A Grant-in-Aid for Scientific Research on Innovative Areas
The Area Number 2509 (2013-2018)

MOLECULAR ARCHITECTONICS

MolArch

Orchestration of Single Molecules for Novel Functions

News Letter No.4 June 2014

Now at Work

A01 Prof. Ogawa's group

Synthesis and measurements of molecular composites bearing non-symmetric and/or non-linear single molecule electronic properties

We are synthesizing new molecules which possibly have non-linear and non-symmetric single molecule electric properties such as rectification, negative differential resistance, and hysteresis. The measurements are performed by a PCI-AFM technique or a mechanical break junction method with helps of other members of this project. Recent results include: "Switching of single-molecule magnetic properties and observation of carbon-surface supramolecular structures of Tb(III) porphyrin double-decker complexes" by Inose *et al.*, "Design and synthesis of perpendicularly connected metal porphyrin-imide dyads for two-terminal wired single molecular diodes" by Handayani *et al.*, and "Synthesis of metal porphyrin arrays with programmable sequences by consecutive Suzuki coupling reaction and investigation of their physical properties" by Tamaki *et al.*, and so on.

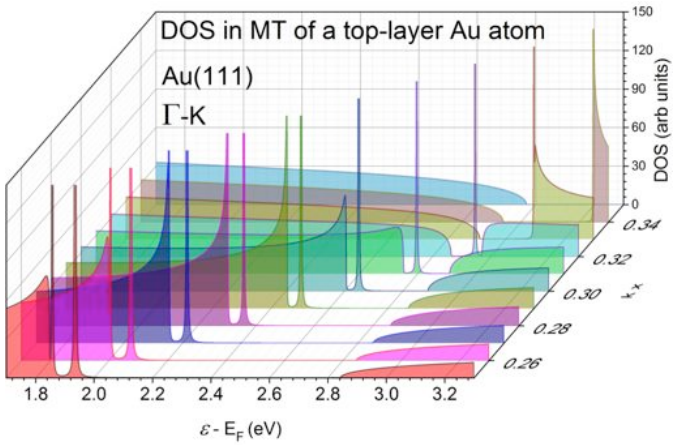
Ms. Inose, Mr. Tamaki, and Ms. Handayani
225th Electrochemical Society in Orlando, U.S.A.

Achievement

A02 Prof. Hiroshi Ishida

Rashba Effect Revisited

While the Rashba effect for the L-gap Shockley surface state on Au(111) was repeatedly studied in the past both experimentally and theoretically, and consensus has been reached on the occupied part of the energy dispersions of the two spin-split surface bands, a basic question regarding at what wave number each of the two modes ceases to persist as a gap state had remained unanswered. Recently we clarified this question by performing an embedded Green's function calculation for a truly semi-infinite Au(111) surface within density functional theory. The answer: The lower branch disappears when it is merged into a projected bulk band below the lower edge of the projected band gap at a relatively small wave number $k \approx 0.27$ a.u., whereas the upper branch persists at larger wave numbers, crossing the projected band gap, and finally absorbed into a projected bulk band above the upper edge of the band gap at $k \approx 0.34$ a.u.

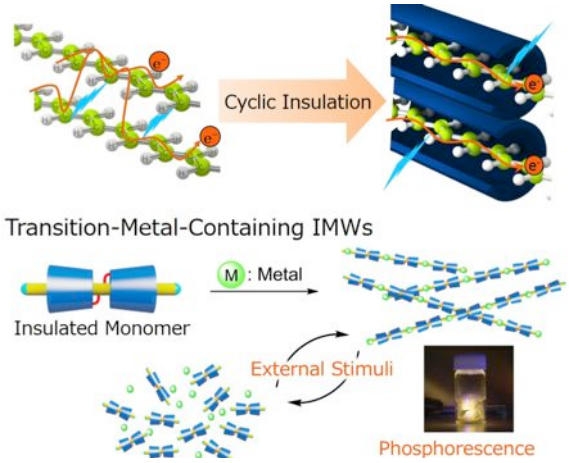


A01
Metal-containing insulated molecular wires

Mr. Hiroshi Masai
(Kyoto University)

π-conjugated polymers, which are called molecular wires, show promising conductivity as wiring materials of molecular electronics. However, strong π-π interaction of general molecular wires causes disorganized aggregation among adjacent polymers, which dramatically decrease their physical properties and wiring efficiency between nanoelectrodes. We have successfully synthesized insulated molecular wires (IMWs), where conjugated chains are covered with cyclodextrin-based macrocycles, achieving high conductivity and efficient wiring.

Our recent research focuses on metal-containing IMWs directing toward stimuli-responsive wiring materials. Their metals are inserted in the backbones and strongly affect the conjugated system. Their macrocycles decrease the thermal motions of polymer backbones under ambient temperature, which archive high conductivity and superior phosphorescence. Moreover, even in the solid state, their triplet species are isolated for micro- or milliseconds from undesirable interactions due to their cyclic protection, displaying fascinating "unimolecular properties" derived from metals in any environment.

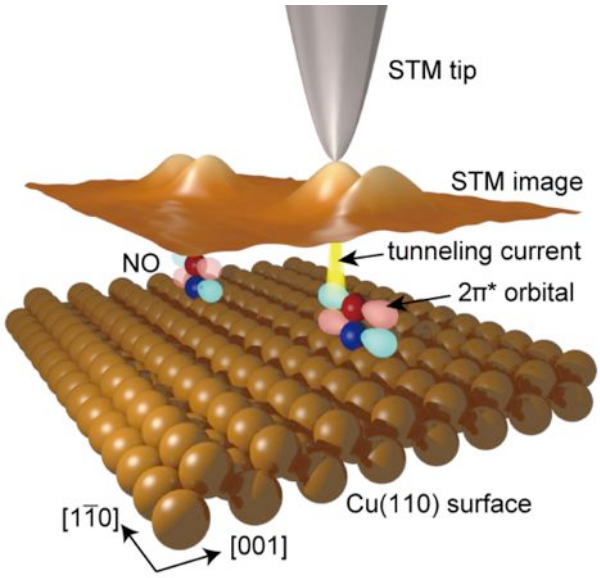


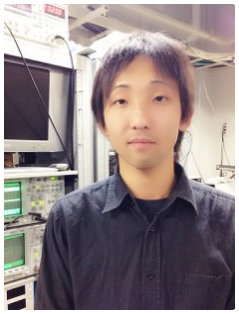
A02
Visualization of valence orbitals of NO *molecules on* Cu *surfaces*

Mr. Akitoshi Shiotari
(Kyoto University)

Interaction of nitric oxide (NO) with metal surfaces has been studied as a model system to understand the adsorption mechanism of diatomic molecules. NO has an unpaired electron in its 2π* orbital, giving rise to various reactivity like dissociation and dimerization on surfaces. We investigated the valence states of NO molecules adsorbed on Cu surfaces with scanning tunneling microscopy (STM) at 6 K, and succeeded in imaging its 2π* valence orbitals located near the Fermi level.

An isolated NO molecule on Cu(111) is imaged as a ring-shaped protrusion, which reflects the doubly-degenerated 2π* orbital. On the other hand, the STM image of NO on Cu(110) shows a dumbbell-shaped protrusion, indicating that the degeneracy of the 2π* orbital is lifted by interaction with the anisotropic substrate. By STM manipulation, we produced a dimer [$(NO)_2$] on the surface, in which the overlap of their 2π* orbitals causes the covalent interaction between the two NO molecules.



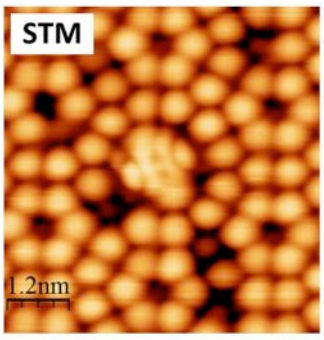


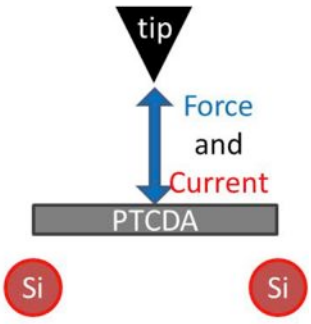
A03
Measurement of single molecule by AFM and STM

Mr. Kota Iwata
(Osaka University)

In the past two decades, Atomic Force Microscopy (AFM) has showed its capability to investigate various surfaces. A measured quantity of AFM is interaction force between tip apex atoms and surface atoms. Thus, AFM can access mechanical properties, such as the stiffness of surface structure [1]. Moreover, using the conductive tip, it is possible to measure the tunneling current and the interaction force simultaneously. Recently, the chemical structure of organic molecule was resolved for the first time [2]. Following this breakthrough, some AFM measurements of single molecules have been reported.

Recently, we have started AFM measurements on single organic molecules. We use Perylene-3, 4, 9, 10-tetracarboxylic dianhydride (PTCDA) deposited on the Si(111)-(7×7) surface, because PTCDA is anchored by strong bonds between O atoms in PTCDA and Si atoms on the surface even at room temperature [3]. Using this system, we are measuring the stiffness and the conductance through a single PTCDA.





[1] K. Iwata *et al.*, APEX, **6**, 155403 (2013)
[2] L. Gross *et al.*, Science, **325**, 1110 (2009)
[3] N. Nicoara *et al.*, PRB, **82**, 075402 (2010)

A04
Single walled carbon nanotube-based stochastic resonance devices

Mr. Agung Setiadi
(Osaka University)

Stochastic resonance (SR) is a phenomenon where the noise can enhance the transmission of signal which lied below threshold level. Previous theoretical calculation shows that multiple junctions, independent noise, and non-linear response are needed to realize SR devices (J. J. Collins, C. C. Chow, and T. T. Imhoff, Nature **376**, 236 (1995)). Devices consisting multiple junctions can be fabricated easily by using SWNTs. Non-linear IV or FET transfer characteristic of the SWNT devices can be used as non-linear response which is needed to define supra- and sub-threshold region. Recently, we obtained non-linear IV response by utilizing APTES-modified chrome electrodes (Fig. 1). We observed SR effect by adding white noise signal to the input signal. Comparing with the theoretical calculation shows that the device has 8-12 current path which has an independent response to the applied signal and noise (Fig. 2). In the future, we will develop SWNT-based SR device which has its own noise via functionalization of the SWNT.

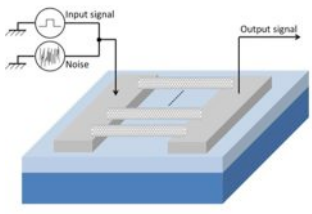


Fig. 1. Measurement configuration

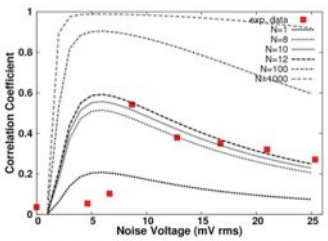


Fig. 2. Correlation coefficient of input – output signal

Report of the 3rd Area Meeting
12-14/June/2014, Tendo, Yamagata

The third area meeting of Molecular Architectonics was held from June 12 to 14, 2014 at the Tendo, Yamagata, being an area famous for the production of shogi pieces. There were about 80 attendees, including members from our area and students. We enjoyed discussion as well as the hot spring and nice food.

With the addition of 18 proposed researchers, our research field expanded significantly. They all introduced their research topics, following which we discussed the future direction of the research, particularly the combination of the molecular science and the informatics with the aid of noise in devices, and possible collaborations between members.

We also had a meeting of young researchers, where we introduced their research groups to each other, for student exchange as well as future collaborations.

There was a poster session for the researchers other than representatives. The Following students received the poster awards. From the left in the photo below:

Mr. Hiroshi Masai (A01, Kyoto Univ.),
Mr. Akitoshi Shiotari (A02, Kyoto Univ.),
Mr. Kota Iwata (A03, Osaka Univ.),
Mr. Masaki Sato (A04, Hokkaido Univ.),
Ms. Mariko Yamaguchi (A03, Osaka Univ.),
Ms. Naoka Ohta (A02, Univ. Tokyo),
Ms. Tomoko Inose (A01, Osaka Univ.).

Next Meeting

4th Area Meeting
24-26, November 2014, Osaka

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