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

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Metal acetylides or metal ethynyl conpounds 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 dendroid sponges exhibiting various functions depending on the metal species. Removal of the metals produces two types of carbon materials: One is mesoporous carbon with graphene walls and the other is amorphous carbon containing small amount of metals.

1. A Novel Functional Carbon Material: Mesoporous Carbon Nano-Dendrite with Graphene Walls

We have succeeded to synthesize a new material, Mesoporous Carbon Nano-Dendrites (MCNDs) with graphenen walls. The novel material exhibits good electric conductance due to large particle sizes and excellent ion fluidity. These properties could be attributed to the dendriform branching structure of the main bodies. Silver acetylide (Ag_2C_2) produces dendriform nanostructures under ultrasonic irradiation. The dendrites were quickly warmed to 150 °C emitting a brilliant flash of reddish orange lighting and thunderous sound indicative of the sudden jump of the local temperature to higher than 2000 °C. This sudden heating boils off the silver from the main body, leaving MCNDs. Raman spectra clearly indicate that the bodies consist of mainly single-layer graphene walls. Scanning Electron Microscope (SEM) and Transmission Electron Microscope (TEM) images as well as EELS spectra show that the main bodies with ~50 nm radii ramifies at every 100–150 nm and composed of the cells with graphene walls. Figure 1a shows a SEM image of MCND. The MCNDs showed a BET surface area of 1600~1800 m^2/g. As shown in Figure 1b, cyclic voltammetry of the supercapacitor with MCND electrodes exhibited good rectangular curves, even at a scanning rate of 400 mV/s, suggesting applicability for high current and high-speed charge-discharge capacitors for motor vehicles. By filling metallic layers or cluster islands in the pores, one can utilize the extremely large surface area for the electrodes of lithium ion batteries or fuel cells, respectively.

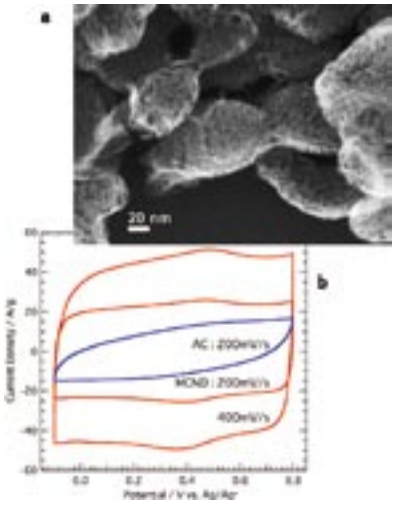

Figure 1. **a**: a high resolution SEM image of the edge region of MCND. **b**: Cyclic voltammograms of a MCND EDLC with an electrode thickness of 80 μm. Although the commercial activated carbon never shows a rectangular response with changing potentials at a scan rate faster than 50 mV/s, MCND can afford high-speed charge-discharge performance at a rate faster than 400 mV/s and current densities higher than 40 A/g.

2. Amorphous Carbon Material Converted from Self-Assembled Copper Acetylide Nanowires

In the next case, we deal with copper acetylide (Cu_2C_2) nanowires as less explosive nano-materials. Cu_2C_2 has been well-known as explosive substance. However, decreasing the size of material into the nanometer makes it possible to control

the explosive segregation reaction. We suggest a new method to produce amorphous carbon material by lower temperature process converted from the less explosive Cu_2C_2 nanowires. Amorphous carbon is normally produced with high temperature process of carbonization. An explosive nature of Cu_2C_2 itself provides segregation reaction into elemental carbon and copper at a temperature below 150 °C. The product by this low temperature process shows unique spectroscopic characters and material properties.

It is very simple to produce Cu_2C_2 nanowires. The fabrication method for Cu_2C_2 nanowire involves bubbling acetylene (C_2H_2) gas into an ammonia solution of copper chloride (CuCl). When the C_2H_2 reacts slowly, Cu_2C_2 molecules can self-assemble into nanowires 5 nm in diameter. Gradual heating of the product up to 150 °C for 1–5 hours in a vacuum transforms Cu_2C_2 nanowire into elemental copper and carbon via a segregation reaction without explosion. Aqueous NH_3 or nitric acid treatment can separate amorphous carbon from Cu element dissolving in solution.

Figure 2 shows Raman spectra of various carbon materials. Graphite displayed sharp peak around 1575 cm^{-1}, which could be assigned to G band of inherent in graphite lattices. For more poorly crystallized graphite, an additional broad band appears at 1350 cm^{-1} (so-called D band. Raman spectra demonstrated difference of crystalline characters between graphite and activated carbon. The amorphous carbon converted from Cu_2C_2 nanowires exhibits no distinct peak in the Raman spectrum. The spectroscopic study tells us that the low temperature process can generate genuine amorphous carbon materials without any trace of crystalline graphite. We attempt this new amorphous carbon evaluated to the application as hydrogen storage and so on right now.

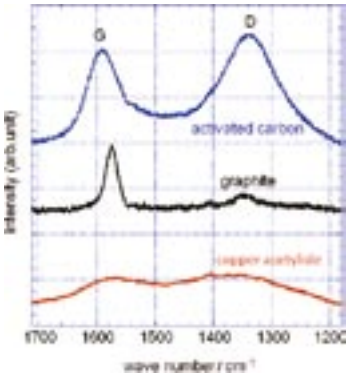

Figure 2. Raman spectra of various carbon materials. Graphite (black line, middle) shows a sharp G band at 1575 cm^{-1}, and active carbon (blue line, top) gives broad G band and also broad D band around 1350 cm^{-1}. Amorphous carbon converted from Cu_2C_2 nanowires shows extremely broad band (red line, bottom).

3. Surface Environment of Ag Nanoparticles Formed by Decomposition of Silver Phenylacetylide

Recently, we developed a facile preparation method of one dimensional Ag nanoparticle arrays via thermal- or photo-decomposition of silver phenylacetylide (Ag–C≡C–Ph). The nanoparticle is stabilized by the surface organic layer which keeps the nanoparticles from aggregation and oxidation. The structure of the surface layer was investigated by surface enhanced Raman spectroscopy and IR spectroscopy.

Figure 3 shows the Raman spectra of as-prepared, thermal- and photo-decomposed Ag–C≡C–Ph. Decomposed samples clearly show broad peaks at around 1970 cm^{-1} regardless of the decomposition process. The peaks are characteristic of the C≡C stretching mode of a surface adsorbed phenylacetylide anion, and indicates that the surface of the Ag nanoparticle is covered with vertically adsorbed phenylacetylene molecules. The peak shows no significant change even after 12 h thermal- or photo- decomposition, indicating the quite strong interaction between Ag nanoparticles and surface adsorbed molecules. Phenylacetylenes except surface adsorbed molecules are rapidly dimerized in decomposition processes to 1,4-diphenylbutadiyne which shows Raman and IR peaks of in- and out-phase =C≡C–C≡C= stretching at 2215 and 2150 cm^{-1}, respectively. In the case of long-time UV irradiated sample, the polymerization continues and results in the graphitic structure as evidenced by the occurrence of D- and G-bands in Raman spectrum at around 1350 and 1580 cm^{-1}, respectively, while the peak of –C≡C–C≡C– in-phase stretching disappears. In contrast, polymerization of 1,4-diphenylbutadiyne is rare in the case of after 12 h heat treatment at 150 °C, where only a small amount of graphitic structure is observed as shown in Figure 3. These results suggest that we can control not only the nanoparticle size of one dimensional Ag arrays but also the conductivity of its intermediate organic matrix from insulating to metallic, in which the Ag nanoparticles are firmly protected by surface adsorbed phenylacetylenes from chemical reactions.

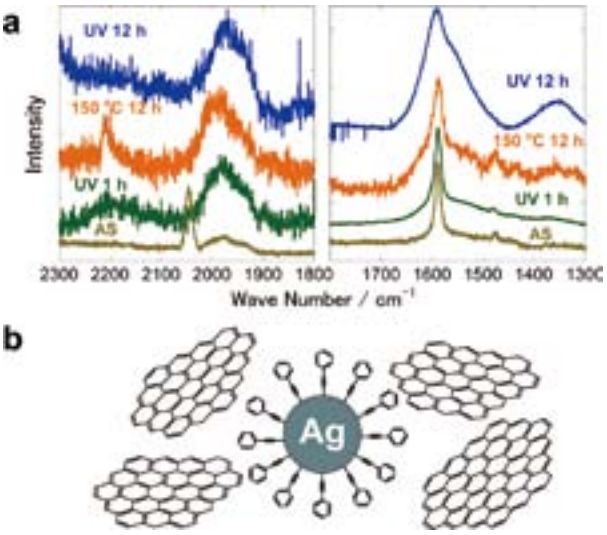

Figure 3. a) Raman spectra of as-prepared and decomposed Ag–C≡C–Ph. b) Schematic drawing of decomposed Ag–C≡C–Ph after 12 h UV irradiation.

Awards

JUDAI, Ken; Young Best presenter Award, 6th Annual Meeting of Society of Nano Science and Technology.
NUMAO, Shigenori; Young Best presenter Award, 6th Annual Meeting of Society of Nano Science and Technology.