# MANA E-BULLETIN

Nano Revolution
for the Future

July
2020

INTERNATIONAL CENTER FOR MATERIALS NANOARCHITECTONICS

## RESEARCH HIGHLIGHTS

[ Vol. 59 ]
AFM's Probe Used to Induce Chemical Reactions at Specific Sites on Single Molecule

[ Vol. 60 ]
New Solid Materials Enable Broader Application of Medical Gases

[ Vol. 61 ]
First Fabrication of fBBLG/hBN Superlattices

## FEATURE

An Interview with

### Prof.
### Hideo Hosono

**NIMS Distingished Fellow**
**Team Leader of the Electro-Active Materials Team**

Vol. 10

# ‘I Love Being a Pioneer’ An Interview with Prof. Hideo Hosono

Hideo Hosono
NIMS Distingished Fellow, Team Leader of the Electro-Active Materials Team

The world-renowned researcher, is famous for creating amorphous oxide semiconductor IGZO-TFTs and room temperature-stable electrides, and discovering iron-based superconductors. He discusses his life and work.

## Make the World Standard in Your Own Research Field

— **You have done important work in a variety of fields. What’s your secret?**

I don’t have any secrets. I’ve just been focusing on what I want to do without restrictions on the technical or academic field. For example, chemistry and physics as two separate disciplines has little meaning in materials science. My main interest is in functional materials utilizing electrons in solids. In the case of semiconductors, I study the movement of electrons under an electric field, and superconductors are similar -- you manipulate electrons in catalysis to react with molecules on a surface.

My PhD thesis was on line shape analysis of electron spin resonance spectra in glass -- rather fundamental work. After that, I did joint work in the material sciences department at Nagoya Institute of Technology, where I worked with ceramics, especially photoactive glasses and protonic conduction in glass. I did ion implantation into $SiO_2$ glass for a year at Vanderbilt University in the U.S. as well as research at Oak Ridge National Lab, in Tennessee.

I returned to Japan, to Tokyo Tech, and changed my research topic from photoactive glasses to oxide semiconductors. The most visible result of my work at that time was the proposal of transparent amorphous oxide semiconductors for thin film transistors, leading to the IGZO TFT, which is now used in high-resolution LCD panels such as tablets and OLEDs for TV screens.

When I started this research in 1993, there was almost no work being done in the field. But now, 25 years later, oxide semiconductors are the world standard for TFTs for flat panel displays and beyond. It was during this work on oxide semiconductors that we discovered iron-based superconductors. This has grown into a huge field comparable to cuprate superconductors -- in the last 10 years, over 50,000 papers have been published on the subject worldwide. But now I’m moving back into electrides.

— **Why electrides?**

The original definition of an electride is a compound in which an electron serves as the anion. The pioneering research was done in the U.S., by James Dye, who first demonstrated the organic electride in 1983. But the compound was very unstable, impossible to treat and quick to decompose, so a low temperature and vacuum were needed. Nobody succeeded in synthesizing a stable electride at ambient conditions until we did, using C12A7 (C is calcium, A is aluminum oxide), a constituent for aluminate cement. Of course C12A7 is a wide-bandgap insulator, but we found that electron can be doped into C12A7 and the resulting C12A7:e converted into semiconductor, metal and eventually superconductor  as the electron concentration goes up.

— **How did you get the idea to investigate C12A7?**

After my PhD work, I got an assistant professor position at Nagoya Institute of Technology. A friend of mine there was in charge of cement materials in the student experiment. I watched them make the cement -- they melted it, then poured it, and it was almost like glass. The ingredients, calcium oxide and aluminum oxide, are both transparent, but to my surprise, even at 200℃ the sample looked pale yellow. At room temperature it turned white, so I thought, something strange is going on here.

That's when I started to study C12A7. My PhD work was related to point defects in glass, so I thought this phenomenon could be due to a defect, which turned out to be the case. This material is now a known as a multi-functional material, but if I hadn't noticed the color that day, it might never have been developed.

— **What are some possible applications for this work?**

Electrides are promising as a catalyst for ammonia synthesis. I started this work in 2011, and a company already has a pilot plant up and running. There is potentially a huge amount of money to be made. Ajinomoto Co., Inc. and a government venture fund invested to create a company, whose name is Tsubame BHB Co., Ltd. (tsubame is Japanese for swallow, the trademark of Tokyo Tech, and BHB is Beyond Haber-Bosch, referring to the industrial process using high pressure for chemical reactions. Haber-Bosch is a large-scale process, requiring huge amounts of energy, to produce ammonia on an industrial scale. Our focus is small scale, with onsite equipment.

You can use renewable energy, like a solar cell or wind power plant. Generated energy is used to electrolyze water to produce hydrogen, which is combined with nitrogen to form ammonia. The biggest use for ammonia is for fertilizer, and onsite synthesis is sometimes called "green ammonia," made from green energy.

Our process requires milder conditions, temperature of 300℃ and a much smaller pump. And it's small enough to be installed at smaller sites. The pilot plant is operating in Kawasaki, at a facility owned by Ajinomoto Co., Inc.

— **You also made a big contribution in demonstrating iron-based superconductors. Why are they significant?**

I turned my attention to magnetic semiconductors after the work on transparent oxide semiconductors involving IGZO was complete in 2006. In the course of my research we demonstrated superconductivity in iron and nickel. At the time I started this research, in 2006, the physics was totally new -- iron was the last constituent of superconductivity because magnetism and superconductivity are in strong competition and iron is a representative magnetic element.

One possible exciting application is in wires used to produce strong magnetic fields. Iron-based superconducting wire could be important in high field applications such as particle accelerators, or in superconducting magnets for medical applications, such as heavy ion radiation for cancer treatments. The magnets for these are enormous right now, but if they were smaller, they could be installed in any hospital.

## Being a Pioneer not a Follower

— **What motivates you in your research?**

I love being a pioneer. I don't like being a follower.

I especially like the initial stages of research, when fundamental science and applications are not separate. It's like two sides of a coin -- different aspects, but integral parts of the same whole. This is a very exciting phase, when a new field begins to take shape. Applications are not always evident at this phase, but they always reveal themselves eventually.

— **Do you have a message for young researchers?**

Well, I still consider myself a young researcher!

I am also a teacher, but I learn a lot from my students. When working with students, the form of interaction is important. Competition is crucial. I don't agree with treating young guys overly politely. Of course, the roles are different, but education is very limited if it's one-way -- it's better to have mutual interaction.

— **What are some things you've learned from your students?**

Just reading published papers is not enough. Learning through direct interaction and sharing your intentions with other team members on a daily basis is the most effective.

Professors get energy from interacting with young people. The difference between young and experienced people is the social responsibilities of roles, not their position "to educate" or to "be educated."

— **Some say you're in the running for a Nobel Prize.**

Well, my research target was never a Nobel Prize. My most interesting research is to solve problems in society, using materials science, hopefully materials born from myself. When I was a high school student, Japan suffered from severe pollution, and diseases like Minamata disease (caused by organic mercury pollution). This inspired me to go into materials science, and that's why I love it -- it's not just interesting, it also has the potential to solve social problems through the application of science.

## Materials Science is Always Closely Connected to Society

— **Which comes first for you, the fundamental science or the application?**
**Do you do research with an application in mind?**

I really don't like this distinction, calling something applied research when it is useful, and fundamental research when it is not immediately applicable. Starting with an application in mind can be a real advantage in materials research, but if you obtain good results, applications will appear automatically. This is not as common in pure chemistry or pure physics. Materials science is always closely connected to society.

Link to this article

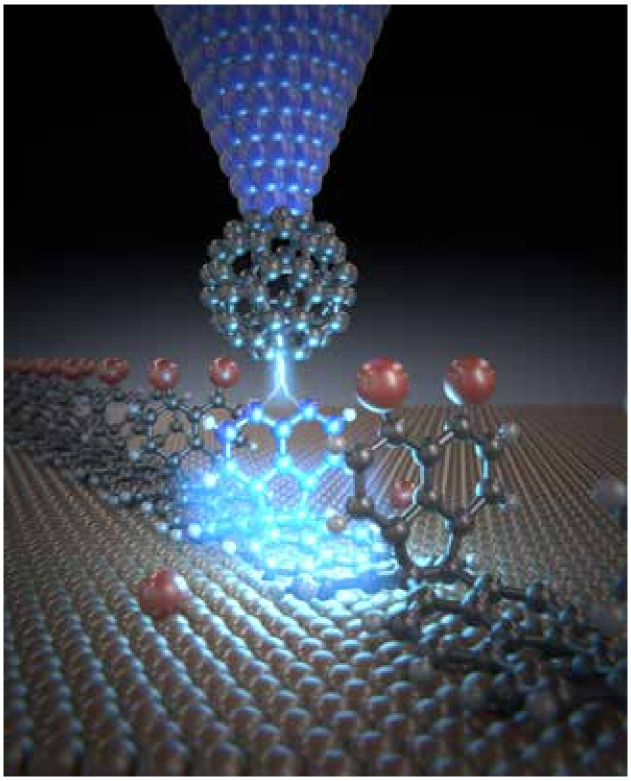
MANA Planning and Outreach Team
International Center for Materials Nanoarchitectonics (WPI-MANA)
National Institute for Materials Science (NIMS)
1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan
TEL: +81-29-860-4710 FAX: +81-29-860-4706
EMAIL: mana-pr@nims.go.jp

### [Vol. 59]

# AFM's Probe Used to Induce Chemical Reactions at Specific Sites on Single Molecule

**A team at MANA has demonstrated controlled addition reactions at specific sites on a single molecule by using an atomic force microscope's (AFM) local probe at low temperature. This work enables the synthesis of functional carbon nanostructures that cannot be obtained by conventional chemistry. Thanks to their superior electrical properties, such nanostructures are expected to find applications in nanoelectronic devices.**

The team synthesized three-dimensional graphene nanoribbons (3D-GNR) by on-surface chemical reaction. Then, taking advantage of the AFM's ability to conduct tip-induced assembly, they demonstrated the nanoribbons' capability as a framework for local probe chemistry. This could allow sequential reactions, particularly addition reactions (in which two molecules combine to create a bigger one), by a local probe at the single-molecule level.



The AFM's probe, terminated with a small carbon monoxide molecule, allows direct observation of the inner structures of both single molecules, as well as the products of on-surface chemical reactions.

It also allows researchers to conduct single molecule chemistry via tip-induced reactions. The local probe can be used to generate highly reactive radical species by tip-induced dehydrogenation, dehalogenation or deoxidization on surfaces. However, since these organic redox reactions are conducted with planar molecules, the molecule-substrate interaction has to be reduced by inserting thin insulating films. In contrast, if a 3D hydrocarbon is used, the out-of-plane moiety can be used for local probe chemistry in a similar way to recent measurements of intermolecular interactions.

The MANA team noted that direct addition reactions at specific sites like the ones they demonstrated can advance chemistry toward synthesis of single compounds atom by atom. Such extremely fine control offers the ability to create unprecedented new functional materials.

This research was carried out by Shigeki Kawai* (Principal Researcher, Nano Functionality Integration Group, Nano-System Field) and his collaborators.

*Present affiliation: Group Leader, Nanoprobe Group, Nano Characterization Field, Research Center for Advanced Measurement and Characterization, NIMS

---

**Reference**

"Three-dimensional Graphene Nanoribbons as a Framework for Molecular Assembly and Local Probe Chemistry", Shigeki Kawai *et al.*
Science Advances [Feburary 28, 2020]
DOI: 10.1126/sciadv.aay8913

### [Vol. 60]

# New Solid Materials Enable Broader Application of Medical Gases

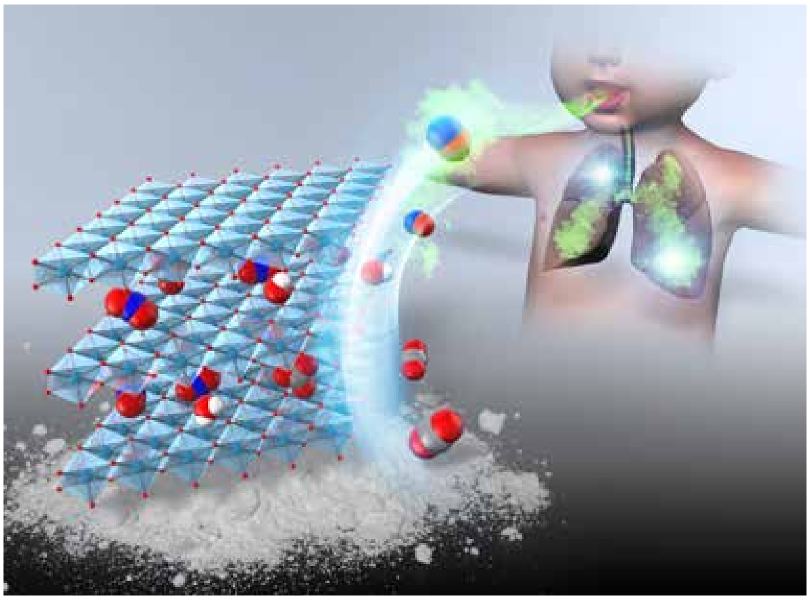
**Hydrogen sulfide ($H_2S$) and nitric oxide (NO) are gases with useful bio-activities, such as anti-oxidation, anti-inflammation and vasodilation. $H_2S$ is an ingredient in hot spring and long known to have positive effects on the skin and cardiovascular system. NO is a selective and fast-acting pulmonary vasodilator, and is used in hospital intensive care units to treat severe respiratory distress, including the so-called "blue-baby syndrome," a life-threatening condition caused by pulmonary hypertension. In addition, the inhaled NO therapy is currently under clinical trials for COVID-19 infection.**

However, the application of these gases is limited since they are toxic at high concentrations and need cumbersome high-pressure gas cylinders. For example, inhaled NO is an advanced medical treatment requiring expensive medical instruments and a trained operator to control and monitor the purity and dose of the NO.

To address these issues, a MANA research team of Shinsuke Ishihara and Nobuo Iyi has developed solid materials that slowly and autonomously release small amounts of $H_2S$ and NO when they contact with $CO_2$ in air.

The materials are based on layered double hydroxide (LDH), a clay mineral, which incorporates gas source anions ($HS^-$ or $NO_2^-$). The materials exchange anions with $CO_2$ and release $H_2S$ and NO.

The concentration and duration of gas release are controllable by adjusting various factors, such as composition of materials, diffusion of gas molecules and anions, and chemical equilibrium.



The team's low-cost and safe-to-handle materials could be used to create a disposable medical system for controlled release of bio-active gases under ambient air. Actually, the team demonstrated the potential utility of new gas-release system by creating a portable, hand-operated (and therefore battery-free) respirator that can supply therapeutically useful quantities of NO into inhaled air.

The work shows that LDH is an attractive material for gas release, and the $CO_2$-driven system is potentially useful for expanding opportunities of utilizing functional gases in a variety of applications.

This research was carried out by Shinsuke Ishihara (Principal Researcher, Frontier Molecules Group) and Nobuo Iyi (Special Researcher, Soft Chemistry Group).

---

**Reference**

"Controlled Release of $H_2S$ and NO Gases Through $CO_2$-Stimulated Anion Exchange", Shinsuke Ishihara and Nobuo Iyi
Nature Communications [January 23, 2020]
DOI: 10.1038/s41467-019-14270-3

## [ Vol. 61]

# First Fabrication of fBBLG/hBN Superlattices

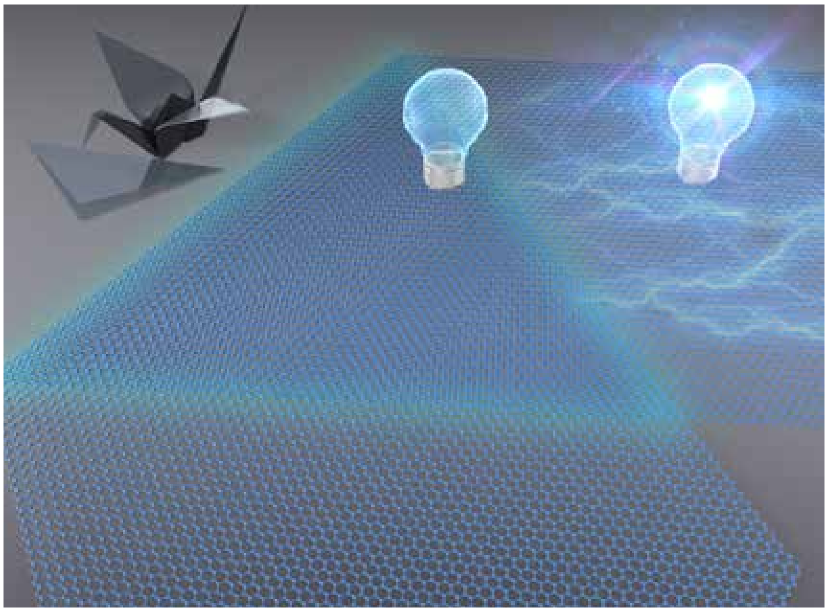
**A team at MANA has demonstrated for the first time the fabrication of folded bilayer-bilayer graphene (fBBLG)/hexagonal boron nitride (hBN) superlattices. This achievement could pave the way for expanded applications of superlattices, such as in a variety of quantum devices.**

Graphene superlattices represent a novel class of quantum metamaterials that have promising prospects. They have been generating a lot of attention recently, ever since the discovery of superconductivity in twisted bilayer graphene (BLG). This was followed by studies related to twisted bilayer-bilayer graphene. Bernal-stacked BLG has a parabolic energy dispersion with a four-fold spin and valley degeneracy.

A superlattice is a periodic structure of layers of two or more materials. Typically, the width of layers is orders of magnitude larger than the lattice constant, and is limited by the growth of the structure. The MANA team's superlattices are made up of vertically stacked ultrathin/atomic-layer quasi 2D materials.

The MANA team's results point to the emergence of a unique electronic band structure in the fBBLG, which could provide a way for investigating correlated electron phenomena by performing energy-band engineering with superlattice structures.

The results of this study indicate the emergence of a unique electronic band structure in fBBLG, which could be modified by the moiré superlattice potential. Although a systematic way to fold graphene is still lacking, it should be a fruitful topic of future research, leading to 2D paper-folding engineering like "origami." The team's results suggest a possible way to engineer 2D electronic systems by mechanical folding, similar to "tear and stack" for twisted heterostructures.



This work could lead the way to expanded applications of superlattices, including quantum devices such as Bloch oscillators, quantum cascade lasers and terahertz source generators.

This research was carried out by Takuya Iwasaki (ICYS-WPI-MANA Research Fellow) and his collaborators.

**Reference**

"Fabrication of folded bilayer-bilayer graphene/hexagonal boron nitride superlattices", Takuya Iwasaki *et al.*
Applied Physics Express [March 5, 2020]
DOI: 10.35848/1882-0786/ab790d

# MANA E-BULLETIN

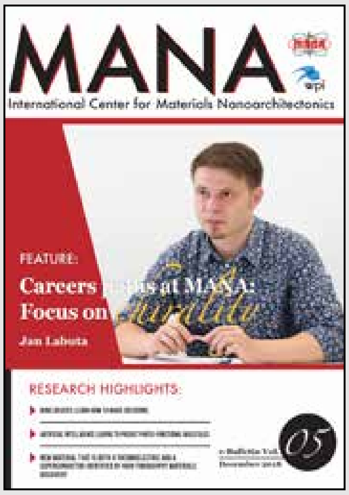
Back issues are available on our website ►►►


MANA
International Center for Materials Nanoarchitectonics
FEATURE:
"Bottom Up Fundamental Research" for Sowing the Seeds of Future Innovation
Takayoshi Sasaki & Tomonobu Nakayama
RESEARCH HIGHLIGHTS:
e-Bulletin Vol. 01
December 2017

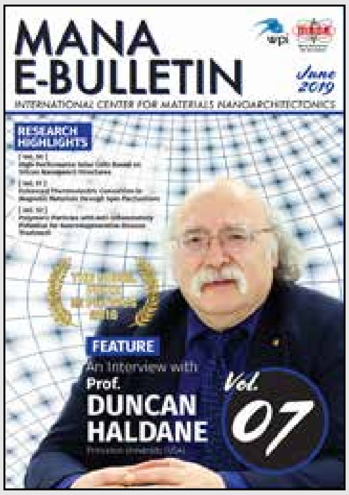

MANA
International Center for Materials Nanoarchitectonics
FEATURE:
MSS: Towards a de facto standard for olfactory sensing
Genki Yoshikawa
RESEARCH HIGHLIGHTS:
e-Bulletin Vol. 02
March 2018

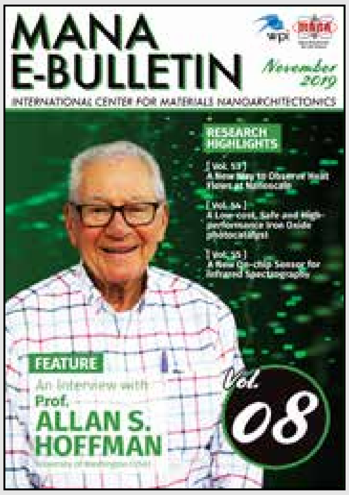

MANA
International Center for Materials Nanoarchitectonics
FEATURE:
Independent Scientists System: Total Freedom to conduct their own research
Yoshio Bando · Akihiro Okamoto · Gaku Imamura
RESEARCH HIGHLIGHTS:
e-Bulletin Vol. 03
June 2018


MANA
International Center for Materials Nanoarchitectonics
FEATURE:
Next Generation Innovative Organic Electronics
Yutaka Wakayama
RESEARCH HIGHLIGHTS:
e-Bulletin Vol. 04
September 2018


MANA
International Center for Materials Nanoarchitectonics
FEATURE:
Careers paths at MANA: Focus on chirality
Jan Labuta
RESEARCH HIGHLIGHTS:
e-Bulletin Vol. 05
December 2018


MANA
International Center for Materials Nanoarchitectonics
FEATURE:
Advanced nanofabrication technology catalyzing discovery and innovation at WPI-MANA
Toshihide Nabatame, NanoFoundry Manager
RESEARCH HIGHLIGHTS:
e-Bulletin Vol. 06
March 2019


MANA E-BULLETIN
June 2019
INTERNATIONAL CENTER FOR MATERIALS NANOARCHITECTONICS
RESEARCH HIGHLIGHTS
FEATURE
An Interview with Prof. DUNCAN HALDANE
Princeton University (USA)
Vol. 07


MANA E-BULLETIN
November 2019
INTERNATIONAL CENTER FOR MATERIALS NANOARCHITECTONICS
RESEARCH HIGHLIGHTS
[ Vol. 53 ] A New Way to Observe Heat Flows at Nanoscale
[ Vol. 54 ] A Low-cost, Safe and High-performance Iron Oxide photocatalyst
[ Vol. 55 ] A New On-chip Sensor for Infrared Spectrographs
FEATURE
An Interview with Prof. ALLAN S. HOFFMAN
University of Washington (USA)
Vol. 08


MANA E-BULLETIN
March 2020
INTERNATIONAL CENTER FOR MATERIALS NANOARCHITECTONICS
RESEARCH HIGHLIGHTS
[ Vol. 56 ] How Do Neuromorphic Nanowire Networks Find Routes to Convey Signals?
[ Vol. 57 ] 'Liquid Electret' Could Offer New Power Source for Wearable Electronics
[ Vol. 58 ] New Insights into Structure of Layered Hydrogen Borides
FEATURE
Creating systems that can think, feel — and smell
Tomonobu Nakayama
×
Genki Yoshikawa
Vol. 09