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Original article

Decoration of CNTs' surface by Fe_3O_4 nanoparticles: Influence of ultrasonication time on the magnetic and structural properties

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ABSTRACT

The decoration of CNTs surface by magnetic nanoparticles was achieved by an ultrasonication-assisted hydrothermal method (UAHM). The effect of ultrasonication time on the crystal structure, magnetic performance, and chemical composition of the magnetic CNT composite material was determined. X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), transmission electron microscopy (TEM), and vibrating sample magnetometry were used to characterize the physical, chemical, and magnetic properties of the composites. The composites synthesized via the UAHM exhibited superparamagnetic properties. The ultrasonication time was a critical factor that affected the structure and magnetic performance of the composites. By simply controlling the ultrasonication time, the crystal phase structure of Fe oxide could be selectively modulated and the magnetic performance of the MCs could be effectively tuned.

1. Introduction

Carbon nanotubes (CNTs) have attracted much attention because of their unique electronic, mechanical, and thermal properties [1,2]. They have been used in many fields including nanoscience, nanotechnology, and bioengineering [3–8]. The decoration of CNTs with magnetic nanoparticles, e.g., the coating or loading of CNTs with Fe/Co/Ni oxides, can improve or modify the optical, magnetic and electrochemical properties of the CNTs [9–16]. These advantages have motivated the expansion of studies on magnetic nano-composites, especially on magnetic CNTs. The exceptional electromagnetic properties and unique structures of magnetic nanotubes also have potential applications in magnetically guided drug delivery systems [17] and other fields.

Among the available magnetic materials, Fe oxides are particularly attractive because of their low cost, especially compared to Ni- and Co-based materials, and low toxicity. Fe oxides are strong candidates for the preparation of magnetic composites materials for industrial scale applications [18,19]. To date, several approaches have been developed for the synthesis of magnetic Fe oxide/CNT composites including chemical precipitation [20], plasma treatment [21], chemical vapor deposition [22], combustion [23], spray pyrolysis [24], hydrothermal/solvothermal methods [25], and self-assembly methods [12]. The methods currently used for the synthesis of Fe oxide/CNTs, however, have some critical disadvantages including the following: (1) several methods suffer from high economic and energy costs [26,27]; (2) other methods are relatively complicated and require the use of organic solvents, which are unsuitable for industrial applications [19,28]. These disadvantages have likely slowed the widespread adoption of Fe oxide/CNT composites for practical applications. Therefore, the development of a simple, cost-effective, time-saving, and environmentally friendly method for the synthesis of magnetically separable Fe oxide/CNT composites is of vital practical significance.

Hydrothermal methods have been used to synthesize Fe_3O_4 nanoparticles in mild organic solvent-free systems [29]. This process is simple and has a low environmental impact. The following steps occur during the typical synthesis of a Fe_3O_4/CNT composite (Scheme 1): (Step 1) Fe^{2+} ions are first bound to the

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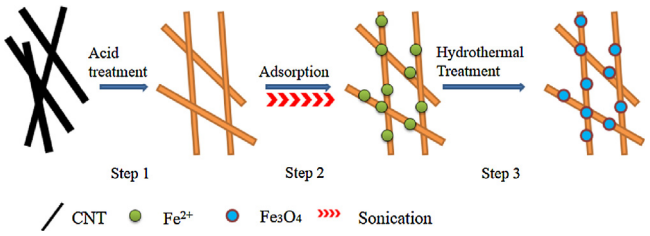


Scheme 1. The illustration of Fe_3O_4/CNT composite synthesis.

CNTs' functional groups, forming a nucleation site for iron oxide crystals. (Step 2) A precipitate gradually forms in an alkaline media. (Step 3) The solution is then sealed in an autoclave for hydrothermal reactions.

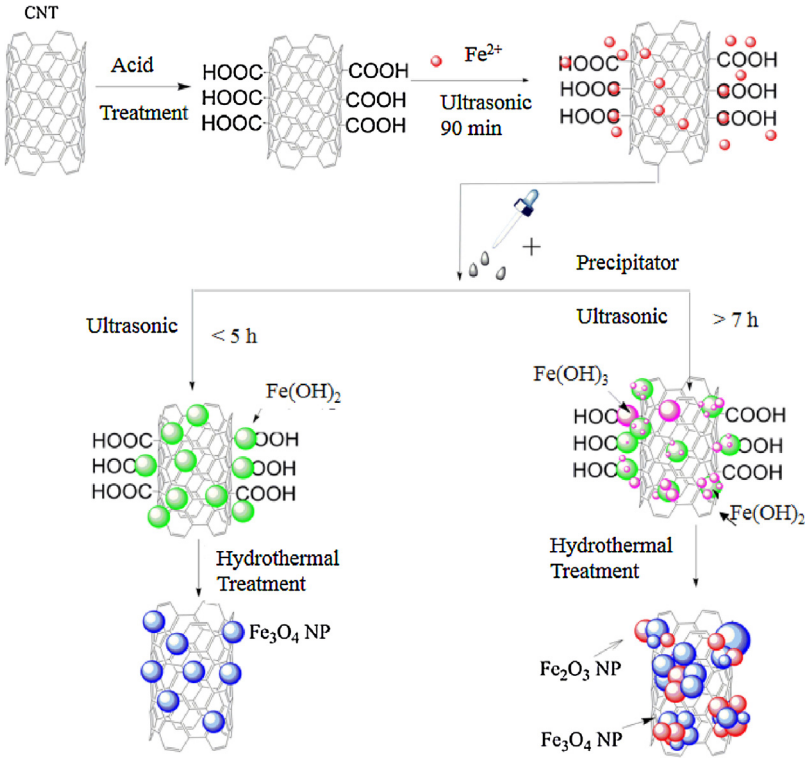
To promote a more uniform dispersion of nucleation centers on the CNTs, ultrasonication was performed during the precipitation process (Step 2) in attempt to synthesize materials with appropriately sized crystalline phases [30]. This combined ultrasonication-assisted hydrothermal method (UAHM) is a straightforward and low-cost approach for the preparation of magnetite nanoparticles/CNT composites (Scheme 2). However, the effect of ultrasonication on Fe_3O_4/CNTs composite synthesis has not previously been determined. In this work, the effect of the duration of ultrasonicationon on the crystal structure, magnetic performance, and chemical composition of the composite was investigated. The morphological, microstructural, and magnetic properties of the obtained nanoparticles were studied using X-ray diffraction (XRD), transmission electron microscopy (TEM), and Fourier transform infrared spectroscopy (FTIR).

2. Experimental

The CNTs were obtained from the Chengdu Organic Chemical limited Company in China, with nanotube's exterior diameter of 20–30 nm. All reactants were of analytical grade and were used without further purification.

The synthesis process for the decoration of magnetic components on CNT surfaces is as the follows: CNT samples were pretreated in concentrated nitric acid (68 wt%) at 140 °C for 2 h to remove the metal catalyst and amorphous carbon species. The purified CNTs were then washed with distilled water, dried at 60 °C under careful stirring in a water bath and finally dried under vacuum at 60 °C for 12 h before further use. Purified CNTs (0.5 g) were added to an aqueous solution of ferrous chloride (0.1 mol/L, 40 mL) and ultrasonicated for 90 min at room temperature to form a homogeneous solution. Aqua ammonia (3:1) was then added into a mixed solution in a drop-wise fashion under stirring until the pH value of the mixture was approximately 10. The mixture was ultrasonicated under stirring for a variable period of time (t = 1, 3, 5, 7 and 9 h). The solution was then transferred to a Teflon-lined autoclave, which was heated to 160 °C in a blast oven for 12 h before being cooled to room temperature. The resulting black magnetic composites were then separated via several rounds of magnetic decantation. The composites were then washed with ethanol and deionized water until the solution reached a neutral pH. The product was dried at 60 °C under careful stirring in a water bath to prevent CNTs' aggregations and form bulks. Finally, the black powdered composites were dried under vacuum at 60 °C for 24 h. The as-prepared magnetic composites (MCs) are denoted as MC-1, 2, 3, 5, 7 and 9 for the different ultrasonication time of 1,2,3,5,7, and 9 h, respectively.

TEM were performed with a JEM-2000 FX transmission electron microscope operating at 200 kV (JEOL Ltd.). The samples were ultrasonically dispersed in ethanol and placed onto a carbon film supported by a copper grid. XRD analysis was conducted using a DX-2700 diffractometer operated at 40 kV and 30 mA (Philips Company). FTIR was performed using a Bruker Tensor 27 Fourier transform spectrometer (Bruker Corporation). The powdered samples were ground with KBr and compressed into a pellet. FTIR spectra from 4000–400 cm^{-1} were recorded in order to



Scheme 2. The formation mechanism of magnetite CNT composites.

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