MANA

International Center for Materials Nanoarchitectonics

FEATURE:

MSS: Towards a *de facto* standard for olfactory sensing

Genki Yoshikawa

RESEARCH HIGHLIGHTS:

- ENVIRONMENTAL MONITORING OF AIR POLLUTION: 'DETECT TO WARN' SENSING SYSTEM FOR MONITORING FORMALDEHYDE
- MODULATING SUPERCONDUCTIVITY OF TWO DIMENSIONAL ATOMIC LAYERS OF INDIUM WITH CHARGE TRANSFER FROM SELF-ASSEMBLED ORGANIC MOLECULES
- METAL OXIDE/GRAPHENE NANOSHEET COMPOSITE EXHIBITS UNPRECEDENTED ENERGY STORAGE PROPERTIES

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Birth of Membrane-type Surface stress Sensor

“My background is surface science and my first interest in sensors was triggered in 2007 during my stay as a visiting scientist at the University of Basel,” says Genki Yoshikawa, Group Leader at the International Center for Materials Nanoarchitectonics (WPI-MANA), at the National Institute of Materials Science (NIMS). “I worked in Dr. Christoph Gerber’s group. I learned a lot from him and his colleagues about cantilever array sensors. Then, I also had collaboration with Dr. Heinrich Rohrer and with the MEMS expert members from the École polytechnique fédérale de Lausanne (EPFL), Lausanne, Switzerland, eventually leading to the invention of the Membrane-type Surface stress Sensor (MSS). We published the technical side of the story in 2011. While there are lots of potential applications for MSS, I decided to focus on smell, because it is the last ‘untapped sensor’ with no commercially available devices in our daily life for more than 30 years at least.”

Characteristics of MSS

The MSS was developed in collaboration with the late Dr. Heinrich Rohrer, and researchers at EPFL, and made public in 2011. The MSS is a compact, ultra-sensitive piezoresistive device fabricated using silicon microfabrication technology with a receptor layer enabling detection of a wide range of molecules including odorous gas molecules, and biomolecules such as DNA and proteins.

Conventional piezoresistive sensors are widely used as strain gauges to measure acceleration and pressure. In its simplest form, the operation of a piezoresistive sensor is based on the physical fact that applying mechanical strain induces changes in the electrical resistivity of silicon or metals and conductors used for fabricating the devices, due to mechanical deformation of the materials. However, for sensing applications, conventional cantilever-type sensors made of silicon requires structural optimization because the uniform stress induced by the adsorption of molecules cannot be efficiently detected.

“The MSS is a unique nanomechanical sensor,” explains Yoshikawa. “We totally redesigned the structure of conventional cantilever-type sensors. Typical MSS consists of a 300 micrometer diameter adsorbate membrane that is suspended by four piezoresistive ‘sensing beams’. So, the MSS is not a conventional cantilever-based sensor. It has a unique structure, exhibiting unsurpassed performance.”

Notably, the limit of detection of the MSS is approximately 0.1 mN/m, a figure of merit that is compatible with laser read-out cantilever sensors and more than 100 times higher than conventional piezoresistive cantilever sensors. Details about the fabrication and wide-ranging applications have been extensively reported by Yoshikawa and colleagues.

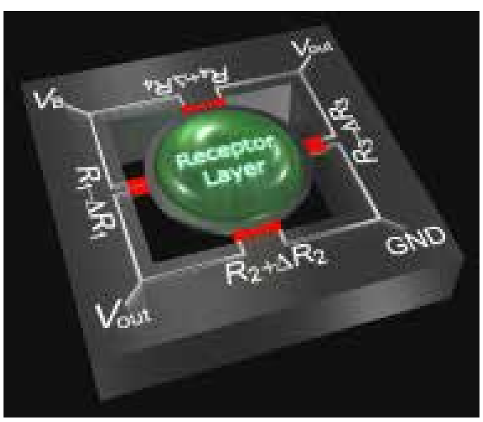


Illustration of the main parts of the MSS. The schematic shows the adsorbate membrane suspended by four sensing beams etched in silicon, and the Wheatstone bridge for the signal read-out.

sensor. It has a unique
sed performance. ”

Genki Yoshikawa
Group Leader

MSS Alliance: Seven organizations join forces to establish MSS-based standardization of odor sensing systems

The MSS Alliance was launched on 25 September 2015 to accelerate the process of taking the MSS technology from the lab to real-world applications. The members of the industry-government-academia alliance include NIMS, Kyocera, Osaka University, NEC, Sumitomo Seika, and NanoWorld. From April 2017, Asahi Kasei also joined the alliance.

"The members of the MSS alliance reflect the multidisciplinary nature of the expertise required for the proliferation of this technology," says Yoshikawa. "We have partners specializing in sensor chips, materials science, standard gases, system integration, analysis of big data with machine learning, and ICT and cloud networks."

Notably, in November 2017, the MSS alliance launched the new framework "MSS Forum" to encourage interested companies and organizations from the public to perform demonstration experiments using the technologies developed by the MSS alliance.

"We are trying to create a *de facto* standard for olfactory sensing based on the MSS technology," says Yoshikawa. "The MSS will cover various applications ranging from health-care by exhaled breath, tests to assessing the quality of fruits and food to environment and security applications. My dream is that this concept will enhance people's lives on a global scale". ■

Further information

G. Yoshikawa, T. Akiyama, S. Gautsch, P. Vettiger, and H. Rohrer, Nanomechanical Membrane-type Surface stress Sensor, Nano Lett. 11, 1044-1048 (2011). DOI: 10.1021/nl103901

Websites

- **MSS Forum: https://mss-forum.com/**
- **Nanomechanical Sensors Lab., Genki Yoshikawa: http://y-genki.net/**
- **Membrane-type Surface stress Sensor (MSS) sold by NanoWorld AG: http://mss-sensor.com/**

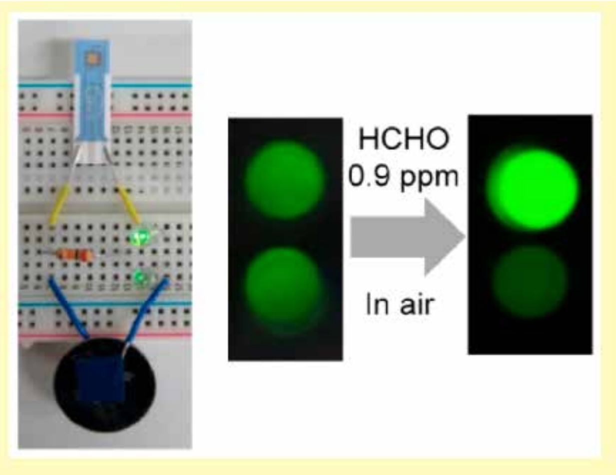
RESEARCH HIGHLIGHTS

01 Environmental Monitoring of Air Pollution: 'Detect to Warn' Sensing System for Monitoring Formaldehyde

Compact 'referenced—chemiresistive-sensors' consisting of network-assembly of semiconducting carbon nanotubes and hydroxylamine hydrochloride enable highly selective and continuous measurement of formaldehyde (HCHO) for environmental monitoring.

HCHO and related chemical compounds used in the construction industry to prevent decay of building materials are known to cause dermatitis, asthma, and other such ailments. Such health issues related indoor air pollution–referred to as 'sick building syndrome'–is a global problem with World Health Organization (WHO) guidelines recommending a maximum permissible concentration of HCHO of 0.08 ppm indoors. But monitoring levels of HCHO is not trivial, with conventional technology being expensive, bulky, and although compact monitoring systems exist, they require renewal of 'detection tags' after each measurement, and have issues related to continuous and long term monitoring.

Here, Shinsuke Ishihara and colleagues at WPI-MANA and collaborators at the Nanomaterials Research Institute, National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, report on the development of an innovative HCHO detection system based on a combination of hydroxylamine hydrochloride and network-assembly of semiconducting single walled carbon nanotube (SWCNTs) sensors capable of highly selective and continuous monitoring. Specifically, the SWCNT sensor is reusable; has a detection limit of 0.016 ppm; HCHO-selectivity of 10^5 to 10^6 times higher than other vapors such as water and methanol; and the implementation of a reference sensor adjacent to an active one prevents false positives.



REFERENCE AND SENSING DEVICES ARE VISUALIZED USING LEDS.
THE PRESENCE OF FORMALDEHYDE IS SHOWN BY THE BRIGHTER LED.

The reaction of HCHO with hydroxylamine hydrochloride generates hydrochloric acid, which causes changes in the conductivity of the SWCNTs that are measured with an external electrical circuit. The reference sensor does not have hydroxylamine hydrochloride present at its surface, hence the sensor does not react to HCHO.

"The high performance and versatility of our sensors were achieved by designing devices with precise separation of semiconducting carbon nanotubes, monodisperse treatment of carbon nanotubes and improvement of active surface area by networking," says Ishihara. "Furthermore, our sensor is low cost, portable, and long lifetime, thereby making it suitable as a 'detect to warn' sensory system."

Reference

SHINSUKE ISHIHARA,*,† JAN LABUTA,† TAKASHI NAKANISHI,† TAKESHI TANAKA,‡ AND HIROMICHI KATAURA,‡ AMPEROMETRIC DETECTION OF SUB-PPM FORMALDEHYDE USING SINGLEWALLED CARBON NANOTUBES AND HYDROXYLAMINES: A REFERENCED CHEMIRESISTIVE SYSTEM. ACS SENS. 2, 1405–1409, (2017).

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02 Modulating superconductivity of two dimensional atomic layers of indium with charge transfer from self-assembled organic molecules

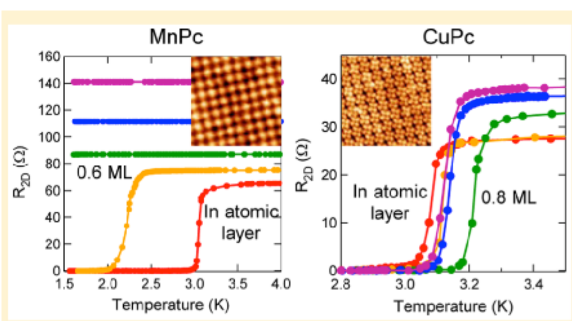
Charge and spin transfer from copper-phthalocyanine organic molecules self-assembled on superconducting atomic layers of indium modifies the superconducting transition temperature of the indium.

There have been tremendous advances in the self-assembly of organic molecules on solid surfaces via non-covalent bonds. Furthermore, research on self-assembly of two dimensional (2D) materials has yielded deep insights into the properties of superconducting 2D materials with atomic-scale thickness that could potentially lead to the creation of new hybrid materials and electronic devices through the so-called 'bottom-up' approach based on self-assembly as opposed to nanofabrication using etching and lithography. Notably, the unique physical proprieties of organic molecules offer advantages in terms of flexible and rational design and are an appealing approach with the possibility of opening up new fields of research.

With a view to controlling superconductivity in 2D atomic layers, Takashi Uchihashi and colleagues at WPI-MANA and collaborators at the Institute for Molecular Science, Okazaki, Japan, and Graduate School of Advanced Integration Science, Chiba University, Chiba, Japan, report the first observation of self-assembled organic molecules modulating the superconducting transport properties of an underlying 2D atomic-layer metallic material.

Specifically, the researchers fabricated 2D heterostructures consisting of an atomic layer of indium (In) epitaxially grown on a silicon substrate and a highly ordered metal-phthalocyanine (MPc, M = Mn, Cu) self-assembled onto the indium layer. In this heterostructure, "charge transfer and local spins due to the presence of organic molecules modified the superconducting properties of the atomic layer".

Examination of the 2D heterostructures led the researchers unexpectedly find that the substitution of the atom of metal-phthalocyanine from Mn to Cu changed the superconducting transition temperature (Tc) from 3.05 K to 3.20 K, that is, from a negative to positive direction. Further analysis combined with scanning tunneling microscopy (STM), X-ray magnetic circular dichroism (XMCD), and ab initio calculations revealed that this distinct phenomenon was due to competition between charge and spin effects.



MODULATION OF TC OF INDIUM BY SELF-ASSEMBLED LAYERS OF ORGANIC MOLECULES.

"Particularly important is the directionality of the relevant d-orbitals that play a decisive role in magnetic interactions," says Uchihashi. "It strongly suggests the feasibility of controlling macroscopic superconducting properties through manipulation of molecular states."

REFERENCE

SHUNSUKE YOSHIZAWA,*,† EMI MINAMITANI,‡ SARANYAN VIJAYARAGHAVAN,§ PUNEET MISHRA,§ YASUMASA TAKAGI,// TOSHIHIKO YOKOYAMA,// HIROAKI OBA,⊥ JUN NITTA,⊥ KAZUYUKI SAKAMOTO,⊥ SATOSHI WATANABE,‡ TOMONOBU NAKAYAMA,§ AND TAKASHI UCHIHASHI*,§, CONTROLLED MODIFICATION OF SUPERCONDUCTIVITY IN EPITAXIAL ATOMIC LAYER−ORGANIC MOLECULE HETEROSTRUCTURES, NANO LETT. 17, 2287−2293, (2017).

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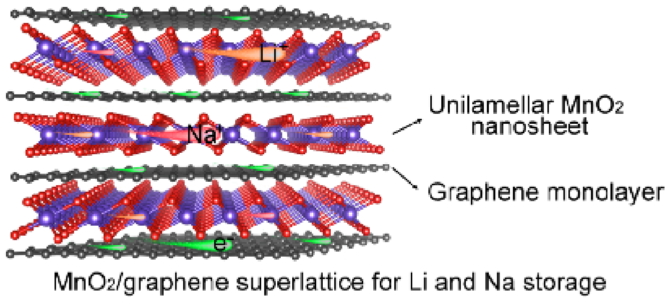
03 METAL OXIDE/GRAPHENE NANOSHEET COMPOSITE EXHIBITS UNPRECEDENTED ENERGY STORAGE PROPERTIES

Single-layer metal oxide nanosheets sandwiched between graphene layers exhibit record energy storage figures of merit.

The unique physical properties of nanomaterials are important for the realization of high performance energy storage devices. For example, the ultra-narrow spaces between multilayered two-dimensional (2D) nanosheets are suitable for high efficiency ion intercalation, namely, reversible insertion of ions into the spaces between layers. Importantly, single-layer nanosheets with nearly ideal atomic-scale thickness exhibit short diffusion distances and large numbers of active sites —properties that are essential for fabricating electrode materials of high performing energy storage devices.

However, despite extensive research on 2D materials such as graphene and transition metal dichalcogenides, the energy storage capacity has not met expectations. More recently, research has also turned to explore 2D metal oxides—materials with many more exposed active sites, and even shorter diffusion lengths. The main issues to resolve include synthesis of genuine single layered metal oxides, prevention of 'restacking' during chemical processes to fabricate electrodes, and improving their electrical conductivity.

Here, a group led by Takayoshi Sasaki at WPI-MANA reported the synthesis of superlattice-like MnO_2/graphene 2D nanostructures that exhibited the best figures of merit for energy storage reported to-date.



STRUCTURE OF MnO_2/GRAPHENE SUPERLATTICE-LIKE STRUCTURE

The researchers synthesized the MnO_2/graphene superlattice structures by 'electrostatic assembly' of single-layer MnO_2 and graphene in a solution, exploiting the differences in the charge states of the respective materials: The MnO_2 nanosheets are negatively charged and modified reduced graphene oxide (rGO) nanosheets are positively charged. The two important points about this fabrication process and the resulting nanosheet superlattices are that the MnO_2 nanosheets were 'genuine unilamellar' structures and each of the MnO_2 nanosheets was 'stabilized' between the atomic layers of graphene.

The MnO_2/graphene nanostructures were used as anodes for Li and Na ion batteries. Electrochemical measurements showed specific capacities of 1325 and 795 mAh/g at 0.1 A/g and 370 and 245 mAh/g at 12.8 A/g for Li and Na storage, respectively. "More importantly, an ultralong cyclability with 0.004% and 0.0078% capacity decay per cycle up to 5000 cycles was achieved for Li and Na storage, respectively, outperforming previously reported metal oxide-based anodes to date," state the authors.

"The superlattice composite material described in this paper is based on MANA's concept of 'Materials Nanoarchitectonics', says Sasaki. "We have taken two types of 2D materials with differing properties and formed an advanced composite material with synergistic characteristics that are not exhibited by a single material."

REFERENCE

PAN XIONG, RENZHI MA, NOBUYUKI SAKAI, AND TAKAYOSHI SASAKI, GENUINE UNILAMELLAR METAL OXIDE NANOSHEETS CONFINED IN A SUPERLATTICE-LIKE STRUCTURE FOR SUPERIOR ENERGY STORAGE, ACS NANO, 12 ,1768–1777, (2018).

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