

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

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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. Following to the invention of graphene-walled Mesoporous Carbon Nano Dendrites (MCND) by evaporating silver from dendroid silver acetylide crystals, we have invented copper nanowires and nanonets by removing the carbon, this time, and also 3D nanonets with copper skeletons with carbon mantles. These electron-conductive materials can be used for energy storage devices.

1. Invention of Electron-Conductive 3D Nanostructure Networks for Energy Storage 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 than those of copper acetylide as shown in the next section. These wire crystals form bundles of the wires and, owing to the catalytic activity of copper, all carbons are removed as volatile hydrocarbon gases leaving copper wires, or 3D copper nets (Figure 1-a). We also succeeded to generate Hollow Carbon Nets by removing copper and the methyl group from copper methylacetylene wire crystals. After the segregation reaction of the acetylide to copper nanoparticles, light hydrocarbon gases, and the carbon matrices with 3D connected net-type structures of 20~150 nm wires (Figure 1-b), mild thermal activation and nitric acid treatment removes copper components from the hybrid materials leaving hollow carbon networks. This material allow to be heated at a high temperature producing conductive graphene and graphitic components around the wall region.

In the empty space of the carbon networks, one can fill tin nanoparticles or silicon submicron particles to make lithium ion batteries or other active metal particles for new batteries.

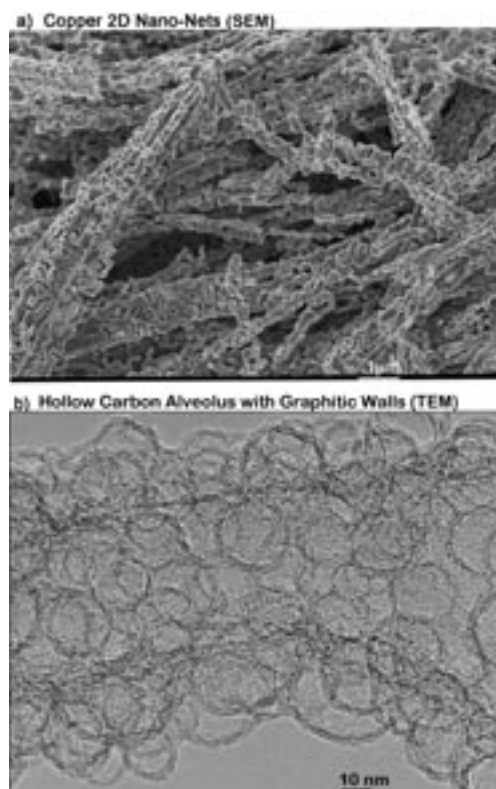


Figure 1. a: a SEM image of the 2D copper nanonets. b: Hollow Carbon Alveolus with graphitic walls. The body is a planer belt shape with many carbon balls connected each other.

2. Self-Assembly of Copper Methyl-Acetylide Nanowires

The methods for nanowire production by highly aniso-

tropic materials are usually based upon the binding with covalent bonds. The Cu_2C_2 molecule is a new category of highly anisotropic crystal, which is based on ionic bonding with a highly anisotropic ligand of a C_2^{2-} unit. Crystal growth of metal atoms is expected to be isotropic and nanowire structures cannot be obtained by a normal method of crystal growth. Our strategy is that the insertion of an acetylenic functional group (C_2^{2-} unit) to metal element provides anisotropic properties. Metal acetylides can be a candidate compound to self-assemble into nanowire morphology.

The substituent effect was examined on nanowire generation of Cu_2C_2 . We have succeeded in producing the copper methyl-acetylene (CuC_2CH_3) nanowires by the simple self-assembly technique. The methyl substitution on an acetylene molecule, can also self-assemble into nanowire morphology through methyl-methyl hydrophobic intermolecular interaction in an aqueous solution. It may mean that an acetylenic or a methyl-ethynyl functional group originally has anisotropic crystal growth properties.

It is very simple to produce CuC_2CH_3 nanowires. The fabrication method for CuC_2CH_3 nanowire involves bubbling methyl acetylene (propyne, HC_2CH_3) gas into an ammonia solution of copper chloride (CuCl).^{1,2} Figure 2 shows a scanning electron microscopic (SEM) image of as-grown product of CuC_2CH_3 . A mat with copper methyl acetylide nanowires was observed. It should be noticed that the amount of impure, amorphous product (not nanowire) for CuC_2CH_3 is much smaller than that for Cu_2C_2 . Not only purity of the CuC_2CH_3 nanowire mats, but also the large surface area of them can link to the capability of good gas adsorbent, gas sensor, or gas storage materials. Indeed, we attempt to check the properties of this nano-material for hydrogen storage, catalysis and so on.

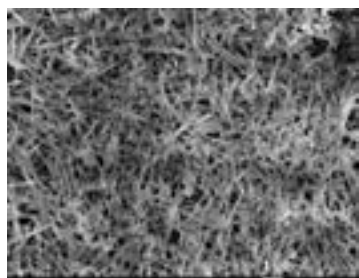


Figure 2. A SEM image of $\text{Cu-C}\equiv\text{C-CH}_3$ bundled nanowire crystals. Organometallic crystals are normally space-charged for SEM observation.

3. Weak Ferromagnetism in Chromium Acetylide Based Magnet

The interest in constructing a transition metal acetylide $[\text{M}(\text{C}\equiv\text{C-R})_n]^{(m-n)+}$ based magnet has been stimulated, in part, by its superior optical properties that raise the possibility of using the materials in various magneto-optical devices.

Recently, we succeeded in constructing the first transition metal acetylide based magnet $[\text{CrCyclam}(\text{C}\equiv\text{C-Ph})_2][\text{Ni}(\text{mdt})_2](\text{H}_2\text{O})$. The crystal structure of the material is characterized by the centrosymmetric unit cell containing a pair of a

cation $[\text{CrCyclam}(\text{C}\equiv\text{C-Ph})_2]^+$ ($S = 3/2$) and an anion $[\text{Ni}(\text{mdt})_2]^-$ ($S = 1/2$), and one water molecule. The cations and anions form one dimensional $[3/2-1/2]$ ferrimagnetic chains. The inter-chain interaction between adjacent cations along the a -axis is mediated by the water molecules which are strongly bound to the cations by hydrogen bonds as shown in Figure 3b. Despite the centrosymmetry of the whole crystal, a water molecule can occupy only one of the two centrosymmetric sites, resulting in the local breakdown of the inversion symmetry between adjacent cations. The observed magnetic susceptibility is in good agreement with the theoretical value of the isolated $[3/2-1/2]$ ferrimagnetic chains down to 3.8 K with the intra-chain interaction $2J/k_B = -5.7$ K. The weak inter-chain interaction through water molecules brings a magnetic phase transition at 3.7 K accompanied with a small spontaneous magnetization as shown in Figure 1d, indicating a weak-ferromagnetic ground state below the temperature. The remanent magnetization monotonically increases from 0.016 to 0.12 μ_B as the temperature decreases from 3.7 to 1.8 K, while coercive force approximately keeps a constant value of 0.8 mT in the temperature range of $2.9 < T < 3.7$ K, followed by a rapid increase below 2.9 K, suggesting the existence of the second phase transition. The existence of the second phase transition is also evidenced by the AC susceptibility, but the detail of the transition remains unclear. The weak ferromagnetism is originated from the local symmetry breakdown that allows the Dzyaloshinsky-Moriya interaction between adjacent cations despite the centrosymmetry of the whole crystal.

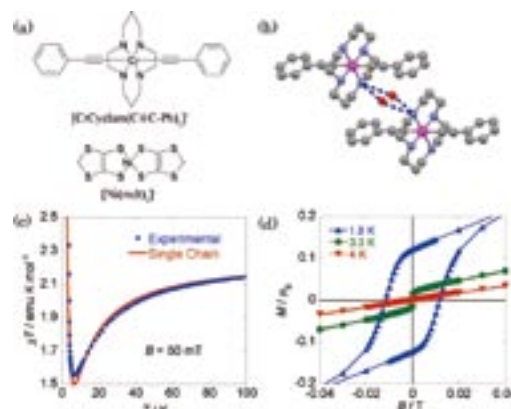


Figure 3. a) The molecular structures. b) The inter-chain interaction path along the a -axis mediated by a water molecule. The red spheres indicate two crystallographically equivalent positions of the water molecule, and the dashed blue lines represent the hydrogen bonds between the oxygen atom of a water molecule and the hydrogen atom of cations. c) The temperature dependence of the χT value. The red solid line indicates the theoretical value calculated by the isolated $[1/2-3/2]$ ferrimagnetic chain model with the intra-chain interaction $2J/k_B = -5.7$ K. d) The magnetization curves measured at 1.8, 3.3 and 4 K.

References

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- 2) K. Judai, S. Numao, A. Furuya, J. Nishijo and N. Nishi, *J. Am. Chem. Soc.* **130**, 1142–1143 (2008).