

### Capturing a Molecule with a Supramolecule Trick

Special Features

- A Crane Game for the Nano World? -

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In nanotechnology, observing, capturing, and functionalizing single molecules are ultimate techniques. However, it is extremely difficult to capture a molecule with man-made devices. Perhaps only a molecule itself is capable of capturing another molecule. This means manipulating a molecule in some way so as to capture a target counterpart molecule. We captured molecules by the following method using an innovative supramolecular trick.

First, a molecule was developed as shown in **Fig. 1A**. This molecule is distinguished by four arms extending from a ring-like structure with a plate-like structure attached to it. Ingenuity was applied to the design of the plate so that the surface is hydrophilic, while the reverse side is hydrophobic. As a result, when this molecule is placed on a water surface, it spreads, extending its "legs" exactly as a Gerridae (pond skater) does (in the following, this is called a Gerridae molecule). A film was created by arranging a large number of these Gerridae molecules on water, forming a supramolecular structure called a monolayer. When the monolayer was compressed, the Gerridae molecules changed shape to minimize the occupied area, creating a closed space under the molecules (**Fig. 1B**). This resembles the action when the fingers of an open hand are bent and closed. < Continued on p.5

Interdisciplinary Research and Development  
Progress in "Supramolecular Materials Science"

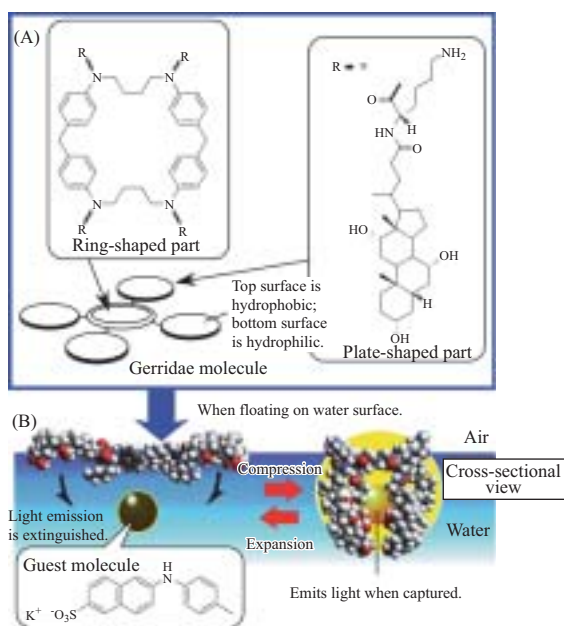


Fig. 1 Structure of Gerridae molecule (A) and function of capturing/releasing molecule (B).

### NIMS Announces New Research Results Database

NIMS News

(June 3, NIMS) -- NIMS has announced a new database which will enable users to search papers, patents, and information on NIMS researchers online. Data on papers and patents are already available and they will be followed by data on researchers which is expected to be available in November of this year.

All those interested in the research results achieved by NIMS and information on NIMS researchers are invited to use this resource.



<http://www3.nims.go.jp/general/>

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# Supramolecule Composed of Soccer-ball Molecules

## - Development of Novel Conductive Material Based on Supramolecules -

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Because nanotechnology is the technology of creating microscopic structures at the 1 nm ( $10^{-9}$  m) level, the methods of organic synthetic chemistry and supramolecular chemistry, which are techniques for assembling molecules, are necessary and indispensable in the bottom-up approach in this field. In order to treat functional molecules as electronic devices, it is necessary to immobilize the molecules on a solid substrate in a structure with the intended molecular arrangement. One substance which has attracted attention as an electronic molecule is the fullerene ( $C_{60}$ ), which is one of carbon nanoclusters.  $C_{60}$  is a soccer ball-shaped  $\pi$ -conjugated molecule with a diameter of 1 nm and is treated as a representative substance in nanochemistry. Because  $C_{60}$  has an electron storage capacity of 6 electrons per molecule, it has been the object of much applied research utilizing its excellent electron transfer characteristics. In the present research, we synthesized a new fullerene derivative with a self-organizing function by introducing a lipid component in the fullerene (Fig. 1a).

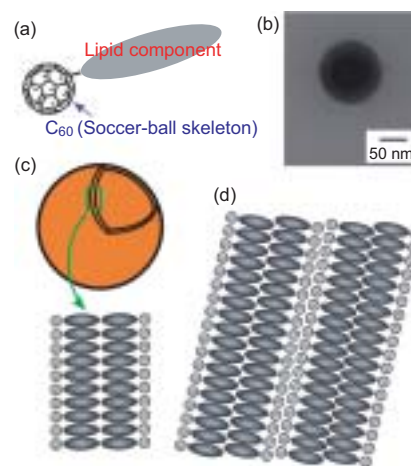


Fig. 1 Molecular structure of a fullerene derivative (a), TEM image of spherical supramolecular structure (b), estimated schematic model of the spherical supramolecular structure (c), and estimated schematic structure of molecular arrangement in AFM image on the substrate (d).

When this fullerene derivative is dispersed in a solution, formation of a spherical supramolecular structure with a diameter on the order of 100 nm could be confirmed by a transmission electron microscope (TEM; Fig. 1b) and a scanning electron microscope (SEM). As the existence of a cavity in the structure was also confirmed by SEM observation, this spherical supramolecular structure is presumed to be a closed spherical endoplasmic reticulum (ER) with a bimolecular film structure, in other words, a vesicular structure (for the estimated schematic model, see Fig. 1c). Because it is possible to enclose various functional substances in the vesicular space, we are now carrying out research targeting the creation of a novel 0-dimensional conductive nanocapsule using the fullerene as the base material.

When a fullerene derivative solution is coated on a substrate, a semispherical structure originating from the spherical supramolecular structure can be observed using an atomic force microscope (AFM). At the same time, a stripe pattern with a pitch of several nm extending up to several hundred nm in length can also be observed on the substrate surface. (AFM images are shown in Fig. 2; the estimated schematic structure is shown in Fig. 1d.) This stripe structure is presumed to have been formed by a self-assembly interaction between the molecules and between the molecules and the substrate surface. We are currently expanding our research focusing on a functional evaluation of fullerene self-assembled 1-dimensional conducting nanowires divided by insulating layers formed by the lipid component and the detailed molecular arrangement structure. In the future, based on various molecular information, we intend to carry out research aiming at the development of novel supramolecular materials which can actually be applied as materials. These research results were obtained through joint research with Dr. Dirk G. Kurth of the Max Planck Institute of Colloids and Interfaces, who is concurrently Director of the Functional Modules Group, AML, NIMS.

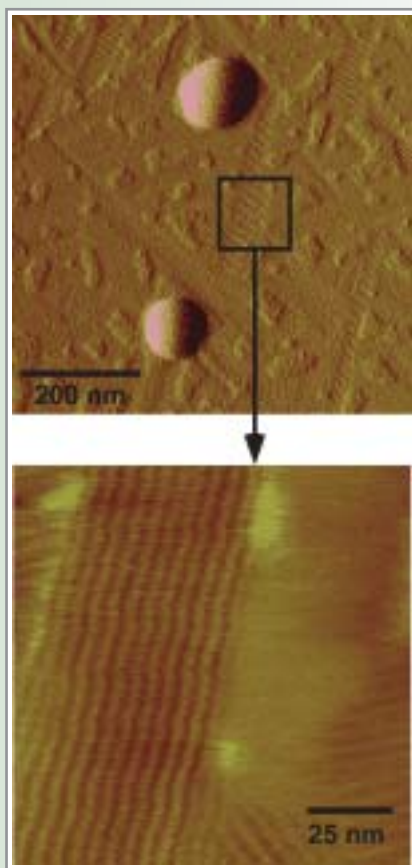


Fig. 2 AFM images of a fullerene derivative coated on a substrate.

For more details: <http://www.nims.go.jp/super/HomePageEng/Top-Eng/>

## Results of FY 2005

## Science & Technology Week Events



Special Program

(April 21-22 & 24, NIMS) -- April 21-22, NIMS held an Open House and this year, almost all NIMS research units opened their laboratories to the public, receiving 430 visitors, which far exceeded last year's total. On April 24, a Special Program was held at the Sengen and Namiki Sites. Blessed with good weather, 503 visitors participated. The Special Program allowed visitors to carry out actual experiments, and the venues were filled to overflowing virtually the entire time. Because this provided a good opportunity for the public to learn about NIMS and its work, NIMS plans to put every possible effort into future events.



# Learning Nature and Making Materials

## - Relationship of Synthetic Polymer Complexes and Proteins -

Masayoshi Higuchi  
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Plastic, rubber and similar organic polymers are among the most useful materials in everyday life, but due to the waste problem and other environmental considerations, they have come to be regarded as something of a "necessary evil" in recent years. On the other hand, proteins and DNA are also organic polymers, but nobody says "no more proteins." Perhaps unique properties of organic polymers are subject to these two extreme views. In other words, the organic polymers are a group of substances with an extremely diverse range of properties in terms of composition, physical properties, and functions.

In photosynthesis and respiratory reactions in living organisms, the trace amounts of metals contained in proteins, which are organic polymers, play a decisive role which is central to reactive activity. When metals are arranged precisely in the 3-dimensional space created by an organic polymer, high efficiency electron transfer and energy conversion can be achieved. If a system similar to a living organism can be created artificially, can functions similar to or even surpassing those of life be obtained? Many polymer complexes (composites of organic polymers and metal ions such as

iron and copper) have been synthesized in an attempt to answer this question.

We have developed a variety of polymer complexes which combine an organic unit and a metallic unit at the nano size with the aim of creating organic-metallic hybrid nanomaterials with functions not found in conventional materials, including new electronic, optical, magnetic, and catalytic properties. For example, in dendritic polymers having a structure in which a polymer chain repeatedly branches and spreads outward like the branches of a tree, we discovered a phenomenon of multi-step sequential assembly of metal ions which

follows the electron density gradient formed internally in the polymer (**Fig. 1**). As another example, a polymer complex in which metal ions are introduced precisely in the main chain of the polymer can be formed by self-assembly of an organic unit and metallic unit (**Fig. 2**). A synergistic action of the different physical properties of the organic unit and the metallic unit can be expected by introducing metal ions in a polymer while precisely controlling their position and number, with the potential for application to diverse functional materials such as organic EL elements, sensors, solar cells, drug delivery, and others.

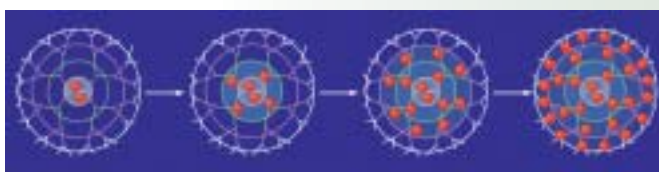


Fig. 1 Multi-step sequential assembly behavior of metal ions in dendritic polymer.

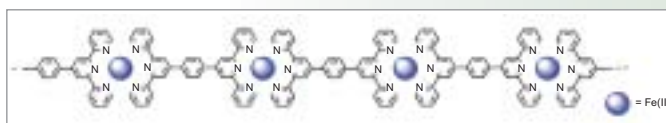


Fig. 2 Formation of polymer complex by self-assembly of organic material and metal.

For more details: <http://www.nims.go.jp/fmg/index>

With President Kishi of NIMS



## Visit by Two Nobel Laureates and Former Minister Koji Omi

(April 22, NIMS) -- NIMS was honored with a visit by two Nobel Prize winners in Physics, Prof. J. I. Friedman of Massachusetts Institute of Technology and Prof. Steven Chu, Director of the Lawrence Berkeley National Laboratory, and Mr. Koji Omi, former Minister of State for Science and Technology Policy and now a member of Japan's House of Representatives. The distinguished guests observed the sites of research and development on laser light frequency conversion materials, atomic electronics, and electro-nanocharacterization.



Prof. Friedman (center), Prof. Chu (second from right) and Mr. Omi (second from left) receiving an explanation from Associate Director Hasegawa (left).

# Inorganic Supramolecular Polymer

- Thin, Long Oxide Nanofiber  
Comparable to DNA -

Izumi Ichinose  
Macromolecular Function Oxides Group  
Advanced Materials Laboratory (AML)

The term supermolecule usually brings to mind organic molecules, macromolecules, and biomolecules such as proteins. These supermolecules are in fact systems which are held together and organized by secondary interactions between molecules, resulting in functions not observed in single molecules. Recently, the concept of supermolecules has expanded to include metal complexes and inorganic clusters. As one group of substances of this type, we are engaged in research on oxide nanofibers.

Raising the pH of an aqueous solution of metal ions generally causes precipitation of the hydroxide, but with salts of copper and cadmium, we discovered that nanofibers precisely like polymers form under certain concentration and pH conditions. Fig. 1 shows an electron microscope image of nanofibers formed in an aqueous solution of cadmium nitrate. The width of the nanofiber is only 1.9 nm. On the other hand, its length extends several microns, which is comparable to the size of colon bacillus plasmid DNA (roughly 6000 bp; bp is the number of base pairings, 1 bp corresponding to approximately 0.34 nm).

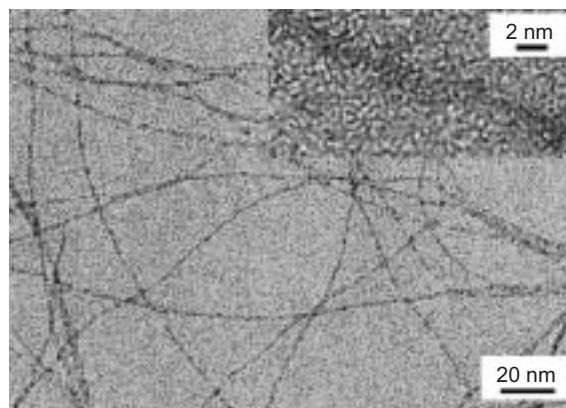


Fig. 1 Electron microscope image of cadmium hydroxide nanofibers (high resolution image is shown at upper right).

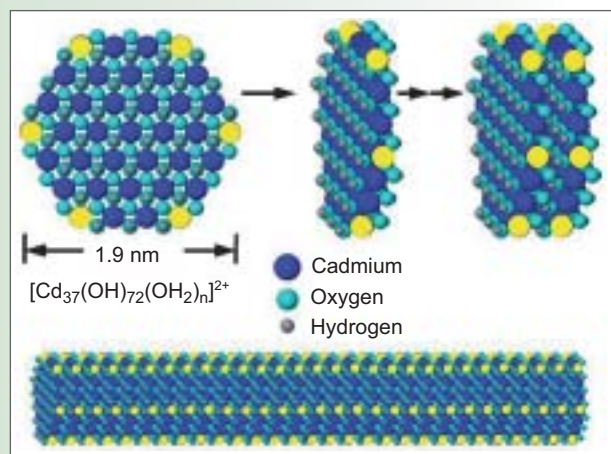


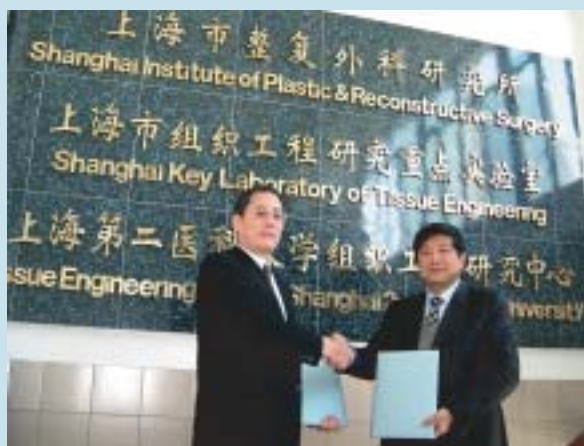
Fig. 2 Proposed structure of nanofiber (yellow shows positively charged cadmium atoms).

We are now in the process of clarifying the internal structure of these oxide nanofibers using a high-resolution electron microscope. The nanofiber obtained from cadmium nitrate is estimated to be a structure consisting of an unlimited number of hexagonal cadmium hydroxide clusters stacked by hydrogen bonding (Fig 2). In a dye molecule adsorption experiment, we found that the surface of the nanofiber has a remarkable positive electrical charge. The charge density is roughly one-third of the surface cadmium atoms, which corresponds to the number of apexes of the hexagonal-shaped cluster. We recently discovered that this type of nanofiber is extremely useful for efficiently extracting short DNA fragments.

Oxide nanofibers are considered an important structural element for constructing 1-dimensional supramolecular materials. We have therefore taken up the challenge of creating new supramolecular materials by designing precise nanocomposites with organic molecules and polymers.

For more details: <http://www.nims.go.jp/mfo/>

## MOU with China's Shanghai Tissue Engineering Center



Prof. Cao (right) shaking hands with Dr. Tanaka, Director-General of BMC.

(March 31, Shanghai) -- The Biomaterials Center (BMC) signed a memorandum of understanding (MOU) with the Shanghai Tissue Engineering Center (STEC) of China. STEC is China's largest tissue engineering organization. The Center carries out national projects in tissue engineering/regenerative medicine and has already achieved clinical application of research results on tissue regeneration, including cartilage and bone. The Center's Director, Prof. Yilin Cao, is among the pioneers in tissue engineering, having succeeded in regenerating a human ear in the back of a mouse. He is now a top researcher of the field of regenerative medicine/tissue engineering in China, and also serves as Vice President of Shanghai 9th People's Hospital, Shanghai Second Medical University. In the future, the two centers will actively promote exchanges of researchers and information, and plan to conduct joint research on biomaterials and tissue engineering.

For more details: [http://www.nims.go.jp/bmc/index\\_e.html](http://www.nims.go.jp/bmc/index_e.html)



# Weak Forces for Strong Materials

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Functional Modules Group  
Advanced Materials Laboratory (AML)

Molecular Materials Group, Department of Interfaces  
Max Planck Institute of Colloids and Interfaces (MPI-KG), Germany

Nature makes extensive use of self-assembly, that is the spontaneous organization of ions, molecules, and polymers to larger well-defined architectures. Self-assembly occurs at all length scales, ranging from the molecular level as in DNA to the macroscopic length scale as in bone or wood. As a result, natural materials have structures at different length scales. The intrinsic structural hierarchy is often responsible for some of the unusual properties such as strength and toughness. Due to the weak and competitive interactions that hold the components in place, biological systems are responsive to external stimuli that is, they can adapt their structure and function.

The implementation of adaptive, stimuli-sensitive and multi-functional properties as well as self-repair in artificial materials is one of the central challenges for research in supramolecular chemistry and materials science. Applying principles of self-organization to device fabrication provides opportunities which go far beyond existing manufacturing technologies such as parallel fabrication (in contrast to conventional sequential fabrication), dimensional control (at the molecular level), component arrangement of alignments, and repair mechanisms. Current artificial materials only provide a single function, rapidly wear out and tear, and ultimately must be disposed.

Advanced materials will contribute to an improved quality of life through multi-functionality, adaptability, longevity, and environment-friendliness. It is safe to predict that these technologies will have a profound impact on the scientific and technological progress, and economic growth far into the 21st century. However, progress in this area will rely on innovative and interdisciplinary approaches. The visionary claims of the supramolecular paradigm may, therefore, provide the incentive for interdisciplinary research and teaching programs which go beyond classical approaches in chemistry, engineering, and physics.

We recently launched the Functional Modules Group in the AML as an international and interdisciplinary program with the aim of contributing to a better understanding of self-assembly for development of new advanced materials. This new group develops and studies self-assembly strategies in order to combine, place, and order structural and functional modules in predictable ways in well-defined architectures, including nanostructures, monolayers, thin films, mesophases and crystalline solids. The components, interactions and structures are designed such as to introduce dynamic properties, such as stimuli-responsiveness, multi-functionality, as well as to exploit the full potential of a given material such as collective properties or gradients. In addition, value-adding proper-

ties shall be encoded in the final materials for technological applications.

Through the incorporation of transition metal ions in the assemblies, the resulting supramolecular modules possess the magnetic, electronic, optical and reactive properties which are relevant for the construction of technologically important devices and materials. The modularity of this approach provides extensive control of the structure and function over a wide range, from the molecular level to macro-length scale. In addition, the use of modules provides an unsurpassed degree of synthetic simplicity, diversity, and flexibility.

As one example, here, we will describe the results of fabrication of an adaptive thin film coating which changes from transparent to blue through application of a potential. The active component, called a polyoxometallate cluster is readily made by water based self-assembly of salts. The cluster is transparent when in the oxide condition, but under reduction, becomes dark blue due to the change in electron state. The coating layer is manufactured by self-assembly using the polyoxometallate and a commercially-available polyelectrolyte. Electrostatic interactions provide adhesion of the components onto the conducting substrate. As shown in the **accompanying figure**, reversible color change in response to potential changes is possible. Such ultra-thin adaptive coatings could find applications for climate control in buildings or automobile sunroofs. Thus, as described above, skillful use of the weak force is expected to lead to the development of high-utility multi-functional materials.

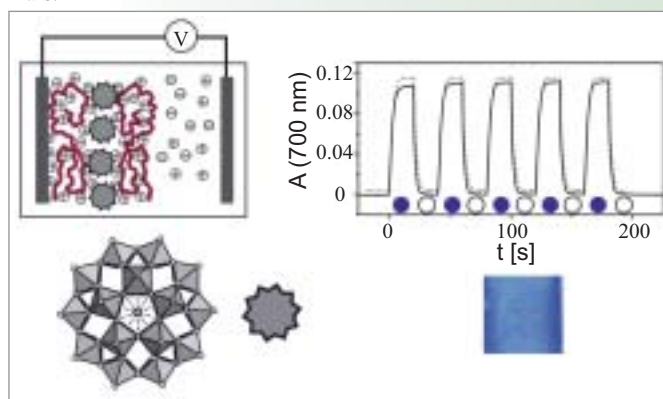


Fig. Top: Schematic diagram of the coating layer (left) and the light absorbance of coating (right). Bottom: Cluster structure of active component, consisting of a europium core in the center surrounded by tungsten oxide (left) and representative photo showing the blue color of the window (right).

For more details: <http://www.nims.go.jp/fmg/index>

< Continued from p.1

## Capturing a Molecule with a Supermolecule Trick

In an experiment, a light-emitting molecule was dissolved in water as the molecule to be captured (called the guest molecule). When light emissions from the water surface were observed while compressing the Gerridae molecule film, it was found that the light became more intense when the film was compressed and weaker when the film was allowed to expand. This shows that the light-emitting molecule is being captured and released by the Gerridae molecule, corresponding to compression and expansion of the film (**Fig. 1B**).

Recognition of a designated molecule by a given molecule is extremely important in supramolecular science and is applied in sensors and other devices. Until now, however, molecular recognition was a passive function, in that it was necessary to wait until the target molecule was entrapped in a prepared structure with a certain probability. In contrast to this, the Gerridae molecule which we developed demonstrates a "function reflecting intentionality" in dynamically capturing and releasing molecules. With additional innovation in the molecule design, it may be possible to create a molecule which, like a "crane game machine," can capture only the target molecule from among numerous mixed substances whenever desired.

For more details: <http://www.nims.go.jp/super/HomePageEng/Top-Eng/>

## Hello from NIMS

My name is Slavomír Nemšák and I'm a Ph.D. student at Charles University in Prague. I joined a NIMS research team in July last year as a member of the Nanomaterials Assembly Group at the Sakura Site. I really enjoy myself being a part of an international team here at NIMS, and I am very thankful for the support from all of my colleagues and my supervisor Dr. Yoshitake-san. The object of our study is formation of ultra-thin well-ordered alumina layers on monocrystalline alloy substrates. Using methods of electron diffraction, microscopy and spectroscopy, we are trying to understand the creation process and dependencies as completely as possible.



[ Samurai! (Me in Samurai armor) ]

Living in Japan might not be easy for Europeans, especially for a relatively young man on his first long-term visit. But after some time, staying in Japan becomes surprisingly pleasant and interesting. Japan is a wonderful country and can be very rewarding when explored through the objective of a still camera. Nature and architectural spots motivated me to return to my old hobby—photographing. Photography is closely connected to another craze of most foreigners in Japan—traveling. So far, I have visited scenic spots like Amanohashidate and Matsushima and the historic places of Kyoto and Nikko, I've seen a bit of nature in Nagano, and I've perspired tons of sweat during climbing Mt. Fuji. I really enjoyed the day I spent at the EXPO Exhibition in Aichi. However, there are so many places left to see, and I'm already looking forward to coming back to Japan someday.

Slavomír Nemšák (Charles University, Czech Republic)  
International Joint Graduate School Program (July 2004-July 2005)  
Nanomaterials Assembly Group, Nanomaterials Laboratory (NML)



[ At Himeji Castle on a study tour, left ]

## ■ Hello from Xiaoli ■

This is a rather new experience for me to say hello to you here, because we may have met at NIMS before. I am Xiaoli Yuan from China. I received my Ph.D. from Nanjing University, China, in 2001. I am now a Research Fellow in the Optoelectronic Nanomaterials Group, working with Dr. Sekiguchi. I came to Tsukuba in the autumn of 2002. I enjoyed the cool atmosphere when I first arrived at Narita Airport. My colleagues were very kind in helping me to settle down in this small, quiet city.



[ China class in NIMS beer party, second from right in first row ]

In the laboratory, I mainly observe secondary electrons and cathodoluminescence from materials generated by electron beams. My colleagues have given me various very good advice. I would like to thank the libraries for the numerous nice books.

I have a lot of good memories from these two years: the annual beer party in the Sengen Site, the trip to Mt. Zao for skiing, the lunch party with colleagues under the sakura trees, the *imonikai* (potato stew party) in a park, and of course, visiting the Lu Xun Monument, which commemorates the great Chinese writer's study in Sendai exactly 100 years ago . . .

Xiaoli Yuan (China)  
Research Fellow (Oct. 2002 - Mar. 2006)  
Optoelectronic Nanomaterials Group  
Nanomaterials Laboratory (NML)



[ With colleagues, second from right, front ]



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