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A facile route to synthesize core/shell structured carbon/magnetic nanoparticles hybrid and their magnetic properties

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ABSTRACT

By controlling the pyrolysis temperature, core/shell structured Fe_3O_4/carbon nanocages, Fe/helical carbon nanotubes and Fe/low helicity of carbon nanotubes could be synthesized selectively over Fe_2O_3 nanotubes generated by a hydrothermal method. The transmission electron microscopic and scanning electron microscopic investigations revealed that the efficiency of generating core/shell structured hybrid was high, exceeding 90%. Because of the magnetic nanoparticles tightly wrapped in graphitic layers, the obtained core/shell structured hybrids showed high stability and good magnetic properties. And the magnetic properties of the obtained core/shell structured hybrid could be tuned by the decomposition temperature and time. Therefore, a simple, inexpensive and environment-benign route was proposed to produce magnetism-tunable core/shell structured hybrid in large quantities.

1. Introduction

In the last decade, various kinds of core/shell nanostructures have attracted intense research interest owing to their multi-functionality and potential applications in more and more fields [1–4]. Among them, magnetic core/shell structured carbon hybrid has received an increasing attention, because they combine the unique properties of magnetic nanoparticles and carbon nanomaterials (CNMs). It is believed that the introduction of CNMs as inert shell is beneficial for protecting magnetic nanoparticles from agglomeration, providing a stabilized magnetic properties and oxidative resistance, and avoiding instability towards dissolution under acidic conditions [5–9], which makes carbon-encapsulated magnetic nanoparticles hold a great promise as multifunctional nanomaterials for their broadened potential applications in areas such as catalysis, giant magnetoresistance sensing, microwave absorption and biomedical area [10–13]. Up to now, several synthesis methods for carbon encapsulation have been attempted, such as chemical vapor condensation, arc discharge, pulsed laser irradiation of solution, hydrothermal or solvothermal method, and so on [14–19]. Nevertheless, most of these routes available now are not satisfactory, and still suffer from complicated and expensive process, low efficiency of encapsulation and uncontrollable properties. Therefore, an efficient strategy that is capable of synthesizing core/shell structured carbon-encapsulated magnetic nanoparticles in high efficiency of encapsulation from a simple, inexpensive and environment-benign process has been in highly demand.

In the previous work, we have employed the chemical vapor deposition technique for the synthesis of carbon nanotubes (CNTs) coated Ni nanoparticles and helical carbon nanotubes (HCNTs) coated Fe nanoparticles over Ni or Fe nanoparticles generated by a combined sol–gel and hydrogen-reduction method, respectively [20–22]. In this article, we report the selective synthesis of core/shell Fe_3O_4/carbon nanocages (Fe_3O_4/CNCs), Fe/HCNTs and Fe/low helicity of carbon nanotubes (Fe/L-HCNTs) directly over Fe_2O_3 nanotubes generated by a hydrothermal method. The obtained Fe_3O_4/CNC, Fe/HCNT and Fe/L-HCNT hybrids show high stability and good magnetic properties, and their magnetic properties can be tuned by the decomposition temperature and time.

2. Experimental

2.1. Synthesis of α-Fe_2O_3 catalyst

Similar to the method reported elsewhere [23], all reagents were of analytical grade and used without further purification. Typically, 9.6 mL of aqueous $NH_4H_2PO_4$ solution (0.02 M), 9.6 mL of aqueous $FeCl_3$ solution (0.5 M) and 150 mL distilled water were

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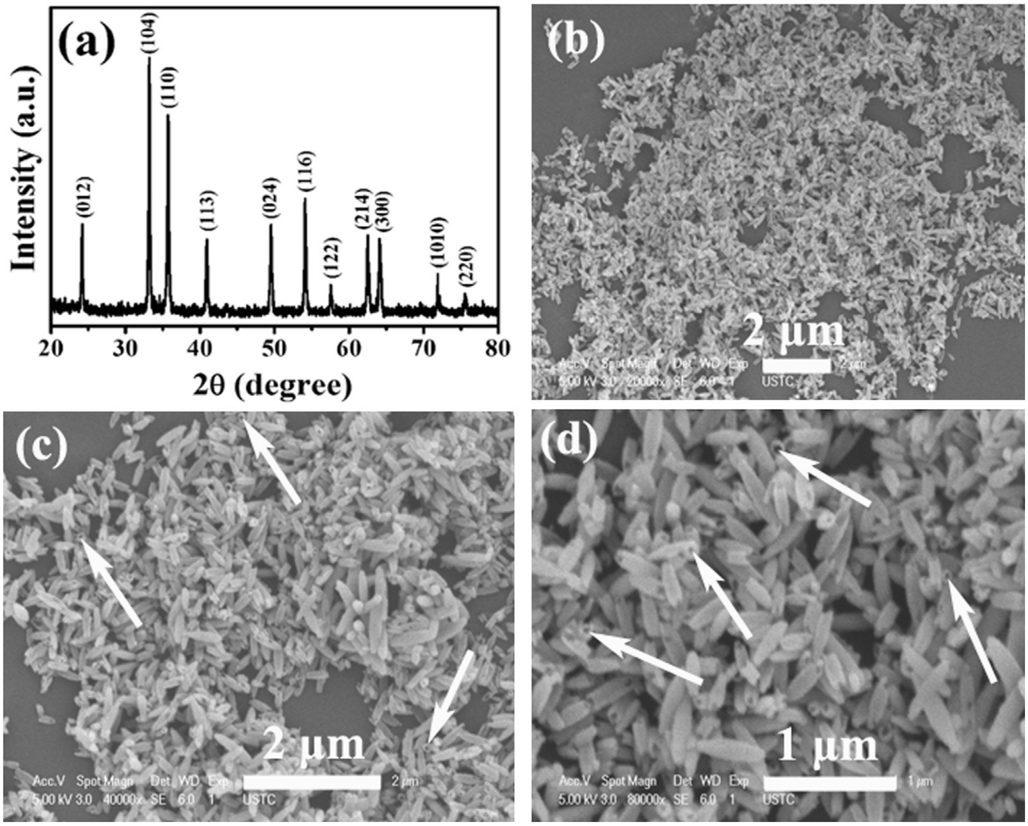

Fig. 1. (a) XRD pattern, and (b–d) FE-SEM images of the as-synthesized catalyst.

mixed together under vigorous stirring at room temperature (RT). Then the obtained solution was transferred into a Teflon-sealed autoclave. The autoclave was sealed and maintained at 220 °C for 48 h. After cooling to RT, the red solid powder could be collected after washed with distilled water and ethanol, and dried at 80 °C for 8 h.

2.2. Generation of 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 through the reaction tube, and acetylene (atmospheric pressure) was introduced into the tube at 400, 500 or 600 °C for 2 h, respectively. After cooling to RT, amounts of black samples could be colleted on the ceramic plate. And the products generated at a pyrolysis temperature of 400, 500 and 600 °C are denoted hereinafter as S-400, S-500 and S-600, respectively.

2.3. Characterization of products

The samples were examined on an X-ray powder diffractometer (XRD) at RT for phase identification using CuKα 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). 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.

3. Results and discussion

3.1. XRD and FE-SEM images of the as-synthesized catalyst

In order to identify the phase and microstructure, the XRD pattern and FE-SEM images of the as-prepared catalyst are shown in Fig. 1. As shown in Fig. 1a, the XRD pattern of the catalyst indicates that all the peaks correspond to Fe_2O_3, which is very close to the literature value (JCPDS No.86-0550). No other peak of impurity can be detected. The FE-SEM investigation (as shown in Fig. 1b–d) shows that the size-uniform Fe_2O_3 nanotubes (the nozzles are indicated by the arrows in Fig. 1c and d) are the majority in the obtained catalyst. Overall, the as-prepared catalyst is Fe_2O_3 nanotubes with an average diameter of ca. 90 nm.

3.2. Phase, Raman spectrum and microstructure of the collected samples

In order to confirm the experimental reproducibility, the experiments were repeated three times. As shown in Table 1,

Table 1
Weight of sample collected over Fe_2O_3 nanotubes at selected temperature in three runs.

Pyrolysis temperature (°C)	400	500	600
Sample	S-400	S-500	S-600
Weight of collected sample in each runs (g)	0.226	1.145	2.076
	0.225	1.151	2.069
	0.231	1.151	2.070