RESEARCH ACTIVITIES

Graphene-Walled Alveolate Carbon & Structures and Functions of Metal–Carbon Nano-Systems Made from Metal-Acetylides

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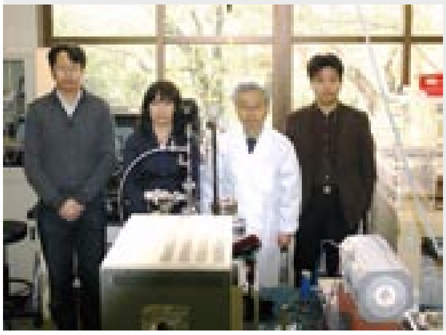

Metal acetylides or metal ethynyl molecules are made of the M^+–C^- ionic bonds. However, the ionic states of the acetylides are essentially metastable resulting in the segregation into metal-carbon or metal-organic polymer nanophases. Following to the invention of graphene-singlewalled Mesoporous Carbon Nano Dendrides (MCND) by evaporating silver from dendroid silver acetylide crystals, we have invented Graphene-multiwalled Alveolate Carbon (GAC), this time, and also 3D nanonets with GAC. These highly electron-conductive materials can be used for the electrodes of various next generation batteries.

1. Invention of Graphene-Multiwalled Alveolate Carbon for Novel Battery Electrodes

As demonstrated by the invention of graphene-walled Mesoporous Carbon Nano-Dendrites (MCND), metal- acetylides are well suited for generating nanostructured conductive materials. In contrast to silver acetylide, copper acetylide or methylethynyl copper normally produces wire-type crystals. Copper methylacetylide ($Cu–C{\equiv}C–CH_3$) also produces wire type crystals bigger and longer than those of copper acetylide. Following to the thermal activation at 230 °C under hydrogen atomosphere, the wire crystals filled in a 300 mL beaker suddenly exhibit the violent segregation reaction producing copper nanocrystals in carbon and a gas mixture of methane and ethylene. A part of copper nanoparticles is removed by the treatment with nitric acid and the residual copper particles are removed at a temperature higher than 1150 °C. The density of the remaining carbon material is 2.07 g/cm^3 that is 4.2% smaller than that of graphite (2.16 g/cm^3). Thermogravimetric Analysis showed a burning temperature as high as 682 °C: A little higher than that of MCND. The small angle X-ray scattering (SAXS) studies suggest that there are three types of the pores; the main part (69% in volume) has empty cores (an average size of 6 nm) surrounded with the shells of 0.83 nm thickness on average, the second one has nearly the same core radii but much thicker shells (17 nm av.), and the third one has

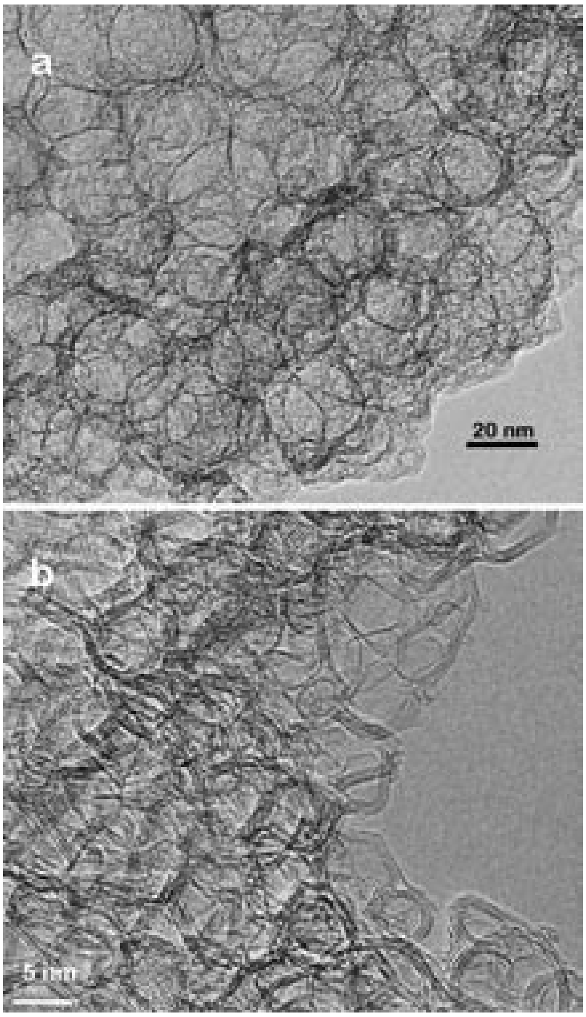

Figure 1. TEM images of a plate-type GAC treated at 1000 °C(**a**), and 1400 °C(**b**).

an average pore size of 40 nm: Each of them is located in the edge area of plate type alveolates, branch-type alveolate rods, and in the middle of big plates, respectively. TEM images of the carbon are shown in Figure 1. Figures 1-a and 1-b show the main component of the plate-type GAC, and the TEM image of the second component showed graphene-multiwalled rod-like alveolate carbon. According to these morphology and various properties, we call this carbon “Graphene-multiwalled Alveolate Carbon (GAC).”

The escape pathways of copper allow other atoms or molecules to be stored in the pores. Thus we have succeeded to store Sn and Si nanocrystals in the pores. Lithium ion batteries with these materials as negative electrodes have exhibited electric capacities as high as 1200–1400 mAh/cm^3 and almost flat charge/discharge cycle performance.

2. In Situ Preparation and Catalytic Activation Method for Copper Nano-Particles from Acetylide Molecules

Metallic surface is too reactive to keep its original structure under usual atmosphere. In order to avoid oxidation and inactivation, we propose a facile preparation method for catalysts of metal nano-particles in situ. Copper acetylide (C_2Cu_2) molecules and copper methyl-acetylide (CuCC–CH_3) molecules can be used as precursors of copper nano-particles. Figure 2 shows a High Resolution (HR)TEM image of which the nano-particle, atomically resolved lattice pattern was clearly observed. The space fringes detected in the HRTEM image are well matched with the d value (0.208 nm) of copper. The Cu nano-particle was covered with amorphous parts. The amorphous carbon layers can function as protection group for oxidation. Actually the metallic copper lattice could be observed even if the TEM specimen was exposed to air during transfer into the TEM apparatus. This means that the outer amorphous carbon could protect the reactive copper nano-particle from oxidizing by air.

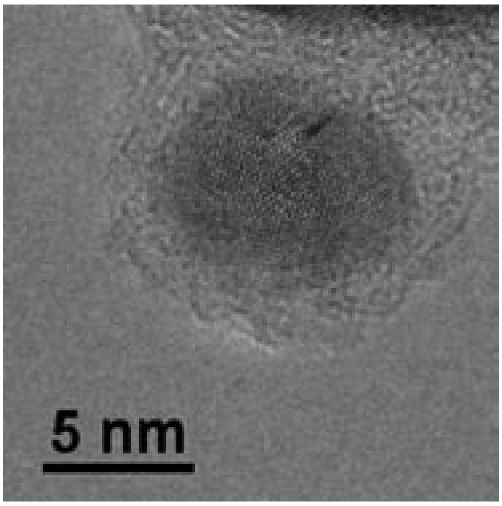

Figure 2. High-resolution transmission electron microscopic (HRTEM) image of annealed CuCC–CH_3 acetylide molecules.

3. Strong Intermolecular Interaction *via* Acetylide Ligands

Transition metal acetylide complex is the isoelectronic carbon analogue of a nitrile complex that is one of the representative building blocks of magnetic materials. In the previous work, we succeeded in constructing the first transition metal acetylide based magnets. However, in those cases, the acetylide ligand itself plays only a subsidiary role in the intermolecular spin–spin interactions because the ligand is placed too far from adjacent molecules to interact. That is, the appropriateness of an acetylide ligand for constructing a molecule based magnet remains unclear.

To evaluate the aptitude of an acetylide ligand for a magnetic material, we tried to construct new molecule-based magnetic materials based on [CrCyclam(C≡C-NaphOMe)$_2$]$^+$ and TCNQ$^-$ (Figure 3a), where the Coulomb repulsion between a negatively charged acetylide ligand and an anion is weakened due to the large π orbital of a naphthyl group and the strong electron affinity of a TCNQ molecule. In consequence, a short contact between an acetylide ligand and a TCNQ anion is expected. The metathesis of [CrCyclam(C≡C-NaphOMe)$_2$]OTf and Bu$_4$N$^+$TCNQ$^-$ in 1,2-dichloroethane (DCE) gives [CrCyclam(C≡C-NaphOMe)$_2$](TCNQ)(DCE) (**1**), while the coexistence of a neutral TCNQ gives [CrCyclam(C≡C-NaphOMe)$_2$](TCNQ)$_2$(DCE) (**2**). The crystal structures of both salts are characterized by the one dimensional alternate stacking of cations and anions (TCNQ$^-$ for **1** or TCNQ$_2$$^-$ for **2**) as shown in Figure 3b, where naphthyl groups and TCNQ molecules are stacked face-to-face. The magnetic susceptibilities of the salts show good agreement with one dimensional S = [1/2, 3/2] ferrimagnetic model with the intra-chain interaction 2J of –19.7 and –4.7 K for **1** and **2**, respectively. These strong interaction via an acetylide ligand evidence the usefulness of transition metal acetylides for a building block of molecule-based magnets.

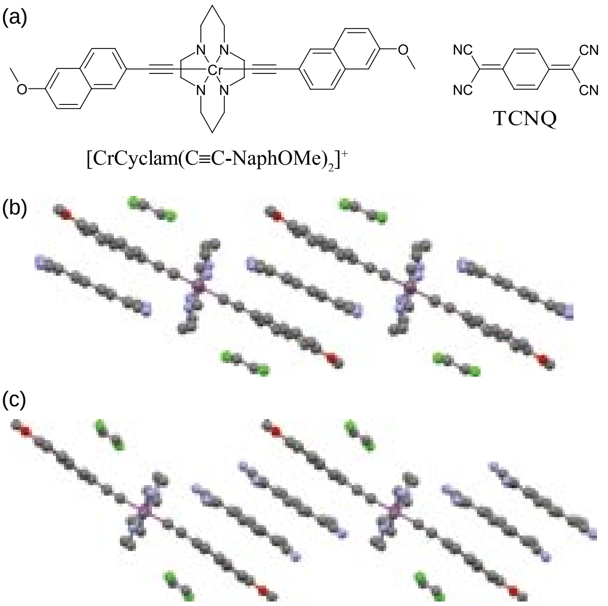

Figure 3. (a): Molecular structures, (b): Crystal structure of **1**, and (c): That of **2**.