



Interpenetration network (IPN) assisted transcription of polymeric hollow spheres: A general approach towards composite hollow spheres

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ABSTRACT

We have demonstrated a general and facile method to synthesize composite hollow spheres by IPN-assisted transcription of polymeric hollow spheres. Starting from a parent PS hollow sphere, IPN polymer composite hollow spheres have been synthesized by a swell polymerization within the shell. The shell thickness and the cavity size are tunable by altering the feeding amount of the monomers. A variety of functional groups are derived by a selective modification of one network of the IPN polymer composite hollow spheres. By specific interactions of desired materials with gels, composite hollow spheres are obtained. The composition of the shell can be controlled within polymer, carbon, inorganic, metal and metallic compounds, and their composites.

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1. Introduction

Hollow spheres, especially composite functional hollow spheres, have spurred increasing interests due to their diverse potential applications such as drug delivery, artificial cells, biosensors, energy conversion and catalysis [1–3]. The key effects on applications are to control both structure and composition. Many methods have been developed to control morphology and composition, including layer-by-layer assisted deposition [4–7], graft onto a core template [8,9], and gel shell induced favorable growth [10]. These methods are essentially based on core-shell structure approach, which usually involves removal of the core templates. The resultant osmotic pressure will usually cause apertures or fragmentation in the shell. In order to avoid removal of the core templates, hollow vesicles or liposome have also been used as templates [11,12]. This method fails to form intact composite shells, due to a poor compatibility after the desired materials are incorporated within the weak thin shell. Emulsion or suspension polymerization has been employed to synthesize polymer hollow spheres [13–15], which also involves a removal of liquid cores. In addition, self-assembly of block copolymer [16–19], core-template-free synthesis [20,21], galvanic metal replacement [22], Kirkendall effect based method [23,24], and gas bubbles as soft-templates [25] are also proposed to prepare composite hollow spheres. These mentioned methods remain to be restricted within special compositions thus lacking generality.

Herein, we present a facile approach to the synthesis of composite hollow spheres with an interpenetration network (IPN) shell. As illustrated in Fig. 1, a commercial polystyrene (PS) hollow sphere A is selected as an example parent template [13]. Composition of the shell can be controlled along series sequential stages. (1) Hydrophobic monomers B can swell the shell and sequentially polymerize forming an A/B binary polymer IPN hollow sphere. In order to strengthen the IPN shell, crosslinkers are usually used together with the monomers. Phase separation during the polymerization is dynamically prohibited within the highly viscoelastic shell, ensuring a bicontinuous IPN structure. (2) Another functional network B1 with desired groups is further derived by a selective modification of desired one polymer network such as B within the composite shell. The physicochemical environment such as being charged and permeable is thus tuned. (3) Desired materials can be favorably grown within network B1 by specific interactions resulting in another composite network B2, whose composition can be varied within polymers, inorganic materials, metals and their compounds. Along the similar procedure, another functional network A1 and composite network A2 can also be derived from the parent network A.

2. Experimental

2.1. Synthesis of IPN composite hollow spheres

2.1.1. PS/(crosslinked PAN) IPN hollow spheres

In 100 mL of water, 5 g of freeze-dried powder of parent polystyrene (PS) hollow spheres HP-433 (a Rohm & Haas product) with

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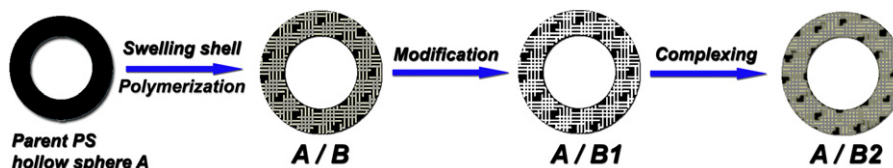


Fig. 1. Schematic synthesis of composite hollow spheres by IPN-assisted transcription of polymer hollow spheres.

an outer diameter of 400 nm and cavity diameter of 250 nm, was dispersed. Then 0.1 g of sodium dodecyl benzenesulfonate (SDS) was added as surfactant. Acrylonitrile/divinylbenzene (5 g, 1:1 wt/wt) and 0.05 g of benzoyl peroxide were added and emulsified under ultrasonication for 10 min. The mixture was held under

mechanical stirring at ambient temperature for 6 h to allow the monomers and initiator to swell the shell. Afterwards, the emulsion was heated to 80 °C to initiate the polymerization in nitrogen for 6 h, and the PS/(crosslinked PAN) IPN hollow spheres were obtained.

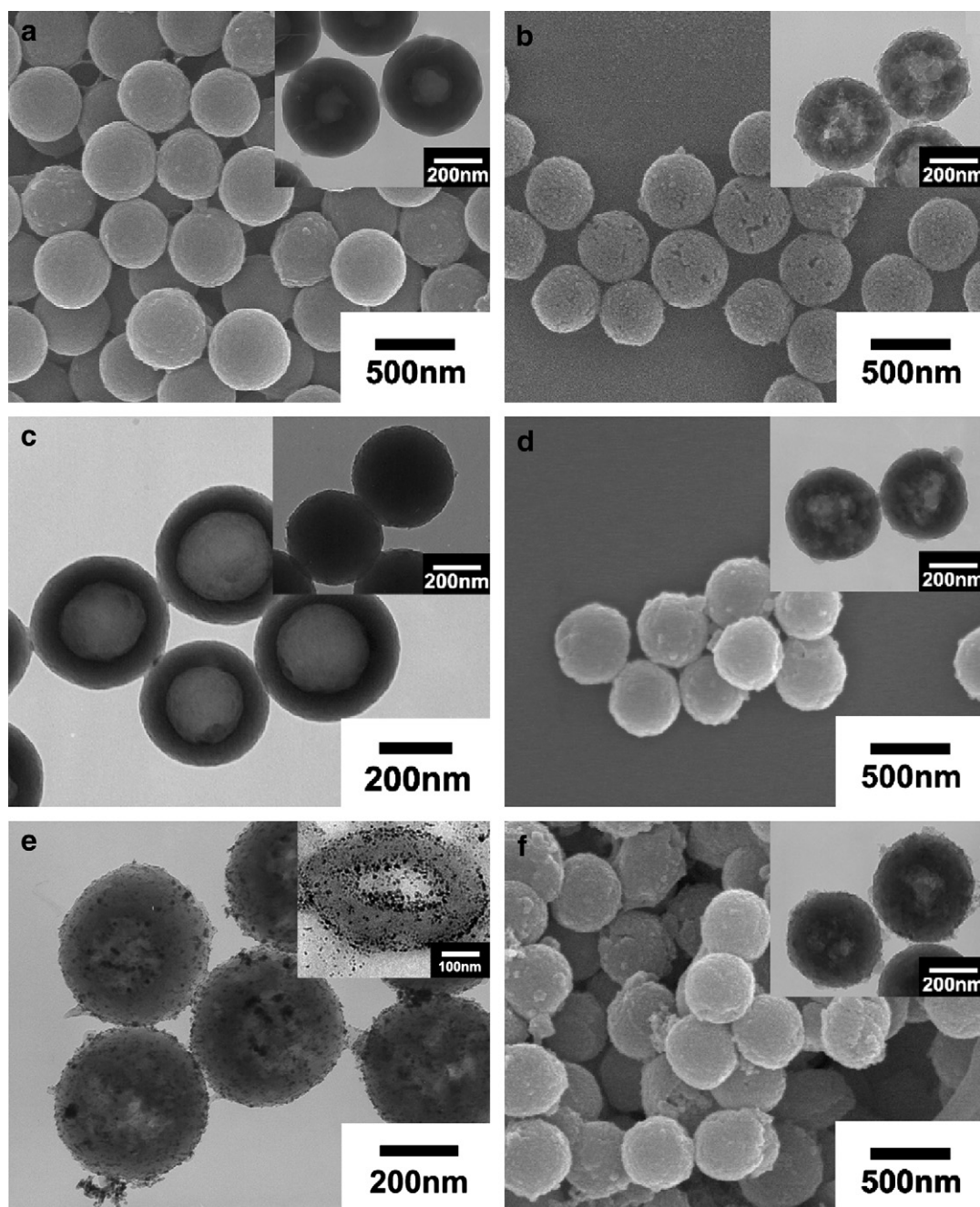


Fig. 2. Electronic images of some representative IPN composite hollow spheres: (a) PS/(crosslinked PAN) at a weight ratio 1:1 of parent PS sphere/monomer ratio; (b) crosslinked PAN after linear polymers were dissolved from those as shown in Fig. 2a with DMF; (c) PS/(crosslinked PAN) prepared at a weight ratio 1:0.4 of parent PS sphere/monomer ratio, and inset image of the sphere at a ratio 1:2; (d) PS/H-PAN with $-\text{COOH}$ and $-\text{CONH}_2$ groups; (e) TEM and inset cross-section TEM images of PS/H-PAN/Pd nanoparticles and (f) PS/silica.

2.2. Modification of IPN hollow spheres

2.2.1. Hydrolysis of PAN

At ambient temperature, 1.0 g of freeze-dried powder of PS/(crosslinked PAN) IPN hollow spheres was dispersed in 20 g of NaOH solution (50 wt%). The mixture was held under reflux for 24 h with mechanical stirring. After a centrifugation and rinsing with water to remove residual NaOH solution and adjusting the pH value close to 7 by hydrochloric acid, the PS/H–PAN IPN hollow spheres were obtained.

2.2.2. Sulfonation of PS

At ambient temperature, 1.0 g of freeze-dried powder of PS/silica IPN hollow spheres was dispersed in 50 g of concentrated sulfuric acid. The mixture was held at 80 °C for 24 h under mechanical stirring. After a centrifugation and rinsing with water to remove residual sulfuric acid solution, the S–PS/silica IPN hollow spheres were obtained.

2.3. Composite hollow spheres

2.3.1. PS/silica hollow spheres

In a mixture of 5 g of water and 5 g of ethanol, 0.1 g of freeze-dried powder of PS/H–PAN IPN hollow spheres was dispersed. To the dispersion, 10 g of tetraethoxysilane (TEOS) and 5 g of ethanol were mixed and added. The sol–gel process was carried out under stirring for 24 h at room temperature. After a centrifugation and rinsing with ethanol to remove residual silica sol outside the spheres, PS/silica composite spheres were prepared.

2.3.2. Pd composite hollow spheres

In 1 g of water, 0.01 g of freeze-dried powder of PS/H–PAN IPN hollow spheres was dispersed, and 3 g of PdCl₂ solution (1 wt%) was added. The mixture was held under stirring for 24 h. After the hollow spheres containing Pd²⁺ were rinsed with water, 0.2 mL of 85 wt% hydrazine hydrate was added under stirring and held for 1 h to reduce Pd²⁺ into metal nanoparticles.

2.3.3. Titania/silica hollow spheres

In 10 g of ethanol and 10 g of tetrabutyl titanate (TBT) 0.1 g of freeze-dried powder of S–PS/silica IPN hollow spheres was dispersed. The mixture was held under stirring for 24 h at room temperature. After the TBT absorbed S–PS/silica IPN hollow spheres were separated by centrifugation and washed with ethanol to remove residual TBT outside the spheres, they were re-dispersed in 10 mL ethanol. At room temperature 10 mL of water was dropped into the dispersion under stirring for 4 h to initiate a sol–gel process. The composite spheres were centrifuged and washed with ethanol/water. The titania/silica composite hollow spheres were obtained after the composite hollow spheres were calcined at 450 °C for 2 h in air.

2.4. Characterization

The structure and morphology of the spheres were characterized using transmission electron microscopy (JEOL 2011 at 200 kV), high-resolution transmission electron microscopy (HITACHI H9000 at 300 kV) and scanning electron microscopy (HITACHI S-4300 at 15 kV). The SEM samples were prepared by vacuum sputtering Pt on the ambient dried samples. TEM samples were prepared by spreading very dilute ethanol dispersions onto carbon-coated copper grids. Ultramicrotomed samples were prepared by embedding the spheres in resins and ultramicrotoming into 30–50 nm thick slices using a Leica ultracut UCT ultramicrotome at room temperature. FT-IR spectroscopy was performed using a BRUKER EQUINOX 55 spectrometer with the samples/KBr pressed pellets.

The crystallinity of the materials was characterized by wide-angle X-ray powder scattering (Rigaku D/max-2500). Nitrogen adsorption/desorption was performed on a Micromeritics ASAP 2020M surface area and porosity analyzer.

3. Results and discussion

As a proof of the concept, a swelling free radical polymerization of acrylonitrile (AN)/divinylbenzene (DVB) mixture was carried out within the shell of the parent polystyrene (PS) hollow sphere. Because the selected monomers can swell the parent template, the monomers were entirely absorbed into the shell of the parent template at room temperature. Then the monomer within the shell polymerized *in situ* at high temperature to form PS/PAN IPN hollow spheres. The hollow cavity is distinguished from the composite hollow spheres (Fig. 2a). Comparing with the parent PS hollow sphere, the cavity diameter decreases from 250 nm to 100 nm, and the shell thickness increases from 75 nm to 150 nm. When the linear polymers were dissolved from the composite spheres with *N,N*-dimethylformamide (DMF), crosslinked hollow spheres were obtained (Fig. 2b). It is interesting that many transverse nanopores were achieved. The shell becomes thicker with further increase in feeding amount of monomers, meanwhile the cavity diameter decreases until eventually the cavity disappears and becomes solid (Fig. 2c).

In order to demonstrate the conversion of polymer B network into functional B1, the PS/PAN hollow spheres were treated with alkali to allow a selective hydrolysis of PAN network, resulting in the formation of functional groups such as carboxylic acid (–COO[–]H⁺) and amide (–CONH₂) (Fig. 2d). The groups were verified by FT-IR spectra (Fig. 3). The characteristic band at 2238 cm^{–1} attributed to –CN group decreases and the new bands at 1670 cm^{–1}, 1239 cm^{–1} and 1156 cm^{–1} indicate the presence of –COOH and –CONH₂ groups. The grey network in the TEM image is corresponded to the hydrolyzed network. Since the groups can easily complex with metal ions, many metal nanoparticles are thus prepared by reduction within the shell. For example, Pd nanoparticles were distributed within the whole shell, indicating that the PAN network was interpenetrated within the parent PS matrix and the whole PAN network has been hydrolyzed (Fig. 2e). The IPN structure of PS/PAN was thus confirmed. In order to show the general approach of favorably forming composite shell within the hydrophilic network, a polymeric gel induced sol–gel process of tetraethyl orthosilicate (TEOS) by acid groups was undertaken forming

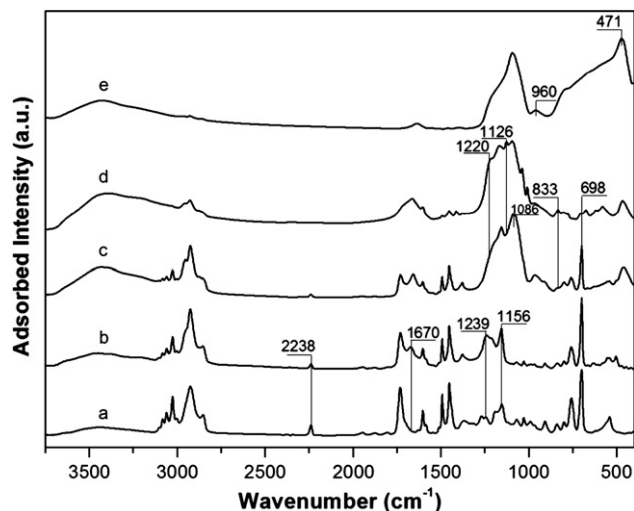


Fig. 3. FT-IR spectra of some representative IPN composite hollow spheres: (a) PS/(crosslinked PAN); (b) PS/H–PAN; (c) PS/silica; (d) S–PS/silica and (e) titania/silica after removing polymer templates at 450 °C in air.

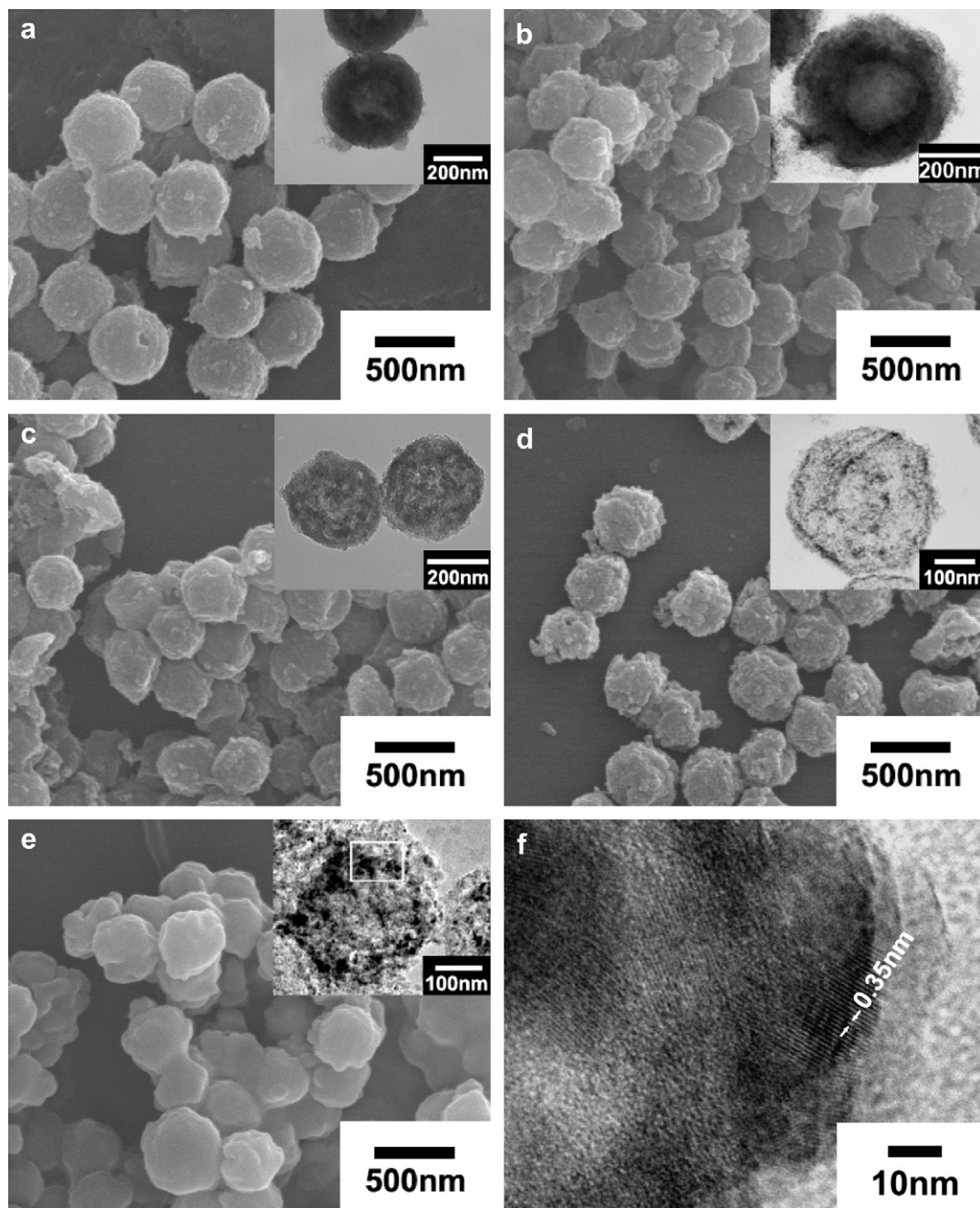


Fig. 4. Electronic images of some representative hollow spheres: (a) S-PS/silica IPN composite; (b) carbon/silica IPN composite by carbonization of S-PS/silica IPN composite hollow spheres at 900 °C in Ar; (c) carbon porous hollow spheres after the silica of carbon/silica IPN composite hollow spheres were treated with hydrofluoric acid to remove silica; (d) silica hollow spheres after removing the carbon of carbon/silica IPN composite hollow spheres at 450 °C for 2 h in air; (e) titania/silica IPN composite hollow spheres after being calcined at 450 °C for 2 h in air and (f) HRTEM image of the framed region in Fig. 3d.

PS/silica IPN hollow spheres (Fig. 2f). As shown in curves b and c (Fig. 3), the characteristic bands at 1670 cm^{-1} , 1239 cm^{-1} and 1156 cm^{-1} attributed to $-\text{COOH}$ and $-\text{CONH}_2$ groups become weaker, and the new broad band around 1000–1120 cm^{-1} attribute to Si–O–Si appearance. This means that there exists interaction between the gel network and silica. The inorganic hollow spheres were prepared after the PS templates were dissolved (not shown here), indicating the continuity of silica network.

The above process of modification and favorable growth of materials can work to another polymer network A. For example, the PS network of the prepared PS/silica IPN hollow spheres was sulfonated with concentrated sulfuric acid at 80 °C for 10 h. The

sulfonated PS/silica (S-PS/silica) IPN hollow spheres were robust to retain the spherical contour (Fig. 4a). The derivation of S-PS from hydrophobic PS network was confirmed by FT-IR spectra (Fig. 3). The characteristic bands at 1220 cm^{-1} and 1126 cm^{-1} are associated with sulfonic acid ($-\text{SO}_3\text{H}$) and sulfone ($-\text{SO}_2-$) groups [10,26–28]. The characteristic peak at 698 cm^{-1} attributed to mono-substituted benzene becomes weaker and the peak at 833 cm^{-1} attributed to bi-substituted benzene becomes stronger, consistent with the conversion of PS into S-PS. Since the sulfonic acid can catalyze PS to convert into carbon, the S-PS/silica composite spheres were treated at a high temperature for example 900 °C in argon (Ar), carbon/silica composite hollow spheres were prepared (Fig. 4b). It was

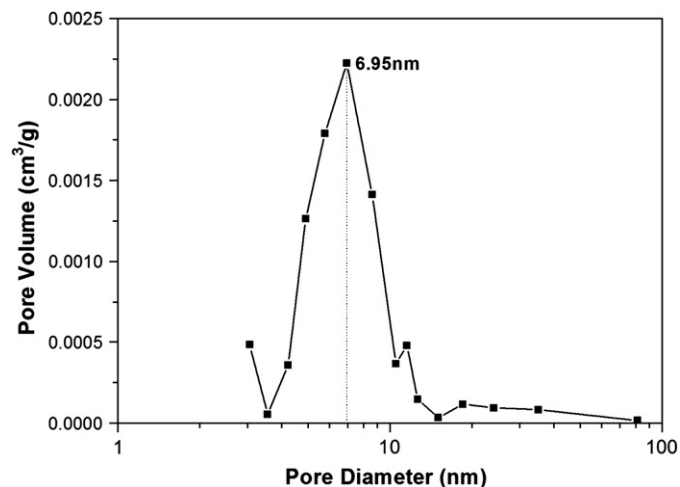


Fig. 5. Pore size distribution of the porous carbon/silica IPN composite hollow spheres.

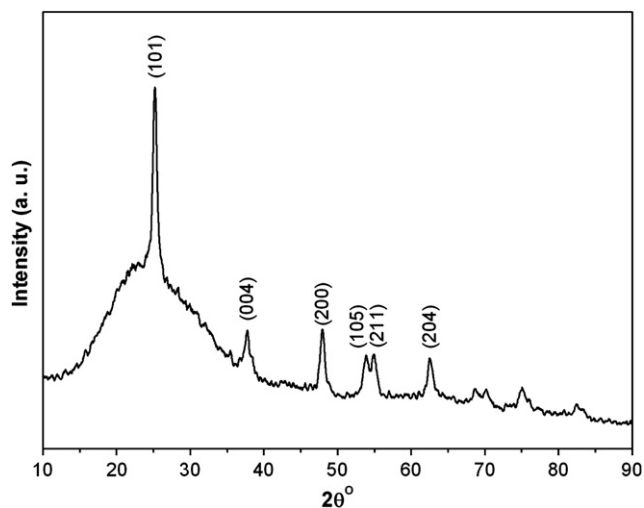


Fig. 6. X-ray powder diffraction spectrum of titania/silica IPN composite hollow spheres after being calcined at 450 °C for 2 h in air.

interesting that the composite shell was mesoporous with a mean pore size of 6.95 nm and a BET specific surface area of 120 m²/g (Fig. 5). After a selective removal of silica with hydrofluoric acid, carbon hollow spheres with a shell thickness about 100 nm were prepared (Fig. 4c). This means that carbon is continuous. When the composite spheres were calcined in air to remove carbon, silica hollow spheres were also prepared (Fig. 4d). Thus, carbon and silica are both continuous constructing the IPN composite shell. Besides conversion of S-PS into carbon, the S-PS gel can also induce a favorable growth of other materials such as titania, polyaniline, Fe₃O₄ [10,26–28]. In order to demonstrate this concept, titania was grown in S-PS network by a sol-gel process of tetrabutyl titanate (TBT). After being calcined at 450 °C in air to remove the organic species, titania/silica IPN composite hollow spheres were prepared (Fig. 4e). The characteristic band at 471 cm⁻¹ assigned to Ti–O–Ti group confirms the presence of titania (Fig. 3). Besides, the new characteristic band at 960 cm⁻¹ is related with Ti–O–Si group, indicating the bonding interaction between titania and silica.

The black network attributed to titania is continuous within the grey silica matrix. The HRTEM image (Fig. 4f) of the black region gives a {101} lattice with a spacing of 0.35 nm assigned to anatase, which is consistent with X-ray powder diffraction (XRD) result (Fig. 6).

4. Conclusion

In summary, we have demonstrated a general and facile method to synthesize composite hollow spheres by IPN-assisted transcription of polymeric hollow spheres. Starting from a parent PS hollow sphere, IPN polymer composite hollow spheres have been synthesized by a swell polymerization within the shell. The shell thickness and the cavity size of the composite hollow spheres are tunable by altering the feeding amount of the monomers. A variety of functional groups are derived leading to polymeric gels by a selective modification of one network of the IPN polymer composite hollow spheres. The physicochemical environment of the shells is thus controlled. By specific interactions of desired materials with gels and gel induced preferential growth, composite hollow spheres are obtained. The composition of the shell can be controlled within polymer, carbon, inorganic, metal and metallic compounds, and their composites.

Acknowledgements

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References

- [1] Wilcox D, Berg M, Bernat T, Kellerman D, Cochran J. Hollow and solid spheres and microspheres: science and technology associated with their fabrication and application. Materials research society proceedings, vol. 372; 1995.
- [2] Graff A, Benito S, Verbert C, Meier W. In: Niemeyer C, Mirkin C, editors. Nanobiotechnology: concepts, applications and perspectives. Weinheim: VCH; 2004. p. 168–84 [chapter 12].
- [3] Meier W. Chem Soc Rev 2000;29:295–303.
- [4] Caruso F, Caruso R, Möhwald H. Science 1998;282:1111–4.
- [5] Caruso F. Chem Eur J 2000;6:413–9.
- [6] Caruso F. Adv Mater 2001;13:11–22.
- [7] Shi X, Shen M, Möhwald H. Prog Polym Sci 2004;29:987–1019.
- [8] Chen Y, Kang E, Neoh K, Greiner A. Adv Funct Mater 2005;15:113–7.
- [9] Cheng D, Xia H, Chan H. Langmuir 2004;20:9909–12.
- [10] Yang Z, Niu Z, Lu Y, Hu Z, Han C. Angew Chem Int Ed 2003;42:1943–5.
- [11] Hotz J, Meier W. Adv Mater 1998;10:1387–90.
- [12] Hubert D, Jung M, German A. Adv Mater 2000;12:1291–4.
- [13] Kowalski A, Vogel M, Blankenship R. U.S. Patent 4427836; 1984.
- [14] Okubo M, Konishi Y, Minami H. Colloid Polym Sci 1998;276:638–42.
- [15] Jang J, Ha H. Langmuir 2002;18:5613–8.
- [16] Zhang Q, Remsen E, Wooley K. J Am Chem Soc 2000;122:3642–51.
- [17] Liu X, Jiang M, Yang S, Chen M, Cheng D, Yang C, et al. Angew Chem Int Ed 2002;41:2950–3.
- [18] Liu F, Eisenberg A. J Am Chem Soc 2003;125:15059–64.
- [19] Dou H, Jiang M, Peng H, Chen D, Hong Y. Angew Chem Int Ed 2003;42:1516–9.
- [20] Zeng HJ. Mater Chem 2006;16:649–62.
- [21] Ding Y, Hu Y, Jiang X, Zhang L, Yang C. Angew Chem Int Ed 2004;43:6369–72.
- [22] Sun Y, Xia Y. Nano Lett 2003;3:1569–72.
- [23] Yin Y, Rioux R, Erdonmez C, Hughes S, Somorjai G, Alivisatos A. Science 2004; 304:711–4.
- [24] Wang Y, Cai L, Xia Y. Adv Mater 2005;17:473–7.
- [25] Peng Q, Dong Y, Li Y. Angew Chem Int Ed 2003;42:3027–30.
- [26] Yang M, Ma J, Niu Z, Dong X, Xu H, Meng Z, et al. Adv Funct Mater 2005;15: 1523–8.
- [27] Yang M, Ma J, Zhang C, Lu Y, Yang Z. Angew Chem Int Ed 2005;44:6727–30.
- [28] Ding S, Zhang C, Yang M, Qu X, Lu Y, Yang Z. Polymer 2006;47:8360–6.