

Synthesis of Asymmetric Inorganic/Polymer Nanocomposite Particles via Localized Substrate Surface Modification and Miniemulsion Polymerization

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Asymmetric nanocomposite particle pairs of polystyrene and silica were prepared via one-step miniemulsion polymerization for the first time. The transmission electron microscopy images showed that these nanocomposite particle pairs were monodisperse and highly asymmetric in morphology. The key to obtaining the asymmetric nanocomposite particle pairs was the combination of miniemulsion polymerization and the local surface modification of silica substrates. Because of localized surface modification on the silica surface, the nucleation and formation of the polymer nodule in miniemulsion polymerization took place only in the modified area on the silica surface, thus ensuring the asymmetric morphology. The asymmetrical materials obtained by the facile and effective method will have significant potential applications in some areas including biomedical fields.

There has been an increasing need for the development of nanocomposite particle pairs in which two components are physically or chemically joined but different in structure, composition, morphology, and properties.^{1,2} These unique nanomaterials have significant potential applications in the stabilization of complex media, electronic displays, and biomedicine.³ In the development of such unique structures, most successfully synthesized asymmetrical systems are polymer/polymer¹ and inorganic/inorganic² nanoparticles. There have been few studies reported on asymmetric nanocomposite particles with a dimer structure composed of inorganic/polymer components. Furthermore, it is of great scientific interest to develop inorganic/polymer nanocomposite particles with the components having different chemical, physical, and surface properties.⁴ One of the potential applications of such material is to be used as carriers for different biomolecules simultaneously, such as proteins and nucleic acids because of the existence of different surface functionalities. Xia et al.^{5a} reported the preparation of asymmetric dimers of silica and polystyrene on the micrometer scale via a template-directed self-assembly technique. Reculusa et al.^{5b} reported the synthesis of snowman-like and dumbbell-like silica/

polystyrene nanocomposite particles by strictly controlling the ratio of silica seeds to growing polystyrene nodules in several other experiments. Using a different approach, Montagne et al.^{5c} obtained asymmetrical morphology by phase separation between the oleic acid-modified magnetic core and polystyrene chains in emulsion polymerization. However, both counterparts of the composite particles exhibited hydrophobic surfaces, which greatly reduced the asymmetric characteristic of the system. Therefore, there is a critical need to search for novel synthesis routes to develop asymmetrical inorganic/polymer systems with remarkably different asymmetrical surface structures and properties.

In this study, we demonstrate a unique and simple synthesis route for developing asymmetric silica/polystyrene nanocomposite particles via one-step miniemulsion polymerization in the presence of locally surface modified silica particles. Figure 1 illustrates the preparation procedure. Monodisperse silica particles of 120 nm diameter are synthesized according to the well-known Stöber procedure⁶ (Figure 1a). The silica particles are partially surface modified with *n*-octadecyltrimethoxysilane (ODMS) using a procedure developed by Ikeda and co-workers with some minor modification to obtain w/o-silica particles.⁷ In this experiment, as shown in Figure 1b, only a localized area on the particle surface is modified to exhibit hydrophobicity while the rest remains hydrophilic. The w/o-silica particles are dispersed into a monomer containing styrene and hexadecane to form the oil phase (Figure 1c, upper part). Surfactant sodium dodecyl sulfate (SDS) and sodium bicarbonate are dissolved in deionized water to form the water phase (Figure 1c, bottom part). Then, the oil and water phases are miniemulsified at a power of 350 W for 20 min by ultrasonication (ultrasound cell disrupter, produced by Ningbo Xinzhi Bio-tech Co.). The asymmetrical compound droplets are formed with a monomer droplet partially

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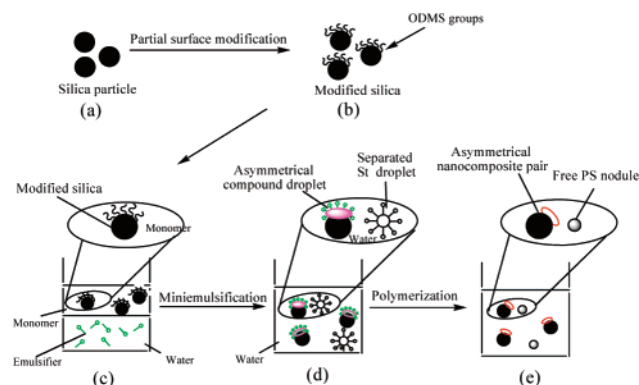


Figure 1. Synthesis strategy in miniemulsion polymerization based on asymmetrically modified silica particles.

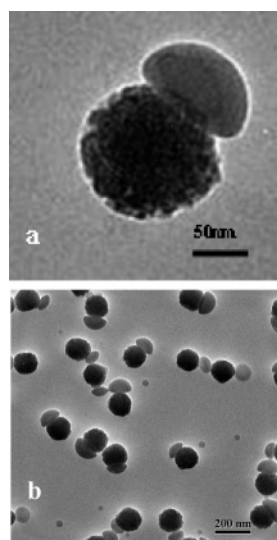


Figure 2. TEM images of mushroom-like silica/polystyrene nanocomposite particles: (a) single pair and (b) multiple pairs.

linked on the silica surface as a result of strong hydrophobic interaction between the monomer molecules and the modified area of the silica surface (Figure 1d). Note that there are free forms of the separated monomer droplets in the miniemulsion system as a result of excessive styrene compared to the number of silica particles. The droplets are initiated by water-soluble initiator potassium persulfate (KPS) and reacted at 70 °C for 3 h to form asymmetric silica/polystyrene nanocomposite particles accompanied by free polystyrene latexes (Figure 1e). The experimental details of this section can be found in Supporting Information.

Figure 2 shows the transmission electron microscopy (TEM) images of the as-synthesized silica/polystyrene nanocomposite particles. (TEM samples were treated by centrifugation at a speed of 10 000 rpm for 3 min to get rid of the free polystyrene latexes.) As can be seen in Figure 2, the polystyrene and silica particles are joined as an asymmetric pair. In Figure 2a, the interface between the silica particle and polystyrene nodule is supposed to be the modified area on the silica surface. This assumption is based on the fact that if the silica was not modified then only free forms of the separated silica particles and polystyrene latexes would be observed.⁸ The TEM images shown in Figure 2 are strong evidence of the asymmetric morphology of the nanocomposite particles.

One of the key challenges involved in the synthesis of the nanocomposite particles lies in the control of the nucleation and

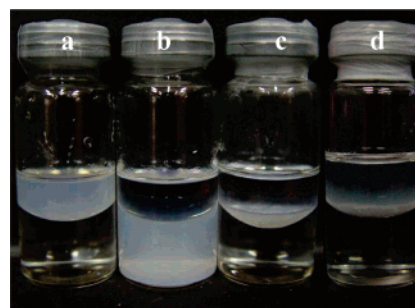


Figure 3. Locations of thoroughly alkylsilylated silica particles (o-silica), unmodified silica particles (w-silica), locally modified silica (w/o-silica), and asymmetric silica/polystyrene nanocomposite particles in a water–toluene dual-phase system: (a) o-silica, (b) w-silica, (c) w/o-silica, and (d) asymmetric silica/polystyrene nanocomposite particles. The average diameter of used silica particles is 120 nm.

growth of the polystyrene nodule on the expected local surface of a silica particle. In this case, that was ensured by an innovative combination of the local surface modification of silica and the miniemulsion polymerization of styrene. These critical steps are depicted in Figure 1b,d,e. The locally modified area on the silica particle serves as a strong linkage site to the monomer droplet, which is the base for developing the asymmetrical morphology. In the miniemulsion polymerization process, droplet nucleation is dominant because of the absence of micelles, whereas the monomer transition between different polymerizing loci is suppressed by the superhydrophobic molecules. Thus, the polymerized latex is approximately a copy of the original droplet in both morphology and size.⁹ Then nanocomposite particles of similar morphology were formed after polymerization. This approach provided a feasible and effective method for the structural design and morphology control of the complex nanocomposite particles.

Another important challenge was to obtain w/o-silica particles via asymmetrical modification of the silica particles. The coupling agents were usually applied to improve the affinity between the hydrophilic silica particles and the organic monomer.¹⁰ However, in this study, the local modification of the silica particles was introduced to ensure the linkage of the styrene monomer onto the silica partial surface (Figure 1b,d). Figure 3 shows the locations of the hydrophobic silica particles, the hydrophilic silica particles, the asymmetrically modified silica particles, and the obtained asymmetric silica/polystyrene nanocomposite particles in the water–toluene dual-phase system. We can see that the asymmetrically modified silica particles (w/o-silica) can preferentially exist at the interface in the water–toluene dual-phase system (Figure 3c). In contrast, the o-silica particles, thoroughly modified by ODMS, are dispersed in toluene (Figure 3a). However, the unmodified w-silica particles are dispersed in water (Figure 3b) as we expected. During miniemulsification, the monomer phase tends to be absorbed onto the hydrophobic part of w/o-silica particle. As a result, the asymmetrical composite droplets are formed with surfactant stabilizing the monomer/water interface. Once the asymmetrical droplets are developed after miniemulsification, the nanocomposite particles are formed via polymerization.⁹ Figure 3d shows that the obtained silica/polystyrene nanocomposite particles exist only at the interface in the water–toluene dual-phase system.

The asymmetric nanocomposite particles were converted into polystyrene hemispheres by treatment with aqueous HF solution.

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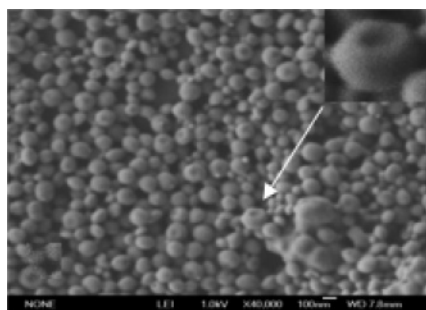


Figure 4. SEM image showing the polystyrene hemispheres remaining after the linked silica particles in the composites are removed by etching. The scale bar is 100 nm.

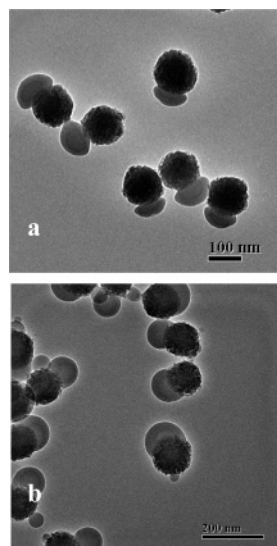


Figure 5. TEM images of asymmetric silica/polystyrene nanocomposite particles: (a) 2.2 g of styrene and (b) 4.8 g of styrene.

The shape of the polystyrene hemispheres was studied by scanning electron microscopy (SEM). In Figure 4, we can see a sunken-like part in nearly every remaining polystyrene hemisphere, which is formed after the linked silica particle is removed by etching. This sunken part of the polystyrene nodules indicates the locally modified surface area in which the polystyrene and silica particle are connected. It can be concluded that the asymmetric nanocomposite particles are developed with control of the polymer nodule nucleation and growth at the modified surface of an inorganic particle.

The asymmetrical morphology of the nanocomposite particles was modified by adjusting the ratio of styrene to silica particles and keeping other parameters unchanged. As shown in Figure 5, when the amount of styrene is changed from 2.2 to 4.8 g (Supporting Information, Table S1, recipes A and B, respectively), the shape of the nanocomposite particles varies from mushroom-like to swaddle-like. Hence, even over this wide range of concentration, the asymmetric morphology of the nanocomposite particles can be well maintained. A conclusion can be drawn here that the formation of asymmetric morphology is independent of the styrene concentration, which is in sharp contrast to results in previous studies.^{5b} The key in the development of asymmetrical morphologies, therefore, lies in the localized surface modification of the silica particles and highly selective nucleation of polystyrene on the modified surface area.

In conclusion, we have developed for the first time a novel method for the preparation of asymmetric nanocomposite pairs via one-step miniemulsion polymerization with particle local surface modification. Nanocomposite particles with different asymmetrical morphology have been obtained by controlling the concentration of styrene. It is a simple and effective approach to synthesizing inorganic/polymer hybrid nanoparticles with asymmetrical morphology. This approach can be further extended to the preparation of other asymmetric nanocomposite particles, such as half-raspberry-like¹¹ and acorn-like systems, by adjusting the density and distribution of the alkylsilane agent on the inorganic particle surfaces and the size of the polymer nodule. These asymmetric nanocomposite particles will find significant applications in complex media, biomedicine, and bioinspired systems.

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Supporting Information Available: Reagent and experimental section including the synthesis of silica particles, surface modification of the silica particles, and synthesis of mushroom-like silica/polystyrene nanocomposite particles. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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