

A facile method to fabricate carbon-encapsulated Fe₃O₄ core/shell composites

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Abstract

One-step synthesis of carbon-encapsulated Fe₃O₄ core/shell composites is reported. The Fe₃O₄ cores were formed via the reduction of Fe³⁺ by glucose under alkaline conditions obtained by the decomposition of urea. The amorphous carbon shells were carbonized from glucose. A possible formation mechanism for the Fe₃O₄@C composite was discussed. In order to characterize these Fe₃O₄@C core-shell composites, high-resolution transmission electron microscopy (HR-TEM), x-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), x-ray photoelectron spectroscopy (XPS) and a superconducting quantum interference device (SQUID) magnetometer were employed to characterize the sample obtained using the above method.

1. Introduction

Magnetic core-shell nanostructured materials have attracted increasing attention due to their various applications in areas such as enzyme and protein immobilization, magnetic resonance imaging and magnetic cell separation and purification [1–4]. To date, the commonly employed approach to synthesize magnetic core-shell nanoparticles is the templating strategy, which consists of two steps. First, magnetic particles are prepared through various methods, and as-prepared particles usually have relatively inert surfaces, which make surface modification almost unavoidable before use as supports or templates. Second, modified magnetic particles are used as templates and they are coated with various materials. Thus, the development of a one-step synthesis strategy for the magnetic core-shell nanostructure has become a pressing need not only for fundamental interest but also for their high efficiency and facility. Thanks to many years of effort from various groups,

various strategies have been developed to construct these magnetic composites [5–8].

In most of the previous studies, both inorganic and organic materials such as chitosan [9], polyamidoamine [10], mesoporous silica [11] etc were employed to coat magnetic particles in order to fabricate core/shell nanoparticles. Compared to polymer and silica shells that have been studied, carbon shells have exhibited much higher stability in various chemical and physical environments such as acid or base media, as well as at high temperatures and pressures. So far, various techniques have been developed to synthesize magnetic metal nanoparticles encapsulated in carbon, including arc techniques [12], magnetron and ion-beam co-sputtering [13], high-temperature annealing of the mixtures of carbon-based materials and metal precursors [14], catalytic chemical vapour deposition [15], pyrolysis of organometallic compounds [16], catalytic decomposition of methane [17], explosion [18], and spraying methods [19]. The intrinsically high energy consumption and intensive use of hardware of these techniques are mainly responsible for the high cost of manufacturing

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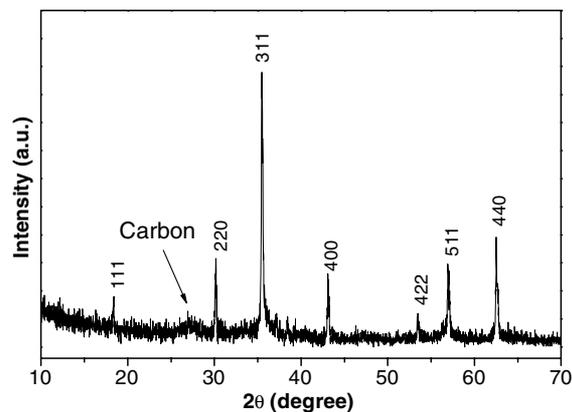


Figure 1. XRD patterns of the magnetic core/shell composites.

nanoparticles encapsulated in carbon, and thus they limit their practical applications.

Recently, Li *et al* [20] reported a way to prepare carbon spheres with a narrow size distribution by heating the aqueous glucose solution at 160–180 °C, which is higher than the normal glycosidation temperature and leads to aromatization and carbonization of glucose, and then such a hydrothermal reaction has been employed to encapsulate Au or Ag nanoparticles in carbon nanospheres. Inspired by the above work, Wei [21] and Wang [22] have successfully prepared carbon-encapsulated magnetic nanoparticles by using FeNi and Fe₃O₄ nanoparticles as the nuclei in the hydrothermal reaction, respectively. However, to the best of our knowledge, there has been no report about the fabrication of Fe₃O₄@C core/shell composites via a one-step hydrothermal carbonization co-reduction technique under such temperatures.

In this work, we describe a convenient method for fabricating carbon-encapsulated magnetic Fe₃O₄ composites through a green wet chemical route under hydrothermal conditions by only one step. Here, these Fe₃O₄ cores were formed via the reduction of Fe³⁺ by glucose under alkaline condition obtained by the decomposition of urea. Synchronously, the carbon shells that carbonized from glucose protected the Fe₃O₄ cores. The carbonization reaction took place in water and no toxic reagents were added; the products may have promising applications in clinical diagnostics, therapeutics, molecular biology, bioengineering, catalysis, and magnetic storage devices.

2. Experimental details

The typical procedure for synthesis is described as follows: glucose (0.01 mol), FeCl₃ (0.006 mol) and urea (0.1 mol) were dissolved in 40 ml of water under vigorous stirring. After being stirred for 10 min, the solution was transferred and sealed in a 50 ml Teflon-sealed autoclave. The autoclave was kept at 180 °C for 14 h before being cooled naturally. The products were separated by magnet, and washed with deionized water and ethanol several times. Then the products were dried at 40 °C in an oven under vacuum for 12 h.

The phase of the samples was examined by x-ray powder diffraction with Cu K α radiation on an MXP18AHF x-ray diffractometer at room temperature. The Raman spectrum

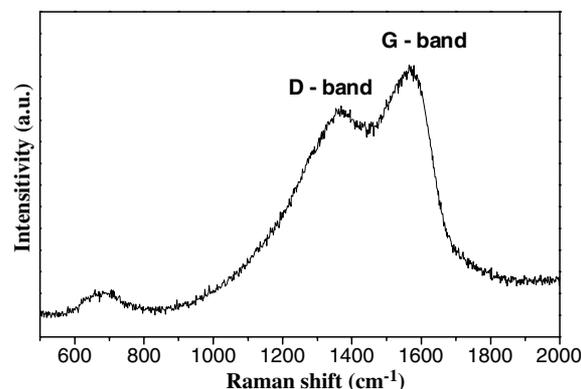


Figure 2. Raman spectrum of the magnetic core/shell composites.

of the sample was taken at room temperature on a SPEX 1403 spectrometer with an argon-ion laser at an excitation wavelength of 514.5 nm. X-ray photoelectron spectra (XPS) were measured on a photoelectron spectrometer using Mg K α radiation. Infrared (IR) spectra were recorded in the wavenumber range 4000–500 cm⁻¹ with a Nicolet Model 759 Fourier transform infrared (FT-IR) spectrometer using a KBr wafer. The morphology of the samples was examined by transmission electron microscopy (TEM) (Hitachi model H-800) and high-resolution TEM (HRTEM) (Model JEOL-2010, Japan). Powder samples for TEM and HR-TEM were prepared by ultrasonically dispersing the products into absolute ethanol, then placing a drop of this suspension onto a copper grid with an amorphous carbon film, and then drying in air. Their magnetic properties (*M-H* curve) were measured at room temperature on an MPMS XL magnetometer made by Quantum Design Corporation.

3. Results and discussion

The crystalline nature of the phase and its purity were determined by x-ray diffraction (XRD). A representative XRD pattern of the as-prepared product is shown in figure 1. All detected diffraction sharp peaks could be indexed as face-centred cubic (fcc) Fe₃O₄ (JCPDS card No. 19-629). No characteristic peaks due to the impurities of hematite or iron hydroxides were detected, which indicates that the products obtained by the present synthetic route consist of a pure fcc phase. The broadened peak with a relatively low peak intensity could be attributed to amorphous carbon [23, 24]. Because the carbon prepared under this method was amorphous, no obvious sharp diffraction peak for the graphite was present. Further information about the structure of the carbon shell was obtained from Raman investigation. A typical Raman spectrum of Fe₃O₄@C core-shell composites (figure 2) showed two main peaks centred at 1357 cm⁻¹ (D-band) and 1566 cm⁻¹ (G-band), the same as those of amorphous carbon [25]. These two vibrational peaks are broad, which indicates the poor crystallinity in the as-formed state, similar to the literature reported by Li *et al* [20]. According to the reports, the peak at 1357 cm⁻¹ is usually associated with the vibrations of carbon atoms with dangling bonds for the in-plane terminations of disordered graphite, and is labelled as the D-band [26, 27],

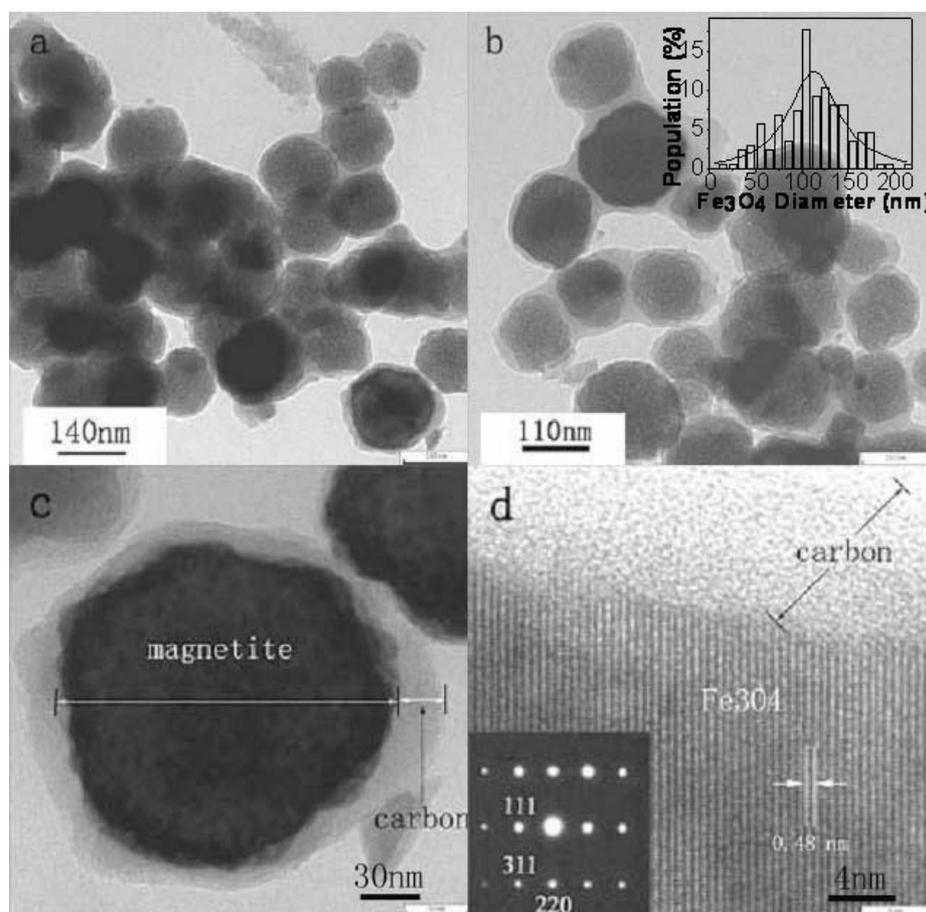


Figure 3. TEM images of the core/shell composites with low magnifications ((a), (b)) and high magnifications (c). High-magnification HRTEM images looking down onto the side surface of a typical Fe_3O_4 /carbon particle (d). The inset at (b) is the size distribution of Fe_3O_4 particles and the inset at (d) is the SEAD of the Fe_3O_4 particle.

and the peak at 1566 cm^{-1} (G-band) (corresponding to the E_{2g} mode) is closely related to the vibration in all sp^2 -bonded carbon atoms in a two-dimensional hexagonal lattice, such as in a graphene layer [26, 28]. The peak (D-band) is relatively high, indicating that in the basal planes there is two-dimensional (2D) disorder [29]. Therefore, the Raman spectrum shows that the carbon in our sample is disordered, in agreement with XRD pattern observations.

Figure 3 shows the typical TEM and HRTEM image of the as-prepared sample. Figure 3(a) shows that the sample consists of well-dispersed particles with an average size range from 100 to 200 nm, and each Fe_3O_4 core was encapsulated in carbon. The size distribution histogram of the Fe_3O_4 cores (the inset of figure 3(b)) indicates the good dispersion. Furthermore, an individual particle obtained with higher magnification, shown in figure 3(c), clearly shows that the particle has a core-shell structure with a Fe_3O_4 core and a carbon shell. The electron diffraction (ED) pattern (the inset of figure 3(d)) confirms the Fe_3O_4 core to be single crystalline; the HR-TEM image (figure 3(d)) shows that the interlayer spacing for the core is about 0.48 nm, which is close to the value for the (111) planes of the Fe_3O_4 , and this agrees very well with the XRD and ED analysis. The average thickness of the coating shell is about 10 nm, and the Fe_3O_4 core is well wrapped in the coating layer. Between the shell and core there exists a clear interface, which

indicates the tight encapsulation. It is also noticeable that some particles are lightly agglomerated by the coalescence of the outer shells (figure 3(b)). The high-resolution TEM image of the product (figure 3(d)) illustrates distinctly that the outer carbon shell consists of amorphous carbon, and this generally supports the above XRD and Raman analysis results.

XPS has often been used for the surface characterization of various materials, and unambiguous results are readily obtained when the various surface components each contain unique elemental markers. Here, in order to further analyse the carbon shell in the core/shell product, XPS (figure 4) were measured to understand the composition of the particle surface. It is obvious that the main content of the surface species is C (71.5 at.%), and the C_{1s} binding energies are 285.1, 287.2 and 289.05 eV, which correspond to C-C/C-H, carbonyl groups and carboxyl groups, respectively [30]. However, the binding energy at 710.20 eV for Fe_{2p3} almost cannot be detected. These results confirm that all Fe_3O_4 cores in the composite are confined within a shell of carbon, and there are certain amounts of functional groups on the carbon surface.

FTIR spectroscopy (figure 5) was further used to measure the product. The peak at 3450 cm^{-1} implies the existence of residual hydroxyl groups, and the peaks at 1710 and 1640 cm^{-1} are attributed to C=O and C=C vibrations, respectively, which supports the concept of the aromatization of glucose during

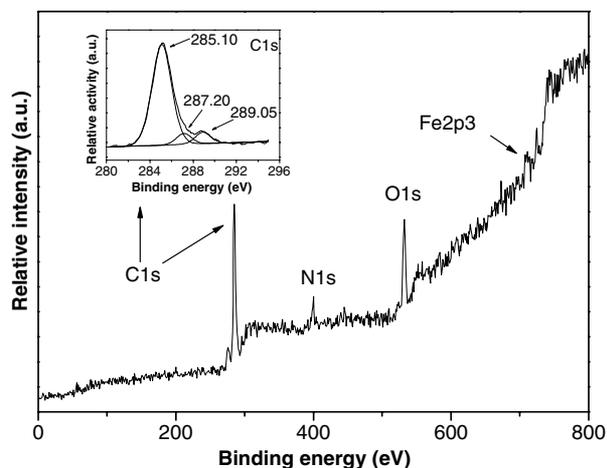


Figure 4. XPS spectrum of the $\text{Fe}_3\text{O}_4@\text{C}$ particles. Inset is the XPS pattern of the C1s.

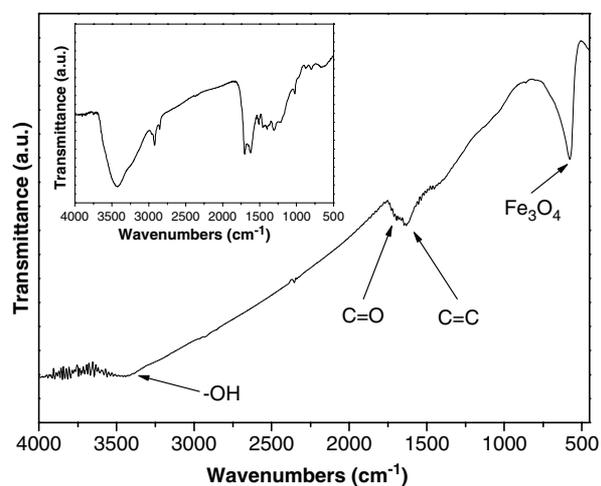


Figure 5. FT-IR spectrum of the magnetic core/shell composites. Inset is the FT-IR spectrum of pure carbon sphere.

hydrothermal treatment [20]. All of these bands reveal that there are functional groups such as $-\text{OH}$ and $\text{C}=\text{O}$ groups on the surface, which will facilitate the linkage of biomolecules or catalytic species to the surface in future application, and this also agrees with the XPS analysis. Considering the low content of carbon in the magnetic composites, it is not surprising to find that the relative intensity of the $-\text{OH}$ bond and the $\text{C}=\text{O}$ bond here are much weaker than that of the pure carbon sphere synthesized by Li's method [20].

The thermogravimetric (TG) analysis curve of $\text{Fe}_3\text{O}_4@\text{C}$ composites is shown in figure 6. The as-prepared sample showed three-step weight loss in the temperature region of 40–700 °C. The initial weight loss from the core/shell composites up to 250 °C was probably due to the removal of surface hydroxyls and/or surface adsorbed water, while the weight loss at higher temperature (250–500 °C) could be attributed mainly to the evaporation and subsequent decomposition of the amorphous carbon coating. As we know, the Fe_3O_4 will transfer to Fe_2O_3 and the weight will increase when the temperature is higher than 500 °C. Therefore, no obvious

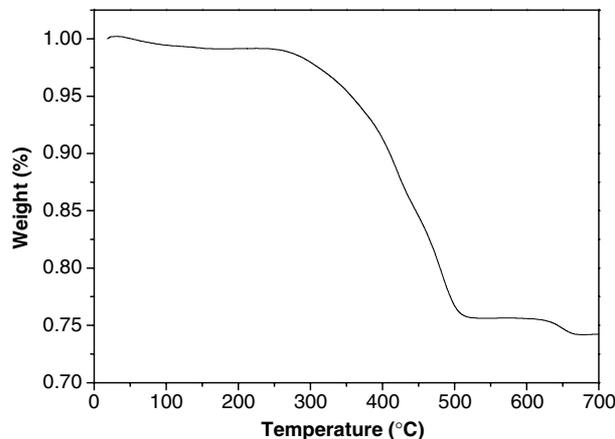


Figure 6. TG of the magnetic core/shell particles.

weight loss could be observed before the temperature is higher than 630 °C. The last weight loss from 625 to 700 °C may be a response to decomposition of the residue carbon. From the TG analysis, the mass ratio of the Fe_3O_4 in the magnetic composite is about 74%.

In comparison with most synthetic routes for $\text{Fe}_3\text{O}_4/\text{C}$ composites, the current approach is characterized by very mild preparation conditions. Therefore, it is necessary to understand the formation mechanism for $\text{Fe}_3\text{O}_4/\text{C}$ particles. In our system, glucose, FeCl_3 and urea were initially dissolved in deionized water and resulted in an homogeneous solution. The Fe_3O_4 nanoparticles were formed via the reduction of Fe^{3+} by glucose under alkaline conditions obtained by the decomposition of urea. When these small magnetic particles (~ 100 nm) formed in solution, they expose a reactive surface outside, catalyze following the carbonization of glucose, and lead to *in situ* deposition of carbonaceous products around the Fe_3O_4 particle surface to form a carbonaceous shell [20, 31]. But, for the magnetostatic energy of ferromagnetic cores, they are very easy to agglomerate, and the achievement of monodisperse particles with a thick shell is still a challenge.

Using this method, we found that the amount of glucose has a great impact on the form of the final products. In the controlled experiments, an experimental session was conducted by adjusting the starting amount of glucose while keeping the other parameters constant. In the absence of glucose, only uniform hexahedral hematite particles were obtained (figure 7(a)). After the amount of glucose was increased to 0.5 g, large Fe_3O_4 particles with both plate-like and octahedron-like morphology were produced (figure 7(c)). It is interesting to find that the Fe_3O_4 size decreases when the amount of glucose increases. When the glucose is 2 g, Fe_3O_4 particles with a size of around 100–200 nm were obtained (figure 7(d)). When an excess of glucose (8 g, reacted for 4 h) was used, nanoparticles of about 10 nm (figure 7(e)) can be obtained, along with some irregular carbon particles that existed on the particle's surface (unfortunately, the magnetic nanoparticles are not pure Fe_3O_4). Although the exact role of glucose in Fe_3O_4 nanoparticle growth is still unclear, it is believed that the presence of glucose molecules play a role in at least four aspects: first, the glucose acts as a reducing reagent; second, the adsorption of glucose molecules

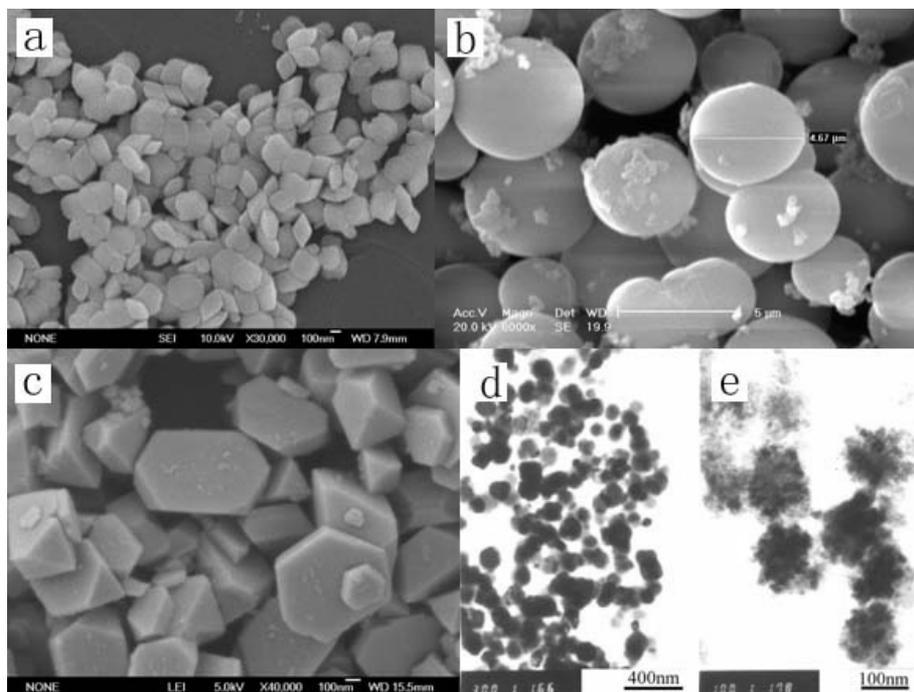


Figure 7. SEM and TEM image of the product, prepared under different amounts of glucose: 0 g (a), 0.5 g (c), 2.0 g (d), 8 g (e); SEM image of the product prepared with the urea missing (b).

onto the surfaces of Fe_3O_4 nuclei can reduce the interfacial tension between the crystallizing phase and the surrounding solution, thus determining the high nucleation frequency of the Fe_3O_4 product and leading to the as-obtained nanosized particles; third, glucose also prevents the chaotic coalescence of nanoparticles but favours their detachment from each other; last, the glucose acts as a precursor, which leads to the formation of the carbon shell. Since glucose is a weak-type reducing reagents, the temperature of the reaction was also investigated. When the temperature is lower than 140°C , glucose cannot be carbonized to carbon; although the carbon was successfully obtained after the temperature is increased to 160°C , pure magnetite still cannot be obtained. Furthermore, the alkaline source also has an important impact on the product. If the urea is missing, the products are mainly composed of carbon spheres with a size range of $1\text{--}6\ \mu\text{m}$ (figure 7(b)). If the urea is replaced by NaOH or $\text{NH}_3\cdot\text{H}_2\text{O}$ as the alkaline source, no magnetic particles are obtained, which means that the urea in our system cannot be substituted.

The magnetic properties of the product were examined using a Quantum Design SQUID magnetometer at room temperature (figure 8). As shown from the magnetic hysteresis loop, the products exhibit typical ferromagnetic curves, with a saturation magnetization of $41.6\ \text{emu g}^{-1}$. Taking into account that the sample contains 74% Fe_3O_4 , this gives a value of $56.2\ \text{emu g}^{-1}$. This value is much lower than that of the corresponding bulk Fe_3O_4 ($92\ \text{emu g}^{-1}$) [32], which may be due to the amorphous carbon shell for the disordered structure at interfaces providing less magnetic moment per unit mass than that of ferromagnetic core regions, which would lead to a decrease in the M_s [33]. The magnetic separability of such magnetic particles was tested in ethanol by placing a magnet near the glass bottle; the black particles were attracted toward

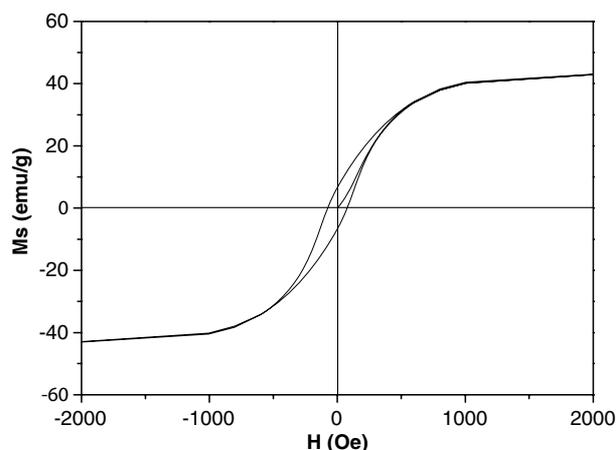


Figure 8. The room-temperature magnetization curve of the $\text{Fe}_3\text{O}_4/\text{C}$ particles.

the magnet within 30 s, demonstrating directly that the core-shell particles possess magnetic properties. This will provide an easy and efficient way to separate $\text{Fe}_3\text{O}_4/\text{C}$ core/shell particles from a suspension system and to carry enzyme or drugs to certain location under an external magnetic field.

4. Conclusion

In summary, we have described a facile strategy for the fabrication of magnetic $\text{Fe}_3\text{O}_4/\text{C}$ composites under hydrothermal conditions by using glucose both as the reducing agent and carbon precursor. Compared to other methods for the formation of magnetic metal@C structures, the one-step

carbonization reaction here is conducted at a relatively low temperature (180 °C). These magnetic particles possessed a certain amount of functional groups. We believe that these biocompatible magnetic composites will have important applications not only in enzyme immobilization but also in targeted drug delivery, biomolecular separations, cancer diagnosis and treatment, and magnetic resonance imaging as well as catalysis.

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