

## Electromagnetic Functionalized Cage-like Polyaniline Composite Nanostructures

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Novel cage-like and electromagnetic functional polyaniline (PANI)/CoFe<sub>2</sub>O<sub>4</sub> composite nanostructures, in which the self-assembled PANI nanofibers (~15 nm in diameter) entwined around the octahedral CoFe<sub>2</sub>O<sub>4</sub> magnet acting as the nucleation site or template, were successfully prepared by FeCl<sub>3</sub> as either oxidant and dopant via a self-assembly process. The coordination effect of the magnet as a nucleation site or template and the magnetic interaction between the PANI nanofibers and CoFe<sub>2</sub>O<sub>4</sub> as a driving force results in such cage-like nanostructures. The cage-like composite nanostructures not only have high conductivity ( $\sigma_{\max} \sim 5.2$  S/cm), but also show a typical ferromagnetic behavior.

## Introduction

Electromagnetic functionality of nanostructured conducting polymers has attracted considerable attention because of their unique magnetic, electric, and optical properties and promising potential applications as electromagnetic interference shielding, microwave absorption materials, nonlinear optical systems, and magnetic storage materials.<sup>1–5</sup> Up to now, many electromagnetic functionalized composites of the conducting polymers have been successfully synthesized by integrating conducting polymers with magnetic nanoparticles via chemical or electrochemical methods.<sup>6</sup> For example, polyaniline (PANI) nanotubes containing Fe<sub>3</sub>O<sub>4</sub> nanoparticles (~10 nm in diameter) and coaxial PANI/ $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> nanofibers have been synthesized by coconstruction of nanoparticles with aniline polymerization via a self-assembly process.<sup>7</sup> Those PANI nanocomposites exhibit electromagnetic properties; however, their conductivity at room temperature is poor. Interestingly, “core–shell” structured polypyrrole (PPy)<sup>8a</sup> and PANI nanocomposites with electromagnetic function have recently been synthesized by a template-free method associated with microspherical hydroxyl iron as a template;<sup>8b</sup> the PPy or PANI/hydroxyl iron micro/nanostructures show an enhanced conductivity at a certain content of the hydroxyl iron caused by conducting PPy or PANI nanofibers formed on the surface of spherical hydroxyl iron. Especially, size effect on physical properties of PANI–V<sub>2</sub>O<sub>5</sub> and PANI–Fe<sub>3</sub>O<sub>4</sub> composites has been also reported.<sup>9</sup> Above-described results suggest that the molecular structure of the electrical and magnetic components in the composites and the morphology of the resultant composites are important in controlling physical properties of the composite micro/nanostructured conducting polymers.

Co ferrites (CoFe<sub>2</sub>O<sub>4</sub>), as one of the most important and abundant magnetic materials, is known to have moderate saturation magnetization, remarkable chemical stability, and a mechanical hardness.<sup>10</sup> In addition, PANI is one of the most promising conducting polymers owing to its high conductivity, low cost, easy of synthesis, excellent environmental stability,

and wide applications as electronic materials.<sup>11</sup> Therefore, it is very interesting in preparing micro- or nanostructures of PANI composites containing CoFe<sub>2</sub>O<sub>4</sub> magnets via a self-assembly process. To our best knowledge, such composite micro/nanostructures have not been reported yet.

Herein novel electromagnetic functional and cage-like PANI composite micro/nanostructures containing ferromagnetic and octahedral CoFe<sub>2</sub>O<sub>4</sub> crystal were successfully prepared by using FeCl<sub>3</sub> as both oxidant and dopant via a self-assembly process. It is found that the octahedral magnetic CoFe<sub>2</sub>O<sub>4</sub> nanocrystal (100–200 nm in diameter) is located in the center of the cage, whereas the self-assembled PANI nanofibers (~15 nm in diameter) entwined directionally around the magnet acting as the nucleation site or template to form unique cage-like structures. The cage-like composites not only have high conductivity of ~10<sup>0</sup> S/cm, but also ferromagnetic function with a high coercive force (1000 Oe). It is also found that the octahedral CoFe<sub>2</sub>O<sub>4</sub> crystal as the nucleation site or template associated with the magnetic interaction between the PANI and CoFe<sub>2</sub>O<sub>4</sub> might result in the PANI nanofibers entwining around the octahedral CoFe<sub>2</sub>O<sub>4</sub> magnet to form the cage-like nanostructures that lead to a maximum conductivity dependent on the content of the magnetic particles. This is significantly different from previous results where the conductivity usually decreases with increase of the content of magnetic nanoparticles caused by insulating magnets in the composites.<sup>7,12,13</sup> The influences of the content of CoFe<sub>2</sub>O<sub>4</sub> magnet on the morphology and the electromagnetic properties of the composites are investigated. The formation mechanism of the self-assembled cage-like PANI/CoFe<sub>2</sub>O<sub>4</sub> nanostructures is also discussed.

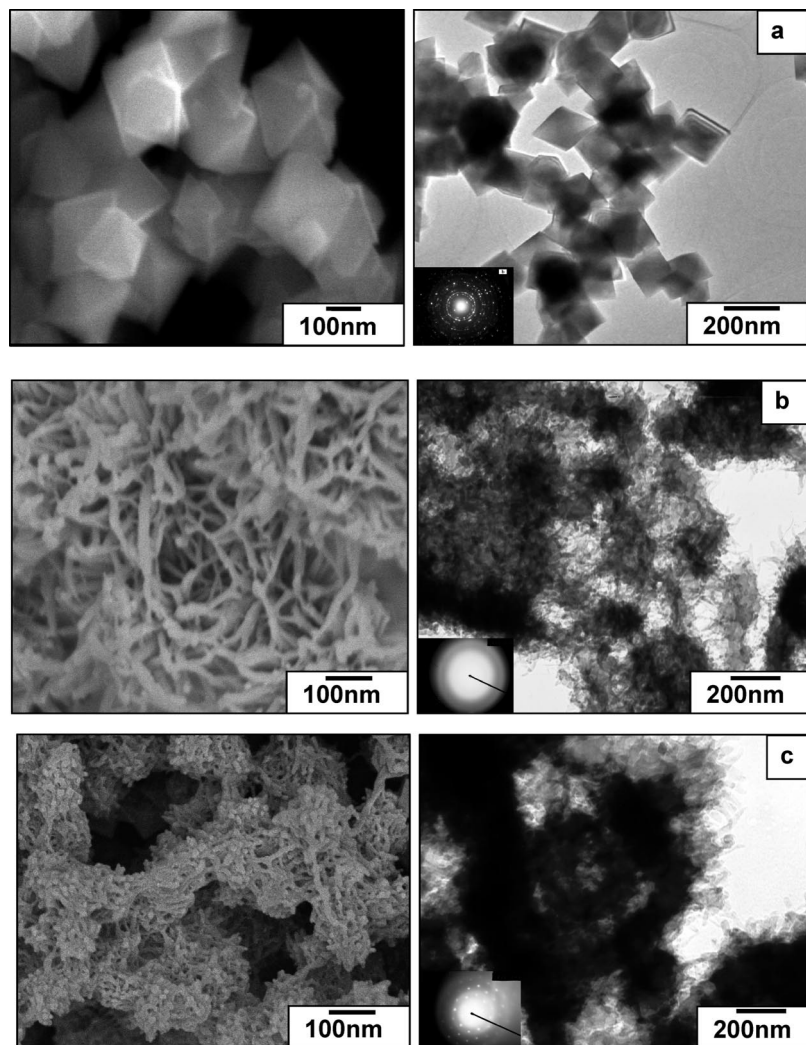
## Results and Discussion

**Morphology of the PANI/CoFe<sub>2</sub>O<sub>4</sub> Composites.** Figure 1 gives typical scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images for pure CoFe<sub>2</sub>O<sub>4</sub> and PANI nanofibers as well as PANI/CoFe<sub>2</sub>O<sub>4</sub> composites, respectively. Pure CoFe<sub>2</sub>O<sub>4</sub> particles are octahedral in shape (100–200 nm in diameter), and the electron diffraction (ED) pattern is in agreement with that of JCPDS (Figure 1a), and is consistent with our previous results<sup>25</sup> indicating the magnetic particles are identical to CoFe<sub>2</sub>O<sub>4</sub> crystal. The PANI oxidized by FeCl<sub>3</sub> as

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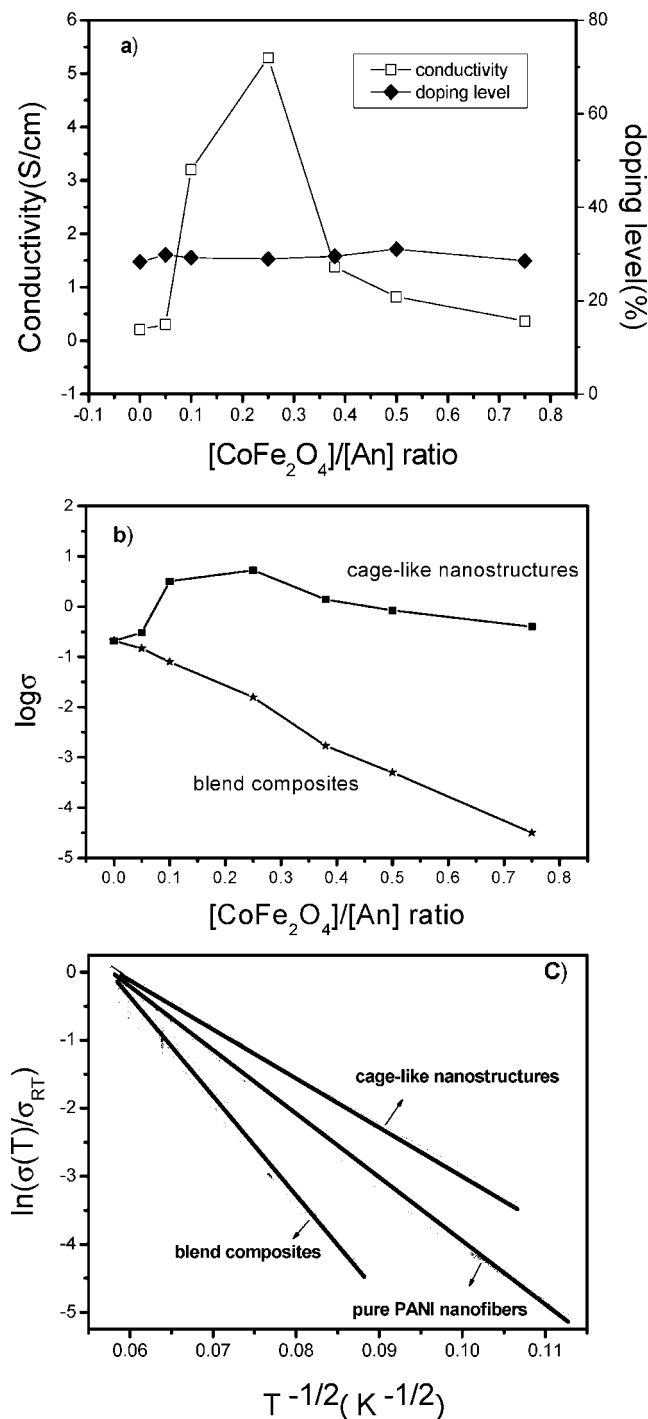
**Figure 1.** Typical SEM and TEM images of (a) pure  $\text{CoFe}_2\text{O}_4$  nano-octahedrons, (b) PANI nanofibers prepared by  $\text{FeCl}_3$  in the absence of the  $\text{CoFe}_2\text{O}_4$  magnet, and (c) cage-like PANI/ $\text{CoFe}_2\text{O}_4$  nanocomposites prepared at  $[\text{CoFe}_2\text{O}_4]/[\text{An}] = 0.25$ .

both oxidant and dopant in the absence of  $\text{CoFe}_2\text{O}_4$  are nanofibers with about 15 nm in diameter, and these nanofibers tend to twist unorderly with each other, indicating the nanofibers are flexible. The TEM image reveals that most nanofibers are solid, and the pure PANI nanofibers are amorphous, as determined by the ED (Figure 1b). Typical SEM and TEM images of the composites synthesized at the molar ratio of magnetic  $\text{CoFe}_2\text{O}_4$  particles to aniline monomer (represented by  $[\text{CoFe}_2\text{O}_4]/[\text{An}]$ ) of 0.25:1 are shown in Figure 1c. It shows the octahedral  $\text{CoFe}_2\text{O}_4$  crystal locates in the center of cage, whereas the PANI nanofibers entwine around the octahedral magnet to form a cage-like morphology of the composites in shape. Obviously, the special cage-like morphology of PANI/ $\text{CoFe}_2\text{O}_4$  composites differs significantly from the electromagnetic composite nanostructures of conducting polymers previously reported,<sup>7,8,10,12–14</sup> where the conducting nanofibers or nanotubes are usually coated or grown on the surface of the magnetic nanoparticles as the templates to form core–shell structured electromagnetic functionalized composites.

It is found that the addition of the magnetic  $\text{CoFe}_2\text{O}_4$  particles does not affect the fibular morphology of the PANI, but changes the arrangement of these fibers to entwine directionally around the magnetic octahedral  $\text{CoFe}_2\text{O}_4$  particles to form unique cage-like nanostructures (see Supporting Information). The  $[\text{CoFe}_2\text{O}_4]/[\text{An}]$  ratio in the range of 0.2:1–0.35:1, for instance, is favorable for forming cage-like composite nanostructures. The morphology

at a low  $[\text{CoFe}_2\text{O}_4]/[\text{An}]$  ratio (e.g., 0.1:1) is similar to that of the pure PANI nanofibers since magnetic  $\text{CoFe}_2\text{O}_4$  particles are insufficient to affect the arrangement of the PANI nanofibers. However, the pure octahedral  $\text{CoFe}_2\text{O}_4$  appears and coexists with cage-like structures when a high  $[\text{CoFe}_2\text{O}_4]/[\text{An}]$  ratio (e.g., 0.5:1) is used because there may not be enough PANI nanofibers to completely envelop all the magnetic particles.

**Electromagnetic Properties of PANI/  $\text{CoFe}_2\text{O}_4$  Composites.** The electromagnetic properties of the cage-like composite nanostructures also depend on the  $[\text{CoFe}_2\text{O}_4]/[\text{An}]$  ratio. The conductivity increases with increase of the  $[\text{CoFe}_2\text{O}_4]/[\text{An}]$  ratio, for instance, until a maximum conductivity is achieved followed by a decrease with increasing the  $[\text{CoFe}_2\text{O}_4]/[\text{An}]$  ratio (Figure 2a). A maximum conductivity ( $\sim 5.52 \text{ S/cm}$ ) is observed at the  $[\text{CoFe}_2\text{O}_4]/[\text{An}]$  ratio of 0.25:1, which is also the optimal condition to form uniform cage-like nanostructures. Unexpectedly, the maximum conductivity of the composites is 1 order of magnitude higher than that of the PANI nanofibers ( $2.24 \times 10^{-1} \text{ S/cm}$ ) synthesized in the absence of  $\text{CoFe}_2\text{O}_4$ . This is also different from the previous results<sup>7,13</sup> in which the conductivity of the electromagnetic composites usually decreases with increase of the content of magnetic nanoparticles due to partial blockage of the conductive path by the insulating magnet. In general, the conductivity of the doped PANI is enhanced by increasing the doping degree.<sup>15</sup> However, the doping degree assigned as  $[\text{N}^+]/[\text{N}]$ , as measured by X-ray photoelectron



**Figure 2.** Effect of the [CoFe<sub>2</sub>O<sub>4</sub>]/[An] ratio on (a) room-temperature conductivity of the PANI/CoFe<sub>2</sub>O<sub>4</sub> nanocomposites and the corresponding doping degree assigned as [N<sup>+</sup>]/[N] measured by XPS; (b) the conductivity of PANI/CoFe<sub>2</sub>O<sub>4</sub> nanocomposites and mechanically blended PANI/CoFe<sub>2</sub>O<sub>4</sub> composites; (c) temperature dependence of the conductivity of cage-like PANI/CoFe<sub>2</sub>O<sub>4</sub> nanostructures, pure PANI nanofibers, and blend PANI/CoFe<sub>2</sub>O<sub>4</sub> composites.

spectroscopy (XPS), is  $\sim 0.35$ , which is independent of the [CoFe<sub>2</sub>O<sub>4</sub>]/[An] ratio, suggesting that the contribution of doping degree to the conductivity of the composites can be negligible. Therefore, the conductivity increases initially as the [CoFe<sub>2</sub>O<sub>4</sub>]/[An] ratio increases up to the maximum value, possibly because of the reduction of the intercontact resistance caused by conducting nanofibers entwining around the CoFe<sub>2</sub>O<sub>4</sub> magnet. Afterward, the decrease in the conductivity with increase of the [CoFe<sub>2</sub>O<sub>4</sub>]/[An] ratio might be partially due to the blockage of

the conductive path by the insulating octahedral magnet incompletely entwined with the PANI nanofibers. In order to prove the above assumption, the conductivity of the composites made by mechanically blending PANI nanofibers with different contents of CoFe<sub>2</sub>O<sub>4</sub> was measured, and the results are shown in Figure 2b. It can be seen that the conductivity decreases with increase of the content of CoFe<sub>2</sub>O<sub>4</sub> magnet as a result of the blockage of the conductive path by the insulating magnet that is consistent with previous reports.<sup>8a</sup>

The temperature dependence of the conductivity of pure PANI nanofibers, PANI/CoFe<sub>2</sub>O<sub>4</sub> cage-like nanostructures, and blended PANI/CoFe<sub>2</sub>O<sub>4</sub> composites was also measured by a four-probe method at temperatures between 30 and 300 K. It is shown that the conductivity of all pellet samples decreases with decreasing temperature, exhibiting a typical semiconductor behavior and following the one-dimensional variable range hopping (1D-VRH) model proposed by Mott,<sup>16</sup> which is expressed as

$$\sigma(T) = \sigma_0 \exp[-(T_0/T)^{1/2}] \quad (1)$$

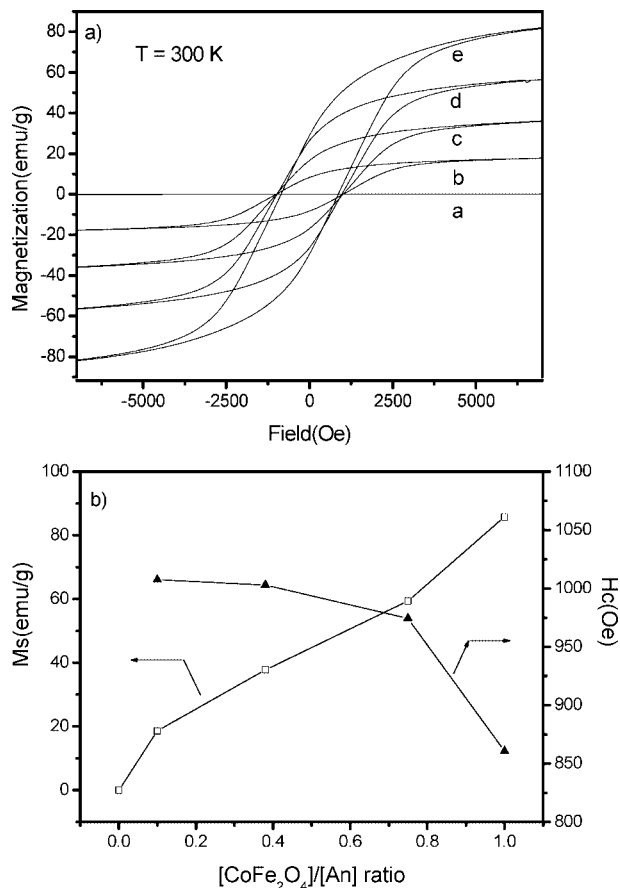
where  $\sigma_0$  is a constant,  $T$  is the Kelvin temperature, and  $T_0$  is the energy needed for charge carriers' hopping conduction related to the intercontact resistance (Figure 2c). It is found that the  $T_0$  value is in the order of cage-like nanocomposites < pure PANI nanofibers < blend composites, which is also consistent with the order of the room-temperature conductivity.

Dependence of the magnetization on the applied magnetic field at 300 K for pure CoFe<sub>2</sub>O<sub>4</sub>, PANI nanofibers, and PANI/CoFe<sub>2</sub>O<sub>4</sub> nanostructured composites synthesized at different [CoFe<sub>2</sub>O<sub>4</sub>]/[An] ratios was measured as shown in Figure 3a. Octahedral CoFe<sub>2</sub>O<sub>4</sub> exhibits ferromagnetic properties with a saturated magnetization ( $M_s$ ) of 85.82 emu/g and a coercive force ( $H_c$ ) of 892 Oe, respectively. The PANI nanofibers show typical paramagnetic properties due to spinning polaron, which is consistent with our previous reports.<sup>7</sup> Obviously, the CoFe<sub>2</sub>O<sub>4</sub> magnet contributes to the ferromagnetic properties of the PANI/CoFe<sub>2</sub>O<sub>4</sub> composites. Interestingly, it is noted that the saturated magnetization increases with increasing the [CoFe<sub>2</sub>O<sub>4</sub>]/[An] ratio (Figure 3b), whereas the coercive force is larger than that of pure CoFe<sub>2</sub>O<sub>4</sub>, indicating a magnetic interaction exists in the cage-like nanocomposites.

**Structural Characterization of the Cage-like Composite Nanostructures.** Figure 4a shows FTIR spectra of the PANI nanofibers, PANI/CoFe<sub>2</sub>O<sub>4</sub> nanocomposites, and blended PANI/CoFe<sub>2</sub>O<sub>4</sub> composites, respectively. One can see that the main chain structure of the cage-like nanocomposites synthesized at a low [CoFe<sub>2</sub>O<sub>4</sub>]/[An] ratio is similar to that of the emeraldine salt form of PANI. All characteristic bands of PANI, the C=C stretching deformation of quinoid at 1580 cm<sup>-1</sup>, benzenoid rings at 1496 cm<sup>-1</sup>, the C-N stretching of secondary aromatic amine at 1302 cm<sup>-1</sup>, the aromatic C-H in-plane bending at 1141 cm<sup>-1</sup>, the out-of-plane deformation of C-H in the 1,4-disubstituted benzene ring at 821 cm<sup>-1</sup> and 505 cm<sup>-1</sup> can all be observed.<sup>17-19</sup> When the [CoFe<sub>2</sub>O<sub>4</sub>]/[An] ratio is increased to 0.75, besides all above bands of PANI, a strong absorption at 550 cm<sup>-1</sup> attributed to Fe-O<sup>20</sup> stretching vibration modes is clearly observed. However, the intensity of the Fe-O stretching vibration modes is affected by the [CoFe<sub>2</sub>O<sub>4</sub>]/[An] ratio: for instance, the band of Fe-O stretching vibration modes in the composites at a low [CoFe<sub>2</sub>O<sub>4</sub>]/[An] ratio is more weak as a result of the octahedral CoFe<sub>2</sub>O<sub>4</sub> magnet completely enwrapped by the PANI nanofibers. Especially, there is no new band in Fourier transform infrared (FTIR) of the composites, indicating that there is no chemical reaction between CoFe<sub>2</sub>O<sub>4</sub> and PANI nanofibers.

Figure 4b illustrates the X-ray diffraction (XRD) patterns of octahedral CoFe<sub>2</sub>O<sub>4</sub> and PANI/CoFe<sub>2</sub>O<sub>4</sub> cage-like composites.

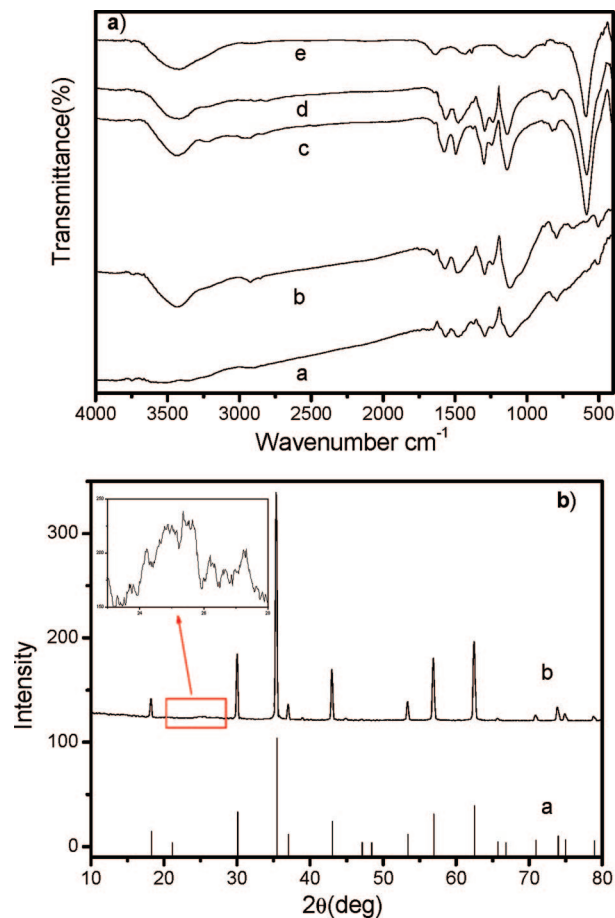




**Figure 3.** (a) Dependence of magnetization with the applied magnetic field at 300 K: (a) pure PANI nanofibers, (b) PANI/CoFe<sub>2</sub>O<sub>4</sub> nanostructures at [CoFe<sub>2</sub>O<sub>4</sub>]/[An] = 0.25:1, (c) PANI/CoFe<sub>2</sub>O<sub>4</sub> nanostructures at [CoFe<sub>2</sub>O<sub>4</sub>]/[An] = 0.5:1, (d) PANI/CoFe<sub>2</sub>O<sub>4</sub> nanostructures at [CoFe<sub>2</sub>O<sub>4</sub>]/[An] = 0.75:1, (e) pure CoFe<sub>2</sub>O<sub>4</sub> magnet. (b) Magnetization and coercive force of the PANI/CoFe<sub>2</sub>O<sub>4</sub> nanostructures versus the change of the [CoFe<sub>2</sub>O<sub>4</sub>]/[An] ratio.

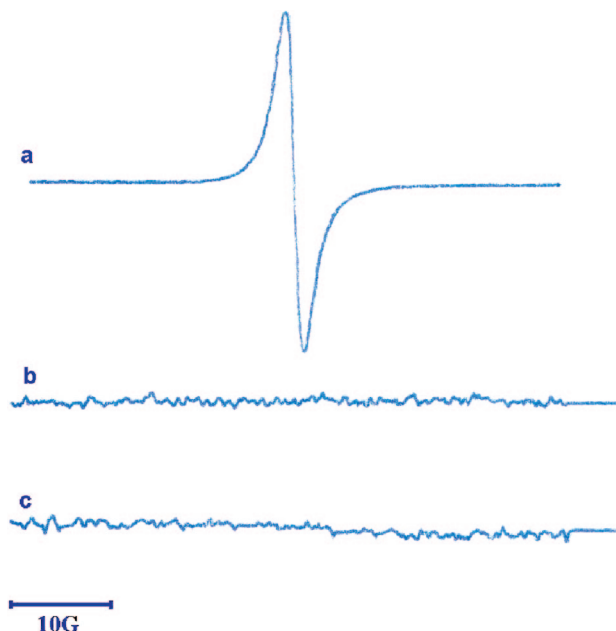
The octahedral CoFe<sub>2</sub>O<sub>4</sub> magnet is crystal, and all sharp peaks at  $d = 18.5, 30.2, 35.6, 37.2, 42.0, 53.4, 57.1,$  and  $62.5 \text{ \AA}$  match well those of CoFe<sub>2</sub>O<sub>4</sub> (JCPDS file no. 22-1086). The pure PANI nanofibers are amorphous, and two broad peaks centered at  $2\theta = 19.76$  and  $25.04$  are observed, which are assigned as planes perpendicular and parallel to the polymer chain,<sup>21</sup> respectively. The characteristic peaks of both PANI and CoFe<sub>2</sub>O<sub>4</sub> crystals are clearly observed from the cage-like composites without new peaks, further indicating there is no chemical reaction between CoFe<sub>2</sub>O<sub>4</sub> and PANI nanofibers.

**Formation Mechanism of Cage-like PANI/ CoFe<sub>2</sub>O<sub>4</sub> Composite.** According to our previous reports,<sup>22</sup> in the absence of CoFe<sub>2</sub>O<sub>4</sub> magnet, it is proposed that the micelles composed of aniline monomer might serve as the “soft-templates” in the formation of the PANI nanofibers because of its hydrophobic group of benzene ring and hydrophilic-NH<sub>2</sub> group. The oxidant of FeCl<sub>3</sub> with a low redox potential (e.g., 0.77 V)<sup>23</sup> results in a thinner diameter of PANI nanofibers (~15 nm) that might be more flexible to twist unorderly with each other, and these PANI nanofibers can be doped by the proton produced via a hydrolysis process of FeCl<sub>3</sub> in aqueous solution. As mentioned in the experimental section, CoFe<sub>2</sub>O<sub>4</sub> magnetic particles were dispersed in aniline monomer before polymerization. The presence of the CoFe<sub>2</sub>O<sub>4</sub> magnetic particles in solution does not change the fibrous shape of the resulting PANI; however, the arrangement of these PANI nanofibers is changed, in which the more



**Figure 4.** (a) FTIR spectra: (a) pure PANI nanofibers, (b) PANI/CoFe<sub>2</sub>O<sub>4</sub> nanostructures at [CoFe<sub>2</sub>O<sub>4</sub>]/[An] = 0.1:1, (c) PANI/CoFe<sub>2</sub>O<sub>4</sub> nanostructures at [CoFe<sub>2</sub>O<sub>4</sub>]/[An] = 0.25:1, (d) PANI/CoFe<sub>2</sub>O<sub>4</sub> nanostructures at [CoFe<sub>2</sub>O<sub>4</sub>]/[An] = 0.5:1, (e) pure CoFe<sub>2</sub>O<sub>4</sub> nano-octahedrons; (b) X-ray scattering patterns: (a) the reference data for the CoFe<sub>2</sub>O<sub>4</sub> standard (std) of the JCPDS file No. 22-1086, (b) PANI/CoFe<sub>2</sub>O<sub>4</sub> nanostructures.

flexible PANI nanofibers entwine directionally around the magnetic octahedral CoFe<sub>2</sub>O<sub>4</sub> particles to form unique cage-like nanostructures. Although we do not clearly understand the formation mechanism of the cage-like composites via a self-assembly process, we proposed that the coordination effect of the octahedral CoFe<sub>2</sub>O<sub>4</sub> crystal as the nucleation or template and the magnetic interaction between the PANI and CoFe<sub>2</sub>O<sub>4</sub> as the driving force for the PANI nanofibers entwining around the octahedral CoFe<sub>2</sub>O<sub>4</sub> magnetic results in the formation of the cage-like composites. The above proposal is supported by the following evidence: (a) As is well-known, the polaron with spin signal is regarded as the charge carrier in the doped PANI,<sup>24</sup> and electron spin resonance (ESR) is a powerful approach to determine the nature of the charge carriers in conducting polymers. For instance, polaron as a charge carrier has spin, while bipolaron is spin-less. When the sample contains some metal ions, the line width of the ESR signal is usually expended, showing no ESR signal as a result of the strong interaction of those metal ions. A strong ESR signal in the PANI nanofibers oxidized by ammonium persulfate (APS) as the oxidant is observed (Figure 5a), indicating the polaron is spinning. Although the polaron in the PANI also serves as the charge carrier, almost no ESR signal is observed in the nanofibers oxidized by using FeCl<sub>3</sub> as the oxidant instead of APS because of the existence of metal ions (Fe<sup>2+</sup> or Fe<sup>3+</sup>),



**Figure 5.** ESR signals of (a) PANI nanofibers oxidized by APS, (b) PANI nanofibers oxidized by  $\text{FeCl}_3$  as both oxidant and dopant, and (c) cage-like PANI/ $\text{CoFe}_2\text{O}_4$  nanocomposites prepared at  $[\text{CoFe}_2\text{O}_4]/[\text{An}] = 0.25$ .

resulting in an expanding line width of the ESR signal (Figure 5b). The similar ESR signal with expanding line width was also observed in the cage-like composites (see Figure 5c) because of the existence of metal ions ( $\text{Co}^{2+}$ ,  $\text{Fe}^{2+}$ , or  $\text{Fe}^{3+}$ ), and the pure  $\text{CoFe}_2\text{O}_4$  exhibits ferromagnetic behavior (Figure 3), which gives us reason to believe that a strong magnetic interaction between the spin polaron in the PANI nanofibers and ferromagnetic octahedral  $\text{CoFe}_2\text{O}_4$  magnet crystal exists in the composites. (b) The coercive force of the cage-like composites is larger than that of the pure magnetic octahedral  $\text{CoFe}_2\text{O}_4$  particles, which further proves the magnetic interaction between PANI nanofibers and  $\text{CoFe}_2\text{O}_4$  magnets exists in the composites. (c) There is no new band in FTIR or new peak in the XRD of the composites, indicating that no chemical reaction between PANI and  $\text{CoFe}_2\text{O}_4$  occurs.

## Conclusion

In summary, novel cage-like PANI/ $\text{CoFe}_2\text{O}_4$  nanostructures with electromagnetic function, where the self-assembled PANI nanofibers ( $\sim 15$  nm in diameter) entwined around the octahedral  $\text{CoFe}_2\text{O}_4$  magnet, were successfully prepared by  $\text{FeCl}_3$  as either oxidant or dopant via a self-assembly process for the first time. The cage-like composites not only have high conductivity ( $\sigma_{\text{max}} \sim 5.52$  S/cm), but also show ferromagnetic behavior with high coercive force ( $\sim 1000$  Oe). It was proposed that the coordination effect of the octahedral  $\text{CoFe}_2\text{O}_4$  magnet as the nucleation site or template and the magnetic interaction between PANI nanofibers and ferromagnetic octahedral  $\text{CoFe}_2\text{O}_4$  crystal as the driving force for the nanofibers entwining around the  $\text{CoFe}_2\text{O}_4$  magnet result in the formation of the cage-like morphology of the composites. The conducting PANI nanofibers entwined around the octahedral magnet result in the occurrence of the maximum conductivity at some  $[\text{CoFe}_2\text{O}_4]/[\text{An}]$  ratio as a result of the decrease of the intercontact resistance between the particles. The electromagnetic properties of the composites are controllable by changing the molar ratio of magnetic particles to aniline monomer.

## Experimental Section

**Synthesis of  $\text{CoFe}_2\text{O}_4$  crystal, PANI Nanofibers and PANI/ $\text{CoFe}_2\text{O}_4$  Composites.** All the reagents used in this study were of analytical grade (purchased from Beijing Chemical Industrial Co.) and used without further purification. Octahedral  $\text{CoFe}_2\text{O}_4$  crystal was prepared by a hydrothermal method based on our previous report<sup>25</sup> as follows: at a given molar ratio of  $\text{Co(II)}$  to  $\text{Fe(II)}$  (e.g., 2:1), 0.5 g of  $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  and 0.86 g of  $\text{C}_6\text{H}_5\text{Na}_3\text{O}_7 \cdot 2\text{H}_2\text{O}$  were dissolved in 20 mL of distilled water under constant stirring at room temperature for 30 min. The green solution turned into a laurel-green solution gradually. Subsequently, 20 mL of NaOH solution (5 mol/L) was slowly dripped without stirring. Greenish precipitate was observed at that time. Afterward, the mixtures were transferred into a 50 mL Teflon-lined autoclave and maintained at  $120^\circ\text{C}$  for 24 h. The black powders collected from the bottom of the container were washed with deionized water and absolute alcohol in turns, and vacuum-dried at room temperature. Cage-like PANI/ $\text{CoFe}_2\text{O}_4$  composites were chemically synthesized by  $\text{FeCl}_3$  as both oxidant and dopant in the presence of  $\text{CoFe}_2\text{O}_4$  magnet via a self-assembly process. The typical synthesis process is described as follows: 0.1 mL (1 mmol) of aniline monomer was mixed with the quantitative of  $\text{CoFe}_2\text{O}_4$  and dissolved in 5 mL of deionized water under supersonic stirring for 30 min to form an emulsion of aniline/ $\text{CoFe}_2\text{O}_4$  complex. Then the precooled 5 mL aqueous solution of  $\text{FeCl}_3$  (6 mmol) as both oxidant and dopant was added into the above mixture under supersonic stirring. When the mixture became green, the supersonic stirring ceased, and the mixture was then left to react for another 15 h under static state at  $0$ – $5^\circ\text{C}$ . The resulting PANI precipitate was washed with deionized water, methanol, and ether several times respectively. Finally, the product was dried in vacuum at room temperature for 24 h to obtain green-black powder of PANI/ $\text{CoFe}_2\text{O}_4$  composites. The PANI nanofibers were also prepared by a similar process in the absence of  $\text{CoFe}_2\text{O}_4$  for a comparable study. The composites with different  $\text{CoFe}_2\text{O}_4$ /aniline molar ratios (e.g., 0.05:1 to 1:1) were prepared by the same process to investigate the effect of  $\text{CoFe}_2\text{O}_4$  content on the structure, morphology, and electromagnetic properties of the composites.

**Structural Characterization and Measurements of Electrical and Magnetic Properties.** XRD and IR were used to characterize the structures of the PANI/ $\text{CoFe}_2\text{O}_4$  composites,  $\text{CoFe}_2\text{O}_4$  magnet, and the doped PANI nanofibers. XRD analysis was carried out on a Regaku D/max2500 diffractometer at a voltage of 40 kV and a current of 200 mA with Cu  $\text{K}\alpha$  radiation ( $\lambda = 1.5406$  Å), employing a scanning rate of  $0.02^\circ \text{s}^{-1}$  in the  $2\theta$  ranging from  $5$  to  $70^\circ$ . The infrared (IR) spectra were recorded on a Bruker Equinox-55 spectrometer on samples palletized with KBr powders. TEM images and the ED patterns were recorded on a Hitachi-600 transmission electron microscope at an accelerating voltage of 200 kV. The SEM images were obtained using a HITACHI S-4300 microscope. XPS data were obtained with an ESCALAB220i-XL electron spectrometer from VG Scientific using 300 W Al  $\text{K}\alpha$  radiations. The base pressure was about  $3 \times 10^{-9}$  mbar. The ESR signal was recorded on an ESP300 (Bruker Co.). The room-temperature conductivity of compressed pellets was measured by a standard four-probe method using a Keithley 196 System DMM Digital Multimeter and Advantest R 1642 programmable dc voltage/current generator as the current source. Magnetic measurements were carried out at 300 K using a vibrating sample magnetometer (VSM, Lakeshore 7307, USA) at a maximum magnetic field of 10 kOe.

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**Supporting Information Available:** SEM images of PANI/CoFe<sub>2</sub>O<sub>4</sub> nanostructures prepared at different [CoFe<sub>2</sub>O<sub>4</sub>]/[An] ratios: (a) [CoFe<sub>2</sub>O<sub>4</sub>]/[An] = 0.1:1, (b) [CoFe<sub>2</sub>O<sub>4</sub>]/[An] = 0.25:1, (c) [CoFe<sub>2</sub>O<sub>4</sub>]/[An] = 0.38:1, (d) [CoFe<sub>2</sub>O<sub>4</sub>]/[An] = 0.75:1. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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