

International Center for Materials Nanoarchitectonics

### FEATURE: "Bottom Up Fundamental Research" for Sowing the Jeeas of Future Innovation

Takayoshi Sasaki & Tomonobu Nakayama

### **RESEARCH HIGHLIGHTS:**

DRIVING SOFT MOLECULAR VEHICLES On a metallic surface

INNOVATIVE TRANSISTORS BASED ON Magnetically induced movement of ions

ATOMICALLY THIN PEROVSKITES BOOST For future electronics



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he International Center for Materials Nanoarchitectonics (WPI-MANA), Tsukuba, Japan, was launched as part of the 10 year World Premier International Research Center Initiative (WPI) program (October 2007-March 2017) funded by Japan's Ministry of Education, Culture, Sports, Science and Technology (MEXT). Now, ten years on, WPI-MANA is internationally recognized as one of the world's leading research institutes focusing on creating innovative functional materials based on in-depth knowledge of the interaction and structure of individual nanoscale components.

### Melting pot of excellence in science and innovation

"I was appointed Director of WPI-MANA in April 2017 and am working with Deputy Director Tomonobu Nakayama and staff at WPI-MANA to expand our research based on our achievements over the last ten years that include MSS, neuromorphic networks, metamaterials, and atomic switches acting as artificial synapses," explains Takayoshi Sasaki. "Research at WPI-MANA is international, multidisciplinary, and dynamic. This reflects the diverse nature of our ideas and global reach of our scientists, approximately 45% of whom are from overseas and 16% are female. WPI-MANA is a 'melting pot' of highly motivated scientists."

### Research organization at WPI-MANA

WPI-MANA is one of seven research centers at the National Institute for Materials Science (NIMS) in Tsukuba with the mission of "bottom up fundamental research". The research is carried out by 228 scientists, covering three major areas of 'nano-materials', 'nano-systems', and 'nano-theory'. The activities at WPI-MANA's Tsukuba research center are complemented by five satellite centers at Georgia Tech and UCLA, USA; University of Montreal, Canada; CNRS, France; and University College London, UK.

#### Major achievements: Scientific publications and intellectual property

WPI-MANA's international status as a scientific powerhouse is based on its tremendous research output during the WPI program. Specifically, a statistical overview shows that scientists at WPI-MANA published 4,219 papers with an average impact factor of 6.09 in 2016, and approximately 49% of the papers were co-authored with international collaborators with a peak of approx. 57% in 2016.

Furthermore, as of January 2017, nearly 4% of these publications were in the top 1% of highly cited papers, that is, 142 out of 3,840. In terms of the field weighted citation impact (FWCI), the FWCI of WPI-MANA is 2.38. This means that WPI-MANA papers were cited 138% more often compared to the world average of FWCI=1.

Innovative research at WPI-MANA

#### Number of Papers and the Average Impact Factor







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Takayoshi Sasaki MANA Director



Tomonobu Nakayama MANA Deputy Director

has also yielded patents and intellectual property. Specifically, between October 2007 and December 2016, WPI-MANA registered 642 patents (489 in Japan and 153 overseas) and applied for 823 patents (578 in Japan and 245 overseas).

#### Deeper exploration of Nanoarchitectonics and artificial perception

"Our plans for the next decade are based on building on the scientific legacy of the last ten years," says Sasaki. "Globally, in addition to our five satellites centers we will also work closely with more than 200 collaborators overseas with whom we have 60 MOUs. In terms of research themes, we will increase efforts on studying larger and more complex hierarchiral organization of nanomaterials, nanocomponents, and advanced nanoanalysis technology."

In addition, WPI-MANA is formulating plans to strengthen links with academia to enable even more young researchers, post-docs and principal investigators (PIs) to join the institute. Outreach and international networking events are also high on the agenda. "We are organizing an international symposium on 'artificial perception' in March 2018," says Nakayama. "This symposium will be an excellent opportunity for scientists at WPI-MANA to share their plans for the future with the larger international nanoscience community."

Sasaki has a clear vision for the future of WPI-MANA. "Our institute has excellent facilities, highly motivated scientists, and administration staff," he says. "We welcome scientists from all over the world to join us, including graduates for our well funded post-doctoral positions." ■

WPI-MANA Website

http://nims.go.jp/mana/

MANA International Symposium 2018 - Toward Perceptive Nanomaterials, Devices, and Systems -

- March 5 March 7, 2018
- International Congress Center
- "Epochal Tsukuba", Tsukuba, Japan
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# Research Highlight

## DRIVING SOFT MOLECULAR VEHICLES ON A METALLIC SURFACE

oft molecules deposited on metallic surfaces were driven using a scanning tunneling microscope (STM) without mechanically pulling or pushing them, but by inducing inelastic excitations with the tunneling current.

In nanoscience, compared to rigid molecules, it is challenging to control the movement of soft molecules due to their flexibility. Notably, only one part of soft molecules is suitable for absorbing tunneling current energy that should be used for inducing motion, and not conformational changes of the molecules.

A collaboration led by Waka Nakanishi and Katsuhiko Ariga at WPI-MANA and We-hyo Soe and Christian Joachim at GNS and WPI-MANA Satellite, CEMES-CNRS in Toulouse designed, synthesized and characterized a conformationally flexible molecule consisting of two binaphtyl paddles mounted on a simple phenyl chassis. The vibration modes of the lateral paddles can be exploited to induce the motion of the molecule on an Au(111) surface using STM inelastic tunneling effects. The molecule has two different nonplanar configurations in solution that it retains when absorbed on the surface. However, on the metallic surface it is possible to switch molecules, one at a time, to a flat configuration



syn-conformation

flat-conformation

moving

SCHEMATIC DIAGRAM SHOWING THE INTERACTION OF TUNNELING CURRENT WITH MOLECULES.

using a specific STM mechanical manipulation protocol. The flat configuration is the most interesting one for this work, because only flat molecules can be controllably moved on the surface by local STM excitations. Once they assume this configuration, the molecules are reasonably stable on the surface.

Molecules in the flat configuration were characterized to determine the spots where tunneling electrons should be injected to make them move on the surface without mechanically pushing them. Indeed, depending on the location at which the tunneling current enters the molecule, this can assume a nonplanar configuration (different from the original one) instead of moving. If the current is applied on the correct spot, the molecule can move in a controlled way. The experimental characterization of the molecules was complemented by molecular dynamics simulations and density functional theory calculations, which helped to uncover the energetics of the

molecules. In April 2017, a 'nanocar race' took place, in which several molecular machines synthesized by groups from around the world competed with the goal of covering a set distance on a gold surface in the minimum possible amount of time, driven by STM tips. The molecule presented in this paper is one of the vehicles that took part to the race. ■

### AFFILIATIONS

- INTERNATIONAL CENTER FOR MATERIALS NANOARCHITECTONICS (WPI-MANA)
- GNS AND MANA SATELLITE, CEMES-CNRS
- GREEN AND WPI-MANA, NATIONAL INSTITUTE FOR MATERIALS SCIENCE
- CENTRE FOR NANOMETER-SCALE SCIENCE AND ADVANCED MATERIALS, NANOSAM
- GRADUATE SCHOOL OF FRONTIER SCIENCES, THE UNIVERSITY OF TOKYO

### REFERENCE

SOE, W.-H., SHIRAI, Y., DURAND, C., YONAMINE, Y., MINAMI, K., BOUJU, X., KOLMER, M., ARIGA, K., JOACHIM, C. AND NAKANISHI, W. CONFORMATION MANIPULATION AND MOTION OF A DOUBLE PADDLE MOLECULE ON AN AU(111) SURFACE. ACS NANO 11, 10357-10365 (2017).

### **NNOVATIVE TRANSISTORS BASED ON MAGNETICALLY INDUCED MOVEMENT OF IONS**

ust as magnets attract iron particles in sandpits, permanent magnetics only attract one type of ion in an electrochemical solution, constituting the basis of magnetically controlled electrochemical transistors.

Electrochemical devices find application in many technologies, including batteries, capacitors, sensors, and transistors. For such electrochemical devices to operate, they need an electric field that causes ionic transport and electrochemical processes. This simple but strict rule has long hindered innovation in electrochemistry and related technologies, however, WPI-MANA researchers recently challenged the rule with their development of 'magnetic control of electrochemical devices'.

WPI-MANA researchers Takashi Tsuchiya and Kazuya Terabe and their co-workers used a small magnet, instead of electrical equipment, to drive ions. The transport of paramagnetic FeCl<sub>4</sub> ions in a liquid electrolyte (including [Bmim]FeCl<sub>4</sub>) was magnetically controlled to operate a typical electrochemical device; an Electric Double Layer Transistor (EDLT), a type of transistor that uses an EDL at a semiconductor/electrolyte interface to tune the electronic carrier density of the semiconductor. An electrical conductance of a two-



dimensional hole gas (several nanometers thick) at a diamond (100) single crystal/electrolyte interface was successfully switched by a magnetic field, although the switching ratio was smaller than in conventional EDLTs that are controlled by an electric field.

The magnetic control of ions adds a new dimension to the 'nanoelectronics achieved by ions' paradigm, invented at WPI-MANA as the atomic switch\*, and such control has a huge impact, even on other electrochemical devices. It has the potential to realize innovative applications that have not been possible using conventional approaches. Furthermore, this discovery stimulates the development of high performance magnetic electrolytes to support such innovation.

In electrochemistry, a branch of chemistry that has already been studied intensively, the interdisciplinary field with magnetism is one of the few great frontiers remaining. Researchers will be undeniably attracted to it, like iron sand is to a magnet. ■

#### \* **REFFERS**

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- INTERNATIONAL CENTER FOR MATERIALS NANOARCHITECTONICS (WPI-MANA)
- RESEARCH CENTER FOR FUNCTIONAL MATERIALS, NIMS
- RESEARCH NETWORK AND FACILITY SERVICES DIVISION, NIMS

### REFERENCE

T. TSUCHIYA, M. IMURA, Y. KOIDE & K. TERABE. MAGNETIC CONTROL OF MAGNETO-ELECTROCHEMICAL CELL AND ELECTRIC DOUBLE LAYER TRANSISTOR. SCI. REP. 7, 10534 (2017)

## ATOMICALLY THIN PEROVSKITES BOOST FOR FUTURE ELECTRONICS

PI-MANA has developed the world's highest performance dielectric nanofilms using atomically thin perovskites. This technology may revolutionize the next-generation of electronics.

This research was conducted by a WPI-MANA research group led by Principal Investigator Minoru Osada and Director Takayoshi Sasaki of WPI-MANA at NIMS.

Electronic devices are getting smaller all the time, but there is a limit to how small they can get using current materials and technology. High- $\kappa$  dielectric materials may be the key for developing electronic devices of the future.

Minoru Osada and colleagues created high-performance dielectric nanofilms using 2D perovskite nanosheets (Ca<sub>2</sub>Na<sub>m-3</sub>Nb<sub>m</sub>O<sub>3m+1</sub>; m =3-6) as building blocks. Perovskite oxides offer tremendous potential for controlling their rich variety of electronic properties including high- $\kappa$ dielectric and ferroelectric.

The researchers demonstrated the targeted synthesis of nanofilms composed of 2D perovskite nanosheets in a unit-cell-upon-unitcell manner. In this unique system, perovskite nanosheets enable precise control over the thickness of the



perovskite layers in increments of ~0.4 nm (one perovskite unit) by changing *m*, and such atomic layer engineering enhances the high- $\kappa$  dielectric response and local ferroelectric instability. The *m* = 6 member (Ca<sub>2</sub>Na<sub>3</sub>Nb<sub>6</sub>O<sub>19</sub>) attained the highest dielectric constant,  $\varepsilon_r = \sim 470$ , ever realized in all known dielectrics in the ultrathin region of less than 10 nm.

Perovskite nanosheets are of technological importance for exploring high- $\kappa$  dielectrics in 2D materials, which have great potential in electronic applications such as memories, capacitors, and gate devices. Notably, perovskite nanosheets afforded high capacitances by relying on high- $\kappa$  values at a molecular thickness. Ca<sub>2</sub>Na<sub>3</sub>Nb<sub>6</sub>O<sub>19</sub> exhibited an unprecedented capacitance density of approximately 203  $\mu$ F cm<sup>-2</sup>, which is about three orders of magnitude greater than that of currently available ceramic condensers, opening a route to ultrascaled high-density capacitors.

These results provide a strategy for achieving 2D high- $\kappa$  dielectrics/ ferroelectrics for use in ultra-scaled electronics and post-graphene technology.

### AFFILIATIONS

• INTERNATIONAL CENTER FOR MATERIALS NANOARCHITECTONICS (WPI-MANA)

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