope that young researchers will display their creativity, and will provide a driving force for this field as top runners. I also hope that Japan will propose a new paradigm for Japanese-originated nanomaterials.




## Mesoporous Materials
### A Potential Source of Innovation

**Katsuhiko Ariga**
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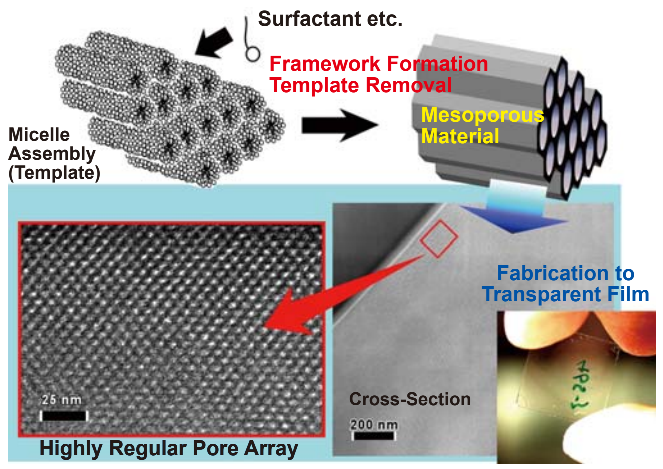
What are mesoporous materials? To explain this in simple terms, with progress in nanotechnology, materials which contain small pores have attracted attention. Although these are called nanoporous materials, this is a somewhat vague definition, as it is merely a general term for materials with nano-sized pores. According to the official definition of the International Union of Pure and Applied Chemistry (IUPAC), materials with a pore diameter of less than 2 nm are termed microporous materials, while those with pores larger than 50 nm are macroporous materials. Intermediate materials with pore diameters from 2 nm to 50 nm are termed mesoporous materials. The range of sizes included in this definition of mesoporous materials is a region in which extremely interesting phenomena can occur in molecular science, supermolecular science, and polymer science, because motion and diffusion of small molecules are possible, but this size range limits the arrangement and mobility of aggregates of those molecules, polymers, etc. Moreover, because it also corresponds to the size of biological materials such as enzymes and nucleic acids, mesopores are a space which is suitable for enclosure of these biomaterials. Thus, the mesoporous materials are attractive materials which provide a field that is capable of manifesting physical properties and other characteristics of interest to scientists.

How are mesoporous materials created? As one simple example, when a surfactant and certain types of polymers are dispersed in a solvent, an aggregate of supermolecules called a micelle is formed. If the conditions are set properly, a precisely-assembled structure can be created. This type of structure is called a mold or a template. Next, a hard material such as silica is solidified around this soft mold. A porous material can then be obtained by removing only the mold part. If silica is used, the result is mesoporous silica. Because the structure of the pores formed in this process reflects the precise structure of the mold, the pore diameter is extremely accurate and the arrangement of the pores is highly-ordered. This kind of dense, accurate porous structure also has an enormous surface area.

Mesoporous materials can be produced using various materials and in various forms, such as powders and transparent films. Furthermore, because the production process is extremely simple and inexpensive, these materials have high potential for application and practical use. Until recently, the main applications of mesoporous materials were considered to be catalyst carriers and adsorbents, taking advantage of their large surface area. However, they also have the potential to bring about a revolution in materials in more advanced applications, not limited to these conventional uses.

Practical application in optoelectronic materials, fuel cell materials, environmental materials, sensing materials, medical materials, and others can be envisioned. For this, it will be necessary to develop mesoporous material based on new materials such as metals and carbon-based materials, to aim at applications such as sensors and drug delivery systems, among others, and to establish new structuring techniques for hierarchical structures.

The following articles introduce recent innovations in these materials by researchers at NIMS. I am confident that our readers will find these recent developments interesting.




Conceptual figure of preparing mesoporous silica and fabricating to film

* International Center for Materials Nanoarchitectonics based on World Premier International Research Center Initiative (WPI) Program

# Synthesis of Mesoporous Metal and Fabrication of Thin Film

Creation of the World's Most Advanced Metallic Nanomaterial by "Electrochemical Plating"

**Yusuke Yamauchi**
MANA Independent Scientist
MANA

Expanding the conventional concept of synthesis of mesoporous materials, we synthesized mesoporous materials with a metal framework by electrochemical deposition of the metal around a molecular assembly, followed by removal of this internal mold. [1,2]

Because mesoporous metals contain an almost infinite number of mesopores, the entire exposed surface area functions as an electrochemical reaction field, forming an electrode with high activity and good diffusivity. Mesoporous platinum and platinum alloys are optimum electrode materials for next-generation direct methanol fuel cells (DMFC). Use of a porous electrode not only increases the reaction area, but also increases the diffusivity of the substance in the electrode, making it possible to achieve higher reaction efficiency. Mesoporous tin (Sn) is a revolutionary material for next-generation negative electrodes for lithium ion secondary cells. At present, carbon is used as a practical negative electrode material for lithium ion secondary cells. However, Sn has a theoretical energy density approximately 2.7 times greater than carbon, and therefore it has attracted strong interest as a new negative electrode material for realizing high performance in cells. On the other hand, because the volume of tin changes greatly during alloying and dealloying with lithium during charging/discharging, the electrode itself is subject to structural collapse/loss. As a result, the life of the electrode is very short, which is a serious drawback. This problem can be solved by using an Sn electrode with a porous structure, i.e., a mesoporous structure, as the volumetric changes during charging/discharging are substantially reduced, greatly extending the life of the electrode.

Recently, our main research target has been the development of thin film of mesoporous metals. Fixing a mesoporous metal on a substrate as a thin film rather than as a powder makes it possible to use this itself as an electrode or base material for sensing. The EDIT (Evaporation-mediated Direct Templating) process, which we developed independently, enables fabrication of various compositions and mesostructures on substrates **(Fig. 1)**. Furthermore, by using a comparatively large molecular assembly as the template, the pore diameter can be controlled precisely from several nm to approximately 100 nm. [3,4] Sensing is possible by controlling the size of the mesopores to screen the molecules that enter the pores by size, and allowing selective reaction of only designated molecules in the electrode. The spaces between pores can be designed hierarchically, from macro to meso scale, by using a substrate which has been prepared by microprocessing, enabling synthesis of fiber electrodes with hierarchical structures, macro-meso hierarchically-structured electrodes, etc. [5,6] **(Fig. 2)**.

To date, synthesis of various metal nanomaterials such as nanoparticles, nanofibers, nanotubes, and others has been the subject of intensive research, and porous materials such as platinum black are used industrially. In comparison with these materials, our mesoporous metals have distinctive features not found in conventional metal materials, in that the size and arrangement of the pores are completely controlled. Thus, functions originating in this regular meso space can also be expected in the future.

References:
1) ***Angew. Chem. Int. Ed.*** 2009, 48, 7792-7797.
2) ***J. Am. Chem. Soc.*** 2009, 131, 9152-9153.
3) ***Angew. Chem. Int. Ed.*** 2008, 47, 5371-5373.
4) ***J. Am. Chem. Soc.*** 2010, 132,208-214.
5) ***J. Am. Chem. Soc.*** 2008, 130, 5426-5427.
6) ***J. Am. Chem. Soc.*** 2008, 130, 10165-10170.

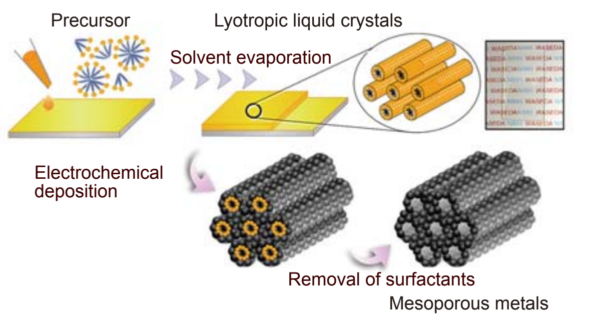



**Fig. 1** Synthesis process for mesoporous metals by the developed solvent evaporation process (EDIT).

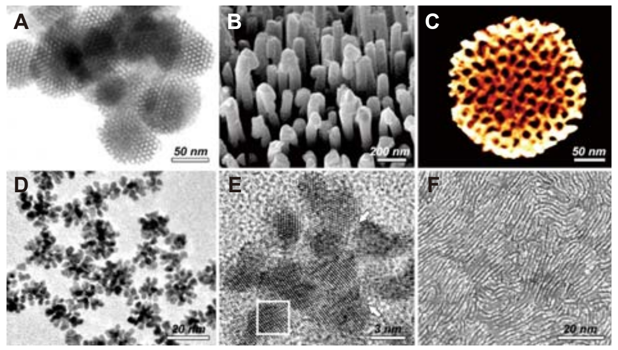



**Fig. 2** Mesoporous metals with various morphologies synthesized to date: **A.** electron microscope image of mesoporous platinum with 2-dimensional hexagonal structure; **B.** fibers of mesoporous platinum-ruthenium alloy; **C.** 3-dimensional tomography of mesoporous metal with gigantic pores exceeding 10nm; **D.** electron microscope image of mesoporous metal nanaoparticles synthesized by solution process; **E.** high resolution electron microscope image of mesoporous metal nanoparticles; and **F.** surface of mesoporous platinum thin film with 2-dimensional hexagonal structure.

# Novel Mesoporous Carbon Based Materials for Energy and Environment

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Since the discovery of mesoporous silica molecular sieves designated as M41S, this field of research has been tremendously focussed and considerable scientific effort has been involved on the preparation, characterization and application of the ordered mesoporous materials. Although mesoporous silica materials possess interesting textural characteristics, the thermal and mechanical stability of these materials are very poor which limit their use for commercial applications. Thus, it is highly critical to explore the synthesis of mesoporous materials other than silica which must be highly stable both thermally and mechanically. As carbon is one of the interesting materials which possess a high thermal and mechanical stability, we are exploring the synthesis of various mesoporous carbon materials with different structure, morphology, and pore diameter by hard templating approach where in inorganic mesoporous metal oxides are employed as the hard template **(Fig. 1)**.

Mesoporous carbons such as carbon nanocage, carbon nanocoops, and glucocarbons have been successfully fabricated using the above approach. Among these materials, carbon nanocage (CNC) is interesting because it exhibits very high surface area of more than $1600 m^2/g$ and pore volume of $2.2 cm^3/g$.[1] It has been successfully synthesized for the first time using nanotemplating technique via "controlled pore filling method" developed by us.

These materials show very high adsorption capacity for proteins, amino acids, DNA and organic dyes.[2] Recently we have demonstrated the importance of pore engineering in CNC design. Very high selectivity for adsorption of tea components (catechin and tannic acid) was achieved through a simple one-pot process using the novel nanocarbon, CNC.[2,3] Although nonspecific hydrophobic interactions play a major role in the current case, functionalization at the cage interior should enable us to achieve a more specific molecular recognition. Since the structural dimensions of CNC are comparable with those of some proteins and peptides, CNC adsorbents could be used for efficient removal of hydrophobic toxic biomaterials such as amyloids and therefore will have a great impact on biomedical fields and could replace the existing toxic and hazardous adsorbent materials.

CNC was also employed as the support for the polymer electrolyte membrane (PEM) fuel cells. It was found that the anodic performance of platinum loaded mesoporous carbon is much higher as compared to that of the commercially available carbon black support even though the platinum content of former is 5 times lower than the later. This indicates that our novel mesoporous carbon could replace the existing support for the PEM fuel cells and reduce the cost of the whole fuel cell system.

The function of the mesoporous carbons can also be tuned by altering the chemical composition of its wall structure with different elements such as nitrogen. Recently we have prepared mesoporous carbon nitride (MCN). which has a highly ordered hexagonal array of two dimensional (2D) pore systems and exhibits much higher specific surface area and specific pore volume, and catalytic activity in the Friedel-Crafts acylation of benzene using hexanoyl chloride for the production of caprophenone which is an important intermediate for organic synthesis, as compared with those of non-porous carbon nitride materials.[4-6] In addition, this material contains inbuilt basic sites which can be used for capturing the $CO_2$ molecules which are the main cause of the recent global warming and may be considered as future "$CO_2$ Eliminator" **(Fig. 2)**. Very recently, we have also prepared novel mesoporous carbon nitride nanoparticles with a size less than 150 nm and a high nitrogen content (C2N) **(Fig. 1)**. These materials showed excellent basic catalytic performances both in the transesterification of beta-ketoesters[7] using different alcohols.

References:
1) Vinu et al. ***J. Mater. Chem.*** 2005, 15, 5122.
2) K. Ariga, A. Vinu, et al. ***J. Am. Chem. Soc.*** 2007, 129, 11022.
3) K. Ariga, A. Vinu, et al. ***Angew. Chem. Int. Ed.*** 2008, 47, 7254.
4) Vinu et al. ***Adv. Mater.*** 2005, 17, 1648.
5) Vinu et al. ***Chem. Mater.*** 2007, 19, 4367.
6) A. Vinu, ***Adv. Func. Mater.*** 2008, 18, 816.
7) Vinu et al. ***Angew. Chem. Int. Ed.*** 2009, 48, 7884.

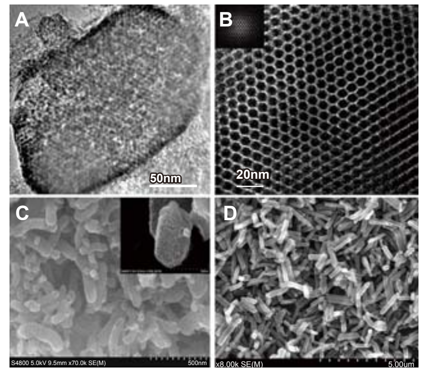



**Fig. 1** A and B) HRTEM images of mesoporous carbon nitride particles and carbon nanocoop, respectively, and C) and D) HRSEM images of mesoporous carbon nitride nanoparticles and mesoporous carbon with rod like morphology, respectively.

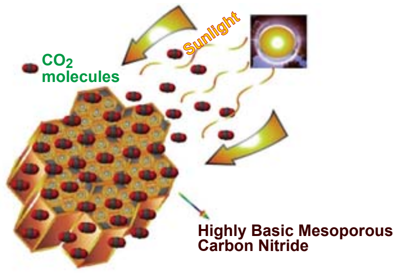
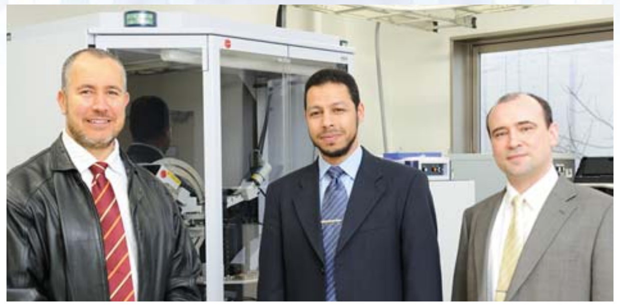



**Fig. 2** Schematic representation of the capturing of acidic $CO_2$ molecules by highly basic mesoporous carbon nitride

# Mesoporous Sensors for Water Purification from Toxic Metals



**Sherif A. El-Safty, Ahmed Shahat, Wojciech Warkocki**
Materials Research Laboratory for Environmental & Energy

Considerable amounts of chemical and bioactive contaminants were released into the environment and water sources from the industrial wastes. Standards for drinking water have been revised several times creating the need for efficient adsorbent of the pollutants. It should be effective even at part-per-billion (ppb) concentrations, according to World Health Organization (WHO).

Here, our optical mesoporous sensors show ability to create sensing systems with indoor and outdoor responses and with revisable, selective and sensitive recognition of toxic metals down to part-per-trillion (ppt), in rapid sensing responses. The fabrication of nanosensor arrays based on the dense pattern of surface functionality and adsorption of the colorant probe dopants with maintaining of the intrinsic mobility and flexibility into the nanoscale ordered materials enabled the development of sensing systems in which high flux of the target metals across the colorant is rapidly achieved within 30 seconds (**Fig. 1**). Indeed, our ordered mesoporous materials that have a uniformly-sized, monodispersed porosity in the range of 2–30 nm, and a large surface area (1000 $m^2$/g) show promise of a new class of sensor materials.

An attempt demonstrated here is the tailoring of colorant probe "azo-chromophore" in compact mesopore membrane-discs, as optical sensor for visual detection of ultra trace $Hg^{II}$ ions (~ppt) (**Fig. 2**) using "low-tech" UV-Vis instrumentation. However, brilliant colour transitions at the same frequency as the human eye could be recognized over a wide-range of $Hg^{II}$ concentrations. Moreover, the mesoporous sensors had the capacity to serve as ion-preconcentrators with efficient reusability up to 20 repeated cycles (**Fig. 3**). The ion-selective workability for optical sensor over multi-ion competitive species led to design of cost-alternative tool to current laboratory sensing methods. Mesoporous optical sensor can ultimately be employed in the basic laboratory assays, in the measurement fields through portable devices, and in the household use as commercial indicators.

The development of these technologies will open new opportunity for environmental cleanup in the world. In this endeavor, we introduce an attractive means of pollution monitoring by the use of simple, inexpensive, rapid responsive and portable mesoporous sensors.

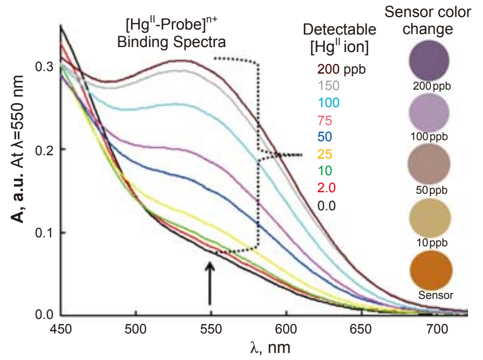



**Fig. 2** Colour transition map and reflectance spectra observed for mesoporous $Hg^{II}$ ion-sensor membrane with increasing concentrations of $Hg^{II}$ ions from 2ppp to 200 ppb, at pH of 7.

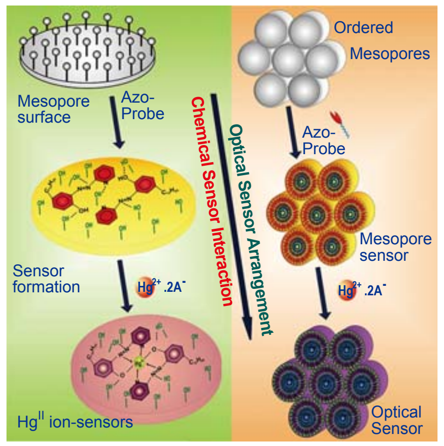



**Fig. 1** Simple design of optical mesoporous sensor for toxic $Hg^{II}$ ions by the chemical construction of "azo-chromophore" with adjacent silanol group at pore surfaces to form well-arrangement azo-probe onto the nanoscale ordered materials. Note: azo-probe formula is 4-dodecyl-6-(2-pyridylazo) phenol

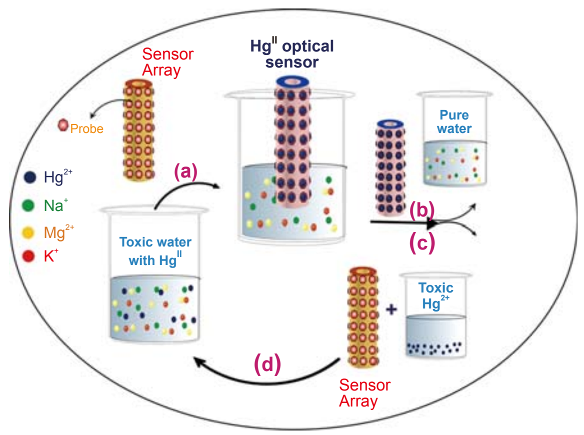



**Fig. 3** Simple design for water treatment system from toxic $Hg^{II}$ ion using optical sensor arrays at complete stages of analyses of (a)optical ion-selective system, (b) removal of toxic ions, (c)extraction of toxic ions, and (d) reusability of the sensor using $C_2O_4^{2-}$ anions as a stripping agents.

# New Hierarchical-type Mesoporous Materials

## Drug Delivery System Featuring Repeated Automatic Release/Stop

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Japan Society of the Promotion of Science (JSPS) fellow

**Katsuhiko Ariga**
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The remarkable functions of living organisms provide a model for artificial functions. We are constantly engaged in research in which we attempt to develop materials with functions like those in the biological world. What is the great difference between living organisms and manmade machines? Is it flexibility and rigidity? No. The great difference is in the coupling of functions. When an artificial machine is switched on, only a certain designated function is initiated. In contrast, when a natural system receives some stimulus, its functions change kaleidoscopically in response to the surrounding conditions. This is possible because its functional coupling and feedback functions are exquisitely harmonized. For this reason, the functions of living organisms are said to be "wise." The secret of sophisticated functions like those in living organisms is a "hierarchical" structural design in which functional structures are intertwined in a complex manner.

Taking this hint from nature, we created the hierarchical structure shown in **Fig. 1**. In the capsules contained in this structure, the large internal space is coated with a silica wall containing small mesopores. The capsules with this hierarchical pore structure are further assembled into a hierarchical structure by fabricating a layered film together with nanoparticles and polymers. This makes it possible to impart a "drug delivery" function, in which a liquid drug is incorporated in the capsules embedded in the film for later release.

When we examined the behavior of the liquid drug, which is absorbed and released when exposed to air, we observed that this operation switches "on" and "off" in a repeated automatic cycle as shown in **Fig. 2**. Although we have not completely elucidated the mechanism responsible for this phenomenon, we believe that it is a function that reflects the hierarchical pore structure, which alternately causes a process of evaporation of the drug in the pores in the capsule wall, and a process of capillary osmosis by which the drug permeates from the interior of the capsule into the pores. Because this material enables periodic release of drugs without external stimulus, application to automatic/periodic drug administration is expected to be possible. For example, if the system is set in the morning, drugs can be administered 3 times during the day. Recent research has also revealed that DNA can be fixed if appropriate processing is applied to the surface of the capsule, and harmful aromatic compounds can be adsorbed if the capsule material is changed from silica to carbon.

The key to the development of this material was creation of a hierarchical structure. This suggests that it may not be possible to realize higher functions, like those seen in living organisms, simply by creating a porous structure without pursuing this kind of systemization/hierarchicalization. Thus, we have now entered an era in which we must say that "not only creating materials, but imparting functions by systemization of those materials is critical."

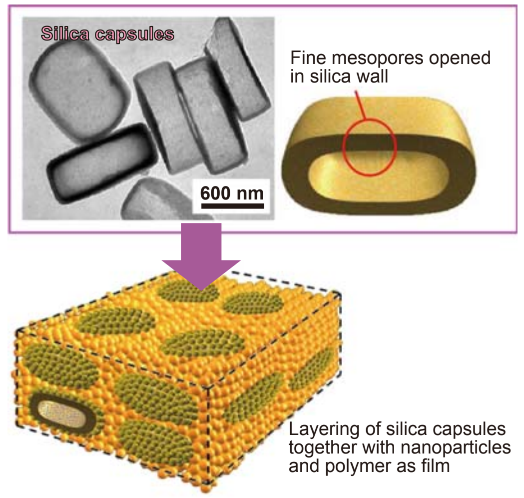



**Fig. 1** Hierarchical system containing silica capsules with mesopores.

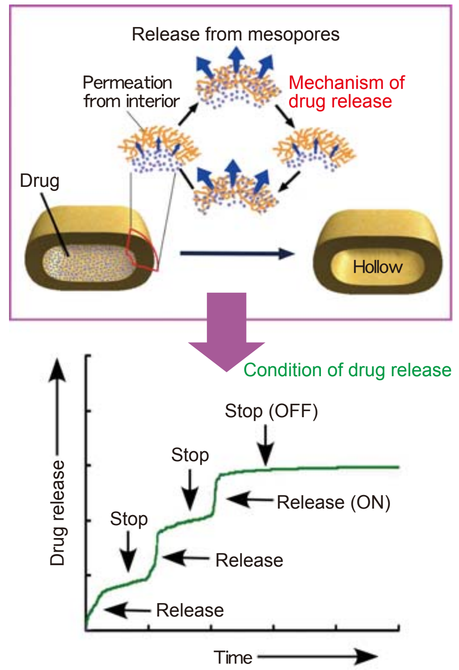


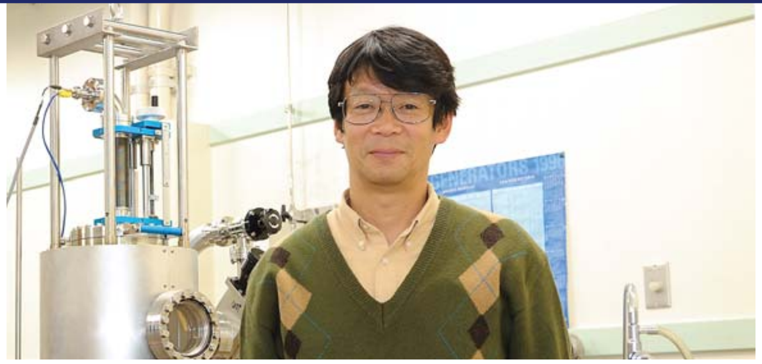

**Fig. 2** Application to automatic cyclical release/stop drug administration.

# Development of Ultrafine Crystalline Cubic Boron Nitride Sintered Cutting Tool

## Toward Realization of Mirror Finish Processing of Steel Materials

High Pressure Group,
Exploratory Nanomaterials Research Laboratory

Group Leader
Takashi Taniguchi



In the processed surfaces of molds for forming contact lenses, optical parts, and similar products, high dimensional accuracy and a mirror finish are required. For this reason, final finishing is normally performed by polishing with a lapping device. Replacing this process with precision cutting, if possible, would make a great contribution both to reducing environmental loads by eliminating the need for polishing powders and lubricants, and to energy saving in the machining process. The development of a new material with excellent cutting performance would also be significant from the viewpoint of pioneering substitute materials for the existing tungsten tools.

Cubic boron nitride (cBN) is the second hardest substance after diamond, and is applied as a tool material for ferrous metal materials with which diamonds cannot be used due to chemical reaction. In particular, high purity binderless cBN sintered bodies, which are obtained by direct phase transformation of hexagonal boron nitride (hBN) under high temperature/high pressure conditions and contain absolutely no sintering binder, are known to possess properties superior to those of conventional sintered tools which contain binders. For precision cutting tools, in addition to hardness and wear resistance, the ability to maintain a sharp edge of the blade during cutting is important. For example, in order to obtain a mirror surface with profile accuracy on the order of 100 nm, a sintered material with a constituent particle size of no more than 100 nm is necessary.

We produced a cBN sintered material, as shown in **Fig. (a)**, with a particle size of less than 100 nm under high temperature/high pressure conditions of approximately 1700°C and 10GPa ($10^5$ atm.) using a belt type high pressure apparatus. Until now, the particle size of binderless cBN sintered bodies has been around 500 nm, and these materials were obtained under synthesis conditions of 8GPa and 2200°C. Refinement of the grain size of the sintered bodies produced in this research was possible due to the successful development of a high pressure synthesis technology which is stable in the 10GPa region,[1] and suppression of cBN grain growth by reducing the temperature necessary for the hBN to cBN phase conversion from 2200°C to 1700°C.

In joint work with RIKEN, this ultrafine particle binderless cBN sintered tool was installed in a high precision milling machine which enables precision cutting, and mirror processing was performed on hardened stainless steel. The results confirmed that a mirror processed surface can be obtained under a dry condition without the use of cutting oils. In this process, surface roughness in maximum height* was <100 nm, and high precision processing having roughness of $R_z$<50 nm on the best processed surface was realized.[2] Important issues for future research include further refinement of the particle size, and reproduction of the properties of the cBN sintered bodies realized in the present research in the low pressure region of 6GPa, enabling general industrial use.

References:
1)T.Taniguchi, M.Akaishi, Y.Kanke, S.Yamaoka, Rev.Sci.Instrum., **75**,1959 (2004).
2)K.Fujisaki,T.Taniguchi,et.al,.J.Mater.Processing Technol.,**209**,5646(2009).

*An index which expresses the finished surface accuracy of material surfaces such as machined surfaces, showing the height from the lowest valley to the highest peak in the standard length in measurement of irregularities (roughness) of the surface.

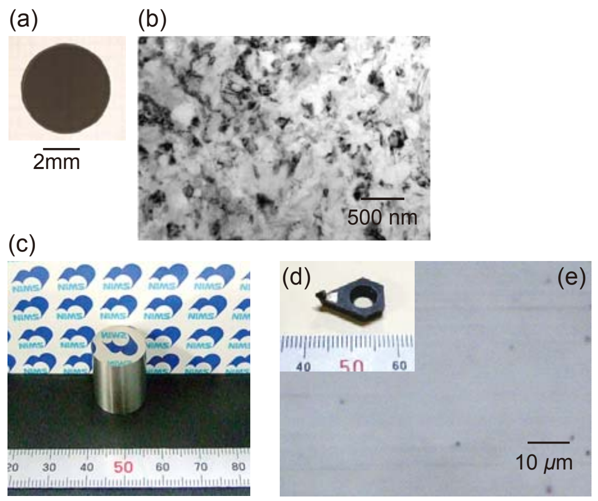



Fig. (a) cBN sintered body, (b) transmission electron microscope image of cBN sintered body, (c) external appearance of test specimen (SUS420J2) after cutting, (d) cBN cutting tool, and (e) optical micrograph of the cut surface.



# New Possibilities of Super-Hard Coating

Coating Materials Group, Hybrid Materials Center

Makoto Watanabe Masayuki Komatsu Managing Director Seiji Kuroda

**Issues for Thermal Spray Coating Technology**

Materials which are produced by mixing and sintering powders of an extremely hard substance such as tungsten carbide (WC) and a soft metal such as cobalt (Co) are called super-hard alloys. Because these materials provide a combination of hardness and wear resistance, they are widely used in tools and machine parts. However, the fact that there are limitations on the size and shape of sintered parts is a drawback. If thermal spraying technology can be used to melt and spray the original feedstock powder, it is possible to coat super-hard alloys on the surfaces of large members and parts with complex shapes. Replacing the conventional approach of producing parts consisting entirely of a super-hard alloy with a system comprising a substrate of some abundant materials and a super-hard coating can be expected to have an important effect in the effective utilization of rare elements such as tungsten and Co.

Fabricated coatings have high hardness and are widely used in applications which require wear resistance, but certain problems are inherent in the conventional process, including oxidation of the sprayed particles during deposition and formation of brittle compounds in the dissolution reaction of Co and WC, which results in weakening of the coating. Furthermore, in many applications, the surface of the coating is polished to a mirror finish, requiring a costly, time-consuming polishing process. Thus, a process which makes it possible to produce a smooth surface in the as-sprayed condition is needed in order to reduce manufacturing costs.

**Results of Joint Research with Industry**

We developed a process called "warm spray" in which the original feedstock powder is accelerated to a high velocity of more than 500m/s while heating the material to a temperature below its melting point. The principle is illustrated in **Fig. 1**. In this process, in addition to heat, the kinetic energy of acceleration is skillfully used in film-forming. Combustion is performed using a mixture of fuel and oxygen to produce a high pressure, high temperature gas. Oxidation of the sprayed particles is avoided by adjusting the gas temperature by mixing a room temperature inert gas with the combustion gas. In this research, our joint research partner, Fujimi Incorporated, developed a small granule-shaped WC-Co powder (granule size: 5-20$\mu$m) containing nano- to submicron-sized WC particles which are suitable for this process. When this powder was deposited by the warm spray process, a coating with a smooth, extremely dense surface was obtained. Because the microparticles of WC in the obtained coating retained their original shape, Vickers hardness exceeding 1500 and surface roughness of Ra<1.8$\mu$m (Ra: arithmetic mean deviation of roughness) were achieved. As shown in **Fig. 2**, these values are significantly improved in comparison with conventional thermal spray coatings. Possible applications of the developed super-hard coating are considered to include industrial manufacturing equipment, construction and civil engineering machinery, and aircraft, among others.

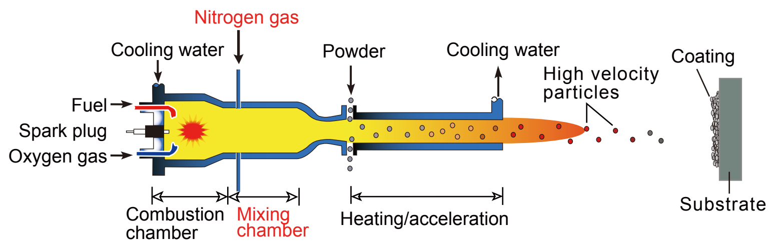



Fig.1 Principle of the warm spray process. Fuel and oxygen are mixed and ignited to produce a high pressure, high temperature combustion gas, and an appropriate amount of nitrogen gas is mixed with the combustion gas to avoid oxidation of the sprayed particles. A dense coating with minimal deterioration is produced by heating WC-Co powder to below its melting point, accelerating the particles and spraying on a substrate at high velocity.

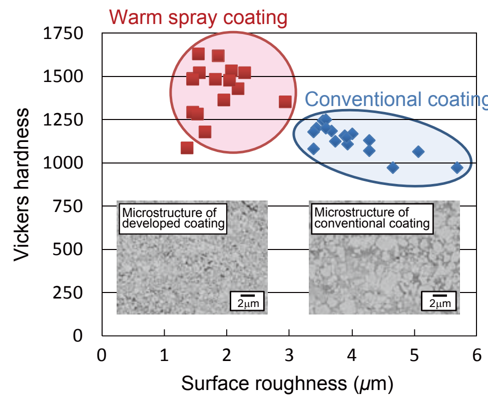



Fig.2 Comparison of the hardness, surface roughness, and cross-sectional microstructure of coatings produced by the developed warm spray process and the conventional process. The developed coating displays a fine microstructure, high hardness, and low surface roughness.

FACE フェイス interview

Unprecedented increases in demand for natural resources have occurred in recent years, driven by increased quantitative demand accompanying rapidly-growing production of industrial products and the necessity of high performance materials which support technical innovation. In particular, increased resource risk is a concern with rare metals and rare earth elements. In view of these circumstances, "urban mines" have attracted attention. The Center for Strategic Natural Resources makes quantitative assessments of the possibility of resource recycling, and devises and proposes optimum methods of resource management, centering on urban mines. In this interview, the Center's Managing Director, Dr. Kohmei Halada, discusses this topic.

**Kohmei Halada**

Managing Director
Center for Strategic Natural Resources

# If it isn't fun, it isn't research!

### I understand that you grew up in Iki Island in Nagasaki Prefecture. What kind of boy were you when you were a child?

Well, when I was a child, I launched a rocket in back of my house. It was the countryside, and there wasn't anything there. When I was a second-grader, my parents bought me a magazine called "Science for Children"(published from Seibundo- shinkosha) and I was completely taken in. I was absorbed in things like launching rockets and building my own hovercraft. The "Blue Backs" series of science books (published from Kodansha) came out when I was in middle school, and I became engrossed in reading them. At the time, I think a great many people were influenced by the "Blue Backs."

### So, I suppose it was inevitable that you'd follow a career in science?

I entered the course of Natural Sciences 1 at the University of Tokyo. In those days, advancing from the course to the Faculty of Physics, Department of Science was considered the "royal road." However, I thought that science was more than just physics, so I entered the Faculty of Metallurgy, Department of Engineering. I like new ideas, so I did research on powder processing, among other topics. I was also interested in biomimetics, which is based on the structures of living organisms. That was where I made the connection with Prof. Ryoichi Yamamoto's concept of ecomaterials. When the Ministry of Education, Culture, Sports, Science and Technology (MEXT) set up a committee on the development of the functions of rare metals and their future image, Prof. Yamamoto was named Chairperson and I was one of the members. When he proposed that we should look at resources from a wider perspective, the concept of Life Cycle Assessment was introduced. And when we were advised to think ways to evaluate ecomaterials, this led to the idea of "urban mines."

### Could you comment on resource management?

This is nothing particularly special. Many companies already apply precise energy management. The same precise management of resources in the supply chain should be required, but Japanese companies tend to take this lightly, even though they depend on overseas sources for virtually all natural resources. As with energy, more comprehensive management of resources integrating geopolitics and other fields is also necessary. Because Japan receives its supplies of resources from all over the world, this is something which Japan should disseminate to the world.

### What are your thoughts on the research environment at NIMS?

Of course, it's a wonderful environment for us. I also feel that the role of NIMS has expanded since becoming an Independent Administrative Institution. I mean that our social impact has become larger. If you're a researcher in a university laboratory, the development of one technology ends with the only evaluation of the technology itself, but at NIMS we can do integrated research. I want to make that environment much, much stronger. Creating groups that can act strategically, bringing together core members for research, providing new ideas to the national government and society – I think that NIMS is required to become a platform for proposing and practicing science and technology strategy through these kinds of activities.

### Finally, what advice do you have for young people?

"Enjoy." When I see young researchers, I feel that everybody is desperately working at their research without any larger sense of freedom. I always think "If it isn't fun, it isn't research." When we advance research, we are also creating culture. Like the musician who composes a piece of music or the artist who paints a picture, research is also a creative and cultural act. Because our field of research is materials, I think it's important that we feel that we're drawing out the goodness of materials possessed by nature.





## The 1st Symposium on ICNSEE

Prof. Louis Schlapbach delivering the keynote address.

(Feb. 9, 2010) The symposium on ICNSEE (Innovative Center of Nanomaterials Science for Environment and Energy) was held at NIMS. This was the first symposium held by the ICNSEE, which began operation in October of last year with the objective of promoting generic research and development of environmental and energy technologies by bringing together leading researchers from Japan and other countries through cooperation among industry, academia, and Independent Administrative Institutions (IAI). The symposium featured a total of 11 lectures, beginning with the keynote address by Prof. Louis Schlapbach, who served previously as the CEO of the Swiss Federal Laboratories for Materials Testing and Research (EMPA) and is scheduled to be appointed Deputy Director-General of the ICNSEE, which was followed by lectures on the four topics related to photovoltaic materials, photocatalytic materials, rechargeable battery materials, and fuel cell materials, which are the Center's target areas, and six topics combining theoretical and computational science and advanced analysis.

## 2010 International Workshop on Photocatalysts and Environmental Purification Materials and 3rd Japan-China Symposium on Photocatalytic Materials

Participants in the workshop and symposium in the NIMS courtyard.

(Feb. 21-24, 2010) The "2010 International Workshop on Photocatalysts and Environmental Purification Materials" and the "3rd Japan-China Symposium on Photocatalytic Materials" were held jointly at NIMS.

Photocatalysts have attracted considerable attention as one technology for solving the increasingly serious problems of global environmental pollution and energy. The development and practical application of materials which display high efficiency photocatalytic effects under the limitless resource of sunlight or indoor light is a starting point toward the solution of environmental pollution and energy problems.

During 3 days, researchers gave a total of 24 oral presentations and 42 poster presentations on topics including nanostructured photocatalytic materials, energy storage and conversion using photocatalysts, together with their evaluation and application, the electronic structure of oxide photocatalysts, photoelectrochemistry, dye sensitization, and others. The conference also featured intense discussions among the many participants, beginning with nearly 30 visiting researchers from China, the United States, and Australia, and also including foreign researchers working at NIMS, and teachers and graduate students from Tokyo Institute of Technology, the University of Tsukuba, and other universities. The event concluded with closing remarks by Prof. Louis Schlapbach, the Deputy Director-General of the ICNSEE.

## Special Symposium on Tsukuba Innovation Arena-nano


From the left, Prof. Sukekatsu Ushioda, Prof. Tamotsu Nomakuchi (President of AIST), Prof. Teruo Kishi, Prof. Nobuhiro Yamada (President of the University of Tsukuba), and Dr. Ryoji Chubachi (Vice Chairman of Sony Corporation and Co-Chair of the Keidanren Committee on Industrial Technology).

(Feb. 17, 2010) A special symposium was held by Tsukuba Innovation Arena-nano (TIA) at the Tokyo Big Sight International Exhibition Center.

TIA is a world-class nanotechnology research and development center located in Tsukuba City, which was launched with the National Institute of Advanced Industrial Science and Technology (AIST), NIMS, and the University of Tsukuba as its core institutions, and brings together the world's highest levels of advanced nanotech research equipment and human resources. The aim of TIA is to turn the results of Japanese nanotechnology research into innovation by a fusion of technologies in different fields desired by private companies through collaboration with the core Institutions.

At this symposium, keynote addresses were delivered by Prof. Tamotsu Nomakuchi, the President of AIST, Prof. Makoto Hirayama of the State University of New York at Albany, and Prof. Ayao Tsuge, President of the Shibaura Institute of Technology, followed by a panel discussion on "Nanotech Research Centers and the Training of Human Resources," which was moderated by Prof. Teruo Kishi, former President of NIMS and now NIMS Advisor, and included, as participants, Prof. Hideaki Takayanagi, Governor of Tokyo University of Science and also Principal Investigator of MANA/NIMS, Prof. Koichi Murakami, Provost of Graduate School of Pure and Applied Sciences at University of Tsukuba, and Dr. Seiichi Yoshikawa, Executive Advisor at Fujitsu Laboratories Ltd.

## NIMS Researchers Win the German Innovation Award, Gottfried Wagener Prize 2009

(Feb. 8, 2010) Dr. Yuji Kimura, Senior Researcher of the NIMS Structural Metals Center, and two Senior Researchers of the Exploratory Research Laboratory for Materials Reliability and Safety, Dr. Tadanobu Inoue and Dr. Fuxing Yin, received the Gottfried Wagener Prize 2009, First Prize for "Development of Stronger and Tougher Steel at Low Temperatures." The award ceremony was held at the Grand Hyatt Tokyo Hotel on February 8, 2010. The German Innovation Award was established in 2008 with the cooperation of the German Chamber of Commerce and Industry in Japan and twelve technology-focused German companies for the purpose of supporting young scientists affiliated with Japanese universities or research institutes. The award is given for application-oriented research which is currently in progress or was completed within the past 2 years in the three fields of Environment and Energy, Health and Medicine, and Safety and Security.


The scene at the award ceremony. The three NIMS researchers are in the center of the front row (from the left, Dr. Yin, Dr. Inoue, and Dr. Kimura).

The award presented to the NIMS team recognized their development of ultra-high strength steel materials which make it possible to realize the development of next-generation steel structures and weight reduction, as required in transportation equipment for resource saving, energy saving, and reduction of $CO_2$ emissions, and development of high strength, high toughness bolts using the ultra-high strength steel materials.

## NIMS Researchers Receive an Award from TMS

(Feb. 15, 2010) Dr. Alok Singh, Dr. Julian Rosalie, Dr. Hidetoshi Somekawa, and Dr. Toshiji Mukai at Lightweight Alloys Group of Structural Metals Center were given "Magnesium Fundamental Research Award" at the 139th Annual Meeting and Exhibition of The Minerals, Metals and Materials Society (TMS) in Seattle, Washington, USA, this month on Feb. 15. TMS is a professional organization headquartered in United States, that encompasses the entire range of materials and engineering, from minerals processing and primary metals production to basic research and the advanced applications of materials.

From left: Dr. Toshiji Mukai, Dr. Alok Singh, Dr. Julian Rosalie, Dr.Hidetoshi Somekawa

## NIMS Signed Comprehensive Collaborative Agreement with Waterloo Institute for Nanotechnology (WIN) at University of Waterloo (UW) Canada

(Feb. 19, 2010) The signing ceremony for NIMS-WIN/UW Comprehensive Collaborative Agreement was held at the Official Residence of Canadian Ambassador to Japan in attendance of the Ambassador Dr. Jonathan T. Fried. The Agreement was signed by Prof. Sukekatsu Ushioda, President of NIMS and Prof. Arthur Carty, President of WIN at UW. The WIN is expected to work as a hub for the development of cooperation including nanotechnology related centers and laboratories in UW.

Preceding to the signing ceremony, there was a visit of 7 members of delegation from WIN/UW Canada to NIMS to have a Workshop on Nanomaterials for Energy, Environment and Biotechnology from Feb. 15th - 16th. The workshop was held mainly by researchers at Innovative Center of Nanomaterials Science for Environment and Energy and Biomaterials Center of NIMS.

Prof. Sukekatsu Ushioda and Prof. Arthur Carty

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