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The preparation and characteristics of poly(methyl methacrylate–methylacrylate acid)/nano-ZnO composite latex particles

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Abstract In this work, poly(methyl methacrylate-co-methylacrylate acid)/ZnO (poly(MMA–MAA)/ZnO) composite latex particle was synthesized by three steps The first step was to synthesize poly(MMA–MAA) copolymer latex particles by soapless emulsion polymerization. Following the first step, the second step was to polymerize MMA, MAA and 3,3-(trimethoxysilyl) propyl methacrylate (MPS) in the presence of poly(MMA–MAA) seed latex particles to form the poly(MMA–MAA)/poly(MMA–MAA–MPS) core–shell latex particles. In the third step, the poly(MMA–MAA)/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)/poly(MMA–MAA–MPS)/ZnO composite latex. In this study, MPS with silanol groups essentially was used as the coupling agent to couple with ZnO nanoparticles, while the results of the study showed that there was not covalent bond existed between ZnO particles and polymer latex. The ZnO particles were adsorbed on the surface of polymer latex by electrostatic interaction. Besides, the linear poly(MMA–MAA)/crosslinking poly(MMA–MAA–MPS) core–shell latex particles which were synthesized in the second step were heated in the presence of ammonia to form the hollow poly(MMA–MAA–MPS) latex particles. The factors of heating time and concentration of crosslinking agent significantly influenced the morphology of hollow poly(MMA–MAA–MPS) latex particles.

Keywords Composite · Methyl methacrylate · Methylacrylate acid · ZnO · Soapless emulsion polymerization

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Introduction

Zinc oxide, ZnO, is one of the multifunctional inorganic materials. They have distinguished performance in electronic, optics, and photonics. For example, versatile application in preparing solar cell [1], gas sensor [2], varistor [3], and piezoelectric device [4] are potentially applied. The methods for preparing ZnO included sol–gel method [5], hydrothermal synthesis [6], chemical vapor deposition [7], and other methods [8, 9]. It is worth noticing that applying suitable surface treatment on ZnO nanoparticles to keep them from aggregation or combining ZnO with polymer particles to become composite latex particles are feasible ways to improve the dispersity of inorganic particles [10]. Miniemulsion polymerization is one of the common methods to prepare composite latex particles. Zhou et al. [11] synthesized SiO_2/poly(styrene-co-butylacrylate) nanocomposite microspheres with various morphologies via miniemulsion polymerization. Ghurmallah et al. [12] used the method of miniemulsion polymerization to encapsulate titanium dioxide in styrene/n-butyl acrylate copolymer and the encapsulation degree was studied.

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 [13]. 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, [14] the deposition of polyelectrolytes on the core particles, 15, 16] and emulsion (microemulsion or miniemulsion) polymerization, [17] have been developed to form hollow latex particles. Recently, the method of layer-by-layer assembly has been proved to fabricate hollow capsules [18, 19]. von Klitzing et al. [20] 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. Karine Glinel et al. [21] 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.

In this work, the poly(MMA–MAA)/poly(MMA–MAA–MPS) latex particles were synthesized first and then reacted with ZnO nanoparticles to form the poly(MMA–MAA)/poly(MMA–MAA–MPS)/ZnO composite latex particle. Besides, the linear poly(MMA–MAA)/crosslinking poly(MMA–MAA–MPS) core–shell latex particles were heated in the presence of ammonia to form the poly(MMA–MAA–MPS) hollow latex particles.

Experiment

Materials

Methyl methacrylate (MMA), methylacrylic 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 work.

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 at the temperature of 50 or 60 °C and stirred using a magnetic stirrer. After the mixture reached to the reaction temperature, ethyl alcohol solution (0.08 g of NaOH dissolved in 15 g of ethyl alcohol) was added into the mixture to react with Zinc acetate dehydrate, therefore obtained the ZnO nanoparticles.

Synthesis of poly(MMA–MAA) copolymer latex particles (first step polymerization)

Methyl methacrylate (MMA, 16.5 g) and methacrylic acid (MAA, 5.5 g) were polymerized to form poly(MMA–MAA) copolymer latex particles. In this reaction, potassium persulfate (KPS) was used as an initiator. The polymerization was carried out at 80 °C for 2 h by the method of soapless emulsion polymerization under a nitrogen atmosphere. The conversion of polymerization was measured in order to make sure that the monomers had been reacted completely. The conversion of polymerization was measured by the method as follows:

After the polymerization was carried out for 2 h, a sample of the emulsion latex was taken out of the reactor and poured into methanol with hydroquinone to stop the reaction. The precipitated polymers were washed with methanol and water several times and then dried in a vacuum oven. The conversion of polymerization was calculated as Eq. 1.

$$\text{Conversion} = \frac{W_2}{W_1 \times M_1(\text{MMA} + \text{MAA})\%} \tag{1}$$

where W_1 is the weight of the sample taken from the vessel; W_2, the weight of dry polymers obtained from the taken sample; $M_1(\text{MMA} + \text{MAA})\%$, the weight percentage of MMA and MAA monomer in the reaction mixture.

The conversion of first step polymerization for the synthesis of poly(MMA–MAA) copolymer latex is about 98%.

Synthesis of poly(MMA–MAA)/poly(MMA–MAA–MPS) latex particle (second step polymerization)

The poly(MMA–MAA)/poly(MMA–MAA–MPS) latex particles were synthesized by the method of soapless seeded emulsion polymerization under the condition listed in Table 1. In the soapless seeded emulsion polymerization, the poly(MMA–MAA) seed latex emulsion was stirred at 80 °C under the atmosphere of nitrogen. At this moment, quantitative monomers (MMA and MAA and MPS) were poured into the reaction system, and then the aqueous solution of $K_2S_2O_8$ was added into

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

Poly(MMA–MAA) seed latex emulsion (g)	50
MMA (g)	7.71–8.25
MAA (g)	0.75–1.29
MPS (g)	0.3–0.5
KPS (g)	0.3
Deionized water (g)	250
Reaction time (h)	2
Reaction temperature (°C)	80
Stirring rate (rpm)	300

the reaction system to begin the reaction. After the reaction proceed for 2 h, the poly(MMA–MAA)/poly(MMA–MAA–MPS) latex particles were produced. The conversion of second step polymerization was calculated as Eq. 2.

$$\text{Conversion} = \frac{W_4 - W_3 \times \mathrm{B}\%}{W_3 \times M_2(\mathrm{MMA} + \mathrm{MAA} + \mathrm{MPS})\%} \tag{2}$$

where W_3 is the weight of the sample taken from the vessel; W_4 is the weight of dry polymer obtained from the taken sample. M_2(MMA + MAA + MPS)% is the weight percentage of monomer (MMA, MAA and MPS) in the reaction mixture for the second step reaction; *B*%, the weight percentage of Poly(MMA–MAA) seed latex in the reaction mixture. The conversion of second step polymerization for the synthesis of poly(MMA–MAA–MPS) is about 98.5%.

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

The poly(MMA–MAA)/poly(MMA–MAA–MPS) latex emulsion mixed with the ZnO particle suspension (the ethyl alcohol medium of ZnO suspension was displaced by deionized water before this process), and then stirred for 48 h at room temperature to produced the poly(MMA–MAA)/poly(MMA–MAA–MPS)/ZnO composite latex particles.

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

The poly(MMA–MAA–MPS) hollow latex particles were synthesized by three steps. The first step was to synthesize the linear poly(MMA–MAA) latex particles. In the second step, the MMA, MAA, MPS and, crosslinking agent (EGDMA), were polymerized in the presence of poly(MMA–MAA) seed latex to form the linear poly(MMA–MAA)/crosslinking poly(MMA–MAA–MPS) latex particles. The conversion of polymerization is about 98.2%. The ingredients and reaction condition were shown as Table 2. Following the second step, the linear poly(MMA–MAA)/crosslinking poly(MMA–MAA–MPS) latex particles were heated in the presence of ammonia to form a hollow structure.

Table 2 Ingredients and reaction condition for the synthesis of 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

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 quantitative of latex particles were purified, and then added into the buffer solution to form the latex suspension. The samples of latex suspension were tested by UV light. The swelling characteristic of latex particles were determined by the UV light transmission.

Result and discussion

Morphology of ZnO nanoparticlers

Figure 1a and b showed the TEM photographs of ZnO nanoparticles, which were synthesized at 50 and 60 °C, respectively. The results showed that the reaction temperature significantly influenced the morphology of ZnO nanoparticles. The ZnO nanoparticles, which were synthesized at 50 °C, showed the rod like structure while that were synthesized at 60 °C showed the spherical like structure (the diameter was about 15 nm). Besides, the X-ray diffraction (XRD) of nanoparticles [22] showed three characteristic peaks of ZnO as shown in Fig. 2. This result decided that ZnO nanoparticles were successfully synthesized by a sol gel method.

Morphology of poly(MMA–MAA)/poly(MMA–MAA–MPS) latex particles

In the process of seed emulsion polymerization, MMA, MAA, and hydrophobic MPS were polymerized in the presence of seed particles to form the poly(MMA–MAA)/poly(MMA–MAA–MPS) latex particles, therefore the diameter of poly(MMA–MAA)/poly(MMA–MAA–MPS) latex particles was larger than that of poly(MMA–MAA) seed latex as shown in Fig. 3a and b. The diameter of

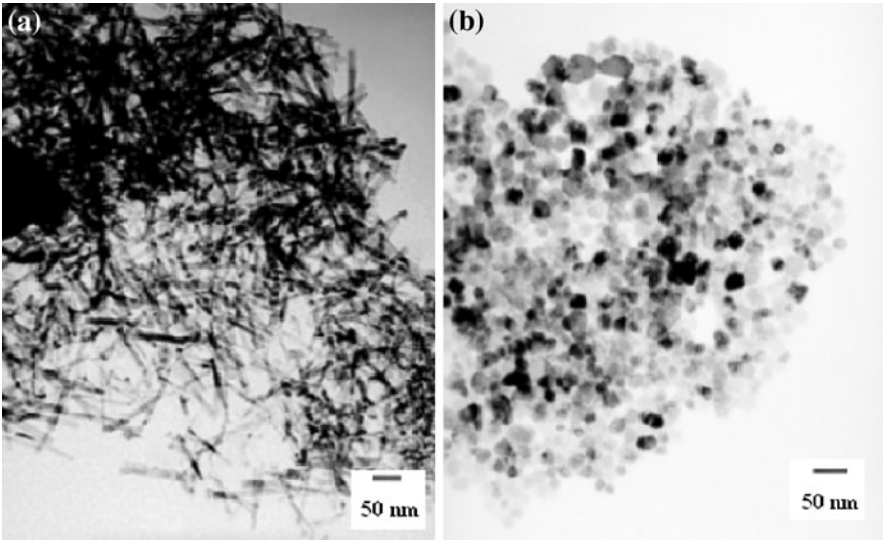

Fig. 1 TEM photographs of ZnO nanoparticle that were synthesized at **a** 50 °C, **b** 60 °C

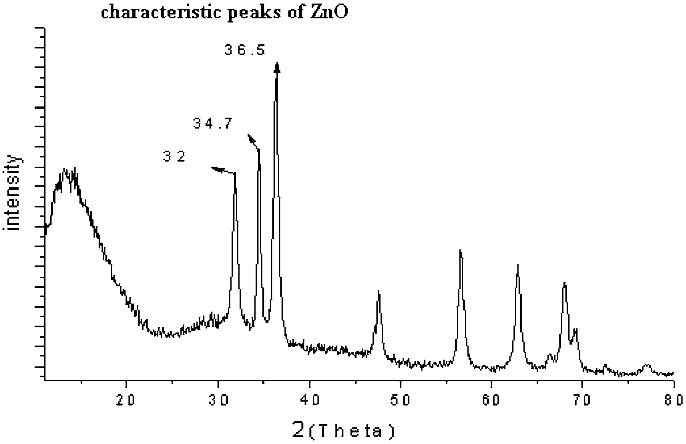

Fig. 2 X-ray diffraction (XRD) of ZnO nanoparticles

poly(MMA–MAA) seed latex was about 314 nm, while the diameter of poly(MMA–MAA)/poly(MMA–MAA–MPS) latex particle was about 400 nm. The composition of latex particle was measured by a energy dispersive spectroscopy (EDS), the result showed that the latex particle contained Si element as shown in Fig. 4. This result decided that MPS had been polymerized on the poly(MMA–MAA) seed latex particle. The boundary of latex particle with more amount of MPS was clearer than that with less amount of MPS as shown in Fig. 3b and c, respectively. The reason was due to that the hydrophobic MPS might restrain the swell state of latex particle.

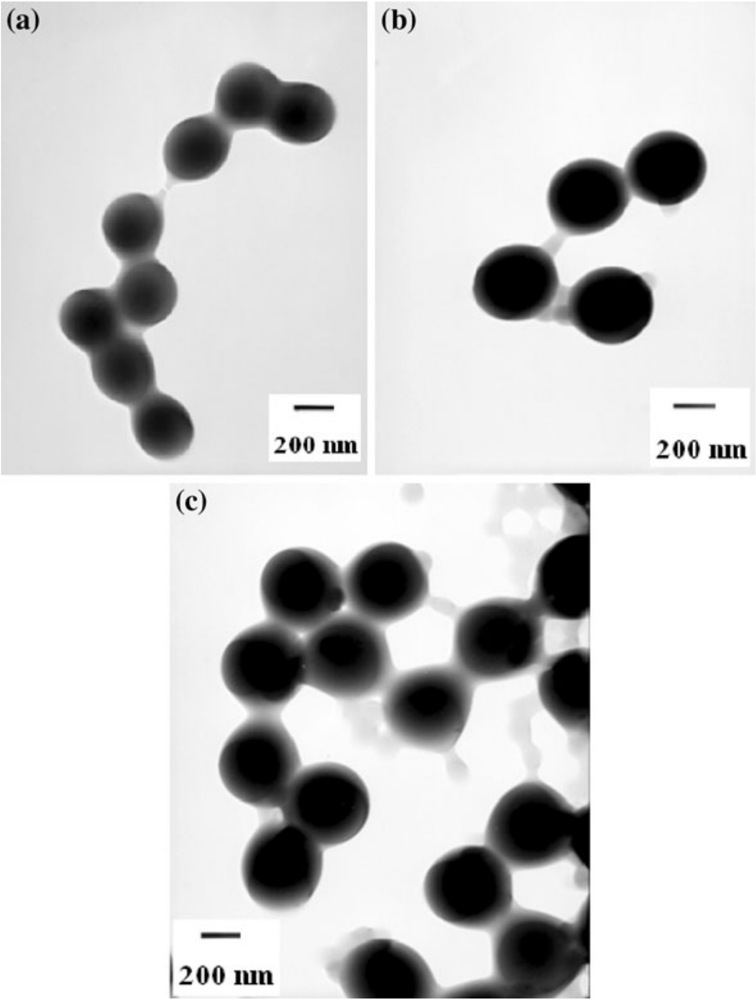

Fig. 3 TEM photographs of **a** poly(MMA–MAA) seed latex particles (MMA:MAA = 3:1 weight ratio), **b** Poly(MMA–MAA)/poly(MMA–MAA–MPS) latex particles (shell composition MMA:MAA = 6:1 weight ratio, MPS 0.5 g), **c** Poly(MMA–MAA)/poly(MMA–MAA–MPS) latex particles (shell composition MMA:MAA = 6:1 weight ratio, MPS 0.3 g)

The swelling property of poly(MMA–MAA)/poly(MMA–MAA–MPS) latex particle

The pH value significantly influenced the swelling state of poly(MMA–MAA)/poly(MMA–MAA–MPS) latex particle. At the condition of high pH value, the carboxylic groups (–COOH) of poly(MAA) were ionized to form $-COO^{-}$ so as to enhance the swelling state of latex particle. Although the pKa of MAA was about 4.66, the poly(MMA–MAA)/poly(MMA–MAA–MPS) latex suspension showed the most significant swelling state at the condition of pH 11 was shown as Fig. 5. The reason was due to that the polymer chains entwined in the latex particle, therefore

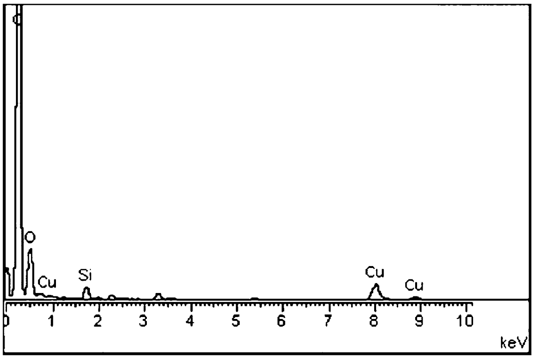

Fig. 4 The spectrum of energy dispersive spectroscopy of poly(MMA–MAA)/poly(MMA–MAA–MPS) latex particles (shell composition MMA:MAA = 6:1, MPS 0.5 g)

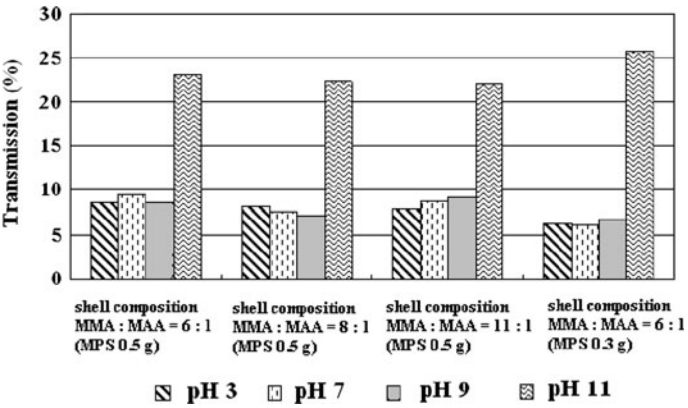

Fig. 5 The effect of pH value and composition on the swelling state of poly(MMA–MAA)/poly(MMA–MAA–MPS) latex particle

the –COOH groups of poly(MAA) were covered by the poly(MMA) segments of polymer chains so that the condition of pH 11 was favorable for the –COOH groups to be ionized completely. Besides, Fig. 5 showed the effect of composition on the swelling state of latex particles. The results showed that the weight ratio of MMA and MAA influenced the swelling state of latex particle insignificantly, while the quantity of MPS influenced the swelling state of latex particle slightly. With the increase of the quantity of MPS would decrease the swelling state of latex particles. The reason was due to that the hydrophobic property of MPS would hinder the swelling behavior of latex particle.

Morphology of poly(MMA–MAA)/poly(MMA–MAA–MPS)/ZnO composite latex particles

The effect of concentration of MAA on the morphology of composite latex particles was shown as Fig. 6a and b. The concentration of MAA influenced the morphology of composite latex particles insignificantly. Besides, the effect of concentration of

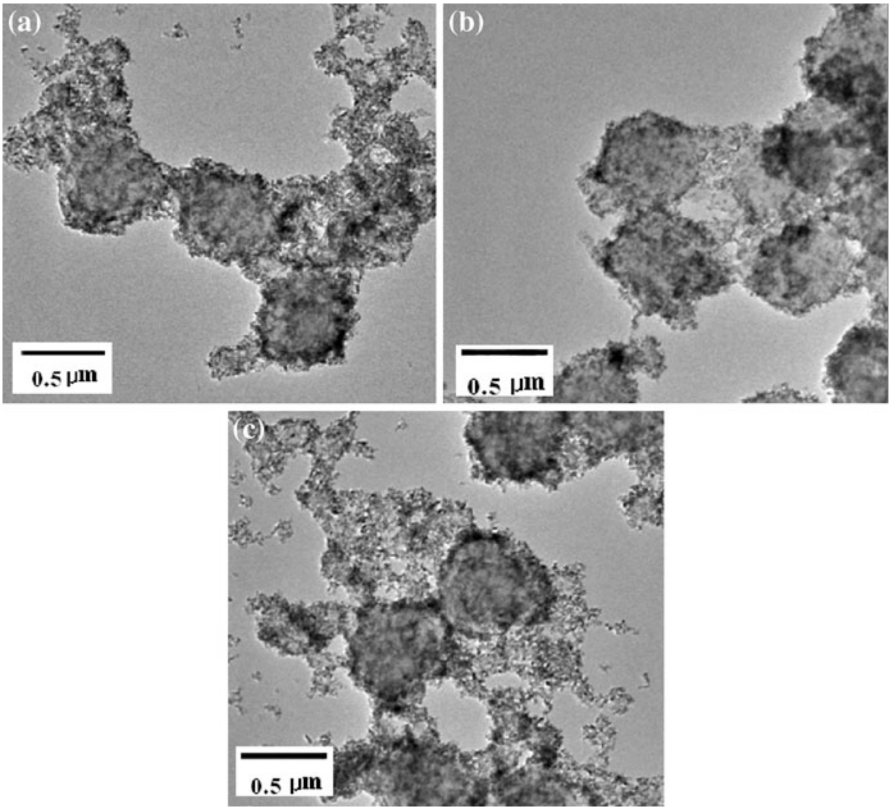

Fig. 6 The effect of concentration of MAA and MPS on the morphology of poly(MMA–MAA)/poly(MMA–MAA–MPS)/ZnO composite latex particles **a** shell composition MMA:MAA = 6:1, MPS 0.5 g, **b** shell composition MMA:MAA = 11:1, MPS 0.5 g (**c**) shell composition MMA:MAA = 6:1, MPS 0.3 g

MPS on the morphology of composite latex particles was insignificant as shown in Fig. 6a and c. In order to ascertain that the ZnO particles bonded to the polymer latex particles firmly, the polymer/ZnO composite latex particles were treated by sonicator. The result showed that the ZnO particles still combined with the polymer latex after the polymer/ZnO composite latex particles were treated by sonicator as shown in Fig. 7.

The bonding between poly(MMA–MAA)/poly(MMA–MAA–MPS) latex particle and ZnO nanoparticle

By referred to the study of chemical bonding between ZnO and polymer chains [23], C^{13}-NMR was used to analyze the composite latex particles. Figure 8a and b showed the ^{13}C-NMR spectrum of poly(MMA–MAA)/poly(MMA–MAA–MPS) latex particles and poly(MMA–MAA)/poly(MMA–MAA–MPS)/ZnO composite latex particles, respectively. Comparing the spectrum of the composite latex particles with that of the polymer latex particles, it could be seen that the peaks of

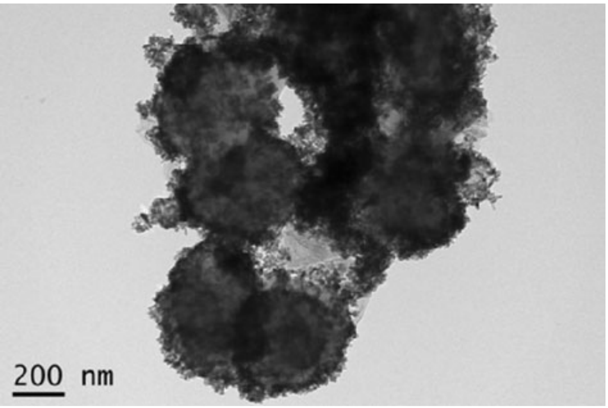

Fig. 7 The morphology of poly(MMA–MAA)/poly(MMA–MAA–MPS)/ZnO composite latex particles that had been treated by sonicator (shell composition MMA:MAA = 6:1, MPS 0.5 g)

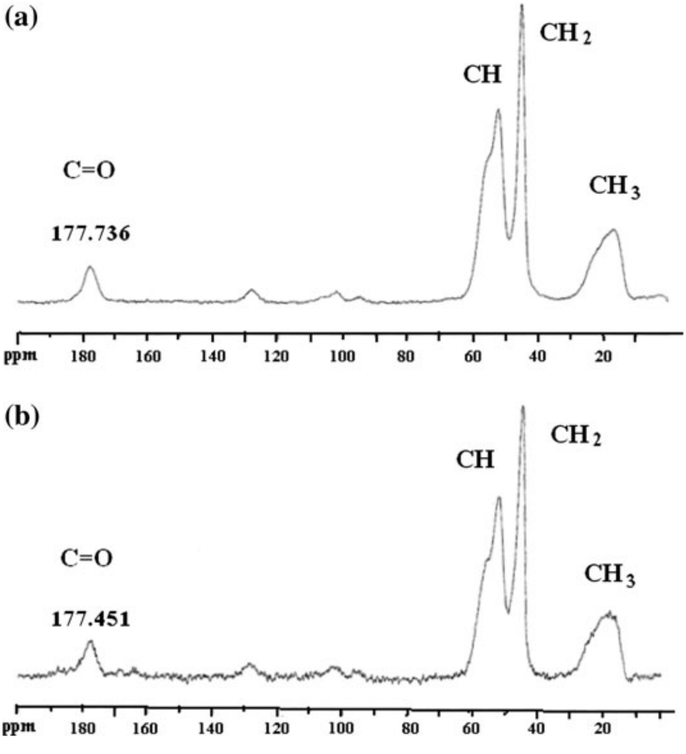

Fig. 8 The ^{13}C-NMR spectrum of **a** poly(MMA–MAA)/poly(MMA–MAA–MPS) latex particles and **b** poly(MMA–MAA)/poly(MMA–MAA–MPS)/ZnO composite latex particles (shell composition MMA:MAA = 6:1, MPS 0.5 g)

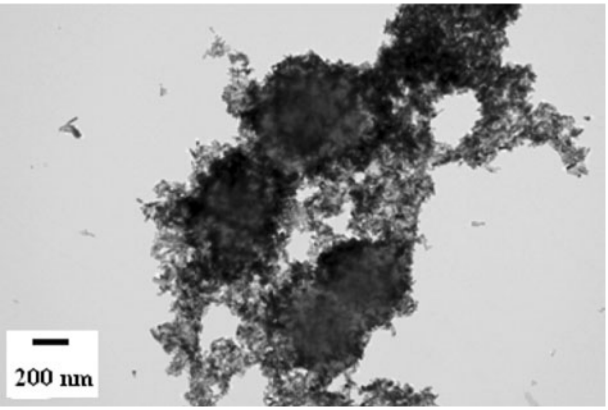

Fig. 9 The morphology of poly(MMA–MAA)/ZnO composite latex particles that had been treated by sonicator (composition MMA:MAA = 6:1)

Table 3 Zeta potential of ZnO particles and polymer latex particles

Sample	Zeta potential (mV)
ZnO	29.18
Poly(MMA–MAA) (Composition MMA:MAA = 6:1)	−37.82
Poly(MMA–MAA)/Poly(MMA–MAA–MPS) (shell composition MMA:MAA = 6:1, MPS 0.5 g)	−31.96
Poly(MMA–MAA)/Poly(MMA–MAA–MPS) (shell composition MMA:MAA = 11:1, MPS 0.5 g)	−27.76
Poly(MMA–MAA)/Poly(MMA–MAA–MPS) (shell composition MMA:MAA = 6:1, MPS 0.3 g)	−31.58

CH_3, CH_2, CH and C=O did not show the chemical shifts almost. It indicated that there was not an interaction existed at the interface of ZnO particles and copolymer chains, implying did not occur the reaction between ZnO particles and poly(MMA–MAA)/poly(MMA–MAA–MPS) latex particles. The result suggested that MPS was not necessary for the bonding between ZnO particles and poly(MMA–MAA)/poly(MMA–MAA–MPS) latex particles. In order to verify the above mention, the poly(MMA–MAA) latex particles (MMA:MAA = 6:1) without MPS were synthesized and then bonded with ZnO nanoparticles to form the poly(MMA–MAA)/ZnO composite latex particles. Besides, the sonicator was used to treat the composite latex particles to prove that the ZnO nanoparticles bonded on the polymer latex firmly. Figure 9 showed the morphology of poly(MMA–MAA)/ZnO composite latex particles, which had been treated by sonicator. The result showed that ZnO nanoparticles adsorbed on the surface of polymer latex particles perfectly. In order to find out what is the bonding force between ZnO particles and poly(MMA–MAA) latex particles, the surface charge of poly(MMA–MAA) latex particles and ZnO nanoparticles were measured by zeta potential analyzer. The result showed that the

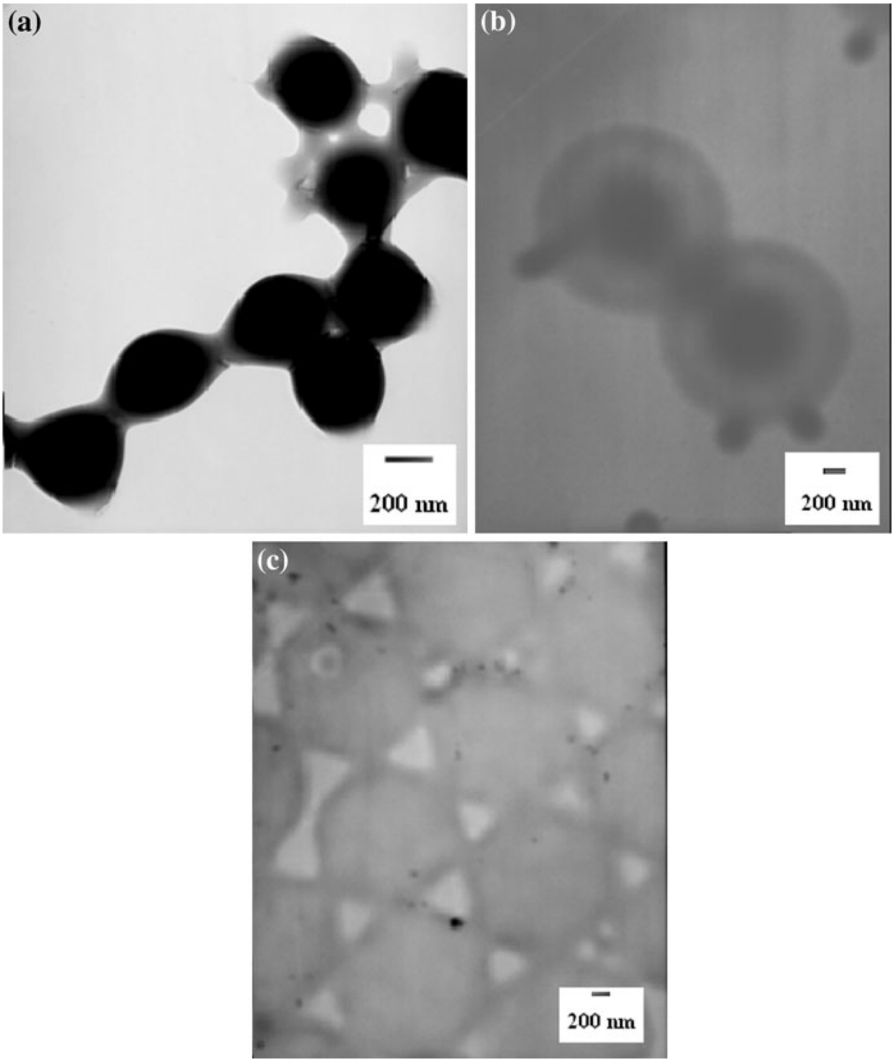

Fig. 10 The morphology of linear poly(MMA–MAA)/crosslinking poly(MMA–MAA–MPS) latex particles that were heated in the presence of ammonia (pH 12) for **a** 0 h, **b** 1 h, **c** 3 h (shell composition of latex particle MMA:MAA = 6:1 weight ratio, MPS 0.3 g, EGDMA 0.5%)

surface charge of poly(MMA–MAA) latex particle was negative while the surface charge of ZnO nanoparticle was positiove, which were shown as Table 3. The above results suggested that there was not covalent bond existed between ZnO nanoparticles and polymer latex. The ZnO nanoparticles were adsorbed on the surface of poly(MMA–MAA) latex particles by electrostatic interaction. This result could explain the reason why the composition influenced the morphology of composite latex particles insignificantly as shown in Fig. 6a–c. It was due to the little variations in surface charge for the composite latex particles with different

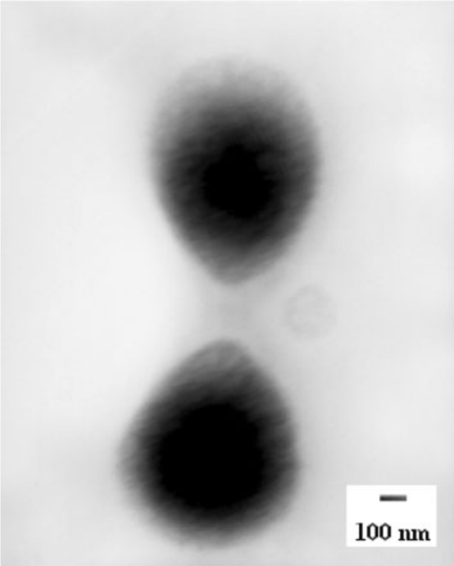

Fig. 11 The morphology of linear poly(MMA–MAA)/crosslinking poly(MMA–MAA–MPS) latex particles, which were heated in the presence of ammonia (pH 12) for 3 h (shell composition of latex particle MMA:MAA = 6:1 weight ratio, MPS 0.3 g, EGDMA 10%)

composition that was shown in Table 3. Therefore, the approximate amount of ZnO particles adsorbed on the surface of poly(MMA–MAA)/poly(MMA–MAA–MPS) latex particles with different composition, and formed the similar morphology.

Morphology of poly(MMA–MAA–MPS) hollow latex particles

The linear poly(MMA–MAA)/crosslinking poly(MMA–MAA–MPS) latex particles with solid structure were heated in the presence of ammonia to form a hollow structure. Figure 10a–c showed the effect of heating time on the morphologies of latex particles. The heating time was the important factor to influence the morphology of latex particles. The latex particles, which were heated at the condition of 25 °C and pH 12 for 1 h, showed the incomplete hollow structure while the latex particles that were heated for 3 h showed the perfect hollow structure. The ammonia needed enough time to diffuse into the latex particles and dissolve the linear poly(MMA–MAA) core to form a hollow structure. Besides, the linear poly(MMA–MAA)/crosslinking poly(MMA–MAA–MPS) core–shell latex particles with the shell of high crosslinking degree showed the imperfect hollow structure as shown in Fig. 11. The shell with high crosslinking degree was the barrier for the diffusion of ammonia, therefore the ammonia could not dissolve the linear poly(MMA–MAA) core completely to form the perfect hollow structure.

Conclusion

In this study, the pH value influenced the swelling state of poly(MMA–MAA)/poly(MMA–MAA–MPS) latex particle significantly. With the increase of pH value would increase the swelling ratio of poly(MMA–MAA)/poly(MMA–MAA–MPS) latex particles. The ZnO nanoparticles bonded with the poly(MMA–MAA)/poly(MMA–MAA–MPS) latex particles firmly by the method of electrostatic interaction rather than chemical bonding. The hollow poly(MMA–MAA–MPS) latex particles were obtained by heating the linear poly(MMA–MAA)/crosslinking poly(MMA–MAA–MPS) latex particles in the presence of ammonia. The heating time and crosslinking degree of poly(MMA–MAA–MPS) shell influenced the morphology of hollow latex particles significantly. The latex particles, which were heated at the condition of 25 °C, pH 12 for 3 h showed the perfect hollow structure. The linear poly(MMA–MAA)/crosslinking poly(MMA–MAA–MPS) core–shell latex with the shell of high crosslinking degree showed the imperfect hollow structure.

References

1. Meng QB, Takahashi K, Zhang XT, Sutanto I, Rao TN, Sato O, Fuji shima A, Watanabe H, Nakamori T, Uragami M (2003) Fabrication of an efficient solid-state dye-sensitized solar cell. Langmuir 19:572–3574
2. Gao T, Wang TH (2005) Synthesis and properties of multipod-shaped ZnO nanorods for gas-sensor applications. Appl Phys A 80:1451–1454
3. Houabes M, Metz R (2007) Rare earth oxides effects on both the threshold voltage and energy absorption capability of ZnO varistors. Ceram Int 33:1191–1197
4. Liu DS, Wu CY, Sheu CS, Tsai FC, Li CH (2006) The preparation of piezoelectric ZnO films by RF magnetron sputtering for layered surface acoustic wave device applications. Jpn J Appl Phys I 45(4):3531–3536
5. Kang XY, Wang TD, Han Y, Tao MD, Tu MJ (1997) Sol-gel process doped ZnO nanopowders and their grain growth. Mater Res Bull 32:1165–1171
6. Lu CH, Yeh CH (2000) Influence of hydrothermal conditions on the morphology and particle size of zinc oxide powder. Ceram Int 26:351–357
7. Kim KS, Kim HW (2003) Synthesis of ZnO nanorod on bare Si substrate using metal organic chemical vapor deposition. Phys B 328(3–4):368–371
8. Audebrand N, Auffredic JP, Louer D (1998) X-ray diffraction study of the early stages of the growth of nanoscale zinc oxide crystallites obtained from thermal decomposition of four precursors. General concepts on precursor-dependent microstructural properties. Chem Mater 10:2450–2461
9. Yang Y, Chen HL, Zhao B, Bao XM (2004) Size control of ZnO nanoparticles via thermal decomposition of zinc acetate coated on organic additives. J Crystal Growth 263(1–4):447–453
10. Luo YD, Dai CA, Chiu WY (2008) Synthesis of P(AA-SA)/ZnO composite latex particles via inverse miniemulsion polymerization and its application in pH regulation and UV shielding. J Polym Sci A 46:8081–8090
11. Zhou J, Zhang SW, Qiao XG, Li XQ, Wu LM (2006) Synthesis of SiO_2/poly(styrene-*co*-butyl acrylate) nanocomposite microspheres via miniemulsion polymerization. J Polym Sci A 44:3202–3209
12. Al-Ghamdi GH, Sudol ED, Dimonie VL, El-Aasser MS (2006) Encapsulatin of titanium dioxide in styrene/*n*-butyl acrylate copolymer by miniemulsion polymerization. J Appl Polym Sci 101:3479–3486
13. Caruso F (2000) Hollow capsule processing through colloidal templating and self-assembly. Chem Eur J 6:413–419
14. Stewart S, Liu GJ (1999) Hollow nanospheres from polyisoprene-block-poly(2-cinnamoylethyl methacrylate)-block-poly(*tert*-butyl acrylate). Chem Mater 11:1048–1054
15. General S, Rudloff J, Thunemann AF (2002) Hollow nanoparticles via stepwise complexation and selective decomplexation of poly(ethylene imine). Chem Commun 5:534–535
16. Gittins DI, Caruso F (2000) Multilayered polymer nanocapsules derived from gold nanoparticle templates. Adv Mater 12:1947–1949

17. Jang J, Ha H (2002) Fabrication of hollow polystyrene nanospheres in microemulsion polymerization using triblock copolymers. Langmuir 18:5613–5618
18. Donath E, Sukhorukov GB, Caruso F, Davis SA, Mőhwald H (1998) Novel hollow polymer shells by colloid-templated assembly of polyelectrolytes. Angew Chem Int Ed 37:2201–2205
19. Sukhorukov GB, Donath E, Davis S, Lichtenfeld H, Caruso F, Popov VI, Mőhwald H (1998) Stepwise polyelectrolyte assembly on particle surfaces: a novel approach to colloid design. Polymer Adv Technol 9:759–767
20. Steitz R, Leiner V, Tauer K, Khrenov V, Klitzing Rv (2002) Ultraviolet and visible Raman spectroscopy characterization of diamond-like carbon film growth by pulsed laser deposition. Appl Phys A 74:519–523
21. Glinel K, Sukhorukov GB, Mőhwald H, Khrenov V, Tauer K (2003) Thermosensitive hollow capsules based on thermoresponsive polyelectrolytes macromol. Chem Phys 204:1784–1790
22. Brayner R, Ferrari-Iliou R (2006) Toxicological impact studies based on *Escherichia coli* bacteria in ultrafine ZnO nanoparticles colloidal medium. Nano Lett 6:866–870
23. Tang E, Cheng G (2006) Preparation of nano-ZnO/PMMA composite particles via grafting of the copolymer onto the surface of zinc oxide nanoparticles. Powder Technol 161:209–214