Preparation of carbon-coated magnetic nanocomposites under inert atmosphere and at low temperature

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HIGHLIGHTS

- The magnetic nanocomposites were prepared by calcining $Fe(NO_3)_3$ and carbon precursor mixture in Ar and at low temperature.
- The magnetic property was tuned by varying calcination temperature, gas flow rate, retention time, and heating rate.
- The saturation magnetization relies on the spatial and temporal contact of Fe intermediates with NO_2 and O_2 byproducts.

GRAPHICAL ABSTRACT
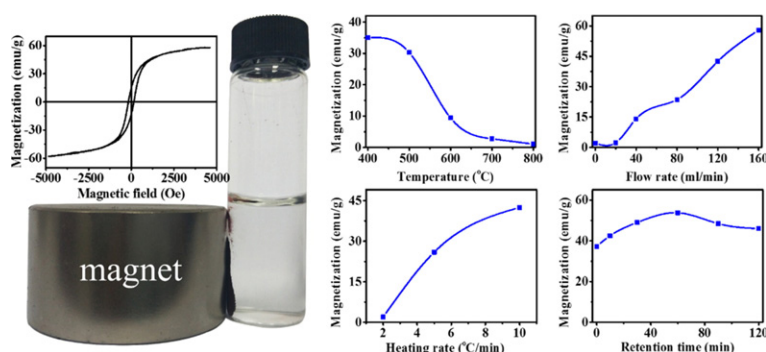
We report that carbon-coated magnetic nanocomposites can be prepared by calcination of the mixture of ferric nitrate $(Fe(NO_3)_3)$ and hydroxyethyl cellulose under benign calcination conditions (argon atmosphere, 400 °C). The magnetic property of the as-prepared samples can be tuned by simply varying the calcination temperature, the flow rate of argon, the retention time, and the heating rate, which would have important implication for the use of $Fe(NO_3)_3$ as iron source for future preparation of carbon-coated magnetic nanocomposites with high saturation magnetization.

ARTICLE INFO

ABSTRACT

We report here that carbon-coated magnetic nanocomposites can be prepared by calcination of the mixture of ferric nitrate $(Fe(NO_3)_3)$ and hydroxyethyl cellulose under argon atmosphere (without hydrogen) and at low temperature (400 °C). The magnetic property of the as-prepared samples can be tuned by simply varying the calcination temperature, the flow rate of argon, the retention time, and the heating rate. The characterization of these samples by XRD, FTIR, TEM and XPS reveals that their magnetic property is closely related with the contents of Fe_3O_4 and Fe_2O_3 in these samples. The proposed mechanism indicates that the reduction of the spatial and temporal contact of the decomposed Fe intermediates with the NO_2 and O_2 byproducts would be favorable for the formation of Fe_3O_4, leading to the higher saturation magnetization of the samples.

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1. Introduction

Magnetic nanocomposites are important materials for many applications such as ferrofluids, information storage, magnetic resonance imaging, as well as bio-technology such as drug delivery and immunoassays [1–6]. However, these materials are unstable under some conditions, for instance, the dissolution of these materials may occur in acidic or basic solution. In order to protect the materials from corrosion, coating of an inert layer is an efficient strategy. In the past decades, numerous materials had been utilized as the protective layer such as polymer [7], silica [2,8,9], carbon [10,11], precious metals [12] and metal oxides [13]. Among these materials, carbon exhibits an excellent stability in both acidic and basic media with additional excellent adsorption ability, for example for removal of organic contaminants or heavy metal ions from aqueous solution [14,15]. Moreover, the precursor sources of carbon are abundant and cheap, which are readily available from cotton fabric [15], rice husk [16], cellulose [10] and so on.

The carbon-coated nanomaterials were first synthesized in 1993 by Ruoff et al. [17] Since then, many methods were developed to produce the carbon-coated magnetic hybrid nanocomposites, such as the chemical vapor deposition [18–20], pyrolysis [21,22], hydrothermal carbonization [23], and so on. Among these methods, pyrolysis is a promising approach for large scale production of carbon-coated magnetic nanocomposites [24]. Zheng et al. [22] reported a one step, rapid, and temple-free method for synthesizing the high density Fe_3O_4 nanoparticles, which was achieved through ultrasonic spray pyrolysis of aqueous solutions containing ferrous chloride and citric acid. Zhu et al. [25] prepared the magnetic graphene nanocomposites by one-pot synthesis followed by annealing at 500 °C under H_2/Ar atmosphere. Gu et al. [26] synthesized carbon-coated Fe_3O_4 nanoparticles via a facile high temperature microwave assisted process. All these methods were conducted under reductive atmosphere (such as hydrogen) or at high temperature (>700 °C), which greatly impeded their industrial application.

In this study, we report a simple method for preparation of carbon-coated magnetic nanocomposites with ferric nitrate ($Fe(NO_3)_3$) as iron source and hydroxyethyl cellulose as the carbon precursor via calcination under inert atmosphere (argon) and at low temperature (400 °C). The effects of the calcination temperature, the flow rate of the argon, the heating rate and the retention time at the target temperature on the magnetic properties are investigated. A mechanism for formation of Fe_3O_4 under these benign conditions is proposed.

2. Experimental

2.1. Chemical

Hydroxyethyl cellulose (HC), ethyl cellulose (EC), $Fe(NO_3)_3 \cdot 9H_2O$ and $Fe_2(SO_4)_3 \cdot xH_2O$ were purchased from Sigma-Aldrich. Glucose was bought from Shanghai Titan Scientific Co., Ltd. Ethyl alcohol and hydrochloric acid were supplied by Sinopharm Chemical Reagent Co., Ltd. All chemicals were used as received without any further treatment.

2.2. Apparatus

Thermal Gravimetric Analysis (TGA) was carried out on a TA Instrument (TGA-Q500) in a nitrogen atmosphere at a heating rate of 10 °C min^{-1}. Magnetic property was analyzed using a vibrating sample magnetometer (VSM, Lake Shore 735) at room temperature. Powder X-ray diffraction (XRD) was measured by a Bruker D8 Focus via ceramic monochromatized Cu Kα radiation of 1.54178 Å, operating at 40 kV and 40 mA. The scanning rate was 5° per min in 2θ and the scanning range was from 15 to 80°. Fourier transform infrared (FTIR) spectra of the samples were taken with KBr pellets using a Thermo Scientific Nicolet iS10 FTIR spectrophotometer. Scanning electron microscope (SEM) images and energy dispersive X-ray analysis (EDX) data were obtained by Hitachi S-4800 equipped with a Horiba EDX system (X-max, silicon

drift X-Ray detector). The specific Brunauer-Emmett-Teller (BET) surface areas of the samples were measured on a Quanta Chrome Nova 2200e by nitrogen adsorption at 77.4 K. The samples were degassed for 3 h at 300 °C prior to measurements. Transmission electron microscopy (TEM) images, high resolution TEM (HRTEM) images and selected area electron diffraction (SAED) pattern were obtained using JEM-2100, JEOL. X-ray photoelectron spectroscopy (XPS) for elemental analysis was conducted on a Kratos Axis Ultra DLD X-ray Photoelectron Spectrometer using 60 W monochromated Mg Kα radiation as the X-ray source for excitation. The 500 μm X-ray spot was used for XPS analysis. The base pressure in the analysis chamber was about 3×10^{-10} mbar. The C 1s peak (284.6 eV) was used for internal calibration.

2.3. Procedure

2.3.1. Preparation of precursor of carbon-coated magnetic nanocomposites (PCMN)

2.0 g of hydroxyethyl cellulose was dissolved in 200 ml water followed by adding 32 g of $Fe(NO_3)_3 \cdot 9H_2O$. To accelerate the solvent evaporation, 200 ml of ethanol was further added into the solution under magnetic stirring. The solution mixture was then dried in a vacuum oven for 72 h at 50 °C to completely remove the solvent. The solid remainder was ground carefully in a crucible and then stored in a sealed glass bottle.

2.3.2. Effect of the calcination temperature

100 mg of PCMN were placed in a horizontal quartz tube and heated to different temperatures (400, 500, 600, 700 and 800 °C) with a heating rate of 10 °C/min under the argon atmosphere at a flow rate of 80 ml/min. After being kept at the target temperatures for 10 min, the samples were allowed to naturally cool down to room temperature. The calcined samples were named as T_m, where the subscript "m" represents the carbonization temperature.

2.3.3. Effect of the flow rate of argon

100 mg of PCMN were heated to 400 °C with a heating rate of 10 °C/min under the argon atmosphere at different flow rates (0, 20, 40, 80, 120 and 160 ml/min). After being kept at the target temperature for 10 min, the samples were allowed to naturally cool down to room temperature. The calcined samples were named as F_m, where the subscript "m" represents the flow rate.

2.3.4. Effect of the heating rate

100 mg of PCMN were heated to 400 °C with a heating rate of 2, 5 and 10 °C/min, respectively, under the argon atmosphere at a flow rate of 120 ml/min. After being kept at the target temperatures for 10 min, the samples were allowed to naturally cool down to room temperature. The calcined samples were named as H_m, where the subscript "m" represents the heating rate.

2.3.5. Effect of the retention time

100 mg of PCMN were heated to 400 °C with a heating rate of 10 °C/min under the argon atmosphere at a flow rate of 80 ml/min. The samples were kept at the target temperatures for 0, 10, 30, 60, 90 and 120 min, followed by naturally cooling down to room temperature. The calcined samples were named as R_m, where the subscript "m" represents the retention time.

3. Results and discussion

The temperatures required for thermal decomposition of PCMN, hydroxyethyl cellulose and $Fe(NO_3)_3 \cdot 9H_2O$ were determined by TGA measurements. As shown in Fig. 1, the thermal decomposition of all these samples proceeds by three stages involving water evaporation, active pyrolysis and passive pyrolysis. The active pyrolysis occurs at 215–390 °C for PCMN, 240–320 °C for HC, and 110–165 °C for $Fe(NO_3)_3 \cdot 9H_2O$, respectively. In the subsequent passive stage, there was a continuous and