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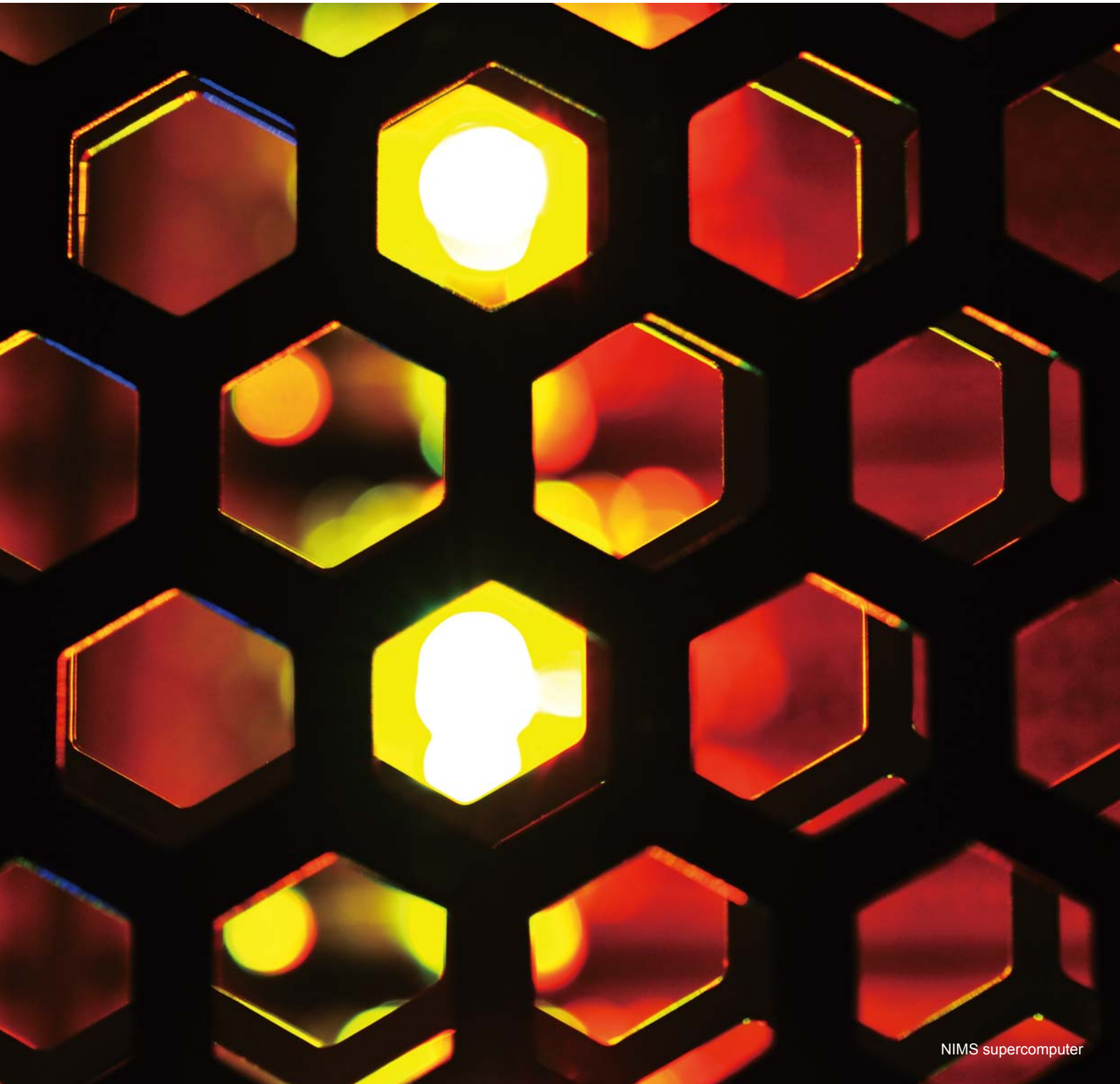
Reflecting Future of Materials with the Computational Science



NIMS supercomputer

Reflecting Future of Materials with the Computational Science

Progress in Computational Science

Takahisa Ohno
Managing Director, Computational Materials Science Center
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The goal of computational science is to understand natural phenomena by numerically simulating those phenomena based on their basic equations, either as they are at natural state or at under controlled environments such as extreme states, ideal states, etc. Called the "third science," computational science is one of the main pillars supporting science in the 21st century, along with the theoretical science and experimental science. The phenomena in the field of materials science encompass a wide range of scales, both temporally and spatially, from the micro level, as exemplified by photoexcitation of the electrons in molecules and surface chemical reactions, to the macro, as seen in secular changes in the mechanical properties of gigantic structures. In understanding the nature and properties of materials, it is necessary to develop computational science techniques which are appropriate for these respective scales. We are engaged in research and development on a variety of techniques, including first-principles calculations, which treat the behavior of electrons and atoms based on quantum mechanics, the classic molecular dynamic method and Monte Carlo method, which are applied at the atomic and molecular scales, the phenomenological phase-field method, which treats the nano/meso regions, and the finite element method and statistical thermodynamics for the macroscopic region. We analyze and understand the physical properties and characteristics of various materials, and search for them with outstanding properties and functions.

To achieve progress in computational science, it is indispensable to advance in analytical theory and numerical analysis methods, and to progress in computer power at the same time. In actuality, computer performance has increased at a rapid speed of approximately 10 times each 3 years, and the development of a next-generation supercomputer with peak performance of the 10 PFLOPS class (FLOPS: Floating-point operations per second; 1 petaflop means computational performance to execute 10^{15} such operations in one second) is in progress. By elucidating the basic principles behind complex phenomena through advanced numerical simulations utilizing this computer environment, computational science is expected to provide a driving force for large advances in materials research.

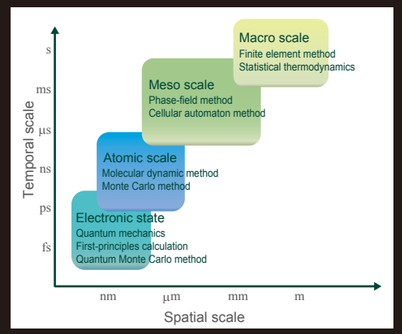

Fig. Temporal and spatial scales of computational science techniques

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Development of Large-Scale First-Principles Calculation Method

Tsuyoshi Miyazaki
First-Principles Simulation Group I,
Computational Materials Science Center

Understanding the properties of surfaces and interfaces at the atomic level is extremely important in basic research on environmental technologies. First-principles calculations based on density functional theory (DFT) make it possible to discover the behaviour of molecules and atoms based on quantum theory, and thus have played a key role in various fields of materials science. In order to simulate phenomena at complex surfaces and interfaces, calculations for systems which consist of large numbers of atoms are necessary. As a result of both the spread of robust DFT programs and the increase in computer power, first-principles calculations for systems consisting of several hundred atoms are now commonly performed. However, with the techniques which are ordinarily used, when the number of atoms exceeds several hundred, the time required for calculations increases rapidly, in proportion to the cube of the number of atoms N. This makes it very difficult to realize first-principles calculations for very large systems comprising more than 1,000 atoms.

To solve this problem, we developed a linear-scaling DFT program, in which the computational cost increases only in proportion to N (also called Order-N or O(N) methods). This work was carried out in joint research with University College London (UCL) in the United Kingdom Our program leads the world in parallelization efficiency and computational stability, and has realized first-principles calculations for systems of more than 10,000 atoms in complex biosystems and nanostructures on the surface of semiconductors. This method is expected to become a basic tool for theoretical research to clarify the reactions at complex surfaces and interfaces.

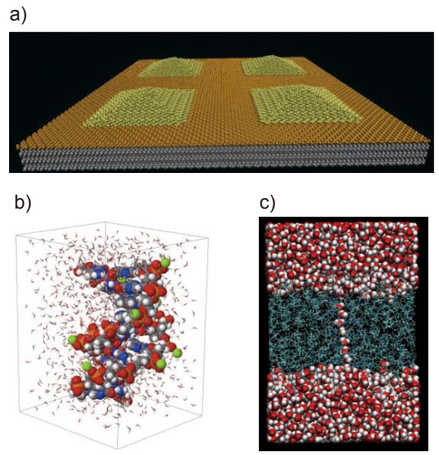

Fig. Examples of systems investigated in theoretical research using Order-N first-principles calculations. a) 3-dimensional island structure of Ge formed on Si(001) surface, b) DNA in an aqueous solution, and c) single file of water molecules in an ion channel in a lipid bilayer.

Approaching to Surface Boraphene

Collaboration of Computational, Experimental, and Theoretical Science

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First-Principles Simulation Group II,
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Recently, a NIMS experimental research group discovered a new boraphene phase on the surfaces of metal diborides (MB_2). Boraphene is a network of boron which has a skeleton similar to that of graphene (carbon atom sheet with single-atom thickness having a hexagonal lattice structure), and gives the MB_2 compound various unique properties, including a high melting point, high hardness, superconducting property, etc. Until this discovery, it had been thought that the boraphene surface was stable in group 5 element compounds of MB_2 (M=Nb, Ta, etc.) and the metal surface was stable in group 4 compounds of MB_2 (M=Zr, Hf, etc.). The fact that an unknown boron surface exists stably, even in the latter systems, was clarified by electron diffraction, which investigates the periodicity of the surface structure, measurements by high-resolution electron-energy-loss spectroscopy, which makes it possible to measure the natural frequency (phonon oscillation) of that surface structure, and other techniques, but, it is no easy matter to determine the detailed atomic configuration from these experiments. Furthermore, although the source of the stability of the surface structure is of great interest from the viewpoint of physical chemistry, it is extremely difficult to understand the origin of this phenomenon based on the empirical facts alone. In cases of this type, use of these experimental techniques in combination with the first-principles calculation method, which is constructed without depending on experiments, is a very effective approach. The figure shows the surface boraphene structure and phonon dispersion, which were clarified by first-principles calculations. The agreement of the phonon dispersion in the experimental results and calculated results demonstrates the appropriateness of the calculation model. The source of the stability of the surface structure was also clarified from the results of electronic state calculations. Combining these calculated results and statistical thermodynamics theory, it was possible to discuss the structural stability under a finite temperature, and to educe the values of various thermal properties, including specific heat, entropy, etc. Thus, first-principles calculation is a technique which provides a clearer outline of various facts related to substances by collaboration with experimental techniques and theoretical science, and is thereby enriching the content of materials science.

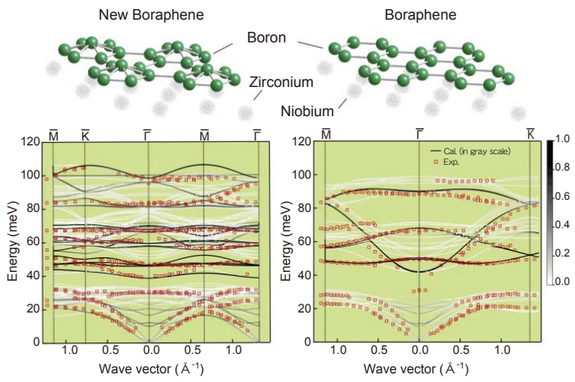

Fig. Surface boraphene structures and their phonon dispersions [from S.Suehara, T. Aizawa, T. Sasaki, Phys. Rev. B81, 085423 (2010)].

First-Principles Simulation of Redox Reaction

Yoshitaka Tateyama
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Redox (reduction & oxidation) reaction plays a key role in many technologies for energy and environmental issues, such as photocatalysis, fuel cell and photovoltaic cell. It is defined as chemical reaction coupled to electron transfer process, which causes energy transfer, formation and dissolution of molecules. Important hydrogen evolution ($2H^+ + 2e^- \longleftrightarrow H_2$) and water dissociation ($O_2 + 4H^+ + 4e^- \longleftrightarrow 2H_2O$) are the representative examples.

In order to perform quantitative simulations of such redox reactions, accurate descriptions of the electron transfer process and the subsequent structural reorganization is essential. Then we have developed and demonstrated first-principles molecular dynamics techniques for free energies and reaction pathways of redox reactions, based on density functional theory (a quantum mechanical theory for many-electron systems). Our calculation techniques are found to be very universal and consistent with the famous Marcus theory of electron transfer.

Recently, we have been working to apply these techniques to redox reactions on solid/solution interfaces, which are the main reaction sites for catalysts and electric cells. Our calculations semi-quantitatively show the change of efficiency of interfacial redox reactions (ex. decomposition of organic species or water molecule), depending on the interfacial structure. With these computational techniques, theoretical design of interfacial redox reactions would be realized in the future.

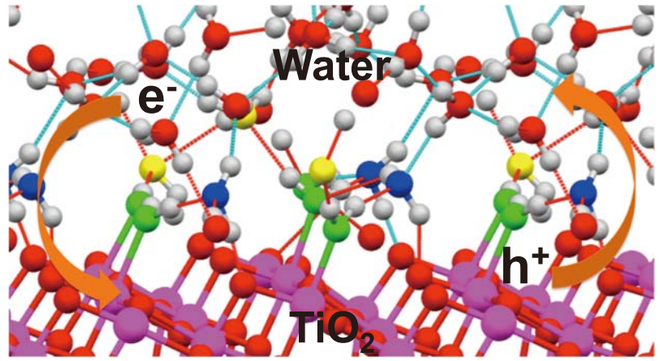

Fig. Molecular model of a photocatalytic system (TiO_2/water interface)

Investigating Nanostructures by Molecular Dynamics Simulation

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Particle Simulation & Thermodynamics Group,
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Experimental techniques for observing the microscopic world, such as electron microscopes, are progressing almost daily. However, these techniques are still at a stage where it is difficult to capture individual atoms as though seen by the eye. On the other hand, because the simulation technique called molecular dynamics (MD) creates a virtual laboratory in the computer and tracks the movements of the individual atoms arranged in that space, MD makes it possible to obtain information that is difficult to obtain experimentally, by determining the positions of atoms in a material and how the configuration and motion of those atoms is related to the properties of the material.

The state in which a material is solidified basically as it existed in the liquid form is called the “glassy state.” Window glass is one example of that state. Metals produced in the glassy state are called *metallic glasses* and display physical properties and electrical properties which differ greatly from those of ordinary metals (in which atoms are arranged in a regular crystalline state), and therefore have attracted considerable attention as new materials. However, the atomic structure of metallic glasses cannot be adequately understood by electron microscopy. Therefore, using an MD simulation, a metallic glass was prepared by rapidly cooling a liquid metal in a virtual laboratory, and its structure was analyzed at the atomic level. The results revealed that the atoms were not arranged randomly, even in the glassy state, but rather, formed icosahedron-shaped clusters, as shown in the accompanying figure.

By making it possible to elucidate the nanostructures of new materials using simulations, as illustrated by this example, this technique is useful in investigating the relationship between the structure and properties of materials and in the development of new materials.

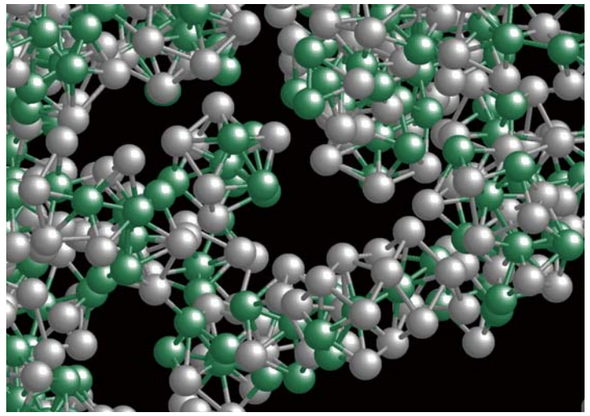

Fig. Network structure of icosahedral clusters found in ZrCu metallic glass (gray: Zr atoms, green: Cu atoms).

Simulation of Solidification Microstructure by Phase-Field Method

Machiko Ode
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Although metal materials may appear flat and featureless to the naked eye, various patterns can be seen when the same metal is observed under a microscope. This pattern is called the “microstructure” and has a great influence on material properties. Many microstructures are formed when materials are melted and then solidified. One typical microstructure of this type is called a “eutectic microstructure.” This is a microstructure which is formed by eutectic solidification, in which two solid phases with different concentrations crystallize simultaneously from a liquid phase having a homogeneous concentration. In this type of microstructure, the two solid phases form a periodic layered structure. Figure shows an example of a calculation of eutectic solidification by the phase-field method.

The phase-field method provides a tool for the simulation of microstructure evolution in complex materials on the mesoscopic scale. In general, microstructures are characterized by a “phase boundary.” For example, in the case of a solidification microstructure, the interface between the solid phase and liquid phase corresponds to this boundary. Because an excess energy, so-called interface energy, exists in the boundary region, the microstructure evolves to reduce the total length of the phase boundary as short as possible. On the other hand, in the solidification process the driving force acting on the solid-liquid interface increases the volume of the solid phase as quickly as possible. The balance of these two forces creates complex microstructual patterns. In the phase-field method, governing equations have been derived in simplified form to reproduce the balance of these two forces without contradiction with the existing theory. Because the formation processes of almost all of “microstructures” can be calculated by the phase-field method, high expectations are placed on this technique in a variety of fields.

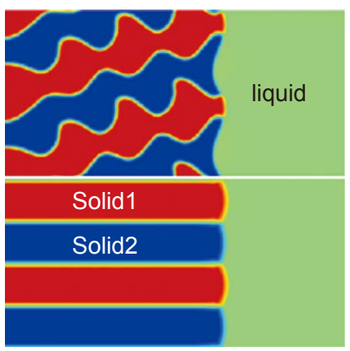

Fig. Calculation example of a eutectic microstructure formation. Top: Interfacial energy, 0.02J/m^2, bottom: 0.1Jm^2. A very small difference in interfacial energy has a large effect on pattern formation.

CALPHAD Modeling of Order-Disorder Transition in $LiCoO_2$

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Computational Materials Science Center
NIMS-TOYOTA Materials Center of Excellence for Sustainable Mobility

Using various thermodynamic quantities of stable / metastable phases obtained from both the first-principles calculations and experiments, the Gibbs energy (energy possessed by a material) of phases is thoroughly assessed based on the simple but adequate thermodynamic models. This procedure is called thermodynamic assessment or CALPHAD (Calculation of Phase Diagrams) method. Since this is based on the thermodynamic models, for extrapolations to temperature, pressure, and compositions, it provides a good estimate of thermodynamic quantities within the accuracy of the model. Thus, the assessed Gibbs energy is one of important parameters for dynamic simulations such as phase field method. In the present work, the thermodynamic assessment was applied to the phase transition in lithium cobalt oxide ($LiCoO_2$), which has been widely used as a positive electrode of lithium ion (Li-ion) secondary batteries.

During charging / discharging of the Li-ion battery, Li atoms migrate between the positive and the negative electrodes; and vacancies form behind on the Li sites in the electrodes. It has been experimentally measured that Li atoms and vacancies form an ordered configuration in the $LiCoO_2$ structure in a certain temperature and composition range, while outside of the range they mix randomly (the order-disorder transition). The Gibbs energy of the $LiCoO_2$ was thermodynamically assessed so as to reproduce well the transition (see **Fig. 1**). From the obtained Gibbs energy, it can be estimated the secondary transition points as presented in **Fig. 2**, and the electromotive force of the Li-ion battery as a function of compositions and temperature. This will be effectively applied for the expansion to the higher order systems with other elements such as nickel and manganese. This result was obtained through the research in NIMS-TOYOTA Materials Center of Excellence for Sustainable Mobility.

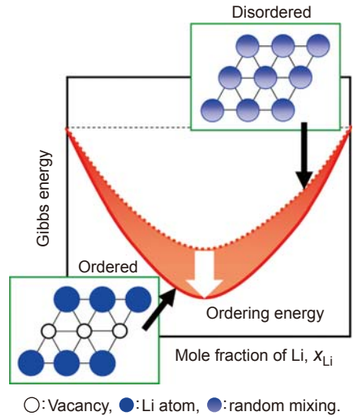

Fig. 1 Gibbs energy of the ordered and disordered phases.

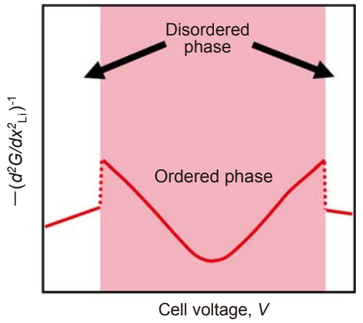

Fig. 2 The second derivative of the Gibbs energy (G) as a function of Li mole fraction. Two horns indicate the second order transitions.

Alloy Design Considering Atomic Arrangement

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Computational Materials Science Center

In alloys, arrangements of atoms with long-range and short-range order exist due to the interactions acting between the atoms, and this feature affects phase stability and material properties. We are engaged in research on alloy design with the aim of predicting the chemical composition and structures of alloys having properties which are considered necessary. We perform thermodynamic analysis from the viewpoint of atomic arrangement, and have clarified the fact that the long-term creep strength (inherent creep strength) of ferritic steels is controlled by atomic pairs formed by solid-solution manganese (Mn) or molybdenum (Mo) and carbon (C) in the ferrite, as well as the effect of short-range order on the mechanism of deformation in titanium-aluminum (Ti-Al) alloys, etc.

We also carried out an analysis of the ordering phenomena of hydrogen in the body-centered tetragonal (bct) structure of a vanadium-hydrogen (V_2H) compound by the cluster variation method (CVM). The vanadium-hydrogen system is the basic system of bcc-type hydrogen storage alloys, and clarification of its hydrogen ordering mechanism is important for establishing the foundations for material design and material development. As shown in the accompanying figure, hydrogen in the ordered state occupies the O_{Z1} site, but when disordered, it randomly occupies both O_{Z1} and O_{Z2} sites. Because both sites have a bct arrangement in the bct structure of vanadium, an analysis of the order-disorder transition was carried out by a tetrahedral approximation using CVM. The results revealed that the critical temperature for ordering of hydrogen is governed by the effective interaction energy of hydrogen with respect to the a_{2L} bond and vacancies (Va, interstitial site) in the accompanying figure.

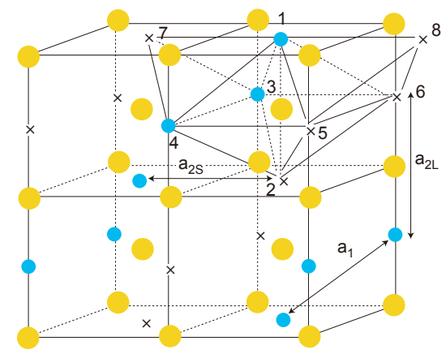

Fig. Six types of basic tetrahedral clusters of V_2H (○: V, ●: hydrogen, (O_{Z1} site), x: empty interstitial site, (O_{Z2} site). Numbers show the positions of the constituent sites of the cluster.

Innovative Center of Nanomaterials Science for Environment and Energy and Computational Science

Takahisa Ohno
Managing Director,
Computational Materials Science Center
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The environmental problems which we face today have their origin in the fact that the total amount of energy used by the human race is approaching the carrying capacity of the planet. From this viewpoint, the development of technologies which reduce loads on the environment is a key issue for sustaining affluent lifestyles.

In response to these conditions, in October 2009, the Innovative Center of Nanomaterials Science for Environment and Energy (ICNSEE), which aims at forming an all-Japan research center with NIMS as its core institute, was selected in the Ministry of Education, Culture, Sports, Science and Technology (MEXT) Program for Development of Environmental Technology Using Nanotechnology.

The ICNSEE conducts basic infrastructural research in order to contribute to the creation of new materials for solving environmental and energy problems. The ICNSEE is targeting materials technologies in connection with energy flows originating from sunlight, that is, energy conversion systems using photovoltaic power generation, photocatalysts, secondary cells, and fuel cells. Here, computational science techniques, together with nanocharacterization technologies, play a key role. The aim is to escape the conventional type of trial-and-error search for materials, and achieve breakthroughs in material technologies related to the environment and energy by understanding surface/interfacial phenomena and establishing control technologies for those phenomena, which are common issues in all energy conversion technologies. This will be accomplished in collaboration with theoretical science and experimental science, utilizing advanced computational science techniques and in-situ measurement technologies.

In energy conversions systems such as photovoltaic power generation, photocatalysts, secondary cells, and fuel cells, diverse heterogeneous interfaces exist. These consist of different material phases such as electrodes, electrolytic solutions, dye molecules, fuels gases, and others. The functions of the system are manifest as a result of phenomena such as charge transfer and ion diffusion which occur at those interfaces.

For example, in dye-sensitized photovoltaic power generation, electron/hole pairs formed by photoexcitation of the dye molecules are responsible for charge separation. Electrons migrate to the electrode surface and move through an external circuit to the opposite electrode, reducing iodine ions, and the reduced iodine ions are transferred through the electrolyte and oxidized by the dye molecules. Light energy is converted to electrical energy by this series of physical and chemical processes. In fuel cells, hydrogen, oxygen, and other fuel gases exchange electrons between the electrode surfaces, converting the chemical energy of the fuel gas to electrical energy (**Fig. 1**).

As these examples suggest, the functions manifested by energy conversion systems are the result of complex multi-scale, multi-physics phenomena involving a large number of physical/chemical processes such as photoexcitation at the surface or interface, electron transfer, charge separation, atomic/ionic transfer, and others. However, at present, these phenomena are not fully understood, and this is a major obstacle to the development of high performance materials. Thus, in order to achieve breakthroughs such as dramatic improvement in energy conversion efficiency, it is important to understand surface/interfacial phenomena and establish technologies for their control utilizing computational science techniques and advanced analytical technologies.

As introduced in pp. 2-5, we are actively engaged in the development of computational science techniques for materials research, elucidation of new physical properties, design of new materials, and related activities. The ICNSEE uses computational science technique to analyze and predict the structures, physical properties, and functions at nano surfaces and interfaces with high accuracy, from the atomic scale to the meso scale, as we work to elucidate the mechanisms of physical and chemical phenomena at diverse nano surfaces and interfaces, including solid-liquid interfaces. As shown in **Fig. 2**, our areas of analysis can be classified as (1) "Electron dynamics" such as charge separation, electron transfer, and redox reactions at nano surfaces and interfaces, (2) "Ion dynamics (atomic dynamics)" such as atomic and ionic diffusion and catalytic reactions, and (3) "Macroscopic dynamics," including the formation of nanostructures in actual materials and the dynamics of atoms in nanostructures.

Concrete research topics using computational science include (1) Photovoltaic materials and photocatalytic materials: Analysis of electronic and structural characteristics of photoexcitation, electron transfer, charge separation, etc. at nano surfaces and interfaces such as inorganic-organic interfaces, solid-liquid interfaces, etc. and (2) Secondary cell materials and fuel cell materials: Analysis of the structural and dynamic characteristics of ion conduction, etc. at nano surfaces and interfaces and in bulk, in materials such as transition metal oxides and others. Based on the results of reliable analyses using an advanced computational environment, as represented by the next-generation supercomputer, our aim is to understand surface/interfacial phenomena, which are fundamental principles common to energy conversion systems, and to construct design guidelines for new materials based thereon.

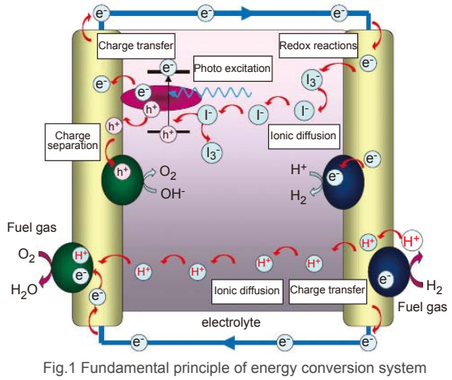


Fig.1 Fundamental principle of energy conversion system

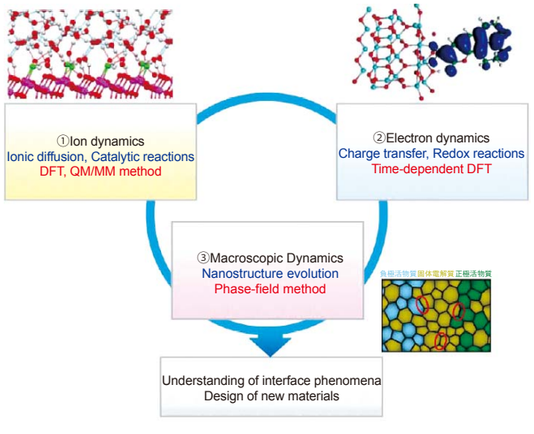


Fig. 2 Computational science approach at the ICNSEE

* Innovative Center of Nanomaterials Science for Environment Energy

Ask the Discoverer The Present, Past, and Future of Carbon Nanotubes

Meijo University **Professor Sumio Iijima**

Carbon nanotubes (CNT) were discovered by Dr. Sumio Iijima in 1991. While consisting entirely of carbon, display a variety of interesting properties. For this reason, CNT have attracted interest as an extremely promising nanotechnology material, and continue to be an object of research by scientists worldwide even today.
In this Special Interview, the discoverer of carbon nanotubes, Dr. Sumio Iijima, discusses the events which led to the discovery of CNT and the barriers to practical application of this substance as a material.

Twenty years have passed since the discovery of CNT in 1991. I think it's fair to say that CNT are now quite well-known.

There are two ways of looking at this. From the viewpoint of pure scientific interest, we can give a passing grade. A large number of researchers are studying CNT, and a great many people have earned doctorates in this field. This is contributing to science. Unfortunately, where practical applications are concerned, there still isn't any talk about profitable work. Because carbon nanotubes are a material, they only have value when they are useful. Somebody has to do this. It may take time, but efforts to break through the economic barrier by university teachers are particularly needed. Likewise, IAIs (Independent Administrative Institution) like AIST (National Institute of Advanced Industrial Science and Technology) and NIMS aren't doing enough in comparison with private companies, probably because this kind of work doesn't result in published papers.

What's interesting, recently, is the fact that this group of materials–fullerenes, nanotubes, and graphene–has successively attracted feelings of expectation. Perhaps news materials will also appear.

A system for smoothly promoting research aimed at realizing materials is inconceivable, I suppose.

I think that's correct. My own idea of materials research is that the extension of the idea of a single individual is the right path, and not everybody joining hands and working together in good fellowship. Research isn't a game, it's a fight with real swords. However, materials research is a bit different from research like biology, where there's no progress without a division of responsibilities.

What kind of applications are you particularly interested in?

Since I have to do something as the pioneer in this field, I'm currently working on use of CNT as an electrode for supercapacitors. We're conducting cooperative research by AIST and private companies to determine whether these can compete with the conventional type. In terms of life time, power density, and certain other properties, we have realized an electrode which is comparable or superior. At present, the problem with CNT is their cost. Activated carbon costs ¥1,000 to several ¥1,000 per kilogram, but the cost of CNT is several ¥10,000 for the same amount. To compete with activated carbon, CNT will have to offer overwhelmingly superior performance.

Now I'd like to ask what led you to the discovery of CNT.

After the invention of the electron microscope in 1932, study of the metallurgy progressed, particularly at Cambridge. Research on displacements and defects of metals was completed, and there was heightened tendency to focus on direct observation of atoms. The historical trend in electron microscopy was from bulk observation silicon and similar substances, to observation of clusters (nanoparticles), and then to nanotubes, individual atoms and molecules, and on to elemental analysis.

I was involved in cluster science, but encouraged by Prof. Kroto (Nobel Laureate in Chemistry), I decided to observe carbon materials. This was just around the time that researchers succeeded in mass synthesis of fullerenes, and the fact that this substance displayed superconductivity caused worldwide excitement. Because Prof. Ando's laboratory at Meijo University had produced carbon by an arc discharge method, I obtained a sample and made microscope observations, which was how I discovered CNT. By accident, as it were.

Even though you call it an accident, it was an accident that required preparation. Wasn't this an example of serendipity?

For this reason, I want to advise young researchers to "resolutely challenge." If you aren't successful, make a graceful retreat. Then go back and make a new start.

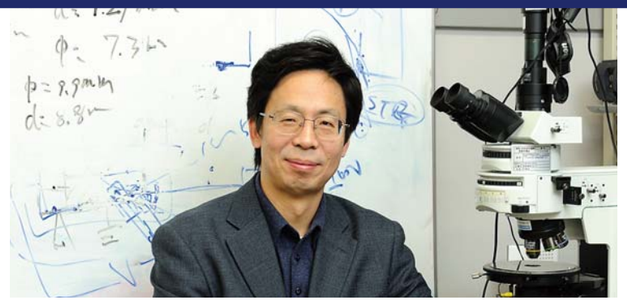
You could say that you have to sow if you expect to reap, or he who shoots oft will hit the mark. Still, if you don't aim at the right place, you won't succeed. . . .

There are 3 types of research in connection with electron microscopes, 1) research that smartly reads the future, 2) creation of devices that others don't have, and 3) doing something different from other people using improved tools (one mustn't go unarmed). My research belongs to the third type.

I hope that young researchers will also "resolutely challenge" their work with such eagerness that they'll want to create their own devices.

Environment-friendly Lead-free Piezoelectric Material Surpassing PZT

Ferroic Physics Group, Sensor Materials Center



Group Leader
Xiaobing Ren

Piezoelectric materials are an important class of energy-conversion materials, which generate electric voltage when mechanical force is applied, and conversely, produce shape change when a voltage is applied (reverse piezoelectric effect). Owing to this smart feature, piezoelectric materials have been used in a great variety of sensors and actuators.

The "king" of these materials is a Pb-containing material PZT, which has been used for over 50 years, and can be found everywhere in our daily life, from lighters, cell phones, personal computers, televisions, and automobiles, to Hi-tech equipment. However, because of the toxicity of Pb, there has been increasing public concern and worldwide legislative laws against the use of Pb-containing products. Unfortunately, despite the effort of many researchers over the last decade, the existing Pb-free materials have been found to show inferior piezoelectricity compared with that of PZT; thus the toxic PZT has been temporally exempted from the restriction of the environmental laws, and our daily life has to rely on the harmful PZT. A big mystery is why Pb-free piezoelectric materials cannot be made as good as PZT.

We have proposed a new theory for achieving high piezoelectricity. The theory suggests that high piezoelectricity can appear in a system having cubic-rhombohedral-tetragonal triple point (which is also a tricritical point); highest piezoelectricity will appear at the composition of a rhombohedral-tetragonal phase boundary (called MPB) **(Fig.1)**. We showed that any system satisfying this condition can yield high piezoelectricity, and PZT is merely one system satisfying this condition. The existing Pb-free systems do not exhibit high piezoelectricity simply because they do not satisfy the above-mentioned condition.

Based on this theory we have designed a new Pb-free piezoelectric ceramic material, BZT-BCT (barium zirconate titanate- barium calcium titanate), which exhibit a triple point in the phase diagram. We found that the MPB composition 50%BCT has an unprecedented high piezoelectricity (piezoelectric constant d_{33} = 620pC/N), which exceeds that of the high-end PZT (PZT-5H). As shown in **Fig.2**, this value is two more times higher than the existing Pb-free materials and even exceed the high-end PZT.

This work provides a hope for developing Pb-free piezoelectric materials which satisfy both environmental requirements and high performance. The theory has the potential for discovering even better Pb-free piezoelectric materials. The present result is expected to have a big impact on the PZT-based piezoelectric industry, as it may lead to the ultimate removal of the current legislative exemption of PZT, thereby we are probably not very far from a "green" piezoelectric world.

References:
W.F. Liu and X.B. Ren, Physical Review Letters, **103, 257602 (2009)**

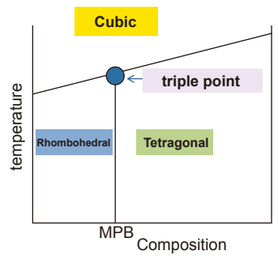


Fig.1 Condition for achieving high piezoelectricity: the existence of a triple point in the composition-temperature phase diagram. Pb-free material is expected to demonstrate a piezoelectricity as high as that of PZT, if satisfying this condition.

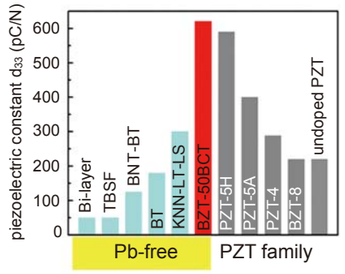


Fig.2 Comparison of piezoelectric constant d_{33} between the new Pb-free piezoelectric material BZT-50BCT (=50%BCT) and the existing Pb-free materials (left side) and PZT family (right side).

Success in Trial Fabrication of BN/Si Heterodiode Solar Cell

Wide Band Gap Semiconductor Group
Advanced Electronic Materials Center
Tokyo Institute of Technology†
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Group Leader
Shojiro Komatsu, Yuhei Satoh†, Daisuke Hirano††, Takuya Nakamura††

Issues in Fabrication of Electronic Device BN Thin Films

BN (sp^3-bonded BN), which has a diamond structure, is an attractive substance from the viewpoint of application, as it possesses hardness second only to that of diamond and is noncombustible. However, sp^3-bonded BN is primarily synthesized by the high pressure method under an extreme environment with a pressure of 10^4 atmospheres and temperature of several 1000°C, and thus was unsuitable for popularization as an industrial material. Therefore, research was carried out on the vapor phase (vapor deposition) method, in which a thin film of BN is fabricated by deposition from a gas containing the raw materials boron and nitrogen by a process using a high energy ion beam or plasma state.

In order to use BN as an electronic material, trace amounts of impurities must be introduced at positions which substitute the constituent atoms of the crystal. This process is called "doping." Doping to create electronic materials has been realized by the high pressure method, and prototype UV-emitting diodes were fabricated by the Nishina Prize-winning NIMS scientist Osamu Mishima and others. However, with the vapor deposition process, formation of the diamond structure and doping tend to be mutually incompatible. As a result, fabrication of BN thin films which function as electronic devices is difficult at present.

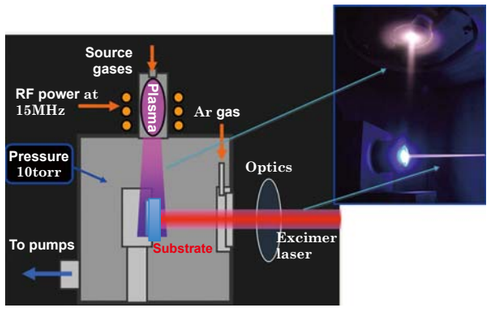


Fig.1 Experimental setup for the preparation of the BN/Si heterodiode structure. The BN film was deposited on a silicon substrate by plasma-assisted laser chemical vapor deposition method. The source gases were diborane (B_2H_6) and ammonia (NH_3), which were dissociated in the plasma and transferred to the substrate as precursor for the deposition. They reacted on the substrate surface to form the BN film. An excimer laser at 193nm activated the surface reactions so as to result in the formation of sp^3-bonded (dense) BN phases.

World's First BN/Si Heterodiode Solar Cell with Excellent Durability

We succeeded in development of a BN thin film which has an sp^3-bonded structure and functions as a semiconductor by an original technique which uses a UV laser in addition to plasma. This is a technique which enables synthesis of new materials by a different reaction route from thermal excitation. With the conventional technique, the surface reaction is excited thermally, but in the newly-developed method, UV laser light is used. A new crystal structure (5H-BN) was also discovered with this technique, and has been registered with the International Center for Diffraction Data. Kobayashi of NIMS also determined the bond structure and space group of 5H-BN, which is essential information for electronic materials. The mechanism by which the high density sp^3-bonding phase forms simultaneously with doping, which is excited/accelerated by UV laser irradiation, is fundamentally interesting, and research is in progress.

As an application of this material, we succeeded in trial fabrication of a hetero-junction solar cell by growing a p-type BN thin film on an n-type silicon substrate. Because the bandgap of BN is too large for terrestrial solar cells, which are used with visible light, in this research, we attempted to use BN in combination with silicon, which has a small bandgap. In the current prototype stage, conversion efficiency is still on the order of 2-4%. However, because BN is an extremely strong material and is also transparent in the visible light region, in the future, it is expected to be possible to realize solar cells for use in severe environments such as outer space, deserts, etc., transparent solar cells which can be applied over window glass, and other innovative applications.

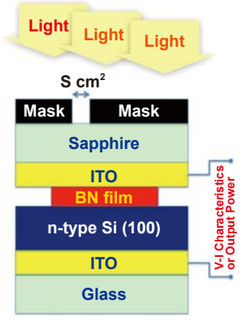


Fig.2 ITO(on sapphire)/BN/Si/ITO (on glass) structure to investigate the photodiode characteristics.

NIMS EVENT REPORT

9th NIMS Forum

"Materials Research Responding to Social Needs"

We have held the NIMS Forum each year since its establishment in order to encourage wide knowledge of the research at NIMS and the results of our works, with particular emphasis on technology transfer.

This year's NIMS Forum was the 9th in the series. With the keywords "Materials research responding to social needs," the Forum introduced nanotechnologies, biotechnologies, and advanced analytical technologies which offer solutions to environmental and energy problems.

Reports were also presented on the establishment and current research of the Innovative Center of Nanomaterials Science for Environment and Energy (ICNSEE), which was launched under the Ministry of Education, Culture, Sports, Science and Technology (MEXT) Program for Development of Environmental Technology using Nanotechnology.


Sukekatsu Ushioda, President of NIMS

The ICNSEE conducts research focusing on four high-priority fields. Because energy conversion systems involve various physiochemical reactions at material surfaces and interfaces, one overarching objective of the ICNSEE is to elucidate the actual condition of these reactions using computational science, and to achieve high efficiency in dye sensitized photovoltaic cells, develop visible light photocatalytic materials, realize high performance secondary cells, and develop materials related to fuel cells.

The followings are the summary of the content of the reports.

Energy and Environmental Materials Realizing Social Needs

1) Innovative Center of Nanomaterials Science for Environment and Energy and the Potential of Computational Science (Takahisa Ohno, Computational Materials Science Center; photo, above)

2) High Efficiency in Dye Sensitized Photovoltaic Cells (Liyuan Han, Advanced Photovoltaics Center; photo, below)

3) Aiming at High Efficiency Secondary Cells (Kazunori Takada, MANA, Nano-Green Field)
4) Development of Materials for Hydrogen Production and Fuel Cells(Chikashi Nishimura, Fuel Cell Materials Center)
5) High Performance in Bismuth-based High Temperature Superconductors and Future Outlook (Hitoshi Kitaguchi, Superconducting Materials Center)

Application of Nanotechnology to Environmental Purification

1) Realizing Ultra-High Speed Filtration of Organic Molecules Using Porous Nanosheets (Izumi Ichinose, Organic Nanomaterials Center; photo)

2) Nano Photocatalysts – Challenging Their Possibilities (Jinhua Ye, Photocatalytic Materials Center)

Progress in Nanotechnology Research

1) Nanostructuring in Atomic Units by Atomic Force Microscopy (Oscar Custance, Advanced Nano Characterization Center; photo)
2) New Optical Functions from Plasmon Nano Resonator (Hideki Miyazaki, Quantum Dot Research Center)
3) Intrinsic Josephson Junctions – Ultra-High Speed/Ultra-Low Power Consumption/3-Dimensionally Integrated Devices Built into Crystal (Takeshi Hatano, Exploratory Nanotechnology Research Laboratory)

4) Development of Nano Probe Sensor for Identification and Detection of Single Molecules (Tomonobu Nakayama, MANA, Nano-Systems Field)

Advanced Analytical Technologies Responding to Materials Research Needs

1) High Field Solid State NMR Breaking Through Pending Issues in Materials Research (Tadashi Shimizu, Advanced Nano Characterization Center; photo)
2) 3-Dimensional Nanostructural Analysis Using Laser Atom Probe (Tadakatsu Ohkubo, Magnetic Materials Center)
3) Visualizing Invisible Semiconductor Interfaces – From Photovoltaic Cells to Next-Generation Semiconductors (Takashi Sekiguchi, Advanced Electronic Materials Center)

Development of Bioresearch

1) Development of Drug Eluting Stent by Hybrid of Medical Metal and Polymer with Bioaffinity (Tetsushi Taguchi, Biomaterials Center; photo)
2) Artificial Bone of Apatite Material with Oriented Continuous Porous Structure (Yasushi Suetsugu, Biomaterials Center)
3) Detection of Biomolecular Recognition by Biotransistor (Yuji Miyahara, Biomaterials Center)

Report on Tsukuba Innovation Arena (TIA) nano (joint project of NIMS, National Institute of Advanced Industrial Science and Technology (AIST), University of Tsukuba, private-sector companies, etc.)

Report
(Kazuo Nakamura, Strategy Office; photo)

nano tech 2010 "International Nanotechnology Exhibition & Conference"

nano tech 2010 was held at the Tokyo Big Sight International Exhibition Center from February 17th (Wednesday) to February 19th (Friday), with exhibitions by more than 600 companies, universities, and public bodies from 20 foreign countries. This event is currently the world's largest nanotechnology exhibition, attracting approximately 50,000 visitors, and has gained worldwide attention.

This year's main theme was "Green Nanotechnology – Sustainability with every nanometer." NIMS won high marks for its unique booth, using innovative ideas in its presentations in the poster exhibition, display of actual items, mini-lectures, and other activities, and was awarded the nano tech Grand Prize 2010 in the Materials Division. NIMS President Ushioda received a plaque from Vice-Chairman Maruyama of the nano tech Executive Committee.

During the 3 days, a constant stream of visitors crowded the NIMS booth. The many visitors posed penetrating questions to the NIMS staff, while also showing keen interest in the actual items and panel displays.

Other events also attracted large audiences, including a mini-lecture session introducing NIMS research, a special symposium on Green Nanotechnology, and a special lecture on the Innovative Center of Nanomaterials Science for Environment and Energy.

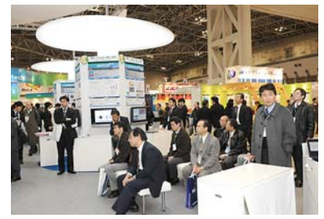
NIMS also learned much through holding the nano tech 2010 Exhibition, and plans to put this knowledge to good use in future research and development and operation of NIMS.


Prof. Eiichi Maruyama (left), Vice-Chairman of the nano tech Executive Committee, and Prof. Sukekatsu Ushioda, President of NIMS.


Special Symposium on Green Nanotechnology: "Efforts of the Innovative Center of Nanomaterials Science for Environment and Energy"
Chikashi Nishimura, Administrative Director, Innovative Center of Nanomaterials Science for Environment and Energy


Scene at the NIMS booth.


Many people visited the NIMS booth.


The audience at the mini-lecture also listened with keen interest.

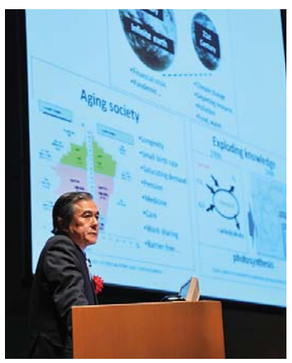
JAPAN NANO 2010 "Challenge of Nanotechnology for Energy and Environment"

JAPAN NANO 2010 was held on February 19th (Friday) as a symposium presenting an overview of recent research and development on nanotechnology for energy and the environment.

The symposium began with a Plenary Lecture by Prof. Hiroshi Komiyama, Director General, Mitsubishi Research Institute, entitled "Smart Strategies for Sustainable Development – Expectations for Nanotechnology", which was followed by lectures on 12 topics, including talks by invited international speakers from the United States, France, and Singapore.

All of the presentations offered visionary new ideas, including "Novel Fuel Cell Catalyst Using Carbon Nanotubes as Material" by Prof. Naotoshi Nakajima of Kyushu University, "Creating New Energy Materials from Commonplace Elements" by Prof. Tatsuya Okubo of the University of Tokyo, and "Production and Use of Cellulose Nanofibers" by Prof. Hiroyuki Yano of Kyoto University, which attracted attention of the large audience.


A scene from Japan Nano 2010



The Plenary Lecture by Prof. Hiroshi Komiyama, Director General of the Mitsubishi Research Institute

The MANA International Symposium 2010

Participants of the Symposium

(Mar. 3-5, 2010) The "MANA (International Center for Materials Nanoarchitectonics) International Symposium 2010" was held jointly with the ICYS (International Center for Young Scientists) at the Epochal Tsukuba International Congress Center. The purpose of the Symposium is to bring together researchers from Japan and other countries and promote research/disseminate information related to the MANA project.

Prof. Toshio Kuroki, the Program Director of WPI (World Premier International Research Center Initiative) and Deputy Director of Research Center for Science Systems at JSPS (Japan Society for the Promotion of Science), and Prof. Gunzi Saito, the Program Officer of WPI and Professor at Meijo University, addressed the opening greetings. A special lecture was presented by Prof. Heinrich Rohrer, Novel Laureate in Physics 1986, and the keynote lecture was given by Prof. C.N.R. Rao, President of Jawaharal Nehru Centre for Advanced Scientific Research in India.

Over the three days, 10 invited lectures were given by the distinguished scientists in the field of nanotechnology and 28 presentations by Satellite Principal Investigators, Independent Scientists, and Scientists at MANA, and ICYS researchers. The presentation by MANA was focused on the four research fields, Nano-Materials, Nano-System, Nano-Bio, and Nano-Green, as well as research at ICYS.

More than 350 participants have joined the Symposium, exceeding the number of the Symposium last year.

NIMS New Partnership

From left: Dr.Mitsuhiro Ebara (NIMS, Senior Researcher), Dr.Takao Aoyanagi (NIMS, Coordinating Director), Prof. Young-Jin Kim (Chonnam National University Hospital, General Director), Prof. Myung Ho Jeong (Chonnam National University Hospital, Director of Heart Research Center)

(Mar. 11, 2010) The NIMS Biomaterials Center signed a memorandum of understanding (MOU) on research cooperation and joint research on "Development of New Materials for Treatment of Heart Disease" with the Heart Research Center, Chonnam National University Hospital, of South Korea. Under this agreement, the Biomaterials Center and Heart Research Center plan to create a system for exchanging researchers, information and research results.

Chonnam National University Hospital performs more than 1,000 coronary angioplasty procedures each year and boasts a success rate of 97.8%. As a key hospital in the Chonnam region, the hospital has recently constructed new facilities, including a Cancer Center and a Diagnostic Imaging Center, among others.

Researchers from NIMS and Chonnam National University Hospital already have a record of obtaining international grants, such as bilateral exchange projects, etc. In the future, the two institutions plan to carry out joint research on drug delivery systems for the treatment of heart disease, gene therapy, and next-generation medical materials for coronary angioplasty.

Hello from NIMS

Canhua Liu
(China)
ICYS-MANA researcher

[Sightseeing at Tomita Farm in Hokkaido last Summer]

After obtaining my Ph.D. at the University of Tokyo four years ago, I joined NIMS and moved to Tsukuba with my wife. She has a job in Tokyo and takes Tsukuba Express to work, so we rent a house very close to Midorino station. In spite of the three hour commute every day, my wife insists on living in Tsukuba not only because of lower house rent, but also because of the better social atmosphere and natural surroundings. On weekends, we often play badminton with friends from NIMS and other institutes including AIST and Tsukuba University. Occasionally, we drive around Tsukuba or the surrounding area for sightseeing and pleasure. We go to Norindanchi and Goraku Garden to see the spring blossoms, to Oarai beach to refresh ourselves in the summer sunshine and sea breeze, to Nikko to enjoy the scarlet maple leaves in autumn, and to Kusatsu and Nasu to ski in winter. Late this past March, we went to Sano Natural Park to hike and view the Katakuri (dogtooth violet) flowers, followed by shopping at Sano Outlet. With such frequent excursions we really enjoy our lives here in Tsukuba.

[Viewing Katakuri flowers at Sano Natural Park this past March]

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