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ScienceDirect
Mendeleev Commun., 2013, **23**, 153–154

Mendeleev Communications

Synthesis of high-quality graphite-coated iron composite nanoparticles by a rapid gas-phase chemical reaction

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DOI: 10.1016/j.mencom.2013.05.011

A new strategy was applied to effectively synthesize spherical core shell structural graphite-coated iron (Fe@G) composite nanoparticles, which were characterized by XRD, TEM, EDX, SAED and XPS.

It is practically important to coat naked metal nanocrystals with an oxygen-impermeable sheath to protect and chemically stabilize them against degradation. The core of graphite-coated metal is a metal nanocrystal, while the outer shell is constituted of several graphite/graphene layers. Graphite-coated iron (Fe@G) nanoparticles are of particular significance and exhibit great potential for numerous applications, such as data storage, magnetic fluids, catalysis, environmental remediation, biotechnology, drug delivery, cell and protein separation.[1–8] Although graphite-coated metal nanoparticles are promising, the poor production rate, complex technological process and high energy consumption hinder the study of this novel material. Recently, different graphite coated strategies and extensive efforts have been explored and developed, such as a modified arc-discharge method, pyrolysis, vapour deposition, catalytic reactions and cumulative, detonation, combustion, hydrothermal and sonochemical methods.[9–20]

Gas-phase shock wave pyrolysis processes for the preparation of functional carbon nanoparticles are of considerable interest.[21] It is well known that a shock tube technique is widely used for the investigation of physical and chemical processes in a broad range of temperatures and pressures. Here, we put forward a rapid chemical reaction for preparing Fe@G nanoparticles using a combustible gas (methane), a gas phase oxidant (oxygen) and other precursors in a shock tube equipment. The rapid gas-phase chemical reaction can provide simple, green and continuous methods for Fe@G nanoparticles.

In a typical synthesis, filling gas (the volume ratio of CH_4 and O_2, 1:2) was first premixed in a shock tube (length, 2200 mm; circular tube, 80 mm) after evacuation and heated up to 200–230 °C (Figure 1). Then, 0.1 mol of $Fe(CO)_5$ were dissolved in 500–800 ml of acetone with stirring to form a wheat solution. The wheat solutions were filled into the shock tube and gasified.

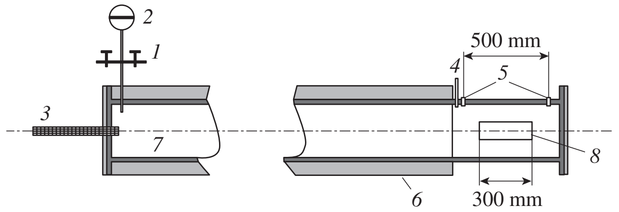

Figure 1 Schematic diagram of the experimental setup: (*1*) inlet/vent hole; (*2*) vacuum watch; (*3*) high energy generator; (*4*) feed inlet; (*5*) pressure sensor; (*6*) temperature controlling apparatus; (*7*) vacuum pump; (*8*) observation window.

The mixed gas phase precursors were ignited and detonated by a high energy shock wave generator. The detonation wave velocity was about 2000 m s^{-1} from the initiation, and the inner pressure rised quickly. The maximum detonation pressure was *ca.* 3 MPa when the chemical reaction was complete. During the rapid chemical reaction, the coating graphite layer mainly originated from methane and acetone. The black products were collected at the inner tube wall by filtration and washing with absolute ethanol several times, and dried in air. The detailed mechanisms of methane chain reactions (including 53 composites and 325 reactions) are fairly complex for gas explosion. The rapid reaction process occurs in accordance with the following equations:

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g) + \Delta Q \quad (1)$$
$$\Delta Q = 831 \text{ kJ mol}^{-1}$$

$$Fe(CO)_5(g) + C_3H_6O(g) + CH_4(g) \rightarrow Fe(l) + C(l) + 2H_2(g) + H_2O(g) + 5CO(g) \quad (2)$$

The products were characterized by XRD, which was used to analyze the phase and crystal structure with a Rigaku D/MAX2400 instrument operated at a step size of 0.02° in a range of 20–80° with CuKα radiation (k = 0.15406 nm, 40 kV voltage, 30 mA current). The morphologies and structures of the as-obtained black products were characterized by TEM using a TECNAI F-30 transmission electron microscope (operated at 300 kV, 0.205 nm point resolution and 0.102 nm line resolution). The chemical compositions of the detonation products were also analyzed using EDS and EDX. The surface compositions and element chemical states of the obtained product were investigated by X-ray photoelectron spectroscopy (XPS) on a Kratos instrument [operated at 15 kV, 15 mA, energy resolution of 0.48eV (Ag $3d^{5/2}$), minimum analysis area of 15 μm and measurement uncertainty of ~0.2 eV]. Electrons ejected from the surface were energy filtered *via* a hemispherical analyzer (HSA) before detection. These measurements were carried out at 300 K. Transmission electron microscopy (TEM) was used to further examine the crystallinity of the as-obtained Fe@G composite nanoparticles. Diameters of the spherical Fe@G nanoparticles ranged from 15 to 50 nm, the average diameter was about 32 nm from the inserted chart fitted by a Gaussian curve [Figure 2(*a*)]. Morphology investigation results showed that the size of the Fe core is about 45 nm, and it was coated in onion-like carbon with a shell thickness of *ca.* 5–8 nm. The energy dispersive X-ray spectrometry (EDX) image of the

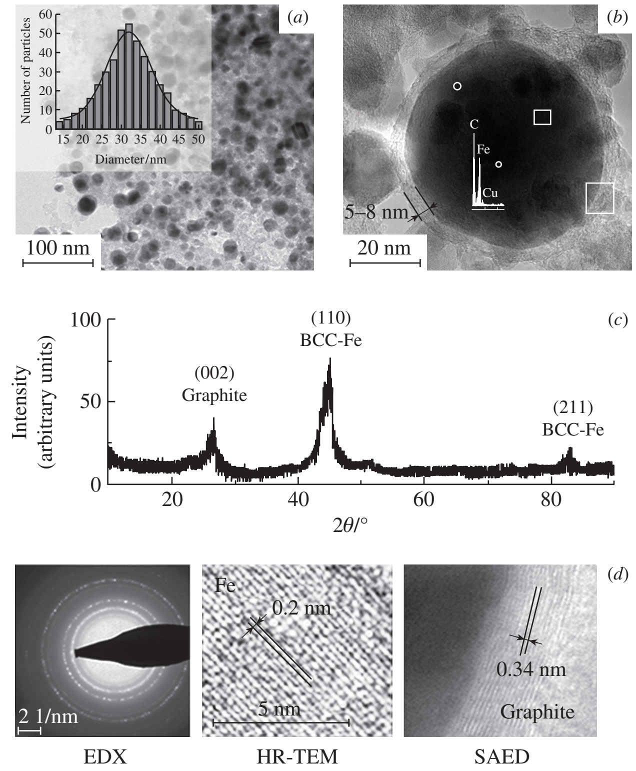

Figure 2 (*a*) TEM image of Fe@G and diameter distribution chart of Fe@G fitted by a Gaussian curve; (*b*) EDX pattern particle partial enlarged image of Fe@G; (*c*) XRD pattern of the obtained product; (*d*) HR-TEM and SAED images of Fe@G.

selected area confirms that there are mainly C and Fe atoms [Figure 2(*b*)]. As shown in Figure 2(*c*), voluminous graphite coated Fe and its composite nanoparticles were obtained from the product, whose peaks at 44.64 and 84.08° can be attributed to the corresponding (110) and (221) reflections of body-centered cubic (bcc) iron according to JCPDS No. 06-0696, and graphite exhibits a clear peak at about 26.4°, which is characteristic of the (002) plane. The interplanar *d*-spacings of the inner Fe core and carbon shell were found to be 0.20 and 0.34 nm, respectively[17] (the square area in high-resolution TEM images), which are in accordance with the (110) planes of bcc Fe and the (002) planes of graphite. Inset (the circle area) is the selected area electron diffraction (SAED) image of the inner Fe core, suggesting that the particle is a bcc iron single crystal. The composite nanoparticles are well crystalline, exhibiting clear crystal diffraction rings in the SAED image [Figure 2(*d*)].

The surface compositions and element chemical states of the product were investigated by XPS analysis. The full-scale XPS spectrum mainly shows only the Fe and graphite carbon at the surfaces (Figure 3), indicating the formation of a single phase Fe and graphite carbon phase material. In Figure 3(*b*), the observed sharp peak at 284.8 eV represents the sp^2 carbon–carbon bond in the graphite carbon shell, which supports the TEM results. The Fe 2*p* spectra of the product are shown in Figure 3(*c*), whose peaks at 706.5 and 720.6 eV indicate the obtained pure Fe nanocrystal according to Graat and Somers.[22]

Thus, we used a rapid chemical reaction of methane to prepare spherical core-shell structural Fe@G composite nanoparticles. The shock wave triggered the mixed multiple gas, meanwhile, induced methane rapid chemical reaction in a closed shock tube in a very short time. The as-obtained products consist of bcc Fe crystals (average diameter of *ca.* 32 nm) with well-crystallized graphite coating layers. The yield of the products was 50–60%. No peaks of impurities such as Fe-based oxides or carbides were observed, suggesting the high purity of the as-obtained products.

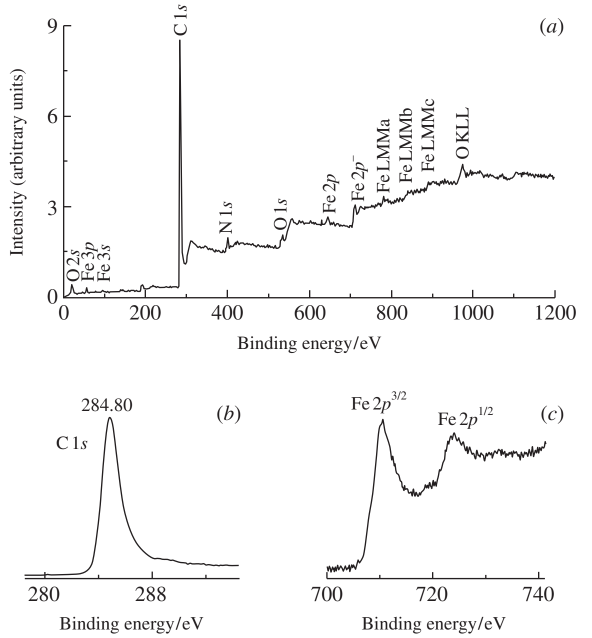

Figure 3 (*a*) Typical XPS spectrum of the obtained sample, (*b*) Fe 2*p* core-level spectrum and (*c*) graphite carbon coating layer spectrum.

This study was supported by the Natural Science Foundation of China (project nos. 10972051, 11272081 and 11028206), the China Postdoctoral Science Foundation (project no. 2012M510270) and the State Key Laboratory of Explosion Science and Technology, Beijing Institute of Technology (grant no. KFJJ13-05M).

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Received: 17th January 2013; Com. 13/4048