Synthesis of composite eccentric double-shelled hollow spheres

Jianjun Li, Shujiang Ding, Chengliang Zhang*, Zhenzhong Yang*

State Key Laboratory of Polymer Physics and Chemistry, Beijing National Laboratory of Molecular Science, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China

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ABSTRACT

Eccentric double-shelled hollow polyethylacrylate (PEA)/polystyrene (PS) crosslinked composite spheres were synthesized by phase separation during swelling polymerization of their mother polymer hollow spheres. The group –NH$_2$ was introduced within the network by ammonization of PEA. Other materials for example silica could be favorably grown within the gel network by a sol–gel process. The polymer/silica hollow spheres gave the corresponding derivative hollow spheres with varied composition including SiO$_2$/carbon, carbon and β-SiC, with the eccentric double-shelled morphology retained.

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1. Introduction

Hollow spheres have attracted considerable attention owing to their potential applications in many fields, such as catalysis, lightweight fillers, controlled release and dye-sensitized solar cells [1–4]. A diversity of hollow spheres of varied composition, such as organic, inorganic and metal, has been successfully prepared [5–16]. They have shown interesting properties. For example, SiO$_2$/carbon hybrid ones can strongly absorb solar light of a broadening wavelength range, and can be in-situ loaded with noble metal nanoparticles with improved electronic properties [17–19]. Recently, complex concentric multi-layered hollow spheres are becoming more interesting for their unique plasma properties [20–23]. We have previously prepared those complex composite hollow spheres using polymer hollow spheres as templates [24–26]. For instance, composite functional hollow spheres with double concentric shells are synthesized using sandwiched hydrogel hollow sphere templates [25]. Compared with the concentric hollow spheres, those eccentric double-shelled hollow spheres have fascinating different characteristics. For example, silica-Au eccentric nanoegg fabricated by anisotropic electroless plating, has different multiple-peaked plasmonic response [27]. Eccentric sphere-in-sphere titanium hollow spheres can scatter UV light more effectively inside the cavity so

as to greatly enhance photocatalytic activity [28]. It should be noticed that the inner sphere is not fixed thus movable, the unique properties will become unstable upon external mechanical vibration. Development of a facile approach to large scale production of eccentric double-shelled hollow spheres with fixed inner sphere is required.

Herein, we report the synthesis of eccentric double-shelled hollow composite spheres using the corresponding ammonized gel hollow sphere templates. As illustrated in Fig. 1, a commercial polystyrene (PS) hollow sphere with transverse hydrophilic channels is selected as an example mother template [25]. The swelling monomers of ethyl acrylate (EA) and divinylbenzene (DVB) can easily diffuse into the cavity via the channels while simultaneously swelling the shell from both the interior and exterior surfaces. At a high content of crosslinking agent DVB, polymerization induced viscoelasticity can drive asymmetric phase separation resulting in anisotropic sandwiched hollow spheres. After dissolution of the middle layer, eccentric double-shelled hollow spheres are derived. Some functional groups for example -NH$_2$ can be introduced within the eccentric hollow spheres by modifying the PEA network through ammonization, which are conducive to further growth of other functional materials. By a sol–gel process forming silica within the gel region, the corresponding silica/polymer composite hollow spheres are derived. Due to the presence of crosslinked network from DVB, the polymer can be easily converted into carbon resulting eccentric silica/carbon double-shelled hollow spheres. For all the double-shelled hollow spheres, the inner sphere is fixed onto the outer shell thus not movable.

* Corresponding authors. Fax: +86 10 62559373.
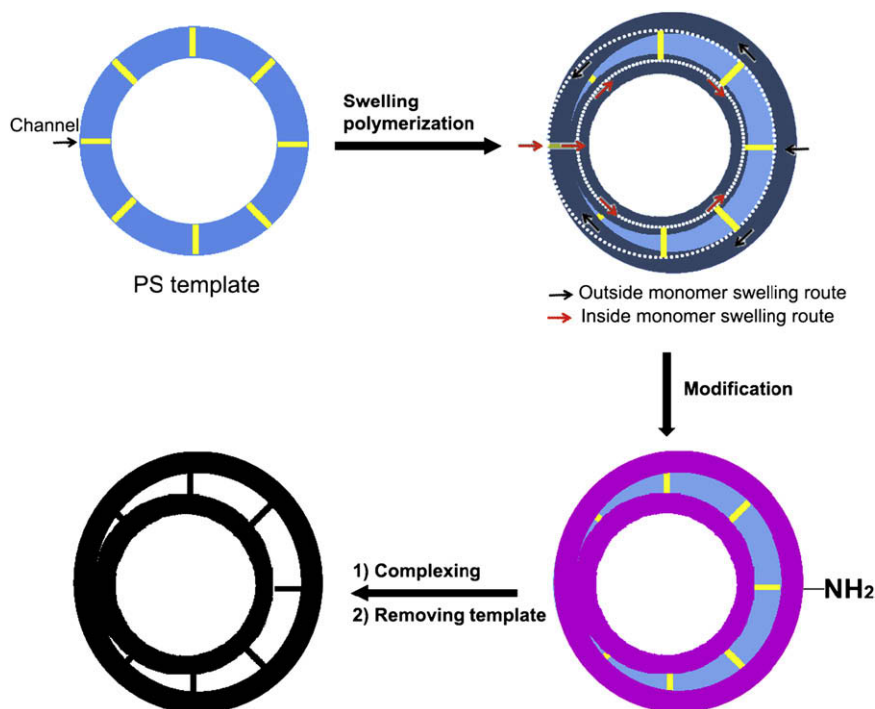*E-mail addresses:* zhangcl@iccas.ac.cn (C. Zhang), yangzz@iccas.ac.cn (Z. Yang).

Fig. 1. Schematic synthesis of eccentric composite hollow spheres.

2. Experimental

2.1. Synthesis of polymer composite sandwiched hollow spheres

13.30 g of HP-433 emulsion (a Rohm & Haas product, solid content 37.5 wt-%) was mixed with a pre-formed emulsion containing 1.00 g of EA, 4.00 g of DVB, 0.05 g of BPO (benzoyl peroxide) and 0.08 g of SDS (sodium dodecyl benzenesulfonate) under stirring for 8 h at ambient temperature for complete swelling of the polymer shell. The polymerization was held at 75 °C for 12 h in nitrogen. By altering the weight ratio of HP-433 to the pre-formed emulsion and the content of DVB, morphology of the composite spheres was tuned.

2.2. Modification of the polymer composite hollow spheres

The ammonization of polyethylacrylate network is given as an example. 3.00 g of freeze dried powder of the above polymer composite hollow spheres was mixed with 100.00 g of triethene-tetraamine in 100.00 g of ethanol. The system was refluxed for varied times in nitrogen to control the ammonization degree. The resultants were centrifuged and washed with ethanol.

2.3. SiO_2/polymer composite hollow spheres

0.50 g of dried powder of modified hollow spheres with –NH_2 group was mixed with 75.00 g of ethanol, 25.00 g of water, 5.00 g of TEOS (tetraethoxysilane) and 1.00 g of 2 M aqueous HCl. The mixture was held at 70 °C under stirring for 12 h to permit a sol–gel process within the gel network. The resultants were centrifuged and washed with ethanol.

2.4. Other derivative double-shelled hollow spheres

The SiO_2/carbon double-shelled hollow spheres were derived after the dried powder of SiO_2/polymer composite hollow spheres

were carbonized at 800 °C in nitrogen for 2 h. At low temperature for example at 450 °C in air for 2 h, the corresponding SiO_2 double-shelled hollow spheres were obtained. Using aqueous HF to remove the SiO_2 from the composite sample, carbon double-shelled hollow spheres were prepared. The corresponding SiC double-shelled hollow spheres were obtained after the SiO_2/carbon double-shelled hollow spheres were further carbonized at higher temperature for example 1450 °C in argon for 2 h.

2.5. Characterization

Morphology of the spheres was characterized using transmission electron microscopy (JEOL 100CX at 100 kV) and scanning electron microscopy (HITACHI S-4800 at 15 kV). The ambient-dried samples were sputtered with Pt in vacuum for SEM observation. Very dilute dispersions in ethanol were spread onto carbon-coated copper grids for transmission electron microscopic (TEM). Fourier transform infrared spectroscopy (BRUKER EQUINOX 55) was performed with the samples pressed into KBr pellets. Elemental analysis was carried out using a Flash EA 1112 apparatus to determine the N content. Nitrogen adsorption was performed on a Micromeritics ASAP 2020M surface area and porosity analyzer. Wide-angle X-ray power scattering (Rigaku D/Max-2500) was used to characterize the crystalline type of the materials.

3. Results and discussion

3.1. PEA/PS composite sandwiched hollow spheres

EA and DVB were used as monomers to swell the shell of the mother PS hollow sphere template (Fig. 2a) following a polymerization forming the crosslinked PEA/PS composite hollow spheres [29]. Two weight ratios are significant to determine structure of the composite spheres: template to monomer mixture, DVB to EA. At a high DVB/EA ratio for example 4:1, all the resultant composite hollow spheres are eccentric with a sandwiched shell. With
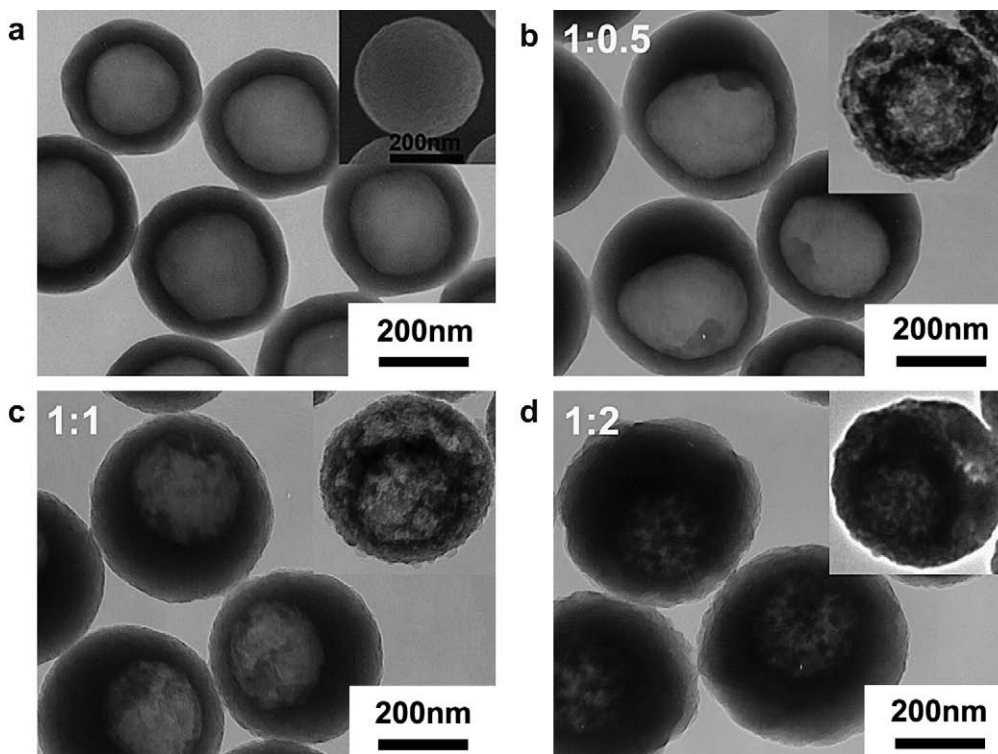
Fig. 2. Morphology of some representative hollow spheres: (a) PS hollow sphere template; (b–d) eccentric hollow spheres with varied template/monomer weight ratio (a = 1:0.5; b = 1:1; c = 1:2) when the DVB/EA ratio is fixed at 4:1. Inset figures (b–d) are the corresponding samples after the composite spheres are treated with DMF.

decreasing template/monomer ratio, cavity of the composite hollow spheres becomes smaller and the whole sphere becomes larger (Fig. 2b–d). With the ratio decreasing from 1:0.5 to 1:2, the average cavity decreases from 230 nm (Fig. 2b) to 150 nm (Fig. 2d),

while the whole sphere becomes from 430 nm to 480 nm. After removal of the linear polymer template from the sandwiched shell with N,N-dimethylformamide (DMF), the corresponding double-shelled eccentric hollow spheres were prepared with both the
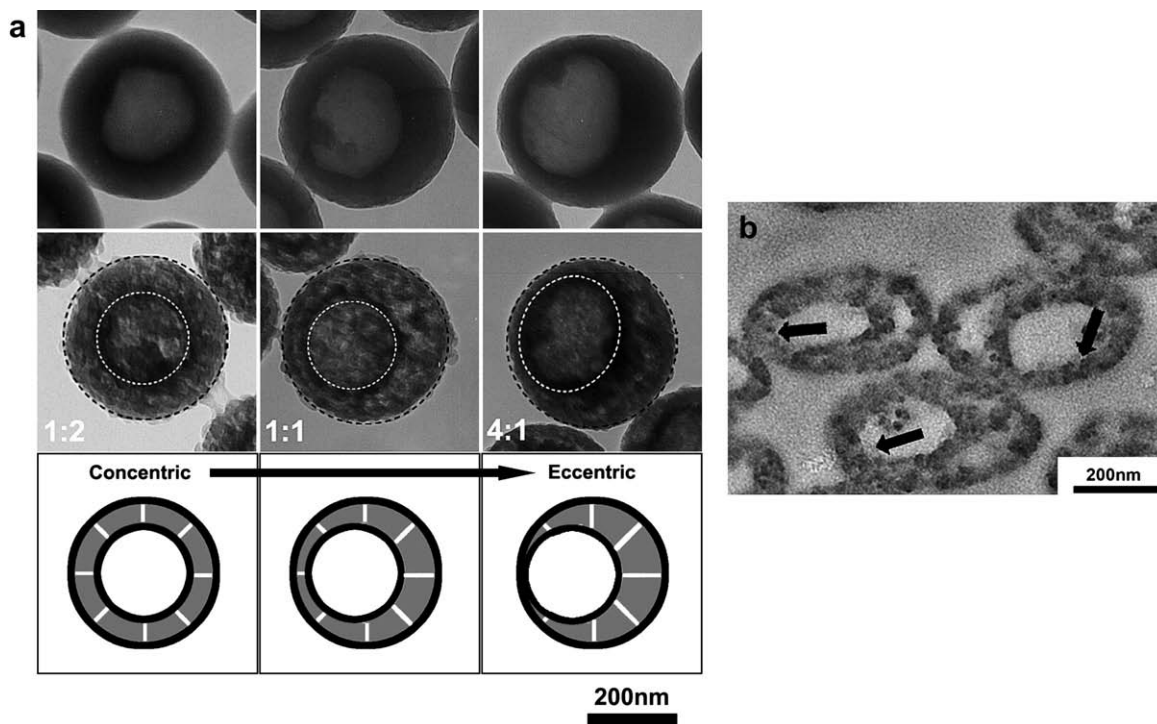

Fig. 3. Morphologies of some representative composite hollow spheres: (a) composite hollow spheres with varied DVB/EA ratio (the left = 1:2; the middle = 1:1; the right = 4:1) before and after the template is dissolved, the corresponding schemes are given; (b) cross-section TEM image of the composite hollow spheres (the right Fig. 3a) after the template is dissolved.
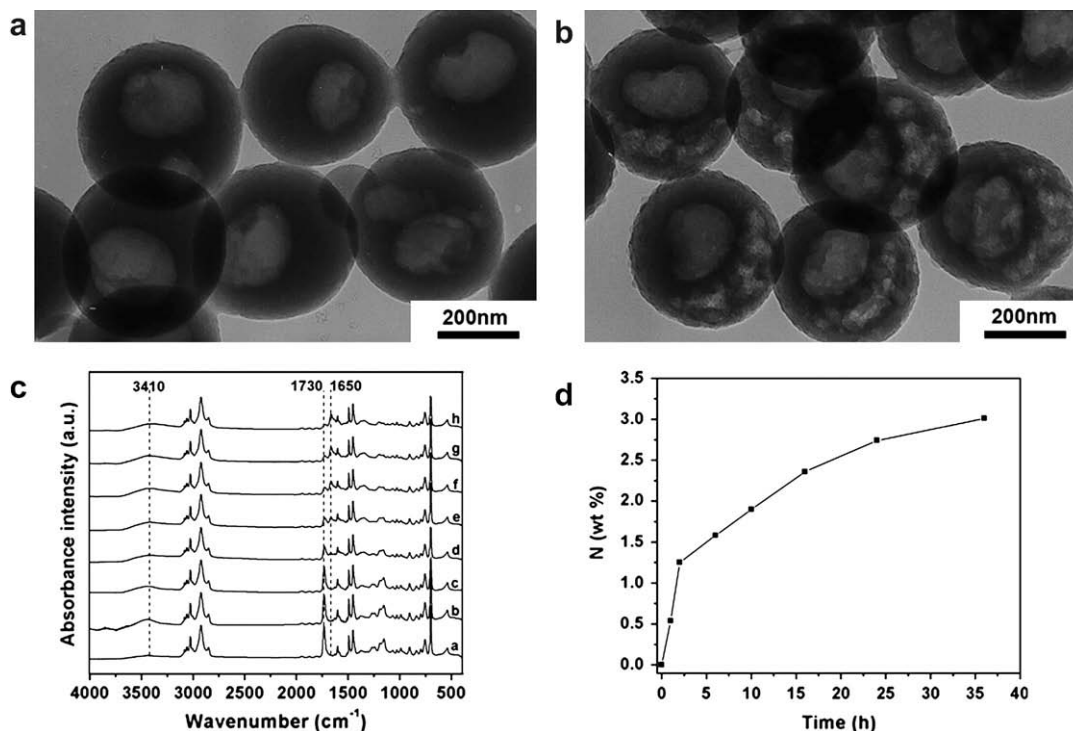
Fig. 4. TEM images of the eccentric double-shelled hollow gel spheres by modification of the sample as shown in Fig. 2c with triethylenetetraamine for 36 h (a) before and (b) after removal of the linear polymer template; (c) FT-IR spectra of the modified hollow spheres for varied ammonization time (h): (a) 0, (b) 1, (c) 2, (d) 6, (e) 12, (f) 16, (g) 24, (h) 36; (d) the corresponding nitrogen elemental analysis of the samples after varied ammonization time.

interior and the exterior shells well discerned (inset TEM images Fig. 2b–d). The gap between the two shells looks like nascent moon under TEM imaging, whose separation is continuously decreased to zero only in one sphere. This unique geometry is important to tune light scattering in a wider wavelength range within a cavity.

Besides strengthening the polymer network, DVB plays another essential role in tuning polymerization thermodynamics and dynamic thus morphology. The morphological evolution of the composite hollow spheres was recorded with different DVB/EA weight ratio at a fixed template/monomer ratio 1:1. At a low level DVB/EA ratio for example 1:2, a homogeneous swelling polymerization is dominant. The composite hollow spheres remain concentric, whose shell becomes thicker and the cavity becomes smaller (Fig. 3a – left). After removal of the linear polymer template with DMF, the corresponding concentric double-shelled hollow spheres were formed. The interior shell is supported by the exterior shell through the pillars formed within the transverse channels. At an increased DVB/EA ratio to 1:1, the hollow spheres become eccentric. With further increasing the ratio to 4:1, the eccentricity becomes more remarkable. In order to elucidate the internal structure of the hollow spheres, cross-section TEM imaging of the samples was undertaken. For the composite spheres prepared at DVB/EA ratio 4:1 as an example, the interior and exterior shells are partially coalesced leaving the nascent moon like gap (Fig. 3b). In this case, the eccentric structure remains permanently rather than movable.
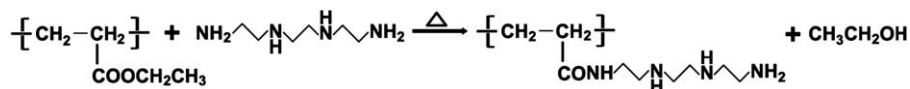
Since the shell of the polymer composite hollow spheres is rather soft at low level of crosslinking agent DVB, ultra-microtoming usually cause deformation of the shell and the internal structural information is lost. As well described, the PEA layer can be easily converted into polyelectrolyte layer with amino group after modification (see the following section), which can selectively induce formation of silica. Meanwhile, the soft shell is

strengthened. In our study, alternatively, the composite spheres after being complexed with silica in the soft gel are ultra-microtomed for TEM observation of the internal structural evolution of the polymer composite hollow spheres (Fig. S1). Both two cross-section TEM images were duplicated from the corresponding two polymer hollow spheres (in Fig. 3a, the left concentric and the middle eccentric one). The evolution from the concentric silica interior shell to the eccentric one indicates the PEA interior shell morphological evolution with the crosslinking agent DVB content.

The polymer hollow sphere template has transverse channels, whose shell is mainly consisted of polystyrene [24–26]. The swelling monomers can easily diffuse inside, and swell the whole shell from both the interior and exterior surfaces simultaneously. As well known, the compatibility between PEA and PS is poor and phase separation occurs for bulk blends. The similar phase separation occurs during polymerization of the monomers [30,31]. Especially, in the presence of crosslinking agent, the PEA network becomes more elastic during polymerization, and the separated PEA domains will be repelled more easily from the PS phase. In fact, many reports have proved that the polymerization can induce phase separation against a solid PS core sphere forming acorn or snowman like structure [32,33]. In our case, the abovementioned phase separation occurs both from the exterior and interior shell surfaces forming double-acorn structures, e.g. the eccentric sandwiched PEA/PS/PEA structure. After removing the linear PS template, the eccentric double-shelled hollow spheres can be obtained instead of one shell.

3.2. Modification of the composite hollow spheres

Some desired functional groups for example –NH$_2$ can be introduced to the PEA/PS composite hollow spheres by ammonization of PEA with triethylenetetraamine as following:

$$\{CH_2-CH_2\} + NH_2 \bigwedge_{H} N \bigwedge_{H} \bigwedge NH_2 \xrightarrow{\triangle} \{CH_2-CH_2\} + CH_3CH_2OH$$
$$\quad\quad\;\; COOCH_2CH_3 \quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad CONH \bigwedge N \bigwedge_{H} N \bigwedge NH_2$$

The modification was carried out in refluxing ethanol, which started from both the interior and exterior surfaces since the polymer shell is not swollen with ethanol. By changing the modification time, the ammonization degree is changed. All the modified hollow spheres can maintain the eccentric structure (Fig. 4a) for example after being modified for 36 h. After dissolution of the linear PS template by DMF, the corresponding double-shelled hollow gel spheres were obtained (Fig. 4b) with the eccentric morphology remained. The ammonization process of PEA with time was investigated by FT-IR (Fig. 4c). With prolonging the reaction time, the characteristic band at 1730 cm^{-1} (assigned to –COOC$_2$H$_5$) becomes gradually weaker, while a new band appears at 1650 cm^{-1} indicating the presence of –CONH–. The band at 3410 cm^{-1} (assigned to –NH$_2$ group) becomes stronger. Nearly all the –COOC$_2$H$_5$ group has transformed into –CONH– group after 36 h. Nitrogen elemental analysis also shows a gradual augmentation of nitrogen amount, which is consistent with FT-IR result (Fig. 4d). At the initial step, the ammonization is fast. The ammonization slows down with prolonging reaction time. Only 0.4% of nitrogen element is increased from 24 h to 36 h, which means that 24 h is sufficient for a nearly complete ammonization.

3.3. Inorganic/polymer composite hollow spheres

Functional groups for example sulfonic acid of polymer gels can induce a favorable growth of functional materials [24,25]. Similarly, the derived –NH$_2$ group can also induce favorable growth of some materials. As an example, SiO$_2$ was induced to grow within the gel forming SiO$_2$/polymer composite double-shelled hollow spheres. The surface becomes coarse (inset SEM image Fig. 5a) and the cavity becomes smaller after the introduction of silica. The crosslinked polymer network consisting of poly(DVB) can easily give carbon at high temperature. The corresponding SiO$_2$/carbon double-shelled hollow spheres were obtained by carbonization of the SiO$_2$/polymer composite hollow spheres in nitrogen at 800 °C for 2 h (Fig. 5b) with the eccentric morphology retained. The hollow spheres were
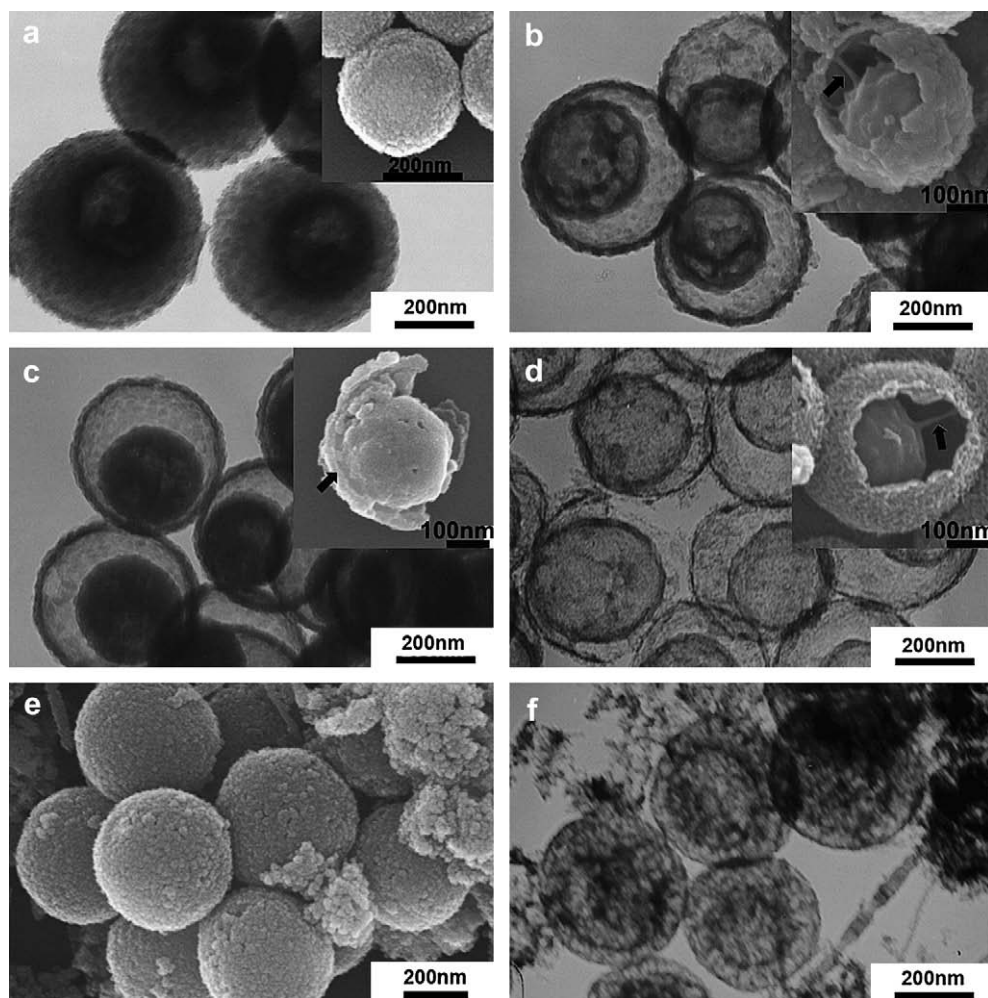
Fig. 5. Morphologies of some representative composite hollow spheres: (a) SiO$_2$/polymer composite eccentric double-shelled hollow spheres; (b) SiO$_2$/carbon double-shelled hollow spheres after calcination of the sample (Fig. 5a) at 800 °C in nitrogen for 2 h; (c) SiO$_2$ double-shelled hollow spheres after calcination of the sample (Fig. 5a) at 450 °C in air for 2 h; (d) carbon double-shelled hollow spheres after removal of silica with aqueous HF from the sample (Fig. 5b); (e) and (f) SEM and TEM images of the β-SiC eccentric hollow spheres.
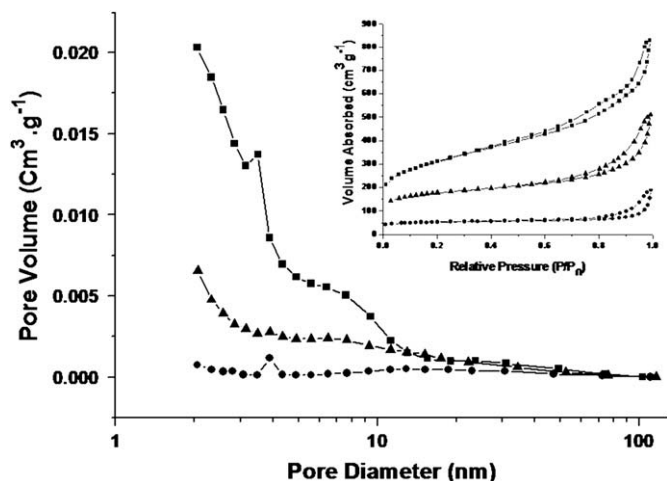
Fig. 6. Nitrogen adsorption/desorption isotherm (inset) and the corresponding pore size distribution of the eccentric double-shelled hollow spheres: ■ C, ▲ SiO$_2$, • SiO$_2$/carbon.

deliberately broken in order to observe the internal structure. Bridging the interior between the exterior shells there exist some pillars (inset SEM image Fig. 5b), which are formed by polymerization of the monomers within the transverse channels. In the presence of those pillars, the eccentric morphology is fixated to avoid the interior sphere to move inside the cavity. As comparison, no carbon hollow spheres were obtained from the polymer composite spheres without SiO$_2$. When the SiO$_2$/polymer composite hollow spheres were calcined at 450 °C in air to remove the polymer, the corresponding SiO$_2$ double-shelled hollow spheres were obtained (Fig. 5c) with the eccentric morphology retained. After removal of silica with aqueous HF from the SiO$_2$/carbon composite hollow spheres, the corresponding carbon hollow spheres were obtained (Fig. 5d). The shell thickness and diameter of the spheres before and after removal of SiO$_2$ are less changed, indicating that both SiO$_2$ and carbon are continuous within the shell. The carbon hollow spheres become highly porous at surface (inset Fig. 5d). Nitrogen isotherm analysis (Fig. 6) was used to further characterize the porosity. The BET specific surface area of the SiO$_2$/carbon hollow spheres is 170 m^2/g, while surface areas of the corresponding SiO$_2$ and carbon hollow spheres are 700 m^2/g and 1080 m^2/g, respectively. The SiC double-shelled
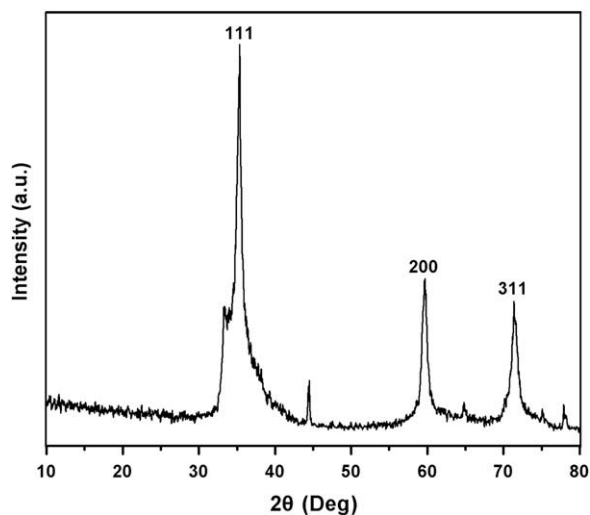
hollow spheres were further derived after the SiO$_2$/carbon composite double-shelled hollow spheres were carbonized at 1450 °C in argon for 2 h. The color changes from black to green. The as-prepared SiC double-shelled hollow spheres were further calcined in air at 700 °C to remove residual carbon, followed by a treatment with aqueous HF at ambient temperature to remove residual silica. Finally, the purified SiC double-shelled hollow spheres maintain their eccentric morphology (Fig. 5e, f). β-SiC form is confirmed by X-ray powder diffraction result (Fig. 7) [16]. The β-SiC hollow spheres remain stable in air at 700 °C, indicating they are potentially useful in fuel cells.

4. Conclusion

Eccentric polymer composite double-shelled hollow spheres were synthesized by swelling polymerization of a polymer hollow sphere. Polymerization induced phase separation is key to give the eccentric morphology. Alkaline groups for example –NH$_2$ was introduced by ammonization of the polyacrylate network, which can induce a favorable growth of other materials for example silica by a sol–gel process. Using DVB monomer for polymerization within the shell plays dual roles: (1) driving the phase separation during polymerization; (2) as a precursor of carbon. After carbonization, the corresponding carbon based composite eccentric double-shelled hollow spheres were derived for example SiO$_2$/C, carbon and β-SiC. The eccentric morphology is fixated by the pillars bridging both the shells formed within the transverse channels.

Acknowledgements

Appendix. Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.polymer.2009.06.008.

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Fig. 7. X-ray powder diffraction spectrum of the SiC double-shelled hollow spheres.

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