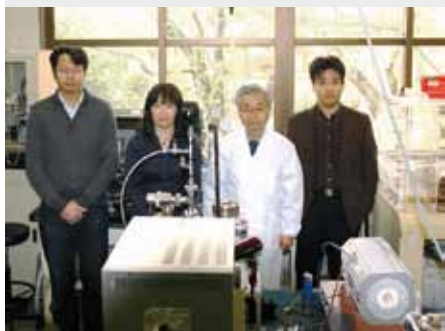


Graphene-Walled Alveolate Carbon & Structures and Functions of Metal–Carbon Nano-Systems Made from Metal-Acetylides

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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 Dendrites (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. Improvement of Graphene-Multiwalled Alveolate Carbon for Novel Battery Electrodes

As demonstrated by many researchers, graphene single sheets and multiple layers are successfully prepared on the ultra-clean surface of metallic copper, nickel or iron. Chemical vapor deposition (CVD) of acetylene or methane produces C_2 radicals that forms condensed hexagonal rings (*i.e.* graphene) with π -orbitals sitting on the d- and s- orbitals of the metal surface. This happens on the gas-solid interface at relatively high temperatures. In order to make a graphene walled mesoporous carbon, copper methylacetylide wire crystals are used with coating iron compound layers that prevent the acetylide segregation reaction explosive. Copper nanoparticles are generated and methyl radicals are converted to methane and ethylene leaving C_2 radicals on the surface of copper particles. On the heating of the reactant, copper metals get away from the inner space to outside leaving the quasi-spherical (originally spherical) pores with walls made of two or three graphene layers as shown in figure 1b. As seen in the figure, all carbons in this alveolate

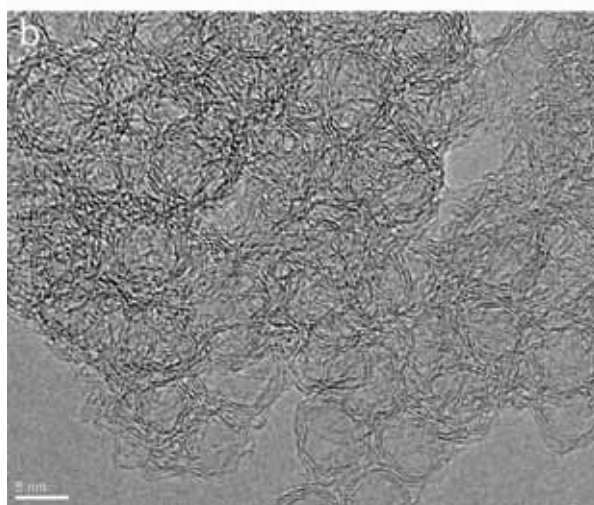
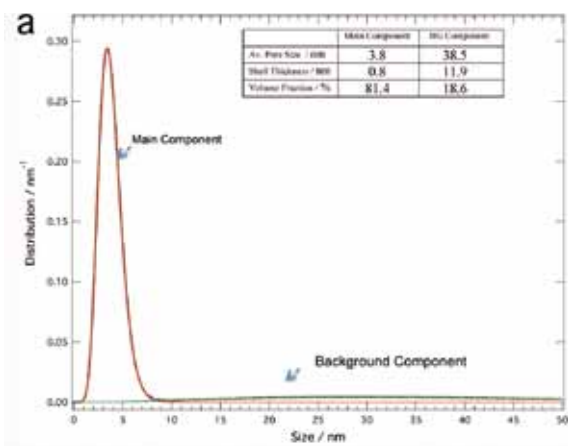


Figure 1. a: Core/shell analysis and the pore size distribution of the improved Graphene-multiwalled Alveolate Carbon. b: A TEM image of the improved Graphene-multiwalled Alveolate Carbon.

carbon are graphene sheets. Amorphous carbon is evacuated as CO₂ gas leaving micro- or meso-pores in the body and increasing the BET surface area of the alveolate carbon. Now, use of this carbon is under aggressive examination for various battery electrodes.

2. In Situ Preparation and Catalytic Activation Method for Copper Nanoparticles from Acetylide Molecules¹⁾

Because metal nanoparticles have a high surface area to volume ratio, they can be highly reactive, cost-effective catalysts. However, metallic surfaces are usually too reactive to maintain their metallic character in the presence of oxygen and/or water vapor. Metal nanoparticle catalysts must be handled carefully to avoid oxidation and inactivation. Here, we suggest a facile in situ preparation method for metal nanoparticle catalysts. Copper acetylide and copper methyl-acetylide molecules are based on ionic bonding, and are relatively stable in air. They can be used as a precursor of copper nanoparticles. Due to their instability at increased temperatures, subsequent annealing promotes a segregation reaction into elemental copper and carbon. Transmission electron microscopy and powder X-ray diffraction revealed that the average diameters of the Cu nanoparticles thus formed were 13.3 and 4.4 nm for C₂Cu₂ and CuCC-CH₃ precursors, respectively. This suggests that the substitution of acetylide molecules can control the size of the resulting copper nanoparticles. The primary advantage of this preparation method is that the functional acetylide group can reduce copper cations. No additional reducing agent is required, so no further separation process is necessary. This presents in situ preparation process. The catalytic activity of the resulting Cu nanoparticles was confirmed for a hydrogen storage system.

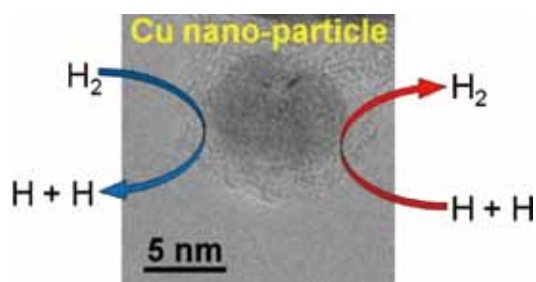
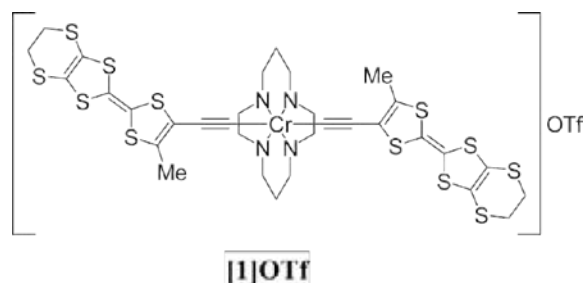


Figure 2. Scheme of hydrogen conversion by Cu nanoparticles covered with amorphous carbon mantles.

3. Weak Ferromagnetism and Strong Spin-Spin Interaction Mediated by the Mixed-Valence Ethynyltetraathiafulvalene-Type Ligand²⁾

A new chromium complex with ethynyl-tetraathiafulvalene (TTF) type ligands, [CrCyclam(C≡C-5-methyl-4'5'-ethylene-dithio-TTF)₂OTf] ([1]OTf), was synthesized. The cyclic voltammetry of the complex shows reversible two oxidation waves owing to the first and second oxidation of TTF unit. The electrochemical oxidation of [1]OTf in Bu₄NClO₄ or Bu₄NBF₄ solution of acetonitrile-chlorobenzene 1:1 mixture gave isostructural crystals of [1][ClO₄]₂(PhCl)₂(MeCN) and [1][BF₄]₂(PhCl)₂(MeCN), where two mixed-valence TTF units of adjacent complexes form dimer cation radical. The crystal structures are characterized by the alternate chain of $S = 3/2$ Cr³⁺Cyclam units and $S = 1/2$ (TTF)²⁺ dimers. These two paramagnetic components are connected directly by ethynyl group, resulting in the strong intra-chain spin-spin interaction of $2J/k_B = -30$ and -28 K for [ClO₄]⁻ and [BF₄]⁻ salts, respectively ($H = -2J\sum_i S_i S_{i+1}$). Both salts show weak-ferromagnetic transition at 23 K thanks to inter-chain anti-ferromagnetic interaction between TTF dimers. The remanent magnetizations and coercive forces of non-oriented samples at 1.8 K are 0.016 μB and 90 mT for the [ClO₄]⁻ salt, and 0.010 μB and 50 mT Oe for the [BF₄]⁻ salt, respectively. The weak-ferromagnetism is attributed to the Dzyaloshinsky-Moriya interaction between adjacent TTF dimers and / or the single ion anisotropy of [1]²⁺.



References

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