Synthesis of SiO$_2$/PS Composite Particles via Emulsion Polymerization

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ABSTRACT: SiO$_2$ particles prepared by Stöber method were modified using 1,3,5,7-tetravinyl-1,3,5,7-tetramethyl-cyclotetrasiloxane (Vi-D$_4$), and SiO$_2$/polystyrene (PS) composite particles with core-shell structure were synthesized adopting mulsion polymerization of PS in a water–ethanol medium. The products were characterized by infrared spectra, X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), and Zetasizer analyzer. The average diameter of SiO$_2$ particles prepared by Stöber method was about 80 nm, the SiO$_2$ particles were modified using the molar ratio of Vi-D$_4$ and SiO$_2$ particles 1 : 10 (the dosage of Vi-D$_4$ benever too much), and the size of modified silica particles was about 90 nm. The infrared spectra indicated that the Vi-D$_4$ had bonded to the silanol groups on surface of SiO$_2$ particles, and XPS indicated the grafting efficiency of Vi-D$_4$ on surface of SiO$_2$ particles had reached 90%. The infrared spectra indicated the PS had been incorporated with SiO$_2$ particles, and TEM indicated the composite particles have obvious core-shell structure. The suitable size of SiO$_2$ particles should be lower than 200 nm, and the optimum volume ratio of ethanol and water should be 1 : 9 or 1 : 4. A kind of monodisperse SiO$_2$/PS composite particles having function of self-assembling was successfully and effectively synthesized. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 122: 43–49, 2011

Key words: silica; polystyrene; composite particle; emulsion polymerization; synthesis

INTRODUCTION

Composite materials consist of organic and inorganic substances, which combines the advantages of organic polymers (flexibility, ductility, dielectric strength, etc.) and those of inorganic materials (rigidity, high thermal stability, UV-shielding property, and high refractive index, etc.).[1–15] These materials can show some special performances, such as optics, electronics, magnetics, and catalysis etc, which are extensively used in the areas of coating, electronics, catalysis, and diagnostics.[16,17]

The composite particles with core-shell can be synthesized through several methods: dispersion polymerization,[18–27] emulsion polymerization,[28–32] miniemulsion polymerization, atom transfer radical polymerization (ATRP),[33] and reversible addition fragmentation chain transfer (RAFT).[34] Dispersion polymerization has been used to synthesize the silica–polystyrene (PS) composite particles. Bourgeat-Lami and Lang[24,25] first modified the silica particles using methacryloxypropyl trimethoxysilane (MPTMS).

Then they synthesized a PS coating on surface of these silica particles using dispersion polymerization in a water/ethanol (5/95 w/w) medium, the initiator, 2,2$'$-azobis (isobutylonitrile), poly (N-vinyl-pyrolidane) and poly(styrene-b-ethylene oxide) stabilizer. Emulsion polymerization is also used to synthesize silica-PS composite particles. Yang and coworkers[28] and Wang and coworkers[29] synthesized monodisperse silica PS core-shell microparticles respectively, and Yang and coworkers investigated the mechanism of the core-shell particles forming.[35,36] Percy et al.[35,36] synthesized polyvinyl–silica composite particles using the "surfactant-free" method. In this way, a small amount of (co)polymerized 4-vinyl pyridine (4VP) or 2-hydroxypropyl methacrylate can ensure a sufficiently strong interaction between the organic and inorganic phase. Tiarks et al.[37] modified the auxiliary protocol of 4VP and synthesized colloidal composite particles with core-shell using miniemulsion polymerization. Subsequently, Wu and coworkers[38] reported a controlled synthesis of silica/PS composite particles with core–shell morphology. In this way, surfactant and cosurfactant are added to increase aggregation efficiency of the silica. Von Werne[33] prepared monodisperse polymer-coated inorganic nanoparticles using ATRP. RAFT polymerization was used to graft PS onto silica nanoparticles by Liu and Pan.[34]

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Obviously, before the core-shell particles is prepared, the surface of silica particle needs to be treated using modification agent,[39,40] or absorbs some macromolecules[41] to improve its dispersibility in organic media. Because the hydroxyl groups of silica particles have strong hydrophilic and can induce aggregations, they are immiscible with organic phase and difficult to react with monomers. To solve this problem, Wu and coworkers[38] used a series of silane coupling agents to hydrophobize the silica particles and found that MPS-modified silica and VTS-modified silica could well disperse in styrene. Wang and coworkers[29] successfully used oleic acid to modify the silica for the first time; Dai and Ma[42] prepared PS-silica core-shell composite particles by one-step emulsion polymerization with a nonionic initiator VA-086; V. Ladmiral et al.[43] made the surface modification of silica using an alkoxyamine derivative.

1,3,5,7-Tetravinyl-1,3,5,7-tetramethylcyclotetrasiloxane (Vi-D_4) with mutisilanol groups and active multivinyl groups has been used in anionic polymerization as a kind of vinylic monomers.[44] The silanol groups of Vi-D_4 can easily bond with the silica surface and the vinyl groups of Vi-D_4 can react with other monomers. Few literatures have mentioned Vi-D_4 as a modification agent used to treat the inorganic particles surface. Therefore, in this article we attempt to modify the silica particles surface using Vi-D_4 as a modification agent, and prepare the silica/PS composite particles adopting emulsion polymerization.

EXPERIMENTAL

Materials

Tetraethyl orthosilicate (TEOS), absolute ethanol, and ammonium hydroxide were analytical grade, 1,3,5,7-tetravinyl-1,3,5,7-tetramethylcyclotetrasiloxane (Vi-D_4) and styrene were distilled under pressure before use, potassium persulfate (KPS) was purified by crystallization, other reagents of analytical grade were utilized without further purification, and deionized water was applied for all polymerization and treatment processes.

Preparation and modification of SiO$_2$ particles

The monodisperse silica (SiO$_2$) particles were prepared in ethanol at room temperature adopting the Stöber method.[45] Unreacted TEOS and ammonia contained in the silica particles were removed using centrifugation and redispersion in ethanol. This purification process was repeated at least five times. After that, the silica particles were dried in an oven at 45°C for 48 h and redispered in ethanol.

Appropriate amount of the Vi-D_4 ethanol solution and the silica particles ethanol solution (the molar ratio of Vi-D_4 and silica particles is 1 : 10)[46,47] were added directly into a 500-mL three-neck reaction flask, and kept stirring and reacting for 24 h at room temperature. Unreacted Vi-D_4 was removed from the product using above purification process. The obtained modified silica particles were dried in an oven at 45°C for 48 h.

Synthesis of SiO$_2$/PS composite particles

Firstly, 1.0 g of the modified silica particles was dispersed in 10 mL of ethanol and treated for 30 min adopting ultrasonication. Then, above all the modified silica particles dispersed in ethanol, 0.1 g of sodium dodecyl benzene sulfonate (SDBS) surfactant, 0.24 g of NaHCO$_3$ buffer, 90 mL of deionized water dispersion medium, 0.1 g of KPS initiator, and 10 mL of styrene monomers were placed into a 250-mL four-neck flask. The polymerization was carried out in an atmosphere of nitrogen for 10 h at 85°C. After filtration, the latex of the silica/PS composite particles was obtained.

Characterization

The morphologies and sizes of modified silica particles and SiO$_2$/PS particles were investigated by transmission electron microscopy (TEM) (JEOL JEM 2010) at an accelerator voltage of 200 kV (the sample : diluted with deionized water, dropped on the copper grids, and dried adopting infrared trip lamp).

The average size and size distribution of these were detected by a Zetasizer 3000HAS analyzer (Malvern).

Infrared spectra of these (the samples: powder, pressed KBr pellets) was measured in the wavenumber range from 4000 to 500 cm^{-1} at a resolution of 4 cm^{-1} adopting a Nicolet Avatar 360 FTIR spectrophotometer.

The surface compositions of these (the samples: powder) were measured by X-ray photoelectron spectroscopy (XPS).

RESULTS AND DISCUSSION

Modification of SiO$_2$ particles

A precondition of successfully synthesized composite particles should make the inorganic particles have good compatibility with monomer phase. The silica particles are usually hydrophilic and not easily dispersed in organic phase, and so their surface needs to be modified using chemical reagents with functional groups. Because Vi-D_4 contains mutisilanol groups and active multivinyl groups, the Vi-D_4
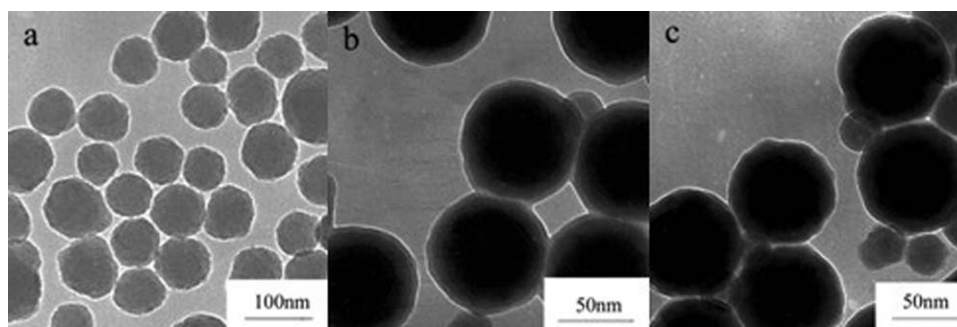
Figure 1 The TEM images of the silica particles: (a) unmodified silica particles; (b) modified silica particles ([Vi-D$_4$] : [SiO$_2$] = 1 : 10 (mol : mol)); (c) modified silica particles ([Vi-D$_4$] : [SiO$_2$] = 1 : 5 (mol : mol)).

is selected as modifying reagent. The modifying reagent not only can graft on surface of silica particles by its mutisilanol groups and form an organic layer being compatible with styrene monomer, but also can polymerize with monomer by its vinyl groups.

Figure 1 is the TEM images of the unmodified silica particles and modified silica particles with different molar ratio of Vi-D$_4$. From Figure 1, we see that the unmodified silica particles [Fig. 1(a)] present sphere-like, surface-coarse, and the average diameter is about 80 nm. When the molar ratio of Vi-D$_4$ and silica particles is 1 : 10, the modified silica particles present the surface smooth, the average diameter not increasing obviously, a few of smaller silica particles (diameter about 10 nm) appearing [Fig. 1(b)]. When the molar ratio of Vi-D$_4$ increases 1 : 5, the number of smaller particles (10 nm) increases [Fig. 1(c)], showing the dosage of Vi-D$_4$ be never too much.

Figure 2 shows the size distributions (determined by Zetasizer 3000HAS analyzer) of three kinds of silica particles. In Figure 2, we can find that the size of unmodified silica particles is about 90 nm, the
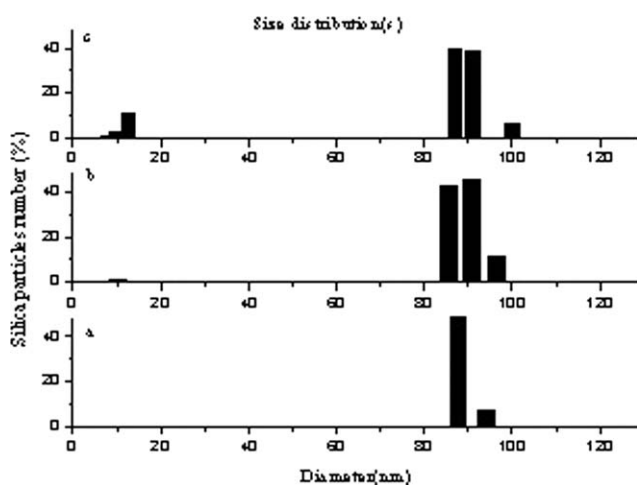
size of modified silica particles is about 90 nm, and that of a few is about 10 nm. The number of small particles increases. The data obtained by Zetasizer 3000HAS analyzer is a little bigger than TEM.

XPS can also be used to assess the surface compositions of the particles and it has good surface-accuracy (that only penetrates 2–10 nm of sampling depth). The atomic ratio determined using XPS indicates the near-surface composites of the particles.[5,42] The C/Si atomic ratio of unmodified silica particles is 0.62; the C/Si atomic ratio of modified silica particles is 0.74, latter was greater than former. It shows that the surface composition of two kinds of silica particles is different. From the molecular formula, we can calculate that the C/Si atomic ratio of Vi-D$_4$ ((C$_2$H$_3$) CH$_3$SiO)$_4$ is 3. The C/Si atomic ratio on the silica particles rising after modification, namely the C/Si atomic ratio growing from 0.62 (unmodified silica particles) to 0.74 (modified particles), should indicate that the Vi-D$_4$ have been grafted on the silica particles. This result is in accordance with that of infrared spectra analysis. The grafting efficiency of Vi-D$_4$ can be calculated from the C/Si atomic ratio, the data obtained by XPS are listed in Table I. From Table I, we can deduce

The mass percentage content of Vi-D$_4$ on surface of the silica particlesis given as: −(difference of C or Si content of silica particle before and after modified)/(difference of C or Si content of Vi-D$_4$ and silica particle after modified)

In the article, the mass percentage content of Vi-D$_4$ on surface of the silica particles is 9%, showing that its grafting efficiency has reached 90%.

Figure 2 The size distributions of silica particles: (a) unmodified silica particles; (b) modified silica particles ([Vi-D$_4$] : [SiO$_2$] = 1 : 10 (mol : mol)); (c) modified silica particles ([Vi-D$_4$] : [SiO$_2$] = 1 : 5(mol : mol)).

TABLE I
The Results of XPS Analysis for Unmodified and Modified Silica Spheres

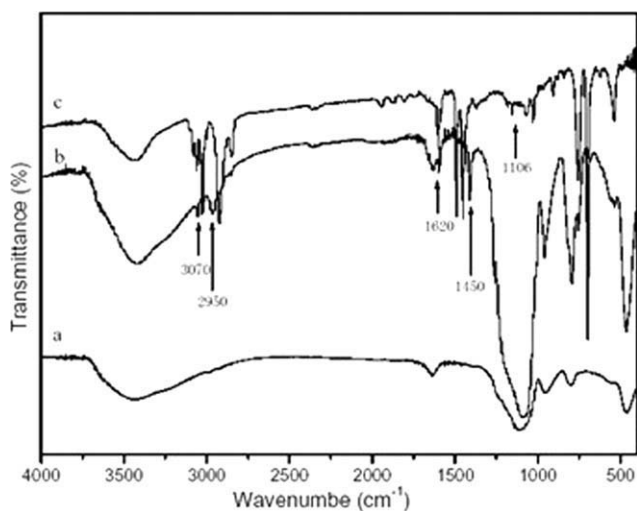| Sample	XPS surface composition		
	C (atom %)	Si (atom %)	C/Si (atom ratio)
Unmodified	24.6	40.0	0.62
Modified	28.5	38.7	0.74

Figure 3 The infrared spectra (range 4000–500 cm^{-1}) of (a) unmodified silica particles; (b) modified silica particles; (c) composite particles.

Synthesis of SiO$_2$/PS composite particles

Monodisperse SiO$_2$/PS core-shell composite particles are synthesized using emulsion polymerization of styrene, the mixture of ethanol and water as reaction medium, the modified silica particles as seeds.

Figure 3 shows the infrared spectra of the unmodified silica particles, modified silica particles, and composite particles respectively. In Figure 3(a), there are absorption bands at 3435 cm^{-1} (OH), 1634 cm^{-1} (H$_2$O), 1100 cm^{-1} and 807 cm^{-1} (Si—O—Si), 950 cm^{-1} (Si—OH), and 471 cm^{-1} (Si—O).[48] Besides above absorption bands, new absorption bands at 1450, 1620, and 2950–3070 cm^{-1} also appear in Figure 4(b), which represent respectively, bending vibration of Si—CH$_3$, stretching vibration of C=C, and stretching vibration of C—H. These data indicate that the Vi-D$_4$ have bonded to the silanol groups on surface of silica particles.

Figure 3(c) is the infrared spectra of the composite particles. The characteristic absorption bands of PS such as 3000, 1600, 1400–1300, and 700 cm^{-1} all appear in Figure 3(c), and vibration of Si—O—C at 1106 cm^{-1}[28,29,49] also appears in Figure 3(c). These data show that the PS has been incorporated with the silica particles.

Figure 4 shows the TEM images of the composite particles. The composite particles have obvious core-shell structures, the dark core is composed of modified silica, and the clear shell is composed of PS. There only is a single core in all these composite particles. This feature shows that the emulsion polymerization is initiated by the modified silica particles as seeds.

From Figure 4, we see that the sizes of modified silica particles strongly influence the formation of composite particles. Under the same emulsion poly-

merization condition, different sizes of modified silica particles used as seed (or core) would obtain different formation of composite particles. When the sizes of modified silica particles is 80 nm, the size of its composite particle is about 240 nm [Fig. 4(a)]. When the sizes of modified silica particles is 140 nm, that of its composite particle is about 320 nm [Fig. 4(b)]. Above two kinds of composite particles all are monodisperse, and have the construct of single core. When the size of modified silica particles exceeds 200 nm, the size of its composite particle would reach 400 nm. Since the number of modified silica particles is very little, an excess of styrene will polymerize to form pure PS particles having not silica core, and the size of those pure PS particles is about 300 nm [Fig. 4(c)]. When the size of modified silica particles is 400 nm, the particle is too big to be used as seed initiated styrene. The particles trend to agglomerate, the styrene will polymerize to form shapeless PS among those agglomerations. From Figure 4(d), we can see that (dark) the silica particles (agglomeration) and (light) the PS get mixed up. So, the modified silica particles used as seed to synthesis the composite particles with obvious core-shell structure need not to be too big, the suitable size of particles should be lower than 200 nm.

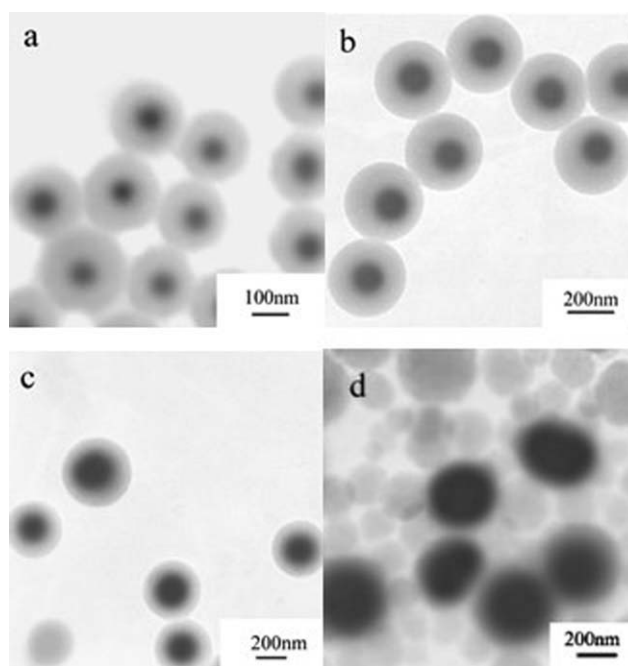The content of SDBS plays an important role in the synthesis process. Under the same polymerization

Figure 4 The TEM images of the composite particles using 0.3 wt % of SDBS in the presence of different size silica particles: (a) with 80 nm silica core; (b) with 140 nm silica core; (c) with 200nm silica core; (d) with 300 nm silica core.
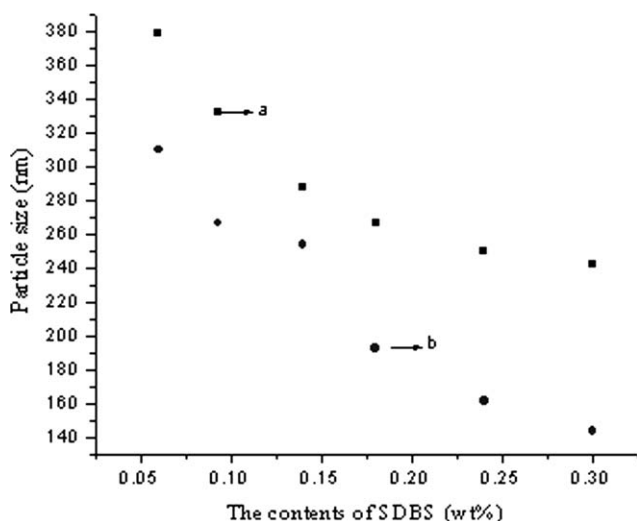
Figure 5 The effects of the content of SDBS on the diameters of composite particles (1.0 g of 80 nm silica particles) and pure polystyrene particles, 0.1 g of KPS, 10 mL of St, the data are measured by Zetasizer 3000HAS analyzer.

condition, the percent content of SDBS changes from 0.06 to 0.3 wt %, the composite particles and the pure PS particles are respectively, synthesized. The size of samples is determined by Zetasizer 3000HAS analyzer. Figure 5 is the effect of percent content of SDBS on the size of particles. As shown in Figure 5, the size of particles is decreasing with increasing of percent content of SDBS. When percent content of SDBS increases from 0.06 to 0.3 wt %, the diameter of the composite particles (the diameter of silica particles used 80 nm) will decrease from 379 to 242 nm [Fig. 5(a)], the diameter of the pure PS particles will decrease from 310 to 144 nm [Fig. 5(b)]. Obviously, the increment of composite particle size should be bound up with thickness of polymer shell. From this, we can conjecture that the limit of polymer shell thickness ∼ 80–150 nm. Although percent content of SDBS can adjust thickness of polymer shell, but this way of doing is not correct. If the composite particle is synthesized using the modified silica particles as seeds, the percent content of SDBS should be determined by experiment. The percent content of SDBS is too low to form the composite particle and too high to avoid generation of pure PS particles. After the size of modified silica particles is fixed, the size of the composite particles will be controlled by regulating of percent dosage of SDBS and styrene, or adopting multistep seed emulsion polymerization (obtained composite particles is successively used as seed).

The composition of medium also plays an important effect on the synthesis of composite particles. The modified silica particles are hydrophobic and can not well disperse in water, so the mixture of ethanol and water is selected as polymerization medium. Under the special polymerization condition, a serial of composite particles are synthesized by changing the volume ratio of ethanol and water. When volume ratio of ethanol and water is 2 : 3, the polymerization is a failure. When the volume ratio of ethanol and water is 1 : 9, the size of composite particle ranges from 230 to 260 nm [Fig. 6(a)]; when the volume ratio of ethanol and water is 1 : 4, the size of the composite particle ranges from 230 to 360 nm [Fig. 6(b)]; when the volume ratio of ethanol and water is 3 : 7, the size of composite particle ranges from 340 to 1100 nm [Fig. 6(c)], the size distribution becomes broad. So, the optimum volume ratio of ethanol and water should be 1 : 9.

Figure 7 is the TEM images of the composite particles in Figure 6. As Figure 7(a,b), the composite particles show very good morphology and ordered self-assembling, there is a single core in the center of each composite particle. In Figure 7(a), the size of composite particles is about 250 nm and in Figure 7(b) that is about 300 nm. In Figure 7(c), the size of composite particles is about 400 nm, because the size of composite particles is too big to be well decentralized, many particles conglomerate together. This makes the size distribution obtained by Zetasizer 3000HAS analyzer to become broad. Obviously, with volume ratio of ethanol and water increasing, the size of composite particles becomes big, the size distribution of that becomes broad, and the stability and self-assembling character of that becomes bad. These phenomena may be caused by the solubility of surfactant or initiator in mixture of ethanol and water, the solubility of SDBS or KPS in water usually is better than that in ethanol. Thus, the volume ratio of ethanol and water ranging from 1 : 9 to 1 : 4 is propitious to control polymerization and stabilization of composite particles. This kind
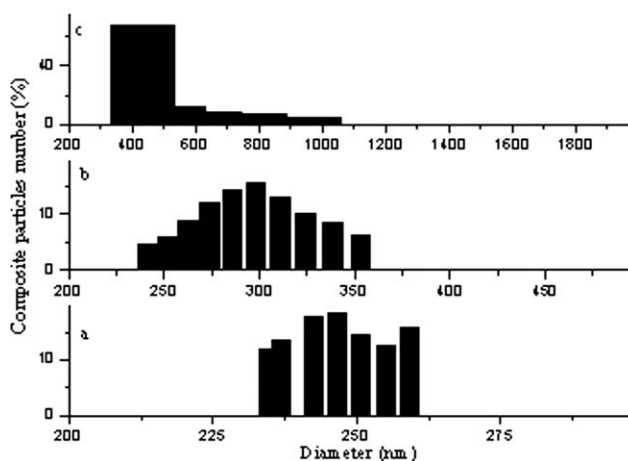

Figure 6 The distributions of composite particles with different solvent compositions (0.3 g of SDBS, 0.1 g of KPS, 10 mL of St, 1.0 g of 100 nm silica particles) in ethanol/water: (a) 1 : 9(v : v); (b) 1 : 4(v : v); (c) 3 : 7(v : v).
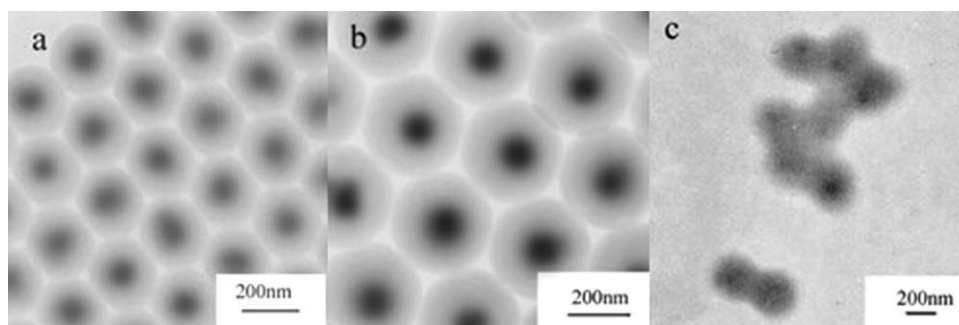
Figure 7   The TEM images of composite particles with different solvent compositions (0.3.g of SDBS, 0.1.g of KPS, 10 mL of St, 1.0.g of 100 nm silica particles) in ethanol/water: (a) 1 : 9(v : v); (b) 1 : 4(v : v); (c) V = 3 : 7(v : v).

of composite particles have character of ordered self-assembling, which will be applied to industry as a kind of nanodevice.

CONCLUSION

In this study, a kind of monodisperse silica/ PS (SiO_2/PS) composite particles is successfully and effectively synthesized.

The average diameter of silica particles prepared by Stöber method is about 80 nm. Because of Vi-D_4 containing mutisilanol groups and active multi-vinyl groups, the Vi-D_4 is selected as modifying reagent. The silica particles are modified using the molar ratio of Vi-D_4 and silica particles 1 : 10 (the dosage of Vi-D_4 benever too much), and the size of modified silica particles is about 90 nm. The infrared spectra indicate that the Vi-D_4 has bonded to the silanol groups on surface of silica particles. When the XPS indicates the mass percentage content of Vi-D_4 on surface of the silica particles is 9%, it shows its grafting efficiency has reached 90%.

Monodisperse SiO_2/PS core-shell composite particles are synthesized using emulsion polymerization of styrene, the mixture of ethanol and water as reaction medium, the modified silica particles as seeds. The infrared spectra show the PS has been incorporated with the silica particles. TEM shows the composite particles have obvious core-shell structure, there only is a single core in each composite particle. The modified silica particles need not to be too big, the suitable size of particles should be lower than 200 nm. The percent content of SDBS can adjust thickness of polymer shell (80–150 nm). After the size of modified silica particles is fixed, the size of the composite particles will be controlled by regulating percent dosage of SDBS and styrene or adopting multistep seed emulsion polymerization. The modified silica particles are hydrophobic and can not well disperse in water, so the mixture of ethanol and water is selected as polymerization medium. The optimum volume ratio of ethanol and water should

be 1 : 9 or 1 : 4. The composite particles have very good morphology and function of ordered self-assembling.

We could forecast that Vi-D_4 will be applied in the surface treatments of other inorganic particles, and the kind of composite particles will be applied to industry as a kind of nanodevice.

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