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ORIGINAL CONTRIBUTION

Study on Fe_3O_4/polyaniline electromagnetic composite hollow spheres prepared against sulfonated polystyrene colloid template

Huifang Xu · Haijiao Zhang · Tong Lv · Huawei Wei · Fei Song

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Abstract Fe_3O_4/polyaniline (PANI) composite hollow spheres were prepared by using sulfonated polystyrene (SPS) microspheres as templates. The sulfonic acid groups were applied to induce absorbing Fe_3O_4 nanoparticle, and subsequently, conductive PANI was grown. Finally, the polystyrene cores were selectively dissolved to yield composite hollow microspheres with electromagnetic properties. The analysis results indicated that the adsorption of Fe_3O_4 on template core by electrostatic interaction resulted in magnetic composite microspheres. The conductivity of composite hollow spheres was remarkably increased after polyvinylpyrrolidone modification which favored the growth of PANI on SPS/Fe_3O_4 and enhanced the integrity of hollow microspheres. The saturated magnetization of the composite hollow microspheres was tuned from 2.7 to 9.1 emu/g, and the conductivity was in the range from 10^{-2} to 10^{0} S/cm.

Keywords Hollow spheres · Template · Electromagnetic · Polyaniline · Fe_3O_4

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H. Xu (✉) · T. Lv · H. Wei · F. Song
School of Chemical Engineering and Technology, Harbin Institute of Technology, Harbin 150001, China
e-mail: xuhf@hit.edu.cn

H. Zhang (✉)
Modern Manufacture Engineering Center, Heilongjiang Institute of Science and Technology, Harbin 150027, China
e-mail: seaboyfang@163.com

Introduction

Hollow microspheres have attracted considerable academic and technological attention in chemistry and materials science because of their advantages of large specific area, low density, and high mechanical stability. The properties of hollow spheres depend on the integrated functionality of shell materials and the low effective density and high specific surface [1–5]. The shells can be made of polymeric, inorganic, or composite materials. Among the shell materials, the electromagnetic materials are proved to be an important class of functional materials for their superior performance as electromagnetic shielding and wave-absorbing materials [6–14]. Combining the electromagnetic properties with hollow geometry is an effective approach to promote their application in new fields [15]. For example, the electromagnetic hollow microspheres could be used as high-performance lightweight wave-absorbing materials [16].

Nowadays, several methods are employed to prepare hollow microspheres. Hollow spheres could be prepared by interfacial reaction [17], combination of sol–gel process with oil–water–oil microemulsion [18], self-assembly of block copolymers [19], aerosol pyrolysis [20], and Kirkendall diffusion [21]. Especially, template synthesis has been well-developed to prepare hollow spheres, in which solid or hollow colloids could be applied as cores [22–24]. The subsequent deposition of shell materials was usually assisted by a layer-by-layer process, and finally, the template cores were selectively removed to obtain the hollow microspheres [25]. Yang et al. proposed a new approach to generally prepare hollow microspheres, where the potential use of polymer colloid as general template was explored, addressing issues related to the derivation of functional groups on template, inducing adsorption of shell materials such as inorganic oxides, metal, and polymer, and the structure–properties relationship [26–30]. They pointed out that the derived functional groups by chemical transformation could induce a diversity of materials including inorganic, metals, and polymers to in situ growth on the template. Additionally, the cavity and shell sizes could be simultaneously tailored due to an inward growth of the shell materials.

The electromagnetic composite hollow microspheres were prepared by using such template [31, 32]. The sulfonated polystyrene (SPS) microspheres were used to adsorb aniline and as acid dopant, and then, the in situ polymerization led to a conductive layer of polyaniline (PANI). The magnetic oxides were deposited by coprecipitation of Fe^{2+} and Fe^{3+} on the conductive microspheres. To some extent, the conductive property was reduced due to de-doping during deposition of Fe_3O_4 by using alkali precipitant. On the other hand, the conductive network was interrupted by the exterior layer of Fe_3O_4.

In this paper, a favorable procedure is proposed to use Fe_3O_4 as interior and conductive PANI as exterior for preparing the electromagnetic composite microspheres against SPS colloid as template. The as-prepared Fe_3O_4 particles were firstly coated on the template via electrostatic adsorption to form SPS/Fe_3O_4, and subsequently, PANI was polymerized as exterior layer. After removing the template, the hollow structure could be achieved. The influences of sulfonation of the template and surface modification on the structure and properties of the electromagnetic hollow microspheres were investigated. The results showed that the magnetization of the electromagnetic hollow microspheres increased by increasing the sulfonation degree of PS. The conductivity was significantly enhanced after SPS/Fe_3O_4 was modified by polyvinylpyrrolidone (PVP) and then PANI was deposited because PVP favored the growth of PANI and formation of contiguous conductive network.

Experimental section

Synthesis

Raw materials

Aniline monomers were distilled under reduced pressure. Styrene (St) was washed with 10 % NaOH and then distilled water to remove the inhibitor. 2,2′-Azobis(2-methylpropionitrile) (AIBN) was recrystallized in absolute ethanol and dried. All other chemical reagents were used as received: PVP, concentrated sulfuric acid, ferrous chloride tetrahydrate ($FeCl_2 \cdot 4H_2O$), ferric chloride hexahydrate ($FeCl_3 \cdot 6H_2O$), sodium hydroxide (NaOH), hydrochloric acid (HCl), ammonium peroxydisulfate (APS), absolute ethanol, and distilled water.

Preparation of polystyrene microspheres

Polystyrene (PS) colloids were prepared by suspension polymerization. Certain amounts of AIBN and PVP were dissolved in ethanol and water under stirring for 30 min, and then, 20 g St was dropped into the mixture. The reaction system was mechanically stirred with 100 rpm and heated at 75 °C for 12 h with N_2 protection. The product was centrifuged, washed with distilled water, and freeze-dried.

Sulfonation of PS microspheres

Sulfonation reaction was according to a typical procedure [27]: 2 g PS was dispersed in 40 ml concentrated sulfuric acid under stirring with 100 rpm. The reaction was conducted at 40 °C for 1, 2, and 4 h to obtain the SPS colloids denoted as SPS1h, SPS2h, and SPS4h, respectively. The SPS was centrifuged and washed with distilled water until the pH value of filtrate was near to 7.

Preparation of Fe_3O_4 nanoparticles

Fe_3O_4 nanoparticles were prepared by a modified coprecipitate method according to the literature [33]. The as-prepared Fe_3O_4 nanoparticles were dispersed in distilled water and filled with nitrogen to form the magnetic suspension.

Preparation of SPS/Fe_3O_4 composite microspheres

A typical procedure was to mix 1.2 g SPS with 0.22 g Fe_3O_4, and 65 ml HCl aqueous solution with pH in the range of 3–5 was added into the mixture. The suspension was stirred for 30 min and then allowed to separate into layers. The underlayer was isolated and then dried at 50 °C.

Preparation of Fe_3O_4/PANI composite hollow microspheres

SPS/Fe_3O_4 (0.5 g) and PVP (2.5 g) were added in 100 ml absolute ethanol at 30 °C and stirred for 5 h. The PVP-modified SPS/Fe_3O_4 was washed with absolute ethanol and then dried at 40 °C. The 0.5 g SPS/Fe_3O_4/PVP was dispersed in 22 ml acidic mixture containing 0.4 ml aniline monomer under constant mechanical stirring at 5 °C for 30 min. Then, 22 ml acidic solution including 0.98 g APS was dropped into the former mixture and the reaction was processed at 5 °C for 12 h. The pH value of the reaction system was 1.5. After reaction, the precipitates were collected and washed with absolute ethanol, distilled water, and then HCl aqueous solution until filtrate was transparent. Finally, the products were freeze-dried. For comparison, the aniline polymerization on SPS/Fe_3O_4 without PVP modification was conducted under the same reaction parameters. Fe_3O_4/PANI hollow spheres were obtained after dissolution

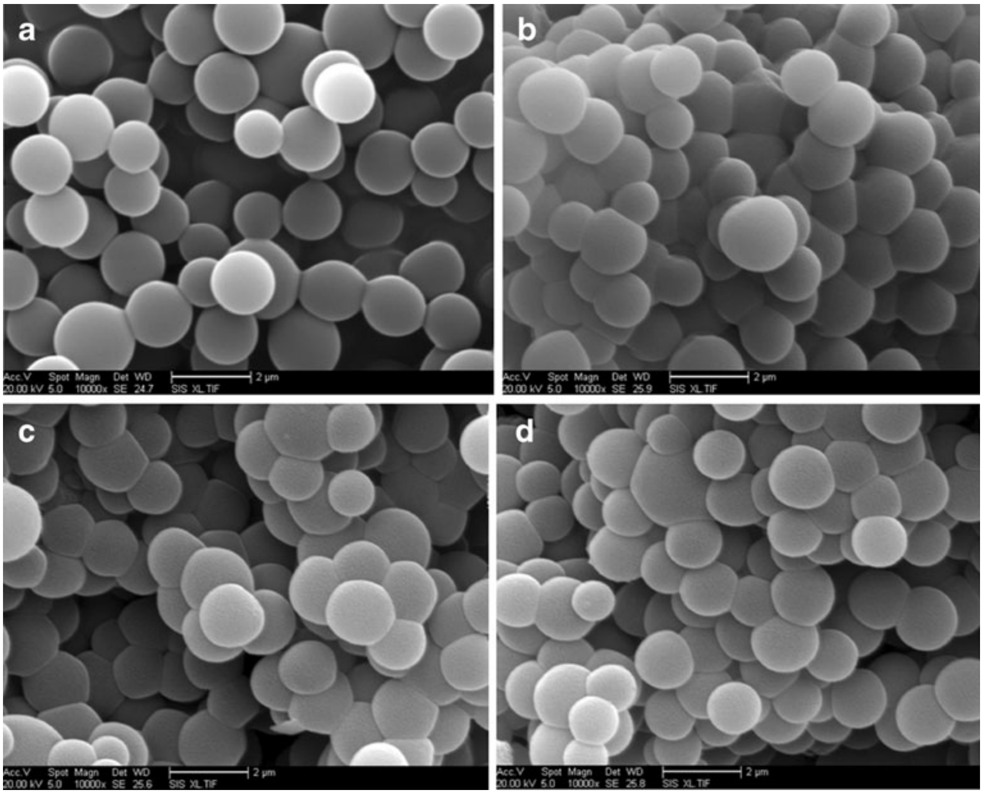

Fig. 1 SEM images of PS and SPS with different sulfonation time. **a** PS; **b** SPS1h; **c** SPS2h; **d** SPS4h

of PS cores with *N*,*N*-dimethylformamide. The Fe_3O_4/PANI hollow spheres were designated as series of H-SPS/Fe_3O_4/PANI or H-SPS/Fe_3O_4/PVP/PANI.

Characterization

Scanning electron microscopy (SEM) measurement was performed with a SIRION200 instrument operated at an accelerating voltage of 20 kV. Particle size analysis was recorded by ZetaPALS of Brookhaven. Fourier transform infrared spectroscopy (FTIR) spectra were recorded on a Thermo Nicolet Nexus 670 spectrometer with samples pressed into KBr pellets. Wide-angle X-ray powder diffraction (D/Max-rB) was used to characterize the crystalline phase of these materials. Conductivity measurement was characterized by the four-point probes method (RTS-8). Vibrating-sample magnetometry (Lake Shore 7410 VSM) was used to characterize the magnetic property of the magnetic spheres. Conductivity measurement was characterized by the four-point probes method (KDY-1).

Results and discussion

The approach to prepare the electromagnetic hollow spheres was based on a template process. PS colloids were used as template to prepare the functional hollow microspheres. The sulfonation process produced the reactive sites for inducing adsorption of shell materials. Adsorption was formed by electrostatic interaction between positively charged Fe_3O_4 nanoparticles and negatively charged SPS. The subsequent growth of PANI on PVP-modified SPS/Fe_3O_4 was conducted, and finally, the template cores were dissolved to form the hollow spheres.

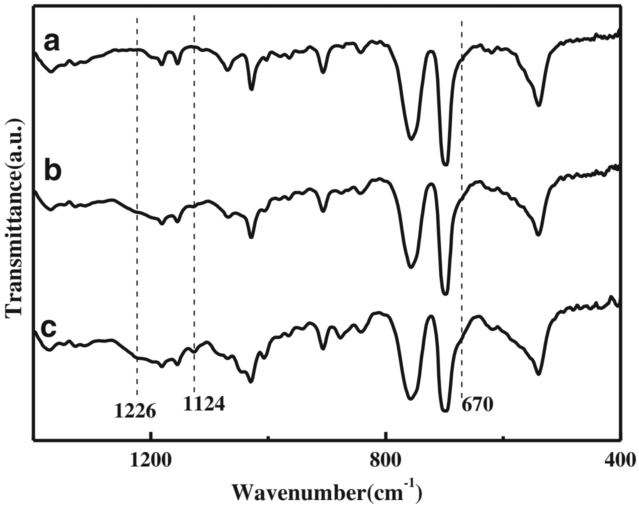

Fig. 2 FTIR spectra. *a* PS; *b* SPS1h; *c* SPS4h

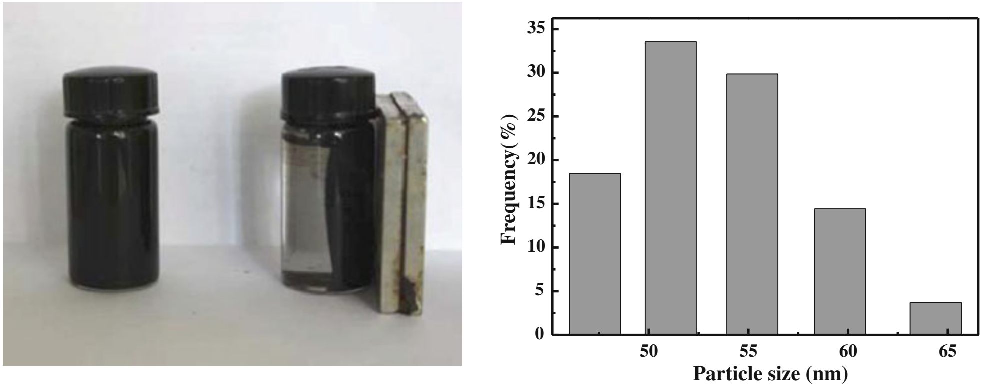

Fig. 3 **a** Photograph of Fe_3O_4 nanoparticles dispersed in water (*left*) and attracted by external magnetic field (*right*); **b** the size distribution of Fe_3O_4 nanoparticles by DLS

The synthesized PS template is shown in Fig. 1. The spherical structure with size concentrated in the range 1.3–1.6 μm was obtained. After sulfonation, the SPS adhered together due to the formation of the gel layer. The average particle size tended to increase with prolonging sulfonation time. FTIR results in Fig. 2 showed that the characteristic bands at 1,226 and 670 cm^{-1} was attributed to the derived sulfonic acid group ($–SO_3H$) and the band at 1,124 cm^{-1} was due to the sulfone group $–SO_2–$. The peak intensities of the functional groups were increased with prolonging sulfonation time, indicating that the contents of the sulfonic acid groups were correspondingly increased.

To obtain the composite hollow spheres with electromagnetic properties, Fe_3O_4 nanoparticles and PANI were applied as the functional shell materials. For ensuring the continuous conductive layer of PANI, the core–shell structure was designed with Fe_3O_4 as inner layer and conductive PANI as the outer layer. The adsorption of Fe_3O_4 particles instead of ferric ions was conducted by sulfonic acid groups via electrostatic interaction as driving force in order to maintain the properties of primitive Fe_3O_4 nanoparticles. Figure 3 exhibited that the synthesized Fe_3O_4 particles could be well-dispersed in water and quickly responded to the external magnetic field. The particle size distribution investigated by dynamic light scattering (DLS) was in the range from 40 to 65 nm.

The adsorption of Fe_3O_4 particles in the sulfonated gel layer could be carried out by electrostatic interaction between sulfonic acid groups and reaction precursor. In this article, the electrostatic adsorption of SPS with Fe_3O_4 was carried out according to the colloid adsorption theory. The pH value was controlled in the range of 3–5 so that sulfonic acid groups were deprotonated to form negatively charged surface, and at the same time, the Fe_3O_4 nanoparticles were positively charged since they have the isoelectric point (pI) of 6.6 [34]. The binding was carried out by the electrostatic interactions between negatively charged SPS spheres and positively charged Fe_3O_4. Therefore, sulfonic acid groups were dissociated to form negatively charged templates when pH values of the system were higher than pK_a of the sulfonic acid groups. Fe_3O_4 nanoparticle will be positively charged when pH values were lower than its pI. The driving force for electrostatic interaction between SPS and Fe_3O_4 was constructed when pH values in the range between pK_a of sulfonic acid groups and pI of Fe_3O_4. After the coating procedure, the SPS/Fe_3O_4 core–shell composites were

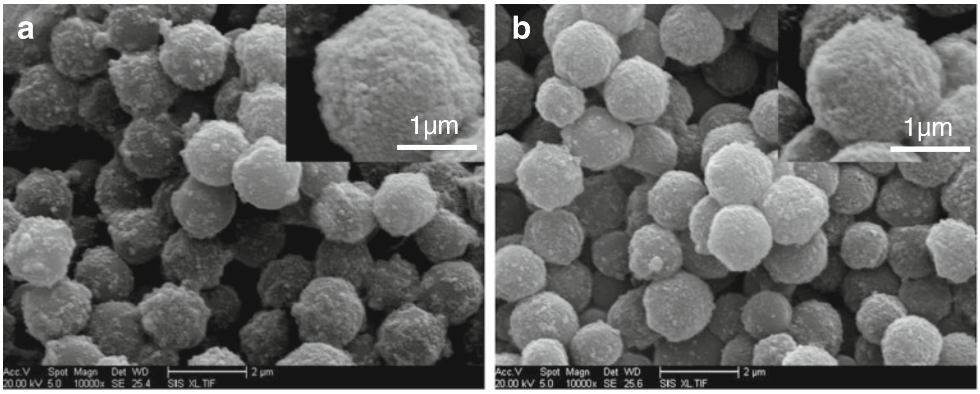

Fig. 4 SEM images of SPS/Fe_3O_4 core–shell composites with different sulfonation degree SPS. **a** SPS1h/Fe_3O_4; **b** SPS4h/Fe_3O_4 (*insets* are the enlarged SEM images)

obtained. Figure 4 showed the SEM images of SPS/Fe_3O_4 composite microspheres with different sulfonation degrees. Compared with SEM images of the corresponding SPS in Fig. 1, it was found that, after coating Fe_3O_4, the composites had coarse surface morphology and the particle size tended to increase. The enlarged SEM in the inset of Fig. 4a, b indicated that SPS were covered by nanoparticles which distributed throughout the whole shell. No free Fe_3O_4 particles were observed in the dispersion medium. FTIR spectra of SPS/Fe_3O_4 in Fig. S1 exhibited that the peak around 539 cm^{-1} of the template weakened and broadened due to the introduction of Fe_3O_4, which had a characteristic adsorption around 560 cm^{-1}.

The in situ growth of PANI on SPS/Fe_3O_4 was conducted to introduce the conductive properties. From Fig. 5, it could be observed that SPS/Fe_3O_4/PANI had different surface structure from SPS/Fe_3O_4. The inset enlarged the SEM images exhibiting that the Fe_3O_4 nanoparticles were covered with polymer layer. After removing the PS cores, the corresponding Fe_3O_4/PANI hollow spheres hardly preserved the spherical morphology, although the integrity could be improved with prolonging sulfonation time. For low sulfonation degree, composite hollow spheres were bowl-shaped hemispheres. The perforation and rupture on the shell resulted from the osmotic pressure during dissolving of the cores. The polymerization of aniline was reacted in HCl aqueous solution, but the

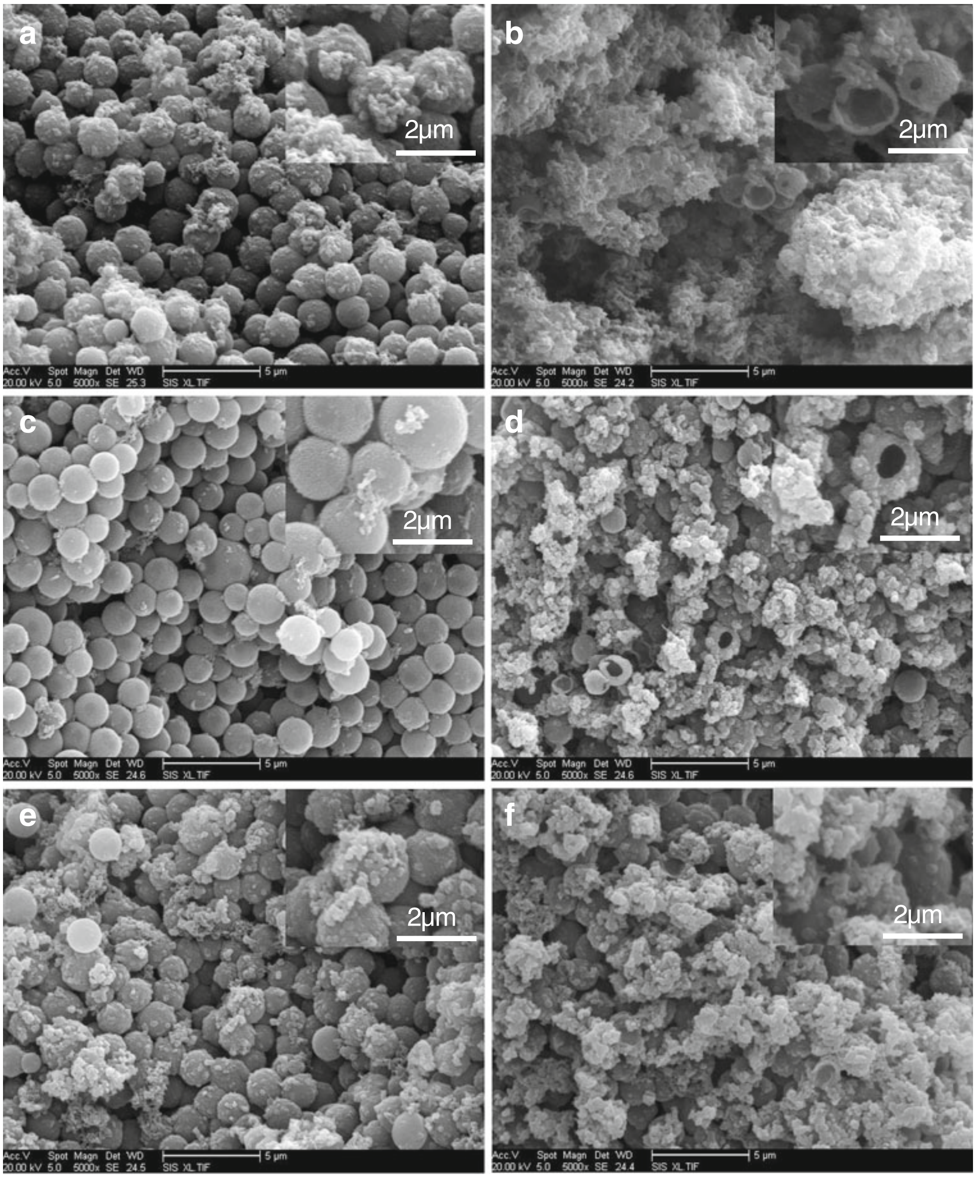

Fig. 5 SPS/Fe_3O_4/PANI before and after removing PS cores (*hollow spheres*). **a** SPS1h/Fe_3O_4/PANI and **b** the corresponding hollow spheres (H-SPS1h/Fe_3O_4/PANI); **c** SPS2h/Fe_3O_4/PANI and **d** the corresponding hollow spheres (H-SPS2h/Fe_3O_4/PANI); **e** SPS4h/Fe_3O_4/PANI and **f** the corresponding hollow spheres (H-SPS4h/Fe_3O_4/PANI) (*insets* are the enlarged SEM images)

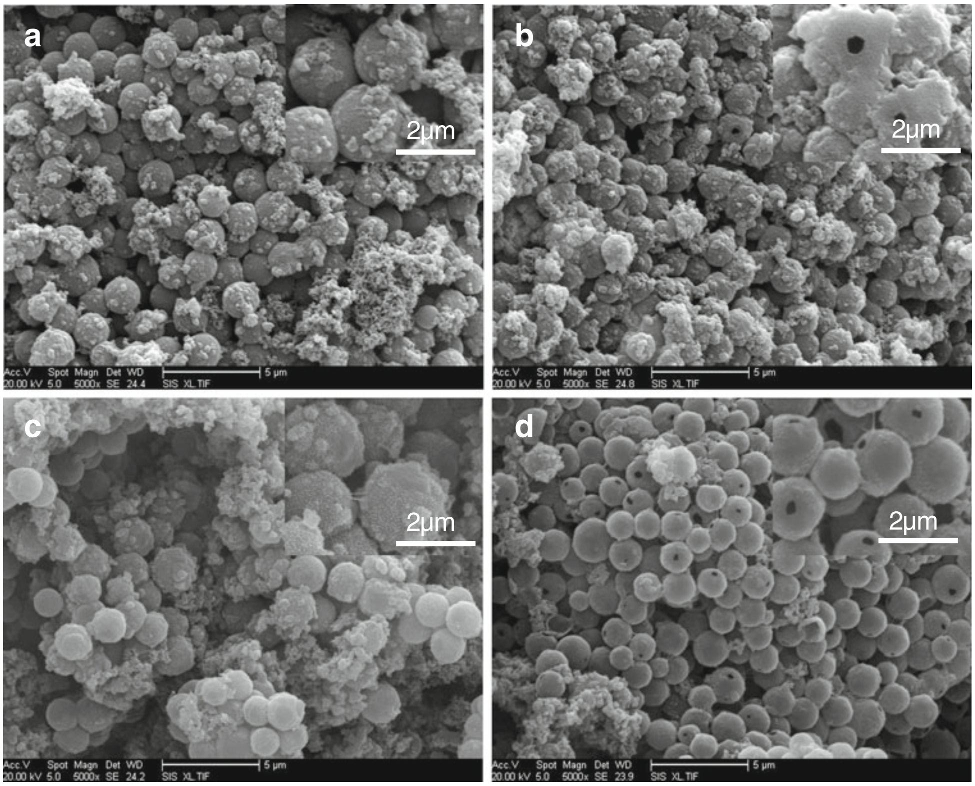

Fig. 6 SEM images of SPS/Fe_3O_4/PVP/PANI before and after removing PS cores. **a** SPS2h/Fe_3O_4/PVP/PANI and **b** the corresponding hollow spheres (H-SPS2h/Fe_3O_4/PVP/PANI); **c** SPS4h/Fe_3O_4/PVP/PANI and **d** the corresponding hollow spheres (H-SPS4h/Fe_3O_4/PVP/PANI) (*insets* are the enlarged SEM images)

aniline monomer was slightly soluble in water, which led to the uneven adsorption on SPS/Fe_3O_4. For promoting the adsorption of aniline and polymerization on SPS/Fe_3O_4, PVP was used to modify SPS/Fe_3O_4 firstly. Aniline polymerization on PVP-modified SPS/Fe_3O_4 composites was carried out under the same condition. After removing the PS cores, the composite hollow spheres with well-defined shell structure were achieved (shown in Fig. 6), indicating the high coverage of PANI because PVP acted both as a site for adsorption of oligoaniline initiation centers and as steric stabilizer of the formed PANI particles [35].

FTIR spectra in Fig. S2 of PANI showed the characteristic adsorption bands at 1,558 and 1,471 cm^{-1} which were due to the C=C stretching vibration of quinoid ring and benzenoid ring of PANI, respectively. The peak at 1,294 cm^{-1} was attributed to the C–N stretching modes of the benzenoid unit. The broad band at 1,114 cm^{-1} was ascribed to the C–H structure of the aromatic ring. These results were in good agreement with previous reports [9]. For SPS4h/Fe_3O_4/PVP/PANI, almost same spectra with PANI were observed.

The crystalline structures of Fe_3O_4, SPS/Fe_3O_4, and Fe_3O_4/PANI hollow spheres were analyzed by X-ray diffraction (XRD) in Fig. 7. From pattern a, it was found that the synthesized Fe_3O_4 could be well-indexed as JCPDS-19-0629. The diffraction peaks at 2θ of 30.1°, 35.4°, 43.0°, 53.4°, 57.0°, 62.5°, and 74.0° were attributed to crystalline planes of (2,2,0), (3,1,1), (4,0,0), (4,2,2), (5,1,1), (4,4,0), and (5,3,3), respectively. The broad diffraction peaks revealed that the nanosized

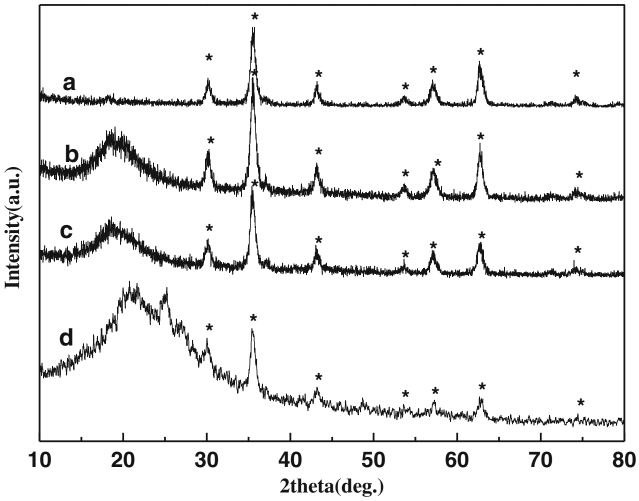

Fig. 7 XRD patterns. *a* Fe_3O_4; *b* SPS1h/Fe_3O_4; *c* SPS4h/Fe_3O_4; *d* typical Fe_3O_4/PANI hollow spheres. *Asterisks* denote the Fe_3O_4 diffraction peaks

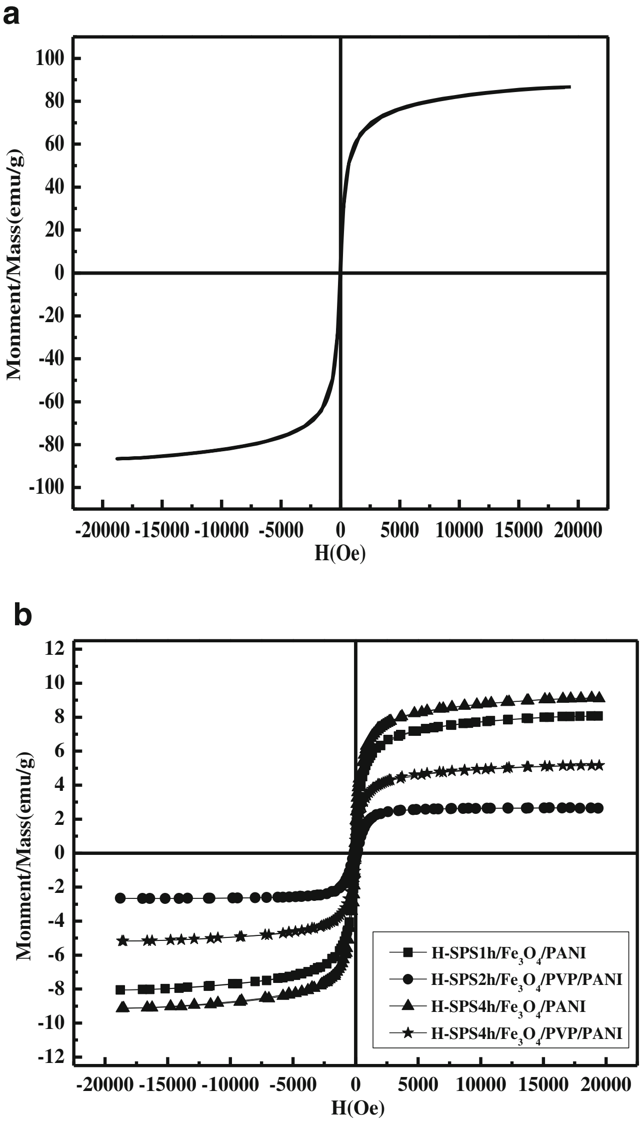

Fig. 8 Hysteresis loops of **a** Fe_3O_4 and **b** electromagnetic composite hollow spheres prepared under different conditions

Fe_3O_4 crystals were obtained. It was observed from patterns b and c that the core–shell SPS/Fe_3O_4 with different sulfonation degrees both included the characteristic diffraction peaks of Fe_3O_4 which were not changed after coating on SPS, indicating that the method to directly absorb Fe_3O_4 could well reserve the structure of Fe_3O_4. A broad peak around 20° in curves b and c was attributed to SPS. The XRD pattern of the typical Fe_3O_4/PANI hollow spheres was shown in curve d. Apart from Fe_3O_4 diffraction peaks, the broad diffraction peaks at $2\theta=20.8°$ and 25.2° were ascribed to the periodicity parallel and perpendicular to the PANI chains, respectively [36].

The electromagnetic properties of hollow microspheres prepared under different parameters were studied by VSM and conductivity. Figure 8 displays the magnetic hysteresis curves of Fe_3O_4 and the hollow spheres by VSM at room temperature. The prepared Fe_3O_4 nanoparticles indicated a superparamagnetic behavior because the remnant magnetization was zero. The saturated magnetization was 86.8 emu/g. The hysteresis curves of hollow spheres also showed that the remnant magnetization was zero, indicating that the superparamagnetic behavior remained after forming magnetic composite hollow spheres. The saturation magnetizations of the hollow spheres were less than that of Fe_3O_4 since it depended on the content of Fe_3O_4 in the composites. By comparing the magnetizations, it was shown that the saturated magnetizations increased with increasing sulfonation degree of the PS templates. The highest value of about 9.1 emu/g was obtained for H-SPS4h/Fe_3O_4/PANI, revealing the highest content of Fe_3O_4 in H-SPS4h/Fe_3O_4/PANI. The two samples of SPS2h/Fe_3O_4/PVP/PANI and SPS4h/Fe_3O_4/PVP/PANI also indicated the same principle, but they had decreased magnetization compared with the sample without PVP modification. The decreased magnetization of the samples modified by PVP resulted from the increased content of PANI because the only difference in the two series was PVP modification. Further supporting the analyses, the conductivities of the hollow spheres were listed in Table 1. The values showed that PVP modification favored the enhancement of conductivity. The increase in conductivity should be attributed to the increase of the loading amount of PANI and the integrity of the conductivity layer, which was consistent with the result of SEM.

Conclusions

In this work, the composite hollow spheres with electromagnetic properties were prepared by applying SPS microspheres as template and Fe_3O_4 and PANI as functional shell. The procedures were conducted to ensure the hollow structure and good properties. The results indicated that the integrity of the hollow spheres was increased by increasing sulfonation degree. The adsorption of Fe_3O_4 nanoparticles on the template instead of their salt reactants ensured better preservation of magnetic properties. PVP modification favored forming continuous layer of conductive PANI and finally increased the conductivity of the sample. The magnetization was tuned by changing the sulfonation degree, and the highest value was 9.1 emu/g and the highest conductivity was 1.27 emu/g.

Table 1 Conductivity of typical samples

Sample	Conductivity (S/cm)
H-SPS1h/Fe_3O_4/PANI	0.169
H-SPS2h/Fe_3O_4/PANI	0.201
H-SPS4h/Fe_3O_4/PANI	0.062
H-SPS4h/Fe_3O_4/PVP/PANI	1.27

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