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Synthesis and characterization of MWCNTs/$Co_{1-x}Zn_xFe_2O_4$ magnetic nanocomposites and their use in hydrogels

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ABSTRACT

A novel magnetic nanocomposite of multiwalled carbon nanotubes (MWCNTs) decorated with $Co_{1-x}Zn_xFe_2O_4$ nanocrystals was synthesized successfully by an effective solvothermal method. The as-prepared MWCNTs/$Co_{1-x}Zn_xFe_2O_4$ magnetic nanocomposite was used for the functionalization of P/H hydrogels as a prototype of device to show the potential application of the nanocomposites. The nanocomposites were characterized by X-ray diffraction analysis, transmission electron microscopy and vibrating sample magnetometer. The results show that the saturation magnetization of the MWCNTs/$Co_{1-x}Zn_xFe_2O_4$ magnetic nanocomposites increases with x when the Zn^{2+} content is less than 0.5, but decreases rapidly when the Zn^{2+} content is more than 0.5. The saturation magnetization as a function of Zn^{2+} substitution reaches a maximum value of 57.5 emu g^{-1} for $x = 0.5$. The probable synthesis mechanism of these nanocomposites was described based on the experimental results.

1. Introduction

One of the most exciting classes of nanomaterials is represented by the carbon nanotubes (CNTs), which are at the center of the nanotechnology research [1,2]. Because of their extraordinary properties, such as mechanical, electric, thermal and structural properties, CNTs can be considered as an ideal building block in hybrid materials [3–5]. Although still in a very early stage of research, the dispersion of metal oxides onto CNTs, forming hybrid materials, could show exceptional performance in many applications. For example, anode materials of lithium-ion batteries (SnO_2/MWCNTs nanocomposites) [6], electrode and electrolyte materials of supercapacitors and other electrochemical energy storage/conversion devices (MnO_2/CNTs and ZnO/CNTs nanocomposites) [7,8], optical limiting application (MWCNTs/SiO_2 bulk materials) [9], ceramic products with good mechanical and tribological properties (CNT(Ni)–Al_2O_3 and CNT/aluminosilicate composites) [10,11], etc.

Co–Zn ferrites, one kind of functional spinels composed of mixed metallic oxides with a general formula AB_2O_4 [12,13], exhibit important properties such as excellent chemical stability, high corrosion resistivity, magneto crystalline anisotropy, magnetostriction and magneto optical properties [14]. Co–Zn ferrites have aroused increasing interest among researchers of various fields due to their extensive applications such as information storage system, medical diagnostics, magnetic drug delivery, hyperthermia for cancer treatment, ferrofluid technology, hard disc recording media, flexible recording media, magnetic static wave devices, surface acoustic wave transducers, vacuum seals [14–18]. Various preparation techniques have been developed to produce $Co_{1-x}Zn_xFe_2O_4$ nanoparticles, such as co-precipitation method [19,20], ceramic technique [21], solid-state reaction technique [22,23], forced hydrolysis method [16], hydrothermal route [18] and solvothermal method [24].

Recently, in order to possess the properties of the individual components with a synergistic effect, composite materials based on the integration of CNTs and ferrite have gained growing interest. Shi et al. [25] synthesized Fe_3O_4/CNTs nanocomposites using ethylene glycol as a reductant under 160 °C. After annealing treatment at different temperatures, the average particle size of Fe_3O_4 was increased with increasing temperature and their size distribution was wider at a higher temperature. Chen et al. [26] prepared $ZnFe_2O_4$/MWCNTs composite via a hydrothermal process. The presence of MWCNTs improved the photocatalytic activity of $ZnFe_2O_4$ significantly. Jiang et al. [27] prepared $CoFe_2O_4$/CNTs magnetic nanocomposites by solvothermal method and showed that the nanocomposites were superparamagnetic at room temperature and have a saturation magnetization of 29.6 emu g^{-1}. Lamastra et al. [28] produced a kind of $CoFe_2O_4$/MWCNTs nanofiber by electrospinning a dispersion of MWCNTs in a solution of polyvinylpyrrolidone, iron nitrate nonahydrate, cobalt acetate tetrahydrate, absolute ethanol and H_2O. Liu et al. [29] deco-

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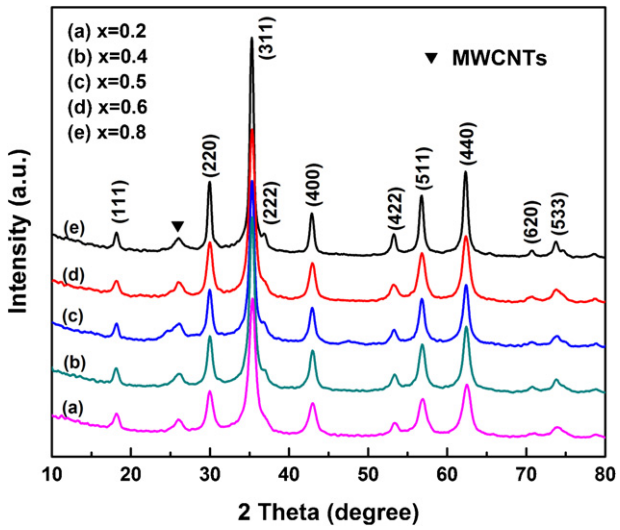

Fig. 1. The XRD patterns of MWCNTs/$Co_{1-x}Zn_xFe_2O_4$ nanocomposites with different compositions (x = 0.2, 0.4, 0.5, 0.6, 0.8).

rated CNTs with nearly monodispersed $M^{II}Fe_2O_4$ (MFe_2O_4, M = Fe, Co, Ni) nanoparticles by *in situ* high-temperature hydrolysis, and the saturation magnetization of Fe_3O_4/CNTs, $CoFe_2O_4$/CNTs and $NiFe_2O_4$/CNTs are obtained as 43.5, 29.6 and 41.7 emu g^{-1}, respectively. Zhang et al. [30] demonstrated a general, efficient and environmentally friendly synthetic strategy for obtaining $Mn_{1-x}Zn_xFe_2O_4$/MWCNTs nanocomposites via a simple solvothermal method. In our previous work, we prepared a series of magnetic monodisperse Co–Zn ferrite nanospheres, which displayed a highest saturation magnetization value of 64.6 emu g^{-1} corresponding to the sample of $Co_{0.5}Zn_{0.5}Fe_2O_4$ nanospheres [24]. Therefore, magnetic Co–Zn ferrite nanospheres are chosen to decorate MWCNTs, in order to improve the magnetic property of the MWCNTs.

Considering the outstanding properties of MWCNTs and $Co_{1-x}Zn_xFe_2O_4$ nanospheres, MWCNTs decorated with $Co_{1-x}Zn_xFe_2O_4$ would have potential applications in many aspects [29,30], for example, the functionalization of hydrogels. Poly(N-isopropylacrylamide) (PNIPAAm) hydrogels are widely utilized in functional hydrogels, which exhibit a clear volume phase transition in response to external stimuli such as temperature, pH, solvent composition, salt concentration, light, mechanical stress and magnetic field [31]. Liu et al. [32] successfully synthesized a series of high hectorite content nanocomposites PNIPAAm/hectorite

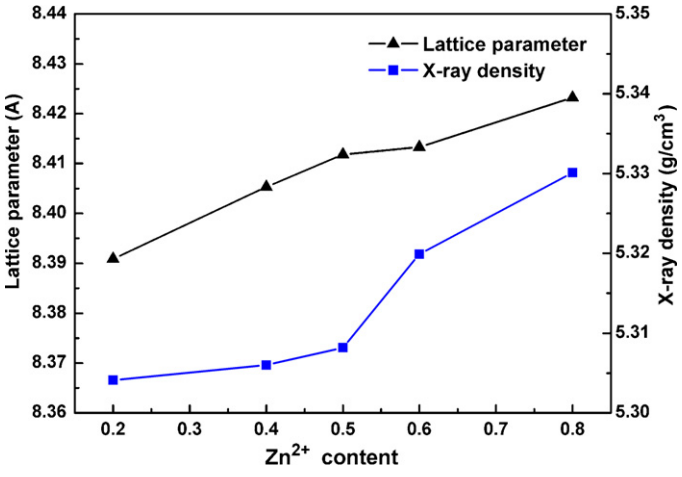

Fig. 2. Lattice parameters and X-ray density of MWCNTs/$Co_{1-x}Zn_xFe_2O_4$ nanocomposites with various Zn^{2+} content.

Table 1
X-ray density and lattice parameters derived from X-ray diffraction pattern of $Co_{1-x}Zn_xFe_2O_4$ nanoparticles with various Zn^{2+} concents.

Zn^{2+} content	0.2	0.4	0.5	0.6	0.8
Lattice parameter a (Å)	8.3909	8.4053	8.4099	8.4133	8.4232
X-ray density (g/cm^3)	5.3041	5.3060	5.3119	5.3199	5.3301

(P/H) hydrogels by choosing a special kind of hectorite (Laponite XLS) modified by tetrasodium pyrophosphate. These hydrogels show surprising mechanical properties and complicated deswelling behavior. Referring to Liu's work [32], the as-prepared MWCNTs/$Co_{1-x}Zn_xFe_2O_4$ magnetic nanocomposites were used for the functionalization of P/H hydrogels as a prototype of device to show the potential application of the nanocomposites.

In this work, we describe a novel, facile, and environmentally friendly synthetic strategy for obtaining MWCNTs/$Co_{1-x}Zn_xFe_2O_4$ magnetic nanocomposites via a solvothermal method. The magnetic properties as well as the microstructures of the nanocomposites have been systematically investigated. Up to now, there are few reports on synthesizing the magnetic nanocomposites of MWCNTs/$Co_{1-x}Zn_xFe_2O_4$, which have a high saturation magnetization. The magnetic properties of the nanocomposites prepared by the solvothermal method were improved greatly compared to other works [27,29]. Furthermore, the MWCNTs/$Co_{1-x}Zn_xFe_2O_4$ magnetic nanocomposite functionalized P/H hydrogels were prepared for the first time and expected to be used as a light-driven and magnetic controlled switch in microreactors.

2. Experimental

2.1. Materials

MWCNTs (length 5 μm; o.d. 50–90 nm; purity: 95–98%) were purchased from Shenzhen Nanotech Port Ltd. Co. (Shenzhen, China). Hectorite-Laponite XLG was purchased from Guangzhou Owen Trade Ltd. Co. (Guangzhou, China). PNIPAAm (purity: 99%) was purchased from J&K Chemical Ltd. The other chemicals, such as hydrated cobalt nitrate ($Co(NO_3)_2{\cdot}6H_2O$), hydrated zinc nitrate ($Zn(NO_3)_2{\cdot}6H_2O$), hydrated iron chloride ($FeCl_3{\cdot}6H_2O$), nitric acid (HNO_3), sodium acetate (NaAc), ethylene glycol (EG), polyethylene glycol (PEG), N,N,N′,N′-tetramethyldiamine (TEMED), and potassium persulfate (KPS), were analytical grade and acquired from Sinopharm Chemical Reagent Co., Ltd.

2.2. Covalent modification of MWCNTs

First, 0.15 g pristine MWCNTs were dispersed into concentrated nitric acid at 100 °C with constant stirring for 24 h. Then, the mixture was diluted with distilled water and rinsed for several times until the pH value reached neutral. Afterwards, the resulting MWCNTs were separated by centrifugation and dried in an oven at 60 °C for subsequent use.

2.3. Synthesis of MWCNTs/$Co_{1-x}Zn_xFe_2O_4$ nanocomposites

MWCNTs/$Co_{1-x}Zn_xFe_2O_4$ magnetic nanocomposites were obtained via a facile solvothermal synthetic route. A series of MWCNTs/$Co_{1-x}Zn_xFe_2O_4$ magnetic nanocomposites were synthesized with different compositions ($0 < x < 1$) under the same conditions. The typical preparation process of MWCNTs/$Co_{1-x}Zn_xFe_2O_4$ (x = 0.2, 0.4, 0.5, 0.6 and 0.8) nanocomposites was described as follows: MWCNTs after acid treated were ultrasonically dispersed in 40 ml ethylene glycol for 30 min. After that, $FeCl_3{\cdot}6H_2O$, $Zn(NO_3)_2{\cdot}6H_2O$ and $Co(NO_3)_2{\cdot}6H_2O$ were dissolved in the resulting MWCNT dispersion according to a certain stoichiometric ratio (5 mmol $FeCl_3{\cdot}6H_2O$, 1.25 mmol $Zn(NO_3)_2{\cdot}6H_2O$ and 1.25 mmol $Co(NO_3)_2{\cdot}6H_2O$ were needed in the case of $Co_{0.5}Zn_{0.5}Fe_2O_4$ and similar for the other value of x). Then, 3.6 g of NaAc and 1 ml of PEG were dissolved in the above mixture solution and vigorously stirred at room temperature for 30 min. Subsequently, the mixture was sealed in a teflon-lined stainless steel autoclave and maintained at 200 °C for 12 h. After reaction, the mixture was cooled to room temperature. The black product was collected by magnet and rinsed with deionized water and ethanol until there were no chloride ions in the solution. Finally, the obtained product was dried in vacuum at 60 °C for 12 h.

2.4. Synthesis of PNIPAAm/MWCNTs/$Co_{1-x}Zn_xFe_2O_4$ hydrogels

PNIPAAm/MWCNTs/$Co_{1-x}Zn_xFe_2O_4$ hydrogels were prepared by simple mixing and solution polymerization. The ratios of raw materials for syntheses of PNIPAAm/MWCNTs/$Co_{1-x}Zn_xFe_2O_4$ hydrogels (P/H/M gels) were as