from Tsukuba, Japan to the world

NIMS NOW International

National Institute for Materials Science

Vol.5 No.2 February, 2007

Special Features

Introduction of 20 New Projects and Recent Achievements
- Organic Nanomaterials Center (ONC) -

Research on Organic/Polymer Materials at NIMS

Izumi Ichinose
Managing Director
Organic Nanomaterials Center (ONC)

The Organic Nanomaterials Center (ONC) was launched in April 2006 as the first research center at NIMS devoted exclusively to organic and polymer materials. Even without mentioning examples such as liquid crystals, gels, rubber, and plastics, organic/polymer materials are important basic materials for Japanese industry. On the other hand, organic/polymer materials are treasure houses of new nanomaterials. In particular, a large number of new material properties which do not exist in conventional materials have been discovered in classes of materials such as shape-regulated polymers, dendrimers, supermolecules, coordination polymers, and so on.

The ONC belongs to the Nanoscale Materials Field at NIMS. Our research is focused on giant molecules with designated sizes, shapes, and functions. Thus, our primary objective is to synthesize new giant molecules and to search for unknown functions in those molecules from the viewpoint of nanoscale materials.

The actual objects of research in the ONC cover a wide range of materials, including porphyrin and fullerene derivatives, coordination polymers having designated sequences, DNA and artificially-designed proteins, and supermolecules and molecular assemblies. In addition, nanoscale fibers and inorganic clusters with unique shapes, living cells, etc. are also included in the ONC's scope of research.

At present, the following 5 groups have been established in the ONC:

(1) Functional Thin Films Group
(2) Functional Modules Group
(3) Supermolecules Group
(4) Nano Architecture Group
(5) Bio Nanomaterials Group

The Functional Thin Films Group conducts research on free-standing films with nanometer thickness, and has taken up the challenge of developing the nano-separation membranes which will support the green society of the future. The Functional Modules Group is engaged in a search for new compounds based on organic synthesis. The Supermolecules Group is involved in material synthesis, and also conducts research in connection with assembly of giant molecules at surfaces and interfaces.

< Continued on p.3

Research areas
Synthesis →
Assembly →

Purposes
Search for unknown functions of giant molecules
Construction of fit-for-purpose molecular systems

Targets
- Biopolymers, nanocomposites
- Supersensitive sensing of biomolecules
- Nano-separation membranes to support a green society

Fig. Concept of the ONC.

in this issue

NIMS News

NIMS Concludes MOU with 3 Institutes

- Further Strengthening of International Cooperation in the ICYS -

From left: Ms. Kobayashi, Leader, General Affairs Dept., ICYS, Prof. Bando, Director-General of the ICYS, Prof. Park, President of the IMS, and Prof. Chan, Vice President of the IMS.

< Continued on p.2

Ultrathin Mesoporous Polymer Films

- Realization of Size-Selective Permeation of Proteins -

Izumi Ichinose
Jian Jin
Xinsheng Peng (ICYS Fellow)
Functional Thin Films Group
Organic Nanomaterials Center (ONC)

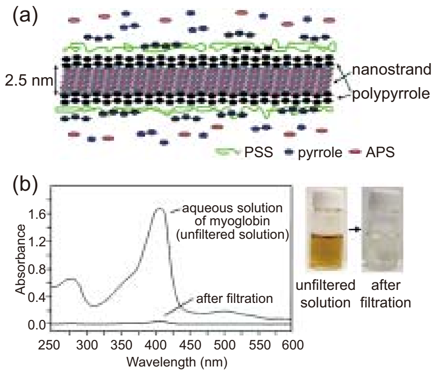


Fig. 1 (a) Coating of nanostrand with polypyrrole. PSS: sodium polystyrene sulfonate, APS: ammonium persulfate. (b) Separation of myoglobin using the above-mentioned free-standing film (40 nm). The left shows UV-vis absorption spectra of the aqueous solution before/after filtration.

The Functional Thin Films Group is engaged in research on nano-separation membranes, which will be indispensable for the realization of "green chemistry" in the future. Production of free-standing films which are mechanically stable at nanometer (nm) thickness is expected to lead to the development of high speed, low energy separation techniques. Therefore, the objectives of the Functional Thin Films Group are to propose new production processes for free-standing films of this type and to elucidate, in physiochemical terms, the permeation characteristics of molecules and ions through such membranes. Although various methods of fabricating nano-separation membranes exist, this article will introduce a method using nanostrands of copper hydroxide.

We discovered that extremely fine fibers of copper hydroxide form spontaneously when the pH of an aqueous solution of copper nitrate is adjusted by adding aminoethanol. Although the diameter of these fibers is only 2.5 nm, their length reaches several 10 µm. These remarkably long, thin fibers are termed inorganic nanostrands based on their resemblance to double-stranded DNA.

Recently, a technique for uniformly coating polymers on the surface of such inorganic nanostrands was developed. As one example, a nanostrand coated with a polypyrrole (PPy) is shown in **Fig. 1a**. If these fibers are produced in a dispersed state in water and are then filtered with a membrane filter, it is possible to obtain a free-standing film (**Fig. 2**) with a thickness of a few tens of nanometers. This free-standing film having a nano-fibrous shape and an appropriate degree of hydrophilicity is stable in the presence of both acids and alkalis, and is not destroyed by heating up to 300 °C. Moreover, due to its extreme thinness, it gives a remarkably high permeation rate with respect to water.

The fact that the free-standing film has a size-selective permeation characteristic (permselectivity) for water-soluble proteins was also confirmed. For example, in a comparison of cytochrome c, which has a diameter of approximately 2.9 nm, and myoglobin, with a diameter of approximately 3.3 nm, the permeability of the former is 2.5 times that of the latter. On the other hand, ferritin, which has a diameter of 12 nm, shows no permeation whatsoever. The aqueous solution before and after separation of myoglobin is shown in **Fig. 1b**. Development of outstanding separation techniques using this type of free-standing film is expected in the future.

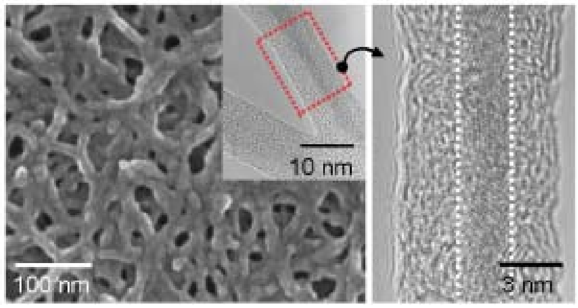


Fig. 2 SEM and high-resolution TEM images of free-standing films consisting of core/shell fibers.

For more details:http://www.nims.go.jp/onc/kinoumaku/index_e.html

NIMS News

< Continued from p.2

NIMS Concludes MOU with 3 Institutes

On December 4, the NIMS International Center for Young Scientists (ICYS) signed a memorandum of understanding (MOU) on "Application of Functional Materials and Device Application" with the Institute of Materials Science (IMS) of the Vietnamese Academy of Science and Technology (VAST) in the joint names of the NIMS Advanced Nano Materials Laboratory and Optronic Materials Center. The two sides pledged positive cooperation, including agreement to cooperate in holding a summer school, cooperation in connection with science and technology in Asia, etc. NIMS also concluded MOUs with the Research Institute for Technical Physics and Materials Sciences (RITPMS) of the Hungary Academy of Sciences on "Science and Technology in Structuring Advanced Materials" on October 27, and with Ireland's Trinity College Dublin on "Nanomaterials and their Environment and Energy Applications" on December 5.

Comprehensive Research Cooperation Agreement with the ENSMP, France

(November 24, Paris) -- NIMS signed an Comprehensive Research Cooperation Agreement with the École Nationale Supérieure des Mines de Paris (ENSMP). Prof. Benoit Legait (President of ENSMP), Prof. Michel Boussuge (ENSMP), and Dr. Yoshio Bando (Director-General of ICYS, NIMS) attended signing ceremony. ENSMP, which was established 1783, is one of the highest level university in science and engineering in France. This agreement will accelerate research collaboration by exchange of young researchers and students.

From right to left; Prof. Boussuge, Prof. Legait, and Dr. Bando.

Nano Measurement, Control, and Manipulation of Biomolecules
- Aiming at Use as Functional Devices -

Hideo Arakawa, Keita Mitsui
Bio Nanomaterials Group
Organic Nanomaterials Center (ONC)

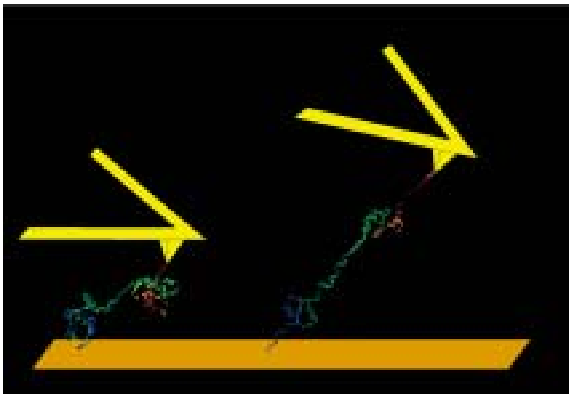


Fig. 1 Nanomechanical extension of a protein molecule. The molecule can be progressively unfolded by pulling apart its two ends.

Biomacromolecules including proteins and nucleic acids are functional at the single molecular level, because these molecules have high-order structures. These molecules are excellent functional "natural nanomachines." When the mechanisms of these molecules have been completely elucidated, we will be able to use these nanomachines properly and even improve them or artificially synthesize new ones, opening a new horizon in nanotechnology. The information about the chemical structures of biomacromolecules is within human grasp, because they are written in their genes, which are being totally decoded in recent genome project research. Exhaustive research is also being carried out with great energy worldwide on questions such as the 3-dimensional structure of the respective molecules and which molecules react with which other molecules in living organisms. Beyond this, however, it will be necessary to develop techniques for controlling and manipulating nanomachine molecules.

We are developing techniques for measuring, controlling, and manipulating biomolecules using nano probe technology. Nano probe technology is a technology which enables measurement of length with sub-nm accuracy and measurement of force with sub-nN accuracy by touching materials with a probe tip. Conversely, the same technique also makes it possible to manipulate materials with nano accuracy. Modification of the surface of a probe made of ordinary silicon enables bonding with biomolecules at designated locations, and we are seeking applications for probes of new nanomaterials such as carbon nanotubes. What is important is that the force should be well controlled at an extremely minute level when the material is manipulated. In the future, such techniques will undoubtedly be necessary in order to manipulate and control soft, complex materials such as biomolecules.

To date, this technique has made it possible to deform single molecules of protein (**Fig. 1**) and to perform mechanical measurements of the force acting between two protein molecules at the nm level and nN level. After the start of the Bio Nanomaterials Group, we developed a method of measuring and controlling force in the direction parallel to the substrate surface (**Fig. 2**). Unlike the conventional method, in which force is applied in the direction perpendicular to the substrate surface, this horizontal nanomechanical measurement method makes it possible to manipulate molecules near the substrate surface. Taking advantage of this feature, further development can be expected, making it possible to measure manipulated molecules by a separate method, followed by other manipulations. Thus, this new technique may become an essential basic technology for the measurement, control, and manipulation of biomolecules.

Fig. 2 Horizontal nanomechanical measurement method. The figure shows the observation of nanomechanical events when a molecule is elongated parallel to the substrate. The blue area is a macromolecule such as a protein. The mechanical properties of the molecule are measured while it is stretched along the substrate surface. The substrate is surface-modified silicon, glass, or the like.

By realizing this kind of nanomechanical technique, we hope to expand research on biomolecules from the chemical to the nano-physical level, and thereby create the foundation for the nano-engineering of the future.

For more details: http://www.nims.go.jp/onc/bio/index_e.html

Special Features

< Continued from p.1

Research on Organic/Polymer Materials at NIMS

On the other hand, the Nano Architecture Group is carrying out research on information processing devices using biomolecules such as DNA, and is studying new systems for molecular information exchange by a fusion of this research with micro-fabrication processes originally developed for semiconductors. The Bio Nanomaterials Group is engaged in research on the mechanical properties of proteins at the single molecule level utilizing advanced SPM* technology, and is continuing to elucidate the relationship between the structure and functions of biomolecules by a physical approach.

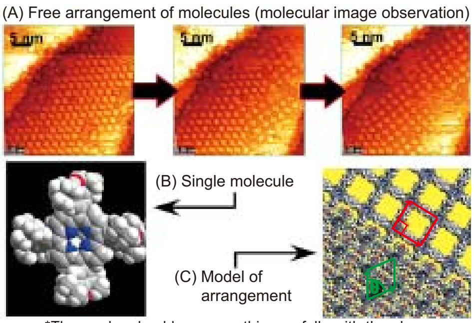
This Special Feature introduces some of the research activities of each group by selecting several recent topics of particular interest.

*SPM: Scanning probe microscope, used here as a characterization technique for micro-regions.

For more details: http://www.nims.go.jp/onc/index_e.html

Future Technologies Made Possible by Supermolecules

Katsuhiko Ariga
Jonathan P. Hill
Takashi Nakanishi
Supermolecules Group
Organic Nanomaterials Center (ONC)



*The reader should compare this carefully with the above molecular image, noting that the angle joining the center of the molecule has changed in the green part and red part.

Fig. 1 Technique for free arrangement of porufirin (dye).

Astonishing technical progress has been achieved in many products such as cell phones and portable computers, contributing to improved convenience in everyday life, resources saving, solution of problems related to overpopulation, and other positive changes. Although these advances were achieved by precisely cutting semiconductors and other parts, the limits of this approach can now be seen. This is because smaller sizes will exceed the capabilities of the cutting tools used in production. As a concept which overcomes this problem, we have adopted the approach of creating tiny functional structures by natural assembly of molecules. Substances which consist of assemblies of some number (or an uncountable number) of molecules and exhibit a structural form and functions that cannot exist in individual molecules are called supermolecules, as they exceed the possibilities of ordinary molecules.

In this article, we will introduce several examples of our research. The first example is a substance consisting of freely-arranged molecules of a functional dye called porufirin (**Fig. 1**). We believe that it will be possible to create electronic circuits, sensors, and other devices of molecular size using this material. The second example is a technique in which the high function molecule called the fullerene is formed freely into spheres, disks, fibers, cones, and other shapes of submicron size (**Fig. 2**). The key point here is that it is possible to obtain various structures from one molecules in a simple manner. In the example in **Fig. 3**, a new carbon material called a "carbon nanocage" was created using supermolecules as a mold. This substance has an extremely large specific surface area and specific porous volume, and shows substance adsorption activity which cannot be observed in conventional substances.

The examples introduced here were the result of joint research with Dr. Yutaka Wakayama of the NIMS Advanced Electronic Materials Center (porufirin dye nanomaterial) and Dr. Ajayan Vinu of the NIMS Fuel Cell Materials Center (carbon nanocage). Because supermolecule technology involves science and technology which extend beyond the bounds of the conventional disciplines, we conduct our research unfettered by these boundaries, as shown by these examples.

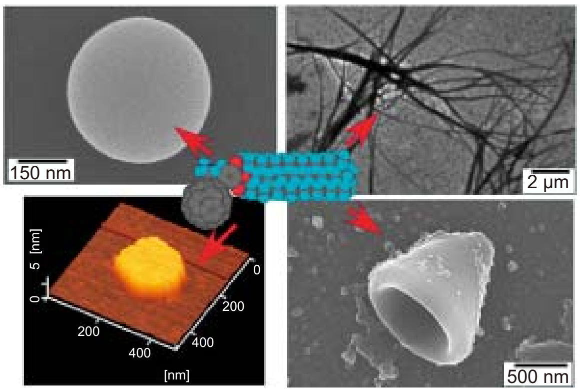
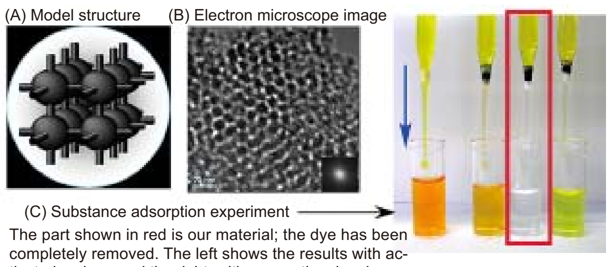


Fig. 2 Free forming technique for fullerenes.



The part shown in red is our material; the dye has been completely removed. The left shows the results with activated carbon, and the right, with conventional carbon.

Fig. 3 Fabrication of carbon nanocage and substance adsorption properties. As can be seen in the red box at the right, the yellow solution has been decolorized, showing an excellent adsorption property.

For more details: http://www.nims.go.jp/onc/super/index_e.html

Special Features Introduction of 20 New Projects and Recent Achievements - Organic Nanomaterials Center (ONC) -

Syntheses of Novel Electronic/Optical Functional Materials and Their Application

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Taichi Ikeda
Functional Modules Group
Organic Nanomaterials Center (ONC)

The Functional Modules Group is involved in the development of novel organic/metallic hybrid polymer materials using comparatively weak intermolecular interactions such as coordinate bonding and hydrogen bonding.

In living organisms, efficient electron transfer and energy conversion are achieved by precise control of metal ions and clusters of iron, copper, and zinc in organic polymers such as the proteins. As familiar examples, these processes can be seen in photosynthesis and respiratory reactions. Learning from these living systems, we are creating various new types of organic/metallic hybrid polymers with precisely controlled structures by designing/synthesizing organic modules using techniques of synthetic organic chemistry,

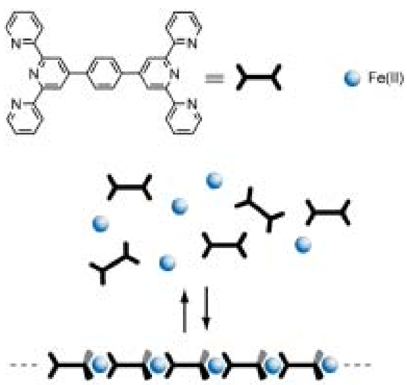

Fig. Organic/metallic hybrid polymer using bis(terpyridyl)benzene as the organic module.

and hybridizing these with metallic ions or clusters by self-assembly utilizing coordinate

Creation of Information Processing Function in Organic Nanomaterials

Kazushi Miki
Kenji Sakamoto
Hideonobu Nakao
Nano Architecture Group
Organic Nanomaterials Center (ONC)

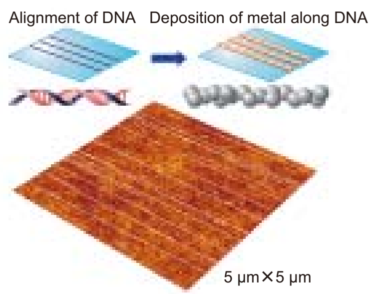

Fig. 1 AFM image of metallic nanoarrays fabricated on aligned DNA.

Fabrication techniques for structures of nanometer scale (1 billionth of a meter) are continuing to be established. However, many are limited to single, independent structures and have not reached a stage where combination of multiple nanostructures is possible. We are carrying out research and development with the aim of realizing information processing devices by functional hierarchicalization of nano functional modules. Because nanoscience is in fact an interdisciplinary field encompassing physics, chemistry, and biotechnology, it has evolved into a new materials technology through crossover between these disciplines, taking advantage of their respective strengths. The focus of our work is nano functional modules consisting of DNA and organic electronic materials.

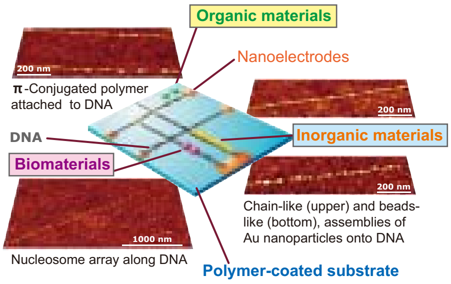

Fig. 2 Nano functional module and application to a new information processing system. The figure shows atomic force microscope (AFM) images of DNA modified with various nanomaterials. Ultimately, a new information processing system will be realized by combining various functional modules, as shown in the center.

Because DNA contains molecular array information at the nanoscale, it may be the ultimate assembly module for constructing nanoarchitectures. In DNA, it is possible to designate locations, or "addresses," where signals are processed in the same manner as in LSIs. If DNA can be arranged in advance on some type of substrate, designated organic materials can be fixed easily at designated locations using specific reactivity. Utilizing this specificity, it is possible to assemble different nano functional modules. To date, we have succeeded in arranging various species of metallic nanoparticles (**Fig. 1**) and organic/biological molecules along DNA. In the near term, we will also explore new materials for nano functional modules such as protein detection devices. Looking further into the future, we hope to realize new information processing functions by functional hierarchicalization of dissimilar nano functional modules (**Fig. 2**).

In research on organic electronic materials, we are focusing on the development of organic materials with high-order hierarchical structures, such as highly-ordered molecular arrangement. Our goal is to fabricate 2-dimensional orientation/array patterns of organic molecules with unique optical/electronic physical properties, with a special resolution of several nm to several µm. A 2-dimensional orientation pattern of polyfluorene (PFO) molecules are shown in **Fig. 3** as an example of high-order hierarchical structures. The orientation of PFO molecules can be controlled using a photo-alignment film developed by us. The photo-alignment film materials are a series of polyimides, which are containing azobenzene in the backbone structure. Their 2-dimensional orientation patterns can be formed easily by irradiation with polarization-controlled ultraviolet light. By depositing PFO molecules on the patterned photo-alignment film and subsequently performing a proper heat treatment, a highly-ordered PFO alignment pattern is induced with the same pattern as the photo-alignment film. With further advances in this photo-alignment technique, it will be possible to realize advanced functional materials for organic devices.

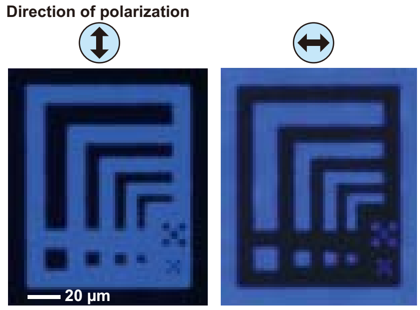

Fig. 3 Polarized fluorescence microscope image of highly-ordered 2-dimensional pattern of PFO molecules formed using a photo-alignment film. Only the PFO which is aligned in the direction of polarization can be seen as blue.

For more details: http://www.nims.go.jp/onc/nano/index_e.html

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bonding. The organic/metallic hybrid polymers are a class of next-generation nanomaterials which are expected to manifest electronic, optical, magnetic, catalytic, and other functions not found in conventional organic polymers and inorganic materials as a result of the nano-level interaction between the organic module and metal species.

For example, by coordination of metallic ions such as Fe to a bis(terpyridyl) benzene derivative as the organic module, we succeeded in synthesizing the straight chain-shaped hybrid polymer shown in the **figure** and analyzing its structure. Because this substance is a polymer, it is possible to fabricate a polymer film in the same way as with ordinary organic polymers. On the other hand, unlike organic polymers, the polymer forms by coordinate bonding, and therefore is easily decomposed and regenerated. This means that it is an extremely suitable polymer material for recycling.

When metal ions and organic modules exist adjacently, the resulting materials can be expected to manifest a variety of physical properties such as electron transfer and energy transfer, magnetic control, etc. The hybrid polymer shown in the **figure** takes on a strong blue coloration due to the absorption based on charge transfer from the metal to the organic module. If a voltage is then applied to this polymer film, the metallic ions are oxidized and the film becomes colorless and transparent (electrochromic property). Moreover, because it shows satisfactory reversibility and response characteristics, this polymer was found to be an excellent electronic/optical functional material. Work has now expanded to applied research in cooperation with a private company with the aim of producing materials which will be useful to society.

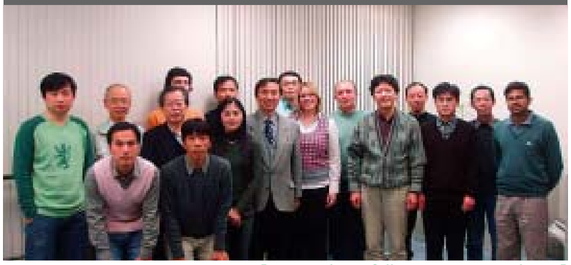
The Functional Modules Group is an international research group with Dr. Dirk Kurth as Group Leader. He also holds an appointment as a researcher in the Max Planck Institute of Colloids and Interfaces (Potsdam, Germany). While studying living systems, we are developing a wide range of research in connection with organic/metallic hybrid polymers, extending from basic science to applied research/practical applications.

For more details: http://www.nims.go.jp/fmg/index_e.html

Hello from NIMS

■ Exploring Japan ■

Annett Thøgersen (University of Oslo, Norway)
NIMS Internship Program (September, 2006 - December, 2006)
Nanotubes Group, Nanoscale Materials Center (NMC) & International Center for Young Scientists (ICYS)



[Me and my fellow group members]

Hi! My name is Annett Thøgersen and I am a PhD student at the Centre for Materials Science and Nanotechnology at the University of Oslo, in Norway. From the end of August to the end of December 2006, I interned at ICYS/NIMS, and my host researcher was Professor Bando. After working two years on my PhD in Oslo, I was ready to try out a new microscope in pursuit of new results and experience a new research facility. NIMS has several really good microscopes and many excellent scientists in my field of interest. A great research environment and the drive to explore a different culture and language made me apply for a research stay in Japan.

I used my time in NIMS working on my PhD thesis. My thesis is about characterizing silicon nanocrystals using the Transmission Electron Microscopy (TEM), Electron Energy Loss Spectroscopy (EELS), and X-ray Photoelectron Spectroscopy (XPS). My main task in Japan was to study the nucleation and diffusion mechanism of additional silicon after heat-treatment and to characterize the atomic structure of the nanocrystals.

[Enjoying ramen noodles]

Tsukuba turned out to be a very friendly city and it was easy to make new friends by going to courses, to our local pub, or during lunch at work. Working in NIMS gave me a lot of wonderful and challenging experiences, and what I learned there will be a big part of my thesis. The weekends I used to travel throughout Japan, experiencing the culture, learning the language, trying different kinds of food, and meeting new people. Japan is a beautiful country and I had a great time. I really enjoyed my time at NIMS, and the people there really made my stay pleasant and educational. I now have a lot of new friends and colleagues that I will stay in touch with. I can't wait to come back.

NIMS News

Reorganization of the Biomaterials Center

(December 1, 2006 & January 1, 2007, NIMS) - The NIMS Biomaterial Center was reorganized and expanded from its current 5 groups to 8 groups, as listed.

Five groups are engaging mainly in research in medical engineering fields, while three groups are conducting research in fields related to nano-bioscience and technology. This reorganization of the Center's groups is intended to make the best use of the specializations of researchers and clarify the proper future directions for research by appropriately organizing the various regions of research carried out in the Biomaterials Center to date.

[Medical Engineering Fields]	Group Leader
Bioceramics Group	Masanori Kikuchi
Biometal Group	Akiko Yamamoto
Biopolymer Group	Hisatoshi Kobayashi
Nano-drug Group	Yoshiyuki Uchida
Organoid Group	Guoping Chen
[Nano-bioscience and Technology Fields]	Group Leader
Cell Sensing Group	Akiyoshi Taniguchi
Bioelectronics Group	Yuji Miyahara
Biosystem and Biomolecule Control Group	Nobutaka Hanagata

For more details: http://www.nims.go.jp/bmc/index_e.html

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Mr. Kensaku Murakawa

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