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Lightweight glass/Fe_3O_4-polyaniline composite hollow spheres with conductive and magnetic properties

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Abstract Lightweight composite hollow spheres with conductive and magnetic properties were prepared by using Hollow Glass Spheres (HGS) as substrate. The morphology, composition, conductive, and magnetic properties of the resultant products were characterized by SEM, EDX, XRD, FTIR spectra, conductivity measurement, and vibrating-sample magnetometry. Polyaniline (PANI) were in situ polymerized on HGS with increasing ratios of PANI to HGS, resulting in the enhanced conductivity of HGS/PANI composites from 1.3×10^{-2} S/cm to 4.4×10^{-2} S/cm. Lightweight glass/Fe_3O_4-PANI composite hollow spheres (HGS/Fe_3O_4-PANI) with conductivity of 5.4×10^{-3} S/cm and magnetization of 9.25 emu/g were prepared by deposition of Fe_3O_4 nanoparticles onto HGS via electrostatic adsorption first, and then polymerization of aniline onto HGS/Fe_3O_4. The glass/PANI-Fe_3O_4 composite hollow spheres (HGS/PANI-Fe_3O_4) composed of Fe_3O_4 as the outmost layer and PANI as the inner layer were prepared for comparison. The conductivity and magnetization of HGS/PANI-Fe_3O_4 were 1.1×10^{-4} S/cm and 2.61 emu/g, respectively.

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Introduction

Inorganic nanoparticles/conducting polymer composites have attracted considerable academic and technological attention because of their unique physical properties and potential applications in drug delivery, microwave absorption, sensors, and memory devices, etc. [1–4]. Among those composites, materials with hollow structure are of particular interest to researchers because of the lightweight and enhanced physicochemical properties when compared with their bulk counterparts [5–7].

Polyanilines (PANI) have been studied extensively among conducting polymers because of their unique doping mechanics, controllable conductivity, and environmental stability [8, 9]. Magnetic nanoparticles, particularly, Fe_3O_4 nanoparticles possess promising applications in magnetic separation, orientation control, and biological applications, etc. [10–13]. Substantial amounts of research have been conducted on preparation of PANI and Fe_3O_4 composites for being used as microwave absorbents, and electrical magnetic shielding materials [14, 15]. In the case of PANI-Fe_3O_4 composite hollow spheres, the core–shell composites were conventionally prepared by using hard cores, such as silica or polymer, e.g., polystyrene spheres as templates [16–19]. The PANI-Fe_3O_4 composite hollow spheres were achieved by using a solvent to remove the templates. In the process of removing core templates, the solvent should have access to the core and the shell is penetrable finally.

Hollow Glass Spheres (HGS) are usually used as fillers in composites due to their lightweight and high mechanical properties [20–22]. The metal, polymer, and inorganic oxides have been deposited onto HGS via various methods [7, 23]. While to the best of the knowledge, little effort has been done to deposit both PANI and Fe_3O_4 on HGS for preparing lightweight composite hollow spheres with conductive and magnetic properties.

Herein, the authors report a facile way to prepare lightweight glass/Fe_3O_4-PANI composite hollow spheres with conductive and magnetic properties by using HGS as a substrate. The study indicates that increase in the PANI loading amount on HGS will cause a rise in electrical conductivity. Addition of Fe_3O_4 nanoparticles leads to formation of lightweight composite spheres with both conductive and magnetic properties. Since the cores of the composites are closed and impenetrable, they show potential to be used as lightweight multifunctional fillers in many materials.

Experimental section

Synthesis

Raw materials

Aniline monomers were distilled under reduced pressure before use; commercially available Hollow Glass Spheres (HGS, silicate glass) were purchased from Shanghai and washed with distilled water and absolute ethanol, respectively for several times. Then, HGS were treated by 0.5 M NaOH aqueous solution for 30 min and were washed to be neutral before use. All the other chemical reagents were used as received: ferrous chloride tetrahydrate ($FeCl_2 \cdot 4H_2O$), ferric chloride hexahydrate ($FeCl_3 \cdot 6H_2O$), ammonium hydroxide ($NH_3 \cdot H_2O$), hydrochloric (HCl), ammonium peroxydisulfate (APS), absolute ethanol, sodium hydrate (NaOH), sodium chloride (NaCl), sodium dodecyl benzene sulfonate (SDBS), poly (sodium 4-styrenesulfonate) (PSS), poly (diallyldimethylammonium chloride) (PDDA), and distilled water.

Preparation of Fe_3O_4 nanoparticles

Fe_3O_4 nanoparticles were prepared by a modified co-precipitate procedure according to literature [24]. 100 mL distilled water was heated up to 80 °C and deaerated by bubbling Nitrogen for 10 min. Then 5.17 g $FeCl_3 \cdot 6H_2O$ and 2.45 g $FeCl_2 \cdot 4H_2O$ were added under mechanical stirring to prepare the aqueous mixture of ferric and ferrous salts. 45 mL NaOH solution (2 M) was added to adjust the system pH to 11, and quickly followed by addition of 0.0252 g SDBS as stabilizer. The reaction was allowed to proceed for 1 h at 80 °C. The precipitate was then isolated from the solution by a magnet and washed by distilled water several times until the filtrate was neutral. The products were re-dispersed in distilled water to prepare the magnetic suspension.

Preparation of HGS/PANI composite spheres

A typical polymerization procedure of Sample 4 was as follows: 1.2 g HGS were dispersed in the 65 mL mixture of 1.2 mL aniline monomer and 2 M HCl aqueous solution (pH = 1.5) under constant mechanical stirring at 5 °C [16]. The reactants were stirred at least 30 min for aniline monomer adsorbed on surface of HGS. Then, 2.94 g APS was dissolved in 65 mL HCl aqueous solution (pH = 1.5). The APS solution was added in the previous mixture slowly, and the reaction was processed at 5 °C for 8 h [16]. After reaction, the precipitates were collected and washed with absolute ethanol and then washed with distilled water until filtrate was transparent. Finally, the products were freeze-dried. Other HGS/PANI (Sample 2 and 3) were fabricated by varying initial HGS/PANI (g/mL) ratio as 1.2/0.4 and 1.2/0.8 while the pH value, ANI and APS concentrations were fixed. Pure PANI (Sample 1) was synthesized under the same reaction condition except for the addition of HGS. The synthesis parameters were specified in Table 1.

Preparation of HGS/Fe_3O_4-PANI and HGS/PANI-Fe_3O_4 composite spheres

The preparation process was described by a schematic drawing (Fig. 1). As shown in Fig. 1a, 1.5 g HGS were dispersed in 100 mL PDDA aqueous solution (0.1 wt% PDDA and 1 M NaCl) under constant stirring for 30 min. PDDA modified HGS were then collected and washed with distilled water for three times, and re-dispersed in NaOH aqueous solution (pH = 9) with constant mechanical stirring. 5 mL magnetic suspension with 0.044 g/mL Fe_3O_4 was mixed with PDDA modified HGS. SDBS modified Fe_3O_4 nanoparticles were, thus, adsorbed on the surface of PDDA modified HGS. PDDA and PSS (0.1 wt% PSS, 1 M NaCl) were deposited on surface of above product in turn, and then the resultant products of HGS/Fe_3O_4 were vacuum-dried at 80 °C for 4 h. The in situ polymerization of 0.5 mL aniline on HGS/Fe_3O_4 was conducted as procedures described in the "Preparation of HGS/PANI

Table 1 Synthesis parameters

Sample	HGS (g)	Aniline (mL)	APS (g)	V_{total} (mL)	Magnetic suspension (mL)
1	–	1.2	2.94	130	–
2	1.2	0.4	0.98	44	–
3	1.2	0.8	1.96	87	–
4	1.2	1.2	2.94	130	–
5	1.5	0.5	1.23	54	5
6	1.5	0.5	1.23	54	5

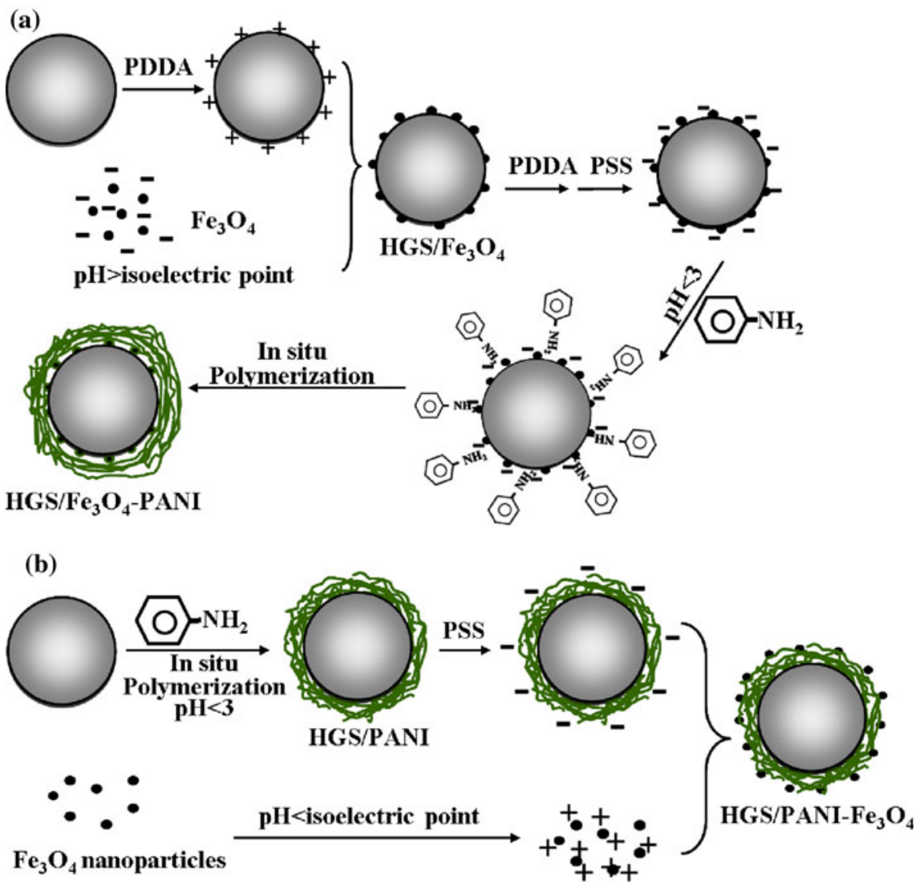

Fig. 1 A schematic drawing illustrated the formation process of lightweight composite hollow spheres with conductive and magnetic properties. **a** the route to prepare Sample 5(HGS/Fe_3O_4-PANI). **b** the route to prepare Sample 6(HGS/PANI-Fe_3O_4)

composite spheres." The products, HGS/Fe_3O_4-PANI (sample 5), were isolated and washed with absolute ethanol and distilled water until the washed liquid was transparent. In comparison, as shown in Fig. 1b, HGS/PANI-Fe_3O_4 (sample 6), were synthesized by depositing Fe_3O_4 nanoparticles on HGS/PANI via electrostatic adsorption.

Characterization

Scanning electron microscopy (SEM) measurement and energy-dispersive X-ray (EDX) analysis were performed with a Jcxa-733 instrument operated at an accelerating voltage of 20 kV and a FEI Quanta 200F instrument. PANI contents of the composites were determined by thermogravimetric analysis (TGA and DTA: Netzsch STA 449 C) in the temperature range of 30–800 °C in flowing air at a heating rate 10 °C/min. FTIR spectra were recorded on a Thermo Nicolet Nexus 670 spectrometer with samples pressed into KBr pellets. Wide-angle X-ray powder scattering (D/max-rB) was used to characterize the crystalline phase of these materials. Conductivity measurement was characterized by four point probes method (RTS-8). A Vibrating-sample magnetometry (Lake Shore 7410 VSM) was used to characterize the magnetic property of the magnetic spheres.

Results and discussion

The microstructure of the synthesized composites

In order to remove the impurity, HGS were treated with 0.5 M NaOH aqueous solutions and washed by ethanol and distilled water before use. The morphologies of HGS were investigated by SEM. As shown in Fig. 2a, the HGS possessed smooth surfaces and a diameter of 10–100 µm. The composition of HGS was examined by EDX spectrum (inset of Fig. 2a). The EDX spectrum revealed that the HGS were mainly composed of O, Si, Na, and Ca, which was consistent with reference [7]. Appearance of Pt element was due to the materials sprayer by a layer of Pt for EDX and SEM characterizations.

The in situ polymerization of aniline on HGS was conducted according to the "Experimental section." Figure 2b–d (Sample 2–Sample 4) showed the typical SEM images of HGS/PANI composites, which were synthesized under the same condition except for the initial ratio of HGS to aniline monomer for exploring its relationship with electrical conductivity. Compared with the original HGS, the surfaces of those composite hollow spheres were rough, indicating that PANI had been deposited on the surfaces of HGS successfully. It was shown from the cross-sectional

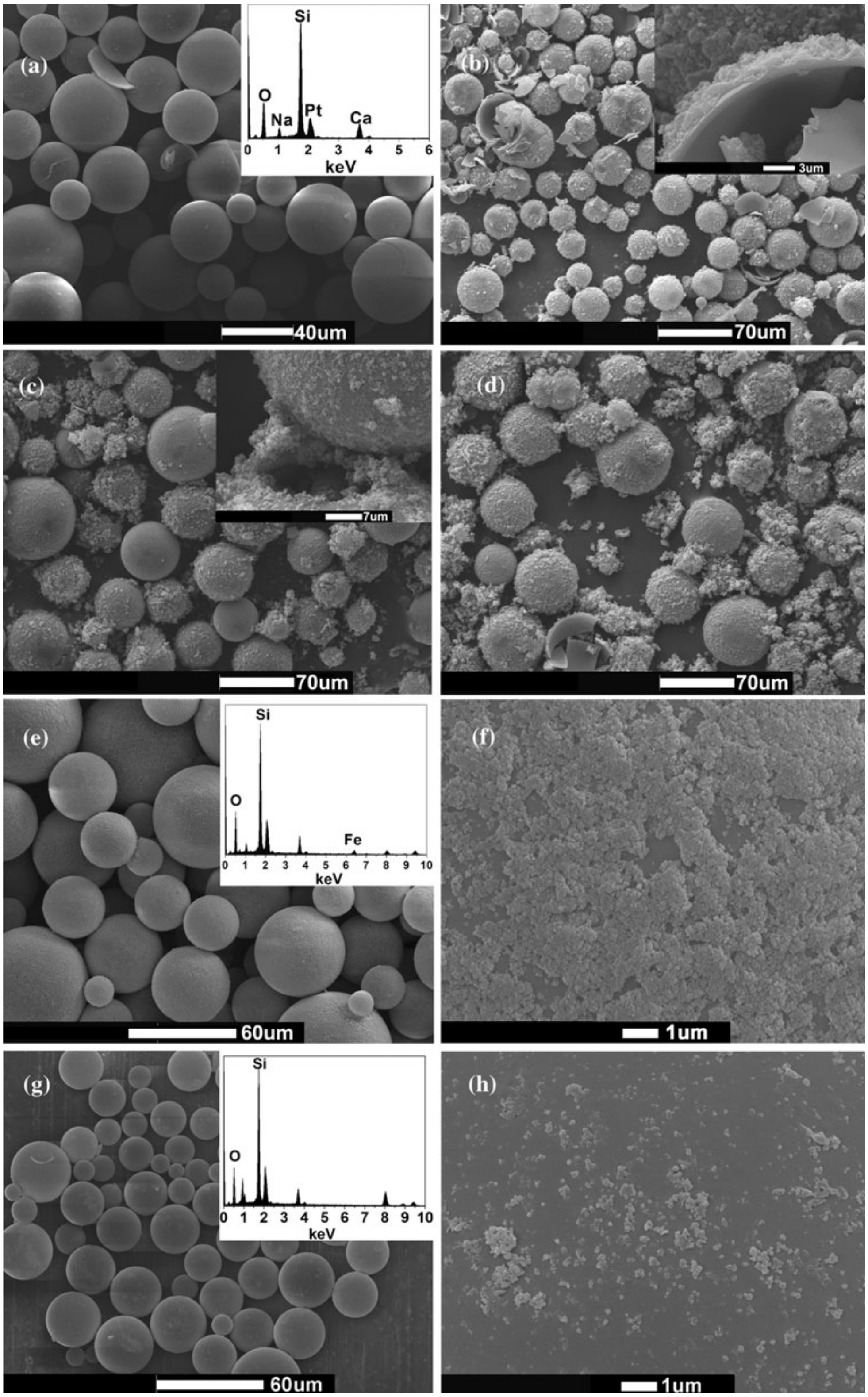

Fig. 2 SEM images. **a** Hollow Glass Spheres and *inset* EDX analysis. **b** Sample 2 and *inset* cross-section of PANI-layer and HGS core of composite spheres. **c** Sample 3 and *inset* the surface morphology of composite spheres. **d** Sample 4. **e** SEM image and EDX result (*inset*) of PDDA modified HGS/Fe_3O_4. **f** a magnified SEM image. **g** SEM image and EDX result (*inset*) of blank HGS/Fe_3O_4. **h** a magnified SEM image

SEM image (inset in Fig. 2b) that the thickness of PANI layer was about 10^2–10^3 nm order of magnitude. However, owing to the large amount of composite spheres, it was difficult to calculate the thickness of PANI layer accurately. It also can be observed that the smaller the HGS were, the rougher the surfaces of composite spheres became. Figure 2b–d further revealed that with the increase of PANI to HGS ratio, PANI may aggregate in bulk rather than continuing to grow on the HGS/PANI surfaces. This suggested that the loading amount of PANI onto HGS had a maximum.

For preparing lightweight composite spheres with both conductive and magnetic properties, two routes were applied by changing the sequences of incorporating Fe_3O_4 nanoparticles in the composites. The detailed preparation process was specified in "Experimental section" and described in Fig. 1. The addition of Fe_3O_4 nanoparticles into PANI system will decrease the electrical conductivity of the composites due to the de-doped caused by in situ growth of Fe_3O_4 on PANI core under alkali solution or the prohibited conductive pathway by Fe_3O_4 nanoparticles in the outer layer of PANI [19, 25]. In order to reduce the negative effects, the authors proposed a HGS/Fe_3O_4-PANI structure (Sample 5) to promote a more continuous PANI network to form in the outmost layer of the composite. As described in schematic drawing of Fig. 1a, the SDBS modified Fe_3O_4 nanoparticles were deposited on PDDA modified HGS by electrostatic adsorption. The polyelectrolyte modification on HGS was favorable for adsorption of Fe_3O_4. The effect was illustrated by comparing the deposition of Fe_3O_4 nanoparticles on blank HGS and PDDA modified HGS. SEM and EDX results confirmed that Fe_3O_4 nanoparticles were more inclined to be deposited on PDDA modified HGS than on blank HGS. EDX result (inset of Fig. 2e) showed that Fe element was tested in PDDA modified HGS/Fe_3O_4. However, the inset of Fig. 2g certified that Fe content was too little to be examined in blank HGS/Fe_3O_4. The magnified SEM images of Fig. 2f, h showed that Fe_3O_4 nanoparticles were densely deposited on PDDA modified HGS, but they were sparsely dispersed on blank HGS. This study presented showed that the Fe_3O_4 contents could be tuned by modifying the HGS.

As shown in Fig. 1a, the assembly of PDDA and then PSS on HGS/Fe_3O_4 was conducted to form a negatively charged surface with sulfonic groups which could promote the adsorption of ANI monomer and an in situ polymerization finally [26, 27]. HGS/PANI-Fe_3O_4 (Sample 6) was prepared as comparison according to Fig. 1b.

Figure 3a–d showed the SEM images of Sample 5 and Sample 6, respectively. The magnified SEM images in Fig. 3b, d indicated that the surface microstructures were different for Sample 5 and Sample 6 due to the different components of the outmost layers. Though the characteristic peaks of Fe were barely observed in EDX spectra, the selected element compositions calculated by the EDX analyses confirmed the existence of Fe element in Sample 5 and Sample 6. The contents of PANI on Sample 5 and Sample 6 were 24.5 and 13.3 wt%, respectively, according to TGA results.

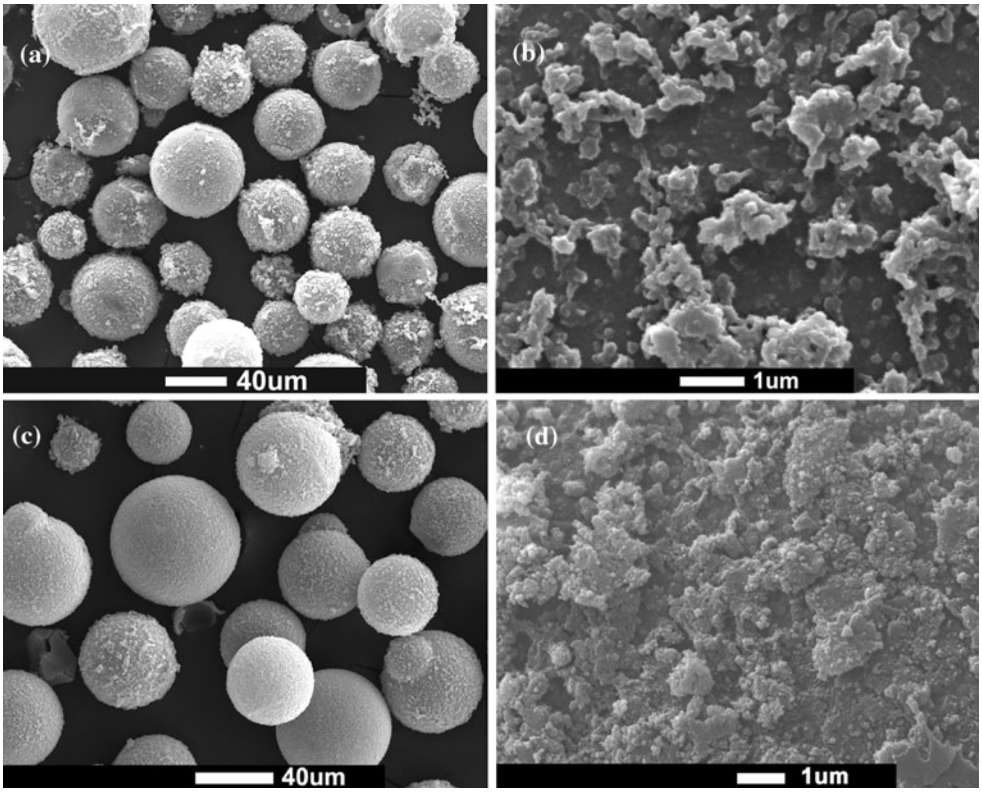

Fig. 3 **a** SEM image of Sample 5. **b** An enlarged SEM image of Sample 5. **c** SEM image of Sample 6. **d** An enlarged SEM image of Sample 6

Photographs shown in Fig. 4 demonstrated that the synthesized composites had a lower density than water and responded quickly to the external magnetic field (inset). If magnetic field were removed, the composite spheres would quickly rise to the water surface. Further, the phenomenon that the composite spheres can float on the surface of water confirmed that they were lightweight with density much lower than that of Fe_3O_4 of 5.2 g/cm^3.

The structural properties studied by FTIR and XRD

The FTIR adsorption spectra for HGS, Sample 3, and Sample 5 were shown in Fig. 5. The adsorption peaks at 1100, 800, and 470 cm^{-1} were characteristic features of Si–O–Si bonds (curve a in Fig. 5) [28]. The characteristic bands of PANI polymeric chain, e.g., quinoid C=C stretching deformation at 1576 cm^{-1}, benzenoid rings at 1493 cm^{-1}, and the C–N stretching of the secondary aromatic amine at 1301 cm^{-1} were observed. In addition, the aromatic C–H in plane bending peak moved to 1128 cm^{-1} and were broadened due to overlapping with Si–O–Si adsorption around 1100 cm^{-1} [29].

The XRD patterns of HGS, Sample 3, Sample 5, Sample 6, and bulk Fe_3O_4 nanoparticles were displayed in Fig. 6. A broad band at 2θ value of 20° can be attributed to amorphous SiO_2 phase in HGS (curve a) [7]. In curve b, c and d, the diffraction at 2θ of 20° became sharper than that of curve a because PANI diffraction peak overlapped with that of SiO_2. The peak centered at 2θ value around 20° in curve b was slightly sharper than those in curve c and d. Curve e in Fig. 6 showed that the diffraction peaks at 2θ values of 30.1°, 35.5°, 43.1°, 53.5°, 57.1° and 62.7° can be attributed to the Bragg reflections from (220), (311), (400), (422), (511), and (440) of Fe_3O_4, respectively [30]. The as-synthesized Fe_3O_4 nanoparticles possessed an average crystalline size at the order of magnitude of 10^1 nm estimated from Scherrer equation. The characteristic peaks of magnetic Fe_3O_4 were observed in curve c and d, which confirmed that the as-synthesized Fe_3O_4 nanoparticles had been incorporated into the composite spheres effectively.

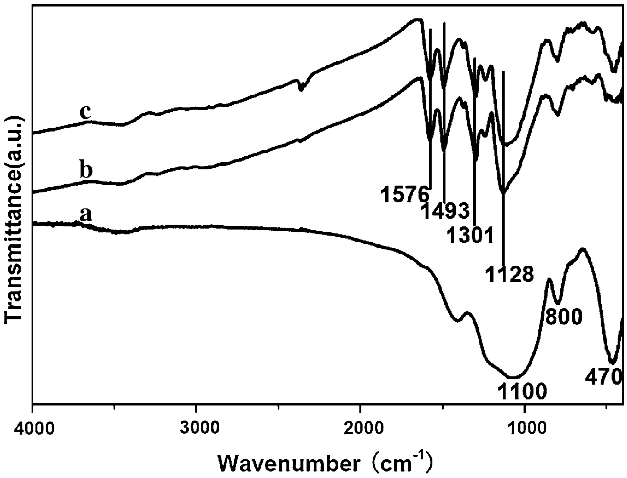

Fig. 5 FTIR spectra: *a* HGS, *b* Sample 3, and *c* Sample 5

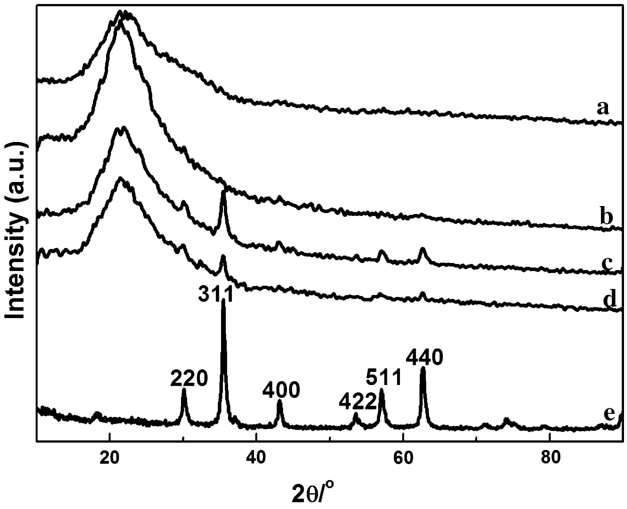

Fig. 6 XRD patterns: *a* HGS, *b* Sample 3, *c* Sample 5, *d* Sample 6, *e* Fe_3O_4 nanoparticles

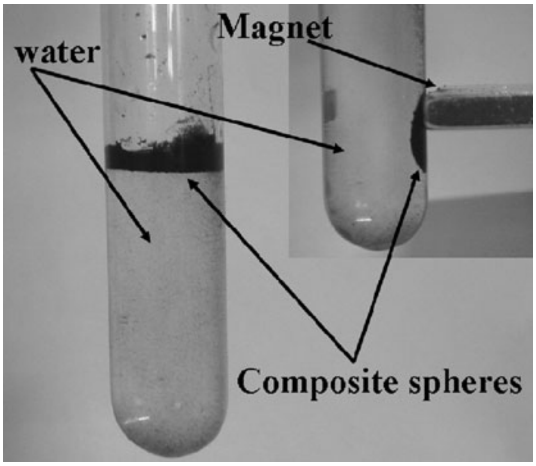

Fig. 4 Photographs showed that the composite spheres (Sample 5) floated on water and were trapped by a magnet (*inset picture*)

Electrical and magnetic properties

The conductivity and magnetization of the synthesized samples were listed in Table 2. As expected, the electrical conductivity increased from 1.3 × 10^{-2} S/cm to 2.8 × 10^{-2} S/cm and 4.4 × 10^{-2} S/cm with decreasing the initial ratios of HGS to ANI monomers (g/mL) from 1.2/0.4 (Sample 2) to 1.2/0.8 (Sample 3) and 1.2/1.2 (Sample 4). The bulk PANI (Sample 1) synthesized with the same reaction parameters had conductivity of 0.5 S/cm.

Table 2 Conductivity and magnetization

Sample	Conductivity (S/cm)	Magnetization (emu/g)
1	5.0×10^{-1}	–
2	1.3×10^{-2}	–
3	2.8×10^{-2}	–
4	4.4×10^{-2}	–
5[a]	5.4×10^{-3}	9.25
6[b]	1.1×10^{-4}	2.61

[a] 24.5 wt% PANI on Sample 5

[b] 13.3 wt% PANI on Sample 6

The electrical conductivity of Sample 5 (5.4×10^{-3} S/cm) was higher than that of Sample 6 (1.1×10^{-4} S/cm) due to the different deposition orders of Fe_3O_4 and PANI layers. The lower electrical conductivity of Sample 6 should be attributed to the negative effects of outer layer magnetic nanoparticles on forming continuous PANI phase and prohibiting conductive pathway. Compared with the original HGS/PANI composites (Sample 2) with the same initial ratio of HGS to ANI, Sample 5 and Sample 6 had lower conductivity, which was consistent with other researches [17, 19].

From Fig. 7, it was observed that the saturated magnetization of Sample 5 and Sample 6 were 9.25 and 2.61 emu/g, respectively. Neither coercivity nor remnant magnetization in Sample 5 and Sample 6 was observed, indicating superparamagnetic particles were deposited on HGS. The lower contents of magnetic nanoparticles in the composite hollow spheres compared to the bulk magnetite should be the major reason of the decreasing saturation magnetizations [16].

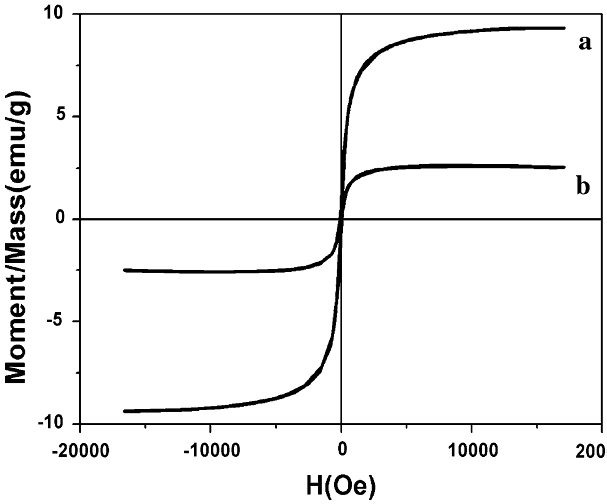

Fig. 7 Magnetic properties of Sample 5 (*curve a*) and Sample 6 (*curve b*)

Conclusions

In summary, the lightweight, conductive, and magnetic composite hollow spheres were prepared by controllable deposition of Fe_3O_4 and polyaniline (PANI) on HGS. The results demonstrated that the conductivity of HGS/PANI composites could be tuned from 1.3×10^{-2} S/cm to 4.4×10^{-2} S/cm by changing the initial ratio of HGS to ANI monomers. The different deposition order of PANI and Fe_3O_4 layers on HGS led to the variant conductive and magnetic properties. The conductivity and magnetization of HGS/Fe_3O_4-PANI were 5.4×10^{-3} S/cm and 9.25 emu/g, respectively, which were more than those of HGS/PANI-Fe_3O_4 of 1.1×10^{-4} S/cm and 2.61 emu/g. The low-density and multifunctional properties of the composite spheres make them promising for applications as functional fillers, microwave absorber, and electronic materials.

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