



Hollow Poly(aniline-co-pyrrole)–Fe₃O₄ Composite Nanospheres: Synthesis and Characterization

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Hollow poly(aniline-co-pyrrole)–Fe₃O₄ nanosphere composites with electromagnetic properties were successfully prepared via oxidative polymerization of a mixture of aniline and pyrrole in the presence of magnetic fluid, using a non-ionic surfactant as template. Field emission scanning electron microscopy (FE-SEM), transmission electron microscopy (TEM), Fourier transform infra-red spectroscopy (FT-IR) and X-ray powder diffraction (XRD) were used to characterize the chemical structure and crystallinity of the nanosphere composites. Thermogravimetric analysis (TGA) was used to determine the thermal stability of the products. X-ray photoelectron spectroscopy (XPS) proved that the Fe₃O₄ magnetic nanoparticles were encapsulated in the poly(aniline-co-pyrrole) hollow nanospheres.

Keywords: Aniline, Pyrrole, Magnetite, Nanosphere.

1. INTRODUCTION

Organic–inorganic composites with micro/nanostructures have attracted significant academic and technological attention because of their unique physical properties and potential applications in nanoelectronics, electrochemical sensors, electromagnetics and microwave-absorbing materials.^{1–3} Integrating magnetic and electrical properties has become a research focus, especially for electromagnetic functionalized conducting polymers and nanoparticles.

Among conducting polymers, polyaniline (PANI) has been considered to be the most promising material for practical applications because of its high electrical conductivity, environmental stability, ease of preparation and favorable physiochemical properties.^{4–5} However, technological applications of PANI are hampered by its poor processability, because of its poor miscibility with other polymers and low solubility in common solvents.⁶ There are several ways to improve processability, such as incorporating functionalized organic acids as dopants, and adding functional groups.⁷ Unfortunately, improvement of the solubility is generally accompanied by decrease in electrical conductivity. To reduce this effect on polymer electrical properties, increasing attention is being paid to

copolymerization of aniline with suitable comonomers. It has been proved that copolymers of aniline and pyrrole have better properties than either homopolymer.^{5, 8, 9}

Nanostructured magnetic particles have attracted much attention over the past decade because of their unique properties and potential applications.^{10–12} Magnetite nanoparticles are the most notable because of their unique magnetic properties and relatively easy synthesis. There are numerous reports on magnetic and conducting polymeric nanocomposites of PANI and polypyrrole (PPY) containing magnetic nanoparticles. Araújo et al. reported preparation and characterization of a PANI/magnetite nanocomposite with tubular morphology.¹³ Yang and coworkers also synthesized hollow PANI/Fe₃O₄ composites with electromagnetic properties by using sulfonated polystyrene as a hard template.¹⁴ Conducting PANI/nano-sized Fe₃O₄ composites were proposed by Kim et al.¹⁵ for adoption as a dispersed phase of magnetorheological fluids. More recently, Wan's group reported a simple self-assembly process for facile one-step synthesis of novel electromagnetic functionalized PPY/Fe₃O₄ composite nanotubes using *p*-toluenesulfonic acid as the dopant and FeCl₃ as the oxidant.¹⁶ However, the morphology of electromagnetic functionalized conducting polymers is still to be investigated. Because the properties are dependent on structure and finite size, the synthesis

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of composite nanostructures with well defined size and morphology is of much interest.

Hollow nanospheres have attracted a great deal of attention because of their hollow interior, which has a wide range of applications.^{17–19} To the best of our knowledge, the preparation of electromagnetic functionalized copolymer hollow structures has not been reported. Herein, we report a facile method for preparing hollow poly(aniline-co-pyrrole)-Fe₃O₄ (HPAP-Fe₃O₄) nanosphere composites via oxidative polymerization of a mixture of aniline and pyrrole in the presence of magnetic fluid, using a non-ionic surfactant as a template. The morphology and molecular structure of the composite hollow nanospheres were determined by scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), and Fourier transform infrared spectroscopy (FT-IR), to understand the unique electromagnetic properties of the nanospheres. Thermogravimetric analysis (TGA) was used to determine the thermal stability of the products, and X-ray photoelectron spectroscopy (XPS) was used to provide elemental analysis and to prove that the Fe₃O₄ magnetic nanoparticles were encapsulated in the poly(aniline-co-pyrrole) hollow nanospheres.

2. EXPERIMENTAL DETAILS

2.1. Materials

Aniline (99%) was supplied by Wako Pure Chemical Reagent Co. Ltd., Japan). Pyrrole (98%, Sigma Aldrich Co. Ltd., USA) was stored below 0 °C. Sodium dodecyl sulfate (SDS), polyoxyethylene(10) octylphenyl ether (Triton X-100), ammonium peroxodisulfate (APS), FeCl₃·6H₂O, FeCl₂·4H₂O, ammonia (28%), and ethanol (99.5%) were of analytical purity and were used as received. Deionized water was used throughout the experiments.

2.2. Experimental Procedure

2.2.1. Synthesis of Fe₃O₄ Nanoparticles

Magnetic nanoparticles Fe₃O₄ were prepared by a modified co-precipitation method. The reaction was carried out in a 250 ml three-necked round-bottom flask equipped with a stirrer. FeCl₂·4H₂O (0.994 g, 5 mmol) in 10 ml of deionized water and 2.73 g (10 mmol) of FeCl₃·6H₂O in 10 ml of deionized water were mixed with vigorous stirring and the mixed solution kept in a water bath at 80 °C. 20 ml of preheated ammonia solution (1.5 M) was added rapidly to the solution, followed by dropwise addition of aqueous ammonia with stirring until the pH reached 10–12, and stirring was continued for 1 h. The Fe₃O₄ nanoparticles formed were collected by magnetic field separation, washed three times with deionized water, and dried under vacuum at 50 °C for 24 h.

2.2.2. Synthesis of HPAP-Fe₃O₄ Nanospheres with Hollow Structure

Hollow poly(aniline-co-pyrrole)-Fe₃O₄ (HPAP-Fe₃O₄) nanospheres were prepared via *in situ* emulsion polymerization in an aqueous solution containing Fe₃O₄ magnetic fluid and surfactant. A typical synthesis for HPAP-Fe₃O₄ nanospheres was as follows. Fe₃O₄ nanoparticles (0.01 g) were mixed with a quantitative amount of surfactant (SDS) dispersed in 20 ml of deionized water with ultrasonication for 2.5 h to obtain a uniform magnetic fluid. Then 1 mmol of pyrrole was added and the suspension was ultrasonicated for 0.5 h. Aniline (1 mmol) and 0.02 g Triton X-100 were added and the mixture ultrasonicated for a further 0.5 h. The mixture was maintained at 0–5 °C for 0.5 h then 0.2 mmol of APS was added to initiate polymerization, which took place at 0–5 °C for 24 h without agitation. The resulting product was collected by filtration and thoroughly washed with deionized water, 95% ethanol, and 0.1 M HCl until the filtrate became colorless. Finally, the hollow poly(aniline-co-pyrrole)-Fe₃O₄ nanospheres were vacuum-dried at 50 °C for 24 h. HPAP nanospheres were prepared in the absence of Fe₃O₄ nanoparticles via *in situ* emulsion polymerization as described above.

3. CHARACTERIZATION

The morphology of the products was investigated by SEM (JEOL S-5000) and TEM (JEOL JEM-2010). XRD patterns were obtained with a RINT 2550H diffractometer using CuK α radiation. FT-IR spectra of KBr powder pressed samples were recorded in the range 400–4000 cm⁻¹ with a Shimadzu IR-prestige21 spectrometer. TGA (TG8120, Rigaku Denki) was used from 50 to 600 °C at a heating rate of 5 °C min⁻¹, then holding at 600 °C for 30 min. XPS was performed using a Kratos Axis Ultra DLD X-ray spectrometer with Mg as the exciting source.

4. RESULTS AND DISCUSSION

4.1. Structure and Morphology of HPAP-Fe₃O₄ Nanospheres

The morphology of Fe₃O₄ nanoparticles dispersed in water as revealed by TEM is shown in Figure 1. The Fe₃O₄ nanoparticles were almost uniform in shape and size, about 10 nm in average diameter, and had relatively high dispersibility. The enlarged TEM image in the inset to Figure 1 suggests that the nanoparticles were well crystallized. FE-SEM images of the HPAP nanospheres and HPAP-Fe₃O₄ composite nanospheres (Fig. 2) show that the samples were uniform nanospheres with average diameter about 100 nm. From the magnified FE-SEM images in Figures 2(c) and (d), it is clear that the HPAP nanospheres had smooth surfaces, while the surfaces

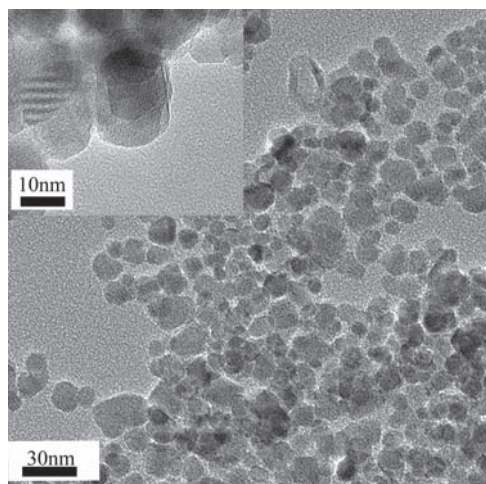


Fig. 1. TEM image of Fe₃O₄ nanoparticles synthesized by co-precipitation (inset: corresponding enlarged TEM image).

of the HPAP-Fe₃O₄ composite nanospheres were relatively rough. The TEM images of HPAP nanospheres and HPAP-Fe₃O₄ composite nanospheres in Figure 3 reveal that the samples had hollow interiors. The magnified TEM images show that the average shell thickness was in the range 20–30 nm. From Figure 3(b) it is clear that the Fe₃O₄ nanoparticles were encapsulated in the HPAP-Fe₃O₄ composite nanospheres, causing the rough surface.

4.2. XRD Analysis

Figure 4 shows XRD patterns of HPAP nanospheres (Fig. 4(a)), HPAP-Fe₃O₄ nanospheres (Fig. 4(b)) and Fe₃O₄ nanoparticles (Fig. 4(c)). The single broad band centered at around 21° for the HPAP nanospheres (Fig. 4(a)) is indicative of an amorphous structure, arising

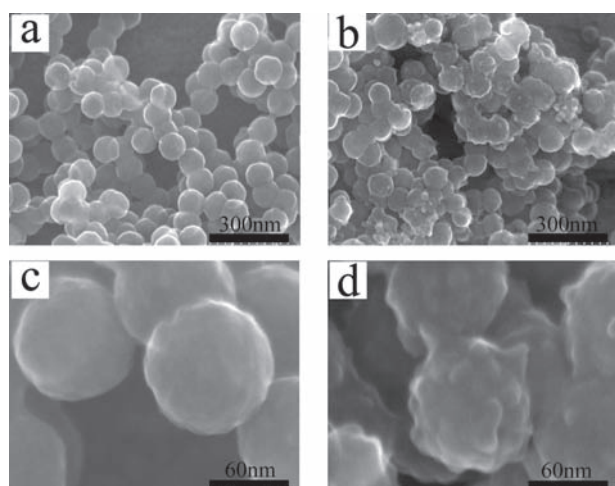


Fig. 2. Typical FE-SEM images of (a) HPAP nanospheres, and (b) HPAP-Fe₃O₄ composite nanospheres. (c) and (d) are high magnification FE-SEM images of HPAP nanospheres and HPAP-Fe₃O₄ composite nanospheres, respectively.

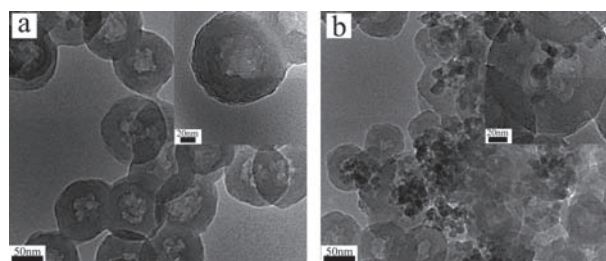


Fig. 3. Typical TEM images of (a) HPAP nanospheres, and (b) HPAP-Fe₃O₄ composite nanospheres. The insets show corresponding enlarged TEM images.

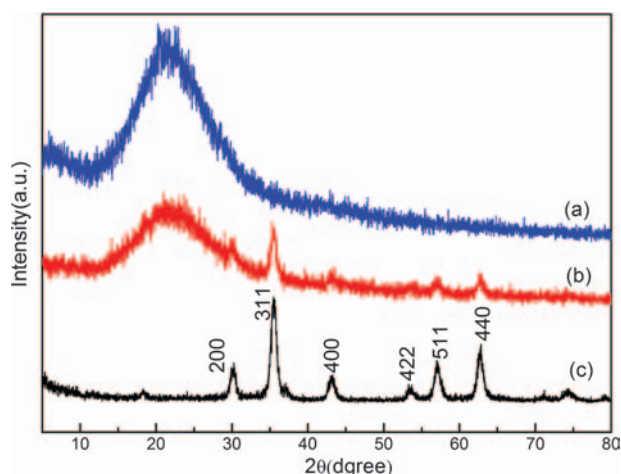


Fig. 4. XRD patterns of (a) HPAP nanospheres, (b) HPAP-Fe₃O₄ composite nanospheres, and (c) Fe₃O₄ nanoparticles.

from the interaction between the different components.^{5,20} The broad band centered at around 21° was also observed for HPAP-Fe₃O₄ nanospheres (Fig. 4(b)), together with diffraction peaks at $2\theta = 30.1, 35.5, 43.3, 53.6, 57.2$ and 62.7° that are in agreement with the XRD peaks of pure Fe₃O₄ nanoparticles (Fig. 4(c)). The peaks correspond to (220), (311), (400), (422), (511), and (440)

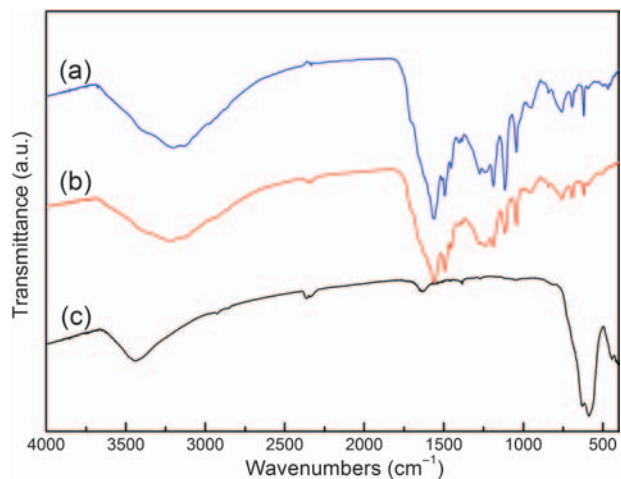


Fig. 5. FTIR spectra of (a) HPAP nanospheres, (b) HPAP-Fe₃O₄ composite nanospheres, and (c) Fe₃O₄ nanoparticles.

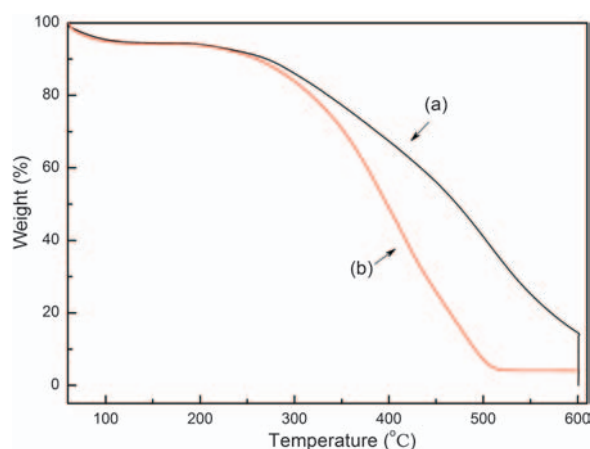


Fig. 6. TGA curves for (a) HPAP nanospheres, and (b) HPAP-Fe₃O₄ composite nanospheres.

Bragg reflections, respectively, of Fe₃O₄, confirming that the HPAP-Fe₃O₄ nanospheres contained Fe₃O₄ nanoparticles. The results also indicate that the Fe₃O₄ nanoparticles had cubic spinel structure identical to that of the reference material in the JCPDS file (PDF No. 65-3107).²¹⁻²³

4.3. FT-IR Spectral Analysis

The molecular structure of the products was determined by FT-IR spectroscopy: spectra are shown in Figure 5. Similar

absorption bands were observed for HPAP nanospheres (Fig. 5(a)) and HPAP-Fe₃O₄ nanospheres (Fig. 5(b)) at 1575, 1564, 1458, 1281, 1190 and 694 cm⁻¹. The bands at 1575 and 1564 cm⁻¹ correspond to the C-C stretch for the quinonoid phenyl rings of PANI and C=C stretching mode of PPY.^{5,24} The peak at 1458 cm⁻¹ is attributed to the benzenoid vibrations, and the bands at 1281 and 1190 cm⁻¹ are due to the presence of aromatic NH groups and the C-N stretching vibration.^{20,25} The band at 694 cm⁻¹ is attributed to C-H in-plane bending in the 1,3-substituted benzene ring, which may be induced by the attachment of pyrrole units at the *meta*-position of the benzene ring.¹³ Figure 5(c) shows the FT-IR spectrum of Fe₃O₄ nanoparticles, with characteristic absorption Fe₃O₄ at 586 cm⁻¹ that is assigned to the Fe-O bond. This band was not observed in the spectrum of HPAP-Fe₃O₄ nanospheres, indicating that the Fe₃O₄ nanoparticles were fully encapsulated in the nanospheres.

4.4. TGA Analysis

TGA curves of the HPAP nanospheres and HPAP-Fe₃O₄ composite nanospheres are presented in Figure 6. The HPAP nanospheres show three step weight loss behavior. The initial weight loss up to 100 °C is due to evaporation of water trapped in the sample. The gradual weight loss up to 280 °C is attributed to loss of low molecular weight

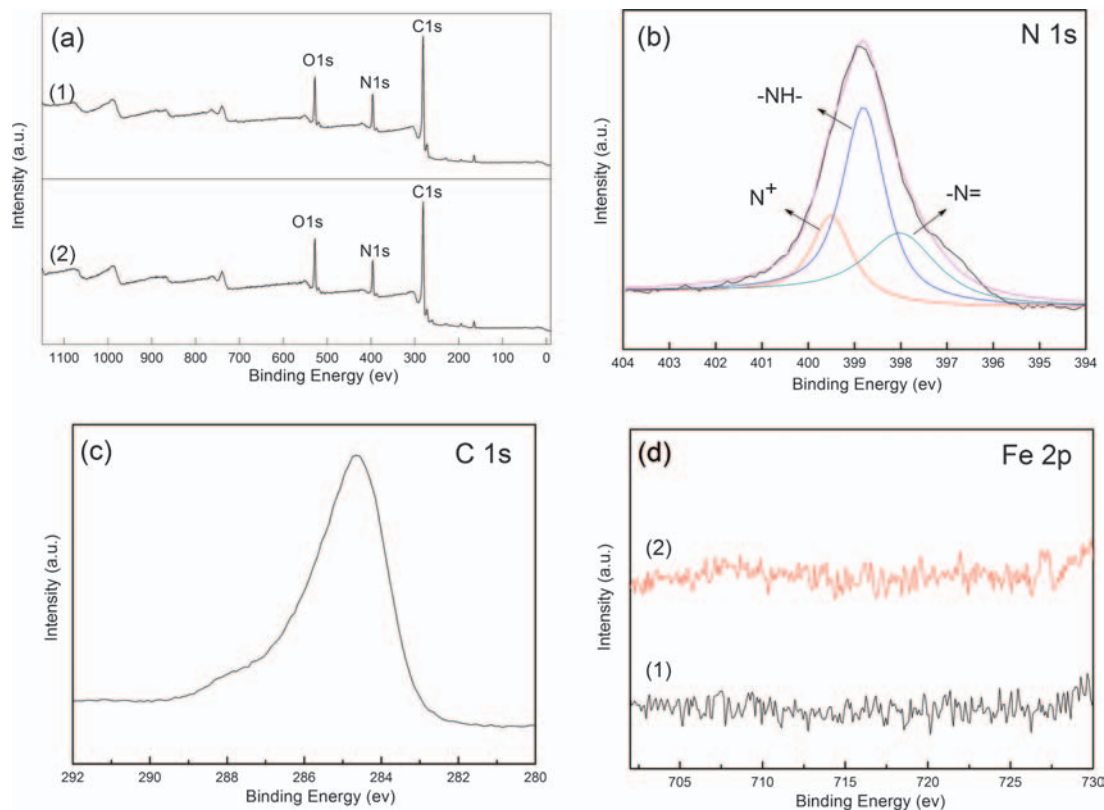


Fig. 7. XPS spectra of (a) HPAP nanospheres (1) and HPAP-Fe₃O₄ composite nanospheres (2); (b) N 1s and (c) C 1s core level spectra of HPAP-Fe₃O₄ composite nanospheres; (d) Fe 2p core level spectra of HPAP nanospheres (1) and HPAP-Fe₃O₄ composite nanospheres (2).

oligomer, and oxidative thermal degradation began above 300 °C. The HPAP-Fe₃O₄ nanospheres showed similar decomposition steps to those of HPAP nanospheres, but the decomposition processes of the two samples above 300 °C indicated that the HPAP-Fe₃O₄ nanospheres had lower thermal stability. The lower thermostability of HPAP-Fe₃O₄ nanospheres may be due to the synthesis by *situ* polymerization in Fe₃O₄ magnetic fluid, which led to the presence of polymer chain defects and broad molecular weight distribution. According to the TGA trace of HPAP-Fe₃O₄ nanospheres Figure 6(b), because of the presence of the Fe₃O₄ nanoparticles the residue from thermal degradation was 4.01% of the initial sample mass.

4.5. XPS Surface Analysis

XPS analysis gave some insight into the chemical composition of the composite nanospheres. Figure 7(a) shows that the composite nanospheres were composed mainly of C, N and O. The N 1s XPS core level spectrum of HPAP-Fe₃O₄ nanospheres is shown in Figure 7(b). The N 1s signal was fitted by three sub-bands, corresponding to quinonoid imine (=N-) at 398.0 eV, benzenoid amine (-NH-) at 398.9 eV, and positively charged nitrogen atoms with binding energy 399.6 eV. This result indicated coexistence of the pernigraniline and emeraldine states of the conducting polymer. However, the binding energies were shifted to lower energy and were slightly different from those reported previously.^{10,19} The energy level shifts can be accounted for by dehydrogenation of pyrrolylium nitrogen and rearrangement of the pyrrole bonds to satisfy the nitrogen valences, and interaction between N and Fe atoms to form a coordinate bond, which could reduce the energy level of the composite nanospheres.^{21,26} The C 1s spectrum of HPAP-Fe₃O₄ nanospheres displays a large peak centered at about 285 eV, as shown in Figure 7(c), which is attributed to aromatic carbons, quinonimine units and charged species. Figure 7(d) shows the XPS spectra in the Fe 2p region. Comparison of the spectrum of HPAP nanospheres with that of HPAP-Fe₃O₄ composite nanospheres shows that no elemental Fe was present, confirming that the Fe₃O₄ nanoparticles were well encapsulated in the nanospheres, in agreement with the FT-IR spectra and the morphology of the HPAP-Fe₃O₄ nanospheres.

5. CONCLUSION

HPAP-Fe₃O₄ composite nanospheres with electromagnetic properties were successfully fabricated by oxidative polymerization of a mixture of aniline and pyrrole in the presence of magnetic fluid, using a non-ionic surfactant as template. FE-SEM and TEM were used to characterize the surface morphology and hollow structure of the

nanospheres, and XRD, FT-IR and XPS provided sufficient data to characterize their chemical structure. The thermostability of the composite nanospheres was examined by TGA. The synthesis method could be extended to other magnetic composite hollow spheres with different compositions.

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