Template synthesis of composite hollow spheres using sulfonated polystyrene hollow spheres

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Abstract

In this paper, we propose a general template synthesis approach towards composite hollow spheres using sulfonated polystyrene gel hollow spheres. The gel hollow spheres are highly crosslinked to well preserve the spherical contour during template synthesis. It is important that the gel shell is infiltrative to many species to allow their further growth therein by specific interaction. The grown materials are well distributed thorough the whole shell forming composite shells. This method is general, which is proved by the growth of many representative materials for example metal Pd nanoparticles, magnetite Fe_3O_4 nanocrystallites, conducting polyaniline, and inorganic titania and silica. It is found that mesoporous inorganic shells are obtained after the template gel is calcined. This concept can be applied to other gel shells and grown materials expecting a new family of composite hollow spheres.
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1. Introduction

Hollow spheres and capsules have spurred great interest due to their potential applications in controlled release, artificial cells, light weight fillers, catalysis and confined reaction vessels [1–7]. Self-assembly of block copolymers can form hollow spheres or micelles [8–12]. Specific molecular chain is required for aiming hollow spheres with defined morphology and stability. Template synthesis based on core-shell structure has been well developed to achieve hollow spheres with varied shell composition. Hard cores such as silica colloids or polystyrene latexes are commonly used as templates for a variety of materials (polymeric, inorganic, biological, metallic) being coated forming the core-shell structures, which is usually assisted by layer-by-layer (LBL) deposition [1–6].

Besides LBL deposition, the shells can also be achieved by other approaches such as surface-initiated polymerization of polymeric brushes [13], redox replacement [14], and Kirkendall diffusion [15–17]. The template cores have to be sacrificed by either dissolution or calcination at high temperature in order to achieve hollow spheres, while the osmotic pressure will usually deteriorate the shell integrity resulting in perforation or fracture. Alternatively, soft template cores for example emulsion droplets [18,19], gas bubbles [20], quasi-reverse emulsions [21] are used to synthesize hollow spheres. The cores can be easily removed by evaporating liquids at elevated temperature. However, composition of the coating materials is rather restricted, and the weak liquid cores are easily deformed and coalesced during synthesis.

To avoid using core templates, hollow spheres such as polyelectrolyte capsules [22–25], viral capsids [26–28], vesicles [29–32] have been recently used as templates to synthesize composite hollow spheres. During the template synthesis using viral capsids, materials usually grow in the cavity rather than within the shell. It is not easy to form composite shells. The

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shell of block copolymer self-assembled vesicles is rather thin, polymerization therein usually induces phase separation leading to parachute-like morphologies. Polymeric gels are such interesting materials with tunable chemistry and physical environment, which can be used as templates to induce favorable growth of materials with varied composition through specific interactions [33−41]. When LBL assisted polyelectrolyte gel hollow spheres are used to prepare composite hollow spheres [22−25], ionic cross-linking nature within the shell significantly sacrifices the functional groups such as proton ions [42]. Based on our previous finding that proton ions can essentially induce favorable growth of functional materials through specific interaction [37,38], insufficient proton ions will lead to failure in favorable growth of materials within the gels. Since chemical modification of polymers can easily derive a variety of functional groups with tunable modification degree, we have extensively synthesized sulfonated polystyrene gels with tunable proton ion content by sulfonation of polystyrene colloids and their stacked opal materials [37−41].

In this paper, we propose a general template synthesis approach towards composite hollow spheres by using robust sulfonated polystyrene gel hollow spheres. The gel hollow spheres are highly crosslinked to well preserve the spherical contour during template synthesis. Sulfonated polystyrene gel shell is infiltrative allowing precursors to diffuse and being favorably absorbed within the whole shell by specific interaction followed by a growth of desired materials thereby forming composite shells. Composition of the materials can be tuned including metals and oxides, inorganic materials, organic polymers and their composites.

2. Experimental

2.1. Preparation of samples

Robust sulfonated polystyrene gel hollow spheres: the parent polymer hollow spheres are mainly composed of a linear polystyrene shell skeleton [40,41]. Crosslinked polystyrene hollow spheres were prepared by swelling radical polymerization of polystyrene/divinylbenzene within the shell of the parent polystyrene hollow spheres at 80 °C. The weight ratio of monomer polystyrene/divinylbenzene (1:1 wt/wt) mixture to parent polystyrene hollow spheres was 1:1. The crosslinked polystyrene hollow spheres were dispersed in concentrated sulfuric acid at 40 °C for varied time deriving robust sulfonated polystyrene gel shell with tunable thickness. The sulfonated polystyrene hollow spheres were washed with ethanol/water. Three representative gel hollow spheres S1, S2, S3 were derived by sulfonation for 4, 16, 24 h. *Metal palladium/gel composite spheres*: 0.1 g dried gel hollow sphere S3 was dispersed in 5 ml aqueous solution containing 0.2 g palladium chloride under stirring in nitrogen for 12 h for absorption. Afterwards the palladium chloride saturated gel S3 was separated by centrifugation and further washed with water to remove residual palladium ions outside the spheres. In a closed vessel, the spheres were re-dispersed in 5 ml water, 1 ml hydrazine hydrate was dropped into the dispersion under stirring followed by a reaction for 0.5 h at ambient temperature leading to Pd/S3 composite hollow spheres. *Magnetite/ S3 composite spheres*: 0.1 g dried gel hollow sphere S3 was dispersed in 5 ml aqueous ammonium hydroxide (10 M) for 12 h. After the ammonium hydroxide absorbed S3 was re-dispersed in 10 ml water, 0.6 ml aqueous mixture of ferrous chloride (1 M)/ferric chloride (2 M) (1:1 v/v) was added under stirring in nitrogen for 1 h [43,44]. The black product was isolated by a magnet and washed with water. *Polyaniline (PANi)/S3 composite spheres*: 0.1 g dried gel hollow sphere S3 was dispersed in 20 ml water, and a desired amount of aniline (0.025−0.400 g) was added into the aqueous dispersion under stirring for 24 h to allow adsorption. A desired amount of aqueous initiator ammonium persulfate (2 M) was added to allow polymerization of aniline at room temperature for 24 h. The PANi/S3 composite spheres were purified by centrifugation and washed with water. *Titania/S3 composite spheres*: 0.1 g dried gel hollow sphere was dispersed in 5 ml tetrabutyl titanate (TBT) under stirring for 24 h. After the TBT adsorbed S3 spheres were separated by centrifugation and washed with ethanol to remove residual TBT outside the spheres, they were re-dispersed in 10 ml ethanol. Water (10 ml) was dropped into the dispersion under stirring followed by a sol−gel process for 4 h at ambient temperature. The composite spheres were centrifugated and washed with ethanol/water. The titania composite hollow spheres were further calcined at high temperature for example 450 °C for 2 h in air. *Silica/S3 composite spheres*: 0.1 g dried gel hollow sphere S3, 2 g water, 2 g tetraethoxysilane (TEOS) were dispersed in 10 ml ethanol under stirring followed by a further reaction for 24 h. Silica/S3 composite spheres were prepared after centrifugation. The composite spheres were calcined at 450 °C in air.

2.2. Characterization

A very dilute dispersion of the spheres in ethanol was dropped onto carbon coated copper grids for transmission electron microscopy (TEM) characterization (JEOL 100CX operating at 100 kV). The composite hollow spheres were embedded in organic glass resin (PMMA) for ultramicrotomed slice samples about 30−50 nm thick using Leica ultracut UCT ultramicrotome at room temperature. Scanning electron microscopy (SEM) measurements were performed with a HITACHI S-4300 apparatus operated at an accelerating voltage of 15 kV. The samples were ambient dried and vacuum sputtered with Pt. The dried sphere samples were pressed into pellets together with potassium bromide (KBr) for characterization by BRUKER EQUINOX 55 FT-IR spectrophotometer. The crystallinity of the materials was characterized by wide-angle X-ray powder scattering (Rigaku D/max-2500). Inorganic content of the composite spheres was measured by Perkin−Elmer TGA 7 in air. Elemental analysis was carried out using a Flash EA-1112 apparatus. Magnetic property of magnetite composite spheres was measured with a vibrating-sample magnetomer (VSM JDM-13). Conductivity of compressed pieces of the dry powders was measured using a standard four-probe method at room temperature. Nitrogen

adsorption was performed on a Micromeritics ASAP 2020M Surface Area and Porosity Analyzer.

3. Results and discussion

3.1. Robust sulfonated polystyrene gel hollow spheres

After the parent hollow spheres with linear polystyrene shell skeleton were completely sulfonated, the gel hollow spheres were rather weak and easily deformed with the spherical shape being lost. The parent hollow spheres were strengthened by radical polymerization of styrene/divinylbenzene monomers within the shell forming a crosslinked polystyrene shell. Shell thickness of the crosslinked hollow sphere increased slightly from 80 nm to 90 nm, and the cavity size decreased from 320 nm to 280 nm (Fig. 1a). The crosslinked shell could well preserve spherical contour after being dissolved with solvents (Fig. 1b), while the parent hollow spheres were completely dissolved. The sulfonation degree was controlled by time at a given temperature 40 °C. After being sulfonated for 4 h, gel hollow spheres S1 were prepared with thicker shell of 140 nm. With sulfonation time further increased from 16 h to 24 h, the gel shell thickness of S2 and S3 was less changed about 150 nm. The derived sulfonic acid and sulfone groups were detected by FT-IR spectra (Fig. 2a). The characteristic bands at 670, 1180 and 1222 cm^{-1} were assigned to the derived sulfonic acid group ($-SO_3H$). The band at 1128 cm^{-1} was related with the sulfone group ($-SO_2-$). The intensity of the characteristic peaks of S2

and S3 were the same, indicating that S3 had been completely sulfonated. Elemental analysis indicated that the sulfur content in a series of gel spheres increased from 4.45 wt% in S1, 7.45 wt% in S2 to 7.99 wt% in S3. The sulfur content increment from S2 to S3 became less remarkable, indicating that the sulfonation of S2 had been nearly completed. This was consistent with equal intensity of the characteristic peaks of S2 and S3 in FT-IR spectra. Gel hollow sphere S3 was selected as the template ensuring complete sulfonation. S3 could well preserve the spherical contour after being ambient dried (Fig. 1c).

3.2. Pd composite hollow spheres

The sulfonated polystyrene gel can be favorably loaded with metal nanoparticles forming composite hollow spheres by ion exchange/reduction. As an example, Pd nanoparticles with a mean size of about 10 nm were formed within the gel shell, which were well distributed through the whole shell (Fig. 1d) indicating that the whole polystyrene shell had been completely sulfonated. Face-centered cubic crystalline structure of Pd nanoparticles confirmed by XRD (Fig. 3) was consistent with the previous reports [45,46]. The peaks at $2\theta = 40.02°$, 46.40°, 68.02°, 82.06° and 86.52° are assigned as the (111), (200), (220), (311) and (222) reflection lines. Broadening of XRD peaks indicated that the size of nanoparticles was about 10 nm, which was consistent with the TEM image (Fig. 1d). Besides metal nanoparticles, metallic oxides can be further derived by precipitation.
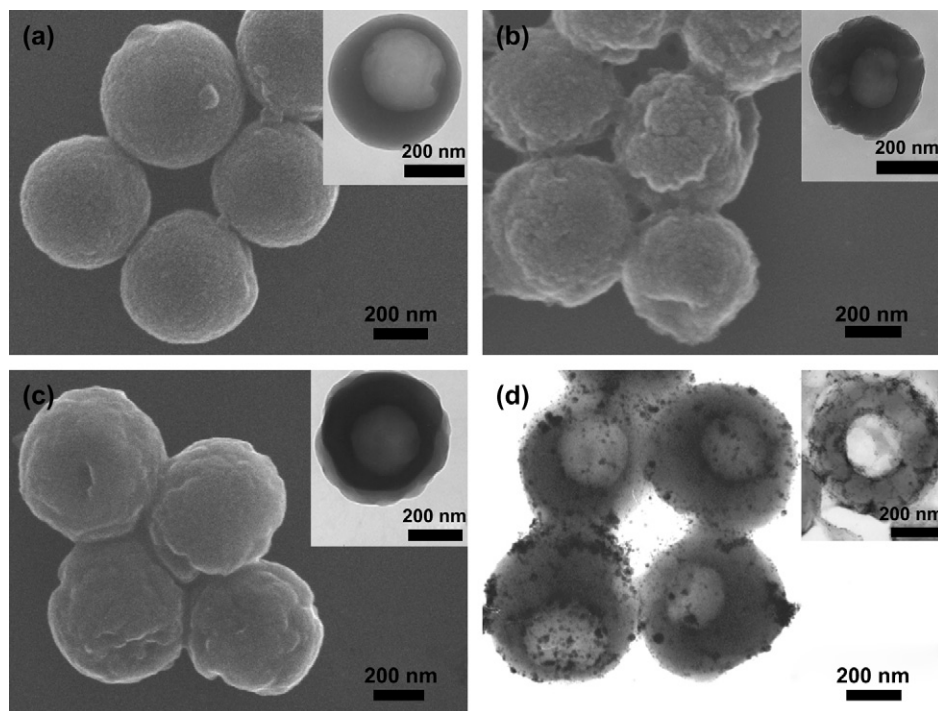

Fig. 1. Morphologies of the representative polymer and composite hollow spheres. (a,b) SEM images of the crosslinked PS hollow spheres by shell swelling radical polymerization before and after being dissolved with DMF, inset: the corresponding TEM images; (c) SEM image of the sulfonated PS hollow spheres S3 after being ambient dried, inset: TEM image; (d) TEM image of Pd/S3 composite hollow spheres, inset: cross-section of TEM image.
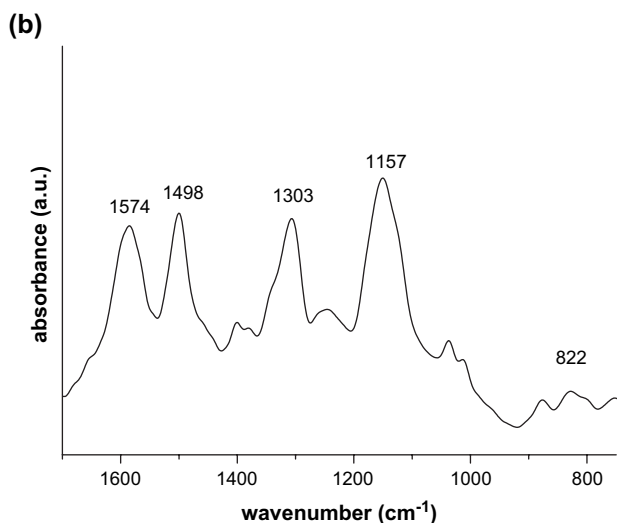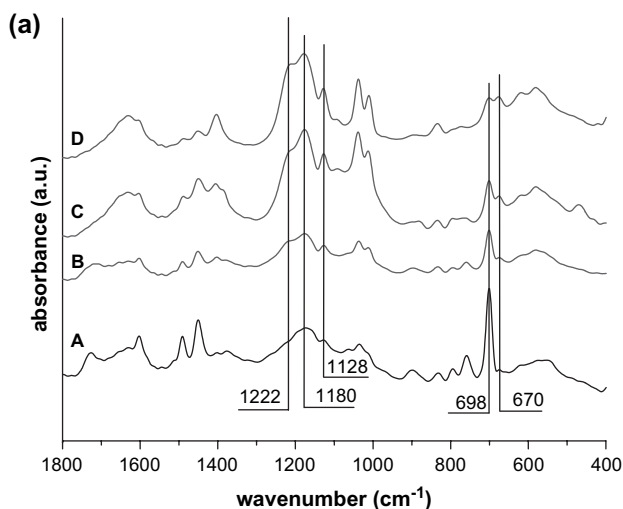
(a)

(b)

Fig. 2. (a) FT-IR spectra of the four representative samples: (A) the crosslinked PS hollow spheres, (B, C, D) sulfonated hollow spheres S1, S2, S3; (b) FT-IR spectrum of polyaniline/S3 composite hollow spheres.

3.3. Fe₃O₄ composite hollow spheres

As a second example, magnetite Fe_3O_4 nanocrystallites were synthesized within the gel shell. The composite spheres had coarse surface consisting of 10–15 nm nanoparticles (Fig. 4a), which were well distributed through the whole shell (inset Fig. 4a). Magnetite Fe_3O_4 was confirmed by XRD (Fig. 5a) consistent with the previous reports [41,43,44]. During measurement of magnetization dependence on field up to 4000 Oe at 300 K (Fig. 6), no coercivity was detected indicating that the nanoparticles were paramagnetic. The magnetite Fe_3O_4 loading was controlled by the ions content added. The saturation magnetite content 73.87 wt% as measured by TGA. Free nanoparticles began to form in the dispersion media when excess ions were added. The saturation magnetization of the composites was tuned by changing the magnetite content for example 19 emu/g (48.21 wt% Fe_3O_4), 29 emu/g (54.23 wt% Fe_3O_4) and 45 emu/g (73.87 wt% Fe_3O_4).
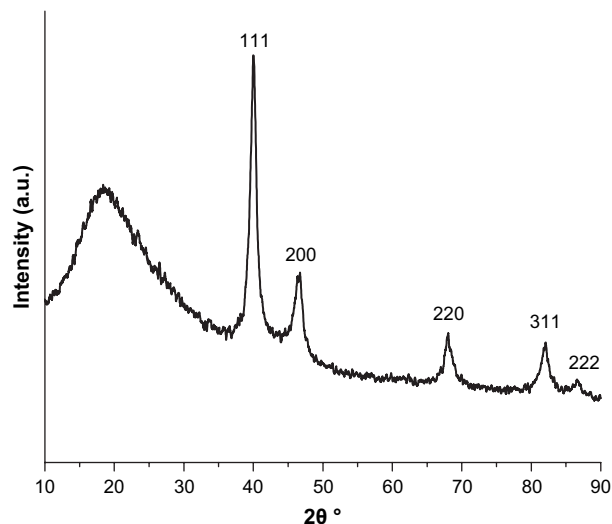

Fig. 3. XRD pattern of the Pd/S3 composite hollow spheres.

3.4. PANi composite hollow spheres

As a third example, monomer aniline was favorably adsorbed within the gel shell by specific interaction and polymerized forming PANi/S3 composite hollow spheres (Fig. 4b). Saturation PANi content reached 75.0 wt%. PANi was in situ doped by the sulfonated polystyrene gel in the form of emeraldine salt evidenced by FT-IR spectrum (Fig. 2b). The bands at 1574 and 1498 cm^{-1} were assigned to quinoid and benzenoid rings, respectively. The other bands at 1303 (C–N stretch), 1157 (C–H plane bend), and 822 cm^{-1} (1,4-disubstituted benzene ring stretch) were identical to the emeraldine salt form of PANi [19,47,48].

The conductivity was controlled within the four-order of magnitude by changing PANi/S3 ratio. When the ratio of PANi/S3 is higher, sulfonic acid is insufficient to dope PANi with lower conductivity. When the ratio is lower, sulfonic acid is in excess to shield the property of doped PANi. A maximum conductivity was 10^{-1} S/cm at an intermediate PANi content 45.3 wt% (Fig. 7). This was explained by an optimal doping of PANi by sulfonic acid group. PANi/Fe_3O_4 composite hollow spheres with the same levels of conductivity and magnetization were accordingly synthesized.

3.5. Titania composite hollow spheres

Inorganic semiconductor titania composite spheres (Fig. 4c) were synthesized by favorable sol–gel process of tetrabutyl titanate (TBT) within the sulfonated polystyrene gel. Both the interior and exterior regions were much denser than the intermediate layer, which could be explained by the precursor TBT diffusion during the sol–gel process. This provides a way to prepare multi-layered hollow spheres in one step simply by controlling reagents diffusion. The composite spheres contained 47.4 wt% titania by TGA measurement. After being calcined at 450 °C, polymers were removed leading to double-layered hollow spheres (Fig. 4d). The phase
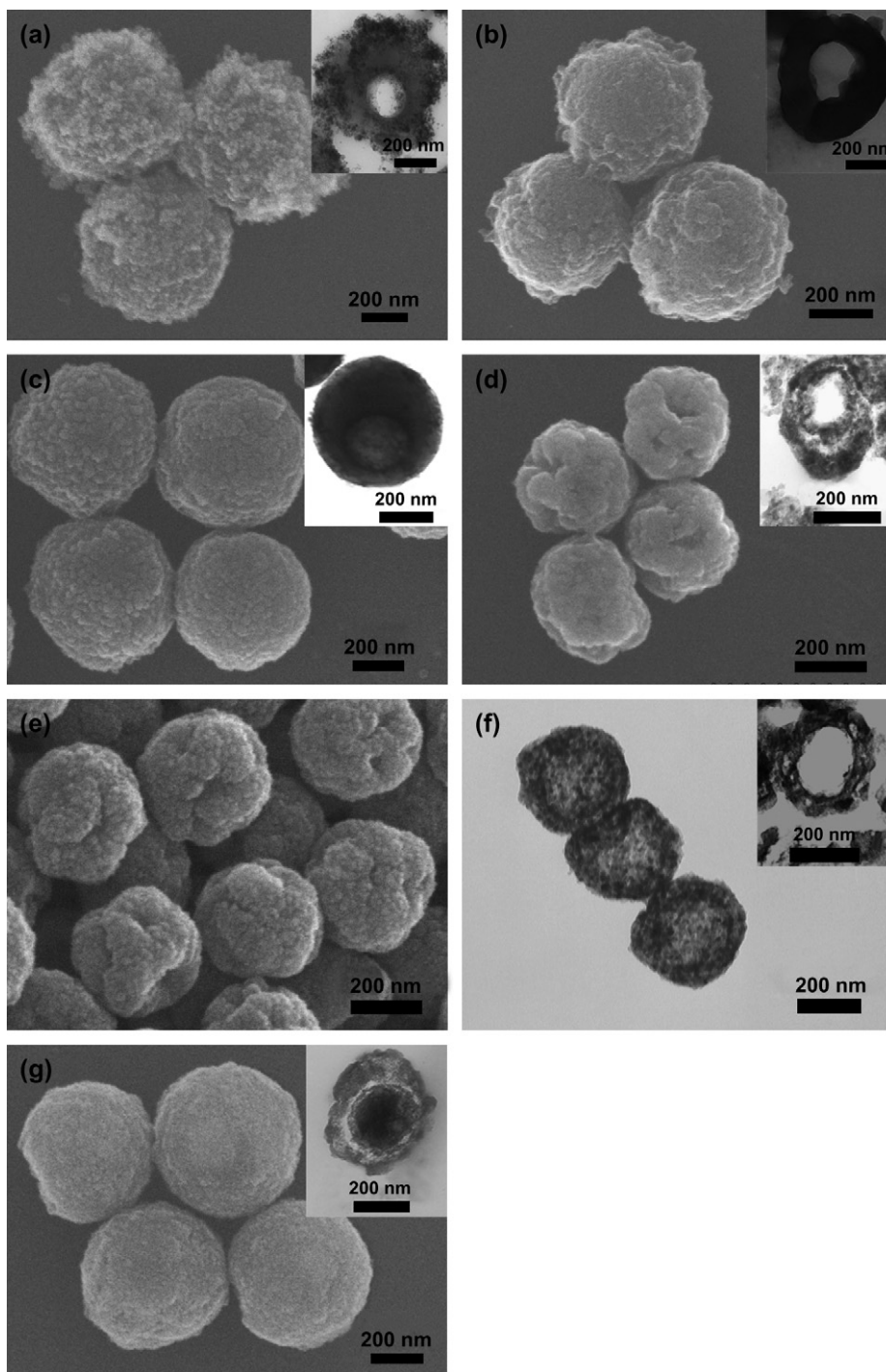
Fig. 4. Morphologies of some representative composite hollow spheres by using template S3. (a) Magnetite Fe₃O₄/S3 composite hollow spheres; (b) polyaniline/S3 composite hollow spheres; (c,d) titania/S3 composite hollow spheres before and after being calcined at 450 °C for 2 h in air; (e,f) titania hollow spheres by using thinner gel shell template; (g) silica/S3 composite hollow spheres before and after being calcined at 450 °C for 2 h in air.

transformation from amorphous to anatase was verified by XRD (Fig. 5b). At high temperature, 600 °C, anatase/titania hollow spheres were derived with the spherical contour well preserved. At 900 °C, pure rutile phase was achieved but the hollow spheres were destroyed. By using a thinner gel shell about 85 nm, single-shelled titania hollow spheres were prepared (Fig. 4e,f).

3.6. Silica composite hollow spheres

By using S3 gel hollow template, silica/S3 composite spheres were prepared (Fig. 4g). After being calcined at 450 °C, silica hollow spheres were prepared. To investigate the pore structure of silica hollow spheres, the nitrogen adsorption test was performed. Hysteresis loop in the
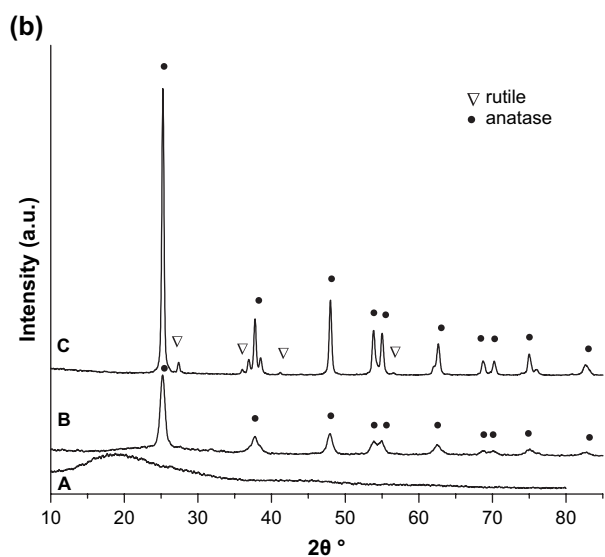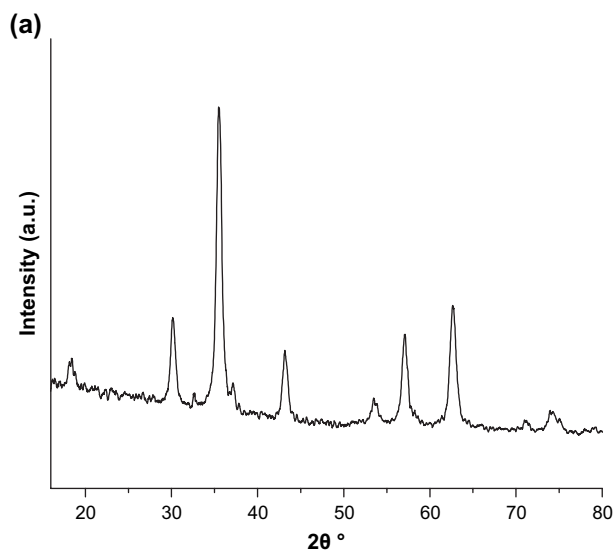
Fig. 5. XRD spectrum of (a) magnetite/S3 composite hollow spheres; (b) titania/S3 composite hollow spheres: (A) untreated, (B) titania hollow spheres after being calcined at 450 °C, (C) 600 °C for 2 h in air (●: anatase; ▽: rutile).
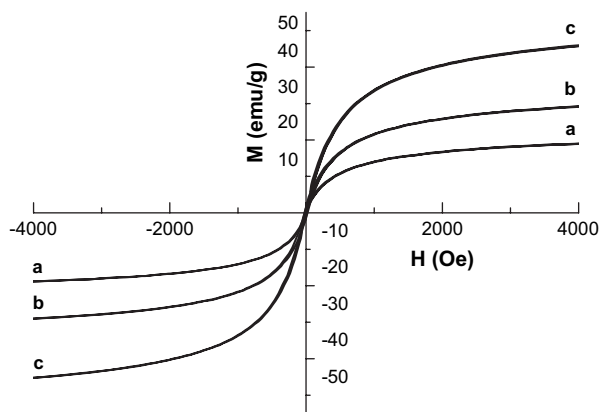

Fig. 6. Magnetization curve obtained at room temperature for magnetite/S3 composite hollow spheres with varied magnetite content: (a) 48.21 wt%, (b) 54.23 wt%, (c) 73.87 wt%.
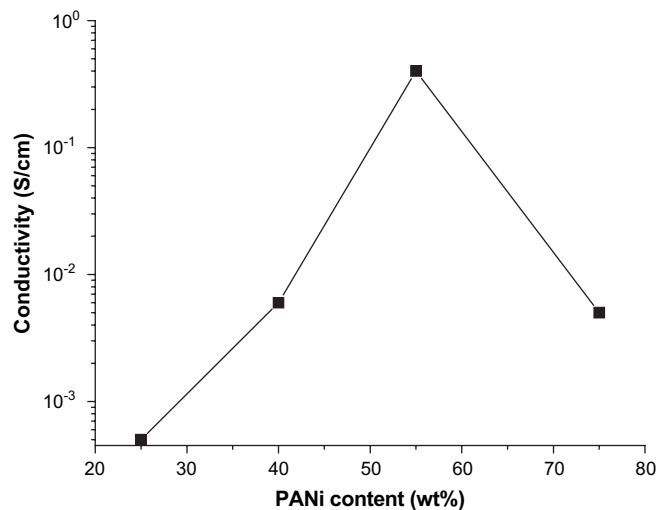

Fig. 7. Conductivity of polyaniline/S3 composite hollow spheres dependent on polyaniline content.
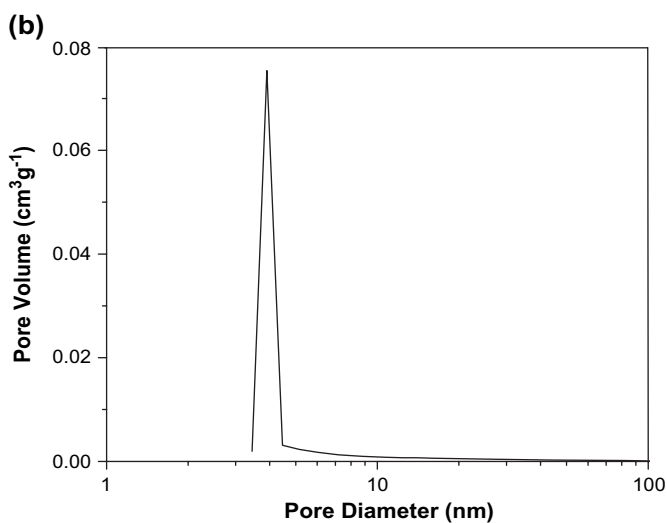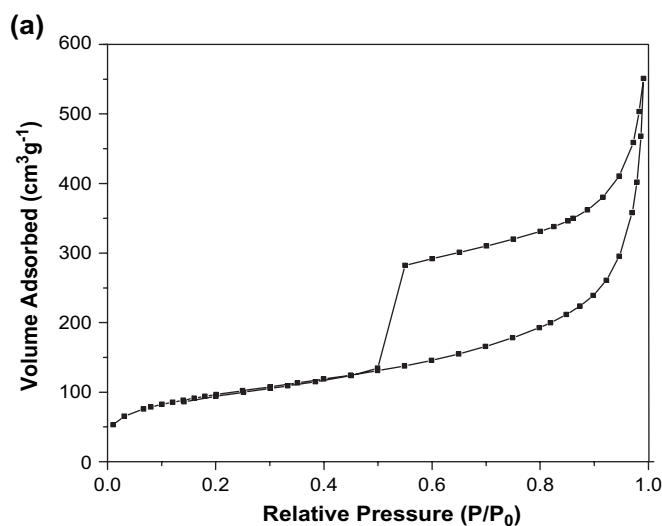

Fig. 8. (a) Nitrogen adsorption/desorption isotherms and (b) the corresponding pore size distribution of the hollow silica spheres.

adsorption/desorption isotherms is the characteristic of mesopore. Their shell was mesoporous with mean pore size about 3.8 nm and BET specific surface area 349 m^2/g (Fig. 8). This means that the gels can be used as a porogen to achieve mesopores.

4. Conclusions

In conclusion, we have demonstrated an approach to fabricate composite hollow spheres by using robust sulfonated polystyrene gel hollow spheres. The methodology is general, a diversity of materials including inorganic, metals and oxides, functional polymers and their composites are favorably grown within the gel shell by specific interaction. This concept can be applied to other gel shells and grown materials expecting a new family of composite hollow spheres.

Acknowledgements

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