

# Fabrication and morphology control of hollow polymer particles by altering core particle size

Wei Deng · Huachao Guo · Wennan Zhang · Chengyou Kan

Received: 16 April 2014 / Revised: 30 May 2014 / Accepted: 23 June 2014 / Published online: 2 July 2014  
© Springer-Verlag Berlin Heidelberg 2014

**Abstract** Particles with various morphologies were fabricated by changing the size of carboxyl-containing core particles and performing seeded emulsion polymerization as well as alkali posttreatment. The distribution of carboxyl groups, size, and morphology of the resultant particles were characterized with conductometric titration, dynamic light scattering (DLS), transmission electron microscopy (TEM), and scanning electron microscopy (SEM). Results indicated that the size of carboxyl-containing core latex particles could be varied from 95 to 240 nm by adjusting the concentration of sodium dodecyl sulfate (SDS). The percentage of carboxyl groups buried inside particles increased clearly along with the encapsulation of core by interlayer and shell polymers, and seeded emulsion copolymerization performed smoothly except the system using core particles with size less than 99 nm. After alkali posttreatment, the morphologies of corresponding particles showed porous, hollow, and bowl-like structure, respectively. Moreover, the relationship between core particle size and alkali-treated particle morphology was elucidated briefly.

**Keywords** Core/shell · Hollow · Porous · Morphology control · Seeded emulsion polymerization

## Introduction

Design and control of the morphology of polymer particles have attained widespread interest because of their theoretical and practical significance. Comparing with the solid polymer particles, hollow structure inside provides the polymer particles many unique characteristics such as low density, effective light scattering, and controlled release, which should enable many applications in coating, filler, catalyst, drug delivery, and biotechnology [1–5].

Since the pioneer synthetic method of hollow polymer particles was patented in 1981, a variety of techniques have been developed to prepare polymer particles with hollow structure, and they can be classified into two general categories: one is to obtain the hollow structure by posttreating multilayer structure polymer particles and sacrificing template [6–9] the other is to encapsulate directly small molecules such as hydrocarbon or water through in situ polymerization [10–13]. Among them, osmotic swelling technique based on emulsion polymerization was the earliest and predominant method for synthesizing submicron sized hollow polymer particles, which was originally invented by Kowalski et al. [6], and its typical processes include the synthesis of core/shell latex particles and the expansion of these particles through creating ions in the core under the appropriate conditions. Subsequently, Vanderhoff et al. discussed the preparation of hollow polymer latex particles from alkali posttreating the latex particles with a soft hydrophilic core/hard hydrophobic shell [14]. Okubo et al. proposed stepwise alkali/acid treatment and alkali/cooling methods to prepare submicron multihollow polymer particles by performing posttreatment on the carboxyl-containing copolymer [15, 16].

Although there have been lots of investigation on the preparation of hollow polymer particles via osmotic swelling technique, the majority of their information was in the patent literature due to the strong commercial interest in these

W. Deng (✉) · H. Guo · W. Zhang  
Key Laboratory of Engineering Dielectrics and Its Application,  
Ministry of Education, Harbin University of Science and  
Technology, 150080 Harbin, People's Republic of China  
e-mail: weideng@hrbust.edu.cn

C. Kan (✉)  
Key Laboratory of Advanced Materials, Ministry of Education,  
Department of Chemical Engineering, Tsinghua University,  
100084 Beijing, People's Republic of China  
e-mail: kancy@mail.tsinghua.edu.cn

particles, which limited the amount of quantitative data. On the other hand, the previous researches were mostly focused on the acquisition of various hollow structures [17–20]. Very little attention has been directed toward controlling the size of hollow polymer particles and investigating the effect of original particle size on the polymerization as well as posttreated particle morphology [21, 22]. Besides the hollow structure, the size and size distribution of hollow polymer particles are important to influence their performance and functionality for many applications [23]. For example, in the field of special coating, the excellent opacity contribution of hollow polymer particles is attributed to the property of efficient light scattering, which depends on the size, size distribution, and different refractive indexes between inner air and outer polymers of hollow polymer particles. According to theoretical calculation and experimental verification, the optimum light scattering efficiency is obtained at a particle diameter of roughly 400 nm and a hollow diameter of roughly 300 nm. In addition, hollow polymer particles with narrow size distribution and similar size to TiO<sub>2</sub> are capable of preventing TiO<sub>2</sub> particles from agglomeration effectively and therefore increasing its efficiency as a primary pigment in coating, contributing to film opacity.

Recently, we have been engaged in the preparation of hollow polymer latex particles and the control of particle morphology from synthesizing multistage hydrophilic core/hydrophobic shell latex particles and performing alkali posttreatment based on the osmotic swelling principle, and some valuable results were obtained [24, 25]. In this article, with the aim of controlling the morphology of hollow polymer particles and discussing the relationship between particle size and morphology, core particles with different sizes were first synthesized under a very low concentration of surfactant, then the influences of core particle size on the emulsion polymerization and the formation of hollow morphology were investigated, and the forming mechanism of different particle morphologies was proposed according to the experiment results and analysis.

## Experimental

### Materials

Methyl methacrylate (MMA), butyl acrylate (BA), methacrylic acid (MAA), and styrene (St) (all A. P. grades, First Chemical Reagent Factory, Tianjin, China) were purified by distillation under reduced pressure and were stored in a refrigerator. Ethylene glycol dimethacrylate (EGDMA) (98.0 % purity, Alfa Aesar, Tianjin, China), divinyl benzene (DVB) (*m*- and *p*-mixture ca. 55 % in ethyl vinyl benzene (EVB) and diethyl benzene (DEB), J&K Scientific Ltd., Beijing, China), sodium dodecyl sulfate (SDS), sodium

hydroxide (NaOH), and H<sub>2</sub>SO<sub>4</sub> (all A. P. grades, Beijing Chemical Works, Beijing, China) were used without further purification. Ammonia (25 wt%, A. P. grade, Beihua Fine Chemical Products Co. Ltd., Beijing, China) was used in alkali treatment process as received. Ammonium persulfate (APS) (A. P. grade, Aijian Modern Reagent Factory, Shanghai, China) was purified by recrystallization twice in water before use. Distilled and deionized water was used throughout.

### Synthesis of multistage core/shell latex

The multistage core/shell latexes were synthesized by multistep seeded emulsion polymerization with different concentrations of emulsifier in a four-necked 250-ml round-bottom flask equipped with an inlet of nitrogen gas, a reflux condenser, a mechanical stirrer, and a thermometer, and the typical recipes were listed in Table 1. The synthetic route included three sequential steps of core, interlayer, and shell preparations as below.

Carboxyl-containing core latexes were prepared via semi-continuous emulsion polymerization as follows. A certain amount of SDS, 90 g of H<sub>2</sub>O, 0.10 g of APS, and 5 wt% of the mixture of MMA, MAA, BA, and EGDMA were charged into the reactor, and the polymerization was carried out at 80 °C for 40 min. Then, the residual monomer mixture and aqueous solution of APS (0.30 g of APS dissolved in 10 ml water) were simultaneously dropwise added into the reactor at 80 °C within 4.5 h, and then the reaction system was heated to 90 °C and maintained at this temperature for 30 min. After that, the system was cooled down to room temperature.

In the interlayer preparation, 10 g of the core latex was first diluted with 25 g of H<sub>2</sub>O, and then the seeded emulsion copolymerization of MAA, St, and MMA onto the core

**Table 1** The recipes of core/interlayer/shell latex particles prepared via multistep emulsion polymerizations

Ingredients	Core (g)	Interlayer (g)	Shell (g)
MMA	16.50	3.66	0
MAA	10.04	0.42	0
BA	14.70	0	0
EGDMA	0.25	0	0
St	0	1.02	11.84
DVB	0	0	0.45
SDS	Variable	0	0
APS	0.40	0.05	0.10
H <sub>2</sub> O	100	30	10
Core latex <sup>a</sup>	0	10.00	0

<sup>a</sup> Core latex represented the emulsion prepared according to the core recipe

particles was carried out at 80 °C by constant feeding the monomer mixture and APS aqueous solution simultaneously into the diluted core latex within 40 min.

At last, St and DVB as well as APS aqueous solution were simultaneously dropwise added into the system at 90 °C within 2 h to form the outer shell. After additional 30 min, the system was cooled down to room temperature to obtain core/interlayer/shell latex particles.

### Alkali posttreatment

A certain amount of the core/interlayer/shell latex was charged into a reactor which was immersed in a water bath at 85 °C, and  $MR_{\text{alkali/acids}}$ , which represented the molar ratio of aqueous ammonia (10 wt%) used in the alkali posttreatment to MAA used in the multistep emulsion polymerization, was fixed to 1.75. After 3 h, the emulsion was cooled down to room temperature.

### Characterization

Monomer conversion was measured by gravimetric analysis. The hydrodynamic diameter ( $D_p^{\text{DLS}}$ ), polydispersity index (PDI), and zeta potential ( $\zeta$ ) of the latex particles were measured on Zetasizer 3000HS (Malvern, UK). The number average diameter ( $D_p^{\text{TEM}}$ ) and morphology of the dried latex particles were characterized using transmission electron microscopy (TEM, JEOL JEM-2100EX, Japan) at 70 kV. The volume expansion ( $\Delta V$ ) of the particles after alkali posttreatment was calculated as below

$$\Delta V = \left( (D_{\text{AP}}^{\text{TEM}} / D_{\text{CS}}^{\text{TEM}})^3 - 1 \right) \times 100 \%$$

where  $D_{\text{CS}}^{\text{TEM}}$  and  $D_{\text{AP}}^{\text{TEM}}$  denote the diameters of the dried particles before and after the alkali posttreatment, respectively.

The distribution of carboxyl groups in the latex was determined by conductometric titration with the following procedure according to the literature [25]; 1.00 g of the original latex was diluted with 100 g of water, and its solid content was measured using a gravimetric method. The pH value of the diluted latex was first adjusted to  $11.5 \pm 0.02$  using 0.385 mol/l NaOH aqueous solution, then the latex was titrated with 0.102 mol/l  $\text{H}_2\text{SO}_4$  aqueous solution, and its conductance ( $\sigma$ ) was recorded using a DDS-307 conductometer (Leici, Shanghai, China). The conductometric titration curve was plotted with the  $\sigma$  value of latex versus the amount of  $\text{H}_2\text{SO}_4$  aqueous solution. The amount of  $-\text{COOH}$  bound on the particle surface and free in aqueous phase corresponding to per gram polymer ( $\text{SF}_a$ ) was calculated directly from the conductometric titration curve, and the amount of  $-\text{COOH}$  embedded inside the particles corresponding to per gram

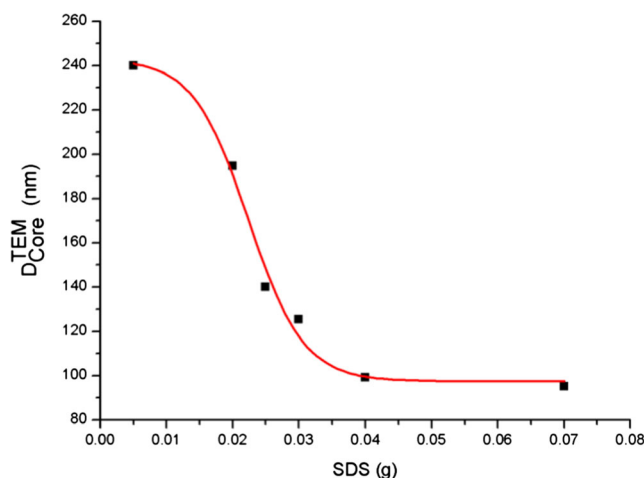
polymer ( $E_a$ ) was obtained from the difference between the initial charge of unsaturated acid monomer and  $\text{SF}_a$ .

## Results and discussion

### Preparation of core particles with different sizes

The ability to make hollow polymer latex particles by alkali posttreatment began with the core/shell structure latex particles which were synthesized via seeded emulsion polymerization using carboxyl-containing core latex as seeds. That means, to get the hollow polymer latex with definite dimension, the core latex particles with appropriate diameter should be synthesized first. Apparently, altering the amount of surfactant is the most convenient and effective method to control the particle size in emulsion polymerization. We have investigated the distribution of carboxyl groups in the core latex particles [25] and found that there was a high content of carboxyl groups bound on the surface of core particles, so the electrostatic effects gave free coagulate even in cases of very low surfactant concentration. Moreover, if there were free micelles in emulsion system, the second micelle nucleation was inevitable in the core/shell preparation process. As a consequence, this finally influenced both the structure and the monodispersity of the hollow particles. Therefore, the concentration of surfactant SDS was fixed under its critical micelle concentration (CMC) in this experiment and the effect of SDS dosage on the size, zeta potential, and morphology of the core particles was investigated.

It was clear from Fig. 1 that the dried diameter of the core particles ( $D_{\text{core}}^{\text{TEM}}$ ) decreased first with the increasing dosage of SDS and then almost unchanged as SDS dosage increased to about 0.040 g (0.10 wt% to monomers). The detailed data



**Fig. 1** Relationship between the diameter of core particles ( $D_{\text{core}}^{\text{TEM}}$ ) and dosage of SDS

**Table 2** Influences of SDS dosage on the core latex properties

Sample	SDS (g)	SDS (wt% to core monomers)	$D_{\text{core}}^{\text{TEM}}$ (nm)	$D_{\text{core}}^{\text{DLS}}$ (nm)	PDI	$\zeta$ (mV)
C-0	0	0	1,030	1,087.0	1.0000	-36.1
C-1	0.005	0.01	240	439.3	0.0027	-47.0
C-2	0.020	0.05	195	266.0	0.0094	-60.0
C-3	0.025	0.06	140	165.9	0.0130	-46.9
C-4	0.030	0.07	126	160.7	0.0160	-47.6
C-5	0.040	0.10	99	130.8	0.0068	-54.2
C-6	0.070	0.17	95	120.6	0.0132	-65.0

of  $D_{\text{core}}^{\text{TEM}}$  were summarized in Table 2. It could be seen that when the concentration of SDS increased from 0.01 to 0.05 wt%, the core size decreased from 240 to 195 nm. As SDS dosage increased to equal or above 0.10 wt%, the core diameter decreased to less than 99 nm. For the polymerization system without SDS (sample C-0), the emulsion system was unstable and coagulation formed so that the particle size was polydisperse and much bigger than the others, exceeding 1  $\mu\text{m}$ . With the addition of SDS, the stability of oligomer and polymer chains in water phase was improved, which led to the increase of initial particle numbers by homogenous nucleation, and as a result, the size of the resultant core particles decreased with the increase of SDS dosage. As SDS dosage increased continuously, the adsorption of SDS at the surface of initial particles reached saturation and the nucleation density of homogenous nucleation tended to unchanged; consequently, the size of the resultant core particles was no longer affected by SDS dosage. A similar tendency was also observed in the hydrodynamic diameter ( $D_{\text{core}}^{\text{DLS}}$ ) of the particles except that the hydration caused the value of  $D_{\text{core}}^{\text{DLS}}$  much bigger than that of  $D_{\text{core}}^{\text{TEM}}$ . Moreover, the

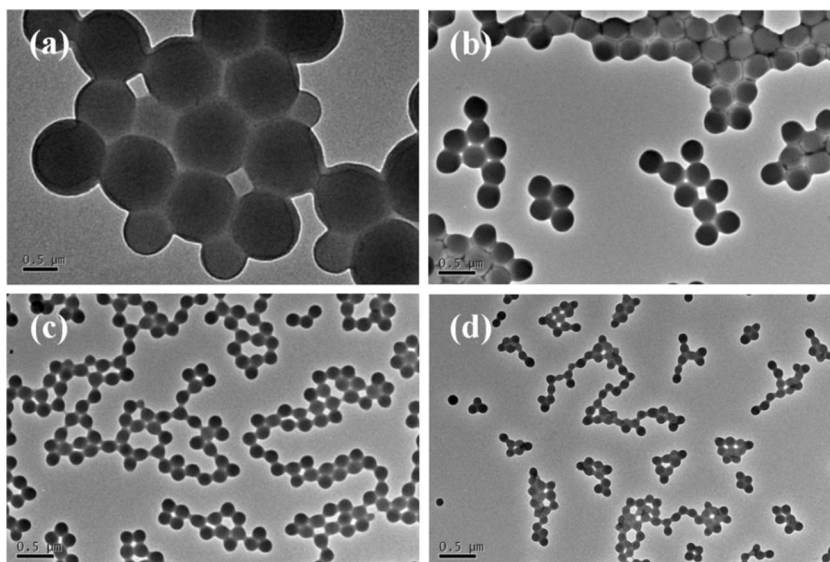
absolute value of zeta potential ( $\zeta$ ) of the sample prepared via soap-free emulsion polymerization was smaller than that of the other samples, which also illustrated that the addition of SDS enhanced the stability of the emulsion system.

The TEM micrographs of the resultant core particles were given in Fig. 2. It was clear that monodisperse latex particles were obtained by emulsion polymerization under low surfactant concentration except for the sample C-0 which was prepared without SDS, and this was in accordance with the results of size PDI listed in Table 2.

#### Preparation of multilayer core/shell particles

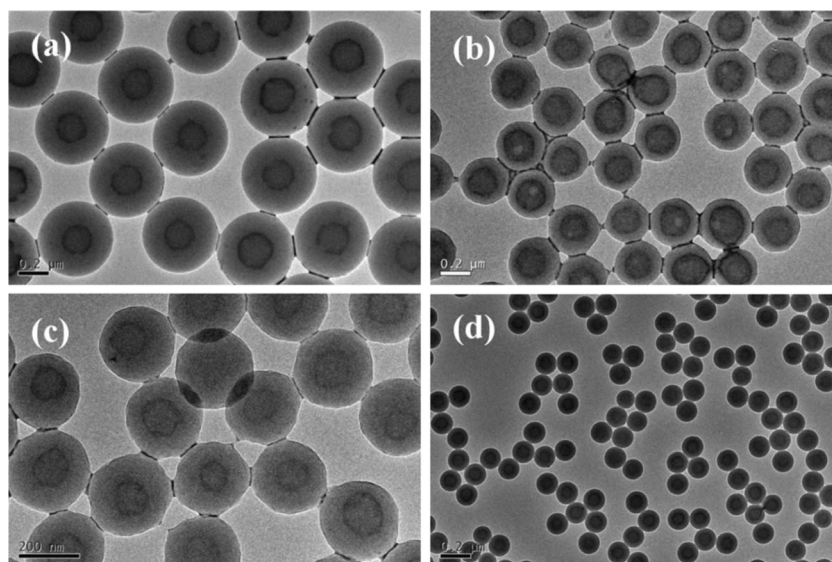
For preparing well-defined polymer latex particles with carboxyl-containing core encapsulated by shell polymers, a polar intermediate layer was designed to insert into the core and the shell to balance their polar difference. Here, core latex particles with different sizes were used as seeds to prepare such multistage core/shell polymer particles, and the typical TEM micrographs of the resultant polymer latex particles were shown in Fig. 3. The results indicated that all the resultant particles CS-1, CS-2, CS-4, and CS-5 prepared with core C-1, C-2, C-4, and C-5 as seeds had obvious core/shell structure with smooth surface, and the dried diameter ( $D_{\text{CS}}^{\text{TEM}}$ ) of CS-1, CS-2, CS-4, and CS-5 were 455, 326, 251, and 138 nm, respectively. Using C-1, C-2, or C-4 as seeds, the seeded emulsion polymerization processes performed smoothly and the monomer conversions of the interlayer and shell preparation both reached higher than 99.4 %. The storage stability of the core/interlayer/shell latexes were more than 3 months at room temperature. On the contrary, the emulsion system was more unstable and some of coagulation was generated when C-5 was encapsulated via seeded emulsion polymerization. For an emulsion system with fixed solid content, the size and

**Fig. 2** TEM micrographs of core latex particles P(MMA-MAA-BA) prepared with different concentration of SDS (wt% to core monomers): **a** 0, **b** 0.01, **c** 0.05, **d** 0.10





**Fig. 3** TEM micrographs of core/interlayer/shell polymer particles P(BA-MAA-MMA)/P(MMA-MAA-St)/P(St-MAA) prepared by using C-1, C-2, C-4, and C-5 as seeds, respectively: **a** CS-1, **b** CS-2, **c** CS-4, and **d** CS-5



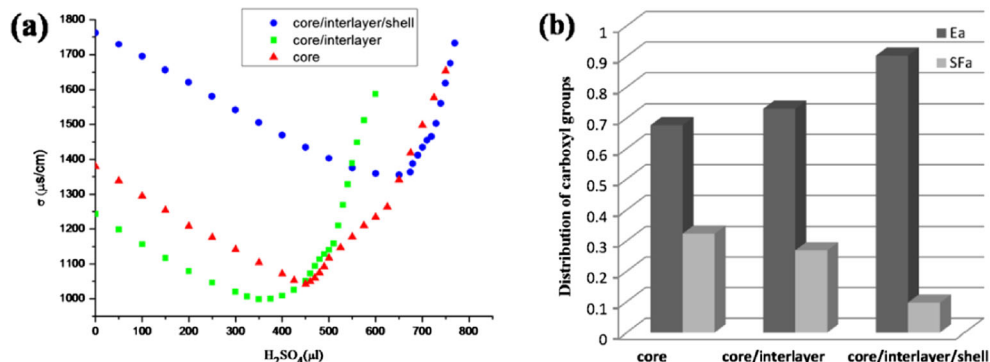
number of the latex particles must be inversely proportional. That meant, the smaller the latex particles size, the more is the amount of latex particles. When same dosage core latexes were employed to perform the following seeded emulsion polymerization, using latex particles with smaller size as seeds would cause the increase of the latex particles amount in comparison with using bigger ones, and then the collision probability of latex particles increased in the system, so during the preparation of multistage core/shell particles in the presence of C-5 as seeds, the system is more unstable and easy to coagulate.

With the purpose of further confirming that the carboxyl-containing core was encapsulated by hydrophobic shell but not migrated toward outside to form the inverted core/shell morphology, C-4 and corresponding core/interlayer as well as core/interlayer/shell (CS-4) were selected to perform conductometric titration to characterize the carboxyl distribution, and the titration curves of latex particles prepared at different stages were illustrated in Fig. 4a. It can be deduced that if the designed encapsulation was effective, the percentage of –COOH buried inside the particles ( $E_a$ ) should increase and the

total percentage of –COOH bound on the particle surface and free in aqueous phase ( $SF_a$ ) should decrease step by step. The values of  $E_a$  and  $SF_a$  of the different latexes were summarized in Fig. 4b. For the core latex C-4,  $E_a$  was only 67.71 % and  $SF_a$  was 32.29 %. After the multistep emulsion copolymerization,  $E_a$  increased to 90.26 % as well as  $SF_a$  decreased to 9.74 % in the latex CS-4, suggesting that the carboxyl-containing core has been well encapsulated by the shell. Since there is always free carboxyl groups in aqueous phase, the percentage of  $E_a$  value could not reach 100 %.

Besides changing the size of core particles, altering the thickness of interlayer/shell is another effective way to control the size of multilayer core/shell particles. We have also prepared core/shell particles in the presence of core latex particles C-4 using different dosages of interlayer and/or shell monomers, and the properties of these core/shell particles were listed in Table 3. As expected, the dried diameter ( $D_{CS}^{TEM}$ ) and hydrodynamic diameter ( $D_{CS}^{DLS}$ ) of the core/shell particles increased with the increase of interlayer and/or shell layer dosage, and the size distribution was narrow.

**Fig. 4** Conductometric titration results: **a** conductometric titration curves of C-4 (triangle), C-4/interlayer (square), and CS-4 (circle) and **b** carboxyl distribution of the particles; black and gray bars represent the percentage of –COOH buried inside the particles ( $E_a$ ) and the total percentage of –COOH bound on the particle surface and free in aqueous phase ( $SF_a$ ), respectively



**Table 3** Properties of core/shell particles prepared by altering the size of core particles and/or the thickness of interlayer/shell layer

Sample	C//I/S mass ratio <sup>a</sup>	$D_{CS}^{TEM}$ (nm)	$D_{CS}^{DLS}$ (nm)	PDI	$\zeta$ (mV)
CS-1	1/1.72/4.16	455	486	0.0358	-43.1
CS-2	1/1.72/4.16	326	375	0.0692	-39.7
CS-4	1/1.72/4.16	251	280	0.0641	-34.3
CS-5	1/1.72/4.16	138	169	0.0597	-38.5
CS-4-a	1/3.46/4.16	266	341	0.0152	-40.7
CS-4-b	1/1.72/2.08	210	252	0.0479	-37.2
CS-4-c	1/1.72/6.24	273	322	0.0380	-35.9

<sup>a</sup> C//I/S mass ratio represented the ratio of monomers dosage used in the core, interlayer, and shell preparation

**Table 4** Properties of alkali posttreated particle properties

Sample	$D_{AP}^{TEM}$ (nm)	$D_{Hollow}^a$ (nm)	$T_{Shell}^b$ (nm)	PDI	Morphology	$\Delta V$ (%)
AP-1	872	–	–	0.259	Hollow and collapse	603.9
AP-2	510	418	46	0.0297	Hollow	282.9
AP-4	400	254	73	0.0958	Hollow	304.7
AP-5	189	–	–	0.0724	Porous	156.9
AP-4-a	429	251	89	0.0786	Hollow	319.5
AP-4-b	380	200	95	0.0858	Hollow	492.5
AP-4-c	475	283	96	0.0778	Hollow	426.7

<sup>a</sup>  $D_{Hollow}$  represented the void size of hollow particles

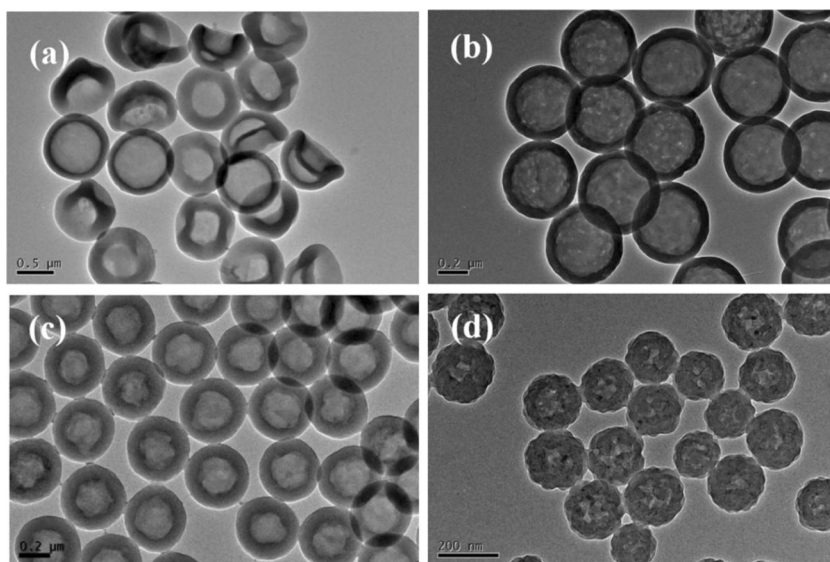
<sup>b</sup>  $T_{Shell}$  represented the shell thickness of hollow particles

### Morphology development of the posttreated particles

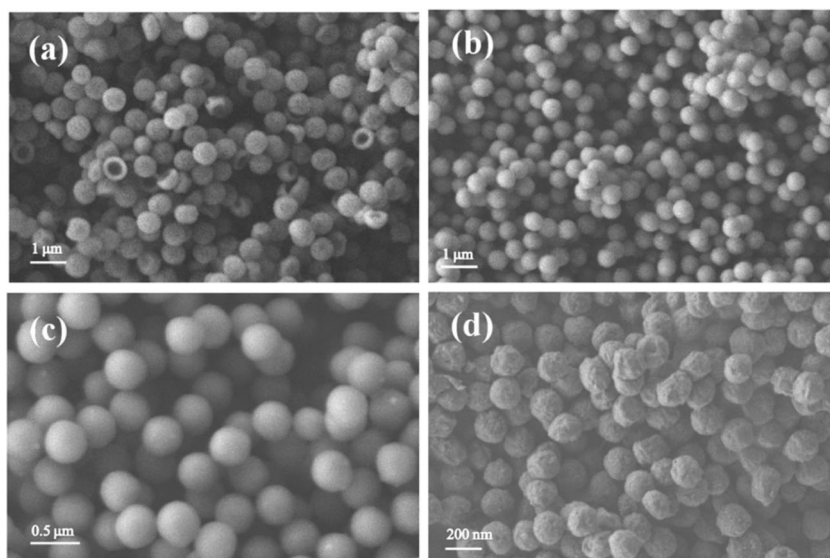
During the alkali posttreatment stage, the multistage core/shell latex particles CS-1, CS-2, CS-4, and CS-5 were treated using 10 wt% aqueous ammonia with  $MR_{alkali/acid}$  1.75 at 85 °C for 3 h. The data of size and morphology of particles were listed in Table 4. It could be seen that obvious raise had taken place in the diameter of the particles after alkali posttreatment ( $D_{AP}^{TEM}$ ), and the volume expansion ( $\Delta V$ ) increased significantly as the diameter of original core/shell particles increased from 138 to 455 nm. Figure 5 shows the TEM micrographs of the corresponding alkali-treated latex particles AP-1, AP-2, AP-4, and AP-5 obtained by alkali posttreating CS-1, CS-2, CS-4, and CS-5. It was notable that hollow and “bowl-like” structure coexisted in AP-1, and AP-2 as well as AP-4 both showed a distinct hollow structure, while AP-5 was more like a porous structure. In order to further investigate the morphologies, the alkali-treated latex particles were also characterized by SEM. Besides some particles had collapsed structure in AP-1, all the alkali-treated particles showed spherical structure. Furthermore, AP-2 and AP-4 had smooth surface, while AP-5 displayed rough surface under SEM observation (Fig. 6).

These results suggested that the decrease of particle size led to the aggravation of the mutual penetration between the core and the shell polymer chains, and some polymer chains with –COOH, which located in the core domain originally, possibly entered into the shell layer during the multistage core/shell preparation stage. Due to the decrease of –COOH amount in the core latex particles, the driving force resulted from the hydration of –COO<sup>–</sup>, and the mobility of polymeric segments in the core was not strong enough to change the particle size obviously during the alkali posttreatment stage, and only several small pores were generated inside. Meanwhile, because the hydration of –COO<sup>–</sup> existed in the shell, loose shell

**Fig. 5** TEM micrographs of the alkali-treated latexes obtained from CS-1, CS-2, CS-4, and CS-5, respectively. **a** AP-1, **b** AP-2, **c** AP-4, and **d** AP-5



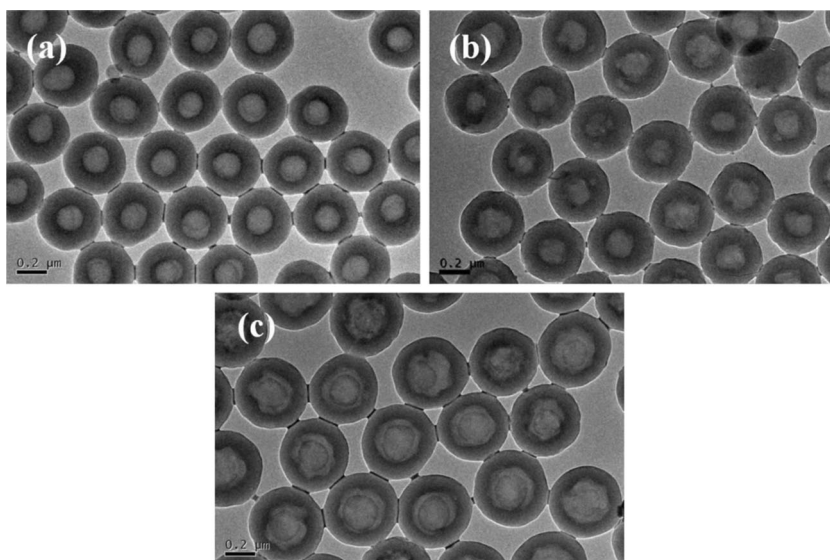
**Fig. 6** SEM micrographs of the alkali-treated latexes obtained from CS-1, CS-2, CS-4, and CS-5, respectively. **a** AP-1, **b** AP-2, **c** AP-4, and **d** AP-5



structure and rough surface appeared in AP-5. Along with the increase of particle size, the mutual penetration of polymer chains would inevitably lessen, the particles possessed more  $-\text{COOH}$  inside and were capable to absorb more water and form more small pores during the alkali post-treatment process, and eventually, the small pores preferred to assemble into one hollow structure to decrease the interfacial free energy through decreasing the interfacial area. If the content of  $-\text{COOH}$  embedded in the core domains was superfluous, the increasing of ionized polymer chains would promote the osmotic swelling greatly during the alkali posttreatment process, and as a result, the excess volume expansion of the latex particles would result in the deformation of shell during the drying process; thereupon, some bowl-like particles were observed when the particle size increased continuously.

As mentioned above, the mutual penetration of polymer chains of different layers played an important role in the morphology change of particles after alkali posttreatment. Not only the size of core particle but also the thickness of interlayer and/or shell layer would affect the penetration degree of polymer chains, so core/shell particles prepared with different dosages of interlayer and shell layer monomers were performed alkali posttreatment under the same conditions to investigate the influences of interlayer and/or shell layer thickness on the size and morphology of final hollow particles. It could be seen from Fig. 7 that all the treated particles presented hollow morphology. Moreover, the influences of interlayer and/or shell layer thickness on the size of final hollow particles were complicated and there is no clear variation tendency could be found from the properties of AP-4 and AP-4-a to AP-4-c listed in Table 4. This might be because although

**Fig. 7** TEM micrographs of the alkali-treated latexes obtained from CS-4-a, CS-4-b, and CS-4-c, respectively. **a** AP-4-a, **b** AP-4-b, and **c** AP-4-c





increasing the thickness of interlayer and/or shell layer could weaken the mutual penetration of polymer chains and ensured more carboxyl groups buried inside the particles so as to offer enough driving force to form hollow structure, it also increased the strength of shell, resulting in the limitation of volume expansion during the alkali posttreatment process.

## Conclusion

In this study, core latex particles containing carboxyl groups with different sizes were first synthesized under low surfactant concentration and used as seeds to prepare core/interlayer/shell structure latex particles via multistep seeded emulsion copolymerization and corresponding hollow polymer particles by further alkali posttreatment. Altering the concentration of SDS provided a facile and effective way to prepare carboxyl-containing core latex particles with different sizes, which played an important role for controlling the size and morphology of alkali posttreated particles. As the diameter of core particles increased from 99 to 240 nm, the diameter of corresponding alkali-treated particles increased significantly from 189 to 872 nm, and the morphology varied from porous, hollow, to bowl-like structure.

**Acknowledgments** This work was financially supported by the training project for innovation and entrepreneurship of the Harbin University of Science and Technology (2013).

## References

- Rennel C, Rigdahl M (1994) Enhancement of the light-scattering ability of coating by using hollow pigments. *Colloid Polym Sci* 272: 1111–1117. doi:10.1007/BF00652380
- McDonald CJ, Devon MJ (2002) Hollow latex particles: synthesis and applications. *Adv Colloid Interface Sci* 99:181–213. doi:10.1016/S0001-8686(02)00034-9
- Fu GD, Li GL, Neoh KG, Kang ET (2011) Hollow polymeric nanostructures-synthesis, morphology and function. *Prog Polym Sci* 36:127–167. doi:10.1016/j.progpolymsci.2010.07.011
- Han J, Liu Y, Guo R (2009) Reactive template method to synthesize gold nanoparticles with controllable size and morphology supported on shells of polymer hollow microspheres and their application for aerobic alcohol oxidation in water. *Adv Funct Mater* 19:1112–1117. doi:10.1002/adfm.200801018
- Yang XY, Chen LT, Huang B, Bai F, Yang XL (2009) Synthesis of pH-sensitive hollow polymer microspheres and their application as drug carriers. *Polymer* 50:3556–3563. doi:10.1016/j.polymer.2009.06.027
- Kowalski A, Vogel M, Blankenshi RM (1981) Preparation of sequential polymers and use thereof in coating compositions and as thickening and/or opacifying agents. EP 0022633A2
- Wang YJ, Angelatos AS, Caruso F (2007) Template synthesis of nanostructured materials via layer-by-layer assembly. *Chem Mater* 20:848–858. doi:10.1021/cm7024813
- Zheng RH, Liu GJ (2007) Water-dispersible oil-filled ABC triblock copolymer vesicles and nanocapsules. *Macromolecules* 40:5116–5121. doi:10.1021/ma070215u
- Caruso F, Caruso RA, Möhwald H (1998) Nanoengineering of inorganic and hybrid hollow spheres by colloidal templating. *Science* 282:1111–1114. doi:10.1126/science.282.5391.1111
- McDonald CJ, Bouck KJ, Chaput AB, Stevens CJ (2000) Emulsion polymerization of void particles by encapsulation of a nonsolvent. *Macromolecules* 33:1593–1605. doi:10.1021/ma991284e
- Gao F, Su ZG, Wang P, Ma GH (2009) Double emulsion template microcapsules with single hollow cavities and thickness-controllable shells. *Langmuir* 25:3832–3838. doi:10.1021/la804173b
- Liu Q, Huang C, Luo S, Liu ZH, Liu BL (2007) Production of micron-sized hollow microspheres by suspension polymerization of St-DEGDA (diethylene glycol diacrylate) with petroleum ether (90–120 °C). *Polymer* 48:1567–1572. doi:10.1016/j.polymer.2007.01.034
- Konishi Y, Okubo M, Minami H (2003) Phase separation in the formation of hollow particles by suspension polymerization for divinylbenzene/toluene droplets dissolving polystyrene. *Colloid Polym Sci* 281:123–129. doi:10.1007/s00396-002-0748-2
- Vanderhoff JW, Park JM, El-Aasser MS (1992) Preparation of particles for microvoid coatings by seeded emulsion polymerization. In: Daniels ES, Sudol ED, El-Aasser MS (eds) *Polymer latexes preparation, characterization, and applications*. ACS, New York, pp 272–281
- Okubo M, Mori H (1997) Production of multi-hollow polymer microspheres by stepwise alkali/acid method. *Colloid Polym Sci* 275: 634–639. doi:10.1007/s003960050129
- Okubo M, Ito A, Kanenobu T (1996) Production of submicron-sized multihollow polymer particles by alkali/cooling method. *Colloid Polym Sci* 274:801–804. doi:10.1007/BF00654677
- Im SH, Jeong U, Xia YN (2005) Polymer hollow particles with controllable holes in their surfaces. *Nat Mater* 4:671–675. doi:10.1038/nmat1448
- Liang FX, Liu JQ, Zhang CQ, Qu XZ, Li JL, Yang ZZ (2011) Janus hollow spheres by emulsion interfacial self-assembled sol-gel process. *Chem Commun* 47:1231–1233. doi:10.1039/C0CC03599H
- Deng JP, Yu Y, Dun S, Yan WT (2010) Hollow polymer particles with nanoscale pores and reactive groups on their rigid shells: preparation and application as nanoreactors. *J Phys Chem B* 114:2593–2601. doi:10.1021/jp909115p
- Zeng HC (2011) Synthesis and self-assembly of complex hollow materials. *J Mater Chem* 21:7511–7526. doi:10.1039/C1JM10499C
- Sun Z, Luo Y (2011) Fabrication of non-collapsed hollow polymeric nanoparticles with shell thickness in the order of ten nanometres and anti-reflection coatings. *Soft Matter* 7:871–875. doi:10.1039/C0SM00983K
- Chang MW, Stride E, Edirisinghe M (2010) Controlling the thickness of hollow polymeric microspheres prepared by electrohydrodynamic atomization. *J R Soc Interface* 7:S451–S460. doi:10.1098/rsif.2010.0092.focus
- Rao JP, Geckeler KE (2011) Polymer nanoparticles: preparation techniques and size-control parameters. *Prog Polym Sci* 36:887–913. doi:10.1016/j.progpolymsci.2011.01.001
- Deng W, Li RL, Zhang MJ, Gong LX, Kan CY (2010) Influences of MAA on the porous morphology of P(St-MAA) latex particles produced by batch soap-free emulsion polymerization followed by stepwise alkali/acid post-treatment. *J Colloid Interf Sci* 349:122–126. doi:10.1016/j.jcis.2010.05.033
- Deng W, Ji WJ, Jiang YM, Kan CY (2013) Influence of unsaturated acid monomer on the morphology of latex particles in the preparation of hollow latex via the alkali post-treatment. *J Appl Polym Sci* 127: 651–658. doi:10.1002/app.37840