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ScienceDirect
Mendeleev Commun., 2012, **22**, 248–249

Mendeleev
Communications

Synthesis of graphite-coated copper nanoparticles by the detonation of a copper-doped emulsion explosive

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DOI: 10.1016/j.mencom.2012.09.006

The graphite-coated copper nanoparticles were synthesized by the detonation decomposition of a copper-doped emulsion explosive and their structure and chemical composition were characterized by TEM, HRTEM, EDX and XRD analysis.

The encapsulation of second phases in graphite is of considerable current interest.[1] Since copper is relatively inexpensive and possesses high electrical conductivity, copper nanoparticles can potentially replace noble metal (silver and gold) nanoparticles used in various materials.[2–4] It is well known that bare copper nanoparticles exposed to air at room temperature are oxidized to form Cu_2O and further CuO in several hours mainly due to a surface effect. The encapsulation of metal nanoparticles into carbon nanoshells significantly changes their thermodynamic, conductive, electronic or mechanical properties.[5,6] Graphite-coated copper nanoparticles (GCNs) can be prepared by a modified arc discharge method,[7,8] a metal-organics pyrolysis method,[9] a modified arc plasma method,[10] a low-temperature thermal treatment,[11] a mechanical activation method,[12] a CVD method[13,14] *etc.* Since the invention of emulsion explosives with good detonation properties, water resistance and flow performance, they have been widely used in civil engineering. Therefore, in principle, any oxidizer and combustible agent can be converted into an emulsion explosive for different purposes. The addition of a nitrate[15] to ammonium nitrate in a classical W/O was found to result in a decrease in the detonation parameters of the emulsion explosive. The nano-$MnFe_2O_4$ and nano-lithium/zinc oxides for new energy battery materials were prepared from emulsion explosives containing Fe/Mn or Li/Zn ions.[16,17] Meanwhile, carbon encapsulated Fe, Co, Ni and Fe based alloys were synthesized by the detonation decomposition of highly explosive mixtures.[18–23] In this work, a copper-doped emulsion explosive was used in the detonation synthesis of GCNs nanostructure materials.

The main ingredients of the copper-doped emulsion explosive are shown in Table 1.[†] The aqueous and oil phases were mixed with a specified ratio and then stirred for about 8–15 min at 1000 rpm to prepare a copper-doped emulsion explosive for synthesizing GCNs. The detonation synthesis was carried out in a closed explosion vessel. The emulsion explosive charge (about 150–200 g) was ignited by shock wave. Argon gas was used for cooling the detonation products. Then, the as-prepared black powder (goal products) was collected from the inner vessel.

Table 1 Main ingredients of the copper-doped emulsion explosive.

Phase	Name	Formula	Content (wt%)
Disperse phase	Ammonium nitrate	NH_4NO_3	10–20
	Copper nitrate	$Cu(NO_3)_2\cdot 3H_2O$	50–70
	Carbamide	CH_4N_2O	5–8
	Water	H_2O	~10–30
Continuous phase	Oleic acid	$C_{18}H_{34}O_2$	5–10
	Paraffin wax	$C_{18}H_{38}$	5–10
	Machine oil	$C_{12}H_{26}$	5–10
Emulsifier	SP-80	$C_{24}H_{44}O_6$	5–10
Sensitizer	RDX	$C_3H_6O_6N_6$	0–5

The morphological and structural details of as-obtained composite nanoparticles were investigated by TEM and HRTEM. All of the spheroidal particles have a core-shell structure with a big black core and a grayish shell. The as-obtained detonation products had diameters of 10–30 nm [Figure 1(*a*)]. Obviously, amorphous carbon occurred among the composite nanoparticles. Insert in Figure 1(*b*) clearly displays the typical magnified single-core shell structure of a nanoparticle shown in Figure 1(*a*). It shows a typical completely sealed carbon shell 3–5 nm in thickness within a big spherical core copper crystal of about 20 nm. No voids could be observed between the core and the shell, and the interlayer distance of coating graphitic lattice was about

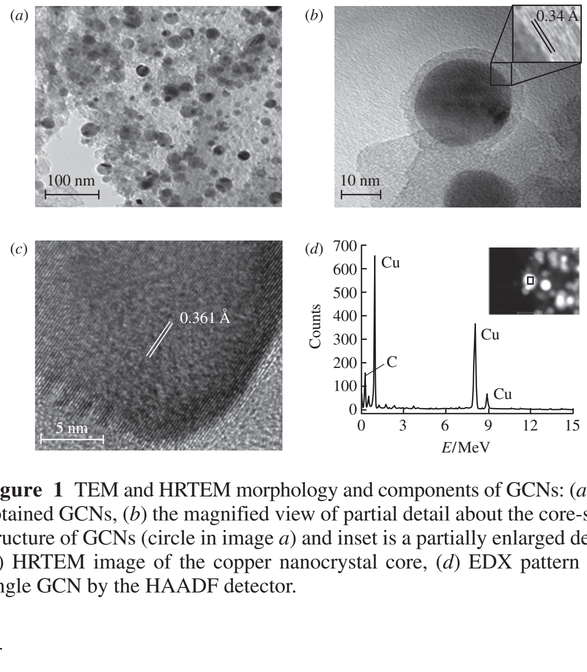

Figure 1 TEM and HRTEM morphology and components of GCNs: (*a*) as-obtained GCNs, (*b*) the magnified view of partial detail about the core-shell structure of GCNs (circle in image *a*) and inset is a partially enlarged detail, (*c*) HRTEM image of the copper nanocrystal core, (*d*) EDX pattern of a single GCN by the HAADF detector.

[†] Analytical-grade ammonium nitrate, copper nitrate and carbamide from Tianjin Fu Chen Chemical Reagent Co., and oleic acid, paraffin wax, machine oil and SP-80 (Zibo Feng Sen Oil Chemical Co.) were used. The dispersed phase (aqueous phase) mainly consisted of copper nitrate (50–70%), ammonium nitrate (10–20%), carbamide (5–8%) and water (15–30%). The continuous phase (oil phase) was mainly composed of oleic acid, paraffin wax and machine oil (5–10%). The emulsifying agent was SP-80 (5–10%). The sensitizing agent was RDX (0–5%).

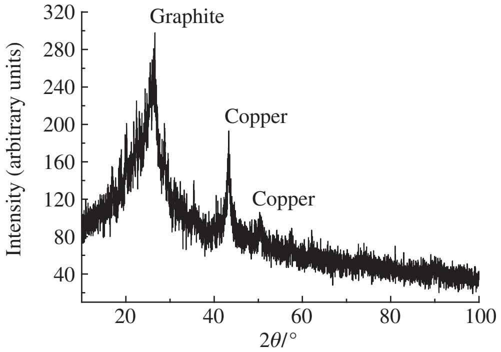

Figure 2 XRD pattern of as-obtained GCNs.

0.34 nm. The measured lattice fringes (~0.361 nm) from the copper core region and the electron diffraction patterns are accordant to fcc-copper planes, clearly indicating differences between the graphitic coating shell [Figure 1(*c*)]. The EDX image of a single GCN (inset in the HAAD local-scan analysis image) exhibits mixed diffraction peaks assigned to copper and carbon [Figure 1(*d*)]. Moreover, the copper diffraction peak is more intense, as compared to that of carbon coating shell, denoting that the spherical copper nanocrystal surface is coated with a thin layer of graphite.

To further verify the composition of the detonation products, the crystallization of the composite nanoparticles was characterized by XRD (Figure 2). The diffraction peak at about 26.37° can be assigned to the (002) plane of a hexagonal graphite structure (JCPDS no. 41-1487) corresponding to the interplanar spacing $d \approx 3.377$ Å. The graphite carbon peak intensity is very high, suggesting that the detonation products are mainly composed of graphite coating shells. The other two peaks are consistent with elemental copper; these peaks at 43.21° and 50.42° can be attributed to the corresponding (110) and (200) reflections of the fcc copper crystal according to JCPDS no. 04-0836.

The interplanar spacing d of the composites corresponding to diffraction peaks can be obtained by the Bragg equation, corresponding to the crystal plane spacings d of bcc copper of ~2.092 and 1.808 Å. The average grain size calculated at ~21.4 nm by the Scherrer equation is consistent with the observed TEM result. It is well known that, when disordered carbon is heated to above 2500 °C, the chaotic carbon layer is gradually moving to the graphite structure, that is, graphitization takes place. The degree of graphitization is $\mathrm{GD} = (3.440 - d_{002})/(3.440 - 3.354)$, where d_{002} is the interplanar spacing of the as-obtained graphite layer, 3.440 Å is the completely graphitized planar spacing, and 3.354 Å is the ideal graphite crystal layer spacing. According to as-obtained graphite lattice spacing ($d = 3.377$Å), the graphitization degree of detonation product is about 0.732. Thus, the graphitization degree of the carbon coating shell from the obtained product is relatively high; that is, the as-obtained product contains a certain amount of amorphous carbon, as evidenced by the XRD pattern.

In conclusion, the spherical and core-shell structural GCNs were successfully synthesized by the detonation of a copper-doped emulsion explosive. The experimental results show that the as-prepared composite nanoparticles are composed of a single-crystalline fcc copper core and a graphite carbon coating. The graphitization degree of the carbon coating shell is relatively high. The average size distribution is in the range of 10–30 nm.

This work was supported by the Natural Science Foundation of China (project nos. 10972010 and 11028206) and the China Postdoctoral Science Foundation (project no. 2012M510270).

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Received: 20th April 2012; Com. 12/3915