



# Preparation and electromagnetic properties of chitosan-decorated ferrite-filled multi-walled carbon nanotubes/polythiophene composites



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## ABSTRACT

The chitosan-decorated ferrite-filled multi-walled carbon nanotubes (MWCNTs)/polythiophene composites were synthesized through *in situ* chemical polymerization of thiophene in the presence of the chitosan-decorated ferrite-filled MWCNTs. The structure of the samples was characterized by Fourier transform infrared spectroscopy, X-ray diffraction. The shape and size were observed by scanning electron microscopy, transmission electron microscopy, and atomic force microscopy. The properties of the samples were tested with the vibrating sample magnetometer and the four-probe conductivity tester. The results showed that chitosan has been decorated onto the surface of MWCNTs. And the MWCNTs have been filled with a large number of ferrite crystals. And the chitosan-decorated ferrite-filled MWCNTs have also been coated with polythiophene. The magnetic saturation value of the chitosan-decorated ferrite-filled MWCNTs/polythiophene composites has achieved 0.18 emu/g, and the conductivity is 1.613 S/cm. Finally, based on the experimental results, the probable formation mechanism of this composite has been investigated.

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## 1. Introduction

In recent years, functional materials have played an important role in the field of civilian economic construction and national defense. In particular, materials with electromagnetic function have been the subject of extensive research. For example, nanoscale particles of oxides have been dispersed in conductive polymers such as polyaniline [1–8], polypyrrole [9], polythiophene derivatives [10,11], polyacrylamide [12] and phenylalanine [13]. The resulting composites of nanoscale magnetic particles and organic polymeric materials have been extensively studied. Because the combination of these materials has the potential to create new electromagnetic materials.

Meanwhile, Carbon nanotubes (CNTs) have been characterized by their high aspect ratio, high Young's modulus, chemical stability, nanometric dimensions, and interesting electrical properties,

especially high permittivity [14]. Multiwalled carbon nanotube (MWCNT)-magnetic composites have been created through the assembly of Zn–Sn substituted strontium ferrite film onto the surface of MWCNTs [15]. Wang et al. [16] have synthesized the ferrite-MWCNT composites using a sol–gel method. And the CNT–SrFe<sub>12</sub>O<sub>19</sub> composites have been produced using a sol–gel method by Li et al. [17]. The CoFe<sub>2</sub>O<sub>4</sub>/MWCNT composites were produced by electrospinning a dispersion of MWCNTs in a solution of polyvinylpyrrolidone, iron (III) nitrate nonahydrate, cobalt (II) acetate tetrahydrate, absolute ethanol, and H<sub>2</sub>O [18]. The  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>/carbon composites exhibit strong absorption characteristics with an absorption peak of –32.0 dB at 6.4 GHz [19]. Despite significant progress with the above studies, new approaches to prepare the multifunctional MWCNT-magnetic composites with control are highly needed.

Herein, we present a general approach to obtaining a new electromagnetic composite. This approach used a wet chemical online-filled method to prepare the ferrite-filled MWCNTs and *in situ* chemical synthesis of the chitosan-decorated ferrite-filled MWCNTs/polythiophene composites. The decoration of chitosan onto the surface of the ferrite-filled MWCNTs has improved the dispersion of the ferrite-filled MWCNTs in the matrix of

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polythiophene. And it reduces the agglomeration of the ferrite-filled MWCNTs. Furthermore, this method has been expected to be applicable for the preparation of other MWCNT-magnetic composites such as surfactant-decorated  $M_xFe_{2-x}O_4$ -filled MWCNTs/conductive polymer composites ( $M = Co, Zn, Ni, Mn, Cu$ ) for use in the electromagnetic devices.

## 2. Experimental

### 2.1. Materials

In this study, MWCNTs (O.D. 20–30 nm, length 10–30  $\mu\text{m}$ , purity >95%, Ash <0.5 wt.%, EC > $10^4$  S/m), purchased from Beijing DK Nanotechnology Co. Ltd., were used directly without further purification. Chitosan (with a degree of deacetylation >90.0%) was obtained from Sinopharm Chemical Reagent Co. Ltd., and thiophene monomer was purchased from Sigma. All other chemicals were all analytical grade.

### 2.2. Preparation of the ferrite-filled MWCNTs

The composites were obtained through a wet chemical filled route. The typical preparation procedure for the ferrite-filled MWCNTs was as follows. A certain amount of ferric nitrate was dissolved in 40 mL deionized water to form a saturated solution at room temperature. 1.0 g MWCNTs were dispersed into 40 mL saturated solution of ferric nitrate stirred at 800 r/min. 15 mL concentrated nitric acid and 5 mL concentrated sulfuric acid were added dropwise into above solution under ultrasonic dispersion for 120 min, and the above mixed solution reacted for 25 days. The substance was filtered and dried, and then transferred into a tube furnace under argon atmosphere using a flowing rate of 0.20 L/min and a heating rate of 10  $^\circ\text{C}/\text{min}$ . The temperature was kept at 950  $^\circ\text{C}$  for 120 min. After that the substance was naturally cooled to room temperature. Then the products were washed with deionized water to a pH of about 7, filtered, and dried again.

### 2.3. Preparation of the chitosan-decorated ferrite-filled MWCNTs

About 1.0 g chitosan was sufficiently dissolved into diluted acetic acid (pH = 2) with vigorous stirring for 15 min to obtain a dispersion system. 0.5 g the ferrite-filled MWCNTs were added into the resulting chitosan dispersion. The mixed system was dispersed ultrasonically for 2 h and mechanically agitated for 60 min, respectively. Then, the ammonia was added dropwise into the above solution obtaining a pH > 10 composite system. After that, the mixed solution was heated to 60  $^\circ\text{C}$ . At the same time, 2 drops of the glutaraldehyde (25 wt.%) were added to the above solution for 2 h to produce a crosslinking reaction. Subsequently, the black products were collected by centrifugation and washed with diluted acetic acid and deionized water. The final products were dried to constant weight under vacuum at 50  $^\circ\text{C}$  for 12 h.

### 2.4. Synthesis of the chitosan-decorated ferrite-filled MWCNTs/polythiophene composites

Composites were prepared by an *in situ* polymerization method as follows. 0.15 g the chitosan-decorated ferrite-filled MWCNTs and 1.0 mL thiophene monomer were added into 15 mL chloroform stirring for 30 min at room temperature. Then, 1.0 mL HCl (1 mol/L) was added into the above solution with ultrasonic dispersion for 10 min. After that, 4.0 g  $\text{FeCl}_3$  was added into the above solution stirring for 10 h. Then, the mixture was poured into 35 mL HCl (1 mol/L) stirring for 12 h. The products were obtained by

suction filtration until the filtrate was colorless. Finally, the composites were dried under vacuum at 50  $^\circ\text{C}$  for 24 h.

### 2.5. Characterization

Fourier transform infrared (FTIR) spectra were obtained using Nicolet 5700 FTIR with a KBr method. X-ray diffraction (XRD) patterns of the samples were characterized using a Philips-pw3040/60 diffractometer with Cu K $\alpha$  radiation ( $\lambda = 0.15418$  nm) at a scanning speed of 4 $^\circ/\text{min}$  in the range of  $2\theta = 5\text{--}60^\circ$ . The morphology and particle sizes of the samples were determined with a Hitachi H-800 scanning electron microscope (SEM), a JEOL JEM-1200EXII transmission electron microscope (TEM), and a Solver P47H atomic force microscope (AFM). The magnetic properties of the final composites were studied with a Lakeshore 7404 vibrating sample magnetometer (VSM), and the conductivity was measured with a four-probe conductivity tester.

## 3. Results and discussion

### 3.1. Polymerization

Fig. 1 illustrates the polymerization procedure for the chitosan-decorated ferrite-filled MWCNTs/polythiophene composites. First,  $\text{Fe}^{3+}$  was self-adsorbed into the inner surface of the MWCNTs through a gross suction effect in the mixed acid environment. The mixed acid environment was produced with a ratio of 3:1 concentrated nitric acid and concentrated sulfuric acid. Ferrite was formed onto the inner wall of MWCNTs during high-temperature calcination under argon. Second, chitosan was deposited onto the surface of the MWCNTs with a high density of carboxylic groups in an alkaline situation. Subsequently, the chitosan crosslinking reaction occurred under the action of glutaraldehyde. Finally, thiophene monomer was attracted by  $\text{Cl}^-$  and carboxylic groups and uniformly distributed over the surface of the chitosan-decorated ferrite-filled MWCNTs. The final products were obtained through *in situ* chemical polymerization of thiophene with anhydrous ferric chloride as an initiator. It has been pointed out in the literature that the aggregation growth of nanocrystallites initiates when the repulsive interactions are not large enough to block their access due to van der Waals force and Brownian motion [20]. In this paper, the gross suction effect and the decreasing surface energy are the main driving forces for the formation of the ferrite-filled MWCNTs. The decoration of chitosan also contributed to the dispersion of the ferrite-filled MWCNTs in the matrix of polythiophene. The MWCNTs, prevented ferrite from contacting with the conductive polymer, can improve the conductivity of the composites, which allows the ferrite to reach the optimum effect on magnetic properties.

### 3.2. FTIR analysis

Fig. 2 shows the FTIR spectra of (a) MWCNTs, (b) the ferrite-filled MWCNTs, (c) the chitosan-decorated ferrite-filled MWCNTs, (d) the chitosan-decorated ferrite-filled MWCNTs/polythiophene, (e) chitosan, and (f) polythiophene. The characteristic absorption peaks of MWCNTs and the ferrite-filled MWCNTs are not obvious. The peak at 1637  $\text{cm}^{-1}$  is assigned to the stretching vibration of C=C (Fig. 2(a) and (b)). The spectrum of the ferrite-filled MWCNTs does not show the characteristic absorption peaks of ferrite, indicating that ferrite may have been formed inside the MWCNTs (Fig. 2(b)). The characteristic peaks of chitosan occur at 2928, 1650, 1462, 1396, 1321, 1156, 1090, and 666  $\text{cm}^{-1}$  (Fig. 2(e)). The peak at 2928  $\text{cm}^{-1}$  is attributed to the C–H stretching vibration, and 1650  $\text{cm}^{-1}$  is assigned to the in-plane deformation

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