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ORIGINAL CONTRIBUTION

Template synthesis of hydrogel composite hollow spheres against polymeric hollow latex

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Abstract Hierarchically structured hydrogel hollow spheres with functional hydrogels located at desired sites are expected to have new properties. We have developed a facile swelling polymerization route using a polymer hollow sphere as template to synthesize hierarchically structured hydrogel hollow spheres. It is significant to pre-swell the template shell with good solvents, such as chloroform containing oil-soluble initiators to control interaction, thus, polymerization locus of different water-soluble functional monomers. Some representative hydrogel composite hollow spheres such as poly(*N*-isopropylarylamide) and poly(acrylic acid) with different morphologies have been synthesized. Hydrogels with functional groups can favorably complex with desired materials; hierarchically structured inorganic or polymer composite hollow spheres are synthesized by a sol–gel process of the inorganic precursor by using different hydrogel composite hollow spheres as templates.

Keywords Template synthesis · Hydrogel · Hollow spheres · Composite · Morphology control

Introduction

Hollow spheres have many potential applications in various fields such as artificial cells, light fillers, catalysis, and controlled delivery systems [1–4]. In comparison with traditional predecessors, the next generation counterparts—complex hierarchically structured hollow spheres—will provide new approaches toward complex structures with superior properties. For example, polymeric hollow spheres with movable gold nanoparticles filled in the interior cavity have been specialized as optical probes for monitoring diffusion of chemical reagents through the polymer shells [5]. A nanoparticle consisting of two concentric metallic nanoshells results in unique plasmon hybridization, allowing nanostructure engineering to tune resonance frequency [6]. Polyelectrolyte hollow capsules with a shell-in-shell structure possess enhanced mechanical and permeation stability compared to the one-shelled capsules [7–9].

It is interesting to synthesize such hollow spheres that consist of stimuli responsive hydrogels with desired functional groups. For instance, the thermo-responsive poly(*N*-isopropylarylamide) (PNIPAM) [10, 11] and pH responsive poly(acrylic acid) (PAA) have been exploited as the shell materials coating onto a core template to obtain the corresponding hollow spheres [12, 13]. So far, layer-by-layer-assisted templating is a major method to synthesize hydrogel hollow spheres, where desired materials are alternatively coated onto a preformed sphere. However, the procedure is time consuming in order to achieve a desired shell thickness, and the templates have to be removed to achieve hollow structures [14–17]. The arisen osmotic pressure during the core removal process sometimes causes the shell to crack or disintegrate. Recently, hollow spheres, e.g., vesicles from amphiphilic molecules have been used as templates, and polymerization of monomers is carried out within the shell forming composite hollow spheres [18, 19]. Unfortunately, this method only works for a few specific monomers owing to a strong polymerization-induced phase separation especially within the rather weak thin shell.

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Herein, we report a general swelling polymerization route for the synthesis of hydrogel hollow spheres by using polymeric hollow spheres as templates and water-soluble monomers as precursors of desired functional hydrogels. The hollow spheres (OP-96) are commercially available from Rhom and Haas, which are mainly composed of a polystyrene shell with nanosized transverse hydrophilic poly (methyl-methacrylate)–poly(methacrylic acid) (PMMA–PMA) channels (Fig. 1a). The average diameter is 450 nm and the shell thickness is about 80 nm. The small transverse channels cannot be discerned owing to a low electron-transmission contrast (Fig. 2a). It is significant that the thick shell of the template hollow spheres assures a well-retained spherical contour of the composite spheres. Polymerization in desired location leads to hierarchically structured composite hydrogel spheres, which is controlled by pre-swelling the shell with chloroform. An oil-soluble initiator is, thus, introduced within the template shell to restrict the polymerization location. Chloroform, as a selective solvent within the shell, can influence the loci of monomers and polymerization, providing a new chance to control morphology of the composite spheres.

Experimental

Samples synthesis

Materials

N,*N*-isopropylacrylamide (NIPAM, 99%) was obtained from J & K Chemical LTD. (ar-Vinylbenzyl) trimethylammonium (VBA, 99%) and 4-styrenesulfonic acid sodium salt hydrate (NaSS, analytical grade) were purchased from Sigma–Aldrich Co. (St. Louis, MO, USA). Tetrabutyl titanate (TBT, chemical pure), *N*,*N*’-dimethylformamide (DMF, analytical grade) and *N*,*N*’-methylene bis(acrylamide) (BIS, 99%), Hydrochloric acid (HCl, analytical grade) were obtained from Beijing Chemical Reagents Company. Sodium dodecyl sulfate (SDS), Poly(vinyl alcohol) (PVA) and acrylic acid (AA) were purchased from Beijing Xingli Fine Chemicals LTD. Benzoyl peroxide (BPO) was obtained from Beijing Jinlong Chemicals LTD. Template hollow spheres HP-433 were obtained from Rhom & Haas Company. All the chemicals were used as received except for AA, which was purified by vacuum distillation prior to use.

BPO or chloroform-swollen template hollow spheres

A solution of 0.04 g of BPO in 2 g of chloroform was emulsified in 110 g of an aqueous solution containing 10 g of PVA and 0.1 g of SDS under sonication forming an O–W dispersion. In a 250-ml three-necked flask fitted with a paddle with Teflon rod and a condenser, 4 g of freeze dried powder of hollow sphere HP-433 was mixed with the above dispersion under stirring at ambient temperature for 6 h, the shell of the hollow spheres was swollen with BPO or chloroform solution.

Synthesis of hydrogel composite hollow spheres

(1) A desired amount of NIPAM and BIS with different weight ratio was dissolved in the above-swollen dispersion at ambient temperature. After the dispersion was degassed with nitrogen, the system was heated to 80 °C to initiate the polymerization for 6 h. Two representative composite spheres: NIPAM(0.5)–BIS(0.5) and NIPAM(0.5) were synthesized (The numbers represent weight ratio of the monomers to template sphere). After the template polymer

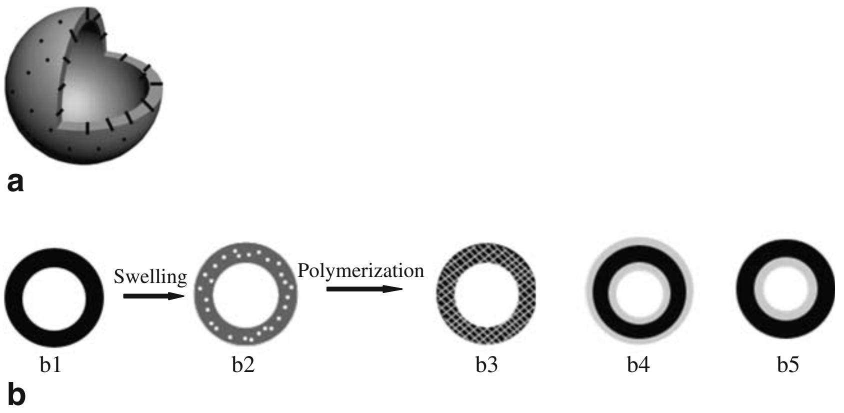


Fig. 1 **a** Three-dimensional model of the template spheres, which are mainly composed of a polystyrene shell with nanosized transverse hydrophilic poly (methyl-methacrylate)–poly (methacrylic acid) (PMMA–PMA) channels. **b** Schematic synthesis of hydrogel composite hollow spheres: *b1* polystyrene template hollow sphere; *b2* swollen hollow sphere with BPO or chloroform solution; *b3–5* hydrogel composite hollow spheres with different morphologies: *b3* within the shell forming IPN structure (NIPAM, NIPAM–BIS, AA–BIS); *b4* mainly onto both the interior and exterior shell surfaces (BIS); *b5* only onto the interior shell surface (BIS–NaSS)

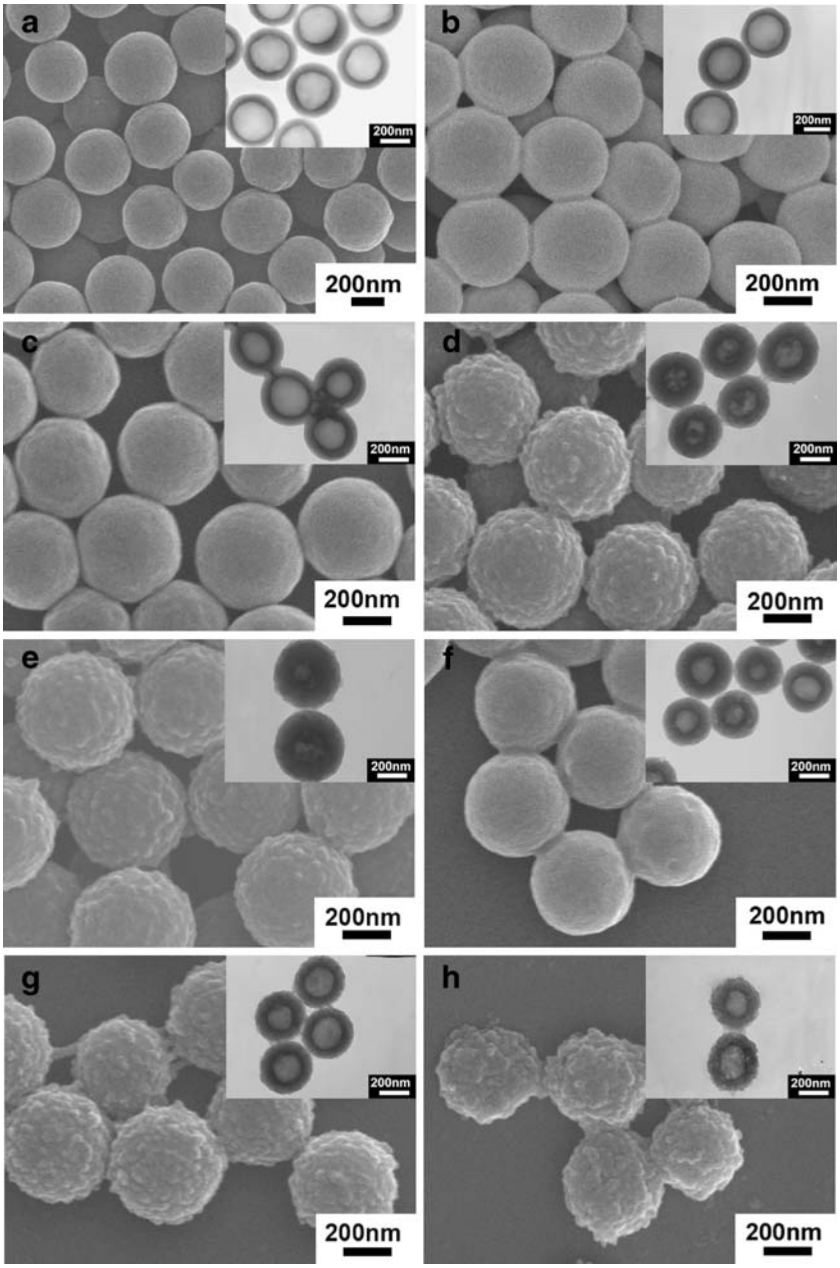


Fig. 2 SEM images with *inset* TEM images of some representative spheres: **a**, **b** template hollow spheres before and after being swelled by chloroform; **c** NIPAM(0.5) composite hollow spheres; **d**, **e** cross-linked NIPAM(0.5)–BIS(0.5) composite hydrogel hollow spheres before and after the template is dissolved with DMF; **f** AA (0.8)–BIS(0.2) composite hollow spheres; **g**, **h** cross-linked AA(0.5)–BIS(0.5) composite hydrogel hollow spheres before and after the template is dissolved with DMF

was dissolved with DMF, the corresponding hydrogel spheres were achieved. (2) Similarly, two representative polyacrylic acid composite hollow spheres: AA(0.5)–BIS (0.5) and AA(0.8)–BIS(0.2) were obtained. PH was adjusted to 4 with HCl before heating the system. (3) Along the similar procedure, a representative composite hollow sphere BIS(0.5) was obtained. Poly(BIS) composite hollow sphere BIS(0.5)–NaSS(0.5) was synthesized using the mixture of 2 g of BIS and 2 g of NaSS instead of pure BIS. (4) PVBA composite hollow sphere was synthesized using a mixture of 2 g of VBA and 2 g of BIS. All the obtained dispersions of composite spheres were washed by water several times and then dispersed in ethanol for further characterizations.

Polymer or titania composite spheres

A typical procedure was given as following: 0.5 g of dried AA(0.5)–BIS(0.5) composite hollow sphere was dispersed in 20 ml of 0.5 M aqueous hydrochloric acid under stirring at 70 °C overnight for a further hydrolysis of polyacrylate. The hydrolyzed composite hollow sphere was washed with water until pH~7. 0.1 g of dried, hydrolyzed composite hollow sphere was dispersed in 5 ml of TBT under stirring for 24 h. The TBT-absorbed sphere was separated by centrifugation and washed with ethanol to remove extra TBT from outside the sphere. The sphere was dispersed in 10 ml of ethanol; 10 ml of water was added into the ethanol dispersion under stirring to allow a sol–gel process of TBT at ambient temperature for 4 h. The synthesized composite sphere was centrifugated and washed with ethanol and water for further characterization.

Characterization

Morphology of the spheres was characterized using transmission electron microscopy (JEOL 2011 at 200 kV) and scanning electron microscopy (SEM; HITACHI S-4300 at 15 kV). The ambient-dried samples were sputtered with Pt in vacuum for SEM observation. Very dilute ethanol dispersions were spread onto carbon-coated copper grids for transmission electron microscopic (TEM) observation. Fourier transform infrared (FTIR) spectroscopy was performed using a Bruker Equinox 55 spectrometer with the samples or KBr pressed pellets. The average hydrodynamic radius of the hydrogel composite hollow spheres was determined using a laser light scattering spectrometer (ALV Co., Germany) with an ALV-5000 digital time correlator and a Helium–Neon laser (Model 127, output power of 40 mW with the wavelength at 632.8 nm). The sample cell was equipped with an oil bath with a temperature accuracy of ±0.1 °C. The measurements were carried out at a fixed angle of 90°.

Results and discussion

The synthesis procedure is illustrated in Fig. 1. The shell of the template hollow spheres is firstly swollen with BPO or chloroform solution at ambient temperature, whose morphology is less influenced (Fig. 2a,b). At a high temperature, BPO starts to decompose forming free radicals within the shell; the monomers dissolved in aqueous continuous phase will be initiated for polymerization to start from interface. Under controlled conditions, polymerization-induced phase separation will finally determine different loci of polymers. It should be noticed that the template shell is mainly polystyrene with PMMA–PMA hydrophilic channels across the shell [20, 21]. Accordingly, different morphologies are achieved when polymeric hydrogel is preferentially formed in different regions: (1) only within the shell; (2) onto both the exterior and interior surfaces of the shell; (3) only onto the internal surface. The interaction between monomer precursors and the swelling agent chloroform will greatly affect the morphology of derived hollow spheres. For those monomers that can swell the PS shell or are soluble in chloroform, they can be easily introduced within the PS shell of the hollow sphere template. Therefore, morphology of the template is transcribed, thus, deriving single-shelled hollow spheres. For those water-soluble monomers, they cannot penetrate the PS shell matrix. After being polymerized, the polymers will be precipitated onto both the interior and exterior surfaces of the PS shell. Thus, double-shelled hydrogel hollow spheres will be derived after the templates are dissolved. For those negatively charged monomers, they can be repelled by both template sphere surface and the charged channels so they can be further used to control morphology of hydrogel hollow spheres. The hydrogel region with specific functional groups can be transcribed by a favorable sol–gel process of TBT forming titania composite hollow spheres, meanwhile the hydrogel locus is determined thereby [22]. Traditional removal of template core is avoided to prepare hollow spheres.

Although NIPAM is water soluble at ambient temperature, the monomer will become hydrophobic, thus, can enter the hydrophobic shell during polymerization at a high temperature 80 °C. The hydrophobic free radicals formed by thermolysis of BPO start to initiate the polymerization dominantly within the shell, leading an interpenetration network with the shell (Fig. 2c). Hollow cavity becomes slightly smaller but remains clearly distinct. The composite shell becomes thicker, revealing that NIPAM is also formed onto both the exterior and interior shell surfaces besides within the shell. PNIPAM was not dissolved from the PS template although no cross-linkers were used. This is probably related to the self-cross-linking through chain transfer reaction [23, 24]. However, the self-cross-linking degree is not high enough to retain the spherical morphology after the removal of the templates. Alternatively, a cross-linker BIS was introduced to make the hydrogel more robust; cross-linked PNIPAM composite hollow spheres were synthesized (Fig. 2d). The surface becomes rather coarse. The cavity size decreases remarkably, and the shell becomes much thicker, meaning polymer are also formed onto interior surface. After the template was dissolved, the corresponding PNIPAM hollow spheres can well preserve their spherical contour even after being dried at ambient temperature (Fig. 2e). The existence of PNIPAM was confirmed by FTIR spectroscopy results (Fig. 4b for NIPAM(0.5), Fig. 4c for NIPAM(0.5)–BIS(0.5)).

Polyacrylic acid, a pH responsive hydrogel hollow sphere will also be promising. The monomer acrylic acid can be mixed with chloroform at any ratio. Because pKa of AA is 4.6, PH value of the reaction was adjusted to 4 to assure the monomers will not be ionized, which will facilitate the monomer to preferentially penetrate into the swollen shell. In the absence of cross-linker, because linear poly(acrylic acid) would be washed away by water, no composite spheres containing linear PAA are synthesized. This has been confirmed by the absence of PAA in the

FTIR spectrum. BIS was also used as cross linker here [25]. At a low level of BIS, for example 25% in respect to acrylic acid, the exterior surface of the composite sphere is smooth (Fig. 2f). After the template was dissolved with DMF, the corresponding hydrogel shell cannot preserve contour. When BIS content was increased, for example to 50%, the exterior surface becomes coarse (Fig. 2g), meaning the hydrogel has also formed onto the shell exterior surface. After the template was dissolved, a cross-linked PAA hydrogel sphere with a single shell was obtained (Fig. 2h). The presence of PAA was confirmed by FTIR results (Fig. 4d for AA(0.8)–BIS(0.2), Fig. 4e for AA(0.5)–BIS(0.5)).

Functional hydrogel containing polyacrylic acid groups can be derived from PBIS via a simple hydrolysis. Because chloroform is a poor solvent for BIS, monomer BIS is prohibited to exist in the chloroform-swollen PS shell matrix. Thus, the polymerization predominantly occurred at the interfaces leading to a sandwiched composite shell (Fig. 3a). After the template locating in middle layer was dissolved, a shell-in-shell PBIS hollow sphere was derived (Fig. 3b). The inner layer collapsed into an individual eccentric hollow sphere due to the absence of the PS shell support. After being hydrolyzed, polyacrylate was transformed into polyacrylic acid. This has been confirmed by FTIR spectroscopy results (Fig. 4f).

Hollow spheres with functional groups inside the cavity are interesting as confined reactors. It is rational to avoid growth of polymers onto exterior surface. A negatively monomer NaSS is selected to play two roles:(1) NaSS poorly dissolved in chloroform will be copolymerized with BIS forming water-soluble polymers [26]; (2) there exists an electrostatic repulsion between the template surface and the polymers with the same negative charges. As a result, the copolymers are mainly formed in continuous phase, which can be removed by centrifugation. The negatively charged monomer NaSS cannot penetrate inside thorough the negatively charged channels due to the electrostatic repulsion, while the polymerization of BIS onto the interior surface is not influenced. The exterior surface of the composite hollow spheres is smooth (Fig. 3c), meaning that no polymers are formed onto the exterior surface. The cavity becomes much smaller, meaning polymers are predominantly formed onto the interior surface. It is also interesting to find that there exists another smaller hollow sphere inside the cavity, indicating that some BIS has polymerized there. After the template was dissolved, the whole particle size is comparable with the PS hollow sphere cavity (Fig. 3d), and the smaller hollow sphere is more clearly to distinguish. No NaSS polymer was detected in the hollow spheres by FTIR spectroscopy (Fig. 4g). As a comparison, when a positively charged monomer VBA was used instead of NaSS, PVBA was polymerized both within the shell and onto the two shell surfaces. Unfortunately, the spheres were heavily aggregated due to opposite charge interaction (Figs. S1a,b). The element chlorine was detected by element analysis. This has verified the key role of charged monomers in morphology control.

Two representatives, PNIPAM and PAA composite hollow spheres, were characterized for their responsive behavior using dynamic light scattering. After temperature was increased from 20 °C to 45 °C in a neutral aqueous, the

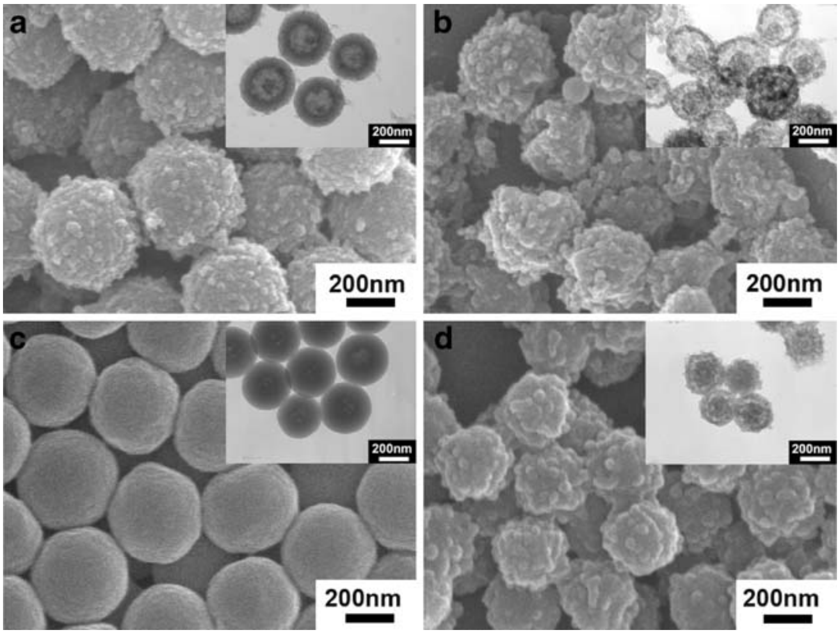


Fig. 3 SEM images with *inset* TEM images of some representative spheres: **a**, **b** the cross-linked BIS(0.5) composite hollow spheres before and after the template is dissolved with DMF; **c**, **d** the cross-linked BIS (0.5)–NaSS(0.5) composite hydrogel hollow spheres before and after the template is dissolved with DMF

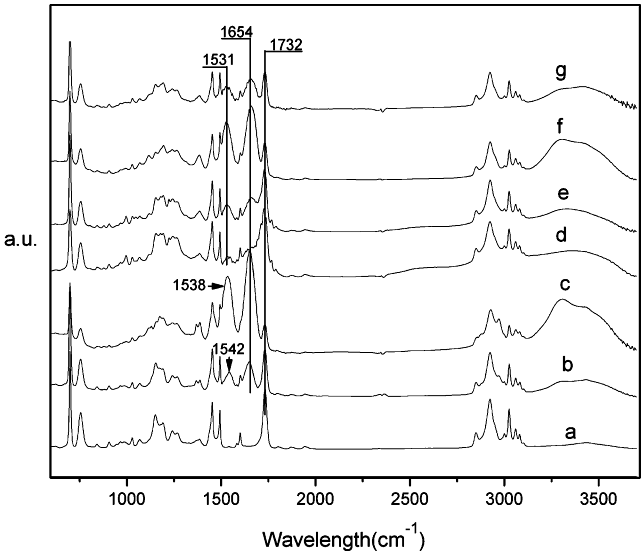
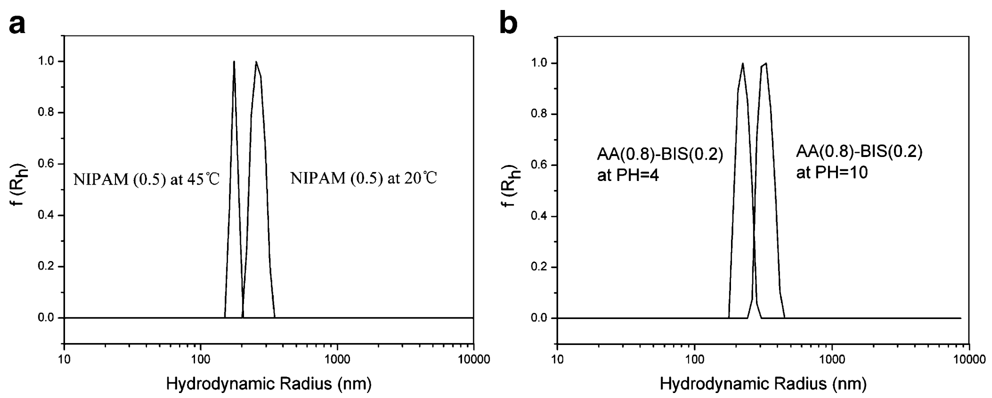


Fig. 4 FTIR spectra of some representative samples: *a* the template hollow sphere HP-433; *b* NIPAM(0.5) composite hydrogel hollow sphere; *c* the cross-linked NIPAM(0.5)–BIS(0.5) composite hydrogel hollow sphere; *d* the cross-linked AA(0.8)–BIS(0.2) composite hydrogel hollow sphere; *e* the cross-linked AA(0.5)–BIS(0.5) composite hydrogel hollow sphere; *f* the cross-linked BIS(0.5) composite hydrogel hollow sphere; *g* the cross-linked BIS(0.5)–NaSS(0.5) composite hydrogel hollow sphere. The characteristic bands at 1,732 cm^{-1} are assigned to the carbonyl group of AA; the bands at 1,654 and 1,542 cm^{-1} of (*b*) are assigned to the carbonyl and C–N groups of NIPAM; the bands at 1,654 and 1,531 cm^{-1} are assigned to the carbonyl and C–N groups of BIS; the characteristic bands at 1,652 and 1,538 cm^{-1} of (*c*) are resulted from overlapping between NIPAM and BIS

hydrodynamic radius of NIPAM(0.5) composite hollow sphere (Fig. 5a) decreases from 264 to 176 nm, equivalent of 33% change. When temperature decreased to 20 °C, the radius increases to 245 nm, indicating a reversible response. It is noticed that PNIPAM has been restricted within the rigid PS matrix; the remarkable radius change is likely related to the surface layer of PNIPAM. When BIS was introduced, although the surface PNIPAM becomes thicker, the radius change becomes smaller because the PNIPAM network is highly cross-linked. For example, the NIPAM (0.5)–BIS(0.5) composite hollow sphere size decreases from 302 to 269 nm, equivalent of 11% change. The cross-linked PNIPAM hollow sphere without the template also experiences a small radius change from 306 to 259 nm, equivalent of 15% change. Polyacrylic acid composite spheres are pH responsive. Comparing AA(0.8)–BIS(0.2) sphere with AA(0.5)–BIS(0.5), the former underwent a much higher radius change at two representative pH values PH=4, 10 at ambient temperature (Fig. 5b).

A series of hydrogel composite hollow spheres with different hierarchical structures have been synthesized. They can be further used as templates to induce a favorable growth of other materials within the hydrogel loci by specific interactions. As a proof of the concept, a series of titania composite spheres with varied morphology were synthesized by a favorable sol–gel process of TBT using different templates because acid groups can catalyze the sol–gel process [22]. Three representative polyacrylic acid composite spheres: AA–BIS, BIS, NaSS–BIS were used to control location of the grown titania. AA(0.8)–BIS(0.2) composite hollow sphere, as shown in Fig. 2f, was used to template synthesis of titania; a smaller hollow titania sphere was formed inside the cavity of the composite template hollow sphere (Fig. 6a). For BIS polymer, polyacrylic acid was derived by acid hydrolysis, which has been confirmed by FTIR spectroscopy (Fig. S3) [27]. The surface of AA (0.5)–BIS(0.5) composite spheres after being hydrolyzed becomes slightly porous and smooth compared with the original ones (Fig. S2a). After a sol–gel process of TBT, the surface pores are filled with titania with the surface roughness increased. The shell becomes thicker and the cavity size decreases remarkably (Fig. 6b). After the template was removed by dissolution, hollow titania spheres were obtained with a smaller cavity even collapsed to solid one (Fig. 6c). For hydrolyzed BIS(0.5) composite hollow spheres (Fig. S2b), both interior and exterior shell

Fig. 5 Particle size distribution of the hydrodynamic radius: **a** NIPAM(0.5) composite hollow spheres at neutral pH; **b** AA(0.8)–BIS(0.2) composite hollow spheres at ambient temperature



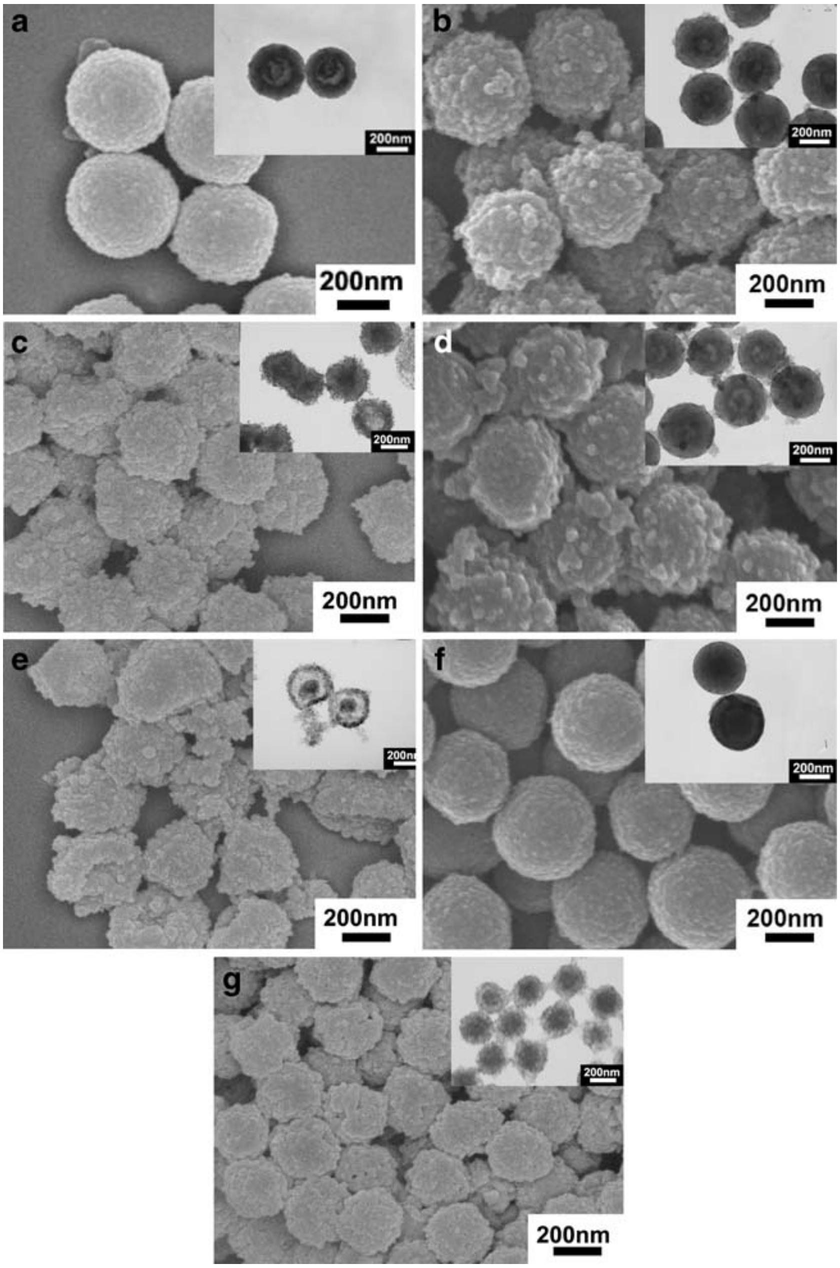


Fig. 6 SEM images with *inset* TEM images of some representative spheres after being complexed with titania: **a** the cross-linked AA(0.8)–BIS (0.2) composite hydrogel hollow spheres after being complexed with titania; **b**, **c** the hydrolyzed AA(0.5)–BIS(0.5) composite hydrogel hollow spheres complexed with titania before and after the template is removed with DMF; **d**, **e** the hydrolyzed BIS(0.5) composite hydrogel hollow spheres complexed with titania before and after the template is removed with DMF; **f**, **g** the hydrolyzed BIS(0.5)–NaSS(0.5) composite hydrogel complexed with titania before and after the template is removed with DMF

surfaces are polyacrylic acid. After titania was formed, the exterior surface becomes more coarse and the cavity size decreases (Fig. 6d). A shell-in-shell structure was achieved after the template was removed (Fig. 6e), revealing that titania has transcribed the morphology of PBIS hydrogel. Because PBIS only exists on the interior surface of the shell of BIS(0.5)–NaSS(0.5) hollow spheres (Fig. S2c), the correspondingly derived polyacrylic acid groups after being hydrolyzed can induce a preferential growth of titania, thereby forming the composite spheres (Fig. 6f). After the template was dissolved, titania spheres were obtained, whose particle size is comparable with the cavity of the templates (Fig. 5g).

Conclusion

Hierarchically structured hydrogel composite hollow spheres have been template-synthesized using a polymer hollow sphere aqueous dispersion. Pre-swelling the shell by solvent chloroform can significantly influence interaction and phase behavior during polymerization, thus, controlling growth locus of hydrogels. Especially, an oil-soluble initiator BPO is also preloaded within the shell, which can further facilitate controlling formation locus of hydrogels. Because hydrogels with specific groups can favorably complex with desired materials, growth of functional materials can be controlled at desired sites when such structured hydrogel composite spheres with different morphologies are used. As a proof of the concept, titania or polymer composite hollow spheres with different morphologies are derived.

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