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Synthesis of uniform MgO/CNT nanorods by precipitation method

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Abstract

In this work, we used carbon nanotubes (CNTs) as a support for synthesis, size control, and morphology of magnesium oxide using the precipitation method. The morphology of MgO nanoparticles varies by changing the weight percent of carbon nanotubes in the solution. Experimental results indicate that, at optimum condition in a mixture of materials, the surface of purified CNTs is covered by MgO nanoparticles completely. The purified CNTs and MgO/CNTs nanorods had average diameters of about 35 and 65 nm, respectively, and their length was in the order of a few micrometers. The structure of CNTs and MgO/CNTs nanopowders has been characterized by analyzing the X-ray diffraction pattern, Fourier transform infrared spectra, and scanning electron microscopy images.

Keywords: Carbon nanotubes, Magnesium oxide, Nanoparticles, MgO/CNT nanorods, Precipitation method

Background

Carbon nanotubes (CNTs) have been extensively studied and known as materials with outstanding properties. Several applications were proposed for CNTs, many of which are concerned with conductive or high-strength composites, in which the inclusion of CNTs in a ceramic matrix is expected to produce composites possessing high stiffness and improved mechanical properties [1-6]. They have also been widely used as support for the controlled synthesis of nanostructures [7].

However, there are major obstacles to overcome in using CNTs as support additives, mainly the difficulty of the uniform dispersion of CNTs, wettability of the CNTs surface, and the load transfer from the matrix to the CNTs [8]. Due to the chemically 'inert' characteristic and the highly hydrophobic nature of the CNT surface, it is difficult to make an attachment with metal precursors [7]. Then, surface modification is required so that efficient tube-matrix interactions are established. The extensive dispersion of various functional groups such as hydroxyl, carboxyl, and carbonyl on the CNT surface could provide active sites for metal ions to attach [9]. Unfortunately, some of the previous studies indicated that these chemical treatments resulted in an extreme

degradation of the tubes and the decrease in Young's modulus [10]. The creation of stable nanotube coatings, which do not significantly alter the tube surface, is expected to exhibit improving mechanical properties when compared with heavily degraded nanotubes [11]. Hernadi et al. [7] have obtained homogeneous coverage of multi-walled carbon nanotubes (MWCNTs) using inorganic materials implementing organometallic compounds. SiO_x-coated CNTs [12] have also been fabricated through a sol-gel technique at room temperature. Chen et al. [13] obtained SnO-CNT composites, using a sol-gel method, as anode-active material for lithium-ion batteries. Sun et al. [14] have coated CNTs with a thin SnO₂ layer using a chemical solution route.

Nanoscale magnesium oxide exhibits unique physical and chemical properties due to its structural characteristic [15]. Several novel methods have been reported in literature for the preparation of nanosized MgO particles [15,16]. The particle size and surface morphology of synthesized MgO by wet chemical procedure depend upon several factors such as the rate of hydrolysis of magnesium salts, temperature, type of base, concentration of the salt, and drying and calcination steps. Proper choice of these parameters can lead to particles of uniform morphology and size [16,17].

The coated nanotubes may improve the adhesion between the nanotubes and the matrix when CNTs are used as fillers in the composite materials. However, the

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mechanical behavior of CNTs is more complicated. Whether or not the strength and stiffness of CNTs can be transferred to the MgO depends on the amount of interfacial bonding between the two phases, which is affected by the CNTs' wettability and interfacial area [18]. Thus, it is important to synthesize CNT-MgO composites and to characterize the interfacial bonding action between the CNTs and the MgO without disruption of the local order of CNTs [9].

In this work, we describe our successful attempt with a simple precipitation method to achieve homogeneous coverage of CNTs with MgO nanoparticles, during which the CNTs were well dispersed in an aqueous solution. The results show that carbon nanotubes can play an important role in controlling the morphology and size of MgO nanoparticles.

Results and discussion

Morphology

The morphology and microstructure of CNTs and MgO/CNT nanopowders were carried out by analyzing scanning electron microscopy (SEM) images. The SEM images of the CNT sample before and after purification are shown in Figure 1. The images show the large amount of impurities attached to the CNT surface (Figure 1a). After the purification steps and the acid treatment, the impurity materials (metal catalyst particles and amorphous carbon) are efficiently removed (Figure 1b). The purification disclosed intertwined CNTs which form a dense 3D-network, extending for several micrometers.

We synthesized nanocomposite powders with different concentrations of CNTs to determine the optimized condition. For now, we discuss the obtained results for the following four concentrations of CNTs in the solution: 0, 0.02, 0.04, and 0.06 g. Figure 2a shows the SEM images of the as-synthesized MgO nanoparticles without any use of CNTs. These nanoparticles are like tiny aggregated nanoparticles which make them bulky. For the 0.02- and 0.04-g concentrations of CNTs, because of the high concentration of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, the CNTs

are invisible (Figure 2b,c). By comparing Figure 2a with Figure 2b,c, we can see that nanoparticles have different morphologies due to the presence of CNTs. Though larger MgO aggregates still exist, many individual nanoparticles are attached onto the CNT surfaces. Thus, the presence of CNTs in the solution can cause the change of MgO nanoparticle morphology.

The SEM image of MgO/CNT nanorods with the 0.06-g concentration of CNTs in the solution is shown in Figure 2d. The images show the development of a large amount of MgO nanoparticles attached to the surfaces of CNTs, making dense and entangled MgO/CNT hybrid nanostructures forming a three-dimensional network structure. For the prepared composites, all of the MgO nanoparticles were firmly deposited on the surface of CNTs, and all of the CNTs are covered by well-dispersed MgO nanoparticles.

In order to obtain the average diameters of CNTs and MgO/CNT nanorods and their range of distribution, we have selected more than 30 per samples and measured their outer diameters from their respective SEM images. It can be seen that the purified CNTs have diameters in the range of 20 to 50 nm (Figure 1b), and MgO/CNT nanorods have diameters within 45 to 150 nm (Figure 2d); their average diameters are about 35 and 65 nm, respectively. Then, the thickness of the MgO layer is about 30 nm.

FT-IR spectroscopy

The nanoparticle loading process was dependent on the functionalization of CNTs. The positive Mg ions may be adsorbed on some sites due to imperfections of the CNT surface and act as preferential nucleation sites for the formation of larger crystals. The functionalization of CNTs using oxidizing acid is one of the most crucial factors, as prerequisite, which would introduce a large number of carboxyl groups on the surface of CNTs, and the high density of functional groups in these restrictive positions would provide great opportunity for further position-selective modification of CNTs with MgO.

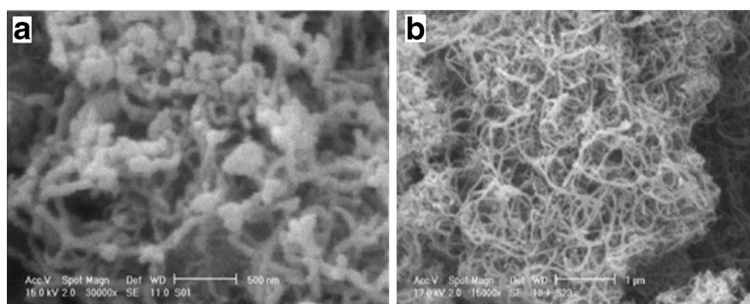


Figure 1 SEM images of CNTs. (a) Before and (b) after purification, showing the long intertwined CNTs.

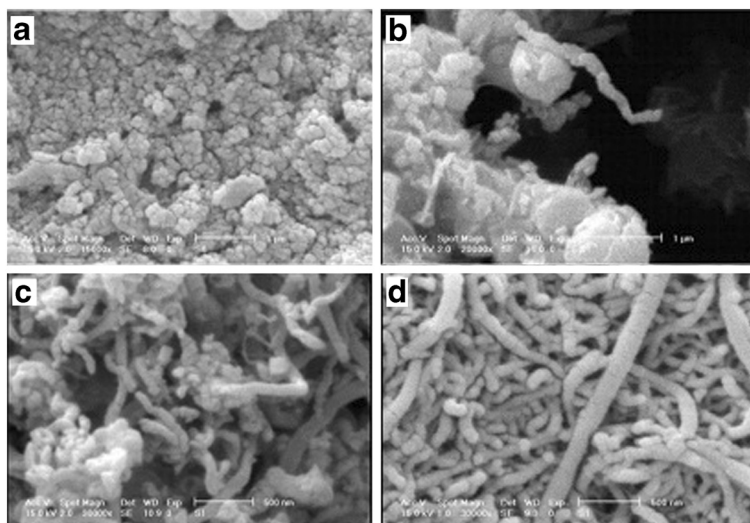


Figure 2 SEM images of MgO nanoparticles and MgO/CNT nanopowders. (a) MgO nanoparticles without using CNTs. MgO/CNT nanopowders synthesized by precipitation method with different concentrations of CNTs in the solution: (b) 0.02, (c) 0.04, and (d) 0.06 g.

A Fourier transform infrared (FT-IR) spectrum was mainly used to identify the presence or absence of functional groups. Figure 3 shows the FT-IR spectra of initial and functionalized CNTs using HNO_3 . As shown on the FT-IR spectra, acid treatment can result in the appearance of some important absorption peaks approximately at $1,210.9$, $1,461.8$, and $1,514.4 \text{ cm}^{-1}$ which correspond to O-C=O, C-O, and C=O, respectively. These peaks are, however, barely noticeable in the functionalization of the CNTs using HNO_3 [6,19-21]. The FT-IR spectra indicate that oxygen with high density is generated from functionalized groups on the surface of CNTs during the acid treatment.

As a result, we herein conjecture that the MgO/CNT nanorods form under precipitation conditions; the redox

reaction between Mg ions will take place on the surface of CNTs. Consequently, MgO nucleated heterogeneously via precipitation deposition because CNTs have prevented MgO from growing into aggregated nanoparticles [22,23].

XRD analysis

The multi-walled carbon nanotubes, MgO nanoparticles, and MgO/CNT nanopowders were analyzed using X-ray diffraction (XRD) analyses. The XRD spectra of CNTs before and after purification with the 2θ range of 20° to 80° are shown in Figure 4. The purified CNTs present a characteristic diffraction peak at about 26.5° , corresponding to the interlayer spacing of multi-walled CNTs,

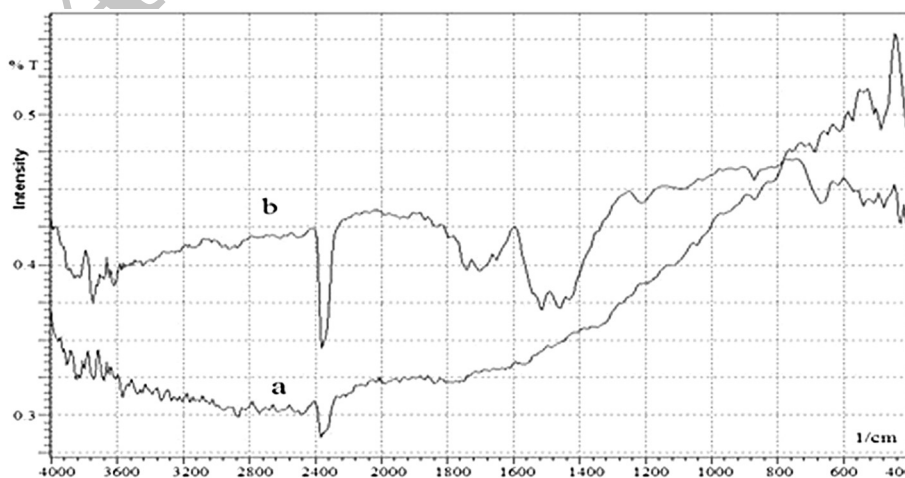


Figure 3 FT-IR spectra of CNTs before (a) and after (b) functionalization.

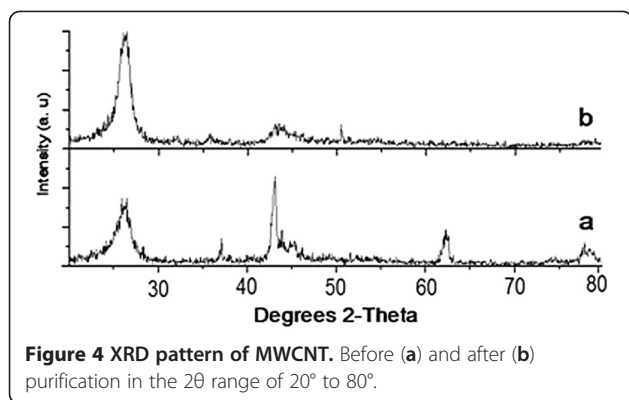


Figure 4 XRD pattern of MWCNT. Before (a) and after (b) purification in the 2θ range of 20° to 80° .

which indicates that the structure of CNTs was not destroyed during the purification process.

Also, the XRD pattern of MgO nanoparticles and MgO/CNT nanopowders (for 0.06 g of CNTs in the solution), in the 2θ range of 20° to 100° , is shown in Figure 5. For both XRD patterns (Figure 5a,b), the intense peaks were observed at 36.8° , 42.7° , 62.1° , and 75.5° , indicating the crystalline nature of the synthesized MgO nanoparticles with fcc structure [16,24]. MgO nanoparticles are composed of pure crystalline MgO since no other impurity peaks are observed in the XRD patterns. In addition, we can see that the characteristic peak of CNTs still exists at $2\theta = 26.5^\circ$ (Figure 5b), but the peak intensity decreases after decorating. The average MgO nanoparticle size for both syntheses (with and without the use of CNTs) was determined from the X-ray diffraction line broadening using the Scherrer formula [25], and their average values are about 11 and 7.1 nm, respectively. The results indicated that the presence of carbon nanotubes in the solution can not only change the morphology of MgO nanopowders, but also decreased the average size of the MgO nanoparticles. We believe that the nucleation and growth processes of MgO were significantly influenced by the introduction of CNTs, which have altered the size and shape of MgO.

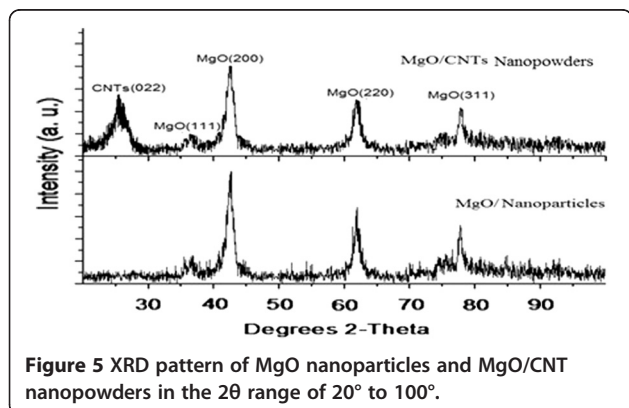


Figure 5 XRD pattern of MgO nanoparticles and MgO/CNT nanopowders in the 2θ range of 20° to 100° .

Conclusions

The results of the synthesis of carbon nanotubes decorated with MgO nanoparticles using the precipitation method were demonstrated in this work. High efficiency of the proposed method was confirmed as well as the possibility of the coating of MgO nanoparticles onto CNTs, without aggregation of these particles. Magnesium ions were attached on CNTs due to the coordination reaction between magnesium ions and polar oxygenated functional groups in the precipitation process. Calculations show that MgO particles appear to have a smaller average size due to the presence of CNTs, and they are durably attached to the nanotubes.

Methods

Synthesis, purification, and functionalization of CNTs

CNTs were synthesized by the catalytic decomposition of ethylene at 930°C over commercial Fe nanoparticles (Sigma-Aldrich, St. Louis, MO, USA; purity was 99% and the average size of nanoparticles was about 25 nm), using catalytic chemical vapor deposition method. It is well known that most produced CNTs contain some impurities such as amorphous carbon, fullerenes, and catalyst particles that could significantly affect the CNT properties, which are a serious impediment for CNTs to be directly used as functional filler in composites. Therefore, such impurities of carbon and metal catalyst particles are encapsulated in the CNT closed tips and walls and need to be removed, trying to avoid a concurrent damage of the tubular structures. In order to remove the impurity, at first, the as-produced CNTs were heated in a horizontal furnace under air flow condition at 500°C for 2 h, sonicated in a mixed solution of HNO_3 (5 M) and HCl (5 M) for 30 min, and stirred for 4 h. This suspension was filtered using a membrane having a $0.2\text{-}\mu\text{m}$ pore size, then washed several times with distilled water until acid-free, and finally dried at 120°C for 2 h. Under these treatments, the product was purified from the impurities, and the surfaces of CNTs were modified, which could alter the surface interactions significantly during the coating procedure.

Synthesis of MgO/CNT nanopowders

The MgO/CNT nanopowders were synthesized by precipitation of the magnesium hydroxide gels in aqueous solution containing CNTs using $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ as a salt and liquid ammonia as the precipitating agent. At first, certain amounts of purified CNTs (0, 0.02, 0.04, and 0.06 g) were dispersed into the distilled water solution of ammonia (50 cm^3 ; $\text{pH} = 10.5$) by ultrasonication for 10 min. Then 1.8 g of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was dissolved in 100 cm^3 of distilled water. With constant magnetic stirring, the solution of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was added dropwise to the above solution at 50°C through a

dropping funnel. The rate of addition of the salt solution was kept approximately at 20 ml/h. During the addition, the pH of the mixture decreased due to hydrolysis of the salt. The pH was maintained at 10.5 by controlling the addition of the liquid ammonia solution. After completion of the precipitation procedure, the mixture was stirred at room temperature for 12 h, washed and filtered continually in distilled water, and dried at 120°C followed by calcination at 450°C for 2 h. During the calcination procedure, the temperature of the furnace was steadily raised from room temperature to 450°C with an increment of 10°C/min. At 450°C, the temperature was maintained for 2 h to achieve the final material.

Characterization of CNTs and MgO/CNT nanopowders

The resulting CNTs and MgO/CNT nanopowders were characterized by SEM images (Philips MAG 15 kV, ×30,000; FEI Co., Hillsboro, OR, USA), FT-IR spectra (8400 S, Shimadzu Corporation, Nakagyo-ku, Kyoto, Japan), and XRD pattern (CuK α spectra, $\lambda = 1.54 \text{ \AA}$; GBC Scientific Equipment LLC, Hampshire, IL, USA). Also, the MgO nanoparticle size was determined using the Debye-Scherrer equation.

Competing interests

The authors declare that they have no competing interest.

Authors' contributions

All authors provided the same contributions in this article. All authors read and approved the final manuscript.

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