from Tsukuba, Japan to the world

NIMS NOW International

National Institute for Materials Science

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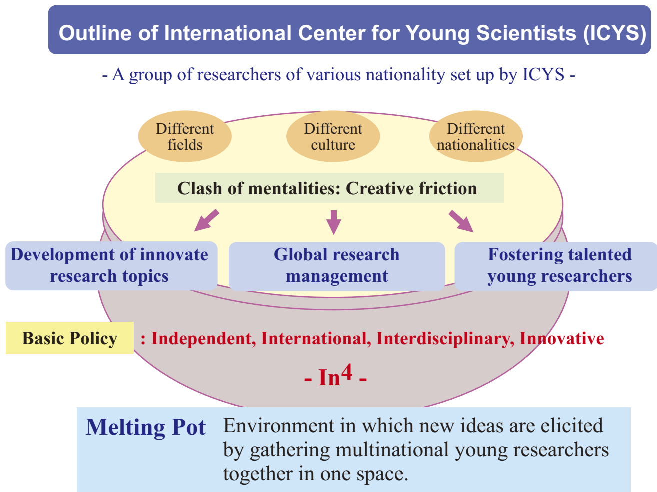
Fostering of Young Scientists

- Exploratory Research and Independence -

Yoshio Bando
Director General
International Center for Young Scientists (ICYS)

Materials research is generally considered a type of "small science," and has a research style which differs greatly from that in developmental research in the "big sciences" such as accelerator research and aeronautics and space exploration. In "big science," the total capabilities of a team are indispensable. On the other hand, in "small science," the individual researcher/abilities of the individual are more essential than team capabilities. In particular, exploratory research demands the originality of individuals. For example, the discovery of the fullerene and carbon nanotube were achievements of individual research. Moreover, it is an extremely interesting fact that major discoveries of the Nobel Prize class are frequently the result of serendipity (unexpected accidental discovery) in fundamental research fields.

Researchers who excel in this kind of original research, and particularly young scientists in their 20s and 30s, are essential to these efforts, which means that we must recruit and foster the best young researchers from countries around the world. Recruiting and fostering these young researchers is the largest challenge not only for NIMS, but also for today's Japan as a whole. In FY2003, NIMS launched the International Center for Young Scientists (ICYS) with the support of the Promotion Subsidy for Science and Technology of Japan's Ministry of Education, Culture, Sports, Science and Technology (MEXT), and is now grappling with the development of young researchers and issues related to internationalization. Our objective in the ICYS is to allow all researchers to demonstrate their research capabilities to the maximum and produce original research results through a fusion of different fields and cultures by creating an attractive research environment where creative young scientists from around the world can gather in one spot and devote themselves independently to research based on their own ideas without language barriers. At the same time, NIMS has also introduced a new research system for attracting young researchers from countries outside of Japan with the intention of "implementation" their achievements to the main NIMS organization.



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ICYS Fellows with Nobel Prize laureate, Sir Harold Kroto (front row, center left) and author (front row, center right).

in this issue

Self-Assembly and Anion Sensing by Nanosized Molecules

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Functional molecules are expected to find application in a variety of nanometer-scale optical and electronic devices which take advantage of their extremely small size and tunable properties. Examples include the development of ultra-high density data storage devices and molecular switches. In the natural world, porphyrinic molecules are known as the substances which give blood its red color and plants their green color (**Fig. 1a**). However, application to molecular electronic devices can be expected, since they possess several desirable properties, including flexibility of synthesis, high thermal stability, and of course, small size (the size of one porphyrin molecule is on the order of 1 nm^2). We have therefore begun work to realize advanced functions in porphyrin molecules with the particular aim of developing sensing and electronic devices.

The porphyrin molecules shown in **Fig. 1** are attractive molecules because they form stable structures at solid substrates while also allowing free introduction of various functional groups. For example, introduction of an electron donor enables construction of intramolecular energy and electron transfer systems, making it possible to develop functions which utilize these processes. **Fig. 2** shows the behavior of a porphyrin which displays designated colors corresponding to various halogen ions. While no previous report has described the possibility of differentiating all halogen ion species simply by mixing a sensing substance with a halogen-containing solution, this result suggests that the porphyrins can be used in anion sensing, which has a wide range of applications. This system can also be used in classifying more complex anion species and the solvent itself. As indicated in **Fig. 1b**, anions are hydrogen bonded by the amine groups at the center of the porphyrin molecules, and the chromogenic response varies depending on the strength of bonding. For example, different coloration can be observed with fluoride and chloride ions because the strength of association is one order stronger with fluoride.

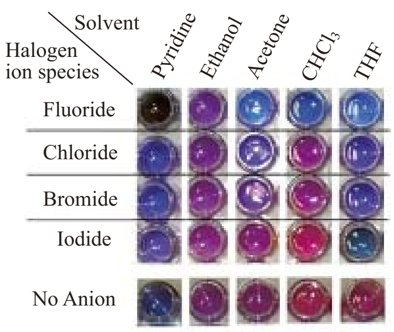

Fig. 2 Color of these porphyrin molecules (OxP) varies depending on the presence of halogen ions and solvent identity (THF: Abbreviation for tetrahydrofuran.)

The structures of these porphyrin molecules are also important in the design of optical materials, and it is a decisive factor in the formation of various supermolecular aggregates, including stacked aggregates, filamentous structures, and molecular monolayers. These structures can be elucidated by techniques such as X-ray crystallography, electron microscopy, and probe microscopy. For example, a direct observation of changes in substrate adsorbed structures due to molecular conformational changes is possible. Further refinement in the molecular structure and electrochemical properties may lead to the development of electrochemical molecular switching devices. It has also been found that, when in an oxidized state, the porphyrinic molecules can be fixed stably at a substrate, and this may be useful not only in the development of new devices, but also in the elucidation of basic phenomena at the molecular level.

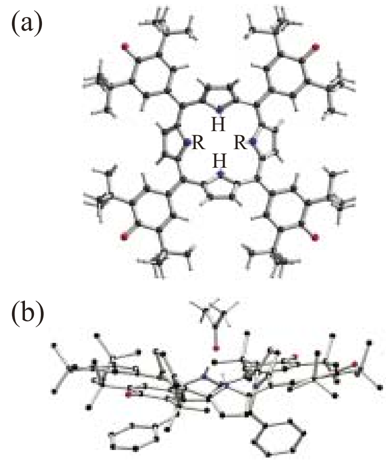

Fig. 1 (a) Porphyrin molecule (OxP) used in this research. Various functional groups can be used for R; H is a hydrogen atom. (b) Binding site in OxP. A small molecule is captured by hydrogen bonding. Black spheres = carbon, blue spheres = nitrogen, and red spheres = oxygen.

Special Features

< Continued from p.1

Fostering of Young Scientists

The ICYS has invited more than 40 young scientists from over 20 countries, who were selected from approximately 800 applications received from more than 60 countries. The average age is around 32. The Center has secured a research environment which enables independent research under a scientific adviser (NIMS staff researcher) and provides research expenses, private rooms, and space for experiments. We believe that allowing researchers with careers of several years after receiving their academic degrees to carry out research independently in a free environment with relaxed supervision from their adviser enables these young researchers to demonstrate their originality to the utmost, and is also the road to growth into outstanding independent researchers.

Of course, "independence" can be dangerous if it leads to "isolation." Therefore, the ICYS consciously creates numerous opportunities for mutual exchanges and mutual enlightenment among its young scientists. For example, 30 minute coffee breaks each day and weekly seminars give members a chance for exchanges. The ICYS also has various training programs which include personal interviews with some of the world's preeminent senior researchers (Nobel Prize Laureate Sir Harold Kroto, Prof. Sukekatsu Ushioda, president of the Japan Advanced Institute of Science and Technology, and others), as well as a summer school and workshops and other activities.

Thus, in the training of young scientists, it is important to build a research system which respects the independence of the researcher and makes it possible to produce original results from free conceptions. Germinal research is by nature one field where young researchers can demonstrate their originality to the maximum. In this issue, we will introduce outstanding recent research achievements by five of our young scientists. The results of the germinal research by these scientists may provide the starting point for new interdisciplinary research, and great development is expected in NIMS.

For more details: http://www.nims.go.jp/icys/

Creation of Novel Materials Using Ultra-High Pressure Synthesis Technique

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Advanced Nano Materials Laboratory

As a recent trend, unconventional new synthesis methods have become necessary for the creation of new materials. Among these, high-pressure synthesis has already been recognized as a powerful new technique for search/preparation of new materials. The advantages of this technique include (1) stabilization of ions in unusual oxidation states which would be impossible to obtain under normal conditions, (2) stabilization of unusual coordination numbers, (3) stabilization of structures which are thermodynamically unstable at ambient pressure, and (4) stabilization of high density compounds. We are using this advanced technique in the preparation of new ferroelectric materials and multiferroic materials (materials which simultaneously display ferroelectric and magnetic properties).

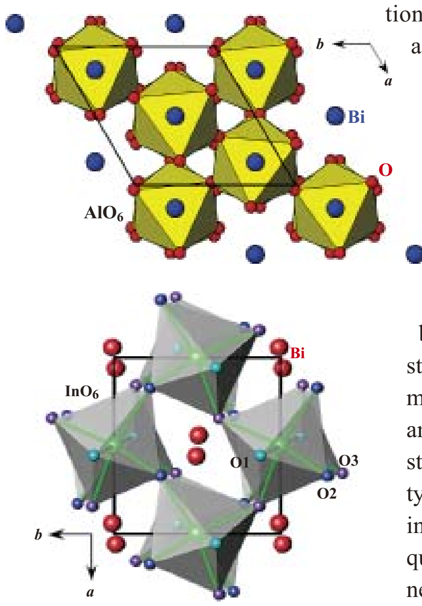

Fig. 1 Crystal structures of $BiAlO_3$ and $BiInO_3$.

We synthesized a new group of compounds which cannot ordinarily be obtained with normal ambient pressure techniques under a high pressure of 6 GPa (approximately 6×10^4 atmospheres) and high temperature. The targets of our system are substances with simple compositions of $BiMO_3$ and $PbMO_3$ (M: metal element). Among these, our work has revealed that $BiAlO_3$, $BiInO_3$ (**Fig. 1**), and $PbVO_3$ (**Fig. 2**) are promising candidates for ferroelectric materials, as they exhibit large spontaneous polarization surpassing that of widely-used ferroelectrics such as $BaTiO_3$ and $PbTiO_3$.

On the other hand, from research on solid solution systems of $BiAlO_3$-$BiGaO_3$, we discovered that this system possesses the same structure as $Pb(Ti,Zr)O_3$, which is an extremely important practical piezoelectric material. In particular, it should be noted that the above-mentioned substances ($BiAlO_3$, $BiInO_3$, and $BiAlO_3$-$BiGaO_3$) are very interesting from the environmental viewpoint as they are lead-free materials.

In other recent research, we showed that the structure of $BiScO_3$, which is obtained by high-pressure synthesis, is close to that of the multiferroic material $BiMnO_3$, but $BiScO_3$ crystallizes in the $C2/c$ centrosymmetric space group. This result brings up an intriguing question about the origin of ferroelectricity in $BiMnO_3$. From this viewpoint, it would be fair to say that $BiScO_3$ is a model system which may provide the key to understanding the role of Mn^{3+} ions when considering the origin of ferroelectricity in $BiMnO_3$.

We also found that $BiGaO_3$ crystallizes in the so-called pyroxene-type structure, in which Ga^{3+} ions occupy tetrahedral sites. Pyroxene-type compounds are interesting from the geological viewpoint, as the pyroxenes are major components of the earth's crust and upper mantle and display a variety of phase transformations under high pressure. Thus, the search for new materials using high-pressure techniques possesses great value both for discovering new material groups which did not exist heretofore and for research on existing substances.

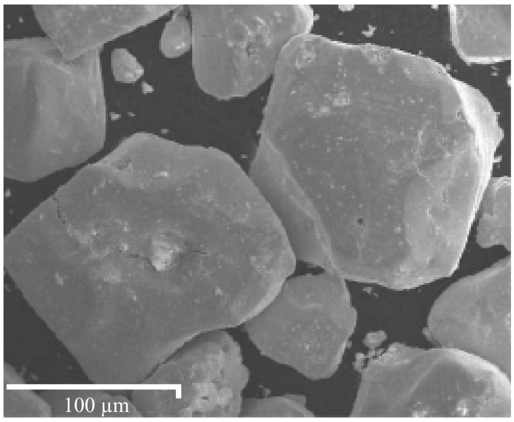

Fig. 2 Crystals of $PbVO_3$ grown under high pressure.

NIMS News

President Kishi Receives the Japanese Society for Non-Destructive Inspection Award

(May 24, Tokyo) -- President Teruo Kishi of NIMS received the Japanese Society for Non-Destructive Inspection Award. This prestigious award is given to persons who have made important contributions in research related to non-destructive inspection (NDI), improvement of NDI technology, and the popularization of NDI techniques. The award given to Prof. Kishi recognizes his research achievements in the field of non-destructive inspection over the course of many years, ranging from basic research to practical applications, and particularly his work on acoustic emission detection of fractures and their quantitative evaluation.

President Kishi (left) at the Award Ceremony.

Mesoporous Carbon and Carbon Nitride Materials

- Application as an Adsorbent for Capture of Dyes and Proteins -

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Fuel Cell Materials Center

Porous silica and carbon materials have attracted considerable attention in recent years due to their applications in many areas, such as gas separation, adsorption of small gas molecules, catalysis, energy storage and capacitors. These porous materials are generally microporous and the creation of mesoporosity is extremely important not only for their applications in the adsorption and separation of molecules and ions that are too large to enter micropores but also for energy applications such as electrical double layer capacitors and fuel cells. Thus, we attempt to develop novel mesoporous carbon and nitrides with various pore diameters using inorganic templating technique and utilize the developed materials in the bulky molecule adsorption and fuel cell applications. This report describes the synthesis and application of novel cage type mesoporous carbon and hexagonal carbon nitride materials.

We succeeded for the first time in preparing the well ordered mesoporous

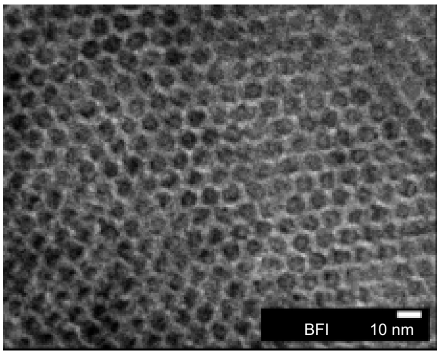

Fig. 1 High resolution electron microscope image of mesoporous carbon nitride.

carbon nitride (MCN) with various pore diameters by inorganic templating method. The material is obtained through a simple polymerization reaction between ethylenediamine and carbon tetrachloride using mesoporous silica with various pore diameters as templates. These materials have a

Special Features Exploratory Research as Promising Further Development

Development of Double-Sided Microfabrication Technique Using Crystal Cleavage Property

- New Development to 3-Dimensional Integration Technique for Superconducting Devices -

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Nano Quantum Electronics Group
Nano System Functionality Center

Copper oxide superconductors are intrinsically of layered structures, with superconducting and non-superconducting layers interleaving each other. Thus a piece of sample consists of thousands of junctions. In the case of $Bi_2Sr_2CaCu_2O_{8+\delta}$ (BSCCO), each junction measures approximately 1.5 nm thick and the junctions are stacked in series in the c axial direction of the crystal. This type of junction is called intrinsic Josephson junction, or IJJ. The discovery of IJJs in high-T_C superconductors opens the path to a new field of 3-dimensional microelectronics at the nanometer scale. Many potential applications are devised in next-generation electronics, including high frequency electromagnetic wave detectors, terahertz oscillators, superconducting digital circuits, quantum computing devices, etc. However, with conventional fabrication process, samples are fabricated on the surface of a single crystal. The surface degradation of superconductivity makes it almost impossible to obtain desired junctions in 3-dimensional stacks.

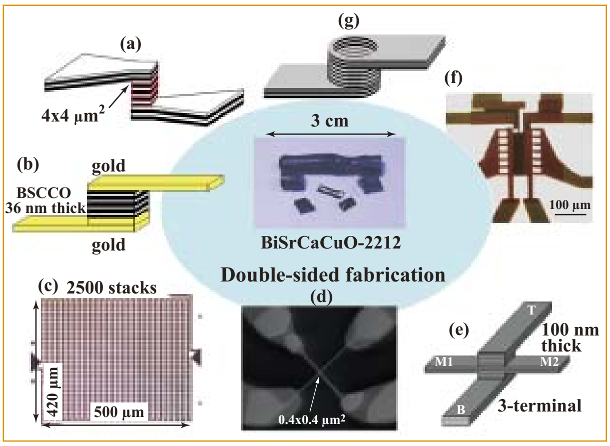

Fig. Various devices fabricated from single crystals of BiSrCaCuO-2212 superconductor, e.g. (a) a single stack of intrinsic Josephson junctions (IJJs) integrated with a superconducting antenna, (b) single-crystal slice 36 nm thick, (c) an array of 2500 stacks of IJJs, (d) single junction 1.5 nm thick, (e) 3-terminal structure of IJJs, (f) integrated array of narrow stacks, and (g) annular device.

To solve this problem, I invented a novel double-sided fabrication method while working in Yamashita Laboratory, Research Institute of Electrical Communication (RIEC), Tohoku University. By this method, a stack of IJJs can be singled out from inside a sample, thus making it possible to fabricate a well-defined number of junctions in well-defined structures (see **Fig.**). We successfully conducted a number of experiments at Tohoku University with samples fabricated by this novel technique. To name only a few examples, a single stack of junctions integrated with a superconducting antenna responded nicely to irradiation up to 2.5 THz (**Fig. a**); single-crystal slices with a thickness as small as 36 nm was successfully handled (**Fig. b**); more than 10^5 junctions were integrated on one chip for applications in quantum voltage standard (**Fig. c**); and a single junction having a thickness of only 1.5 nm was fabricated (**Fig. d**).

Since I joined NIMS, the versatility of double-sided fabrication has been further explored and the physics and possible applications of IJJs further revealed or demonstrated. For example, a central electrode 100 nm thick can be fabricated in a stack of IJJs between the top and bottom electrodes (**Fig. e**) so that the physical processes (such as self-heating) happening in the stack can be more thoroughly understood than without it. Such a stack can also serve as the basic building block for 3-dimensional integration of digital circuits. Using integrated narrow IJJ stacks, we have succeeded in observing THz excitation as evenly-spaced voltage steps on their current-voltage characteristics. We have also succeeded in achieving an oscillation power of several 10 µW by integrating these devices (**Fig. f**).

Recent observations of annular devices (**Fig. g**), the macroscopic quantum tunneling effect, Josephson magnetic flux ratchet, and numerous other interesting phenomena are continuously demonstrating that this double-sided fabrication technique will play increasingly important role in bridging the gap between the material research and the applications in biotechnology and nanotechnology.

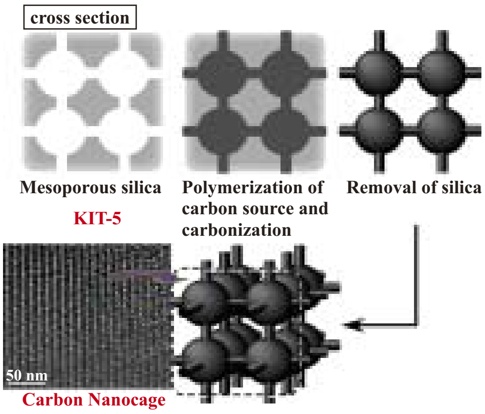

Fig. 2 Carbon nanocage (CNC) fabrication method.

highly ordered hexagonal pore system (**Fig. 1**) and the structure of the MCN is composed of ordered carbon nitride rods, which was originally formed inside the cylindrical mesopores of silica template. These carbon nitride rods are rigidly interconnected by smaller carbon nitrides which are formed inside the micropores of main cylindrical pores of silica template. They also exhibit high surface area, pore volume and uniform mesopores size distribution. They are promising materials and could offer great potential for the applications such as catalytic supports, gas storage, lubricants, and drug delivery.

Recently we also succesfully developed a method to prepare a novel mesoporous carbon, ***Carbon Nanocage*** (CNC), with various pore diameters using cage type mesoporous silica templates (KIT-5) (**Fig. 2**). The textural parameters of the CNC can be easily tuned by a simple adjustment of the weight ratio of the carbon and the silica source. The specific pore volume and the specific surface area of CNC are much higher as compared to CMK-3 mesoporous carbon prepared from hexagonally ordered mesoporous silica (SBA-15) and are the champion data in the world. The carbon nanocage also shows a superior performance in the adsorption of biomolecules and dyes as compared to CMK-3 and activated carbon (AC) (**Fig. 3**). As CNC possesses very high surface area, pore volume and interesting cage type porous structure, we are currently studying the application of the material for size selective adsorption of various organic bulky molecules and as a support for fuel cells.

Fig. 3 Capturing of alizarin yellow dye using CNC.

For more details: http://fuelcellmaterials.jp/en/

Biomolecular Recognition on Silicon

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In order to create a society in which people can live their everyday lives safely and securely in spite of the constantly changing environment, the requirements placed on (bio)chemical monitoring/sensing have increased at an accelerating pace, and now include environmental monitoring of viral contagion, chemical sensitivity, and other problems which have become increasing threats in recent years, as well as countermeasures for bioterrorism, which is a subject of heightened tensions. To realize this, we have focused on the sugars which exist in the cell surface in the form of glycolipids, glycoproteins and proteoglycan.

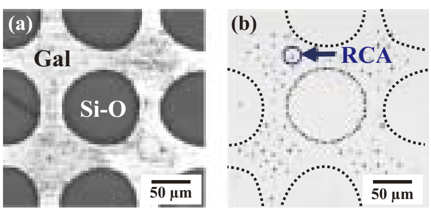

Fig. 2 Optical microscopic images showing the specific molecular recognition between lectin and sugar monolayer. (a) Photomask for use in optical patterning: Because the black circular region passes UV light, the sugar monolayer which formed in this region is removed by photooxidation, and silicon oxide (shown as Si-O) is newly formed. (b) Molecular recognition test using the micro-patterned sample. The circle in (b) corresponds to the black circular region in (a). The silicon oxide surface has the effect of preventing nonspecific adsorption of lectin.

Such sugar moieties play the role of a "face" which allows a wide variety of guest molecules, beginning with viruses, to enter living organisms from the outside environment. Monitoring and sensing of the biomolecular interactions which occur inside and outside of living cells can be expected to realize a better understanding of the unique recognition mechanism of sugars for guest molecules and quantification of their specific recognition events. However, it is difficult to treat the specific recognition event quantitatively using commercially available arrays of sugar molecules because their molecules are distributed randomly on the arrayed regions.

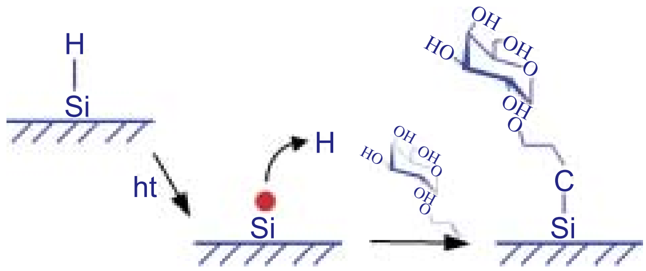

Fig. 1 Formation process of sugar monolayer. Si-H bond is thermally cleaved to give a silicon-centered radical (red circle), and then is terminated with a 1-alkene of sugar to form an interfacial C-Si covalent bond. As a result, sugar monolayer is directly immobilized on a bare silicon surface.

As a first step to overcome this shortcoming, we succeeded in covalently immobilizing sugar monolayer on a non-oxidized silicon surface, which made it possible to control in molecular orientation, molecular spacing, and stability as a device of sugar monolayer. The immobilization process employed a thermal radical reaction between a 1-alkene terminated with a sugar molecule and hydrogen-terminated silicon (**Fig. 1**). Since the sugar molecule was gradually terminated over the silicon surface, the water-contact angle at the substrate surface gradually decreased. Using X-ray photoelectron spectroscopy, an interfacial C-Si covalent linkage could be detected, and thus we resulted that the sugar monomolecular film was successfully formed through the thermal radical reaction shown in **Fig. 1**.

Next, by preparing a micropatterned sugar-modified substrate through an optical lithography, we simultaneously examined the specific biomolecular interaction of the protein-sugar, and whether the nonspecific adsorption of proteins onto unintended areas could be prevented. Furthermore, when we micropatterned a sugar-modified surface using the photomask shown in **Fig. 2a**, the lectin aggregate was observed in the shape of the pattern and was limited to the region of sugar moiety, as shown in **Fig. 2b**. This reveals that our prepared sugar monolayer still shows the specific recognition ability to lectin even after its immobilization. Our future objectives include the development of a high performance biomolecular device utilizing the characteristics of silicon.

Recruitment

We are seeking highly motivated people in biomaterials field!

1. Job clarification: Researchers
2. Recruiting fields:
   a. Polymeric biomaterial synthesis, bio-functional surface chemistry, nano-micro structure control
   b. Polymeric scaffold biomaterials for medical engineering
   c. Study of cells/materials interface for sensor cells
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3. Requirements: Applicants should have a PhD in biology, chemistry, or a related field.
   (a-d) Applicants should be no older than 35.
   (e) Applicants should be aged over 35 (Group-Leader level).
4. Position available from October, 2006
5. Application dead line: July 31, 2006
6. Application form and detailed information:
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Hello from NIMS

Jonathan Hill (U.K.)
Senior Researcher
Supermolecules Group
Organic Nanomaterials Center

[Working in my office at the Supermolecules Group]

Greetings from the Supermolecules Group at NIMS. My name is Jonathan Hill and I am working as a researcher here. Although I was educated in England, I have spent most of my research career living and working outside that country with stays in Osaka, Japan and Karlsruhe, Germany. Now I am happy to call Tsukuba my home.

Tsukuba is a town of great contrast. On one hand, it has the relaxed attitude befitting a provincial town while on the other it has become the epicenter for research in Japan. Besides that, the flux of researchers, both Japanese and foreign, lends a cosmopolitan mood to Tsukuba against the backdrop of its rural surroundings. NIMS reflects well these features having a friendly, international environment, at the same time being dynamic and progressive in its attitude to research. Also, the term 'materials' (the 'M' in NIMS) covers a diverse range of topics: I am working largely on organic chemistry but I have colleagues involved in nanotech, biotech and combinatorial science.

[Having fun at home in Ninomiya House; from left Yuujin, Erin and Jinko]

Finally, my life here is made very much more comfortable and fun by my family who are my wife Jinko (仁子) and kids Yuujin (悠仁, 4 years) and Erin (愛凜, 10 months). At the weekend, we can play in the many public parks in Tsukuba or catch a train to Tokyo to visit the zoo.

NIMS
National Institute for Materials Science

PUBLISHER
Dr. Hisao Kanda

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