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A facile controlled in-situ synthesis of monodisperse magnetic carbon nanotubes nanocomposites using water-ethylene glycol mixed solvents

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A B S T R A C T

In this paper, a facile and controllable method for in-situ synthesis of the magnetic carbon nanotubes nanocomposites (Fe/CNTs) in water-ethylene glycol (EG) mixed solvents is reported by the deposition–precipitation method following annealing. The effect of water/EG ratio on the physico-chemical properties of magnetic Fe/CNTs is investigated by X-ray diffraction, transmission electron microscope, scanning electron microscopy, thermogravimetric analysis and physical property measurement system. The results indicate that the iron particle size distribution and grain size can be well-tuned by adjusting the water/EG ratio. With the variation of EG fraction in the mixed solvent, the nucleation, growth and crystallization of magnetic iron oxides with a controllable morphologies and particle sizes attached on the exterior surface of CNTs can be achieved. The as-prepared Fe/CNTs nanocomposites display superparamagnetic property at room temperature and the water/EG ratio determines the magnetization of the sample. Possible formation mechanism for magnetic Fe/CNTs is proposed based on the characterization results.

1. Introduction

Carbon nanotubes (CNTs) with the unique electrical, thermal, mechanical and optical properties has been widely used in energy storage materials, sensors, electronics and catalysis [1,2] since Iijima discovered the CNTs in 1991 [3]. Magnetic nanoparticles such as magnetite and maghemite have attracted growing attention since their promising application in magnetic force, water treatment, biosensors and drug delivery [4–7]. To combine the advantages of both, the state-of-the-art of preparation methods have been developed to assemble the magnetic material such as deposition on functionalized CNTs, electrochemical deposition, electroless deposition and physical approaches [8]. Among these methods, nanoparticle deposition on functionalized CNTs is hopefully a simple and efficient chemical method to synthesize the magnetic Fe/CNTs catalyst. The monodispersion and particle size distribution of magnetic material determine their own properties.

There are two main categories of the preparation method for nanoparticle dispersion on functionalized CNTs: one is adhering the iron particles onto the CNTs surface through covalent or non-covalent bond; the other is in situ synthesis [9]. In situ synthesis is a time-saving, cost-effective and reproducible process for large-scale production compared to the former method. During the synthesis process, some challenges should be faced to improve the performance and enlarge the applications of magnetic CNTs nanocomposites, such as the suitable dimension of magnetic nanoparticles, a narrow size distribution, high crystallinity and the reproducible procedure without any purification operation. As far as the fine-tuned size distribution of the magnetic nanoparticles, the precipitation method is restrained due to only kinetic factors deciding the growth of the crystal [5]. The above difficulties are real challenges faced by researchers attempting to develop a facile, reproducible and cost-saving method. It is noted that the precipitation process involves two steps, namely, nucleation and growth. To get a monodisperse and narrow size distribution of iron oxide particles, these two steps should be seriously separated, that is, the nucleation should be avoided in the growth process [10].

Ethylene glycol (EG) is the simplest diol with enormous

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potential in various applications such as antifreeze formulations in automobiles, a deicing fluid for windshields and aircraft, a desiccant for natural gas production, and a raw material for manufacture of polyester fibers and resins industry [11]. It should be noted that EG has extensively been used as a reducing agent for the preparation of metal and metal oxide nanoparticles [12]. Though application of EG has recently proliferated in the area of nanoparticles synthesis, efforts in using it as a solvent are lacking. EG is a polar solvent and is thoroughly miscible with water at any ratio. After mixing them, the EG and water molecules are homogeneously mixed [13] and hence the physicochemical properties could be tuned by mixing them. It is reported that the liquid with surface tension higher than 0.1–0.2 N m^{-1} can't get the CNTs wetted [14]. Therefore, the CNTs could be wetted by the water and EG mixture. By filling the tube with solvent, the magnetic nanoparticles attached on exterior surface of CNTs would be obtained subsequently. In early reports, a surfactant would be added to prevent the iron particle from agglomeration during the formation of magnetic particles. Here, the EG was used as not only a solvent but also a stabilizer. By changing the solvent ratio (water/EG ratio), EG would demonstrate its versatility in the formation, growth and crystallization of magnetic oxides with a controllable morphologies and particle sizes as expected. Hence, a nearly monodisperse magnetic particles decorated CNTs nanocomposites can be manufactured via a facile in-situ synthesis method: deposition–precipitation process at different water/EG ratios followed by annealing. Additionally, the influence of the water/EG ratio on the physicochemical properties of magnetic nanocomposites was investigated by a series of characterization techniques. To further confirm the unique properties of EG, the influence of solvent on the magnetic Fe/CNTs nanocomposites preparation was investigated in this paper.

In this study, a facile and controlled in-situ synthesis method in the solvent with different water/EG ratio is reported to fabricate magnetic Fe/CNTs catalyst followed by annealing. The size distribution of magnetic nanoparticles located on the CNTs surface are fine-tuned by adjusting the water/EG ratio in this method. Furthermore, the possible formation mechanisms of the magnetic nanocomposites are discussed.

2. Experimental section

2.1. Synthesis of magnetic CNTs

Pristine CNTs (multi-wall CNTs) was obtained from Chengdu Organic Chemical Co. of Chinese Academy of Sciences. Iron (III) nitrate nonahydrate, ammonium carbonate and EG were supplied by Tianjin Kermel Co., LTD of China. All the reagents used in this research were analytical grade without any further purification.

Before synthesizing the magnetic composite, CNTs were functionalized as follows: 5.0 g raw CNTs were refluxed at 122 °C (azeotropic point) for 6 h in 300 mL concentrated nitric acid (65 wt.%). After cooling down to room temperature, the carbon material was filtered and washed with deionized water until a neutral pH was reached, followed by drying at 110 °C overnight for further use. This acid treatment can not only remove the residual contaminants but also introduce more functionalized carbon sites on the surface [15].

The magnetic Fe/CNTs nanocomposites were prepared by the deposition–precipitation method followed by annealing. In a typical experiment, 2.0 g purified CNTs and 3.607 g iron nitrate nonahydrate were dispersed in 60 mL water and heated to 60 °C in a round bottomed flask. Ammonium carbonate (1.714 g, dissolved in 120 mL EG) was added drop-wise to the mixed solution under continuous stirring for 2 h and the resulting precipitant was kept in this medium overnight. After filtration and washing three times with ethanol and distilled water, the aged suspension was dried at 110 °C for 12 h and calcined in an Ar flow at 400 °C for 5 h with a rate of 3 °C/min. The resulting sample was named as Fe/CNTs-E2W1. Fe/CNTs-W2E1 (120 mL water/60 mL EG) was derived by exchanging the solvent with Fe/CNTs-E2W1. The samples Fe/CNTs-W and Fe/CNTs-E were prepared when the solvents used were water and EG, respectively. To investigate the effect of the solvent, the ethanol was used as solvent and the corresponding sample was denoted as Fe/CNTs-e with the same preparation method mentioned above.

2.2. Characterization of materials

The morphological features of the samples were measured on a Hitachi S-4800 Scanning electron microscopy (SEM) at an accelerating voltage of 3.0 kV. The structures of samples were characterized with a JEM-2100F transmission electron microscope (TEM) at 200 kV. Sample specimens for TEM studies were prepared by ultrasonic dispersion of the catalysts in ethanol and the suspension were dropped onto a carbon-coated copper grid before TEM images were recorded. The powder X-ray diffraction (XRD) characterization was performed on a RigakuD/max-2500 diffractometer with a CuKα radiation (40 kV, 200 mA). The scan speed was 8°/min, with a scanning angle ranged from 10° to 80°. The magnetic measurements of the samples were conducted on SQUDI-VSM to the field strength of 2 T. Thermogravimetric analysis (TGA) was carried out using a thermal analysis system (STA449F3, NETZSCH Crop.). The sample was heated from room temperature to 800 °C with a heating rate of 10 °C/min in air (50 mL min^{-1}).

3. Results and discussion

3.1. Magnetic CNTs morphology and structure

Fig. 1 illustrates the morphologies of the as-prepared samples investigated by SEM. As seen in Fig. 1, some aggregation of iron particles outside the CNTs for Fe/CNTs-W (Fig. 1a) and Fe/CNTs-W2E1 (Fig. 1b) can be observed, while the other samples display a uniform coated with the iron particles along the CNTs (Fig. 1c and d).

The representative TEM images of as-prepared samples further verify the decoration of magnetic particles on CNTs and are shown in Fig. 2. It is evident that the distribution of iron magnetic nanoparticles becomes better with the increase of EG content in the mixed solvent. An obvious iron particles agglomeration on the external surface of CNTs are observed for Fe/CNTs-W (Fig. 2a) and Fe/W2E1 (Fig. 2b) with more serious agglomeration on Fe/CNTs-W, whereas for Fe/CNTs-E2W1 and Fe/CNTs-E, an uniform iron particles without detectable aggregation is found on the exterior surface of CNTs (Fig. 2c and d). Furthermore, both Fe/CNTs-E2W1 and Fe/CNTs-E show a comparable narrow size distribution of iron particles. The magnetic nanoparticles tend to be aggregated and agglomerated due to the anisotropic dipolar attraction [16]. From the above results, we can deduce that the distribution and dispersion of iron magnetic nanoparticles located on CNTs surface would be well controlled by adjusting the water/EG ratios.

Fig. 3 shows the XRD patterns of the Fe/CNTs nanocomposites prepared by different water/EG ratios. As shown in Fig. 3, the diffraction peak at 25.9° and 43.0° are attributed to the (0 0 2) and (1 0 0) planes for graphitic walls of CNTs [17]. It is interesting to note that the crystal phases for Fe/CNTs-W and Fe/CNTs-W2E1 are a mixture of α-Fe_2O_3 (hematite) and γ-Fe_2O_3 (maghemite), while for the other samples they are single phase γ-Fe_2O_3 according to the JCPDS cards no.33-0664 and no.39-1346 [18–20]. No peaks