from Tsukuba, Japan to the world

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Special Features

New Nanotube Research Gives Hints of Boundless Possibilities

Ferromagnetic Nanowire in Carbon Nanotube

—Application to Magnetic Disks—

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Fabrication of regular arrangements of nanostructured materials which display ferromagnetism is expected to lead to application to high density magnetic disks and other devices. In particular, because bulk FeCo alloys are important magnetic materials, if nanowires of them can be fabricated, dramatic improvement in memory density is expected to be possible in quantized magnetic disks, taking advantage of the small size and magnetic anisotropy of the nanowires. In the present research, we succeeded in creating a single-crystal nanowire having an FeCo composition in a carbon nanotube, and elucidated its structure and magnetic properties.

First, equal parts of organic substances containing iron $Fe(C_5H_5)_2$ and cobalt $Co(C_5H_5)_2$ were mixed in equal proportions in a toluene solvent, and the solution was atomized and subjected to heating/pyrolysis in an argon gas atmosphere at 600-800 ℃. When this was done, multi-layered carbon nanotubes with diameters of 10-20 nm formed, and nanowires which showed a black contrast formed inside the tubes (**figure**). Lattice image observation and composition analysis revealed that the nanowires (diameter, approx. 5 nm, length, approx. 50 nm) which formed in the tubes are an alloy with an Fe-Co composition and furthermore, their structure is a single crystal having a body-centered cubic (bcc) atomic arrangement. It was particularly interesting that the interface between the metal nanowire and carbon nanotube has a conforming arrangement, and a step at the single-atom layer level can clearly seen (enlarged photo at right of **figure**). These facts suggest that the tube wall of the carbon nanotube grew preferentially from the step on the metal surface and are important as experimental evidence showing why transition metals such as Fe and Co, etc. function effectively as catalysts for carbon nanotubes. Recently, a growth theory proposing that steps on the surface of transition metal particles accelerate the growth of carbon nanotubes by acting as activation points has been reported. The present result is expected to attract attention as an empirical finding supporting this theory.

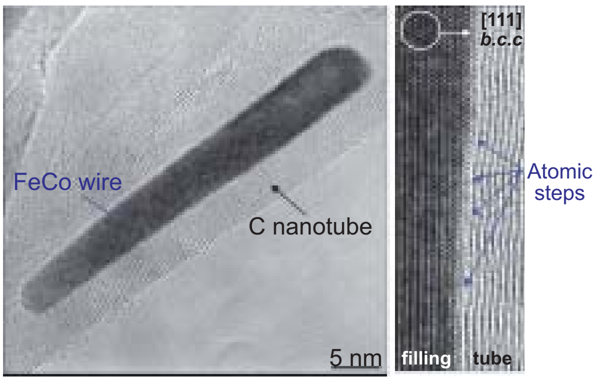

Fig. FeCo ferromagnetic single-crystal nanowire enclosed in carbon nanotube. The enlargement at the right shows a step at the single-atom level on the alloy single crystal. The graphite layer of the carbon nanotube has grown from this step.

< Continued on p.4

in this issue

NIMS News

Prof. Matolin of Charles University, Czech Republic, receiving Overseas Fellow certificate from President Kishi.

< Continued on p.5

Creation of Semiconducting Nanotube

—Si Nanotubes and Microtubes—

Junqing Hu, Yoshio Bando
International Center for Young Scientists (ICYS)

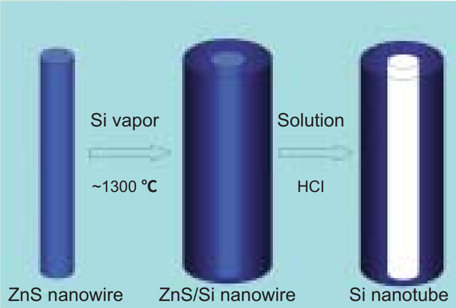

Fig. 1 Si nanotube synthesis method.

It is well known that the properties of carbon nanotubes change, displaying the characteristics of both metals and semiconductors. At present, however, no new synthesis methods capable of controlling this feature has yet been developed, and selective synthesis of carbon nanotubes having only semiconducting characteristics is difficult. If semiconductor nanotubes other than carbon nanotubes can be synthesized and applied as ultrafine wires, a great advance in the miniaturization of electronic circuits can be expected, and high density integration of semiconductors and high speed, low power consumption devices will become possible.

We are involved in the creation of nanotubes of semiconducting materials and recently succeeded in fabricating nanotubes from silicon (Si), gallium nitride (GaN), silicon carbide (SiC), aluminum nitride (AlN), and other materials.

Fig. 1 shows the synthesis method used with Si nanotubes. First, fine needles (nanowires; diameter, approx. 50 nm, length, several µm) of single-crystal zinc sulfide (ZnS) are formed. An Si film is coated on the surface of the ZnS, forming a 2-layer core-shell type nanowire consisting of ZnS and Si. As a feature of this process, because the crystal structure of Si closely resembles that of ZnS, the Si thin sheath nanowire also easily forms a single crystal. An Si nanotube (diameter, approx. 100 nm) can then be formed by dissolving the ZnS with hydrochloric acid (**Fig. 2** and **Fig. 3**). Electron diffraction and observation of lattice images confirmed that the Si nanotube is a single crystal, which is a world's first research achievement. The structure of the Si nanotube is an sp^3 atomic arrangement, which is the same as that of the bulk.

Fig. 4 shows an SEM image of an Si microtube which formed when SiO powder was subjected to pyrolysis at a high temperature of 1650 ℃. The tube diameter is approximately 1-5 µm, and its length is several µm. Unlike the nanotubes described above, the microtube wall consists of amorphous Si. Development of new synthesis methods for Si nanotubes and microtubes is indispensable, as both have poor yield with the current techniques, at no more than approximately 10 %. Theoretically, the existence of Si nanotubes with an sp^2 atomic arrangement is also predicted, and creation of this type can be considered an important challenge for the future. While application of Si nanotubes and microtubes to the field of electronics as ultrafine wiring can be expected, taking advantage of their semiconductor properties, a wide range of other applications to catalysts, filters, biosensors, and other devices is also foreseen, utilizing their unique pore structure.

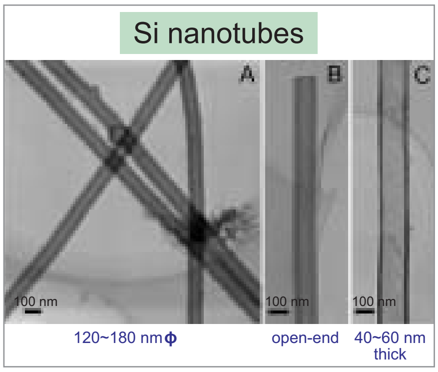

Fig. 2 Transmission electron microscope image of single-crystal Si nanotube.

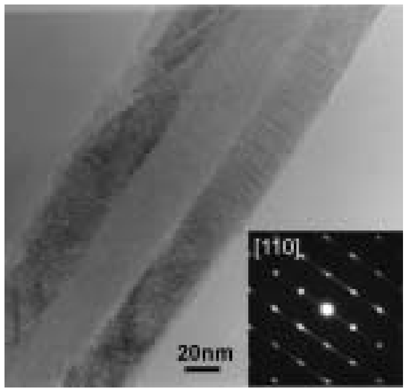

Fig. 3 High resolution electron microscope image and the electron diffraction pattern of Si nanotube.

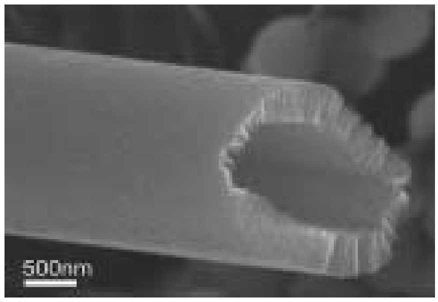

Fig. 4 Si microtube.

Development of Nanothermometer for High Temperature Measurement

—New Applications for Oxide Nanotubes—

Yubao Li, Yoshio Bando
Advanced Beam Analysis Group
Advanced Materials Laboratory (AML)

Liquid gallium enclosed in a carbon nanotube expands and contracts in response to the external air temperature, making it possible to measure the temperature by measuring the length of the liquid column using an electron microscope. Nanotubes which contain a liquid metal are called nanothermometers, and can be used in temperature measurements of local spaces of submicron order. However, carbon nanotubes easily oxidize in air at high temperatures exceeding approximately 500 ℃, and the structure of the tube wall is destroyed. For this reason, there are limitations on the application of nanothermometers using carbon nanotubes in high temperature measurement in the air. On the other hand, oxides are stable in the air even at high temperatures. Therefore, if oxide nanotubes can be fabricated and a liquid metal can be injected into the tube, use as an oxide nanothermometer is expected to be possible in the same manner as with carbon nanothermometers. Recently, we successfully synthesized various kinds of oxide nanotubes, including MgO, In_2O_3, SiO_2, and others, and developed nanothermometers using oxide nanotubes containing liquid gallium and liquid indium.

Fig. 1 shows an electron microscope image of a single-crystal MgO nanotube. A MgO nanotube with a diameter of approximately 30-100 nm and average length of several µm were synthesized, as shown in **Fig. 1**, by reacting metallic Mg powder and gallium oxide (Ga_2O_3)

Development of Nanothermometer for Low Temperature Measurement

—New Applications for Carbon Nanotubes—

Zongwen Liu, Yoshio Bando
Advanced Beam Analysis Group
Advanced Materials Laboratory (AML)

In previous work, we discovered that a carbon nanotube containing liquid gallium could be used as a thermometer and christened this the "nano thermometer." The nanothermometer is based on the principle that the length of a column of liquid gallium enclosed in a nanotube changes due to volumetric expansion and contraction caused by temperature changes; thus, the temperature can be measured from the length of this liquid column. We have already reported that temperature measurements are possible from room temperature to high temperatures of approximately 500 ℃. The nano thermometer has been listed as the world's smallest thermometer in the *Guinness Book of World Records* (2004). In the present work, we discovered the phenomenon of volumetric expansion/contraction of liquid gallium in a nanotube at low temperatures well below room temperature.

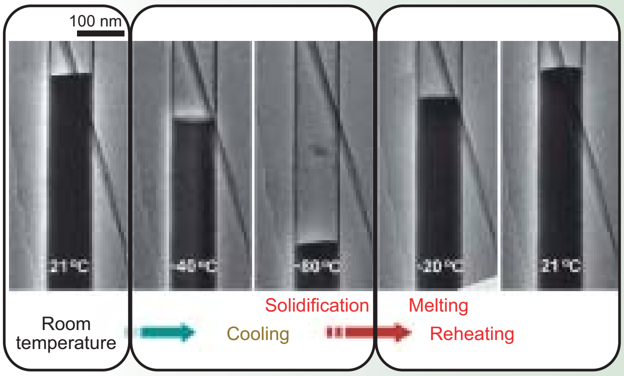

Fig. 1 Behavior of nanothermometer at low temperature. The length of the liquid gallium column enclosed in the carbon nanotube decreases with temperature. The gallium solidifies at -80 ℃ and when heated, melts at -20 ℃.

Fig. 1 presents electron microscope images showing the process of change in the height of the liquid column with temperature decreases, when a liquid gallium column enclosed in a multi-layered carbon nanotube (approx. 100 nm diameter) is cooled from room temperature to -40 ℃ and -80 ℃. It is interesting to note that the liquid gallium remains even below room temperature, and only solidifies at a temperature of -80 ℃. When reheated, the gallium becomes liquid at -20 ℃. **Fig. 2** shows the results of a quantitative investigation of these changes in the liquid gallium column accompanying temperature changes by observation with an electron microscope. A large hysterics loop occurs during the cooling-heating cycle of the nanothermometer, caused by supercooling. We attribute this phenomenon to the fact that the liquid gallium is enclosed in a carbon nanotube.

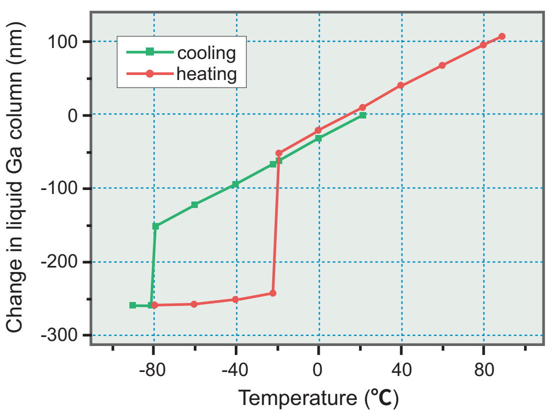

Fig. 2 Changes in liquid gallium column due to temperature changes.

The present experiments revealed that the nano thermometer can be used not only in high temperature measurements up to 500 ℃, but also in temperature measurements at low temperatures down to nearly -80 ℃. For practical applications, some method of recording the maximum and/or minimum temperatures is extremely important. Recently, it was found that the maximum temperature can be recorded by controlled oxidation of the surface at the tip of the gallium column. Nanothermometers will be indispensable in fields of research related to nanotechnology, providing local temperature measurements at submicron length scales. The successful development of a nanothermometer capable of measuring low temperatures significantly expands the temperature measurement range of nano thermometers from the high temperature region to the low temperature region, and is expected to dramatically enlarge the future range of applications of nanothermometers.

For more details: http://www.nims.go.jp/abg/eng/

powder at 1300 ℃ for approximately 1 hr in a vacuum and liquid gallium was injected into the tube. From the electron diffraction and observation of lattice images, it was confirmed that the formed MgO nanotube is a single crystal (tube growth direction is [100]). The successful synthesis of a single-crystal MgO nanotube in this work is a world's first. As features, the cross-sectional profile of the MgO nanotube forms a cyclo-shaped quadrilateral, and the shape of the cavity inside the tube is also a quadrilateral which follows the external shape of the tube. This differs greatly from the shape of carbon nanotubes, which have an cylindrical external shape. This work revealed that the liquid gallium enclosed in the tube undergoes volumetric expansion and contraction due to temperature changes, in the same manner as in carbon nanotubes.

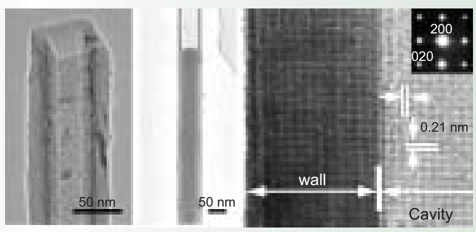

Fig. 1 Shape of single-crystal MgO nanotube containing liquid gallium and its lattice image.

Fig. 2 shows the temperature change in an SiO_2 glass nanotube which contains liquid indium in the tube. The SiO_2 nanotube has a large reservoir part (nanoball) which the liquid indium fills, as can be seen in the photograph. As features, the formed SiO_2 glass nanotubes have diameters from 30-120 nm, their length is an extremely long filament of approximately 1 mm, and this grows regularly in one direction. This successful development of nanothermometers using an oxide nanotube is expected to further expand the applications of nanothermomemeters.

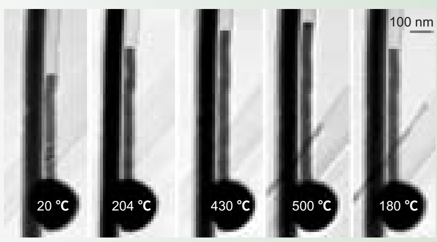

Fig. 2 Nanothermometer using SiO_2 glass nanotube (substance in tube is liquid indium).

For more details: http://www.nims.go.jp/abg/eng/

Room Temperature Liquid Phase Synthesis of Fullerene Nanotubes

—Creating Nanotubes with Fullerene Molecules—

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Ecomaterials Center (EMC)

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Nippon Sheet Glass Co., Ltd.

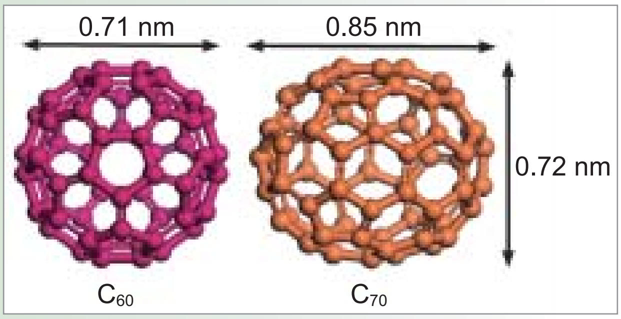

Fig. 1 Models of C_{60} and C_{70} molecules.

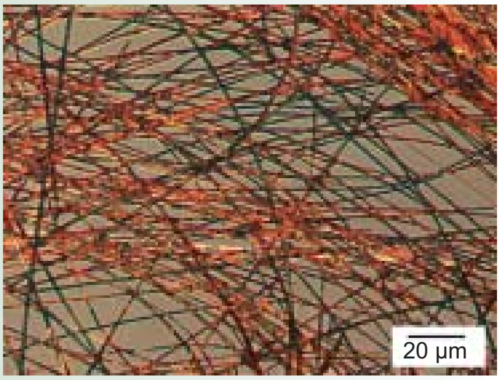

Fig. 2 C_{70} nanotubes created by room temperature liquid phase synthesis (optical micrograph).

Fig. 3 Optical micrograph of C_{70} nanotubes.

Fullerene nanotubes (FNT) are a class of hollow crystalline fibers made up of fullerene molecules (basket-shaped molecules consisting of carbon atoms) such as C_{60} and C_{70} (**Fig. 1**). FNT were discovered by the authors in 2004 while synthesizing fullerene nanowhiskers (FNW; fine whisker-shaped crystals consisting of fullerene molecules).

The first example of FNT was a C_{60} nanotube, which was discovered while synthesizing C_{60} nanowhiskers. The C_{60} nanotube is a hollow needle-shaped crystal with a diameter of several hundred nanometers and length of several microns, and was synthesized by the liquid-liquid interface precipitation method using isopropyl alcohol (IPA) and a C_{60}-saturated toluene solution containing a platinum derivative of C_{60}. A C_{70} nanotube, which is the second example, was formed using a C_{70}-saturated pyridine solution and IPA system. As shown in **Fig. 2** and **Fig. 3**, the C_{70} nanotube has an outer diameter of several hundred nanometers and displays a reddish-brown metallic luster. It grows to a length of several millimeters or more. Moreover, as shown in the transmission electron microscope image in **Fig. 4**, a distinct hollow structure can be observed. It was found that C_{70} nanotubes dried at room temperature have a face-centered cubic (fcc) structure and a structure in which C_{70} molecules are densely aligned in the axial direction of the tube growth. Similarly, we also succeeded in synthesizing a C_{60}-C_{70} binary system FNT using inexpensive fullerene soot. An important feature of FNT is that the properties of the individual fullerene molecules are reflected in the properties of the tube as a whole.

Continuing basic research will open the way to an infinite range of applications, including the environment, energy, electronics, pharmaceuticals, and MEMS, among others. This research achievement is expected to provide the starting point for synthesis of diverse types of FNT which take advantage of the features of respective fullerene molecules.

Fig. 4 Transmission electron microscope image of C_{70} nanotubes.

Special Features

< Continued from p.1

Ferromagnetic Nanowire in Carbon Nanotube

When magnetic measurements of the synthesized FeCo nanosubstance were performed by SQUID, it was found that the substance displays high coercivity of 928 oersted (Oe) at room temperature. As a distinctive feature, this value is more than 3 orders higher than the coercivity of FeCo bulk material. This kind of new FeCo nanowire enclosed in a carbon nanotube is expected to be widely used in the future in data storage devices, high sensitivity magnetic sensors, and the manufacture of magnetic ink for copiers, among other potential applications.

For more details: http://www.nims.go.jp/abg/eng/

Platinum Nanotube with Outer Diameter of 6 nm

—Expectations for Application to Fuel Cell Catalyst—

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(Former Researcher at NIRIM)
CREST

In recent years, rising expectations have been placed on the development of automobiles equipped with polymer electrolyte fuel cells (PEFC) as a clean energy source which produces electricity from hydrogen and oxygen. However, popularization of this technology will require broad improvement in both the price and performance aspects. Thus, a technical breakthrough which makes it possible to produce a platinum catalyst with especially high activity and thereby reduce the quantity of catalyst used has been required.

We have been engaged in research on new materials which use cylindrical rods made up of surfactant molecules as a template, and have created new substances including mesoporous and nanotubular rare earth materials having pore diamters of 3 nm and outer diameters of 6 nm, respectively, and macromolecular nanotubes of the same size. However, where metals are concerned, because metal atoms have the property of easily cohering, extremely fine metal nanotubes with outer diameters of 10 nm or less were unknown until recently. Moreover, in synthesis using a surfactant as the mold, use of one type of surfactant was the general practice.

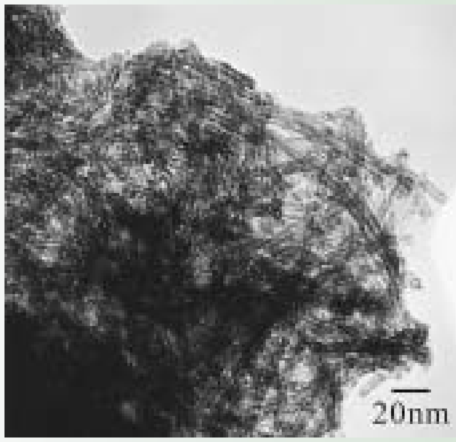

Fig. 1 Platinum nanotubes.

In contrast to this, we devised a novel method which uses a template combining two types of surfactants and succeeded in synthesizing platinum nanotubes (**Fig. 1**) which have an outer diameter of 6 nm and ultrafine pores on an order that would just allow entry by DNA molecules with a diameter of 2 nm. The results of model calculations showed that molecules of the two surfactants are combined to form liquid crystals composed of their cylindrical rodlike assemblies, and the platinum tubes are formed within the outer aqueous shell of the cylindrical rods (**Fig. 2**).

When ultrafine platinum particles are used as a catalyst, it is known that the atomic arrangement at the exposed surface of the particles and lattice defects such as loss/displacement of atoms, etc. affect their activity. Accordingly, it is also possible that platinum nanotubes may manifest a catalytic ability originating in their unique shape. In particular, unlike ordinary particle catalysts, an increase in catalytic activity associated with the convex surface of the tube inner wall is expected. For this reason, platinum nanotubes can be expected to drastically improve the utilization factor of platinum as an electrode catalyst in fuel cells. In addition, application to catalysts for automotive exhaust gas purification, petrochemical processes, synthetic gas production, and production of pharmaceuticals and fats, etc. is also conceivable. As immediate tasks, we are conducting further research to establish synthesis conditions, including yield improvement, etc.

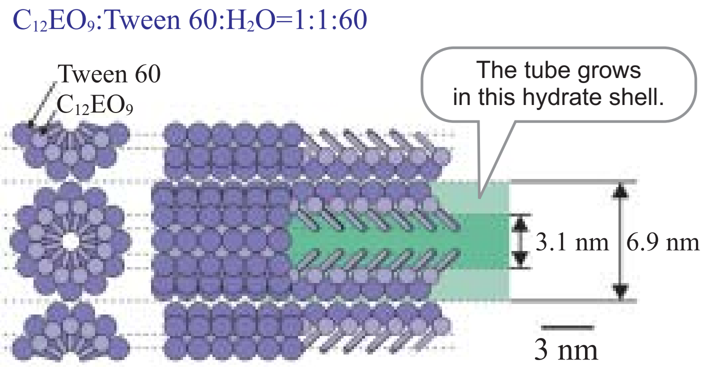

Fig. 2 Model of liquid crystal template.

coffee break

"Camellia in snow" March 4


Photo by Marat B. Gaifullin

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Start of Overseas Fellow System

NIMS is launching an Overseas Fellow System under which NIMS Overseas Fellows will be selected from among non-Japanese researchers who have carried out research during long-term stays at NIMS and non-Japanese researchers who have made major contributions to NIMS research and international cooperation. The selected Fellows will receive certificates and ID cards from the President of NIMS.

The aim of this system is to create a network of outstanding cooperating persons associated with NIMS, who can provide positive cooperation in joint research, information, and introduction of human resources after they complete their work at NIMS and return to their own countries. To support this program, Fellows will also receive *NIMS NOW International* and other publications on a regular basis.

Hello Everybody!

[In front of the National Museum in Ueno, Tokyo]

My name is Samuela Rigozzi and I came from the Italian speaking part of Switzerland. Last year, I graduated from the Swiss Federal Institute of Technology in Lausanne (EPFL), as engineer in material science. I decided to come to Japan for a limited period of stay before starting a PhD, to see how it is to work in a research centre such as the NIMS and, at the same time, discover a new country.

I started working for NIMS last September as Junior Researcher in the Regeneration Materials Group. My work consists in studying the biocompatibility between rat osteoblast cell and different pre-treated hydroxyapatite surfaces, by gene expression, and observation of cell attachment with SEM and AFM.

This was my first visit to Japan, and I definitely love it. I remember that during the first few weeks here I felt so lost because of the big differences between home and the island of the rising sun. Slowly, I met very nice people who told me about Japan and its customs, and now I know that I will never forget my stay here. I'd like to thank NIMS for giving me the chance of getting closer to such a far country.

Samuela Rigozzi (EPFL, Switzerland)
NIMS Junior Researcher (Sep. 2004 - Feb. 2005)
Regeneration Materials Group
Biomaterials Center (BMC)

[On the Shinkansen bullet train before the trip to Kyoto]

Living in Tsukuba

Ding Rong Ou (China)
Research Fellow (Aug. 2004 - Aug. 2006)

Fei Ye (China)
JSPS Fellow (Oct. 2004 - Oct. 2006)

Eco-Energy Materials Group, Ecomaterials Center (EMC)

We are a couple from the Department of Materials Science and Engineering, Tsinghua University, China. Last year, we got our PhD degree and started our life in Tsukuba. As a couple, we are very lucky to work in a same institute. Now we both work with Dr. Toshiyuki Mori (Eco-Energy Material Group), investigating the relationship between microstructure and electrolytic properties in doped ceria electrolyte for fuel cell. We like our challenging and interesting work.

[With Japanese friends; first (Ye) and second (Ou) from the right in the upper row]

Living in Japan is totally a new experience for us. Fortunately, we met a lot of kind people. Dr. Mori, the group members and other new friends always give us a lot of helps on work and daily life. Tsukuba is a quiet and beautiful city. In holiday, we can climb Mt. Tsukuba, or walk in the parks and visit the museum and library, or spend time with friends. It is convenient and comfortable to work and live in here.

Although we do not speak Japanese, we have learned some about the Japanese culture from daily life, as well as from our Japanese friends. It is good for us to know more about different cultures, and thereby understand the world better.

NIMS Public Relations Office
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PUBLISHER
Dr. Masatoshi NIHEI

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