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Preparation and magnetic property of multi-walled carbon nanotube/α-Fe_2O_3 composites

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Abstract: In order to attain new functional nanomaterials with good magnetic property, multi-walled carbon nanotubes/hematite (MWNTs/α-Fe_2O_3) composites were synthesized using the co-deposition method. MWNTs/α-Fe_2O_3 composites were characterized by X-ray diffractometry (XRD), scanning electron microscopy (SEM), transmission electron microscopy(TEM), Raman spectroscopy and vibrating sample magnetometry (VSM). The experimental results show that the structure and magnetic properties of the MWNTs/α-Fe_2O_3 composites are related to the heat treatment temperature. MWNTs are modified by α-Fe_2O_3 nano-particles and α-Fe_2O_3 nanorods with a diameter of 10−50 nm after being treated at 450 ℃. When the heat treatment temperature exceeds 600 ℃, MWNTs are only modified by Fe_3O_4 particles. Furthermore, the MWNTs composites treated at 450 ℃ and 600 ℃ have good magnetic behaviour.

Key words: carbon nanotubes; α-Fe_2O_3; magnetic property

1 Introduction

Because of its non-toxicity, low cost, and relatively good stability, α-Fe_2O_3 is widely used in catalysts, pigments, and sensors[1−3]. In particular, to optimize the applications of α-Fe_2O_3 in these fields, it is necessary to prepare new α-Fe_2O_3 nanomaterials and to create new hybrid materials with various properties and applications. In recent years, synthesis and assembly of hematite particles with various morphologies have attracted intensive interest. So far, hematite structures of various morphologies have been reported, such as shuttle-like α-Fe_2O_3[4], plate-shaped α-Fe_2O_3 nanocrystals[5], ring-like α-Fe_2O_3[6], urchin-like α-Fe_2O_3[7], wire of α-Fe_2O_3 [8], rod of α-Fe_2O_3[9] and flower-like α-Fe_2O_3 [10].

Carbon nanotubes (CNTs) have attracted considerable research interest in the past decade, and were regarded as promising candidates for reinforcement in composite materials due to their excellent mechanical, unique electronic, magnetic, and gas adsorption properties. It was found that CNTs reinforced composites have prominent enhancement in the properties, such as hardness[11], bending strength[12], fracture toughness [13], wear resistance[14], corrosion resistance[15], electrical conductivity[16], and thermal stability[17−19]. Therefore, these unique properties make CNTs very useful for supporting Fe_2O_3 in many potential applications. In this work, a simple synthetic route to prepare multi-walled carbon nanotubes/hematite (MWNTs/α-Fe_2O_3) composites is reported through co-deposition method and thermal treatment. Moreover, the magnetic properties of MWNTs/α-Fe_2O_3 composites are investigated.

2 Experimental

2.1 Preparation, oxidization and amination of MWNTs

The MWNTs used in this work were produced by

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catalytic decomposition of acetylene[20]. The products were oxidized by immersing in mixture acid of concentrated H_2SO_4 and HNO_3 and refluxed for 2 h at boiling, and then suspended and refluxed in 3 mol/L HCl solution for 2 h at boiling. In order to further functionalize MWNTs, the oxidized MWNTs were further refluxed in concentrated ammonia for 2 h at boiling, and then filtered and washed with de-ionized water again. Finally, the black precipitate was dried at 90 ℃[21].

2.2 Modification of MWNTs with citric acid

The aminated MWNTs and citric acid (CA) were mixed and sonicated in de-ionized water for 30 min. Sulfuric acid (10 mL) was dropped into the suspension of MWNTs, which was then stirred and refluxed at 80 ℃. The reaction mixture was cooled to ambient temperature, then filtered and washed with deionized water. The black precipitate was collected by filtration and dried at 60 ℃.

2.3 Synthesis of MWNTs/Fe_2O_3 composite

All the reagents used in the experiments were analytically pure and purchased from the Tianjin Chemical Reagent Company, China. The experimental details were as follows. Firstly, 5 g $Fe(NO_3)_3$ was dissolved in 500 mL deionized water under continuous stirring for 3 h. Secondly, 5 g polyethylene glycol (analytical pure, relative molecular mass 20 000) and 0.2 g MWNTs modified with CA were added, and the mixture was sonicated for 2 h after stirring for 0.5 h. Thirdly, the ammonia solution ($V(NH_3)$:$V(H_2O)$=1:1) was slowly dropped under continuous sonicating until the precipitation was complete. Fourthly, after the suspension was stable for 48 h, the resultant products were filtered, washed several times with deionized water and ethanol. Finally, the resultant precipitation was dried at 80 ℃ in air, and then calcined at 450, 600 and 750 ℃, respectively, for 2 h under the protection of nitrogen. In order to study the influence of MWNTs on the magnetic property of α-Fe_2O_3, pure α-Fe_2O_3 and MWNTs/α-Fe_2O_3 composites (containing 0.2 g MWNTs) were prepared under the same conditions.

2.4 Characterization

The composites were observed with a JSM−6700F field emission scanning electron microscope. Transmission electron microscopy (TEM) observation and energy dispersive X-ray (EDX) analyses were conducted on a JEM−3010 transmission electron microscope of high magnification. The X-ray powder diffraction (XRD) analyses were carried out using the Philips PW 1710 diffractometer with Cu $K_{\alpha 1}$ radiation. Raman spectroscopy was performed using a Jobin Yvon Labran−010 spectrophotometer at room temperature. Magnetic measurements for the samples in the powder form were carried out at room temperature using a vibrating sample magnetometer (VSM HH−50).

3 Results and discussion

3.1 SEM analysis

Fig.1 shows the SEM images of MWNTs composite after being heat treated at different temperatures. It is found that the samples are composed of MWNTs, nanoparticles and nanorods after heat treatment at 450 ℃, and MWNTs are dispersed uniformly. When the heat treatment temperature is 600 ℃, the MWNTs can be modified by nanoparticles with size in the range of 100−200 nm, as shown in Fig.1(b). However, when the heat treatment temperatures is 750 ℃, the size of particles is about 500 nm, and MWNTs agglomerate severely (Fig.1(c)).

3.2 TEM analysis

The TEM morphologies of MWNTs composites after being heat treated at different temperatures are shown in Fig.2. Fig.2(a) shows the TEM morphology of

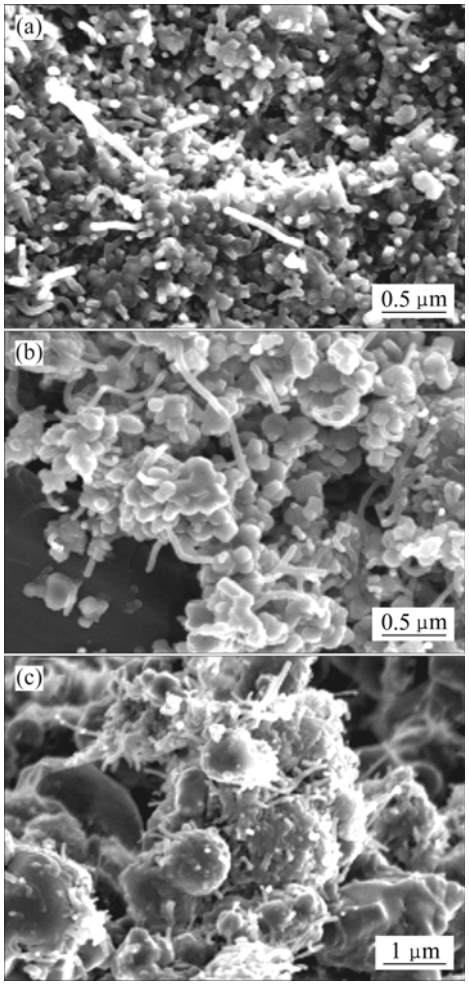

Fig.1 SEM images of MWNTs composites after heat treatment at different temperatures: (a) 450 ℃; (b) 600 ℃; (c) 750 ℃

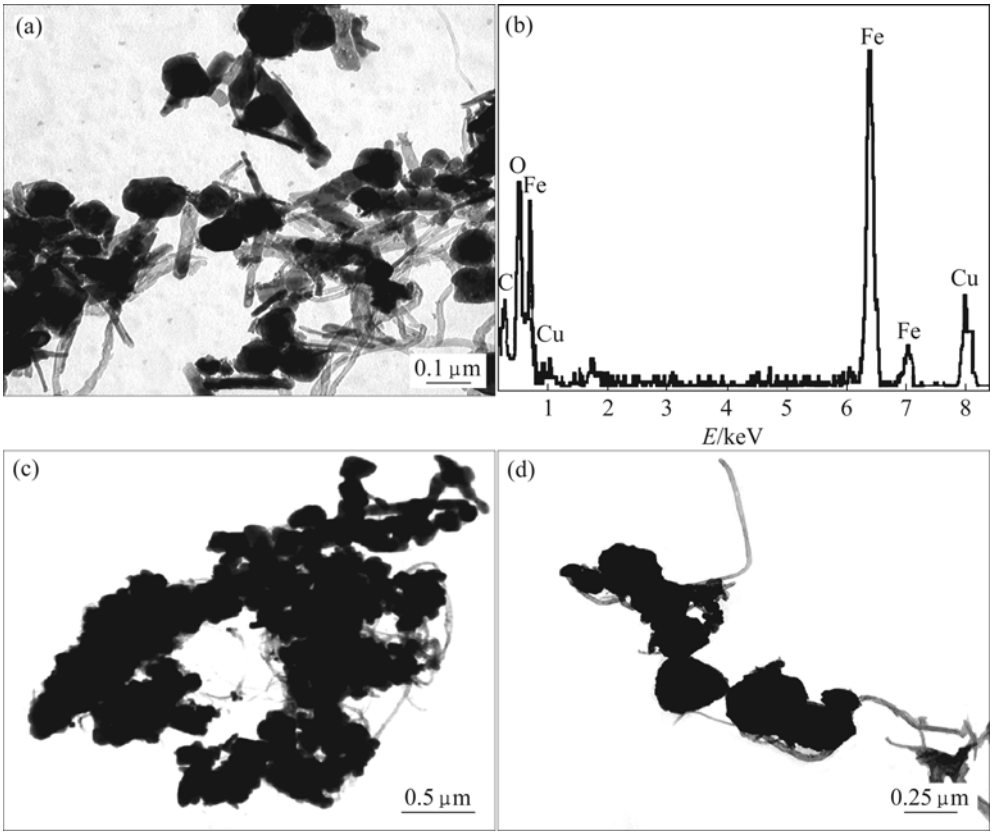

Fig.2 TEM morphologies of composite treated at 450 ℃ (a), 600 ℃ (c), and 750 ℃ (d) and EDX spectrum of composite treated at 450 ℃ (b)

composites heat treated at 450 ℃. It is obvious that the MWNTs are modified by nanoparticles with sizes of 50−100 nm and nanorods with diameter of 50−100 nm and length of 0.1−1 μm. The corresponding EDX spectrum of MWNTs composites is shown in Fig.2(b). It reveals the presence of C, O, Fe and Cu elements in the composites. The peaks of element Cu are attributed to the Cu grid that supports the sample. Moreover, the relative concentration ratio of Fe to O is approximately 2:3. These results indicate that the nanoparticles and nanorodes are Fe_2O_3. Fig.2(c) reveals TEM morphology of MWNTs composites after being heat treated at 600 ℃. It can be observed that MWNTs are only modified by nanoparticles. When the heat treatment temperature increases to 750 ℃, MWNTs can be modified by particles, but the size of particles grows dramatically (Fig.2(d)).

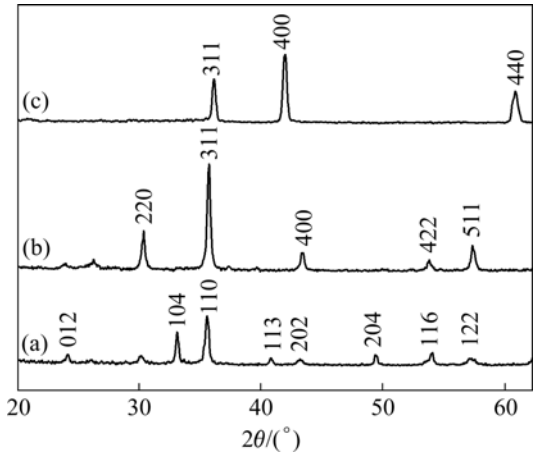

Fig.3 XRD patterns of MWNTs/α-Fe_2O_3 composites treated at different temperatures: (a) 450 ℃; (b) 600 ℃; (c) 750 ℃

3.3 XRD analysis

The XRD patterns of MWNTs/α-Fe_2O_3 composite heat treated at different temperatures are shown in Fig.3. It is clear that the sample treated at 450 ℃ is identified as the single-phase α-Fe_2O_3 with a suitable crystalline hexagonal structure (JCPDS file No. 86-0550) (Fig.3(a)), while the sample treated at 600 ℃ shows Fe_3O_4 phase (Fig.3(b)). Compared with Fig.3(a), the diffraction peaks of Fig.3(b) become sharper and narrower with the increase of heat treatment temperature, indicating the improvement of crystallinity and the increase of particle size. However, when the heat treatment temperature reaches 750 ℃, the sample only shows Fe_3O_4 phase.

In order to further identify the MWNTs/Fe_2O_3 composite treated at 450 ℃, the Raman spectrum analyses were conducted. The Raman spectrum is shown in Fig.4. The two peaks at 221.8 and 491.1 cm^{-1} arise from the A_{1g} mode of Fe−O band, and the other five

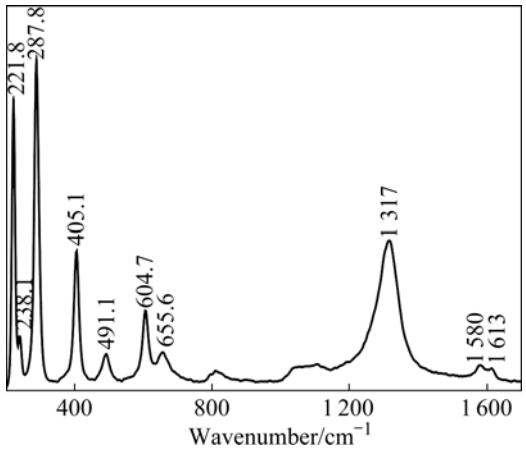

Fig.4 Raman spectrum of MWNTs/Fe_2O_3 composites treated at 450 ℃

peaks are attributed to E_g mode of Fe—O band. These peaks correspond well to the reported values of hematite (α-Fe_2O_3)[2, 22]. Furthermore, there are three peaks at about 1 317, 1 580, and 1 613 cm^{-1}. These three peaks are attributed to the D mode, G mode, and D′ mode of MWNTs, respectively.

3.4 Magnetic properties

Fig.5 depicts the variation of the magnetic properties of samples with MWNTs contents. It is very evident that the MWNTs/α-Fe_2O_3 composites treated at 450 ℃ all exhibit typical magnetic hysteresis loops. The saturation magnetization of composites decreases with increasing the MWNTs content, and the coercive force of composites increases with increasing the MWNTs content. The saturation magnetization and coercive force of pure α-Fe_2O_3 are approximately 64.65 A·m^2/kg and 1 204.6 A/m, respectively. When the MWNTs content is 0.2%(mass fraction), the saturation magnetization of composites is reduced to 27.19 A·m^2/kg, but the coercive force is enhanced to 2 364.6 A/m. The results implies that MWNTs can enhance the coercive force of α-Fe_2O_3.

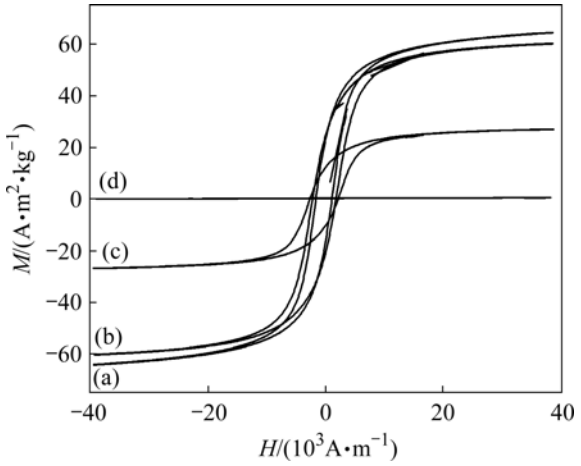

Fig.5 Room temperature magnetization curves of samples heat treated at 450 ℃ with different MWNTs content: (a) Fe_2O_3 without MWNTs; (b) Fe_2O_3 containing 0.1% MWNTs; (c) Fe_2O_3 containing 0.2% MWNTs; (d) MWNTs

In addition, the effect of heat treatment temperature on the magnetic property of MWNTs/α-Fe_2O_3 composite containing 0.1% MWNTs was studied. Fig.6 shows the room temperature magnetization curve of MWNTs composites treated at different temperatures. It is obvious that the magnetic properties of the MWNTs/α-Fe_2O_3 composites show great dependence on the heat treatment temperature. When the heat treatment temperatures are 450 ℃ and 600 ℃, the composites exhibit typical magnetic hysteresis loops. However, the composites treated at 750 ℃ reveal paramagnetism. This phenomenon can be explained by the Fe_3O_4 crystals growth and agglomeration of MWNTs, which results in decreasing of the magnetic property of composite.

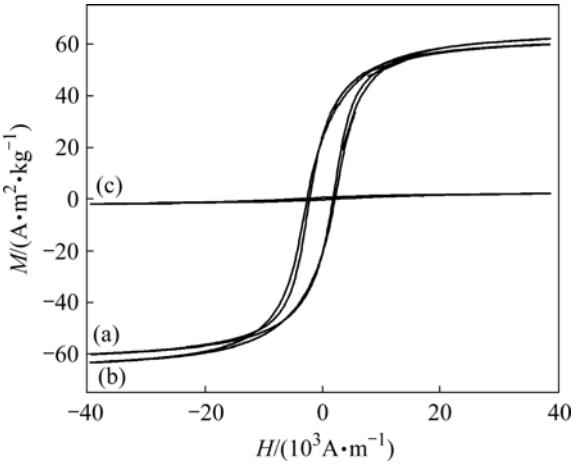

Fig.6 Room temperature magnetization curves of MWNTs/Fe_2O_3 composites treated at different temperatures: (a) 450 ℃; (b) 600 ℃; (c) 750 ℃

4 Conclusions

MWNTs/α-Fe_2O_3 composites were prepared by co-deposition method. Experimental analyses reveal that heat treatment temperature influences the structure and magnetic properties of the MWNTs/α-Fe_2O_3 composites. When the heat treatment temperature is 450 ℃, MWNTs are modified by α-Fe_2O_3 nanoparticles with sizes of 50−100 nm and α-Fe_2O_3 nanorods with diameter of 50−100 nm. However, the MWNTs are modified by Fe_3O_4 nanoparticles when the heat treatment temperature exceeds 600 ℃. Moreover, the composites treated at 450 ℃ and 600 ℃ exhibit good ferromagnetic property, whereas the composites treated at 750 ℃ reveal paramagnetism.

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