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Synthesis of Fe_3O_4/CNTs magnetic nanocomposites at the liquid–liquid interface using oleate as surfactant and reactant

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ABSTRACT

Carbon nanotubes (CNTs)-based magnetic nanocomposites have attracted significant research interest owing to their great potentialities in various technological fields. In this investigation, a kind of novel Fe_3O_4/CNTs magnetic nanocomposites were prepared by in situ chemical precipitation using oleate as reactant and surfactant at the liquid–liquid interface of cyclohexane/ethanol/water mixture solvent. The as-prepared samples were characterized via transmission electron microscopy (TEM), X-ray diffractometry (XRD), X-ray photoelectron spectroscopy (XPS), Fourier transform infrared (FTIR) and vibration sample magnetometry (VSM). Results indicated that the Fe_3O_4/CNTs magnetic nanocomposites dispersed well in organic medium were prepared organic medium, were prepared. The magnetic nanocomposites were proved to be superparamagnetic with coercive force of 3.69 Oe. A mechanism scheme was proposed to illustrate the formation process of the magnetic nanocomposites.

1. Introduction

Because of exhibiting interesting electronic, mechanical and structural properties, carbon nanotubes (CNTs) are extremely promising for applications in materials science and medicinal chemistry [1]. Decoration of CNTs with magnetic nanoparticles, such as coating or loading CNTs with γ-Fe_2O_3, $NiFe_2O_4$ and Fe_3O_4 [2–4], can improve or impart new optical, magnetic and electrochemical properties of CNTs. Therefore, the studies on magnetic nanocomposites, especially on magnetic CNTs, are rapidly expanding. Moreover, the exceptional electromagnetic properties and the unique structure of magnetic nanotubes could have an important potential in many other applications ranging from electromagnetic devices to biomedical fields such as magnetically guided drug delivery systems [3,5].

Various chemistry-based processing routes have been developed to synthesize Fe_3O_4/CNTs magnetic nanocomposite, Qu et al. [6] used chemical coprecipitation of Fe^{2+} and Fe^{3+} in the presence of CNTs in an alkaline solution to prepare Fe_3O_4/CNTs. Jia et al. [4] achieved the magnetic functionalization of CNTs by coating with Fe_3O_4 nanoparticles via a simple hydrothermal process, in which the Fe_3O_4 beads orderly self-assembled on some restricted positions along CNTs and formed necklace-like nanostructures. Tan et al. [7] obtained the magnetic Fe_3O_4/CNTs by decoration of metal-oxide nanoparticles on or in CNTs. The method involved the dispersion of CNTs in $Fe(CO)_5$ followed by vacuum thermolysis and subsequent oxidation. The above methods are suitable for producing hydrophilic magnetic composites, while in actual application, they should have good solubility in organic solvents especially used in biomedical fields [8].

Herein, we described a facile and effective chemical coprecipitation method to synthesize a magnetic Fe_3O_4/CNTs nanocomposite exhibiting a good compatibility with organic solvents at the liquid–liquid interface of cyclohexane/ethanol/water mixture solvent. Finally, the formation process of the magnetic nanocomposites was discussed.

2. Experiment

2.1. Chemicals

The CNTs (diameter: 40–60 nm, purity: 95–98%) were kindly provided by the Shenzhen Nanotechnologies Co. Ltd of China. The other chemicals were of analytical grade and purchased from Shanghai Chemical Company.

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2.2. Purification of CNTs

The commercial CNTs were purified in the mixture of concentrated sulfuric and nitric acids (1:3 by volume) at 80 °C with constant stirring for 6 h. Afterwards, the solution was diluted with distilled water and rinsed for several times until the pH value reaches neutral, and then filtered and dried in vacuum at 60 °C for further use.

2.3. Preparation of Fe_3O_4/CNTs nanocomposites

A mass of 0.12 g purified CNTs and 3.2 g sodium oleate were added into a 500 mL bottom-round flask filling with 40 mL ethanol and 80 mL deionized water with ultrasonic agitation for 30 min, and then 200 mL cyclohexane was introduced. Above suspension was deoxygenated via bubbling N_2 for 30 min at 75 °C and recorded as system (I). Subsequently, 0.675 g $FeCl_3 \cdot 6H_2O$ and 0.372 g $FeCl_2 \cdot 4H_2O$ were dissolved in ethanol aqueous, and the solution was added into system (I) to form system (II). System (II) was refluxed for 1 h in N_2 atmosphere, then 5 wt% NaOH aqueous was dropped into until the pH value reached 11. After stirring for 2 h at 75 °C, the reaction system aged at 50 °C for 2 h again. Subsequently, the production was separated from the reaction system by a strong NdFeB Magnet ((BH)max = 30 MG Oe). Via lavation and evaporation in vacuum at 40 °C, the Fe_3O_4/CNTs nanocomposites were fabricated.

2.4. Characterization

The magnetic Fe_3O_4/CNTs nanocomposites were characterized by transmission electron microscopy (TEM, accelerating voltage/120 kV, Philips Tecnai 12), X-ray diffractometer (XRD, D/max 18 kV, Bruker D8 Super Speed) with Cu Kα radiation, X-ray photoelectron spectroscopy (XPS, Thermo, ESCALAB250), Fourier transform infrared (FTIR, MB154S, Bomen, Canada) and vibrating sample magnetometer (VSM, EV7, ADE, USA), respectively.

3. Results and discussion

3.1. Characterization of sample

The morphology of the as-produced samples was investigated by TEM and shown in Fig. 1. Fig. 1(a) reveals that the purified CNTs, with diameter of 40–60 nm, present well-graphitized walls and basically have no extra materials. Obviously, unlike the uniform micron-structure of pure CNTs, Fe_3O_4/CNTs nanocomposites exhibited in Fig. 1(b) show many additional tiny particles (diameter $D \approx 8$–10 nm) attached on the surface of the CNTs. Although the distributing of these nanoparticles depict some nonuniformity produced from the extremely high curvature of CNTs ($D_{MWNT} \approx 15$–30 nm [9]) which is adverse for the formation of dense coatings, while no free nanoparticles were found in the whole grid.

The XRD pattern in Fig. 2 indicates that the crystal structure of magnetic nanocomposites comprises two phases of cubic Fe_3O_4 (pdf card: 65–3107) and CNTs. Well-resolved diffraction peaks

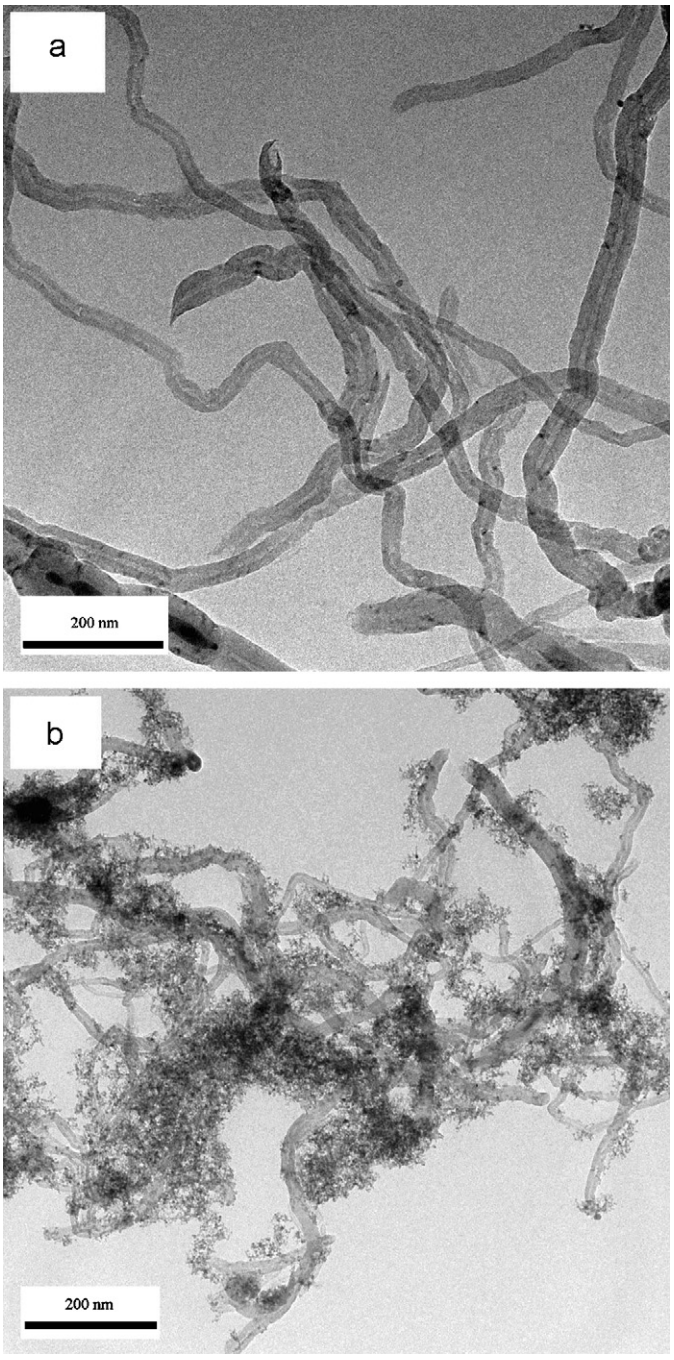

Fig. 1. TEM micrograph of (a) CNTs and (b) nano-Fe_3O_4/CNTs.

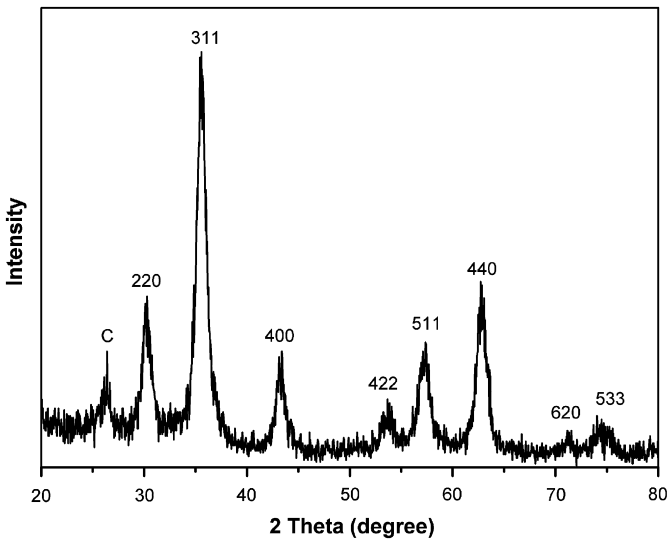

Fig. 2. XRD patterns of CNTs decorated with Fe_3O_4 nanoparticles.