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# Assembly of Magnetic Nanospheres into One-Dimensional Nanostructured Carbon Hybrid Materials

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The synthesis and characterization of carbon-coated ferromagnetic nanoparticles that organize into 1-D assemblies of micrometer-sized ferromagnetic chains is described. A controlled aromatization and carbonization of glucose under hydrothermal reaction conditions enabled the preparation of carbonaceous surfactants that were used as shells for the coating of ferromagnetic Fe<sub>3</sub>O<sub>4</sub> nanospheres with a uniform size distribution. Under controlled experimental conditions, it was, for the first time, demonstrated that glucose could be employed as the carbon source in the preparation of continuous 1-D carbon nanoparticle chains with magnetic nanosphere inclusions. The functional groups on the carbon surface will facilitate the linkage of functional groups or catalytic species to the surface in future application. The salient feature of the reported method was the assembly of magnetic nanospheres under hydrothermal reaction conditions in the absence of external fields.

## Introduction

Recently, the controlled self-assembly of magnetic nanoparticles has stimulated a great interest since this method represents a convenient tool for the fabrication of magnetic nanodevices.<sup>1–11</sup> The magnetic assembly of dipolar colloids is an intriguing strategy for materials synthesis, as the directionality of magnetic dipoles enables a selective one-dimensional (1-D) organization of ferromagnetic nanoparticles.<sup>12,13</sup> In certain cases, it may be desirable to preserve the chain structure once the field is removed, and it has been shown that these magnetically driven self-assembled structures can be linked by polymers or other linkages<sup>14–17</sup> to form flexible chains of permanently linked superparamagnetic beads. Such chains have been used, for instance, as probes of MR fluid

behavior,<sup>18</sup> as micromechanical sensors,<sup>19</sup> and in DNA and other bioseparation processes.<sup>20</sup>

With the development of 1-D magnetic materials, the self-dipole-directed assembly of magnetic nanoparticles into ordered structures has stimulated a great interest.<sup>21–23</sup> A number of groups have reported on the fabrication of functional 1-D magnetic nanoparticle chains with polymeric coatings,<sup>24–26</sup> or with carbon coatings.<sup>27–30</sup> Our motivation in this area is to use the inherent magnetic dipoles between ferromagnetic colloids as a novel approach for controlling nanoparticle assembly.

## Experimental Section

**Materials.** All reagents were purchased from Beijing Chemicals Co., Ltd., and used without purification.

**Synthesis of the Fe<sub>3</sub>O<sub>4</sub> Nanospheres:**<sup>31</sup> FeCl<sub>3</sub>·6H<sub>2</sub>O (1.35 g, 5 mmol) was dissolved in ethylene glycol (40 mL), forming a clear solution, after which NaAc (3.6 g) and polyethylene glycol (1.0 g) were added. The mixture was stirred vigorously for 30 min and then sealed in a Teflon-lined stainless-steel autoclave (50 mL

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capacity). The autoclave was heated to and maintained at 200 °C for 8–72 h and then was allowed to cool to room temperature. The resulting black product was washed several times with ethanol and dried at 60 °C for 6 h; the yield of the Fe<sub>3</sub>O<sub>4</sub> nanospheres was about 85%. The above process could be extended to the synthesis of MFe<sub>2</sub>O<sub>4</sub> (M = Co, Zn) nanospheres by coprecipitation of M<sup>II</sup> and Fe<sup>III</sup> chlorides (M<sup>2+</sup>/Fe<sup>3+</sup> = 0.5).<sup>31</sup> For example, a mixture of ZnCl<sub>2</sub> (0.34 g, 2.5 mmol) and FeCl<sub>3</sub>·6H<sub>2</sub>O (1.35 g, 5 mmol) under the same reaction conditions as these was used for the synthesis of ZnFe<sub>2</sub>O<sub>4</sub> nanospheres.

**The Typical Procedure for the Assembly of the 1-D Magnetic Chains Was the Following.** Fe<sub>3</sub>O<sub>4</sub> nanospheres were first immersed in a 0.1 M HNO<sub>3</sub> solution for 5 min, after which the nanospheres were separated with a magnet and washed several times with deionized water. Subsequently, glucose (0.005 mol), Fe<sub>3</sub>O<sub>4</sub> nanospheres (0.002 mol) and urea (0.05 mol) were dissolved in 40 mL of water under vigorous stirring. After stirring for 10 min, the solution was transferred to a 50-mL Teflon-sealed autoclave. The autoclave was kept at 200 °C for 10–36 h before being cooled naturally. The products were separated by a magnet and washed several times with deionized water and ethanol. The so-obtained products were dried at 40 °C in an oven under vacuum for 12 h. The yield of the 1-D magnetic chains was about 52%. The products were fully carbonized at 500 °C in argon for Raman spectra characterization.

**Characterization.** The crystalline structure of the samples was examined by X-ray powder diffraction with Cu K $\alpha$  radiation on a Rigaku D/max-2500 X-ray diffractometer at room temperature. Moreover, Raman spectra were taken on the samples at room temperature on a Renishaw 2000 spectrometer with an argon-ion laser at an excitation wavelength of 514.5 nm. Fourier transform infrared (FT-IR) spectra were recorded in the wavenumber range 4000–500 cm<sup>-1</sup> with a Bio-Rad digilab Division FTS-80 spectrometer using a KBr wafer. The morphology of the samples was examined by transmission electron microscopy (TEM) (JEOL 2000) as well as by an XL30 ESEM FEG field emission scanning electron microscope (FE-SEM, FEI Company with 20 kV operating voltage). Powder samples for the TEM and FE-SEM investigations were prepared by ultrasonically dispersing the products in absolute ethanol, placing a drop of this suspension on a copper grid with an amorphous carbon film, and then drying it in air. The magnetic properties of the samples were studied by a superconducting quantum interference device (SQUID) magnetometer.

## Results and Discussion

The present communication reports on the development of a novel two-step synthesis route for the preparation of 1-D Fe<sub>3</sub>O<sub>4</sub>/C ferromagnetic chains. During the first step, Fe<sub>3</sub>O<sub>4</sub> magnetic nanospheres with diameters of 80 nm were synthesized via a solvothermal reaction, using FeCl<sub>3</sub> as the source of magnetic, and ethylene glycol as both the solvent and reductant. Subsequently, the magnetic nanospheres were coated with a thin layer of carbon by the polymerization and carbonization of glucose through a hydrothermal reaction, which gave rise to continuous 1-D carbon chains with Fe<sub>3</sub>O<sub>4</sub> inclusions.

Glucose was selected as the carbon source in the assembly of these 1-D magnetic chains through a hydrothermal reaction in the absence of external fields, since (1) the successful assemblies of hollow nanocrystals of cobalt chalcogenides at elevated temperatures have indicated that magnetic self-dipoles obtained from a large volume of nanocrystals are sufficient in order to maintain 1-D assemblies of the nanocrystals in solution;<sup>32</sup> (2) the recently reported formation of core-shell-structured materials, such as

FeNi/C<sup>33</sup> and Fe<sub>3</sub>O<sub>4</sub>/C,<sup>34,35</sup> in hydrothermal reactions has suggested that a similar process could be used to generate carbon-coated magnetic chains from 1-D assemblies of Fe<sub>3</sub>O<sub>4</sub> magnetic nanospheres; (3) glucose is a less expensive carbon source than other polymers due to its regenerative production in nature; (4) the assembly of carbon-coated Fe<sub>3</sub>O<sub>4</sub> magnetic chains under hydrothermal reaction conditions is unreported; and (5) functional groups, such as -OH and C=O, are present on the surfaces of the carbon shells, thus facilitating the linkage of functional groups or catalytic species to the surfaces in future applications. This strategy enables a modular assembly route to 1-D carbonaceous materials using soluble glucose precursors that previously required colloidal polymers,<sup>27</sup> block copolymer phase-separated thin films<sup>36,37</sup> or hard templates.<sup>38,39</sup> Similar core-shell colloids, or carbonized thin films composed of metal nanoparticle cores and carbon shells, have been obtained using arc-discharge methods,<sup>40</sup> ion-beam sputtering,<sup>41</sup> or carbonizing polymer precursors.<sup>42,43</sup> However, there were few applications of these carbon hybrid magnetic materials in bioseparation processes, because these materials were lacking functional groups on carbon shells. The methods presented herein represent a mild synthesis route for preparing carbon-coated 1-D core-shell-structured materials with functional groups which facilitate the linkage of other functional groups or catalytic species to the surface. The salient feature of the reported method is the assembly of magnetic nanospheres under hydrothermal reaction conditions in the absence of external fields.

Figure 1 presents a field-emission scanning electron microscopy (SEM) image as well as a transmission electron microscopy (TEM) micrograph displaying that the as-synthesized Fe<sub>3</sub>O<sub>4</sub> nanospheres had a mean diameter of 80 nm and a narrow size distribution (Figure 1). The crystalline structures of the Fe<sub>3</sub>O<sub>4</sub> were characterized by X-ray diffraction (XRD), and as shown in Figure 2, the patterns could be easily indexed to Fe<sub>3</sub>O<sub>4</sub> (JCPDS 75-1609). XRD was also employed to determine the crystalline nature of the as-prepared Fe<sub>3</sub>O<sub>4</sub>/C composite along with its purity. All detected sharp diffraction peaks could be indexed as Fe<sub>3</sub>O<sub>4</sub>. No obvious sharp diffraction peak corresponding to the graphite was present, indicating that most of the carbon prepared with this method was amorphous.

The as-made Fe<sub>3</sub>O<sub>4</sub> nanospheres were coated with hydrophilic carbon by a hydrothermal reaction of glucose. According to previous reports,<sup>44,45</sup> the carbonization of glucose during a hydrothermal treatment is due to the cross-linking of the intermolecular dehydration products of the glucose, oligosaccharides and/or other macromolecules derived from glucose. Fourier transform infrared (FTIR) spectra of the as-made magnetic chains are shown in Figure 3. The peak at 3460 cm<sup>-1</sup> implied

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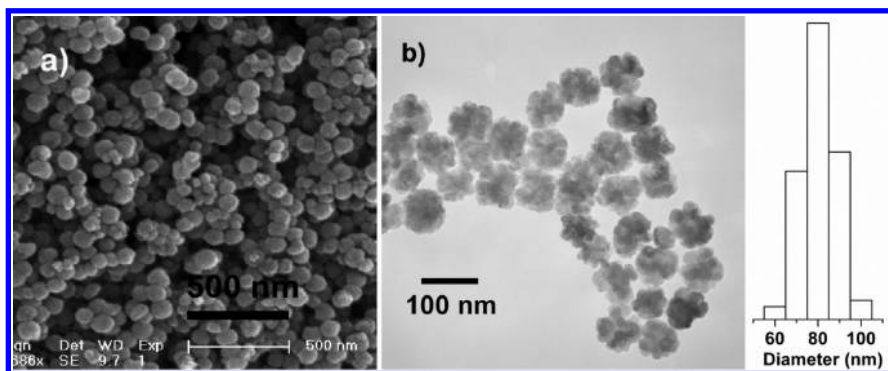
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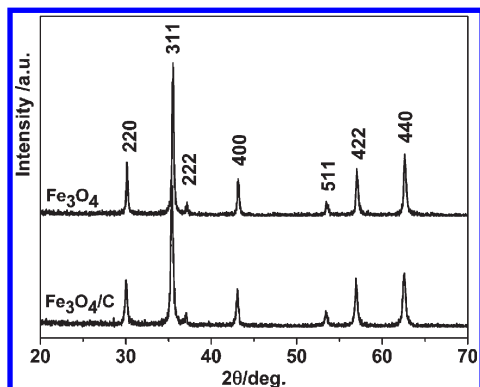
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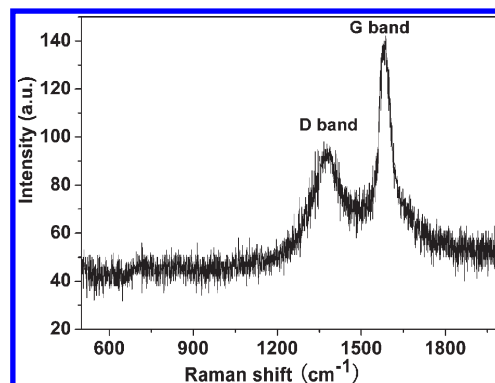
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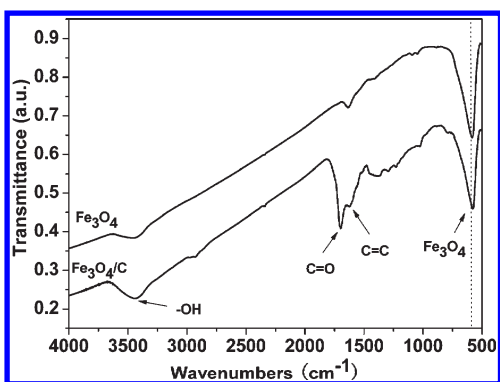
**Figure 1.** (a) SEM and (b) TEM micrographs of the  $\text{Fe}_3\text{O}_4$  nanospheres.



**Figure 2.** XRD patterns of  $\text{Fe}_3\text{O}_4$  nanospheres and  $\text{Fe}_3\text{O}_4/\text{C}$  composite.



**Figure 4.** Raman spectrum of the  $\text{Fe}_3\text{O}_4/\text{C}$  composite.



**Figure 3.** FT-IR spectra of the  $\text{Fe}_3\text{O}_4$  nanospheres and  $\text{Fe}_3\text{O}_4/\text{C}$  composite.

the existence of residual hydroxyl groups, and the peaks at  $1720$  and  $1650\text{ cm}^{-1}$  were attributed to  $\text{C}=\text{O}$  and  $\text{C}=\text{C}$  vibrations, respectively. Their presence supports the concept of an aromatization of glucose during the hydrothermal treatment.<sup>44,45</sup> All of the observed bands revealed that there were functional groups, such as  $-\text{OH}$  and  $\text{C}=\text{O}$ , on the surface, thus facilitating the linkage of functional groups or catalytic species to the surface in future applications.

Further information concerning the structure of the carbon shell was obtained from Raman investigation (Figure 4). The two distinct peaks at  $1348$  and  $1598\text{ cm}^{-1}$  were assigned to the “D” band and the “G” band of carbon materials, respectively. The “G” band, associated with an  $\text{E}_{2\text{g}}$  mode of graphite, is ascribed to

the vibration of  $\text{sp}^2$ -bonded carbon atoms in a two-dimensional hexagonal lattice.<sup>46,47</sup> The fact that such a band was observed confirms the presence of graphitic carbon. The band peaking at  $1348\text{ cm}^{-1}$  was a consequence of carbon atom vibrations with the dangling bonds in the plane terminations of a disordered graphite phase or glassy carbon. These two vibrational peaks were broad, revealing a poor crystallinity in the as-formed state, and this result correlated well with that reported in literature by Li et al.<sup>44,45</sup> In summary, the Raman spectrum demonstrated a disorder of the carbon in the sample, in agreement with the XRD observations.

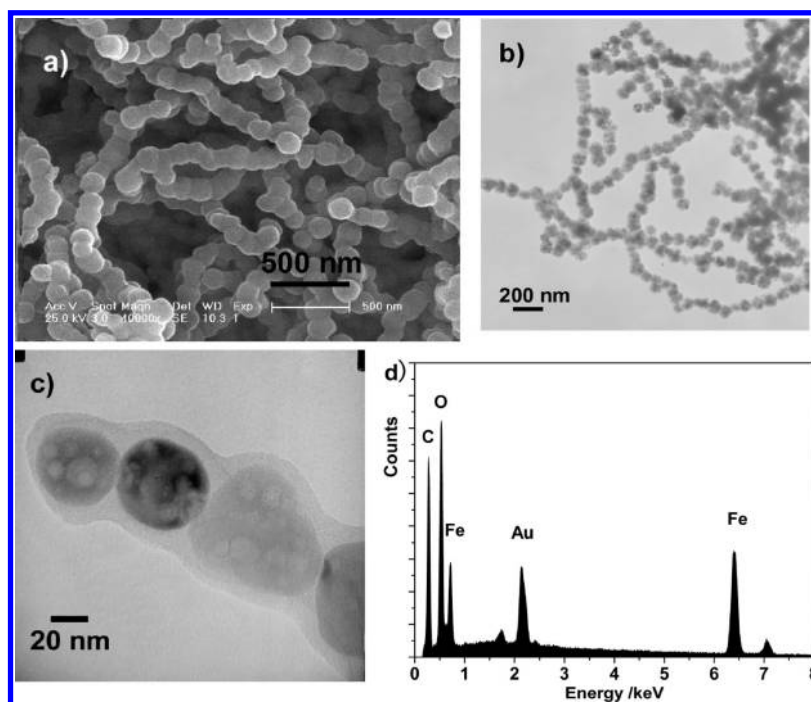
Figure 5d displays the energy-dispersive X-ray analysis (EDXA) of the obtained  $\text{Fe}_3\text{O}_4/\text{C}$  chains and reveals the existence of elemental Fe, C and O. These carbon-coated  $\text{Fe}_3\text{O}_4$  hybrid materials were also characterized by TEM and FE-SEM to determine the particle size and morphology of the nanoparticle chains. The FE-SEM image in Figure 5a demonstrates that the  $\text{Fe}_3\text{O}_4$  nanospheres were organized into extended nanoparticle chains with lengths as long as  $2\text{ }\mu\text{m}$  and with diameters of  $100\text{ nm}$ . The FE-SEM image also indicated that the chainlike  $\text{Fe}_3\text{O}_4/\text{C}$  was the major nanostructure formed, and this observation suggests that the chainlike structure was obtained in high yield, which may allow for large-scale production. The TEM images of the nanoparticle chains revealed that the  $\text{Fe}_3\text{O}_4$  nanospheres were aligned one by one during the hydrothermal reaction of glucose and that this resulted in core-shell-structured  $\text{Fe}_3\text{O}_4$  chains covered with a uniform carbon layer with a thickness of about  $10\text{ nm}$  (Figure 5b, c).

The above results led to the following proposition for the formation mechanism of the chainlike hybrid structures (Scheme 1). Each  $\text{Fe}_3\text{O}_4$  nanosphere was believed to behave as a single magnetic dipole at room temperature, where no chainlike

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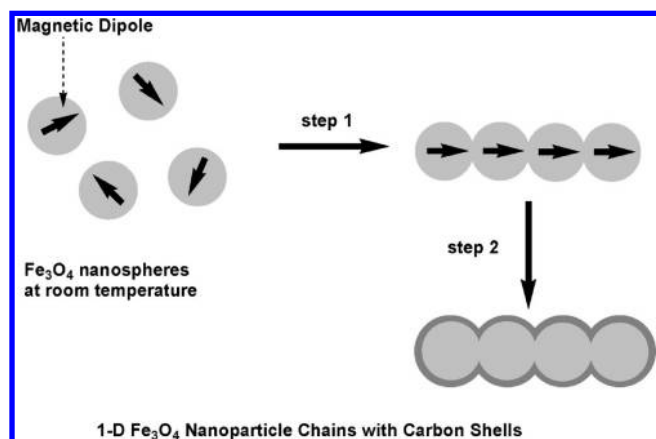
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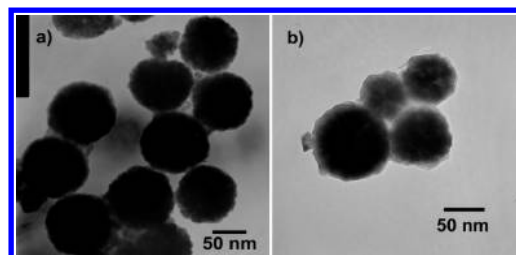
**Figure 5.** (a) FE-SEM image and (b,c) TEM micrographs of  $\text{Fe}_3\text{O}_4/\text{C}$  composite. (d) Energy-dispersive X-ray analysis of the obtained  $\text{Fe}_3\text{O}_4/\text{C}$  composite.

**Scheme 1. Schematic Assembly Model for the 1-D  $\text{Fe}_3\text{O}_4/\text{C}$  Ferro-magnetic Chains in the Absence of an External Field: (Step 1) Self-Dipole Action at 200 °C in the Absence of an External Field; (Step 2) Aromatization and Carbonization of Glucose at the Surface of the 1-D  $\text{Fe}_3\text{O}_4$  Chains**



structures were observed, probably because the magnetic dipolar interactions between these nanospheres were too weak to form such structures (Figure 1). Under the hydrothermal reaction conditions,  $\text{Fe}_3\text{O}_4$  nanospheres form 1-D chains in solution because of strong magnetic dipolar interactions and an elevated temperature, which was similar to the Xu's report.<sup>32</sup> After formation of the magnetic chains, a thin layer of carbon started to grow around the  $\text{Fe}_3\text{O}_4$  chain without causing a disintegration of the chain. A further carbonization reaction of glucose afforded a 1-D assembly of carbon-coated  $\text{Fe}_3\text{O}_4$  nanochains. According to this mechanism, a reduction of the magnetic dipolar interactions should prevent the formation of the chainlike structure. To illustrate this point, the following experiments were conducted.

$\text{Fe}_3\text{O}_4/\text{C}$  hybrid materials were synthesized in an alternating magnetic field,  $B(t) = B_0 \sin(\omega t)$ , where  $B_0 = 35$  G and  $\omega = 2\pi f$  with  $f = 50$  Hz, generated by a Helmholtz coil.<sup>32</sup> In such a field,

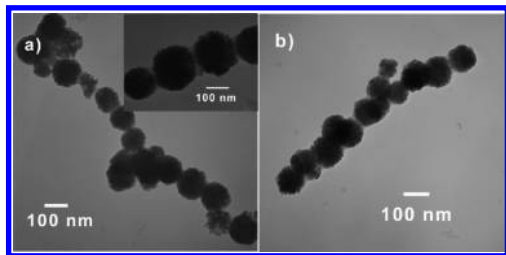


**Figure 6.** TEM micrographs of shell–core  $\text{Fe}_3\text{O}_4/\text{C}$  nanoparticles.

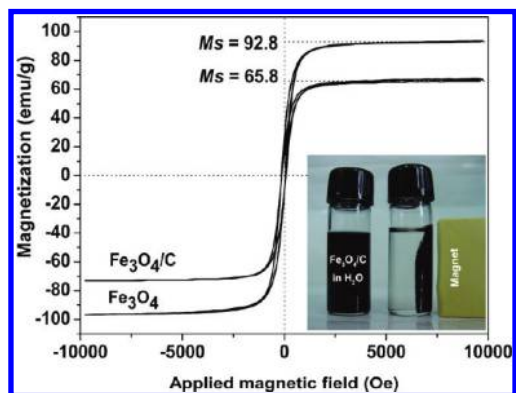
the reaction of glucose with  $\text{Fe}_3\text{O}_4$  led only to numerous disorder shell–core  $\text{Fe}_3\text{O}_4/\text{C}$  nanospheres, and no chainlike structures were formed (Figure 6). The underlying explanation is that the alternate magnetic field caused the magnetic  $\text{Fe}_3\text{O}_4$  chain to break due to the vibrational magnetic torque applied. This, in turn, disrupted the dipolar interactions between the particles. Once the chain was broken, the alternating magnetic torque caused the particles to rotate and prevented them from reconnecting. Such a mechanism agrees with the observations of strong dipolar–dipolar attractions between magnetic dipoles being able to induce the formation of a chainlike structure.

To establish the generality of this procedure,  $\text{Fe}_3\text{O}_4$  was replaced by  $\text{ZnFe}_2\text{O}_4$  or  $\text{CoFe}_2\text{O}_4$  in the assembly process. As shown in Figure 7, it was possible to obtain 1-D chainlike structures of carbon-coated  $\text{ZnFe}_2\text{O}_4$  and  $\text{CoFe}_2\text{O}_4$  composites, which presented morphologies similar to those of the 1-D  $\text{Fe}_3\text{O}_4/\text{C}$  composites. These studies indicate that the assembly of magnetic dipoles in the hydrothermal reaction of glucose enabled a modular assembly route to 1-D carbonaceous materials. The assembly of other magnetic nanoparticles into similar chainlike structures is currently ongoing.

The magnetic behavior of  $\text{Fe}_3\text{O}_4/\text{C}$  nanochains, which is of importance for practical applications, was investigated as comparison to that of  $\text{Fe}_3\text{O}_4$  nanospheres. Figure 8 shows magnetic hysteresis curves, measured at room temperature, for the two samples. The hysteresis loop of the  $\text{Fe}_3\text{O}_4/\text{C}$  nanochains exhibited



**Figure 7.** TEM micrographs of (a)  $\text{ZnFe}_2\text{O}_4/\text{C}$  composite and (b)  $\text{CoFe}_2\text{O}_4/\text{C}$  composite.



**Figure 8.** Hysteresis curve and the magnetic separability of the  $\text{Fe}_3\text{O}_4/\text{C}$  nanochains at room temperature.

a ferromagnetic behavior with values of saturation magnetization ( $M_s$ ), remnant magnetization ( $M_r$ ), and coercivity ( $H_c$ ) of  $\sim 65.8$ , 20.2 emu/g, and 76.5 Oe, respectively. The obtained saturation

magnetization ( $M_s$ ) was lower than that of the  $\text{Fe}_3\text{O}_4$  nanospheres (92.8 emu/g), and this was believed to be due to the amorphous carbon shell in the chainlike structure at the interface providing a smaller magnetic torque per unit mass as opposed to that of the ferromagnetic cores.<sup>48</sup> The magnetic separability of such magnetic chains was tested in water by placing a magnet near the glass bottle; the black chains were attracted toward the magnet within 20 s, clearly demonstrating the magnetic properties of the  $\text{Fe}_3\text{O}_4/\text{C}$  nanochains. Thus, an easy and efficient way to separate the  $\text{Fe}_3\text{O}_4/\text{C}$  nanochains from a suspension system is to use an external magnetic field.

## Conclusions

In summary, the synthesis and characterization of carbon-coated ferromagnetic nanoparticles that organize into 1-D assemblies of micrometer-sized ferromagnetic chains was described. A controlled aromatization and carbonization of glucose under hydrothermal reaction conditions enabled the preparation of carbonaceous surfactants that were used as shells for the coating of ferromagnetic  $\text{Fe}_3\text{O}_4$  nanospheres with a uniform size distribution. Under controlled experimental conditions, it was demonstrated, for the first time, that glucose could be employed as the carbon source in the preparation of continuous 1-D carbon nanoparticle chains with magnetic nanosphere inclusions. The functional groups on the carbon surface will facilitate the linkage of functional groups or catalytic species to the surface in future applications.

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