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Controllable synthesis, characterization, and magnetic properties of magnetic nanoparticles encapsulated in carbon nanocages and carbon nanotubes

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ABSTRACT

By controlling the pyrolysis temperature, core/shell materials with Fe_3O_4 encapsulated in carbon nanocages (Fe_3O_4@CNCs) and Fe encapsulated in carbon nanotubes (Fe@CNTs) were synthesized selectively from acetylene using Fe_2O_3 nanoparticles as catalyst in chemical vapor deposition. Scanning electron microscopic study showed that the efficiency of generating Fe_3O_4@CNCs and Fe@CNTs was high, exceeding 95%. Transmission electron microscopic study confirmed the high selectivity to Fe_3O_4@CNCs and Fe@CNTs, with the former having morphology similar to that of the catalyst particles. With Fe_3O_4 and Fe nanoparticles tightly wrapped in graphitic layers, the obtained Fe_3O_4@CNCs and Fe@CNTs materials show high stability and good magnetic properties.

1. Introduction

Due to surface and/or quantum-size effects, metal nanoparticles especially those of magnetic materials exhibit unique physical properties and have potential applications in many areas [1–4]. However, metal nanoparticles are usually highly active and easily oxidized in air, resulting in deterioration of characteristics such as magnetism. The breakthrough in this regard was the encapsulation of metal nanoparticles in carbon layers. Since the discovery of fullerenes, there was much advance in the development of carbon nanomaterials (CNMs) and carbon-coated nanocapsules [5–7]. Compared with other inert materials such as silica, metal oxides and polymer shells [8–10], carbon shells exhibited much higher stability in chemical and physical environments. With the metal nanoparticles encapsulated in carbon shells, they are protected from oxidation. Also, with the encapsulation, there is reduction of magnetic coupling between magnetic phases, opening the possibility of optimizing the intrinsic magnetic properties of the metal nanoparticles [11–15]. In the past years, carbon nanocages (CNCs) and CNMs that were filled with ferromagnetic materials have attracted considerable attention due to their potential applications such as electromagnetic wave absorption [12], magnetic data storage and human tumor therapy [16,17]. There are methods for the synthesis of metal-filled CNMs or CNCs [18–22]. Nonetheless, most of the adopted procedures were complicated, and the efficiency of metal encapsulation needs improvement [23–25].

Based on knowledge revealed in the past [26–29], we worked on the controllable synthesis of CNCs-encapsulated Fe_3O_4 (Fe_3O_4@CNCs) and carbon nanotubes (CNTs)-encapsulated Fe (Fe@CNTs). We selectively generated these core/shell structures with high efficiency over Fe_2O_3 nanoparticles by controlling the pyrolysis temperature of acetylene in chemical vapor deposition. To the best of our knowledge, our proposed route is very simple and has not been reported before.

2. Experimental

2.1. Synthesis of α-Fe_2O_3 catalyst

All reagents were of analytical grade and used without further purification. Typically, 30 ml of aqueous $NH_4H_2PO_4$ solution (0.05 M) was added to 30 ml of aqueous $Fe(NO_3)_3$ solution (0.3 M; yellowish in color) under vigorous stirring at room temperature (RT). After stirring for another five minutes, the resulted slurry was transferred into a Teflon-sealed autoclave and subject to hydrothermal treatment at

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220 °C for 48 h. With the setting cooled to RT, the as-obtained solid substance (red in color) was filtered out, washed three times with distilled water, and dried at 80 °C for 8 h.

2.2. Generation of Fe_3O_4@CNCs and Fe@CNTs core/shell materials

First, the as-obtained red powder (0.1 g) was dispersed on a ceramic plate that was positioned inside a quartz tube. Then the temperature of the furnace was raised from RT to a designed temperature with Ar flowing (controlled by flowmeter at a flow rate of 40 sccm) through the reaction tube. After that, the gas supply was shifted from Ar to acetylene for the synthesis of carbon-encapsulated nanomaterials. The decomposition of acetylene (atmospheric pressure, 2 h) was conducted at 400, 500 or 600 °C (heated at a rate of 10 °C/min). The products generated at pyrolysis temperatures of 400, 500 and 600 °C are denoted hereinafter as C-400, C-500 and C-600, respectively.

2.3. Characterization of products

The samples were examined on an X-ray powder diffractometer (XRD) at RT for phase identification using CuK_α radiation (model D/Max-RA, Rigaku). Raman spectroscopic investigations were performed using a Jobin-Yvon Labram HR800 instrument with 514.5 nm Ar^+ laser excitation. The morphology of samples was examined using a transmission electron microscope (TEM) (model JEM-2000EX, operated at an accelerating voltage of 80 kV), and field emission scanning electron microscope (FE-SEM) (model FEI Sirion 200, operated at accelerating voltages of 5 kV and equipped with a energy dispersive X-ray spectrometer (EDS)). The magnetic properties of samples were measured at 300 K using a Quantum Design MPMS SQUID magnetometer (Quantum Design MPMS-XL) equipped with a superconducting magnet capable of producing fields of up to 50 kOe. Fourier Transform Infrared (FTIR) spectra of samples (in KBr pellets) were recorded over a Nicolet 510P spectrometer.

3. Results and discussion

3.1. FE-SEM, XRD and EDS characterizations of catalyst

The FE-SEM images of the as-synthesized catalyst are shown in Fig. 1a and b. One can see a large amount of size-uniform hollow nanoparticles (as indicated by arrows), exceeding 94% of the entire content. The XRD pattern shows lines corresponding to α-Fe_2O_3 and P (as indexed in Fig. 1c). The EDS result shows the presence of Fe, O and P (Fig. 1d). Based on the results, it is deduced that the catalyst is mainly composed of hollow α-Fe_2O_3 nanoparticles with an average diameter of ca. 200 nm.

3.2. Microstructure and magnetic property of C-400

In each run, about 0.131 g of C-400 was harvested on the ceramic plate. The FE-SEM image (Fig. 2a) indicates that C-400 is mainly composed of hollow nanoparticles, with morphology similar to that of the α-Fe_2O_3 catalyst (Fig. 1a and b). The EDS result indicates the presence of C, Fe and O (Fig. 2b), and the Fe:O molar ratio of C-400 is much higher than that of the α-Fe_2O_3 catalyst (Fig. 1d). The XRD result of the obtained C-400 is shown in Fig. 2c. One can find that the diffraction peaks corresponding to α-Fe_2O_3 catalyst disappears completely after the reduction of α-Fe_2O_3 by C_2H_2 at 400 °C. And the diffraction peaks corresponding to phases of C, Fe_3O_4, $Fe_{0.942}O$ and Fe_2C can be observed clearly (as indicated by the symbols in Fig. 2c), indicating that the obtained C-400 is a composite made up of C and Fe_3O_4. Fig. 2d shows the Raman spectrum of C-400; there are a total of four peaks. The one at ca. 1602 cm^{-1} (called G-band, indicative of graphitic layer of high crystallinity) is corresponding to the E_{2g} mode of graphite that is related to the C – C vibration of carbon materials with sp^2 orbital structure. The one at ca. 1336 cm^{-1} (called D-band) is a consequence of resonance scattering with the emission of phonon [30,31]. The intensity ratio of the G and D bands (I_G/I_D) is commonly used to characterize the crystallinity of carbon materials. In the study, an I_G/I_D of ca. 1.09 was recorded for C-400, implying high crystallinity. The peaks at 281 and

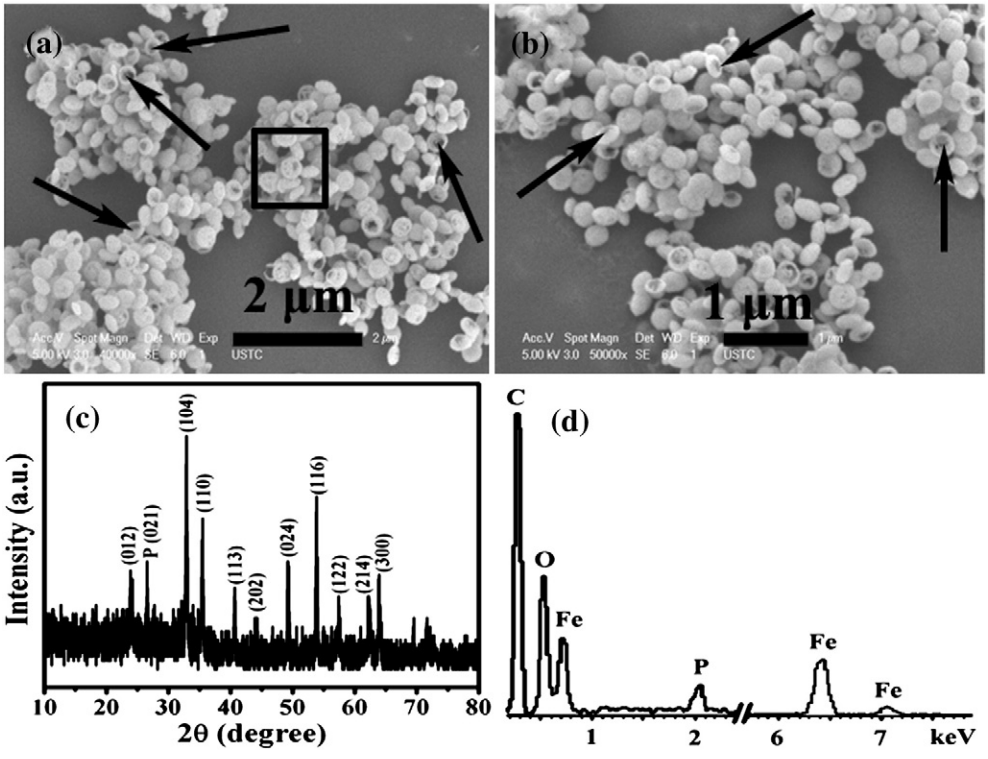

Fig. 1. (a,b) FE-SEM images, (c) XRD pattern, and (d) EDS result (collected from the area marked in 1a) of catalyst.