Preparation of Highly Monodisperse Hybrid Silica Nanospheres Using a One-Step Emulsion Reaction in Aqueous Solution

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Highly monodisperse hybrid spherical silica nanoparticles with diameters ranging from 30 to 200 nm were prepared by a one-step emulsion polymerization in aqueous solution. In contrast with the former method for preparing the hybrid silica materials, our method has three advantages. (1) Through this one-pot route, hybrid silica particles with organic functional groups on the surface are prepared in aqueous solution. (2) The particles are created in a size range of 30−200 nm and highly monodisperse. (3) The size of the particles can be effectively well-defined and precisely controlled depending upon the synthesis conditions such as the concentration of surfactant. Other kinds of organosilane monomers have also been tried in the same way. Scanning electron microscopy (SEM), transmission electron microscopy (TEM), and dynamic light scattering (DLS) were performed to elucidate the morphologies of the hybrid silica particles. Thermogravimetric analysis (TGA), ^{29}Si NMR, and ^{13}C NMR were used to gain information about thermal properties and detail structure. This approach may open a new broad avenue for the hybrid material in the field of photocrystal, electronic enveloping.

1. Introduction

Monodisperse nanosized colloids are greatly important in the field of nanoscience and nanotechnology due to their well-defined dimensions and functional properties.[1,2] Today they are widely used in the field of biosensors,[3] luminescence,[4] catalysis,[5,6] sensitive gas sensors,[7,8] and magnetic materials.[9]

Silica is one of the most widely used colloidal materials.[10] Silica colloids have a remarkable colloidal stability due to their large negative surface charge under neutral and basic conditions.[11] These characters make silica the most attractive issue in colloidal science.

In 1968, Stöber et al.[12] developed a procedure for synthesizing monodisperse silica colloids in a water/ethanol solution with silicon alkoxides as the precursor and ammonia as the catalyst. Subsequently, this method was streamlined to use tetraethylorthosilicate (TEOS) as the precursor, and the concentrations of ammonia and TEOS were regulated to control the particle size in a range of several hundred nanometers. Seeded regrowth was an important development of the Stöber method which improved the monodispersity.[13] However, small silica particles

(typically < 20 nm) produced by the Stöber method were of poor dispersity. Recently, Yokoi et al. reported preparation of monodisperse silica particles with sizes ranging from 12 to 23 nm.[14] They utilized lysine as a catalyst in aqueous media to hydrolyze TEOS heterogeneously and achieved an unprecedented good monodispersity in that size range.

Besides the Stöber method, there were also microemulsion ways of obtaining monodisperse silica particles. The microemulsion approach works particularly well for the smaller size (< 100 nm) with high monodispersity.[15] Finnie et al. prepared silica nanoparticles by the reaction of tetramethylorthosilicate (TMOS) in a water-in-oil microemulsion.[16] Baek et al. developed a method for preparing the nanosized spherical SiO_2 particles using the emulsion method with the sodium silicate.[17]

Today the organic−inorganic hybrid materials are of great interest in the material field. To improve the interaction of fillers and substrates, covalent linking is needed. It means there is a need to introduce active organic groups (such as vinyl, thiol, and amine) into the fillers (such as silica colloids). There are two different methods, postgrafting and co-condensation, that can be employed to modify silica colloids. Postgrafting is a two-step method for covalently linking the silane coupling agent with the surface silanol groups and has been widely used in the modification of silica colloids.[18−20] Meanwhile, an overdue silane coupling agent often necessitates extensive cleaning, and the particle surfaces could be only partially modified. On the other hand, the co-condensation method is for copolymerizing the silane coupling agent with silica precursors (such as tetraethyl

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Table 1. Concentrations of SDBS Used in the Preparations

	A	B	C	D	E	F	G
concentration	0.1CMC	0.2CMC	0.3CMC	0.4CMC	0.5CMC	0.7CMC	1.0CMC

orthosilicate). This one-step approach enables a higher and more homogeneous surface coverage of functional groups.[20−25]

Recently, Lee et al. reported preparation of monodisperse silica particles with a range of sizes from one to several micrometers. The advantages of the method are a one-pot route and size selectivity controlled by the concentration of organosilane and the reaction temperature.[26] The main limitation of the Lee process remains in the preparation of smaller particles. A highly monodisperse silica sphere is very challenging to achieve in a size range of nanometers.

Here, we report a facile, reproductive one-step synthetic approach for preparing silica particles having many organic groups on their surfaces with sizes ranging from 30 to 200 nm. It is an effective method for obtaining monomodal particles using a water-based synthesis. The hybrid nanoparticles have a tendency to dissolve in nonpolar polymer monomers, for example, styrene, and thus could potentially be composited with polymer bulk materials. The efficient one-step preparation of hybrid silica particles needs only an organosilane without other precursors. The high monodispersity of the prepared silica nanospheres renders them perfectly suitable for colloidal array formation. Moreover, the size of the nanoparticles can be easily defined and controlled by the concentration of the surfactant under certain circumstances. All of the factors mentioned above enable a plethora of potential applications of these particles in the field of photocrystal, biosensor, luminescence, catalyst, sensitive gas sensor, and electronic enveloping.

2. Experimental Section

Materials. Vinyltriethoxysilane (VTES), triethoxyphenylsilane, methyltriethoxysilane, and 3-aminopropyltriethoxysilane were acquired from Liyang Mingtian Chemical Co. Ltd. Ammonium hydroxide and sodium dodecylbenzene sulfonate (SDBS) were supplied by Jiangsu Yonghua Fine Chemistry Co. Ltd. All chemicals were used as received without further purification. Water was obtained from a Sartorius arium 611DI water purification system.

Synthesis. VTES (3.8 g) and SDBS (0.013 g) were added to 30 mL of water under vigorous stirring until an emulsion formed. $NH_3 \cdot H_2O$ (0.5 mL) was added dropwise to the emulsion (pH 11.5), and the reaction mixture was kept at 50 °C for 48 h. A homogeneous colloidal dispersion (sample G) was obtained. The colloidal dispersion was centrifuged, and the resulting precipitate was washed several times using water. The VTES silica spheres (fuctionalized by vinyl groups) were fabricated at room temperature and 50 °C.

Samples A−F were prepared in the same way except with the addition of SDBS in different amounts. The concentration of SDBS used in the preparation of sample G was the CMC (critical micelle concentration). The concentrations of SDBS used in the preparations of the samples are listed in Table 1.

The Stöber nanoparticles which were used as a reference were synthesized by the Stöber method.[12]

Characterization. Transmission electron microscopy (TEM) was conducted on a JEM-1005 instrument (JEOL Co.) at 80 kV. One drop of the colloidal emulsion was placed on the sample grid, and the solvent was allowed to evaporate.

Scanning electron microscopy (SEM) was performed using a Hitachi S-4800 instrument. Samples were prepared by directly spin-coating the emulsion onto the silicon slice. An accelerating voltage of 10 kV with a Au coating of the sample was used to image these particles.

Dynamic light scattering (DLS) which provided us with average particle sizes and size distributions was conducted by using a 90 plus particle size analyzer (Brookhaven Inc.): temperature of 25.0 °C, aqueous suspension, viscosity of 0.890 cP, reference index fluid of 1.330, angle of 90.00, and wavelength of 660.0 nm.

Infrared spectra were recorded with a Nicolet 5DX Fourier transform infrared spectrometer using membranes as samples.

Thermogravimetric analysis (TGA) was conducted with a PE TGA thermogravimetric analyzer at a heat rate of 20 °C/min from room temperature to 1000 °C under both a continuous nitrogen flow and an air flow.

^{29}Si NMR and ^{13}C NMR spectra were recorded at room temperature using a Varian Infinityplus-400 wide-bore (89 mm) NMR spectrometer.

As the IR and NMR spectra and thermal properties of these samples are almost the same, we used sample B as an example.

3. Results and Discussion

We used only hybrid nanoparticles made from VTES as an example to carry out the following characterization.

TEM Image of Hybrid Silica Particles. TEM images of silica particles fabricated with vinyltriethoxysilane (VTES) are shown in Figure 1. Clearly, these images demonstrate that the silica particles are nanometer-sized and highly monodisperse. The average particle sizes are listed in Table 2(the *X* axis stands for the concentration of the surfactant, and the *Y* axis stands for the size of the particles). The result shows that the particle size is systematically controlled by adjusting the concentration of the surfactant (SDBS), while the other conditions remain the same. When the concentration of SDBS reaches the CMC, highly monodisperse silica particles with a diameter of 32 nm are obtained, and the particle size will not decrease any more according to the trend of this curve. As the concentration of SDBS decreases to one-tenth of CMC, the diameter of these monodisperse particles increases significantly. For example, the particle diameter shows a noticeable change from 32 to 141 nm when the concentration of SDBS is decreased from CMC to 0.1CMC (Table 1). These could be explained by the traditional surfactant theory. When the concentration of the surfactant decreases from the CMC, there is not enough surfactant to reduce the surface tension of these small nanodroplets of monomer, and this results in larger nanodroplets which leads to the final larger nanoparticles. When the concentration of surfactant is higher than the CMC, the nanodroplets of monomer will not be reduced any longer, as the surface tension has reached the minimum.

As in the case of VTES, triethoxyphenylsilane (TEPS), methyltriethoxysilane, and 3-aminopropyltriethoxysilane can form the similar monodisperse nanoparticles using the same emulsion system.

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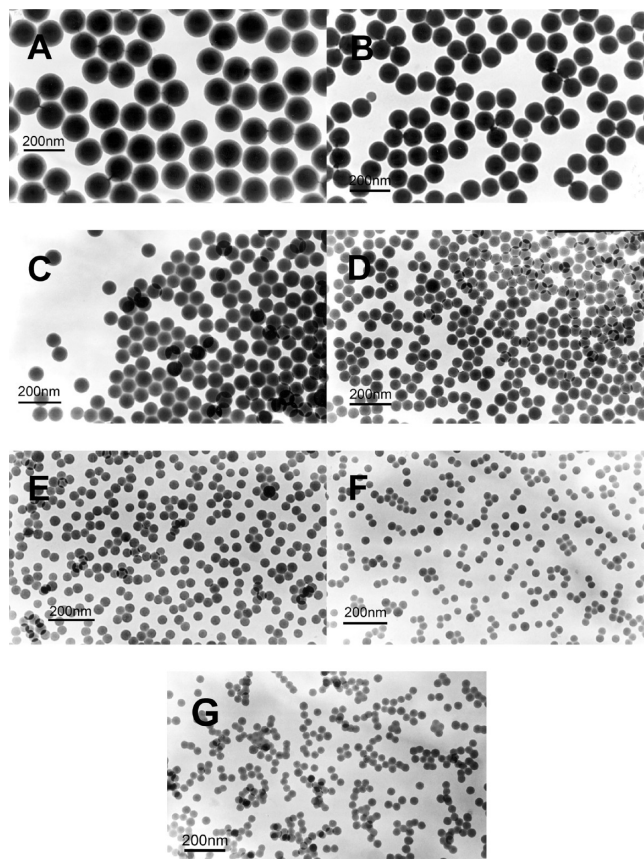(26) Lee, Y. J.; Park, J. H.; Oh, C.; Oh, S. G.; Kim, Y. C. *Langmuir* **2007**, *23*, 10875–10878.

Figure 1. TEM images of samples A−G.

Table 2. Diameters from TEM Images of Samples

	A	B	C	D	E	F	G
diameter (nm)	141	100	75	58	43	35	32

Commonly, nanometer-sized particles tended to form agglomerates that might stem from the fact that they have a very high specific surface area and a high surface energy.[27] However, the synthesized particles were perfect nanospheres and not aggregated in this way. It is possible that the triethoxy group restricted polymerization in three dimensions and the surfactant inhibited particle growth, in which the surfactant might play a more important role.

SEM Image of Hybrid Silica Particles. SEM images of these hybrid silica particles fabricated by VTES are shown in Figure 2. It is obvious from these images that the silica particles are highly monodisperse and are nanometer-sized. The particle size could be controlled in the way which has been indicated in the previous section (Figure 3).

DLS Analysis. DLS analysis was used to obtain the diameters and polydispersity of these particles with a particle size analyzer. As listed in Table 3, we found that the particle size from DLS is always slightly larger than that from TEM. This difference might stem from the hydrated radius used in DLS. However, the change in diameters is parallel between TEM and DLS results. With the decrease in the particle diameter, there is a slight increase in the polydispersity, but the result still shows very good monodispersity.

TGA. TGA was performed to study the thermal properties of these hybrid particles under both N_2 and air atmosphere.

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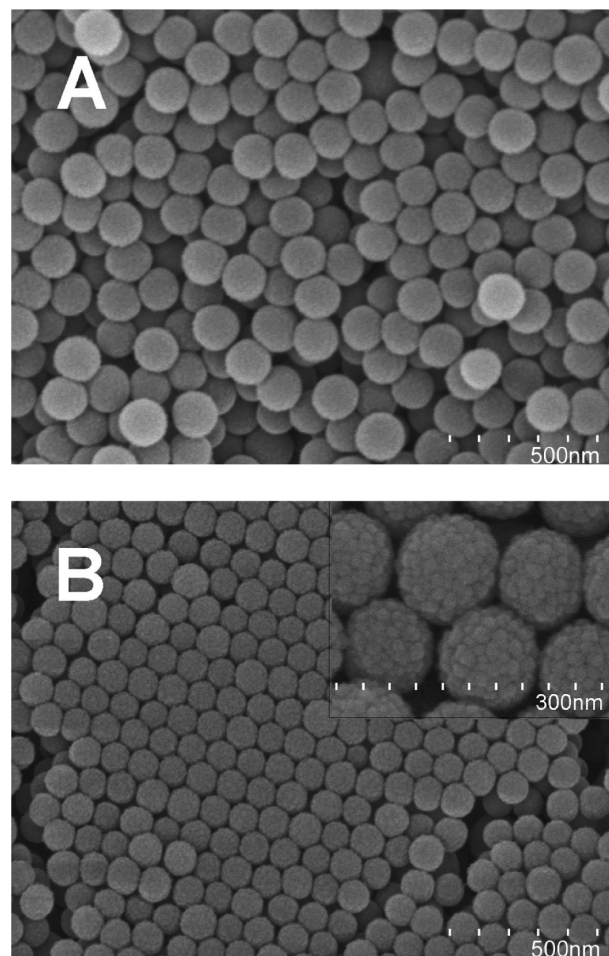
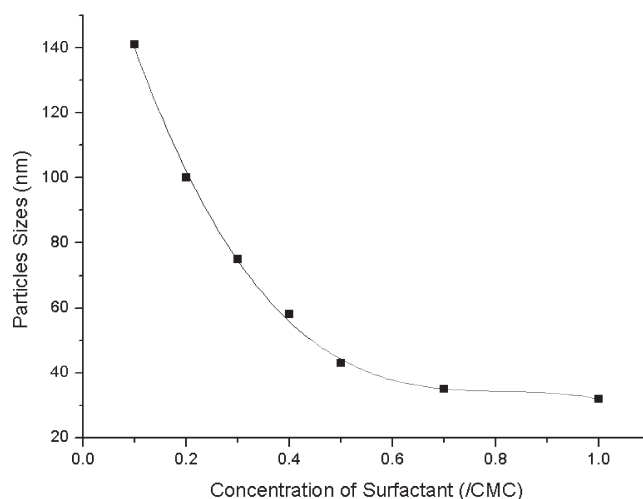**Figure 2.** SEM images of two samples (samples A and B).

Figure 3. Relation of the sizes of particles and the concentrations of surfactant.

The TG curve (Figure 4) of sample B under a N_2 atmosphere displays two weight losses. The first loss of 2.2% beginning at 200 °C is attributed to the decomposition of unhydrolyzed EtO-Si, whereas the second loss of 6% beginning at 450 °C can be attributed to the degradation of the C=C bonds of $[CH_2=CH-SiO_{1.5}]_n$. The total weight loss (8.2% at 738 °C) is less than 15.2% which is calculated as C=C bonds fully decomposed. It is possible that those C=C bonds located at the core of these particles did not fully degrade. In summary, the samples did not

Table 3. Results from DLS Analysis

	A	B	C	D	E	F	G
effective diameter (nm)	161.8	123.0	95.1	79.1	57.7	44.5	40.9
polydispersity	0.005	0.005	0.005	0.019	0.041	0.042	0.035
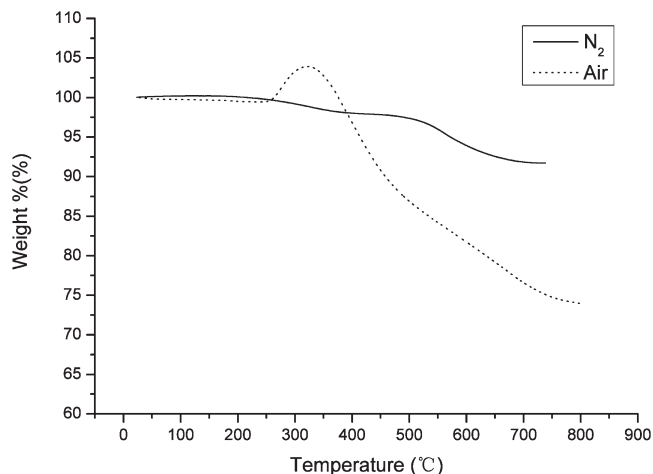
Figure 4. TGA of sample B (under N_2 and air).

significantly decompose from room temperature to 750 °C under a N_2 atmosphere. It means the particles have a good thermal stability.
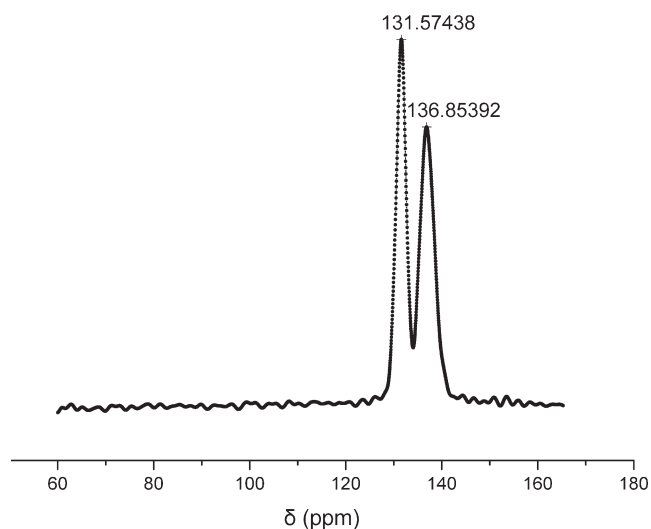
The TG curve of sample B under an air atmosphere showed both a weight increase and a weight loss. The weight increase stage ($\sim$4%) beginning at 250 °C was partially attributed to the partial oxidation of the C=C bonds (the full oxidation would give a weight increase of 20.3%), while the latter weight loss (30%) beginning at 320 °C possibly resulted from the degradation of the [vinyl-$SiO_{1.5}$]$_n$ bonds. The total weight loss (26% at 799 °C) was less than 32.9%, corresponding to the total degradation of the vinyl groups. The explanation might be the same as that given above, that those [vinyl-$SiO_{1.5}$]$_n$ bonds which were located at the core of these particles did not degrade fully.

^{29}Si NMR Analysis. In the ^{29}Si NMR spectrum, the resolution of signals was very good and certain Si chemical shifts correspond to certain Si−O−Si structure. For our hybrid silica particle, the Si chemical shift of the silicon can provide us with the quantity of mono-, bi-, and tridentate silicon.

The ^{29}Si NMR spectrum of the organic−inorganic hybrid nanoparticles exhibited two distinguished peaks in the T region. They are T_3 (−80.40006 to approximate −79 ppm) and T_2 (−70.90771 to approximate −70 ppm) (Figure 5). This result suggests most of the ethyloxy groups have been hydrolyzed and the cross-linking structure is formed.[28]

^{13}C NMR Analysis. The ^{13}C NMR spectra show that the organic−inorganic hybrid nanoparticles prepared in this way have a very strong peak of the vinyl group (δ 131.57 and 136.85)[28] (Figure 6). This is solid proof of the vinyl group located in the particles.

Controlling the Size of These Hybrid Silica Nanoparticles. Monodisperse and hybrid silica particles were synthesized by a one-step emulsion reaction in aqueous solution. The average size of the hybrid silica nanoparticles synthesized here was determined by two different methods: DLS and TEM. The results obtained from these two methods were similar. The average particle sizes obtained from DLS were always

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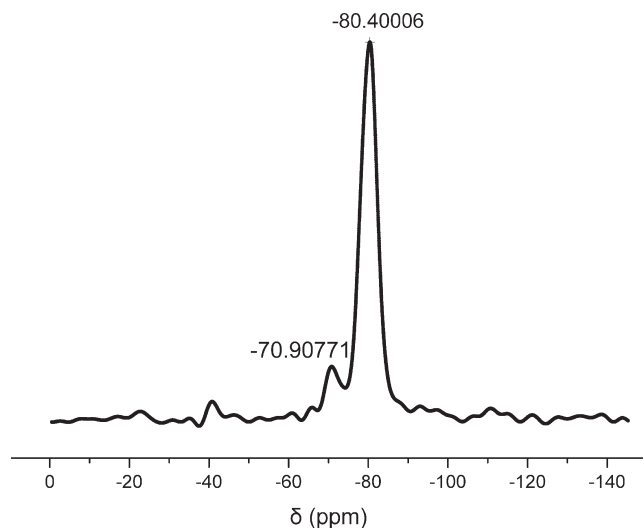
Figure 5. ^{29}Si NMR spectrum of sample B.

Figure 6. ^{13}C NMR spectrum of sample B.

larger than those obtained from the TEM images for the same samples. It might stem from the data we obtained from DLS for the effective diameter. So the results obtained from the TEM image might be closer to the true size of the hybrid silica particles.

In this emulsion system, the size of the silica particles was mainly dependent on the amount of surfactant while the polydispersity was mainly affected by the amount of catalyst (ammonium hydroxide). The amount of the reactants (water and VTES) did not play such an important role in this system. Note that the results presented in Figure 1 were obtained under the same condition (1.9 g of VTES, 15 mL of H_2O, 50 °C, pH 11.5) with different amounts of surfactant. This result exhibited changes in the particle size with the amount of surfactant when the concentrations of VTES and the pH were fixed. The decline in particle size was observed with an increase in the amount of surfactant. This phenomenon was attributed to the decrease in surface tension when the surfactant concentration increased.

No particle with good shape was achieved when the $NH_3 \cdot H_2O$ concentration was low (for example, pH 9.5) which might be caused by the incomplete hydrolysis, and when the concentration of $NH_3 \cdot H_2O$ is too high (for example, pH 12.5),
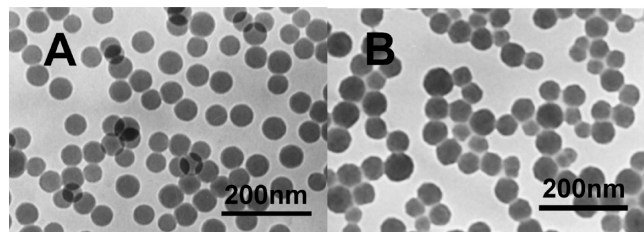
Figure 7. TEM images of the particles synthesized by (A) phenyl-triethoxysilane and (B) methyltriethoxysilane.
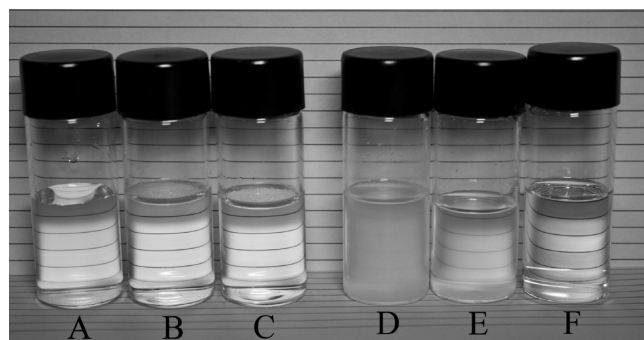

Figure 8. Different phenomena for vinyl group and phenyl group hybrid nanoparticles dispersed into aqueous and styrene solutions compared with traditional Stöber nanoparticles: (A) Stöber nanoparticles in aqueous solution, (B) vinyl group hybrid nanoparticles in aqueous solution, (C) phenyl group hybrid nanoparticles in aqueous solution, (D) Stöber nanoparticles in styrene, (E) vinyl group hybrid nanoparticles in styrene, and (F) phenyl group hybrid nanoparticles in styrene

the hydrolysis−condensation reaction may become too fast to form monodisperse particles (Supporting Information).

Using Other Precursors To Synthesize Such Hybrid Silica Particles. Experiments with different precursors (triethoxyphenylsilane, methyltriethoxysilane, and 3-aminopropyltriethoxysilane) were conducted in the same way. All of them except 3-aminopropyltriethoxysilane could form fine particles (Figure 7). This might stem from the fact that when the 3-aminopropyltriethoxysilane was added in water, intermolecule interaction began. As the amine groups are positively charged and the silanol groups are just oppositely charged, strong intramolecule interaction like a zwitterion-like species ($\equiv$SiO$^-$, $^+$H$_3$NC$_3$H$_6$−Si$\equiv$) occurred.[29] This may influence the emulsion polymerization.

Special Surface Character of These Organic−Inorganic Hybrid Nanoparticles. Due to organic groups (such as the vinyl group and the phenyl group) located on the surface, these hybrid nanoparticles have a tendency to dissolve in some nonpolar solvents or nonpolar polymer monomers, for example, styrene. On the other hand, the traditional inorganic

nanoparticles made by the Stöber method are inclined to dissolve in some polar solvents, for example, water. When the same amount of Stöber nanoparticles and our vinyl group and phenyl group hybrid nanoparticles were dispersed into water and styrene, different phenomena were detected. From these figures, we could find that our vinyl group and phenyl group hybrid nanoparticles are totally nonsoaked by water and floating on the surface, but the Stöber nanoparticles could disperse into the water to form a homogeneous solution. In contrast, when the same amount of these nanopartilces was dispersed into styrene, they acted contrarily. The Stöber nanoparticles could not dissolve and just formed a suspension, and the suspension would precipitate latter. The vinyl group hybrid nanoparticles could disperse in styrene to form a more pellucid dispersion, while the phenyl group hybrid nanoparticles could totally dissolve in the styrene to form a transparent liquid (Figure 8).

4. Conclusion

In summary, we have successfully developed a facile one-pot emulsion method for synthesizing monodisperse hybrid vinyltriethoxysilane nanoparticles with sizes ranging from 30 to 200 nm. The size of the particles can be effectively well-defined and precisely controlled depending upon the synthesis conditions such as the concentration of surfactant. It is an effective method for obtaining monomodal particles in aqueous solution. The hybrid nanoparticles have a tendency to dissolve in nonpolar polymer monomers, for example, styrene, and thus could potentially be composited with polymer bulk materials. The synthesis using other kinds of organosilanes such as triethoxyphenylsilane, methyltriethoxysilane, 3-aminopropyltriethoxysilane has also been attempted. All of them except 3-aminopropyltriethoxysilane could form fine particles. The organic groups located on the surface provide the silica particles with chemical active sites which can improve the interaction between the particles and the substrate materials. This effective approach can open a new avenue for the hybrid material in the field of photocrystal, biosensor, luminescence, catalyst, sensitive gas sensor, and electronic enveloping.

Supporting Information Available: Full vibrational spectrum (IR) of the hybrid silica particles, the ^{1}H solid NMR analysis, and results of experiments at different pH values (9.5 and 12.5). This material is available free of charge via the Internet at http://pubs.acs.org.

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