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# Nanotechnology Giving a New Shape to Environmental Remediation

Project on Research and Development of  
Innovative Materials for Environmental Remediation

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## Project on Research and Development of Innovative Materials for Environmental Remediation

Soil, water, and the atmosphere. Without these, human life would be impossible, yet we are constantly sacrificing these essential natural blessings.

Radiation spilled by the accident of Fukushima Daiichi Nuclear Power Plant that caused by East Japan Earthquake has contaminated much seawater, air, and soil, and even if decontamination work is carried out, treatment of the waste generated in this process will still be a problem.

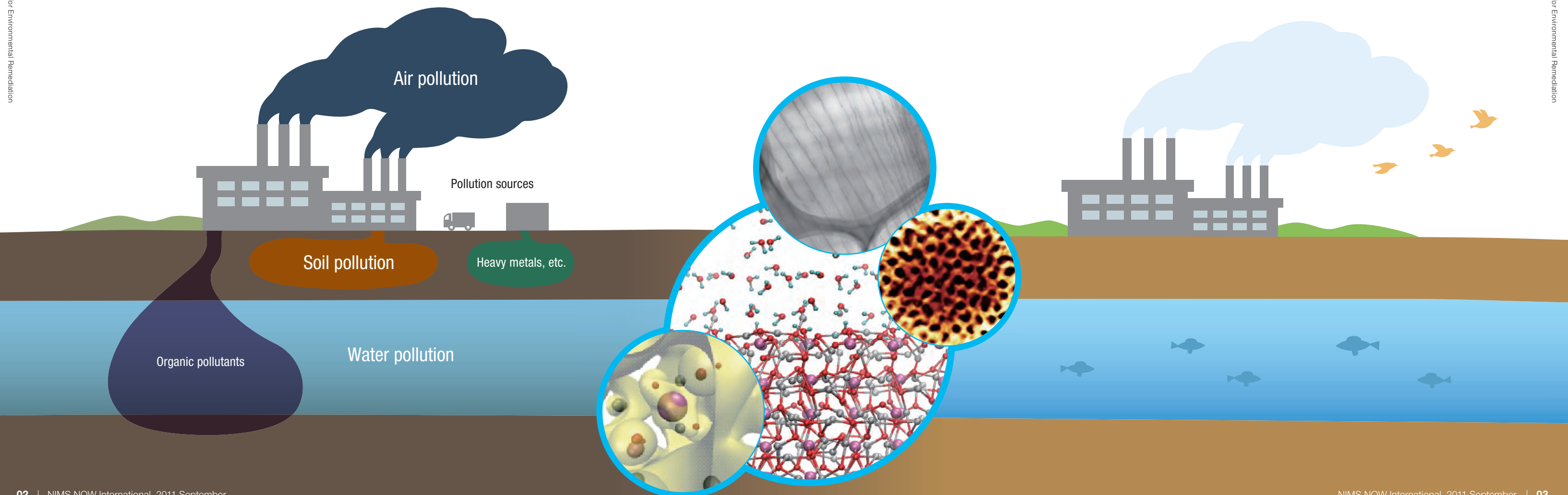
These issues are not limited to radiation. The problem of environmental pollution involves an extremely large number of harmful substances which are a familiar part of our everyday lives, such as heavy metals, organic compounds, CO, NO<sub>x</sub>, and others.

Up to the present, a wide range of methods have been used to remove pollutants. However, there is not a single technology which can solve all kinds of environmental pollutions. The approach which NIMS is pursuing is embodied in the "Project on Research and Development of Innovative Materials for Environmental Remediation."

From the viewpoint of nanotechnology, pollution can be considered to be a surface/interfacial phenomenon. It is thought that harmful substances adhere not only to the surfaces which are visible to the eyes, but also to the surfaces and interfaces of particles and molecules. For this reason, nano-level catalytic action (photocatalyst [P.4](#), metal catalyst [P.5](#)) and mesoporous materials [P.6](#) have become research themes. Moreover, natural detoxification processes for harmful substances are an essential part of our planetary system, and we are establishing concepts and processes for [geomaterials P.7](#) modeled on these natural processes.

We are also working toward theoretical interpretations of the nano-level mechanisms of these surface and interfacial phenomena [P.8](#) and will return this knowledge to more efficient materials development.

NIMS brings together pioneering intelligence to address one of the great issues of our times – realizing a sustainable society.





## Research on Advanced Photocatalytic Materials

Unit Director, Environmental Remediation Materials Unit,  
Environment and Energy Materials Division

Jinhua Ye

### Environmental remediation materials and photocatalysts

Photocatalytic materials are materials which make it possible to decompose and remove harmful organic substances, produce hydrogen from water, and convert carbon dioxide to methane and other useful chemical resources by using the reduction action of electrons and the oxidation action of holes excited by irradiation with light.

Using only the energy of light, these photocatalytic materials can contribute to solving increasingly complicated, diversified, and globalized problems such as global warming due to increased CO<sub>2</sub> in the atmosphere, atmospheric pollution by exhaust gas and flue gas, problems of water and soil pollution due to the discharge of untreated industrial effluents into rivers, and disruptions of the ecosystem by endocrine disrupters, among others. We can say that these materials are truly one ultimate low environmental impact purification/remediation technology.

### Success in the development of visible light photocatalytic materials

The greatest challenge with photocatalysts is limitations on their use environments. Because conventional photocatalytic materials only display activity under ultraviolet light (wavelength: <400 nm), their efficiency and applications had been limited.

Therefore, in the NIMS 2nd Five-year Plan, we promoted the development of visible light responsive photocatalysts and research to realize higher functions in those materials.

To date, we have succeeded in the development of new photocatalyst materials which respond not only to ultraviolet light but also to visible light by controlling the band structure of oxide-based

semiconductor materials. Together with this, we have also carried out fundamental and basic research aimed at theoretical and experimental elucidation of the controlling factors in photocatalytic efficiency and realization of high performance in photocatalysts applying nanotechnology.

As a result, as research achievements during the 2<sup>nd</sup> period, we developed a large number of new high efficiency/visible light responsive photocatalytic materials, and also developed and applied nano-structure fabrication technologies for realizing high functionality in those materials.

In addition, in research on the reaction mechanisms of photocatalysts, we obtained important principles for the development of advanced photocatalyst materials, for example, by clarifying the relationship between band structure and photocatalytic activity, elucidating the surface adsorption structure and identifying the dissociative adsorption conditions for water molecules, etc.

One noteworthy achievement, which occurred in material design/development based on a new strategy focusing on the mobility of excited carriers, was the discovery of the material Ag<sub>3</sub>PO<sub>4</sub>, which has oxidizing power comparable to the quantum yield of photosynthesis in plants, even though this is an inorganic material.<sup>1)</sup>

In the theoretical aspect, the fact that the high activity of Ag<sub>3</sub>PO<sub>4</sub> is caused by its unique electronic structure was clarified by first-principles calculations.<sup>2)</sup> Referring to recent theoretical predictions (for details, see p. 8), we succeeded in developing a technique which enables selective growth of the {110} crystal plane, which has high surface energy (Fig. 1), and in achieving higher functionality in Ag<sub>3</sub>PO<sub>4</sub> materials by fabricating a nano hetero core shell structure with a heterogeneous material.<sup>3-4)</sup>

### Strengthening collaboration with theoretical calculations

In the future, we plan to promote continuing related research in a form that further develops our achievements to date. In particular, we will strengthen our collaboration with theoretical calculations in order to design and create excellent materials based on knowledge of surface and interfacial properties utilizing computational science.

We intend to elucidate the surface and interfacial oxidation/reduction reaction paths by a tie-up between experimental science and computational science. We also aim at construction of innovative materials systems for effective decomposition/removal of harmful substance and CO<sub>2</sub> photoreduction/recycling by hybridization with other environmental remediation element materials, such as adsorbents, mesoporous materials, intermetallic compound catalyst materials, etc., which are objects of research and development in other sub-themes.

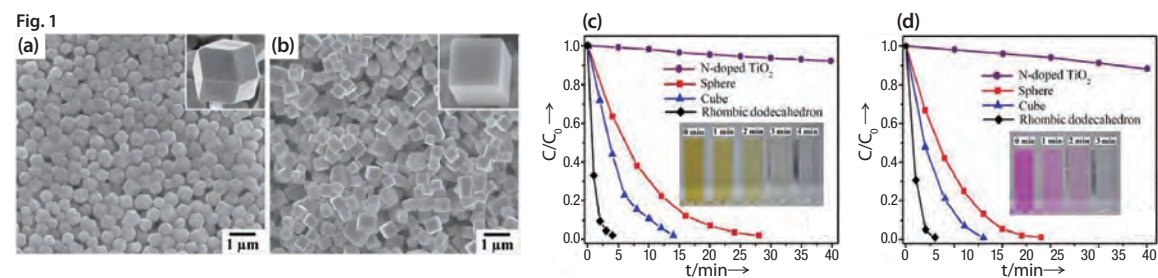
The research in this sub-theme is expected to make an important contribution to realizing "Environmental remediation and restoration technologies," which is the target of the project "Research and development of innovative materials for environmental remediation."

1) Z.Yi, J.Ye, N.Kikugawa, T.Kako, et al, *Nature Mater.*, 9, 559-564, 2010.

2) N.Umezawa, S.Ouyang, and J.Ye, *Phys. Rev. B* 83, 035202, 2011.

3) Y. Bi, S. Ouyang, N. Umezawa, J. Cao, and J. Ye, *J. Am. Chem. Soc.*, 133, 6490-6492, 2011.

4) Y. Bi, S. Ouyang, J. Cao, and J. Ye, *Phys. Chem. Chem. Phys.* 13, 10071-10075, 2011.



**Fig. 1** SEM images of Ag<sub>3</sub>PO<sub>4</sub> nano-single crystals with controlled growth planes. (a) {110} nano dodecahedron, (b) {100} nano cube (c) comparison of activity in MO dye decomposition under visible light irradiation, and (d) comparison of activity in RhB dye decomposition under visible light irradiation. In both cases, the {110} nano dodecahedron showed the highest activity.

## Research and Development of Impurity Poisoning-Resistant Intermetallic Compound Catalysts

Catalytic Materials Group, Environmental Remediation Materials Unit,  
Environment and Energy Materials Division

Hideki Abe

### Two problems of metal catalysts used in exhaust gas purification

One of the materials which is at the heart of environmental and energy technologies, represented by automobile exhaust gas purification and fuel cells, is catalytic materials with metals as their active center, namely, metal catalysts. Metal catalysts demonstrate an excellent ability in chemical reactions involving small molecules, such as the purification reaction of NO<sub>x</sub> (nitrogen oxide) molecules and the electrochemical oxidation reaction of methanol molecules. We are engaged in research and development of high performance metal catalyst materials for the main purpose of purification of fossil fuel engine exhaust gases.

The existing metal catalysts have two unsolved problems. One is the large amount of precious, or noble metals used. In many cases, noble metals such as platinum, palladium, rhodium, etc. are used as the active substance in metal catalysts. In fact, nearly 90% of annual production of rhodium is consumed as a catalyst material for automobile exhaust gas purification. The noble metals are a representative example of "rare metals," meaning metals with low production volumes and geographically limited production areas. In the future, increasing calls to reduce consumption of noble metals in catalyst materials are expected.

The second issue is the problem of impurity poisoning. One weak point of metal catalysts is "impurity poisoning," which means the catalytic reaction is impeded by surface adsorption of impurity chemical species. Actually, it is known that palladium, which is widely used as an exhaust gas purification catalyst, easily loses its activity due to surface adsorption of the sulfur dioxide contained in exhaust gas. Thus, future metal catalysts must not only have excellent activity in the object reaction, but must also have high resistance to impurity poisoning.

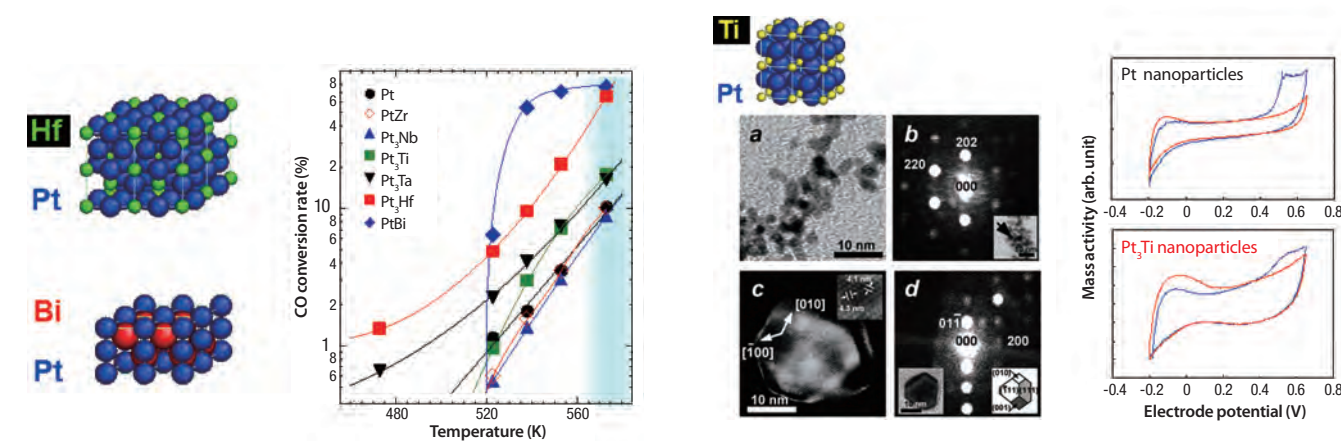
### Toward realization of high performance, noble metal-free catalysts

In this sub-theme, we are taking on the challenge of solving the two above-mentioned problems of metal catalysts by using "intermetallic compounds" as catalytic active substances. Intermetallic compounds consist of combinations of metallic elements other than noble metals, and have a specific atomic order and electronic structure different from both elemental metals and alloys.

First, by collaboration with "Theoretical design of environmental remediation materials," we will ascertain the correlation between the atomic order/electronic state of the catalyst surface and the strength of adsorption of the reactive chemical

species, and search for new catalytic compounds which simultaneously realize a low content of noble metals and high impurity resistance (Fig. 1). Finally, our aim is to realize "noble metal-free catalysts" which render the conventional noble metal-system catalyst materials obsolescent.

Second, utilizing an independently-developed liquid phase synthesis method, we intend to realize high performance metal catalysts which are superior to the conventional noble metal system catalysts by dispersion/support of catalyst compound nanoparticles on the surfaces of "photocatalyst materials," "mesoporous materials," and "geomaterials" (Fig. 2).



**Fig. 1** Activities of various intermetallic compound exhaust gas purification catalysts.

**Fig. 2** Images of intermetallic compound nanoparticles created by the liquid phase synthesis method (left) and their impurity poisoning resistance (right).

**Jinhua Ye** Ph.D. Completed the doctoral degree at the School of Science, the University of Tokyo in 1990. Dr. Ye was appointed to Managing Director of the NIMS Photocatalytic Materials Center in April 2006 and has been a Principal Investigator at the International Center for Materials Nanoarchitectonics (MANA) since 2007. She has also held a concurrent post as Professor at the Hokkaido University-NIMS Joint Graduate School Photo Functional Materials Laboratory since 2008. She was appointed to her present position as Unit Director, Environmental Remediation Materials Unit in 2011. Her research fields are research and development of photocatalyst materials and their application to the environmental and energy fields.

**Hideki Abe** Ph.D. Withdrew from the doctoral course in chemistry at the School of Science, University of Tokyo in 1995 and joined the National Research Institute for Metals (NRI, now NIMS) in the same year. Dr. Abe is currently a Senior Researcher at NIMS.



## Development of Functional Mesoporous Materials

MANA Independent Scientist  
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**Yusuke Yamauchi**

### Satisfying both reduced use of platinum and high activity

Our group is developing material technologies for reduction/substitution of rare metals in order to contribute to solving the serious global-scale problems that we currently face, represented by environmental, energy, and resource problems. In particular, platinum (Pt), which is a noble metal, is known to display high activity as a catalyst and is widely used in electrodes of batteries, etc. and as an industrial catalyst (in the case of automobiles, as a purification catalyst for exhaust gas). If the surface area of platinum is increased, its exposed surface also increases, resulting in extremely strong activation of the catalytic function. However, because world reserves of platinum are small and Pt is an extremely expensive metal, how to maintain/realize high activity with a small amount of platinum (or with a substitute metal) will become increasingly important in the future.

### Mesoporous platinum holds the key

The key technology is a process for producing mesoporous platinum. In the synthesis of general mesoporous materials, first, a regular assembled structure is created by assembling surfactant molecules, an inorganic reaction is then performed around the assembled structure, which serves as a

mold, solidifying the target substance, and finally, the surfactant is removed. This concept of synthesis of mesoporous substances has been applied to a wide range of compositions, and diverse functional porous materials have been reported from many countries. However, there have been few examples in which the skeleton was a metal. In order to synthesize mesoporous metals, the conventional concept of synthesis of mesoporous substances must have been greatly expanded.

Under the NIMS 2nd Five-year Plan, we succeeded in synthesis of mesoporous metals with large surface areas using various surfactants and also reported control of the material morphology, not limited to nanoparticles, but also including thin films, monoliths, nanoparticles, fibers, and others. These materials have larger surface areas than the conventional platinum black or carbon supported platinum, and were found to have activity several 10s of times greater in methanol oxidation capacity.

For the 3rd Five-year Plan, our aim is to improve activity by one order by applying various surfactants and further refinement of the synthesis conditions.

Another area of research is mesoporous silica. Mesoporous silica is used in adsorption of harmful substances. The reader may know that zeolite and similar materials are being used in the cleanup of contaminated water at the Fukushima nuclear power plant and

elsewhere, but zeolite has the drawback of also adsorbing various metal species.

### Targeting – an important focus of future research

We believe that selectivity in adsorption of only the target harmful substance will become the most important issue in the future. In the synthesis of mesoporous substances, nanometer order functional building blocks which show strong interaction with designated harmful substances are used as the starting material, and the mesoporous substance is assembled in a skeleton by using those substances. This design concept makes it possible to manifest the desired adsorption function by high order advanced design of the starting molecule which will be used as the building block.

At present, research on mesoporous materials is developing over a wide range, from synthesis and structural analysis to various types of applied research, beginning with use in catalyst supports, adsorbents, optical materials, and biomedical applications. In the future, the discovery of remarkable examples of application of mesoporous materials will lead to further breakthroughs in mesoporous materials. Our group will narrow its target to environmental purification applications which make the best use of the distinctive features of the mesoporous structure such as large surface area and uniform pore size.

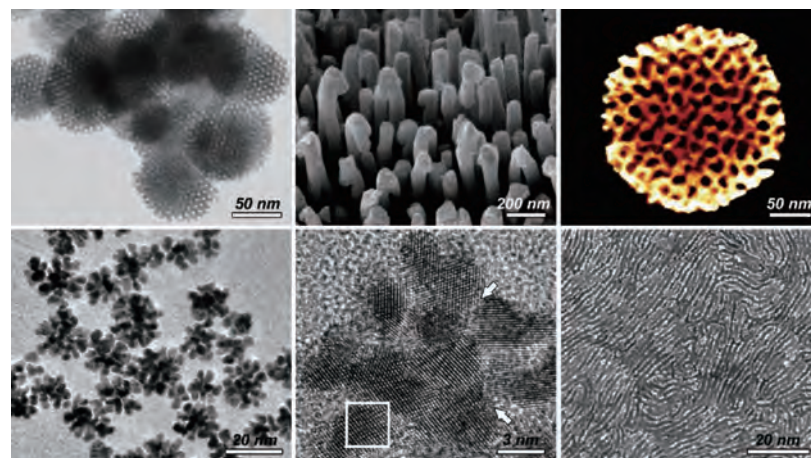


Figure: Library of platinum nanostructures developed to date.

**Yusuke Yamauchi** Dr. Eng. Graduated from the Department of Applied Chemistry, School of Science and Engineering, Waseda University in March 2003 and completed the doctoral course at the Graduate School of Science and Engineering, Waseda University in March 2007. Dr. Yamauchi joined NIMS in April 2007 and has been MANA Independent Scientist since October 2007. At present, he is a Japan Science and Technology Agency (JST) PRESTO Researcher and holds a current position as Guest Lecturer in the Faculty of Science and Engineering at Waseda University.

## Possibilities of Geomaterials

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### Geomaterials – Perfect circulation with the lowest environmental load

In order to overcome the enormous damage caused by the Great East Japan Earthquake and Tsunami and Fukushima No. 1 Nuclear Power Plant problem, we also are made to consider what we should do as researchers in the field of materials science.

While nature may present a threat to us, as the earthquake and tsunami demonstrated, it also teaches us various kinds of wisdom, as can be verified from the 4.6 billion year history of our planet. That wisdom is “perfect circulation and high functionality with the minimum load on the environment.”

Understanding these lessons as science, we are attempting to design and develop high functional materials with ultra-low environmental load by imitating, technologizing, and utilizing the constituent rocks and minerals (geomaterials) which make up the planet and their structures as one element technology in environmental remediation materials.

For this, we will investigate the phyllosilicates, layered double hydroxides (LDH), and others which consist of ubiquitous elements and non-toxic elements, with the aim of greatly enhancing their performance by studying their compositions and physical properties, optimizing their nanostructures, and developing nano-composites from both the experimental and theoretical aspects.

We also hope to contribute to practical application of environmental remediation technologies by hybridization of the adsorption properties and other properties of geomaterials with other technologies, such as photocatalyst

materials, mesoporous materials, etc.

For the Fukushima No. 1 Nuclear Power Plant problem, a technology for removal of radioactive substances from agricultural soil etc. is already developed for “Establishment of foundation for countermeasures against environmental impacts of radioactive substances” under the leadership of the Council for Science and Technology Policy.

### Application of geomaterials to environmental remediation

While developing a radioactive substance removal technology, we are also engaged in research focusing on layered materials such as phyllosilicate smectite, LDH, and others, paying our respects to the wisdom of the Earth. We are working on issues including synthesis and characterization, manifestation of adsorption properties and catalytic capacity, and creation of nano-composites with organic materials and polymers. Concretely, our research comprises the following 4 themes.

1. Focusing on combinations of phyllosilicates and LDH with semiconductor ZnO, we optimized the synthesis conditions for phyllosilicates and LDH containing Zn in their structures, and discovered manifestation of photocatalytic properties such as decolorization and decomposition of rhodamine dye, etc (Fig. 1). Because of their affinity with organic substances and high adsorption capacity, it is expected to be possible to achieve improved efficiency in decomposition of harmful organic substances and thereby make a major contribution to global environmental problems.
2. We discovered that an anion-exchangeable

chloride-type LDH (Cl-LDH) can be obtained by decarbonation of carbonate-type LDH (CO<sub>3</sub><sup>2-</sup>-LDH), which has had only limited application as an anion exchange material, at room temperature and in a short time using a weakly acidic solution of an acetate buffer and NaCl. The decarbonation of CO<sub>3</sub><sup>2-</sup>-LDH is a key reaction for recycling of anion exchange material (Fig. 2). In particular, high expectations are placed on application of this anion-exchangeable LDH as a water purification material, taking advantage of anion affinity ranking, which is different from anion exchange resins, and its high affinity for anions such as fluoride, borate, arsenate, etc.

3. We succeeded in producing nanosheets (delamination phenomenon) of various types of layered silicates and control of their surface properties and were able to promote nano-compositization with polymers (Fig. 3). Furthermore, we also succeeded in improving their functionality and properties (mechanical strength, gas barrier, etc.) and demonstrated the possibility of their application to new photocatalyst material/structural material fields.
4. We succeeded in forming monodisperse nanoparticles of layered silicates by applying a hybrid atomization method used in producing micro-sized spherical metal particles to layered silicates, and demonstrated the possibility of improving their specific surface area, adsorption properties, etc.

By investigating these themes, focusing on the old, yet new “geomaterials,” we believe that we can contribute to solving global environmental problems with diverse, complex aspects, and can thereby contribute to a sustainable society.

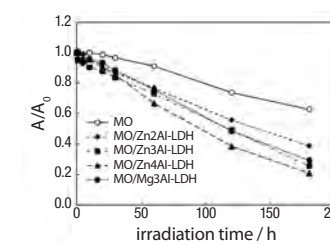


Fig. 1 Photodegradation of the organic dye, methyl orange, and the complex of methyl orange-LDHs with various Zn/Al ratios, monitored as the normalized absorbance vs irradiation time.

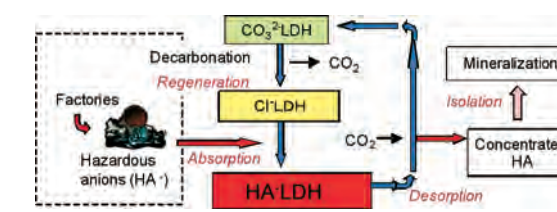


Fig. 2 Application of LDH as an adsorbent of hazardous anion.

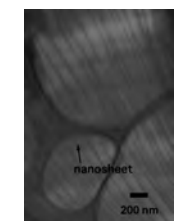


Fig. 3 TEM image of epoxy/mica nanocomposite

**Hirohisa Yamada** Dr. Sci. Completed the doctoral course at Graduate School of Science, Kyoto University and joined the National Institute for Research in Inorganic Materials (NIRIM, now NIMS) in 1986. Prior to his present position, Dr. Yamada worked in the NIMS Ecomaterials Research Center and Photocatalyst Materials Center as a Group Leader. / **Kenji Tamura** Dr. Sci. Completed the doctoral course at Graduate School of Science, Hokkaido University and joined Showa Denko K.K. in 1990. Joined NIMS in 2003 and is currently a Senior Researcher. / **Nobuo Iyi** Dr. Sci. Graduated from the Faculty of Chemistry, Kwansei Gakuin University and joined the NIRIM in 1977. At present, he is engaged in research on the synthesis and reaction of layered double hydroxides (LDH). Dr. Iyi is a Senior Researcher in the Geomaterials Group. / **Kazumi Minagawa** Dr. Eng. Graduated from Department of Mechanical Engineering No. 2, Tokyo Denki University and received his doctorate from Graduate School of Engineering, Kyushu University. Joined the NIRIM in 1975. Prior to his present position, Dr. Minagawa worked in the NIMS Ecomaterials Research Center and Structural Metals Center as a Senior Researcher. / **Shigeru Suehara** Dr. Eng. Graduated from Waseda University. Member of the Material Properties Theory Group, Computational Materials Science Unit. Dr. Suehara is engaged in computational research centering on first-principles MD simulation.



## Outlook for Theoretical Design of Environmental Remediation Materials

Catalytic Materials Group, Environmental Remediation Materials Unit,  
Environment and Energy Materials Division

Naoto Umezawa

### The functions of environmental remediation materials are surface and interfacial phenomena

The functions of environmental remediation materials are characterized by the common keywords, surface and interfacial phenomena. Understanding those phenomena makes us possible to design better materials. However, because surface and interfacial chemical reactions proceed through complex processes, such as electron transfer and the formation of intermediates, elucidation of the mechanisms involved is extremely difficult. Therefore, it is necessary to construct theoretical models which extract only the critical essence by focusing on the property of interest. We are working to elucidate the key mechanism by eliminating the side issues in complex phenomena based on the concept called "first-principles modeling," which combines the type of model described above and first-principles calculations. Furthermore, we also reiterate predictions and verifications to accelerate development by close collaboration with experimental researchers, with the purpose of predicting better materials based on the knowledge obtained. This article introduces the results to date.

### Understanding the band structure of silver-based oxides

Under the NIMS 2nd Five-year Plan, we investigated the source of the high photo-oxidation force of silver phosphate,<sup>1)</sup> which had been discovered by the NIMS

Photocatalytic Materials Center. We performed first-principles calculations for silver phosphate ( $\text{Ag}_3\text{PO}_4$ ), silver oxide ( $\text{Ag}_2\text{O}$ ), and silver niobate ( $\text{AgNbO}_3$ ), and succeeded in determining the unique electronic structure of  $\text{Ag}_3\text{PO}_4$  by comparing the electronic structures of these silver compounds.<sup>2)</sup>

The band structures of these silver-based oxides are shown in Figure 1. With  $\text{Ag}_3\text{PO}_4$ , it can be understood that the bottom of the conduction band is widely dispersed because it is formed by an Ag s orbital, and this is an effective shape for electron transfer (Fig. 1(a)). The contour surface of the wave function shown on the right side of the figure suggests that this state is itinerant. This means that electrons are readily transferred in any direction and is considered to contribute to high photocatalytic activity.

In  $\text{Ag}_3\text{PO}_4$ , P and O are strongly bound, suppressing hybridization of Ag d and O p. Therefore, virtually no localized level originating in the Ag d orbital appears at the bottom of the conduction band. Instead, it was found that a band with large dispersion is formed due to hybridization of Ag s – Ag s, and the effective mass of electrons is small and isotropic in comparison with other silver-based photocatalysts.

On the other hand, the bottom of the conduction band of  $\text{Ag}_2\text{O}$  is localized because an Ag d – O p anti-bonding state has formed (Fig. 1(b)). In the case of  $\text{AgNbO}_3$ , it can be understood that the d orbitals of Nb are distributed anisotropically, limiting the directions in which electrons can move (Fig. 1(c)).

From these results, we concluded that the

isotropic, itinerant band structure at the bottom of the conduction band of  $\text{Ag}_3\text{PO}_4$  contributes to high photocatalytic activity. Although hole carriers are mainly related to the oxidation reaction, recombination with holes is suppressed by the rapid movement of photoexcited electrons formed in the bulk to the surface. Therefore, if the effective mass of electrons can be decreased, it is considered that this will in effect accelerate the oxidation reaction. Moreover, a comparison of  $\text{Ag}_3\text{PO}_4$  and  $\text{AgNbO}_3$  revealed that the effective mass of holes is also smaller in  $\text{Ag}_3\text{PO}_4$ , and this contributes to high oxidation activity.

### Extracting higher activity from silver phosphate

In order to extract higher activity from  $\text{Ag}_3\text{PO}_4$ , we also attempted to expose a designated plane orientation.<sup>3)</sup>

Catalytic activity is deeply related to surface energy and generally increases due to instability in planes with high surface energy.

In the case of  $\text{Ag}_3\text{PO}_4$ , our calculations showed that the surface energies of the (110) plane and the (100) plane are 1.31 J/m<sup>2</sup> and 1.12 J/m<sup>2</sup>, respectively, surface energy being larger in the (110) plane. In fact, it has been confirmed experimentally that rhombic dodecahedron crystals, which have an exposed (110) plane, have higher photocatalytic activity than cubic crystals, in which the (100) plane is exposed, and our work provided a clear interpretation of this experimental result.

Furthermore, a calculation of the surface

energy when oxygen deficiency (reduction) was introduced in these respective planes and comparison of their stability with the ideal surface suggested theoretically that oxygen deficiency can occur comparatively easily in the (110) plane (Fig. 2). This is also considered to contribute to high activity.

As outlined above, an understanding of the source of photocatalytic activity is possible to some extent based on the properties of the bulk and surface, but more powerful design principles can be obtained from a detailed understanding of the surface chemical reaction process at the atomic level. The computational science technique used for this purpose is "molecular dynamics (MD) simulation." At present, a simulation of the oxidation reaction of water at the surface of  $\text{Ag}_3\text{PO}_4$  is in progress (Fig. 3), and an elucidation of the reaction path is expected in the near future.

### Bandgap control using surface contact of nanoparticles

As one example of surface/interfacial design, this section introduces a bandgap control technique using surface contact between nanoparticles.

In order to form photocatalysts with high activity, it is necessary to amplify absorption of visible light, which accounts for more than 40% of sunlight, by adjusting the bandgap to an appropriate width. In this research, we attempted to develop a new type of visible light sensitive photocatalyst by modifying the band structure by aggregation of photocatalytic

nanoparticles.<sup>4,5)</sup>

Surface contact between nanoparticles was expressed by a simple model in which two surfaces were placed in confrontation, and the effect of aggregation was investigated theoretically. Fig. 4(a) shows a model in which ideal surfaces of CdS (110) were arranged with mirror symmetry, and Fig. 4(b) is the model when sulfur deficiency was introduced at the contact interface in (a). From a density-functional calculation, it was found that structural relaxation results in the formation of a Cd-Cd bond at the contact interface when a sulfur deficiency is introduced (Fig. 4(b)).

The density of states (DOS) of the respective models are shown in Fig. 4(c) and (d). In the case of simple confrontation of the ideal surfaces, the same bandgap as in the bulk was obtained (Fig. 4(c)). However, when the sulfur deficiency was introduced, an interface state formed in the gap, and this effectively narrowed the bandgap (Fig. 4(d)).

From the density distribution of electrons occupying one of the gap states, it is understood that it mainly consists of the Cd-Cd bonding state (Fig. 4(d)). Formation of the Cd-Cd bond was also supported by a calculation of formation energy and experimental results, including XPS and others.

The fact that visible light absorption is amplified by aggregation of CdS nanoparticles, resulting in enhanced photocatalytic activity, has also been confirmed experimentally, demonstrating the appropriateness of the model.<sup>4)</sup> A similar effect has also been observed with  $\text{TiO}_2$ .<sup>5)</sup>

In the case of isolated nanoparticles, the

bandgap increases due to the effect of quantum confinement (QC). However, in the case of aggregated nanoparticles, the bandgap is determined by competition between the QC effect and bonding and anti-bonding states in the gap formed by surface contact between the particles. If the bandgap of the aggregated nanoparticles can be controlled by the particle size of the constituent particles, this will provide a simple technique for enhancing the visible light absorption efficiency. Thus, these are important results which opened a new route to bandgap control.

This article has introduced the theoretical approach and its results in examples of photocatalysts. The NIMS 3rd Five-year Plan, which began in April, expands the objects of research to environmental remediation materials as a whole, based on a unified understanding of surface and interfacial phenomena, with the aim of contributing to the development of excellent materials capable of responding to the needs of the times.

1) Zhiguo Yi, Jinhua Ye, Naoki Kikugawa, Tetsuya Kako, Shuxin Ouyang, Hilary Stuart-Williams, Hui Yang, Junyu Cao, Wenjun Luo, Zhaosheng Li, Yun Liu, and Ray L. Withers, *Nature Materials* 9, 559 (2010).

2) Naoto Umezawa, Shuxin Ouyang, and Jinhua Ye, *Phys. Rev. B* 83, 035202 (2011).

3) Yingpu Bi, Shuxin Ouyang, Naoto Umezawa, Junyu Cao, and Jinhua Ye, *J. Am. Chem. Soc.* 133, 6490 (2011).

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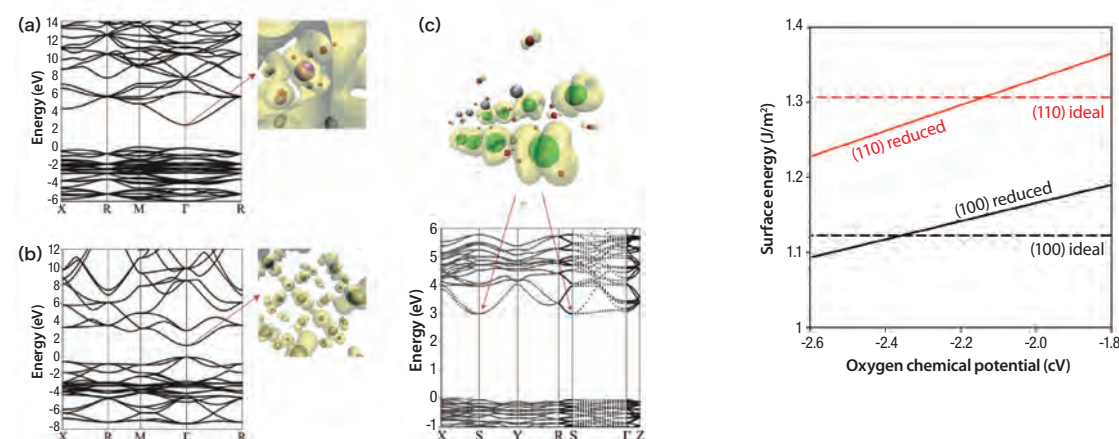


Fig. 1 Band structures of silver-based oxides and wave functions of the bottom of the conduction band.<sup>2)</sup> (a)  $\text{Ag}_3\text{PO}_4$ , (b)  $\text{Ag}_2\text{O}$ , and (c)  $\text{AgNbO}_3$ .

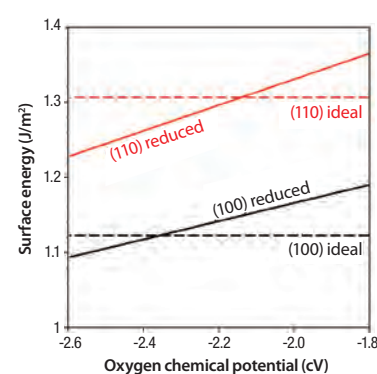


Fig. 2 Results of calculation of the surface energy of the ideal plane and oxygen deficient (reduced) plane at the respective plane orientations of the  $\text{Ag}_3\text{PO}_4$  (110) plane and (100) plane.<sup>3)</sup> It can be understood that not only is the surface energy of the (110) plane comparatively high, but the value of the oxygen chemical potential when the oxygen reduced plane stabilizes is also high, indicating that oxygen deficiency occurs easily.

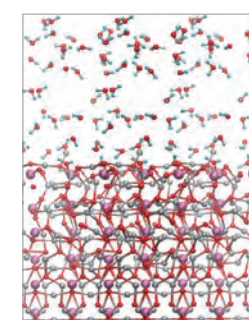


Fig. 3 Simulation of the chemical reaction at the interface between  $\text{Ag}_3\text{PO}_4$  surface and water, showing the positions of atoms of Ag (silver), P (magenta), O (red), and H (cyan), respectively.

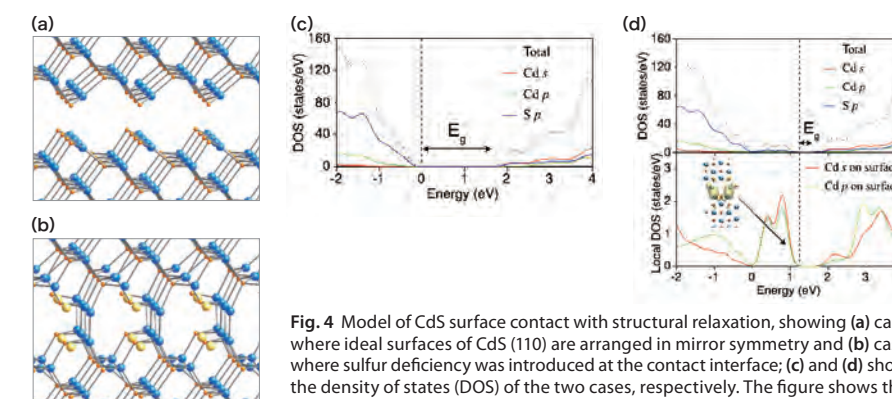


Fig. 4 Model of CdS surface contact with structural relaxation, showing (a) case where ideal surfaces of CdS (110) are arranged in mirror symmetry and (b) case where sulfur deficiency was introduced at the contact interface; (c) and (d) show the density of states (DOS) of the two cases, respectively. The figure shows the positions of atoms of Cd (blue) and S (orange) and sulfur deficiencies (yellow).

**Naoto Umezawa** Ph.D. Completed the doctoral course in the Department of Physics, University of Tokyo Graduate School of Science in 2003 and was employed as a Postdoctoral Scientist at the University of Southern California in April of the same year. Joined NIMS as a Special Researcher in 2004 and was appointed to his present position as Senior Researcher at NIMS in 2008. In 2007, he was a Visiting Scientist at the University of California at Santa Barbara. He also received the 29th Japan Society of Applied Physics Best Original Paper Award in 2007. His research field is materials design using first-principles calculation.



## Optical Control of Nuclear Spins in Solid-state NMR Quantum Computers

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High Magnetic Field Station, Research Network and Facility Services Division  
**Shinobu Ohki**

Group Leader, High Field NMR Group, Nano Characterization Unit,  
 Advanced Key Technologies Division  
**Tadashi Shimizu**

### Quantum computers with nuclear spins

For decades, nuclear spins (the rotations of stable nuclei) in materials have been utilized as probes in nuclear magnetic resonance (NMR) and magnetic resonance imaging (MRI), which are now indispensable in a variety of fields ranging from physics, chemistry, biochemistry, to medical treatments. Recently, the initiative has been created to devise a quantum computer\* using nuclear spins in materials. The scheme, called "NMR quantum computer", is now known as one of the most advanced testbeds for quantum computations; in fact, simple calculations have been demonstrated with several qubits in organic molecules in solutions. Nevertheless, the quantum computers can exert their ability only in large-scale problems with much larger number of qubits; i.e., the scale-up is an essential step toward the practical quantum computation.

It is now believed that large-scale NMR quantum computers will be built on semiconductor technologies; in fact, some practical schemes have been proposed along this line. The implementation of the schemes, however, is a great challenge even with the state-of-the-art technologies. One of the challenges is to provide control schemes for

inter-nuclear (=inter-qubit) couplings: they should be "on" during operations, and "off" otherwise, i.e. they should be switchable. This feature is essential especially in large-scale quantum computers because the number of inter-nuclear couplings increases drastically with the number of qubits, which brings a great deal of complexity into the calculations; the switching simplifies the couplings, hence facilitates the calculations.

### Control of inter-nuclear couplings by light irradiation

We have discovered a scheme for controlling inter-nuclear couplings in semiconductors by light irradiation. The scheme, when applied to properly arranged nuclear-spin systems, may allow optical switching of the couplings (Fig. 1). Furthermore, we find that the reach of the optically-induced couplings can be longer by increasing the light intensity. This feature may allow a variety of options for arranging qubits, as they need not be next to each other to secure couplings, in contrast to the case of the "short-ranged" couplings.

It is expected that quantum computers will be a key player in the future information technologies, and that nuclear spins will be their essential ingredients because of their extremely long decoherence times. Although

there still remain many challenges to implement the scheme presented here, such as to devise a method to properly arrange the qubits in semiconductors, we believe that the present scheme should be a key contribution to the quantum computing in the future.

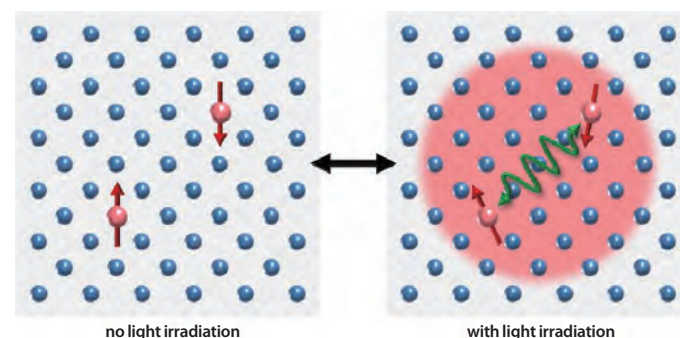
\* Quantum computer: a new paradigm of computer science, which operates making use of the principles of quantum mechanics. It is expected to have the ability to solve problems that are practically insolvable with existing computers due to the extremely long computation time required. In particular, it can break the present cryptography that guarantees the security of the modern information communications; therefore, it is regarded as a fundamental technology that brings about a paradigm shift in the modern information technologies. "NMR quantum computer" is the scheme that employs nuclear spins in materials as quantum bits (qubits)

(Acknowledgement) This work was supported by JST PRESTO program and Grants-in-Aid for Scientific Research from JSPS.

(Reference) Atsushi Goto, Shinobu Ohki, Kenjiro Hashi & Tadashi Shimizu, *Nature Communications* 2:378 doi:10.1038/ncomms1378 (2011).  
 Nature Research Highlight:  
<http://www.natureasia.com/en/highlights/details.php?id=1335>



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**Fig. 1** Schematic diagram of "switching operation". The red spheres with arrows and the blue spheres represent atoms with, and without nuclear spins, respectively. In the dark, all the couplings (including the known "short-ranged" ones) between nuclear spins apart from each other by a few lattice points are "off". The light irradiation (red circle) turns on the coupling (green line).

## Next-Generation Memories Made From Nanocrystals

Soft Chemistry Group, Soft Chemistry Unit, MANA  
**Minoru Osada, Bao-Wen Li**

NIMS Fellow, Unit Director, Soft Chemistry Unit, MANA  
**Takayoshi Sasaki**

### Nonvolatile memory using ferroelectrics

Hasn't everyone encountered the problems of irritatingly slow startup and short battery life with the personal computers? One technology to solve these problems is to use ferroelectric nonvolatile memory in your personal computers. Ferroelectric is one type of insulators, which have the ability of nonvolatile switching of polarization states. In ferroelectric crystals, a strong external electrical field can reverse the plus and minus poles of the polarization. The crystals also hold their polarization direction until forced to change by another applied electric field. Thus, they can be coded as nonvolatile binary memory, representing "0" in one direction and "1" in the other.

Ferroelectric random access memory (FeRAM) has the crucial ability of computers to store information even after the power source is removed. The most widely used form of primary storage today is a volatile form of random access memory (RAM), meaning that when the computer is shut down, anything contained in RAM is lost. In FeRAMs, on the other hand, not only would such technology save energy, but it would allow for the computers that could be turned on and off

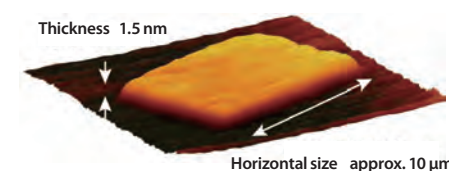
almost instantly, bypassing the slow start-up and shutdown sequence. However, most forms of FeRAMs have limitations that make them unsuitable for use as primary storage. Typically, FeRAMs either cost more or perform worse than volatile RAMs. Denser, faster, low-energy FeRAMs are highly desired and nanostructured ferroelectrics are one of the key challenges in FeRAMs.

### Nano-engineered ferroelectric material

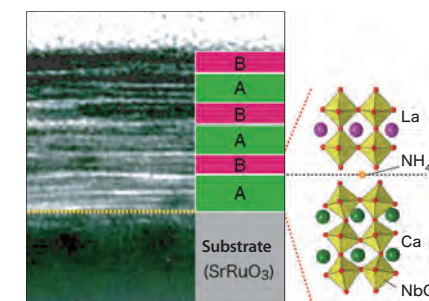
In designing nanostructured ferroelectrics, we focus on oxide nanosheets, which are obtained by delaminating a layered compound into its single layers through soft-chemical procedures. We have synthesized perovskite nanosheets ( $A = \text{Ca}_2\text{Nb}_3\text{O}_{10}$ ,  $B = \text{LaNb}_2\text{O}_7$ ) (Fig. 1). Perovskites form the basis of interesting classes of dielectric and ferroelectric materials. We fabricated an artificial superlattice by alternately stacking of two perovskite nanosheets via solution-based layer-by-layer assembly (Fig. 2). By such an artificial structuring, we found that the  $(\text{Ca}_2\text{Nb}_3\text{O}_{10}, B/\text{LaNb}_2\text{O}_7)$  superlattice possesses a new form of interface coupling, which gives rise to ferroelectricity at room temperature (Fig. 3). This artificial

superlattice exhibited robust ferroelectric properties even at several nanometer thicknesses, which is essentially required for future FeRAMs.

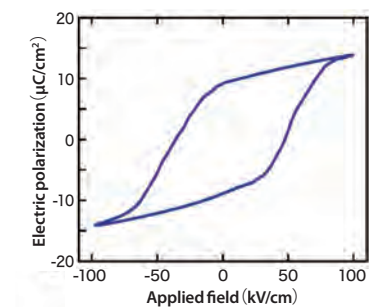
Our work is a proof-of-concept, showing that high-performance electronic devices can be made from perovskite nanosheets via the solution process in beakers. Our new recipe is not suitable for immediate use but it could offer the next big change in our computers in the coming decades.



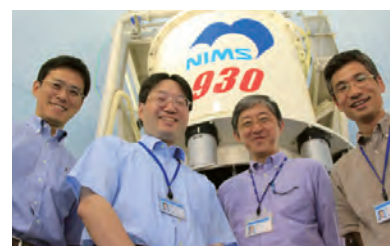
**Fig. 1** AFM image of an individual oxide nanosheet ( $\text{Ca}_2\text{Nb}_3\text{O}_{10}$ ).



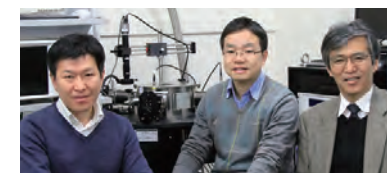
**Fig. 2** Cross-Sectional HRTEM image of the superlattice  $(B/A)_3$  fabricated on a  $\text{SrRuO}_3$  substrate.



**Fig. 3** Polarization-Electric field ( $P$ - $E$ ) hysteresis loop of the superlattice  $(B/A)_3$ . The ability of polarization switching by applying an external electric field indicates the ferroelectric nature of this film.



**Atsushi Goto** (center left): Senior Researcher, Ph.D. in Physics (The University of Tokyo, 1996). He joined National Research Institute for Metals (NIRIM) as researcher in 1996, and has been appointed as senior researcher at NIMS since 2001. He also served as visiting scholar at UCLA in 2000, and JST-PRESTO researcher from 2007 to 2011. / **Shinobu Ohki** (center right): Principal Engineer. He graduated from Graduate School of Science and Engineering, University of Tsukuba in 1994. He joined NIMS as JST-CREST engineer in 2001, and was appointed as NIMS research staff in 2004. He has been in the current position since 2009. / **Kenjiro Hashi** (right): Senior Researcher, Ph.D. in Human & Environmental Studies (Kyoto University, 1998). He was appointed at NIRIM as COE researcher in 1998, and at RIKEN as post-doctoral fellow in 1999. He joined NIMS in 2001. He has been in the current position since 2004. / **Tadashi Shimizu** (left): Group leader, Ph.D. in Physics (The University of Tokyo, 1987). He was employed as research associate at the Institute for Solid State Physics, the University of Tokyo in 1987. He joined NIRIM in 1990 as researcher, and was later appointed as senior researcher and subgroup leader. He has been in the current position since 2006. He also served as visiting scholar at Los Alamos National Laboratory, and visiting professor at Kyoto University. Since 2009, he has served as professor of Department of Quantum and Condensed Matter Physics, Hokkaido University.



**Minoru Osada** (left). He received his PhD in Materials Science from Tokyo Institute of Technology in 1998. Prior to joining NIMS in 2003, he was a RIKEN Special Postdoctoral Researcher and a JST PRESTO Fellow. He is currently a MANA Scientist and Associate Professor of the Waseda University-NIMS Joint Graduate School. / **Bao-Wen Li** (center). He received his PhD in Materials Science and Engineering from University of Tsukuba in 2010. He is currently a NIMS Postdoctoral Researcher. / **Takayoshi Sasaki** (right). He received his PhD in Chemistry from the University of Tokyo in 1985. Since 1980, he has worked for NIRIM. He is now a NIMS Fellow and MANA Principal Investigator.

## 1 Report on NIMS-Warsaw University of Technology-Hitachi High-Tech Joint Seminar

The NIMS-Warsaw University of Technology-Hitachi High-Technologies Corporation Joint Seminar was held at the NIMS Sengen Site on July 21 with approximately 70 participants.

NIMS concluded an International Joint Graduate School Agreement with Warsaw University of Technology (WUT) in June of last year. This is an extremely distinctive program, under which 7 researchers from WUT and 6 researchers from NIMS form pairs and jointly select students, and in principle, these students receive basic training at WUT for 1 year and then carry out research toward their doctoral dissertations at NIMS for a period of 2-3 years.

As part of this program, NIMS welcomed 9 WUT students as internship students for an 8-week period this summer. Supporting the program, the three-party seminar was held with the participation of Hitachi High-Technologies Corp., which is actively cooperating in improving the analytical devices of the WUT Department of Materials Engineering.

At the seminar, opening remarks were given by Prof. Sukekatsu Ushioda, President of NIMS, and Prof. Kurzydowski of WUT, reconfirming the importance of research and educational activities through

international exchanges, even under the difficult conditions following the earthquake and tsunami disaster. Promotion of deeper exchanges among NIMS, WUT, and HHT in both the research and scientific aspects is expected in the future.



Participants in the Joint Seminar.

### Announcement: The 11th NIMS Forum

The NIMS Forum, which gives a full view of recent research achievements at NIMS, will be held again this year! This event will feature a special lecture by Mr. Tsuguo Nobe of Nissan Motor Co., Ltd. on "Smart Grids, Smart Communities, and Electric Vehicles – A Vision of the Future of Automotive Society and Environment & Energy." This is a "must-see" presentation on two critical issues now facing Japan –

the environment and energy – from the viewpoint of the automobile. In addition, researchers at NIMS/GREEN will deliver lectures on all-solid-state lithium ion batteries and electrode surface/interfacial reactions, and there will be more than 60 poster sessions where participants can ask questions on recent research results directly to the researchers. There is no admission charge for this event. We

warmly invite everyone to attend.

**Date: October 26 (Wed), 2011**

**Site: Tokyo International Forum Hall B7 (Yurakucho)**

<http://www.t-i-forum.co.jp/english/>  
(The forum will be held in Japanese)

## Hello from NIMS

Dear NIMS NOW readers,

'Endless Discovery' is the first phrase, which is seen at the baggage claim of Narita airport. Glad to meet you. My name is Jung-Sub Wi. I and my family came to Japan one year before, and still we have been continued to discover new fun in Japan.



Astronomical museum in JAXA

My three-year-old boy, Junbeom, loves vehicles, just like other

kids of his age. In Japan, every single day he is finding a new car-toy and collecting. Even at a grocery store, there are plenty of toys. It makes my little boy's life in Japan happy, and makes me start to learn how to persuade him. My wife's major is education of earth science and she teaches middle school science in Korea. Here, she has been impressed by variety of science museums. Tsukuba nicknamed as a science city has many nice museums of geology, astronomy, map & survey, botanic and so on, and many of them have no admission fee! My wife is dreaming to make her own teaching materials with many photos from here. In NIMS, I am a one of ICYS (International Center for Young Scientists)

researchers. With many ICYS colleagues of various nationalities and research backgrounds, we are studying together, and sometimes discovering diverse Japanese foods, beers and sakes.

From Tsukuba, Jung-Sub Wi



Historical garage in Tokyo



**Jung-Sub Wi** (Korea)  
ICYS researcher, MANA  
2010.04. - present



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