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ORIGINAL PAPER

Synthesis and characteristics of poly(methyl methacrylate-methacrylic acid-3,3-(trimethoxysilyl) propyl methacrylate) hollow latex particles and their application to drug carriers

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Abstract In this study, the hollow latex particle was synthesized by three processes. The first process was to synthesize the poly(methyl methacrylate-*co*-methacrylic acid) (poly(MMA-MAA)) copolymer latex particles by the method of soapless emulsion polymerization. Following the first process, the second process was to polymerize MMA, MAA, 3,3-(trimethoxysilyl) propyl methacrylate (MPS), and ethylene glycol dimethacrylate in the presence of poly(MMA-MAA) latex particles to form the linear poly(MMA-MAA)/crosslinking poly(MMA-MAA-MPS) core–shell latex particles. In the third process, the core–shell latex particles were heated in the presence of ammonia to form the poly(MMA-MAA-MPS) hollow latex particles. A sufficient heating time and high-heating temperature were necessary for the ammonia to dissolve the linear poly(MMA-MAA) core to form a perfect hollow structure. The crosslinking poly(MMA-MAA-MPS) shell was a barrier for the ammonia to diffuse into the latex particles so that the latex particle with the high-crosslinking shell showed an imperfect hollow structure. Besides, the hollow poly(MMA-MAA-MPS) latex particles reacted with ZnO nanoparticles, which were synthesized by a traditional sol-gel method, to form the polymer/inorganic poly(MMA-MAA-MPS)/ZnO composite hollow latex particles. With the increase of crosslinking degree would increase the amount of ZnO bonding. Moreover, the poly(MMA-MAA-MPS) hollow latex particles were used as carriers to load with the model drug, caffeine. The release of caffeine from poly(MMA-MAA-MPS) hollow latex particles was investigated.

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Introduction

Hollow polymeric spheres have been widely applied in many fields because of their potential application, which range from targeted drug delivery to advanced functional materials [1]. The hollow core structure can encapsulate large quantities of materials and release them by a controlled manner. Several methods, such as self-assembly of block copoloymers in a solvent [2], the deposition of polyelectrolytes on the core particles [3], and emulsion (micro- or mini-emulsion) polymerization [4], have been developed to form hollow latex particles. Synthetic methods leading to particles with core–shell, micro-domain, and interpenetrating networks have been published [5, 6]. Recently, the method of layer-by-layer assembly has been proved to fabricate hollow capsules [7]. The process consists of the successive deposition of polyelectrolytes of opposite charge on latex particles and then removed the core. The capsules that were produced by alternate adsorption of poly(styrene sulfonate salt) (PSS) and poly(allylamine hydrochloride) (PAH) and then were extensively characterized [8–10] with respect to their morphology, their surface charge, their mechanical properties, and their permeability. The development of "intelligent" capsules with thermoresponsive behavior is particularly attractive. Klitzing and co-workers [11] reported the self-assembly of a negatively charged copolymer containing a thermosensitive poly(*N*-isopropylamide) (PNIPAM) block and poly(diallyldimethyl ammonium chloride) (PDADMAC) polyaction on the planar surface. Glinel et al. [12] reported on the layer-by-layer assembly of diblock copolymers consisting of a positively or negatively charged block and a thermosensitive PNIPAM block. Besides, they used confocal microscopy to study the variation of the capsule morphology and permeability with increasing temperature. Moreover, the combination of nanosized inorganic particles with organic polymers to form the nanocomposites with good processability and improved physical, mechanical properties, and especial application such as biotechnology and medicine has drawn considerable attention recently [13–17].

In this study, the poly(MMA-MAA-MPS) hollow latex particles were synthesized first and then reacted with ZnO nanoparticles to form the poly(MMA-MAA-MPS)/ZnO composite hollow latex particle. The morphologies of composite hollow latex particles were investigated. Besides, the poly(MMA-MAA-MPS) hollow latex particles were used as carriers, and the control release behavior of poly(MMA-MAA-MPS) hollow latex particles was studied.

Experimental

Materials

Methyl methacrylate (MMA), methacrylic acid (MAA), 3,3-(trimethoxysilyl) propyl methacrylate (MPS), ethylene glycol dimethacrylate (EGDMA), potassium persulfate (KPS), zinc acetate dehydrate, and ammonium were used as supplied. Other chemicals were of analytical grade and used without further purification. Distilled and deionized water was used throughout the study.

Synthesis of ZnO nanoparticles

Ethyl alcohol (40 g) and zinc acetate dehydrate (0.219 g) were placed in the reaction vessel with condenser, and then heated and stirred using a magnetic stirrer. After the mixture reached to the reaction temperature, the sodium hydroxide solution (0.08 g NaOH dissolved in 15 g ethyl alcohol) was added into the mixture to react with zinc acetate dehydrate, therefore obtained the ZnO nanoparticles.

Synthesis of poly(MMA-MAA-MPS) hollow latex particle

The poly(MMA-MAA-MPS) hollow latex particles were synthesized by three processes. The first process was to synthesize the linear-poly(MMA-MAA) latex particle by the method of sopaless emulsion polymerizations. In this reaction, about 16.5 and 5.5 g MAA were polymerized under a nitrogen atmosphere by using KPS as initiators. In the second process, the MMA, MAA, MPS, and EGDMA were polymerized in the presence of poly(MMA-MAA) seed latex particles to form the linear-poly(MMA-MAA)/crosslinking poly(MMA-MAA-MPS) core–shell latex particles. The ingredients and reaction condition were shown as Table 1. Following the second process, the core–shell latex particles were heated and stirred in the presence of ammonia at the temperature of 25, 50, and 80 °C, respectively, by the stirred speed of 300 rpm to dissolved the poly(MMA-MAA) linear core and form the poly(MMA-MAA-MPS) hollow latex particles.

Synthesis of poly(MMA-MAA-MPS)/ZnO composite latex particle

The poly(MMA-MAA-MPS) hollow latex emulsion mixed with the ZnO nanoparticle suspension (the ethyl alcohol medium of ZnO suspension was displaced by deionized water before this process), and then stirred for 48 h by the stirred speed of

Table 1 Ingredients and reaction condition for the synthesis of the linear-poly(MMA-MAA)/crosslinking poly(MMA-MAA-MPS) latex particles

Poly(MMA-MAA) seed latex emulsion (g)	50
MMA (g)	7.71
MAA (g)	1.29
MPS (g)	0–0.3
EGDMA (g)	0.0475–0.9
KPS (g)	0.3
Deionized water (g)	250
Reaction time (h)	4
Reaction temperature (°C)	70
Stirring rate (rpm)	300

500 rpm at room temperature to produced the poly(MMA-MAA-MPS)/ZnO composite hollow latex particles.

Caffeine loading experiment

In this study, caffeine was used as model drug to investigate the control release behavior of latex particles. Pre-weight sample, poly(MMA-MAA-MPS) hollow latex particles, was immersed in a buffer solution-containing caffeine, followed by ultrasonication for 10 min, and kept at the temperature of 25 °C to proceed the caffeine loading experiment. After the caffeine loading experiment proceed for a definite time, a centrifuge was used to separate the hollow latex particles from the caffeine solution. The centrifugal upper solution was taken out and measured by using a UV–Vis spectrophotometer to decide the concentration of unloading caffeine. The amount of caffeine loading (WL) could be calculated as follow:

$$\mathrm{WL} = (A1 - A2) \times (C2 - C1)/C1 \tag{1}$$

where $A1$ is the caffeine concentration for the experiment of caffeine loading, $A2$ is the caffeine concentration of the upper solution, $C1$ is the weight of dried hollow latex particle for the experiment of caffeine loading, and $C2$ is the weight of hollow latex emulsion for the experiment of caffeine loading.

Caffeine releasing experiment

The hollow latex particles, which had loaded with caffeine, were immersed into a buffer solution to release caffeine. After the caffeine releasing experiment proceed for a definite time, a centrifuge was used to separate the hollow latex particles from the buffer solution, and then the buffer solution was measure by using a UV–Vis spectrophotometer (detect the characteristic absorbance of caffeine at 272 nm) to decide the quantity of releasing caffeine. The caffeine release (Wn) could be calculated as follows:

$$\mathrm{Wn} = R1 \times (D2 - D1)/D1 \tag{2}$$

where $R1$ is the caffeine concentration that releases from the hollow latex particles to the buffer solution, $D1$ is the weight of dried hollow latex particles for the experiment of caffeine releasing, and $D2$ is the weight of hollow latex buffer suspension for the experiment of caffeine releasing.

Morphology of the latex particles

The morphology of the latex particles was observed by a JEOL JSM-1200 EX II transmission electron microscope (TEM).

Swelling characteristic of latex particles

A quantity of latex particles were purified firstly, and then added into the buffer solution to form the latex suspension. Following, the latex suspension was measured by using a UV–Vis spectrophotometer to detect the characteristic absorbance of latex particles. The UV–Vis spectrum of the latex suspension showed a significant absorbance at 500 nm. Therefore, the latex suspension was measured using a UV–Vis spectrophotometer by detecting the characteristic absorbance at 500 nm to determine the swelling characteristic of latex particles.

Results and discussion

Effect of heating time on the morphology of poly(MMA-MAA-MPS) hollow latex particles

Figure 1a, b showed the morphologies of poly(MMA-MAA-MPS) hollow latex particles that were produced by heating the linear poly(MMA-MAA)/crosslinking (MMA-MAA-MPS) latex particles in the presence of ammonia at 50 °C for 1 and 3 h, respectively. The linear-poly(MMA-MAA)/crosslinking poly(MMA-MAA-MPS) latex particles, which were heated for 1 h, showed an incomplete hollow structure while a perfect hollow structure was shown after the latex particles were heated for 3 h. The ammonia needed sufficient time to dissolve the poly(MMA-MAA) linear zone of latex particles to form a perfect hollow structure.

Effect of heating temperature on the morphology of poly(MMA-MAA-MPS) hollow latex particles

Figure 2a, b showed the effect of heating temperature on the morphology of poly(MMA-MAA-MPS) hollow latex particles. The linear-poly(MMA-MAA)/

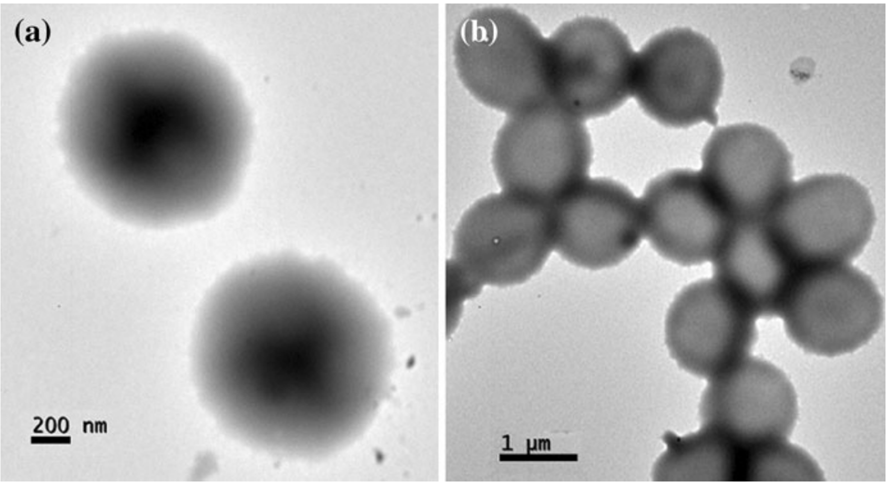


Fig. 1 The morphologies of poly(MMA-MAA-MPS) hollow latex particles that were produced by heating the linear-poly(MMA-MAA)/crosslinking poly(MMA-MAA-MPS) latex particles (EGDMA 0.5 %) in the presence of ammonia (pH 12) at 50 °C for **a** 1 h and **b** 3 h

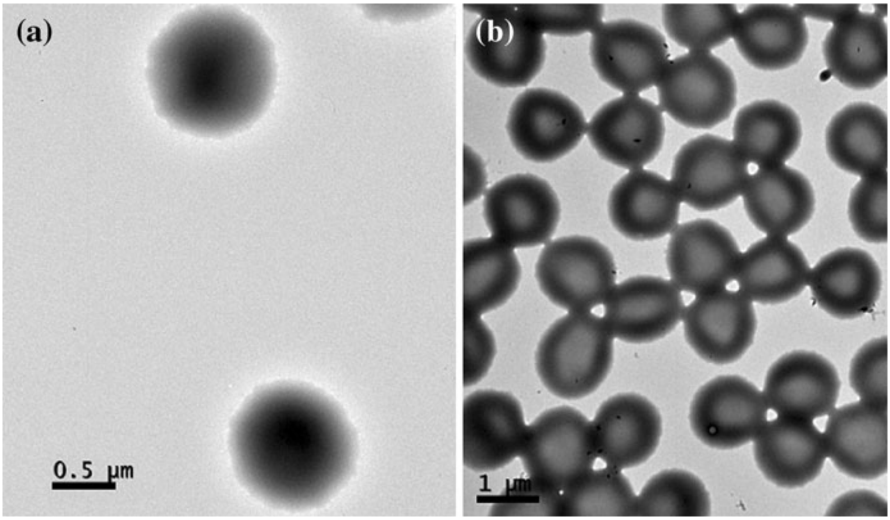


Fig. 2 The morphologies of poly(MMA-MAA-MPS) hollow latex particles that were produced by heating the linear-poly(MMA-MAA)/crosslinking poly(MMA-MAA-MPS) latex particles (EGDMA 0.5 %) in the presence of ammonia (pH 12) at **a** 25 °C and **b** 80 °C for 1 h

crosslinking poly(MMA-MAA-MPS) latex particles, which were heated in the presence of ammonia at 25 °C, displayed an incomplete hollow structure while the latex particles that were heated at 80 °C showed a prefect hollow structure. High temperature was advantageous for the ammonia to dissolve the poly(MMA-MAA) linear zone of latex particles to form a perfect hollow structure.

Effect of crosslinking degree on the morphology of poly(MMA-MAA-MPS) hollow latex particles

The crosslinking degree of poly(MMA-MAA-MPS) shell was an important factor to influence the morphology of hollow poly(MMA-MAA-MPS) latex particles as shown in Fig. 3a, b. The linear-poly(MMA-MAA)/crosslinking poly(MMA-MAA-MPS) latex particles with the crosslinking agent of 1.5 % were heated in the presence of ammonia at 80 °C for 3 h showed a perfect hollow structure while the latex particles with crosslinking agent of 10 % showed an incomplete hollow structure. The crosslinking structure of poly(MMA-MAA-MPS) might hinder ammonia from diffusion into the linear-poly(MMA-MAA)/crosslinking poly (MMA-MAA-MPS) latex particles to dissolve the poly(MMA-MAA) linear zone, therefore the latex particles with higher crosslinking degree would form an incomplete hollow structure.

Effect of pH value on the morphology of poly(MMA-MAA-MPS) latex particles

The pH value of ammonia significantly influenced the morphology of latex particles were shown as Fig. 4a, b. The linear-poly(MMA-MAA)/crosslinking

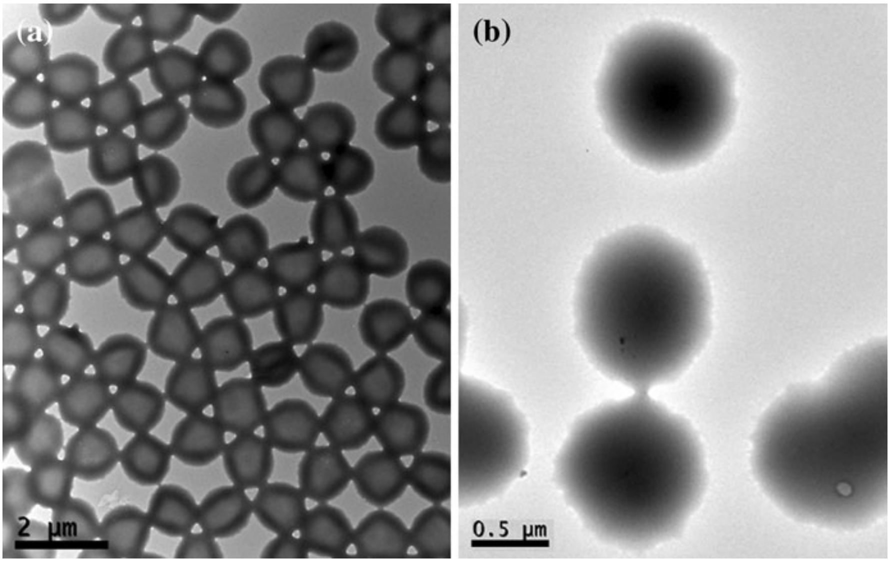


Fig. 3 The morphologies of poly(MMA-MAA-MPS) hollow latex particles that were produced by heating the linear-poly(MMA-MAA)/crosslinking poly(MMA-MAA-MPS) latex particles with EGDMA **a** 1.5 % **b** 10 % in the presence of ammonia (pH 12) at 80 °C for 3 h

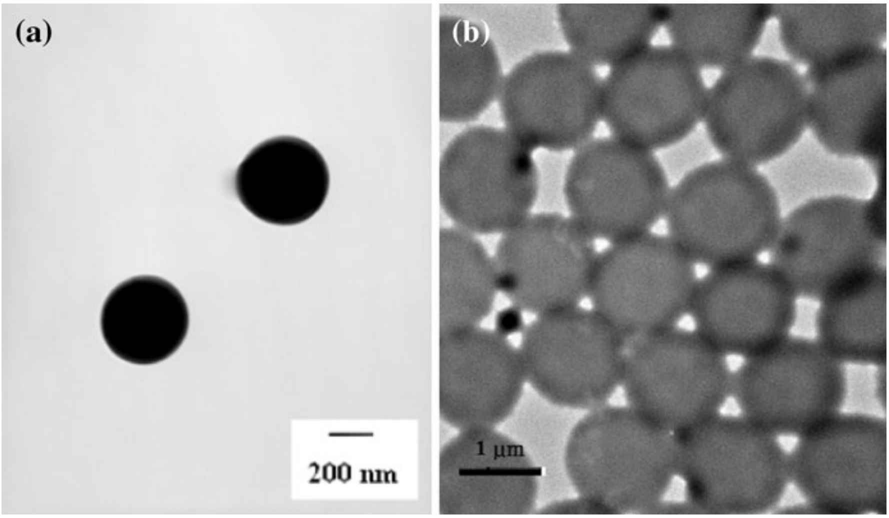


Fig. 4 The morphologies of poly(MMA-MAA-MPS) hollow latex particles that were produced by heating the linear-poly(MMA-MAA)/crosslinking poly(MMA-MAA-MPS) latex particles (EGDMA 0.5 %) in the presence of ammonia **a** pH 11 **b** pH 12 at 80 °C for 3 h

poly(MMA-MAA-MPS) latex particles, which were heated at the condition of pH 11, showed a dense structure while the latex particles, which were heated in the presence of pH 12 ammonia, showed a perfect hollow structure. At the condition of high-pH value, the carboxylic groups (–COOH) of poly(MAA) were ionized to form $–COO^{-}$ so as to enhance the hydrophilic of poly(MMA-MAA) polymer chains. Therefore, the ammonia of pH 12 dissolve the poly(MMA-MAA) linear core of linear-poly(MMA-MAA)/crosslinking poly(MMA-MAA-MPS) latex particles completely to form the poly(MMA-MAA-MPS) hollow latex particles.

Effect of crosslinking degree on the morphology of poly(MMA-MAA-MPS)/ ZnO composite hollow latex particles

Figure 5a, b showed the morphologies of poly(MMA-MAA-MPS)/ZnO composite hollow latex particles with EGDMA 0.5 and 1.5 %, respectively. The results showed that the hollow latex particles with 1.5 % EGDMA bonded with more amounts of ZnO nanoparticles. The reason was due to that the poly(MMA-MAA-MPS) hollow latex particles were produced by heating the linear-poly(MMA-MAA)/crosslinking poly(MMA-MAA-MPS) latex particles in the presence of ammonia so that part of poly(MMA-MAA-MPS) chains might separate from the

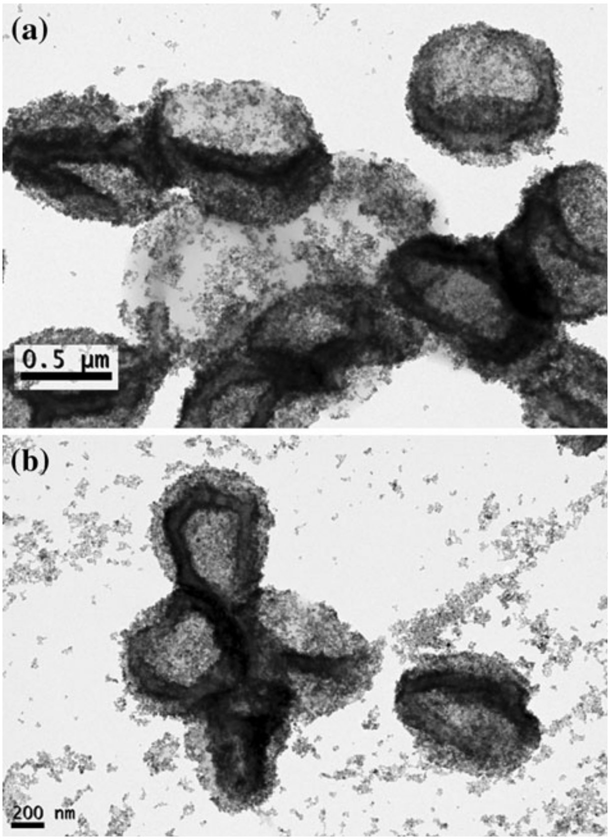


Fig. 5 The morphologies of poly(MMA-MAA-MPS)/ZnO composite hollow latex particles with EGDMA **a** 0.5 %; **b** 1.5 %

Table 2 The surface charge of ZnO nanoparticles and hollow latex particles

Sample	Surface charge (mV)
ZnO nanoparticles	29.18
Poly(MMA-MAA-MPS) hollow latex particles (EGDMA 0.5 %)	−44.73
Poly(MMA-MAA-MPS) hollow latex particles (EGDMA 1 %)	−51.70
Poly(MMA-MAA-MPS) hollow latex particles (EGDMA 1.5 %)	−52.84
Poly(MMA-MAA-MPS)/ZnO composite hollow latex particles(EGDMA 0.5 %)	−40.82
Poly(MMA-MAA-MPS)/ZnO composite hollow latex particles(EGDMA 1 %)	−38.25
Poly(MMA-MAA-MPS)/ZnO composite hollow latex particles(EGDMA 1.5 %)	−34.26

poly(MMA-MAA-MPS) hollow latex particle with low crosslinking degree, while large part of poly(MMA-MAA-MPS) chains might retain on the surface of hollow latex particles with high-crosslinking degree. In the presence of ammonia, the carboxylic acid group (–COOH) of poly(MAA) segments were ionized to form $–COO^{-}$, therefore the increase of crosslinking degree would increase the amount of negative charge on the surface of hollow latex particles as shown in Table 2. The ZnO nanoparticles with positive surface charge were favorable to bond with the poly(MMA-MAA-MPS) hollow latex particles with large amount of negative surface charge. Therefore, the latex particles with high-crosslinking degree might bond with more amounts of ZnO particles so as to increase the surface charge of latex particles. After the poly(MMA-MAA-MPS)/ZnO composite hollow latex particles were treated by sonicator, the ZnO particles still bonded with the latex particles firmly as shown in Fig. 6a, b.

The swelling state of poly(MMA-MAA-MPS) hollow latex particle

The pH value significantly influenced the swelling state of poly(MMA-MAA-MPS) hollow latex particles. At the condition of pH 3, the hollow latex particles showed the least significant swelling state of the four conditions as shown in Fig. 7. At the condition of high pH value, the carboxylic groups of poly(MAA), which consisted in the poly(MMA-MAA-MPS) hollow latex particle, were ionized to form $–COO^{-}$ so as to enhance the swelling state of hollow latex particle. However, the pH value insignificantly influenced the swelling state of poly(MMA-MAA-MPS) hollow latex particles with either 1 % EGDMA or 1.5 % EGDMA. The reason was due to that the structure of high-crosslinking degree restricted the swelling behavior of hollow latex particles.

The morphology of poly(MMA-MAA-MPS) hollow latex particles that were loaded with caffeine

Figure 8a, b showed the morphologies of poly(MMA-MAA-MPS) hollow latex particles before and after were loaded with caffeine, respectively. Before loaded with caffeine, the latex particles showed a brighter image while the latex particles showed a darker image after loaded with caffeine. These results indicated that the hollow latex particles were loaded with caffeine perfectly.

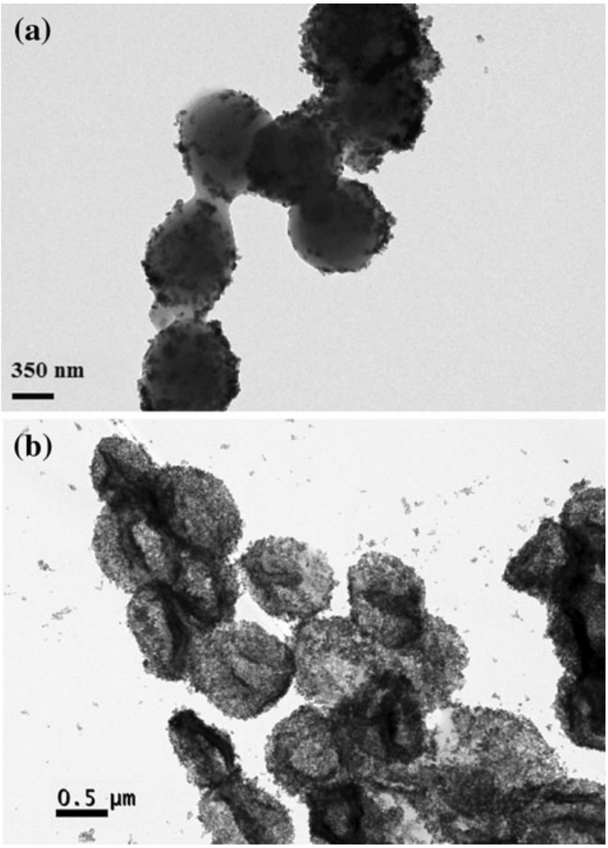


Fig. 6 The morphologies of poly(MMA-MAA-MPS)/ZnO composite hollow latex particles with EGDMA **a** 0.5 % **b** 1.5 % that had been treated by sonicator

Effect of hollow structure and crosslinking degree on the amount of caffeine loading

The crosslinking structure of hollow latex particle significantly hindered the caffeine from diffusing into the latex particle. With the increase of crosslinking agent would decrease the amount of caffeine loading as shown in Fig. 9. Besides, Fig. 9 showed that the hollow structure of latex particle was favorable for the caffeine loading. The latex particle with hollow structure was loaded with larger amount of caffeine than that with dense structure.

Effect of pH value on the amount of caffeine loading

Figure 10 showed the effect of pH value on the amount of caffeine loading. The results showed that the poly(MMA-MAA-MPS) hollow latex particles loaded with the least amount of caffeine at the condition of pH 11 than any others pH values in the experiment. At the condition of pH 11 the carboxylic groups of poly(MAA),

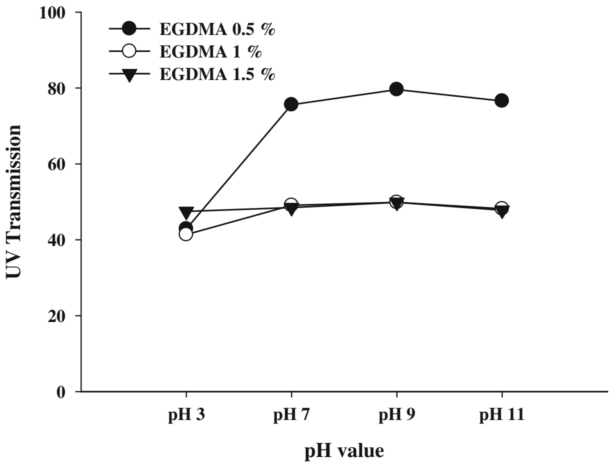


Fig. 7 The effect of crosslinking agent on the swelling state of poly(MMA-MAA-MPS) hollow latex particles

which consisted in the poly(MMA-MAA-MPS) hollow latex particle, were ionized to form –COO$^-$ so as to enhance the swelling state of hollow latex particle. The caffeine not only loaded into but also diffused out of the well-swollen latex particles so that the hollow latex particles loaded with the least amount of caffeine at the condition of pH 11. Moreover, at the condition of pH 3, the hollow latex particles showed a poor swelling state so that the caffeine was difficult to load into the latex particles while the caffeine, which had loaded into the latex particles, was difficult to diffuse out of the latex particles. At the condition of pH 7, the appropriate swelling state made the hollow latex particles retained a large amount of caffeine.

Effect of pH value on the control release of caffeine

Figure 11 showed the effect of pH value on the control release of caffeine, which was loaded in the hollow latex particles at the condition of pH 3. The results showed that the largest amount of caffeine released from the hollow latex particles at the condition of pH 3 than any others pH value in the experiment. After the hollow latex particles were loaded with caffeine, a large part of caffeine stayed at the shell zone but not stayed at the hollow zone due to the shrunken structure of latex particle at the condition of pH 3 so that the caffeine was easy to release from the shell zone of hollow latex particles during the release process. However, the hollow latex particles swollen well at the condition of pH 11 so that the caffeine, which stayed at the shell zone, not only diffused out of the latex particle but also diffused into the hollow zone of latex particles during the process of caffeine release, hence only a little amount of caffeine released from the hollow latex particle. Besides, a large amount of aqueous medium diffused into the well-swollen latex particle at the condition of pH 11 so as to lower the concentration gradient of caffeine between interior and external of latex particle, therefore only a little of caffeine released from the hollow latex particle. The control release of caffeine, which was loaded in the

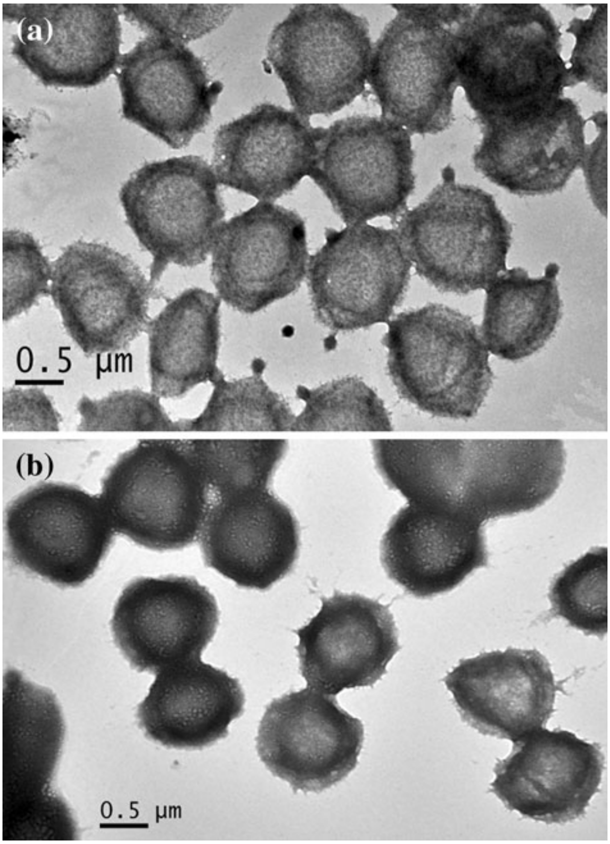


Fig. 8 The morphologies of poly(MMA-MAA-MPS) hollow latex particles (EGDMA 0.5 %) **a** before were loaded with caffeine **b** after were loaded with caffeine at the condition of pH 7

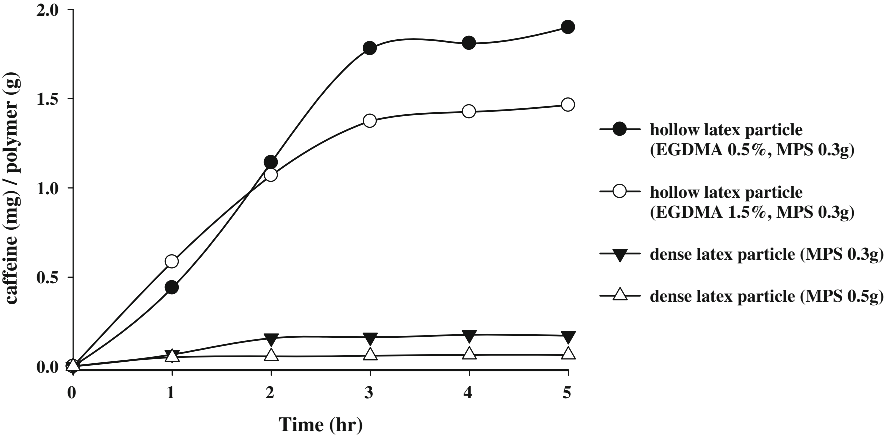


Fig. 9 The effect of structure and crosslinking degree of latex particles on the amount of caffeine loading

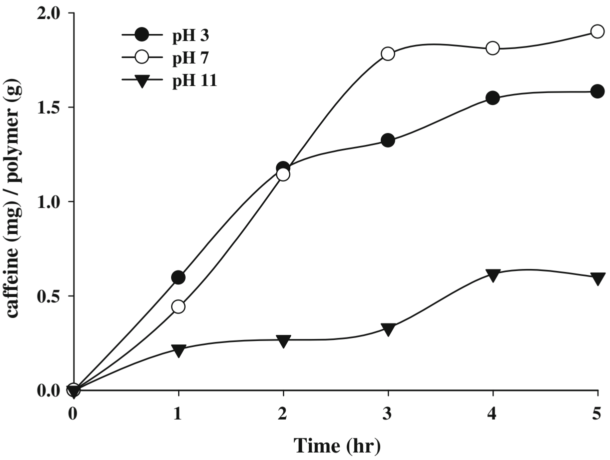


Fig. 10 Effect of pH value on the amount of caffeine loading

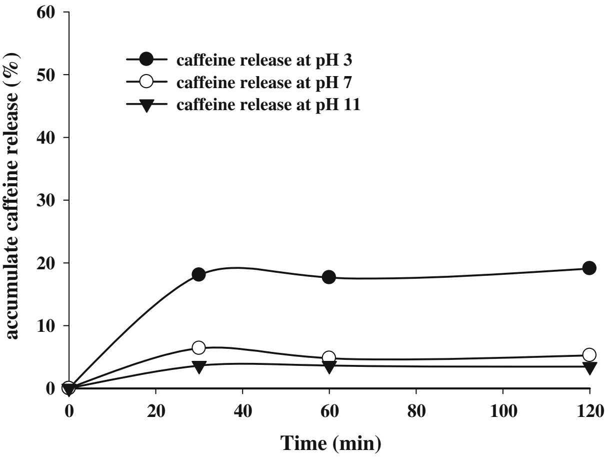
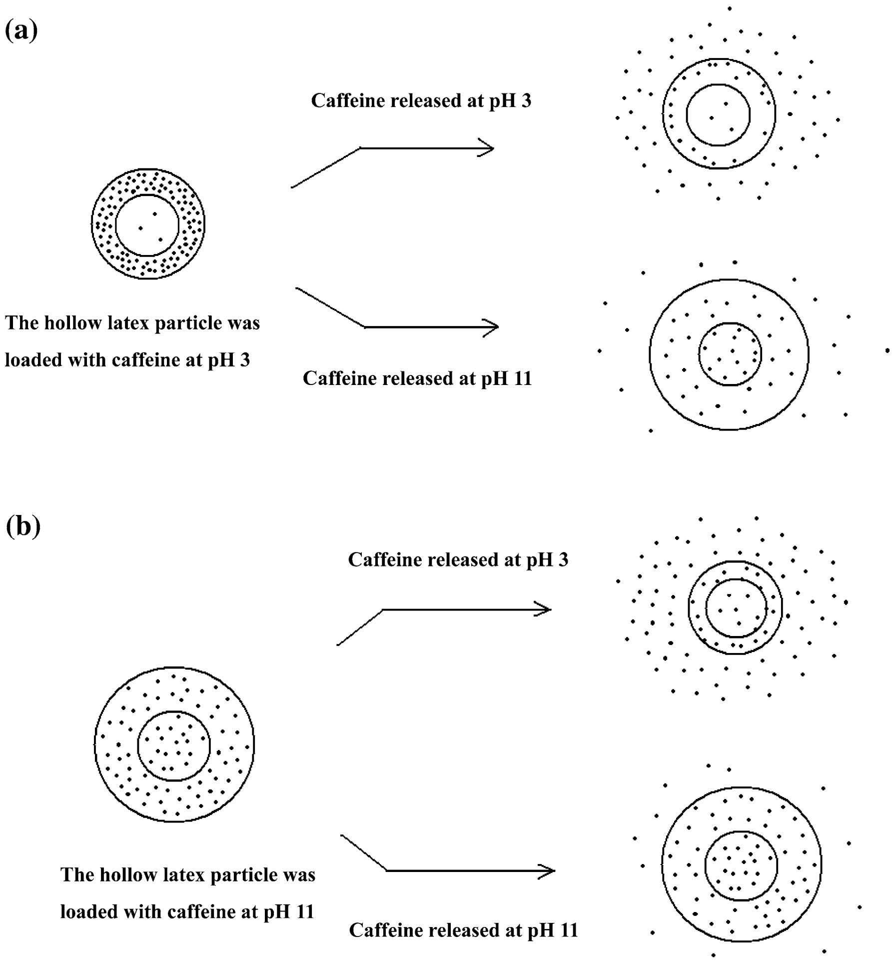


Fig. 11 The effect of pH value on the amount of caffeine release (the hollow latex particles with EGDMA 0.5 % were loaded with the caffeine at the condition of pH 3)

hollow latex particle at the condition of pH 3, was shown as scheme 1a. Figure 12 showed the effect of pH value on the control release of caffeine, which was loaded in the hollow latex particles at the condition of pH 11. The results showed that the largest amount of caffeine released from the hollow latex particles at the condition of pH 3 than any others pH value in the experiment. After the hollow latex particles were loaded with caffeine at the condition of pH 11, the caffeine not only stayed at the shell zone but also diffused into the hollow zone due to the well swollen structure of latex particles. During the process of caffeine release at the condition of pH 3, the well-swollen hollow latex particles shrunk to form a compact structure so as to extrude the caffeine out of the latex particle quickly. On the contrary, when the caffeine was released at the condition of pH 11, the well-swollen hollow latex



Scheme 1 The control release of caffeine that was loaded in the hollow latex particle at the condition of **a** pH 3; **b** pH 11

particles still showed a swollen structure, so that the caffeine did not be extruded out but stayed in the inner zone of latex particle. The caffeine almost did not release from the hollow latex particles at the condition of pH 11. Scheme 1b showed the control release of caffeine, which was loaded in the hollow latex particles at the condition of pH 11.

Conclusion

In this study, the poly(MMA-MAA-MPS) hollow latex particles were produced successfully by the method of heating the linear-poly(MMA-MAA)/crosslinking

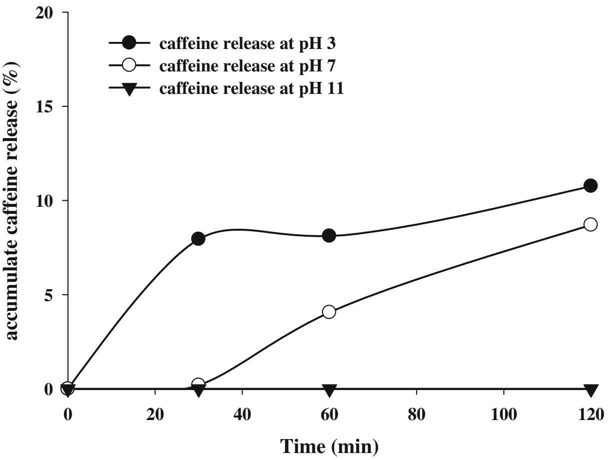


Fig. 12 The effect of pH value on the amount of caffeine release (the hollow latex particles with EGDMA 0.5 % were loaded with caffeine at the condition of pH 11)

poly(MMA-MAA-MPS) latex particles in the presence of ammonia. Sufficient heating time and high-heating temperature were necessary for the ammonia to dissolve the linear core of latex particles to form a perfect hollow structure. The crosslinking structure of poly(MMA-MAA-MPS) shell was a barrier to hinder the ammonia from diffusing into the latex particles to dissolve the poly(MMA-MAA) linear core so that the latex particles with high crosslinking degree of poly(MMA-MAA-MPS) shell would form an incomplete hollow structure. The hollow latex particles were used as carriers to load with caffeine perfectly. No matter whether the caffeine was loaded in the hollow latex particles at the condition of pH 3 or pH 11, the caffeine was easier to release from the latex particles at the condition of pH 3 than that released at the condition of pH 11.

The poly(MMA-MAA-MPS) hollow latex particles mixed with ZnO particle suspension to form the poly(MMA-MAA-MPS)/ZnO composite hollow latex particles. With the increase of crosslinking degree of latex particles would increase the amount of ZnO bonding. After the poly(MMA-MAA-MPS)/ZnO composite hollow latex particles were treated by sonicator, the ZnO particles still bonded with the latex particles firmly.

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