Construction and Nano-scale Measurements of Molecular Nanostructures for Molecular Electronics

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Molecular electronics is a relatively new and fascinating area of research. However, as most single organic molecules are not conductive in a classical sense, long-range electronic transport through single molecules is unlikely to be useful for practical electronic circuits. Our group is interested in composites of conductive nano-materials with functional organic molecules as attractive bases for molecular electronics. Structures such as carbon nanotubes and metal nanoparticles incorporating functional organic molecules have been shown to be possible candidates. We have prepared two dimensional, one dimensional Au nano-particle assemblies using organic molecules, and carbon nanotube/organic molecule composites. Their electric properties were studied using nanogap electrodes and PCI-AFM.

The subjects of our group can be classified into three categories: (1) Preparation and self organization of functional organic molecules, metal nano-particles, and carbon nanotubes, (2) development of new scanning microscopic methods, and (3) development of new lithographic technique utilizing self assembling of molecules. By the combination of these three theme we are aiming to realize molecular scale electronics.

1. Metal-Semiconductor Transition Induced Visible Fluorescence in Single Walled Carbon-Nanotube/Noble Metal Nanoparticle Composites1)

We show that single walled carbon nanotube (SWNT) bundles emit visible fluorescence in the presence of noble metal nanoparticles and nanorods in the solid state. Conductivity measurements with metallic nanotubes, isolated from pristine SWNTs show that they become semiconducting in the presence of the metal nanoparticles. Nanoparticle binding increases the defects in the nanotube structures which is evident in the Raman spectra. The metal–semiconductor transition removes the non-radiative decay channels of the excited states enabling visible fluorescence. Nanotube structures are imaged using this emission with resolution below the classical limits.

2. A New Utilization of Organic Molecules for Nanofabrication Using the Molecular Ruler Method2)

Oligothiophenes and porphyrin oligomers were exploited as new molecules for the “molecular ruler” (MR) method in the form of simple molecular monolayers. When handled in air, oligothiophenes yielded extremely homogeneous nanogaps about 30 nm wide, while handling under N_2 produced nanoscale gaps of around 10 nm between parent and daughter structures. The difference between these two results indicated that it was possible to control the width of this gap by varying the extent of oxidation of the oligothiophenes. Porphyrin oligomers also yielded nanogaps about 10 nm wide. Therefore, these two types of molecules are promising candidates for use in MR methods.

3. Scanning Tunneling Microscopy Investigation of Vanadyl and Cobalt(II) Octaethylporphyrin Self-Assembled Monolayer Arrays on Graphite3)

Two-dimensional crystals of [2,3,7,8,12,13,17,18-octaethyl-21*H*,23*H*-porphine] vanadium(IV) oxide and cobalt(II) (VOOEP and CoOEP, respectively) at the interface of 1-tetradecene and highly oriented pyretic graphite (HOPG) were studied by scanning tunneling microscopy (STM). The lattice parameters were determined for VOOEP (a = 1.6±0.1 nm, b = 1.46±0.05 nm, Γ = 61±3°) and CoOEP (a = 1.48±0.08 nm, b = 1.42±0.07 nm, Γ = 62.0±4°). The lattice parameters were calibrated using the HOPG lattice as a reference. The center metal dependenceobserved by high-resolution STM analysis of octaethylporphyrin and the differences between VOOEP and CoOEP are proved.

4. Different *I-V* Characteristic of Single Electron Tunneling Induced by Using Double-Barrier Tunneling Junctions with Differing Symmetric Structures[4)]

I-V characteristics of single electron tunneling from a symmetric and an asymmetric double-barrier tunneling junction (DBTJ) were examined. A single Au nanoparticle was trapped in nanogap whose size was precisely controlled using a combination of electron beam lithography and molecular rulertechnique. Though the symmetric junction showed a monotonic rise with a bias beyond the Coulomb gap voltage, the asymmetric junction showed Coulomb staircases. The capacitance of the junction estimated from the fitting curves using the Coulomb conventional theory was consistentwith the capacitance calculated from the observed structure. The authors quantitatively found the correlation between the electrical and structural properties of DBTJ.

5. Halide Anion Mediated Dimer Formation of a *meso*-Unsubstituted N-Confused Porphyrin[5)]

The new N-confused porphyrin (NCP) derivatives, *meso*-unsubstituted *b*-alkyl, 3-oxo-N-confused porphyrin (3-oxo-NCP) and related macrocycles, were synthesized from appropriate pyrrolic precursors *via* a [3+1] type condensation reaction. 3-Oxo-NCP forms a self-assembled dimer in dichloromethane solution that is stabilized by complementary hydrogen bonding interactions arising from the peripheral amide-like moieties. The protonated form of 3-oxo-NCP was observed to bind halide anions (F^-, Cl^-) through the outer NH and the inner pyrrolic NH groups, affording a dimer in dichloromethane solution. The structure of the chloride-bridged dimer in the solid state was determined by X-ray diffraction analysis.

6. Photo Responsibility of Au Nano-Particle/Porphyrin Polymer Composite Device Using Nano-Gap Electrodes[6)]

Electrodes with a gap size of 15 ~ 80 nm could be bridged by porphyrin molecular wires with 50 ~ 300 nm length. The porphyrin units could be coordinated with Au nano-particles having pyridinyl moiety. The device with both the porphyrin and Au nano-particles showed photo-response characteristics while those without the Au nano-particles showed no response.

7. Synthesis of Dendron Protected Porphyrin Wires and Preparation of a One-Dimensional Assembly of Gold Nanoparticles Chemically Linked to the π-Conjugated[7)]

A one-dimensional assembly of gold nanoparticles chemically bonded to π-conjugated porphyrin polymers was prepared on a chemically modified glass surface and on an undoped naturally oxidized silicon surface by the following methods: π-conjugated porphyrin polymers were prepared by oxidative coupling of 5,15-diethynyl-10,20-bis-((4- dendron)phenyl) porphyrin, and its homologues (larger than 40-mer) were collected by analytical gel permeation chromatography. The porphyrin polymers were deposited using the Langmuir-Blodgett method on substrate surfaces, which were then soaked in a solution of gold nanoparticles (2.7±0.8 nm) protected with *t*-dodecanethiol and 4-pyridineethanethiol. The topographical images of the surface observed by tapping mode atomic force microscopy showed that the polymers could be dispersed on both substrates, with a height of 2.8±0.5 nm on the modified glass and 3.1±0.5 nm on silicon. The height clearly increased after soaking in the gold nanoparticle solution, to 5.3±0.5 nm on glass and 5.4±0.7 nm on silicon. The differences in height corresponded to the diameter of the gold nanoparticles bonded to the porphyrin polymers. The distance between gold nanoparticles observed in scanning electron microscopic images was *ca*. 5 nm, indicating that they were bonded at every four or five porphyrin units.

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Awards

MIYAKE, Yusuke; Outstanding Research Award, AsiaNano 2006.
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