Synthesis of ZnO/polystyrene composites particles by Pickering emulsion polymerization

Jui Hung Chen^a, Chu-Yun Cheng^a, Wen-Yen Chiu^{a,b,*}, Chia-Fen Lee^c, Nai-Yun Liang^d

^a Institute of Polymer Science and Engineering, National Taiwan University Taipei 106, Taiwan

^b Department of Chemical Engineering, National Taiwan University Taipei 106, Taiwan

^c Department of Cosmetic Science, Chia Nan University of Pharmacy and Science, Tainan 717, Taiwan

^d Taiwan Textile Research Institute, Taipei 236, Taiwan

ARTICLE INFO

Article history:

Received 3 September 2007

Received in revised form 26 February 2008

Accepted 18 July 2008

Available online 24 July 2008

Keywords:

ZnO

Polystyrene

Composite particles

Pickering emulsion polymerization

ABSTRACT

ZnO/polystyrene composite particles were synthesized by Pickering emulsion polymerization. ZnO nanoparticles were first prepared by reaction of zinc acetate and sodium hydroxide in ethanol medium. Then different amount of styrene monomer was emulsified in water in the presence of ZnO nanoparticles either by mechanical stirring or by sonication, followed by polymerization of styrene. Two kinds of initiators were used to start the polymerization, azobisisobutyronitrile (AIBN) and potassium persulfate (KPS). The X-ray diffraction pattern verified the crystal structure of ZnO and FT-IR spectra evidenced the existence of ZnO and polystyrene (PS) in ZnO/polystyrene composite particles. Different morphologies were observed for the composite particles when using different initiators. From TEM photographs, AIBN-initiated system produced mainly core-shell composite particles with PS as core and ZnO as shell, while KPS-initiated system showed both composite particles and pure PS particles. Two schemes of reaction mechanism were proposed to explain the morphologies accordingly. Both systems of composite particles showed good pH adjusting ability.

© 2008 Elsevier Ltd. All rights reserved.

1. Introduction

In recent years, many efforts have been focused on the inorganic/organic composite materials with various compositions. By combining organic and inorganic materials, the resulting composites can possess advantages of both organic and inorganic components, thus creating extensive usages in many areas. Among the many inorganic materials, zinc oxide, ZnO, is a direct band-gap ($E_g = 3.37$ eV) semiconductor with a large exciton binding energy (60 meV) [1]. Therefore ZnO is useful in many application areas such as solar cell [2], gas sensor [3,4], varistors [5], acoustic, and luminescent devices [6–8]. Generally, ZnO can be synthesized by sol–gel method [9,10], homoge-

neous precipitation [11], chemical vapor deposition [12], thermal decomposition [13,14], hydrothermal synthesis [15], and reaction of zinc salt with base [16]. Different synthesis routes result in different ZnO morphology, including particle, rod, tube, and flower-like. Moreover, ZnO is also an amphoteric substance and has the ability to sense [17] and adjust pH value, making it useful in biomaterial and textile.

Traditional oil-in-water emulsion polymerization was preceded by adding surfactant to stabilize hydrophobic monomer in aqueous medium. The conventional choice of surfactants includes anionic type, cationic type, zwitterionic type, and nonionic type. Most of them are usually organic compounds containing hydrophilic and hydrophobic group on the molecule or polymer with long chain structure. If the organic surfactants are replaced by inorganic nano-sized particles it is referred as Pickering emulsion polymerization, which was proposed by Pickering in

* Corresponding author. Address: Department of Chemical Engineering, National Taiwan University Taipei 106, Taiwan. Tel.: +886 2 23623259.

E-mail address: ycciu@ccms.ntu.edu.tw (W.-Y. Chiu).

1907 [18]. Theoretical and experimental researches of Pickering emulsion polymerization were developed by He [19–21] and Blinks [22,23]. When the size of inorganic particle is reduced to nanoscale, they are able to assemble on the surfaces of monomer droplets form a stable dispersion. After polymerization inorganic/polymer composite particles can be obtained. Many kinds of inorganic nanoparticles have been reported to be utilized in Pickering emulsion polymerization, including magnetite, cobalt ferrite [24,25], cerium dioxide [26], titania [27], and silica [28,29]. The Pickering emulsion polymerization provides a simple and effective way to prepare inorganic/organic composite materials. In this paper, ZnO/polystyrene composite particles were prepared by Pickering emulsion polymerization. ZnO nanoparticles were first synthesized from reaction of zinc acetate and sodium hydroxide in ethanol. Then polymerization of styrene with different initiators was conducted in the presence of ZnO nanoparticles as stabilizer. The morphology of resulting composite particles varied with the selection of initiator of polymerization. The crystal structure was studied with X-ray diffraction and the functional groups of both inorganic and organic components were characterized with Fourier transform infrared spectroscopy. The morphology of ZnO/polystyrene composite particles was studied with transmission electron microscopy. Finally the pH adjusting ability of ZnO/polystyrene composite particles was investigated.

2. Experiments

2.1. Materials

Zinc acetate and sodium hydroxide (NaOH) purchased from Acros were used as precursor and base in the synthesis of ZnO nanoparticles. Styrene monomer (St) was also

purchased from Acros and used as received. Azobisisobutyronitrile (AIBN) and potassium persulfate (KPS) were used as initiators of polymerization of styrene. Ethanol and DI-water were used as solvents of synthesis of ZnO nanoparticles and Pickering emulsion polymerization, respectively.

2.2. Preparation of ZnO nanoparticles

ZnO nanoparticles can be prepared by the reaction of zinc acetate and a base in the alcohol medium. In this study, 1.314 g zinc acetate and 0.48 g NaOH were dissolved in 330 ml ethanol and refluxed at 60 °C for 1 h. The acetate group reacted with base, converting zinc acetate into zinc oxide. The ZnO dispersion synthesized in alcohol medium was clear and transparent and was able to maintain stable for at least 2 weeks. After reaction, the zinc oxide ethanol dispersion was mixed with DI-water for purification. ZnO particles were then separated from the dispersion supernatant by centrifugation at 7000 rpm for 5 min repeatedly. Finally the ZnO particles were redispersed in DI-water to obtain ZnO water dispersion. TEM result indicated that the size of ZnO particles were about 10–30 nm, as shown in Fig. 1.

2.3. Pickering emulsion polymerization of ZnO/polystyrene composite particles

For AIBN system, styrene monomer and AIBN were first mixed with 10 ml DI-water and then added to 50 ml of ZnO water dispersion prepared as described in Section 2.2. The mixture was then emulsified either by mechanical stirring (300 rpm) or sonication with a Dr. Hielscher UP50H at 100% amplitude at 0 °C for 10 min. After emulsification, the miniemulsion was heated to 75 °C to start the polymerization of styrene under stirring (300 rpm) and a nitrogen atmosphere. After 6 h of polymerization, the ZnO/polystyrene composite latex was diluted with methanol and separated from the dispersion supernatant by centrifugation at 13000 rpm for 15 min repeatedly. As for KPS system, KPS was added after the emulsification of ZnO and styrene being heated to 75 °C. The ZnO/polystyrene composite particles were dried to powder in an oven for further characterization. The compositions of recipes to prepare different ZnO/polystyrene composite particles were listed in Table 1.

Fig. 1. TEM of ZnO nanoparticles.

Table 1

Composition of recipes to prepare ZnO/polystyrene composite particles

Sample	Styrene monomer (g)	ZnO dispersion (ml)	Emulsification	Initiator ^a
PS1ZnO(A)	0.1	50	Mechanical stirring	AIBN
PS2ZnO(A)	0.2			
PS3ZnO(A)	0.3			
PS1ZnOs(A)	0.1	50	Sonification	AIBN
PS2ZnOs(A)	0.2			
PS3ZnOs(A)	0.3			
PS1ZnO(K)	0.1	50	Mechanical stirring	KPS
PS2ZnO(K)	0.2			
PS3ZnO(K)	0.3			
PS1ZnOs(K)	0.1	50	Sonification	KPS
PS2ZnOs(K)	0.2			
PS3ZnOs(K)	0.3			

^a Weight of initiator is 1% of weight of styrene monomer.

Fig. 2. XRD patterns of ZnO, ZnO/polystyrene composites and polystyrene.

2.4. Characterization

X-ray diffraction (XRD) patterns were taken to analyze the crystal structures of ZnO, using a MAC Science/MXP X'pert diffractometer with CuK α radiation at 40 kV and 30 mA. ZnO/polystyrene composite particles were pressed into KBr pellet and the Fourier transform infrared spectrum (FT-IR) was obtained with BIO-RAD FTS40 in the

400–4000 cm^{-1} range with 16 scans. The morphology of ZnO/polystyrene composite particles was observed with a Hitachi H-7100 transmission electron microscope (TEM).

2.5. pH adjusting ability

The pH adjusting ability of ZnO/polystyrene composite particles was investigated by dispersing dried ZnO/poly-

Fig. 3. FT-IR spectra of ZnO, polystyrene, and PS3ZnO composite particles.

Fig. 4. TEM of (a) PS1ZnO(A), (b) PS3ZnO(A), and (c) PS3ZnOs(A).

styrene composite particles into water solution with different pH value to form 1000 ppm ZnO/polystyrene water dispersion. For example, 0.01 g PS1ZnO(A) was added to 10 ml of water solutions with pH 3, 5, 7, and 9 for 10 min. Then the steady-state pH values before and after ZnO/polystyrene dispersion were recorded and compared.

3. Results and discussions

3.1. XRD analysis of ZnO/polystyrene composite particles

The XRD patterns of ZnO, ZnO/polystyrene composites and polystyrene were shown in Fig. 2. Pure ZnO particles

has wurtzite structure and possess main peaks at $2\theta = 32^\circ$, 34.4° , 36.6° , corresponding to (100), (002), and (101) planes, respectively [30]. In this study, ZnO was synthesized from zinc acetate and base. The by-product sodium acetate could be dissolved in water and removed by centrifugation. Therefore sodium acetate was not observed on XRD pattern. The XRD patterns of ZnO/polystyrene composite particles of different compositions were almost the same as that of ZnO, indicating that the crystal structure of ZnO was not altered by the presence of polystyrene. In a Pickering emulsion polymerization, ZnO particles played a role as surfactant, which adsorbed on the surfaces of polystyrene/St particles to form a stable latex. As a result

Fig. 5. TEM of (a) PS1ZnO(K), (b) PS3ZnO(K).

Fig. 6. TEM of (a) PS1ZnOs(K), (b) PS3ZnOs(K).

the XRD pattern of ZnO/polystyrene composite particles exhibited the same characteristics of ZnO.

3.2. FT-IR analysis of ZnO/polystyrene composite particles

Fig. 3 showed the FT-IR spectra of ZnO, polystyrene, and PS3ZnO composite particles. ZnO/polystyrene composite and polystyrene presented the same spectra in the wavenumber range of $700\text{--}3100\text{ cm}^{-1}$ while the weak peak located at $500\text{--}700\text{ cm}^{-1}$ is attributed to the stretching of Zn–O bond. Since the characteristic peaks of polystyrene and ZnO are both presented on PS3ZnO spectrum, it is clear

that ZnO/polystyrene composite was successfully synthesized in this work.

3.3. Morphology study of ZnO/polystyrene composite particles

The ZnO/polystyrene composite particles in this study can be classified as polymerization initiated by AIBN and by KPS. During the emulsification process of styrene monomer and ZnO dispersion, styrene is a hydrophobic monomer and no surfactant was added, phase separation was expected. Nevertheless, this phenomenon was not observed. It indicated that styrene monomer is

Scheme 1. Mechanism of Pickering emulsion polymerization of ZnO and polystyrene initiated by AIBN.

Scheme 2. Mechanism of Pickering emulsion polymerization of ZnO and polystyrene initiated by KPS.

well-protected by ZnO nanoparticles to form a stable suspension in water and ZnO nanoparticles functioned as surfactants.

3.3.1. AIBN system

The hydrophobic initiator AIBN was existing in the styrene droplets to initiate polymerization. The nucleation mechanism of polymer particles in such case is mainly droplet nucleation. AIBN molecules would diffuse from water into styrene monomers and initiate the polymerization reaction at 75 °C. The sizes of monomer droplets and polymer latex particles were almost identical. Fig. 4(a) and (b) showed the morphologies of PS1ZnO(A) and PS3ZnO(A). It was seen that the surfaces of polystyrene particles were covered with ZnO nanoparticles,

showing a core-shell structure. As the content of styrene increased from 0.1 to 0.3 g in the reaction recipes in Table 1, the size of ZnO/polystyrene composite particles increased from 50 to 200 nm. When the content of monomer was higher, the relative concentration of ZnO to styrene decreased. The amount of ZnO particles was insufficient and it tended to form larger droplets during emulsification, resulting in larger size of ZnO/polystyrene composite particles. The emulsification methods also affected the particle size. When the content of styrene monomer was 0.1 or 0.2 g, the degree of emulsification by mechanical stirring and that by sonication were comparative. The particle sizes of PS1ZnO(A) and PS1ZnOs(A) or PS2ZnO(A) and PS2ZnOs(A) were similar. As the content of styrene monomer increased to 0.3 g, the viscosity

Fig. 7. (a) pH adjusting ability test of ZnO/polystyrene composite particles initiated by AIBN (x axis: the initial pH value of solution; y axis: the pH value after ZnO/polystyrene composite particles dispersion; open squares: the blank test). (b) pH adjusting ability test of ZnO/polystyrene composite particles initiated by KPS (x axis: the initial pH value of solution; y axis: the pH value after ZnO/polystyrene composite particles dispersion; open squares: the blank test).

of solution started to have an effect on the sized of latex particles. Sonication provide more energy and resulting in smaller latex particle. In Fig. 4(c), the particle size PS3ZnOs(A) is 120 nm, nearly half of that of PS3ZnO(A). Therefore, the size of ZnO/polystyrene composite particles can be controlled by monomer content (or relative concentration of ZnO to styrene) and emulsification methods.

3.3.2. KPS system

When KPS was used as the initiator, the morphology of composite particles was very different. KPS is a hydrophilic initiator and it alone is capable to stabilize PS particles and form stable latex solution. In the experimental procedure, KPS was added after emulsification of styrene monomer with ZnO. Therefore the stabilization of styrene droplets was attributed to ZnO particles. The nucleation of polymer

particles occurred not only in monomer droplets but also in water phase. When the content of styrene was low, as for PS1ZnO(K) shown in Fig. 5(a), large portion of pure PS particles was observed in addition to composite particles with ZnO nanoparticles on the surface, which indicated that major part of the nucleation of polymer particles occurred in water. As the content of styrene increased to 0.2 and 0.3 g for PS2ZnO(K) and PS3ZnO(K), respectively, the number of styrene droplets increased. Therefore more radicals from KPS would be captured by styrene droplets and the probability of nucleation in droplets would be raised. On the other hand, the ratio of ZnO to styrene decreased as a consequence of styrene increasing. The ZnO/polystyrene composite latex became less stable for the lack of ZnO nanoparticles as stabilizer. As a result, coagulation occurred because of the interaction between ZnO and the PS latex particles. Morphologically, ZnO would be embedded inside the large coagulation of PS particles as shown in Fig. 5(b) for PS3ZnO(K). In sum, three kinds of particles were observed: PS with ZnO nanoparticles on the surfaces due to nucleation in droplets, pure PS particles due to nucleation in water, and ZnO-embedded PS particles due to coagulation of particles.

Looking into the morphologies of latex particles emulsified by sonication instead of mechanical stirring, since the number of styrene droplets increased after sonication, the probability of droplet nucleation would be enhanced, as shown in Fig. 6(a) for PS1ZnOs(K). However, when styrene monomer was increased to 0.2 or 0.3 g for PS2ZnOs(K) and PS3ZnOs(K), respectively, the relatively insufficient ZnO nanoparticles resulted in less stable droplets, thus both nucleation in water and coagulation of particles increased. It can be seen from Fig. 6(b) for PS3ZnOs(K) that pure PS particles nucleated in water and coagulation thus formed large composite particles were together existing in the reaction systems.

From the discussion above, the mechanism of Pickering emulsion polymerization of ZnO and polystyrene can be summarized as Schemes 1 and 2. For AIBN system, styrene monomer was well-protected by ZnO nanoparticles and polymerization reaction occurred mainly in styrene droplets, since AIBN was a hydrophobic initiator. The resulting composite particles showed core-shell morphology. The difference in morphology of particles between mechanical stirring and sonication on emulsification was only apparent when the content of styrene was high. For KPS system, the proportion of polymer particle nucleation in droplets decreased but nucleation in water increased due to the hydrophilic property of KPS. Both pure PS particles and ZnO/PS composite particles were observed. Besides, coagulation of particles resulted in ZnO-embedded morphology.

3.4. pH adjusting ability investigation

ZnO is an amphoteric substance that can react with either an acid or a base. In a acid medium, ZnO reacts with proton to form Zn^{2+} and H_2O , while in a base medium, ZnO reacts with hydroxide group to form $[\text{Zn}(\text{OH})_4]^{2-}$. This property makes ZnO a good material for pH adjusting. In this study, the variation of pH value of 1000 ppm of ZnO/polystyrene water dispersion with different pH was com-

pared. As shown in Fig. 7, both ZnO/polystyrene composite particles initiated by AIBN and KPS adjusted water solution from pH 3, 5, 7, or 9 to 7–8. That is, ZnO/polystyrene composite particles as-prepared could adjust acid and base solution to neutral. They are potential to be good pH adjusting materials. To increase the range of pH adjusting and their application are under study.

4. Conclusion

By Pickering emulsion polymerization, ZnO/polystyrene composite particles were successfully synthesized. ZnO nanoparticles acted as surfactant in the polymerization of styrene. The crystal structure of ZnO in ZnO/polystyrene composite particles was not altered. Using different initiators in the polymerization, it resulted in different morphologies of ZnO/polystyrene composite particle. Due to the difference of degree of hydrophilicity, AIBN-initiated system resulted in ZnO-shell and PS-core composite particles while KPS-initiated system resulted in pure PS particles and composite particles with ZnO on the surface or ZnO-embedded inside. ZnO/polystyrene composite particles showed good pH adjusting ability and they are potential as a pH buffering material.

Acknowledgement

The authors are grateful to the financial support from Ministry of Economic Affairs “Technology Development Program for Academia” under contract 95-EC-17-A-08-S1-015.

References

- [1] Yi G-C, Wang C, Park WJ. ZnO nanorods: synthesis, characterization and applications. *Semicond Sci Tech* 2005;20(4):S22–34.
- [2] Beek WJE, Wienk MM, Janssen RAJ. Hybrid polymer solar cells based on zinc oxide. *J Mater Chem* 2005;15:2985–8.
- [3] Sahay PP. Zinc oxide thin film gas sensor for detection of acetone. *J Mater Sci* 2005;40:4383.
- [4] Jiaqiang X, Yuping C, Daoyong C, Jianian S. Hydrothermal synthesis and gas sensing characters of ZnO. *Sensor Actuat B Chem* 2006;113(1):526–31.
- [5] Kong L, Li F, Zhang L, Yao X. Sol-gel glass-coated zinc oxide for varistor applications. *J Mater Sci Lett* 1998;17(9):769–71.
- [6] Hao XT, Zhu FR, Ong KS, Tan LW. Hydrogenated aluminium-doped zinc oxide semiconductor thin films for polymeric light-emitting diodes. *Semicond Sci Tech* 2006;21(1):48–54.
- [7] Shih W-C, Wu M-S. Growth of ZnO films on GaAs substrates with a SiO₂ buffer layer by RF planar magnetron sputtering for surface acoustic wave applications. *J Cryst Growth* 1994;137(3–4):319–25.
- [8] Radovanovic RV, Norberg NS, McNally KE, Gamelin DR. Colloidal transition-metal-doped ZnO quantum dots. *J Am Chem Soc* 2002;129(51):15192–3.
- [9] Khrenov V, Klapper M, Koch M, Mullen K. Surface functionalized ZnO particles designed for the use in transparent nanocomposites. *Macromol Chem Phys* 2005;206(1):95–101.
- [10] Toutorski IA, Tkachenko TE, Pokidko BV. Mechanical properties and structure of zinc-containing latex-silicate composites. *J Sol-Gel Sci Tech* 2003;26(1–3):505–9.
- [11] Taubert A, Palms D, Weiss Ö, Piccini M-T, Batchelder DN. Polymer-assisted control of particle morphology and particle size of zinc oxide precipitated from aqueous solution. *Chem Mater* 2002;14(6):2594–601.
- [12] Purica M, Budianu E, Rusu E, Danila M, Gavrilă R. Optical and structural investigation of ZnO thin films prepared by chemical vapor deposition (CVD). *Thin Solid Films* 2002;403–404:485–8.
- [13] Audebrand N, Auffrédic J-P, Louër D. 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* 1998;10(9):2450–61.
- [14] Yang Y, Chen H, Zhao B, Bao X. Size control of ZnO nanoparticles via thermal decomposition of zinc acetate coated on organic additives. *J Cryst Growth* 2004;263(1–4):447–53.
- [15] Lu C-H, Yeh C-H. Influence of hydrothermal conditions on the morphology and particle size of zinc oxide powder. *Ceram Int* 2000;26(4):351–7.
- [16] Trindade T, Jesus JDP, O'Brien P. Preparation of zinc oxide and zinc sulfide powders by controlled precipitation from aqueous solution. *J Mater Chem* 1994;4(10):1615–7.
- [17] Al-Hilli SM, Al-Mofarji RT, Willander M. Zinc oxide nanorod for intracellular pH sensing. *Appl Phys Lett* 2006;89:173119.
- [18] Pickering SU. *J Chem Soc* 1907;91:2001–21.
- [19] He Y. Preparation of polyaniline/nano-ZnO composites via a novel Pickering emulsion route. *Powder Technol* 2004;147(1–3):59–63.
- [20] He Y. A novel emulsion route to sub-micrometer polyaniline/nano-ZnO composite fibers. *Appl Surf Sci* 2005;249(1–4):1–6.
- [21] He Y, Li K. Novel Janus $\text{Cu}_2(\text{OH})_2\text{CO}_3/\text{CuS}$ microspheres prepared via a Pickering emulsion route. *J Colloid Interf Sci* 2007;306(2):296–9.
- [22] Binks BP, Lumsdon SO. Influence of particle wettability on the type and stability of surfactant-free emulsions. *Langmuir* 2000;16(23):8622–31.
- [23] Binks BP, Clint JH. Solid wettability from surface energy components: relevance to Pickering emulsion. *Langmuir* 2002;18(4):1270–3.
- [24] Sacanna S, Philipse AP. A generic single-step synthesis of monodisperse core/shell colloids based on spontaneous Pickering emulsification. *Adv Mater* 2007;19(22):3824–6.
- [25] Hasell T, Yang J, Wang W, Li J, Brown PD, Poliakoff M, et al. Preparation of polymer-nanoparticle composite beads by a nanoparticle-stabilised suspension polymerisation. *J Mater Chem* 2007;17(41):4382–6.
- [26] He Y. Synthesis of polyaniline/nano- CeO_2 composite microspheres via a solid-stabilized emulsion route. *Mater Chem Phys* 2005;92(1):134–7.
- [27] Liu Y, Chen X, Wang R, Xin JH. Polymer microspheres stabilized by titania nanoparticles. *Mater Lett* 2006;60(29–30):3731–4.
- [28] Binks BP, Philip J, Rodrigues JA. Inversion of silica-stabilized emulsions induced by particle concentration. *Langmuir* 2005;21(8):3296–302.
- [29] Binks BP, Whitby CP. Nanoparticle silica-stabilised oil-in-water emulsions: improving emulsion stability. *Colloids Surf A Physicochem Eng Aspects* 2005;253(1–3):105–15.
- [30] He Y, Sang W, Wang J, Wu R, Min J. Polymer-assisted complexing controlled orientation growth of ZnO nanorods. *J Nanoparticle Res* 2005;7:307–10.