

# Structures and Functions of Metal–Carbon Nano-Systems Produced from Metal-Acetylides

Department of Materials Molecular Science  
Division of Electronic Structure



NISHI, Nobuyuki  
JUDAI, Ken  
NISHIJO, Junichi  
OISHI, Osamu  
MATSUMOTO, Chie  
FURUYA, Ari  
NUMAO, Shigenori  
UBAHARA, Wakana

Professor  
Assistant Professor  
Assistant Professor  
Technical Associate  
IMS Fellow  
Post-Doctoral Fellow  
Graduate Student  
Secretary

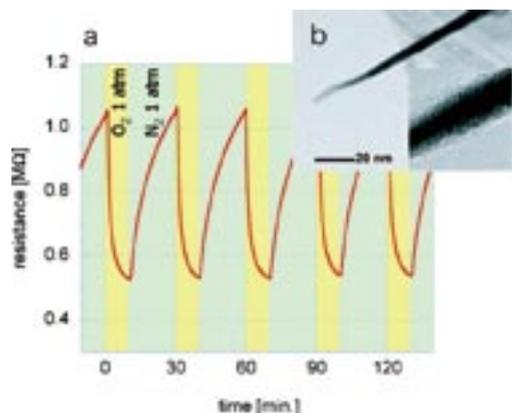
Metal acetylides or metal ethynyl compounds are made of the  $M^+-C^-$  ionic bonds. However, the ionic states of the acetylides are essentially metastable resulting in the segregation into metal-carbon or metal-organic polymer nanophases. This segregation still maintains  $M^+-C^-$  ionic bonds around the interfaces of the metal wire, particles, and dendric sponges exhibiting various functions depending on the metal species.

## 1. Increased Electric Conductance through Physisorbed Oxygen on Copper Nanocables Sheathed in Carbon

Solid gas sensors, which are operated at high temperature, are normally based on chemisorption for modification of the electronic band conduction. Sensing of  $O_2$  has been widely investigated. Recent advances in nanotechnology allow  $O_2$  sensors, such as carbon nanotubes, to work at lower temperatures. We found that copper nanocables sheathed in carbon can detect physisorbed  $O_2$  at room temperature by just measuring electric resistance. We have recently reported a low-cost, simple, and large-scale production method of nanowires involving the self-assembly of copper acetylide ( $Cu_2C_2$ ) molecules in an aqueous solution. The conductance of a pressed tablet of nanocables fabricated by annealing  $Cu_2C_2$  nanowires varies reversibly with adsorption and desorption of  $O_2$  at room temperature.

$Cu_2C_2$  nanocables consist of metallic Cu nanowires sheathed in amorphous carbon layers. It is very simple to produce a sensor using  $Cu_2C_2$  nanocables. Current-voltage ( $I$ - $V$ ) measurement of the  $Cu_2C_2$  nanocables was carried out under  $O_2$ - $N_2$  gas mixtures with a total pressure of 1 atm. The  $Cu_2C_2$  nanocables exhibited an ohmic, proportional  $I$ - $V$  character. The constant voltage used for the measurement was typically 1 V. Figure 1 shows the transient conductivity on the  $Cu_2C_2$  nanocables obtained by alternately exposing the nanocables to pure  $O_2$  (1 atm) and pure  $N_2$  (1 atm) gas. The conductance more than doubled during the 10-min  $O_2$  expo-

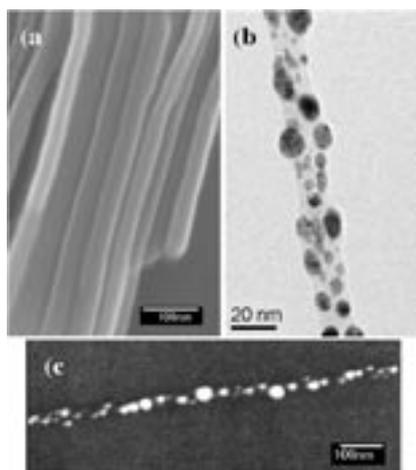
sure, and recovered reversibly during the subsequent  $N_2$  exposures. It must be noted that the reversible fluctuations in conductance were observed at room temperature. The presence of the charged species changes the semiconductor's Fermi level and the conduction of carriers. However, reversible absorption and desorption cycles at room temperature are generally believed to involve physisorption of molecules. Physisorption of  $O_2$ , which is not accompanied by charge transfer, is extremely unlikely to modify the electronic band structure for sensing by conductance.



**Figure 1.** a: Reversible changes in  $Cu_2C_2$  nanocable conductivity. The resistance of the  $Cu_2C_2$  nanocables decreased under  $O_2$ . b: TEM image of a  $Cu_2C_2$  nanocable.

## 2. Template-Free Fabrication of One-Dimensional Ag Nanoparticle Arrays

Development of a new facile preparation method of one-dimensional (1D) metal nanoparticle (NP) arrays is significant for both application and fundamental studies. We demonstrate a new facile and mass productive fabrication method for diameter-controlled 1D NP arrays *via* decomposition of silver phenylacetylide [ $Ag-C\equiv C-Ph$ ] nanowires. The ligand dissociation



**Figure 2.** (a) SEM image of [Ag-C≡C-Ph] nanowires separated from EtOH. (b) TEM image of UV irradiated nanowire. (c) SEM image of nanowire after 1h of UV.

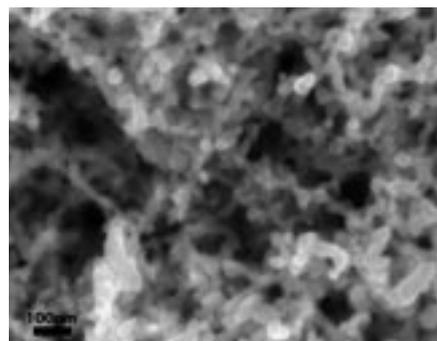
tion of [Me<sub>3</sub>P-Ag-C≡C-Ph] in a polar solvent gives [Ag-C≡C-Ph] nanowires as shown in Figure 2a. The average diameter of nanowires depends on the solvent: for examples, using MeOH and 1-BuOH gives nanowires with the average diameter of 30 and 100 nm, respectively. The nanowire is easily decomposed into

an assembly of Ag NPs embedded in a polymerized phenylacetylene matrix by UV irradiation or heating thanks to the strong reducing power of ethynyl anions. The transmission electron microscope (TEM) image of UV irradiated nanowire is shown in Figure 2b. It is obvious that a nanowire is converted into an assembly of Ag NPs after irradiation, whereas the wire shape of an assembly is kept by polymerized phenylacetylene. The NP arrays can be easily fixed on the substrate by heating the nanowire above 150 °C under vacuum after 1 h of UV irradiation as shown in Figure 1c, where the surface of each Ag NP is covered with thin layer of polycyclic aromatic hydrocarbons.

### 3. Dendric Nano-Sponge of Silver Acetylide (Ag<sub>2</sub>C<sub>2</sub>) and Its Conversion to Silver Dendric-Skeletons Sheathed in Carbon Mantle

In contrast to the wire-type nano-structure formation of copper acetylide, silver acetylide (Ag<sub>2</sub>C<sub>2</sub>) produces nano-sponge composed of dendric nano-rods with diameters of 20–30 nm under a certain synthetic condition as seen in Figure 3. Annealing at a temperature lower than 85 °C exhibits the segregation into inner silver and outer carbon with maintaining the dendric shape. This heating procedure in vacuum sometimes causes explosive reaction when the temperature of the powder increases this upper limit. Nitric acid treatment removes metallic silver but remains carbon and a small amount of silver strongly bound to carbon. EDS and TGA spectra of this sample revealed the presence of the remaining metallic silver. BET area (number of molecules adsorbed  $\times$  area per an N<sub>2</sub> molecule) is estimated to be 157 m<sup>2</sup>/g from the BET adsorption isotherm equation for the acid treated sample.

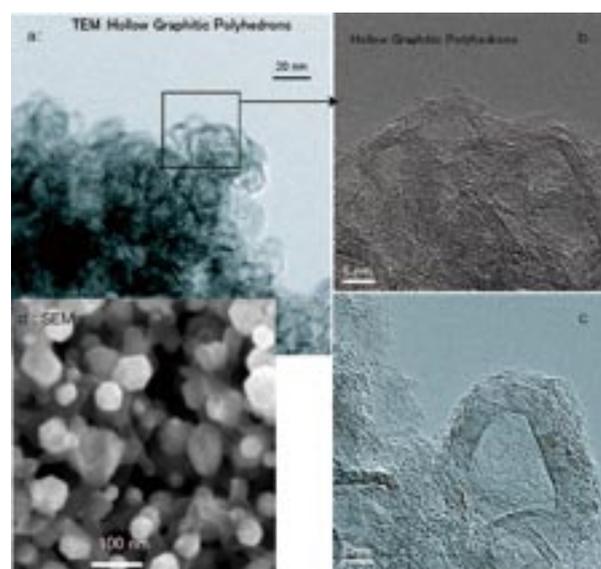
Although the characterization of the residual silver remains, we expect high catalytic activities of the silver on the carbon sponge with mesopore structures.



**Figure 3.** SEM image of the dendric nano-sponge structure of crystalline Ag<sub>2</sub>C<sub>2</sub>.

### 4. Hollow Graphitic Nano-Polyhedrons Produced from Silver Acetylide (Ag<sub>2</sub>C<sub>2</sub>)

A thoughtful graduate student can sometimes have a chance to change a bad accident to a very lucky discovery of a new material. The student performed the explosive reaction in a glass tube situated in a vacuum and collected the carbon product left inside the tube. Silver was evaporated and coated a mirror film inside the inner surface of the glass tube. Then he observed the TEM images of the carbon products. What he saw is the carbon onion type graphitic nano-structures with large empty holes, as shown in Figure 4. Strangely or reasonably, most of graphite layers are straight with bent corners with angles 90° ~ 120°. The SEM image in Figure 4-d shows the polyhedron balls of 20–100 nm. The presence of many defects (holes and layer mismatchings) in the graphitic shells suggests the potentials for gas storage.



**Figure 4.** a: TEM image of Hollow Graphitic Polyhedrons. The part in the black frame is expanded in b. c: Another expanded TEM image exhibiting imperfect graphitic shells. d: SEM image of the samples.

#### Award

NISHIJO, Junichi; Excellent Presentation Award, 87<sup>th</sup> Spring Meeting of Chemical Society of Japan.