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MOLECULAR ARCHITECTONICS

olArch Orchestration of Single Molecules for Novel Functions

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A01 Prof. Hirofumi Tanaka

Fabrication and electric properties of graphene nanoribbon

We succeeded to develop a simple unzipping method for fabricating single-layer graphene nanoribbons (sGNRs) from double-walled carbon nanotubes (DWNTs) (H. Tanaka et al., Sci. Rep. 2015, 5, 12341) by collaboration with A03 and A04. A sonication treatment was employed to unzip the DWNTs by inducing defects in them through annealing at 500 °C. The unzipped DWNTs yielded double-layered GNRs (dGNRs). Further sonication allowed each dGNR to be unpeeled into two semimetal sGNRs. Purification performed using a high-speed centrifuge ensured that more than 99% of the formed GNRs were sGNRs. The absorption of nanoparticles of planar molecule, naphthalenediimide (NDI), allowed the changes of the electrical properties of the obtained sGNRs. The shape of the I-V curve obtained by the sGNRs varied with the number of NDI nanoparticles adsorbed. This was suggestive of the existence of a band gap at the narrow-necked part near the NDI-adsorbing area of the sGNRs. After the report, we also succeeded to unzip of SWNT to obtain less than 10 nm width semiconducting sGNRs by the unzipping treatment. The width of GNR can be controlled by selecting a chiral vector of the SWNT.



<u>Achievement</u>

A01 Prof. Michio M. Matsushita *Current-induced mutual conductivity change along orthogonal crystal axes in an ion-radical salt of cyclophane-type donor*

A bromide salt of TTF-based cyclophane-type donor shows a characteristic structural phase transition around 170 K accompanied with a hysteretic behavior. In this phase transition, equivalent *a*- and *b*- axes in the high temperature phase (Tetragonal, P4,) become non-equivalent (*Monoclinic*, P2,) in the low temperature phase although there is some mosaicity. Due to the change of the molecular structure in the phase transition, conductivity becomes ca. 10 times larger in LTP compared to that in HTP. We found that the conductivity along a- and c- axes in the LTP (correspond to the *a*- and *b*-axes in HTP) could be changed mutually by loading relatively large current (up to 100μ A) along the *a*- and *c*-axes, alternately. The resistance along the current-loaded axis decreased whereas the resistance along the other axis increased as shown in the graph. This process could be repeated, and the change through the process reached up to 15 times larger/smaller in maximum. Since this crystal has mosaicity, a high-resistance domain will be converted to through low-resistance state the current application. Although this is a crystalline sample, it could be a model of integrated molecular circuit.



~Molecular



A01 Strictly size controlled synthesis of tin oxide clusters by using dendrimer template method Mr. Yusuke Inomata (TIT)

Cluster science has been attracted owing to their specific properties compared to the bulk materials. The properties of clusters are varied dramatically by changing the composed atomicity. Therefore, a method for strictly size and atomicity controlled cluster synthesis method is eagerly anticipated. In order to achieve this objective, we have established a template synthetic method using phenylazomethine dendrimer (DPA) for size and atomicity selective metal and metal oxide clusters.

We focused on clusterization of tin dioxide because the properties vary uniquely by changing the morphology and defect state. In a recent study, tin dioxide clusters have different structures compared to bulk state in a small cluster size region (< 2 nm): Rutile type SnO2 phase and pseudo SnO phase caused by lattice defects. It was found that the latter phase was increased as the cluster size is reduced and contributed to the paramagnetivity of tin dioxide. The increase of the band gap energy due to the quantum confinement effect was also confirmed and the leakage of the electron was indicated from the comparison of the effective mass models.





A02 Inter-electrode stretched and immobilized DNA nanowires associated with $Ru(bpy)_{3}^{2+}$ Mr. Taiki Kunikyo (Chiba University)

DNA, one of the most known biopolymers, possesses unique features for creating functional complexes by interacting with other materials. Therefore, DNA and its complexes have attracted much attention for fabricating various DNAbased functional devices. In this research, we aim to characterize photo-electronic properties of single molecular DNA complexes. First, we stretched and immobilized DNA nanowires by dielectrophoretic trapping method.[1] By applying high-frequency and high electric field to DNA aqueous solution between a pair of Au electrodes with 25 μ m inter-electrode distance, the DNA nanowires were stretched between the electrodes (Fig. 1). Height of the DNA nanowires were 0.4~1.3 nm, indicating single-molecularly alignment of DNA nanowires. Then, we functionalized the DNA nanowires by association with $Ru(bpy)_{3}^{2+}$ complex, known as photo-electronic functional molecule, through electrostatic fluorescence interaction. By microscope measurement, orange emission lines from the $DNA/Ru(bpy)_3^{2+}$ nanowires were observed between the electrodes (Fig. 2). The DNA/ $Ru(bpy)_3^{2+}$ nanowires are expected to perform their unique photo-electronic functionalities.

We pursue further investigation on single-molecular DNA complexes for fabricating of highly-functional DNA-based nanowires.

Fig. 1 AFM image of DNA nanowires.



Fig. 2 Fluorescence microscopic image of DNA/Ru(bpy)s²⁺ nanowires.

[1] O. Kurosawa, et al., JJAP 39, 7164 (2000).

Architects~



A03 Width-Controlled Sub-Nanometer Graphene Nanoribbon Films Synthesized by Radical-Polymerized Chemical Vapor Deposition Mr. Shaotang Song (Kyoto University)

The methods of GNR synthesis can be classified top-down or bottom-up approaches. into Comparing with the top-down approaches, the bottom-up approaches which include organic synthesis in solution by a combination of aromatic coupling and dehydrogenation of soluble organic building-blocks, and surface-assisted polymerization with subsequent dehydrogenation in an ultra-high vacuum environment, can give a relatively easy controllable width and edge structure. However these methods are facing some challenge on the systematic synthesis of GNRs with different width at larger scales because of the low solubility of GNRs and need for special conditions. Therefore, a simple method for large-scale production of GNR is eagerly required. Here, we demonstrated large-scale growth of armchair-edged GNRs on Au (111) even in extremely low-vacuum conditions using our newly developed method, radicalpolymerized chemical vapor deposition. Armchair-edged GNRs with a width of 2, 3, or 4 benzene rings, grown on a large scale, can form the isolated films, which can be used to experimentally characterize the unknown width-dependent band gap and can also be used to fabricate devices such as field effect transistors and photoconductive devices.





A04 Coulomb blockade on DNA-protein networks

Mr. Harumasa Yamaguchi (Osaka University)

Measurement of harmonic electric properties of nanoscale molecular networks is important in molecular electronics, and effective methods are required for building up each functional molecule as an electronic component. In particular, deoxyribonucleic acid (DNA) has been widely investigated as a scaffold due to its unique capabilities to build up complex nanostructures by self-assembly.

We have investigated the electric properties for DNA-protein networks such as cytochrome c, cytochrome c3 and lysozyme with DNA scaffold. Observed current-voltage (*I-V*) characteristics show nonlinear properties with the threshold voltage. The *I-V* curves are well fitted by the Coulomb blockade (CB) network model. We found that these localized Coulomb islands are induced by DNA-protein interactions. In the CB network model, the CB sites are assumed to be biased in cascade by the external voltage. These findings suggest that DNA has the potentiality to act as a nanoscale scaffold.



9th Joint Research Meeting of MEXT National Projects 13-15 November, 2015, Tokyo



The 9th Joint Research Meeting of MEXT National Projects on Condensed-Matter Science was held from November 13 to 15, 2015 at The University of Tokyo. More than 80 members from seven national projects (Molecular Architectonics, Ultra Slow Muon Microscope, Synergy of Fluctuation and Structure, Nano Spin Conversion, 3D Active Site Science, Topological Materials Science, and Physics of Conductive Multipole Systems) got together.

Our area representative, Prof. H. Tada, introduced our project's goals and activities (how to promote interdisciplinary collaborations and how to encourage young researchers). In addition, Prof. H. Tanaka and Dr. M. Akai presented their achievements and on-going work. We had fruitful discussion with attendees from a wide variety of national projects.

4th Workshop for Young Researchers 24-25 November, 2015 Kanagawa and Tokyo



The 4th Workshop for Young Researchers, attended by approximately 10 students and staff from our area, was held from November 24 to 25, 2015.

On the first day, we visited Nippon Telegraph Telephone (NTT) Basic Research Laboratories and discussed "the future of semiconductor electronics and the potential of single molecular electronics". Discussions with company researchers in other fields were a good experience and made us think about our research. The next day, we made transistor logic circuits and checked their operations using Arduino. This was first time for us to assemble discrete components and we learned the basics inorganic semiconductor of electronics. Furthermore we also learned how to use Arduino, and that this device can be applied to the operation of our instruments.

(A01 Takashi Tamaki)





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