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Facile synthesis of silica/polymer hybrid microspheres and hollow polymer microspheres

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Abstract

Monodisperse silica/polydivinylbenzene (SiO_2/PDVB) and silica/poly(ethyleneglycol dimethacrylate) (SiO_2/PEGDMA) core–shell hybrid microspheres were prepared by a two-stage reaction with silica particles' grafting of 3-(methacryloxy)propyltrimethoxysilane (MPS) as core and PDVB or PEGDMA as shell, in which the MPS-modified silica core with diameter of 238 nm was synthesized by Stöber method and subsequently grafted with MPS as the first-stage reaction. The PDVB or PEGDMA shell was then encapsulated over the MPS-modified silica core by distillation precipitation polymerization of divinylbenzene (DVB) or ethyleneglycol dimethacrylate (EGDMA) in neat acetonitrile with 2,2′-azobisisobutyronitrile (AIBN) initiator as the second-stage reaction. The encapsulation of PDVB and PEGDMA on modified silica core particles was driven by the capture of DVB or EGDMA oligomer radicals via the vinyl groups on the surface of the modified silica cores during the second-stage polymerization in the absence of any stabilizer or surfactant. The shell thickness of the core–shell hybrid particles was controlled by the feed of DVB or EGDMA monomer during the polymerization. Hollow PDVB or PEGDMA microspheres with various shell thickness were further developed after selective removal of the modified silica cores with hydrofluoric acid. The resultant core–shell hybrid materials and hollow microspheres were characterized by transmission electron microscopy (TEM), and Fourier transform infrared spectra (FT-IR).

Keywords: Inorganic–organic hybrid microsphere; Distillation precipitation polymerization; Hollow microsphere

1. Introduction

During the last two decades, the inorganic/polymer hybrid materials have attracted increasing interest for the researchers both in academic and engineering fields because these new materials combine the advantages of the organic polymer matrix having the facile process-ability, flexibility and the various functional groups, together with the properties of the inorganic particles in terms of mechanical strength, modulus, and thermal stability. These hybrid materials may exhibit novel and excellent properties, such as mechanical, chemical, electrical, rheological, magnetic, optical and catalytic, by altering the compositions, dimensions and structures of the components, which have promised many applications such as drug delivery system, diagnostics, coatings and catalysis [1–8].

Silica particles, which can be conveniently prepared by the hydrolysis of organic-silicate via a sol–gel process, have wide applications in many fields including cosmetics, printing and electronic industries. However, these particles tend to coagulate due to their high surface energy and polycondensation of their surface hydroxyl groups. Therefore, it is necessary to prevent such coagulation as silica/polymer hybrid particles with modification of the surface property originating from the polymer component. The synthesis of the silica/polymer hybrid particles can be generally classified into two categories: the self-assembly of the resultant silica and polymer particles via physical or physicochemical interaction, and direct polymerization of monomer on the surface of silica particles. The silica/polymer hybrid particles with various interesting morphologies have been prepared, including core–shell

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microspheres [9,10], raspberry-like [11], snowman-like [12], daisly-shaped and mutipod-like [13], and raisinbun-like [14]. Dispersion polymerization has been used to prepare the silica/polymer hybrid particles, in which the vinyl groups were introduced by 3-(trimethoxysilyl) propyl methacrylate on the surface of the silica seeds [15–17]. Bourgeat-Lami et al. [18] synthesized silica/poly(methyl methacrylate) nanocomposite particles by emulsion polymerization with a cationic initiator 2,2′-azobis(isobutyraidine) dihydrochloride (AIBA·2HCl) in the presence of a non-ionic polyoxyethylenic surfactant. However, it was difficult to control the morphology of the resultant silica/polymer hybrid particles and the encapsulation efficiencies of the polymer on the silica core were much low for both dispersion polymerization [15–17] and emulsion polymerization [19]. Surface-initiated atom transfer radical polymerization (ATRP) technology has been utilized to synthesize well-defined silica/polymer core–shell hybrids with the initiator-modified silica particles as macroinitiator [19–21], in which the synthesis needed long reaction time and conversion of monomer to polymer was low.

Recently, polymer hollow microspheres have attracted much attention for their wide applications, such as encapsulation for controlled-release of drugs and enzymes, fillers, pigments, catalysts, and adsorption materials for sound [3,22–25]. A variety of physical and chemical techniques have been reported for the synthesis of polymer hollow microspheres. Voided particles were obtained by emulsion polymerization via encapsulation of a hydrocarbon non-solvent, which was a complicated process controlled by a number of convoluted, thermodynamic and kinetic factors [26]. Electrostatic interaction as a driving force was only suitable for layer-by-layer assembly of polymer electrolytes [26,27]. Micelle formation of block copolymer afforded hollow polymer microspheres, which needed delicate design of block copolymer with UV-crosslinking of the shell-layer and subsequent tedious ozonolysis of core [27]. Hollow polymer microspheres were prepared by surface-initiated ATRP of styrene with subsequent UV-treatment for shell-crosslinking, which involved complex and tedious processes for synthesis [28].

In our previous work, distillation precipitation polymerization has been developed as a facile and powerful technique for the preparation of monodisperse poly(divinylbenzene) (polyDVB) [29], poly(ethyleneglycol dimethacrylate) (polyEGDMA) [30], poly(*N*,*N*′-methylenebisacrylamide) (polyMBAAm) [31] and other polymer microspheres with various functional groups [32–34]. More recently, we reported the synthesis of monodisperse silica/polyMBAAm core–shell composites with regular shape by distillation precipitation polymerization of MBAAm in neat acetonitrile with silica particles as seeds, in which the hydrogen-bonding interaction between the active hydroxyl groups on the surface of the silica particles and the amide groups of MBAAm played a key role for efficient encapsulation of polyMBAAm over the silica cores [35]. In the present work, we describe the preparation of monodisperse silica/polyDVB and silica/polyEGDMA core–shell hybrid microspheres by encapsulation of the MPS-modified silica cores during the distillation precipitation polymerization of divinylbenzene (DVB) or ethyleneglycol dimethacrylate (EGDMA) in neat acetonitrile in the absence of any stabilizer or surfactant. Further, the corresponding polyDVB and polyEGDMA hollow microspheres having a well-defined size and controlled shell thickness were developed after selective removal of the silica core in hydrofluoric acid.

2. Experimental

2.1. Chemicals

Tetraethyl orthosilicate ($Si(OEt)_4$, TEOS)) was purchased from Aldrich and used without any further purification. 3-(Methacryloxy)propyltrimethoxysilane (MPS) was available from Aldrich and distilled under vacuum. Divinylbenzene (DVB, 80% divinylbenzene isomers) was supplied as technical grade by Shengli Chemical Technical Factory, Shandong, China) and was washed with 5% aqueous sodium hydroxide and water, then dried over anhydrous magnesium sulfate prior to use. Ethyleneglycol dimethacrylate (EGDMA) was of chemical grade from Alfa Aesar and used without any purification. 2,2′-Azobisisobutyronitrile (AIBN) (analytical grade from Chemical Factory of Nankai University) was recrystallized from methanol. Hydrofluoric acid (HF, containing 40% of HF) was available from Tianjin Chemical Reagent Institute. Acetonitrile (analytical grade, Tianjin Reagents II Co.) was dried over calcium hydride and purified by distillation before use. All the other reagents were analytical reagents and used as received without any further purification.

2.2. Synthesis of MPS-modified silica microspheres

Silica microspheres were prepared according to the classical Stöber method [36]: 12 mL of TEOS was added to the mixture of 200 mL ethanol, 20 mL de-ionized water and 15 mL aqueous solution of 25% ammonium with vigorous stirring at room temperature and the reaction was continued further for 24 h with stirring. The MPS-modified silica microspheres were afforded by coupling silica alcosol particles according to the literature [15]: excess MPS (1.0 g, 4.0 mmol) was introduced into 20 mL of the silica mixture under stirring in a 50 mL round-bottom flask. Coating of silica particles with MPS was achieved by stirring the mixture of alcosol silica particles and MPS for 48 h at room temperature. The resultant MPS-modified silica particles were purified by three cycles of centrifugation, decantation, and resuspension in ethanol with ultrasonic-bathing. The MPS-modified silica particles were dried in a vacuum oven at 50 °C till constant weight.

2.3. Preparation of silica/polyDVB hybrid microspheres

The MPS-modified silica core particles were prepared as described above for the further polymerization to afford silica/polymer core–shell hybrid microspheres. A typical procedure for the distillation precipitation polymerization was as following: 0.10 g of MPS-modified silica microspheres were suspended in 40 mL of acetonitrile as a white suspension in a 50 mL two-necked flask under ultrasonic-bathing. Then DVB (0.40 mL, 0.37 g, as 1.0 vol% of the reaction system) together with AIBN initiator (0.008 g, 2 wt% relative to DVB monomer) were dissolved in the suspension. The two-necked flask attached with a fractionating column, Liebig condenser and receiver was then submerged in a heating mantle. The reaction mixture was heated from ambient temperature till the boiling state within 15 min and the reaction mixture was kept under reflux state for further 10 min. The white color was deepened during the heating and the solvent was then distilled off the reaction system. The reaction was stopped after 20 mL of acetonitrile was distilled from the reaction system within 70 min. After the polymerization, the resultant silica/polyDVB core–shell hybrid microspheres were purified by repeated centrifugation, decantation, and resuspension in acetone with ultrasonic-bathing for three times. The hybrid particles were finally dried in a vacuum oven at 50 °C till constant weight.

The other distillation precipitation polymerizations were much similar to that of the typical procedure by varying the DVB feed in the range of 0.20–0.40 mL, while the amount of AIBN initiator was maintained at 2 wt% relative to the monomer. The treatment of the resultant silica/polyDVB core–shell hybrids was the same as that for the typical process.

2.4. Preparation of silica/polyEGDMA core–shell hybrid microspheres

The basic preparation procedure used for silica/polyEGDMA was very similar to that described above for silica/polyDVB hybrids and involved altering the monomer from DVB to EGDMA, while the monomer loading was varied in the range of 0.20–0.50 mL and AIBN initiator was kept at 2 wt% corresponding to the EGDMA monomer. The reaction mixture was heated from ambient temperature till the boiling state within 8 min and the reaction system was kept under reflux state before distilling the solvent out of the reaction mixture. The white color was deepened during the heating process and the reaction was stopped after 20 mL of acetonitrile was distilled off the reaction system within 35 min. The treatment of silica/polyEGDMA hybrid particles was the same as that for the typical procedure of silica/polyDVB hybrids.

The reproducibility of the polymerizations was confirmed through several duplicate and triplicate experiments.

2.5. Synthesis of hollow polyDVB and polyEGDMA microspheres

The resultant silica/polyDVB and silica/polyEGDMA core–shell hybrid microspheres were immersed in 40% HF solution for 2 h. Then the excess HF and newly formed SiF_4 were expelled out of the polymer microspheres by several centrifugation/washing cycles in water till the pH of 7. The resultant polyDVB and polyEGDMA hollow microspheres were dried in a vacuum oven at 50 °C till constant weight.

2.6. Characterization

The size, size distribution and morphologies of MPS-modified silica core, silica/polyDVB, silica/polyEGDMA core–shell microsphere, the corresponding polyDVB and polyEGDMA hollow microspheres were characterized by transmission electron microscopy (TEM, Tecnai G2 20 S-TWIN). All the size and size distribution reflect the averages of about 100 particles each, which are calculated according to the following formula:

$$U = D_w/D_n \quad D_n = \sum_{i=1}^{k} n_i D_i \Big/ \sum_{i=1}^{k} n_i \quad D_w = \sum_{i=1}^{k} n_i D_i^4 \Big/ \sum_{i=1}^{k} n_i D_i^3$$

where, U is the polydispersity index, D_n is the number average diameter, D_w is the weight-average diameter, D_i is the diameter of the determined microspheres.

Fourier transform infrared analysis was performed on a Bio-Rad FTS 135 spectrometer with scanning over the range of 400–4000 cm^{-1}.

3. Results and discussion

Monodisperse MPS-modified silica microspheres were prepared from the hydrolysis of siloxane TEOS via a sol–gel process having active hydroxyl groups with the successive coating of MPS to incorporate the reactive vinyl groups on the surface [15]. The TEM micrograph of MPS-modified silica microspheres as shown in Fig. 1A indicated that these particles had spherical shape and smooth surface with an average size of 238 nm and monodispersity index (U) of 1.012. The modification of the silica microspheres by further hydrolysis of MPS with the aid of surface hydroxyl groups on the surface of silica particles was confirmed by FT-IR spectra as shown in Fig. 2a, which displayed the bands at 1632 and 1699 cm^{-1} corresponding to the stretching vibrations of the vinyl groups and carbonyl groups of MPS component, respectively. These reactive vinyl groups would permit the growth of the silica particles by radical capture of the newly formed oligomers and monomers during the second-stage distillation precipitation polymerization to result in silica/polymer core–shell hybrid microspheres. The detailed procedures for the preparation of silica/polymer hybrid particles and the corresponding hollow polymer microspheres are illustrated in Scheme 1.

3.1. Silica/polyDVB core–shell hybrid microspheres

The formation of monodisperse polyDVB [29] and poly(EGDMA) [30] indicated that acetonitrile met the solvency condition requirement for such polymerizations, during which acetonitrile dissolved the monomer used but precipitated the resultant polymer network. The residual reactive vinyl groups on the surface of polyDVB cores were essential to obtain monodisperse core–shell functional microspheres by two-stage precipitation polymerization [38], in which the newly formed oligomers and monomers were captured by these

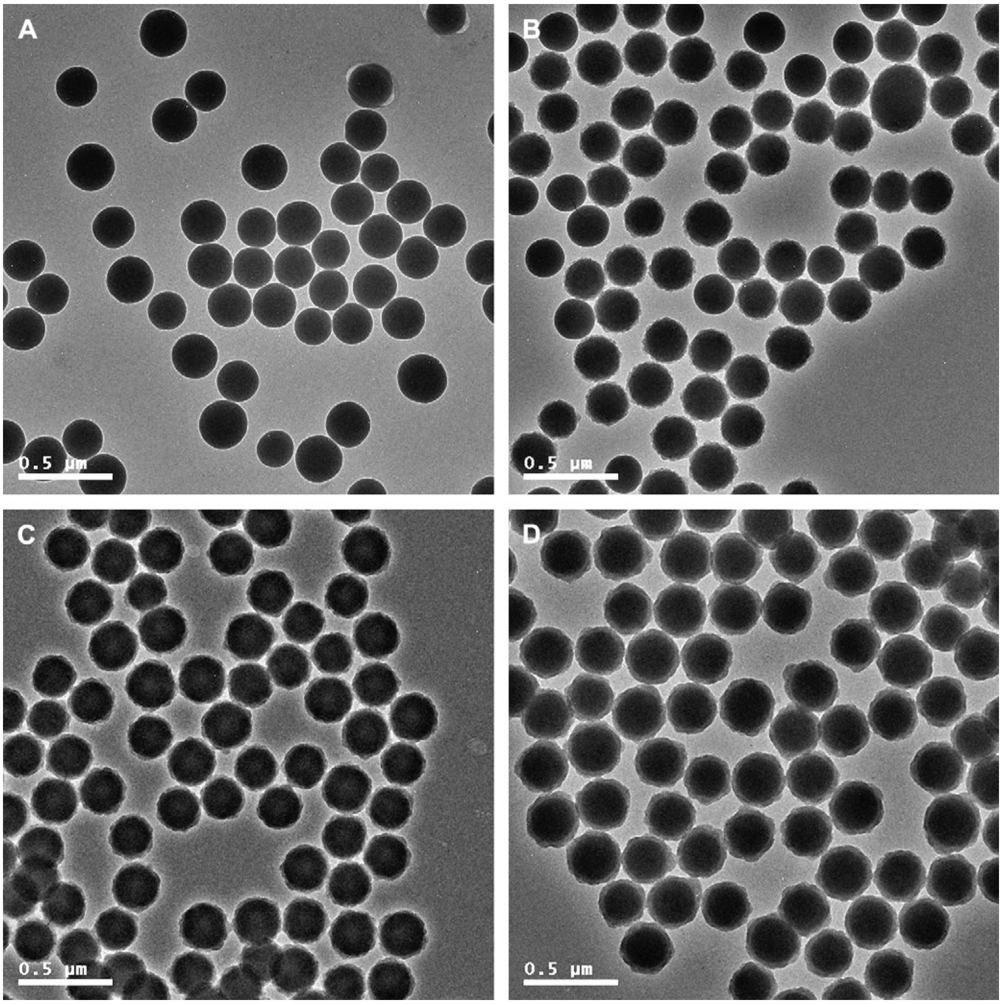


Fig. 1. TEM micrographs of silica/polyDVB microspheres with different DVB feed during polymerization: (A) APS-modified silica particles; (B) 0.2 mL; (C) 0.3 mL; (D) 0.4 mL. Reaction conditions: 40 mL of acetonitrile and AIBN as initiator of 2 wt% relative to the monomer.

reactive vinyl groups in the absence of any second-initiated small particles during the second-stage polymerization. In the present work, the MPS-modified silica particles with vinyl groups on the surface were used as seeds in the second-stage distillation precipitation polymerization for the growth of the shell-layer to afford monodisperse silica/polyDVB and silica/polyEGDMA core–shell hybrid microspheres as shown in Scheme 1.

A series of experiments were initially conducted to investigate the effect of the DVB feed on the formation of silica/polyDVB during the second-stage polymerization. TEM micrographs of the resultant silica/polyDVB core–shell hybrid particles with different DVB loadings are shown in Fig. 1B–D. The results indicated that the final silica/polyDVB hybrid microspheres had spherical shapes with smooth and non-segmented surfaces without formation of any second-initiated particles in the cases of DVB feed ranging from 0.20 to 0.40 mL for the second-stage polymerization, which was difficult for both dispersion polymerization [15–17] and emulsion polymerization [18].

The reaction conditions, size, size distribution of the resultant silica/polyDVB hybrid microspheres and the conversion of DVB to hybrid particles are summarized in Table 1. The size of the core–shell particles increased considerably from 238 nm of silica seeds with increasing DVB feed in the range

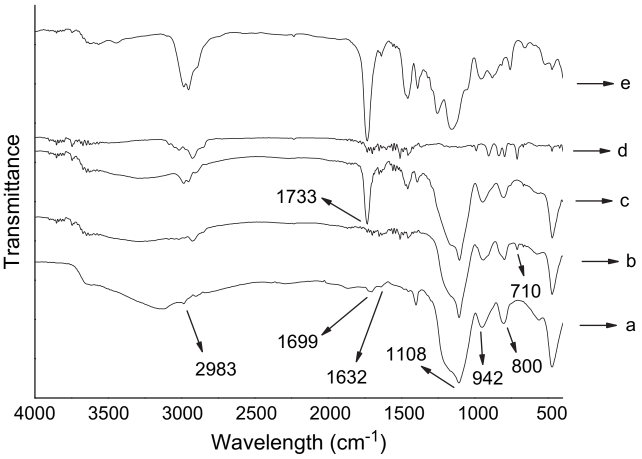
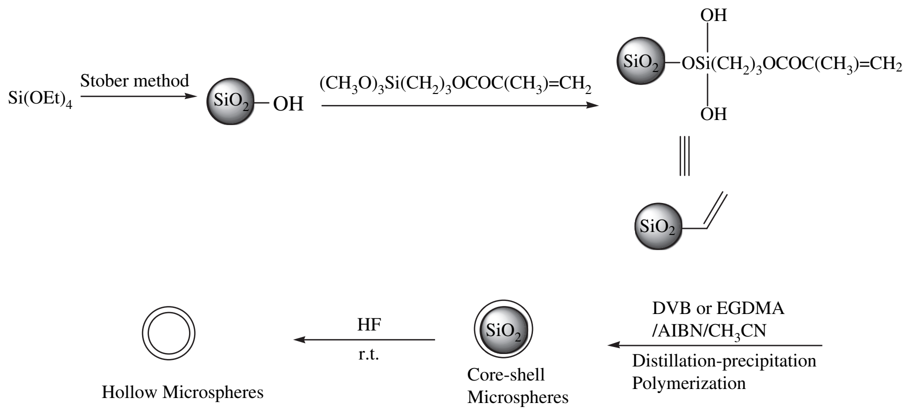


Fig. 2. FT-IR spectra of the hybrid microspheres: (a) MPS-modified silica; (b) silica/polyDVB; (c) silica/polyEGDMA; (d) hollow polyDVB; (e) hollow polyEGDMA.



Scheme 1. Preparation of silica/polymer core–shell hybrid microspheres and the corresponding hollow polymer microspheres.

of 0.20–0.40 mL, and the maximum diameter of 284 nm and monodispersity index of 1.006 of the resultant silica/polyDVB was obtained at DVB loading of 0.40 mL. All of the afforded silica/polyDVB hybrid microspheres had monodispersed size with a monodispersity index below 1.008. In the present work, the shell thickness of the polymer layer was calculated as the half of the difference between the diameter of the resultant silica/polymer core–shell hybrid microsphere and that of MPS-modified silica core. In other words, the monodisperse silica/polyDVB core–shell hybrid microspheres with polyDVB thickness ranging from 3 to 23 nm can be conveniently controlled by varying the DVB monomer loading during the second-stage polymerization. The conversion of DVB to the hybrid core–shell particles during the encapsulation was increased significantly from 9 to 27% when DVB loading was slightly enhanced from 0.20 to 0.30 mL.

The surface modification of the polyDVB component leading to silica/polyDVB core–shell hybrid particles was proven further by FT-IR spectra as shown in Fig. 2b (with entry C in Table 1 as a sample), which had a weak peak at 741 cm^{-1} corresponding to the typical adsorption of the phenyl group of the polyDVB unit. This meant that polyDVB shell was successfully encapsulated over the MPS-modified silica core during the second-stage polymerization.

3.2. Silica/polyEGDMA core–shell hybrid microspheres

An important concern for the present work is to afford silica/polymer core–shell hybrid microspheres and to retain the particle monodispersity in the absence of secondary-initiated particles through the second-stage distillation precipitation polymerization. The TEM images of silica/polyEGDMA core–shell hybrid microspheres with different EGDMA feed for the polymerizations are illustrated in Fig. 3. The results demonstrated that the core–shell hybrid microspheres had spherical shapes with smooth surfaces without any secondary-initiated particles.

The reaction conditions, size, size distribution of the final silica/polyEGDMA hybrid core–shell microspheres and the conversion of EGDMA to the corresponding hybrid particles are tabulated in Table 2. The results indicated that all the resultant hybrid microspheres were monodisperse with a size distribution index around 1.006–1.008 without any coagulation. The conversion of the silica/polyEGDMA was increased from 13 to 28% when EGDMA feed was increased from 0.20 to 0.30 mL during the second-stage polymerization. The diameter of silica/polyEGDMA was increased significantly from 238 nm of silica core with increasing the EGDMA feed in the range of 0.20–0.50 mL for the second-stage polymerization, and the largest size of 303 nm with monodispersity index of 1.007 was obtained in the case of 0.50 mL EGDMA loading. In short, monodisperse silica/polyEGDMA hybrid core–shell microspheres with polyEGDMA shell thickness in the range of 9–33 nm were facially prepared by altering the EGDMA feed from 0.20 to 0.50 mL during the second-stage polymerization.

The successful encapsulation of polyEGDMA shell over MPS-modified silica core was studied further by FT-IR spectra as shown in Fig. 2. The FT-IR spectrum in Fig. 2c of silica/polyEGDMA (with entry C in Table 2 as a sample) has a strong peak at 1733 cm^{-1} corresponding to the vibration of the carbonyl unit in ester group of polyEGDMA component.

Monodisperse silica/polyDVB and silica/polyEGDMA core–shell hybrid microspheres were formed without any secondary-initiated particles after the second-stage distillation precipitation polymerization of DVB and EGDMA, respectively, during which the thickness in a definite range for the polymer shell was controlled via the feed of DVB and EGDMA monomers. These results indicated that all the polymer species were exclusively encapsulated over the

Table 1
The size, size distribution, shell thickness, yield and of silica/polyDVB hybrids with different recipe in the feed and the fraction of shell-layer in the hybrid

Entry	SiO_2 (g)	DVB (mL)	D_n (nm)	D_w (nm)	U	Shell thickness (nm)	Conversion (%)[a]
A	0.1	0	238	240	1.012	0	0
B	0.1	0.2	244	247	1.008	3	9
C	0.1	0.3	256	258	1.008	9	27
D	0.1	0.4	284	285	1.006	23	23

[a] Conversion = $(M_{\text{core-shell}} - M_{\text{core}})/M_{\text{DVB}} \times 100\%$.

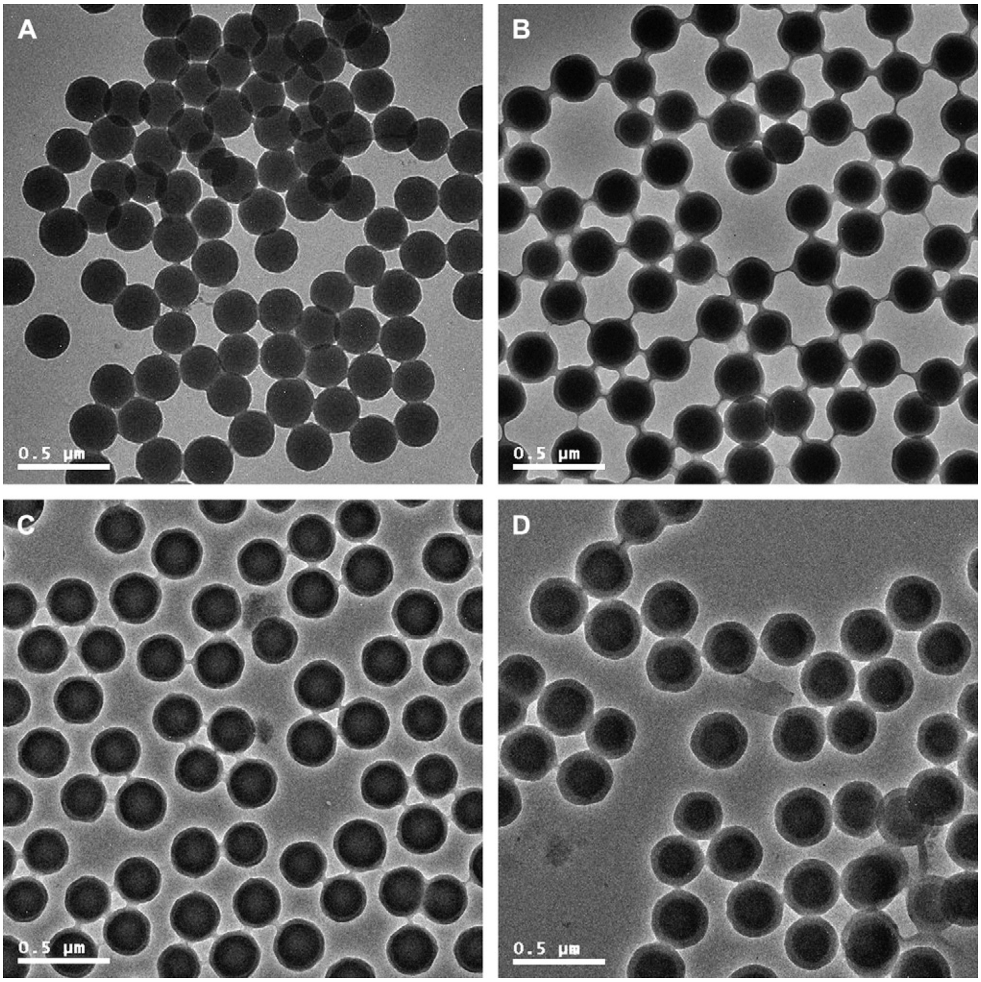


Fig. 3. TEM micrographs of silica/polyEGDMA microspheres with different EGDMA feed during polymerization: (A) 0.2 mL; (B) 0.3 mL; (C) 0.4 mL; (D) 0.5 mL.

MPS-modified silica cores during the polymerization. Here, the encapsulation of the polyDVB and polyEGDMA shells onto the MPS-modified silica core was performed by the capture of the newly formed oligomers and monomers during the polymerization via the vinyl groups on the surface of the MPS-modified silica particles during the polymerization. The presence of the vinyl groups on the surface of MPS-modified silica seeds was proven by FT-IR spectra as discussed above. The essential role of the vinyl groups on the surface of MPS-modified silica cores was confirmed further by the formation of the separated-irregular particles (TEM image not shown here) in the presence of silica particles as seeds for the polymerization of DVB and EGDMA, in which neither DVB nor EGDMA can be encapsulated onto the silica core due to its hydrophobic nature lacking efficient interaction with the silica particles. It was reported that the residual vinyl groups located on the surface of polyDVB microspheres favored the capture of the radical oligomers and monomers from the solution to grow the particles in precipitation polymerization [38] and distillation precipitation polymerization [29].

Table 2
The size, size distribution, shell thickness, yield and of silica/polyEGDMA hybrids with different recipe in the feed and the fraction of shell-layer in the hybrid

Entry	SiO_2 (g)	EGDMA (mL)	D_n (nm)	D_w (nm)	U	Shell thickness (nm)	Conversion (%)[a]
A	0.1	0	238	240	1.012	0	0
B	0.1	0.2	256	257	1.006	3	13
C	0.1	0.3	264	266	1.008	9	28
D	0.1	0.4	272	274	1.007	23	27
E	0.1	0.5	303	305	1.007	33	18

[a] Conversion = $(M_{\text{core-shell}} - M_{\text{core}})/M_{\text{EGDMA}} \times 100\%$.

3.3. Preparation of polyDVB and polyEGDMA hollow microspheres with various shell thickness

In our previous work, the crosslinked polyDVB core in the functional core–shell polymer microspheres [37,39] cannot be selectively removed by either dissolution with solvent or degradation with suitable reagent for the preparation of hollow polymer microspheres. Silica cores of the resultant silica/polyDVB and silica/polyEGDMA core–shell hybrid microspheres were selectively removed by the degradation of silica core with elution of SiF_4 gas from the system in HF aqueous solution to afford the corresponding polyDVB and polyEGDMA hollow microspheres.

The TEM micrographs of polyDVB hollow microspheres with different thickness are illustrated in Fig. 4. When DVB monomer feed during the second-stage polymerization was lower than 0.30 mL, the results in Fig. 4A with collapsed particles and Fig. 4B with irregular particles were observed, which indicated that the shell-layer was not thick (less than 9 nm) enough to support the cavities formed during the selective removal of silica cores in HF solution. The monodisperse hollow polyDVB microspheres as shown in Fig. 4C with thickness of 23 nm were obtained with DVB loading of 0.40 mL for the polymerization, in which the convincing hollow-sphere structures were observed with the presence of circular rings of non-segmented spherical structure and a cavity in the interior. The fraction of polyDVB in the silica/polyDVB core–shell hybrids was 60% with DVB feed of 0.40 mL as listed in Table 1, which confirmed further the successful removal of silica core by hydrofluoric acid during the etching process.

Fig. 5 showed the TEM micrographs of the resultant polyEGDMA hollow microspheres with different thickness. The results in Fig. 5A with deformed particles implied that the shell-layer was not thick (less than 10 nm) enough to sustain the cavities developed from the selective degradation of silica core when the EGDMA monomer feed during the polymerization was lower than 0.20 mL. The hollow polyEGDMA microspheres were obtained with EGDMA feed in the range of 0.30–0.50 mL for the formation of the polyEGDMA shell-layer. In the TEM images as illustrated in Fig. 5B–D, convincing hollow-sphere structures were inspected with the presence of circular rings of sectioned spheres and a cavity in the interior. The thickness of the polyEGDMA shell-layer was calculated increasing from 13 to 33 nm as summarized in Table 2 from TEM characterization, when the EGDMA feed was increased from 0.30 to 0.50 mL during the second-stage polymerization. In other words, the shell thickness of the resultant polyEGDMA hollow microspheres could be controlled by the amount of EGDMA monomer during the encapsulation of polyEGDMA over MPS-modified silica core. The fraction of polyEGDMA component in silica/polyEGDMA core–shell microspheres was increased from 30 to 60% with EGDMA feed increasing from 0.20 to 0.40 mL as listed in Table 2, which proved the successful encapsulation of polyEGDMA over the MPS-modified silica core by the distillation precipitation polymerization. The preparation of the other core–shell

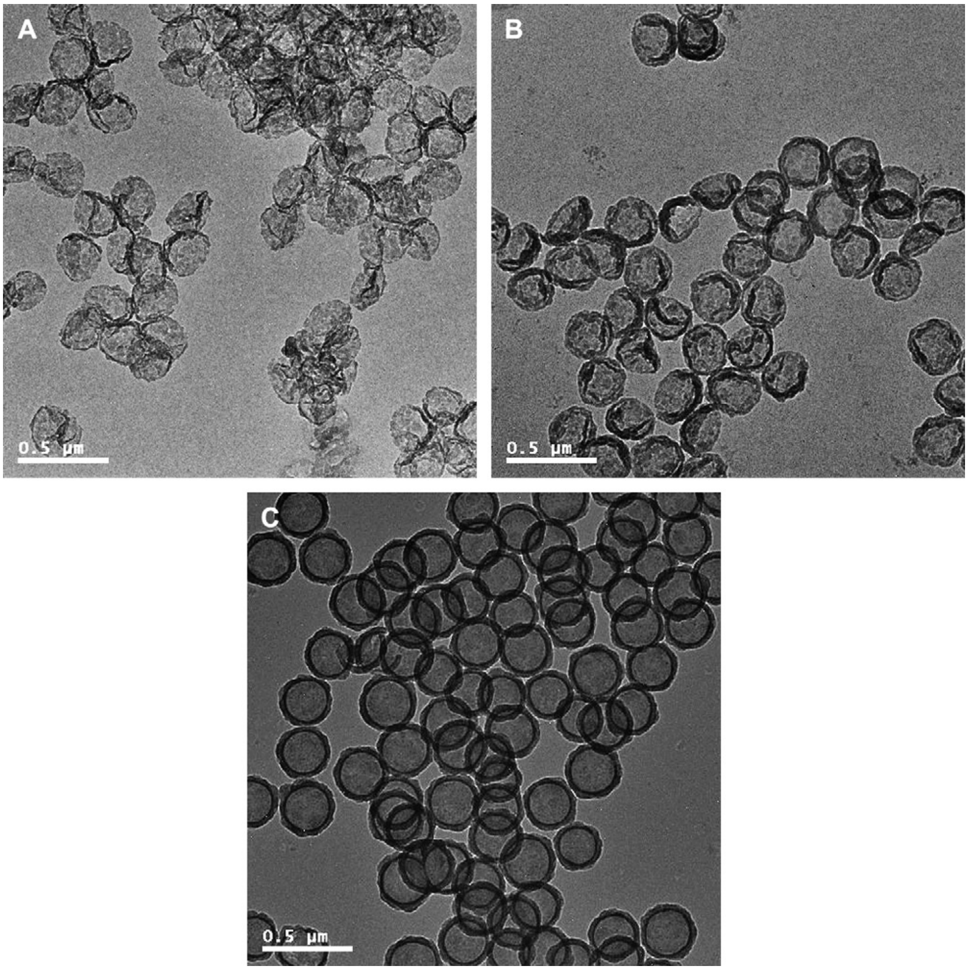


Fig. 4. TEM micrographs of hollow polyDVB microspheres with different thickness: (A) 3 nm; (B) 9 nm; (C) 23 nm. The thickness is calculated as the half of difference of silica/polyDVB hybrids and silica microsphere from TEM characterization.

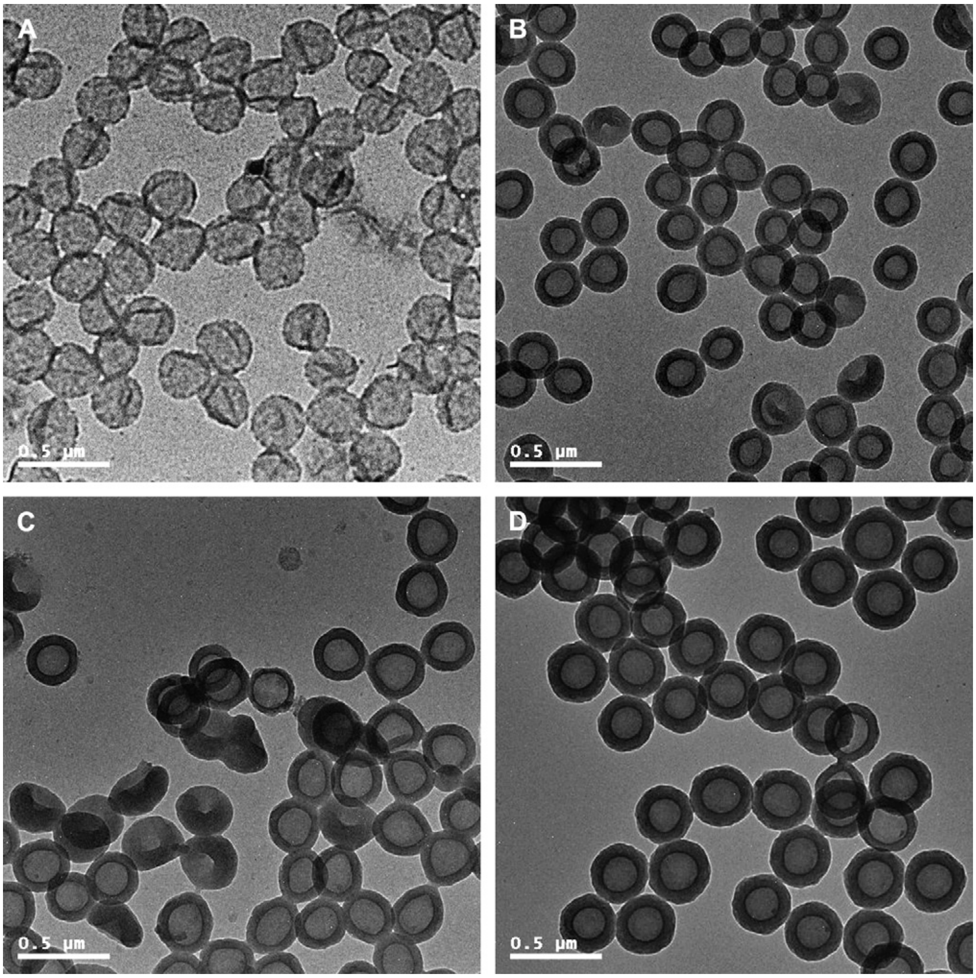


Fig. 5. TEM micrographs of hollow polyEGDMA microspheres with different thickness: (A) 9 nm; (B) 13 nm; (C) 17 nm; (D) 33 nm. The thickness is calculated as the half of difference of silica/polyDVB hybrids and silica microsphere from TEM characterization.

inorganic/organic hybrid particles and the application of these hollow polymer microspheres are in progress.

4. Conclusion

Monodisperse silica/polyDVB and silica/polyEGDMA core–shell hybrid microspheres with spherical shape and smooth surface were synthesized by distillation precipitation polymerization of DVB and EGDMA in neat acetonitrile with MPS-modified silica particles as seeds and AIBN as initiator in the absence of any additive. The reactive vinyl groups on the surface of MPS-modified silica core played an important role for the encapsulation of the polymer shell-layer over the silica seeds through the capture of the newly formed oligomers and monomers during the polymerization, in which the vinyl groups were incorporated by the first-stage modification of MPS with the aid of active hydroxyl groups on the surface of silica particles. The thickness of the polymer shell-layer of the resultant silica/polyDVB and silica/polyEGDMA core–shell hybrid microspheres was conveniently controlled by DVB and EGDMA feed during the second-stage polymerization. The corresponding polyDVB and polyEGDMA hollow microspheres with various shell thickness in the range of 9–33 nm were further developed by the selective etching of the silica cores in HF solution from silica/polyDVB and silica/polyEGDMA core–shell hybrid microspheres, respectively.

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