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Facile Fabrication of Inorganic/Polymer Janus Microspheres by Miniemulsion Polymerization

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Inorganic/polymer Janus microspheres were fabricated successfully in a one-step process by miniemulsion polymerization. Our method involved the in situ miniemulsion polymerization of styrene and the in situ hydrolysis–condensation of tetraethoxysilane under basic conditions. By taking full advantage of phase separation between the growing polystyrene particles and tetraethoxysilane, Janus microspheres were obtained with silica constituting one hemisphere by the hydrolysis–condensation and polystyrene the other hemisphere after the polymerization of monomers. The Janus microspheres showed amphiphilicity due to the different chemical composition of each hemisphere.

Recently, Janus particles have received much attention in nanoscience due to the interesting properties for academic and technological reasons.[1] Janus particles are named after the two-faced Roman god Janus representing particles with different polarity, morphology, color, or any other property.[2] Therefore, they find applications in an increasing diversity of areas by using as building blocks for supraparticular assemblies, dual-functionalized carriers useful for catalysis, sensing and drug delivery, particular surfactants, etc.[3]

Because of the minimization of interfacial tension energy, nanoparticles are typically prepared in spherical shape and their surface chemical groups are isotropically arranged. For the fabrication of Janus particles, different approaches have been developed, such as from the controlled phase separation of polymer mixtures, from the self-assembly of sophisticated terpolymers, from controlled surface nucleation, and from the urface modification of symmetric particles.[4] More often, Janus particles are prepared in a two-step process via altering the symmetry elements of the precursor particles by chemical or physicochemical processes. A facile method for the production of Janus particles still remains a major challenge. Recently, organic–inorganic hybrid asymmetric dimer particles have been fabricated successfully via miniemulsion polymerization. The formation of dimer particles was realized by taking full advantage of phase separation between the growing polystyrene (PS) particles and tetraethoxysilane (TEOS).[5] Inspired by the interesting result, we investigate the feasibility for the preparation of Janus microspheres by controlling phase separation within polymer microspheres.

Here we show for the first time that inorganic/polymer Janus microspheres were prepared by controlled phase separation in a one-step process. The mixture of TEOS and styrene (St) was confined in monomer droplets via a miniemulsification process. Janus microspheres were obtained with silica constituting one hemisphere by hydrolysis–condensation under basic conditions and PS the other hemisphere after the polymerization of monomers.

The formation of silica/polymer Janus microspheres via miniemulsion polymerization is displayed in Figure 1. First of all, St, γ-(trimethoxysilyl)propyl methacrylate (MPS), and TEOS were restricted in miniemulsion microreactor droplets (Figure 1a) under high-speed shearing, which was stabilized by sodium dodecyl sulfate (SDS) and costabilizer hexadecane (HD). After the polymerization was carried out at 75 °C under N_2 atmosphere for 0.5 h, the pH value of the dispersion was adjusted to around 9.0. The great differences in the miscibility of PS and TEOS resulted in the phase separation.[5] TEOS phase was compressed and pushed to one side of the initially formed PS particles (Figure 1b). By the hydrolysis–condensation reaction under basic conditions, TEOS turned into silica. Janus microspheres with silica constituting one hemisphere were obtained after the polymerization was carried out for another 10 h. (Figure 1c). Details of the method are given in Supporting Information.[6]

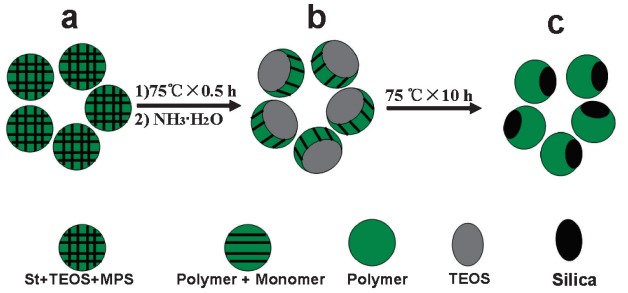

Figure 1. Schematic illustration for the preparation of hybrid Janus microspheres via miniemulsion polymerization. a) Miniemulsions of St, TEOS, and MPS were formed by using a Fluko® homogenizer to apply a shear force. b) After the polymerization of styrene was carried out for ca. 0.5 h at 75 °C, the pH value of the aqueous dispersion was adjusted by ammonia to around 9.0. c) Polymerization was carried out for ca. 10 h and hybrid Janus microspheres were obtained after silica hemisphere was formed under basic conditions.

Figure 2a shows the TEM image of hybrid microspheres prepared by the miniemulsion polymerization. By using water-soluble initiator, the potassium persulfate (KPS) decomposed in the water phase, and the polymerization of St was initiated by radical entry into the preexisting miniemulsion droplets. The naturally different miscibility between TEOS and polymer resulted in the phase separation and the TEOS phase was compressed. However, the increased viscosity of the shell of the monomer/polymer mixed droplets inhibited the TEOS phase from being extruded out and settled at one internal side of the initially formed

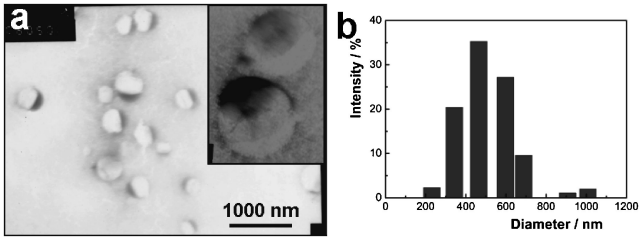

Figure 2. Typical nonstained TEM image (a) and size distribution (b) of the as-prepared Janus microspheres showing the morphology and size distribution of microspheres, respectively.

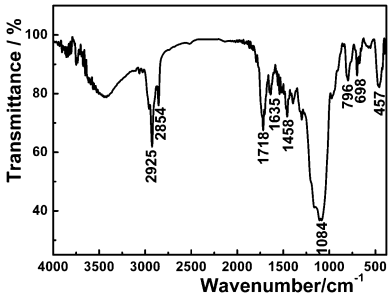

Figure 3. FT-IR spectroscopy of the Janus microspheres.

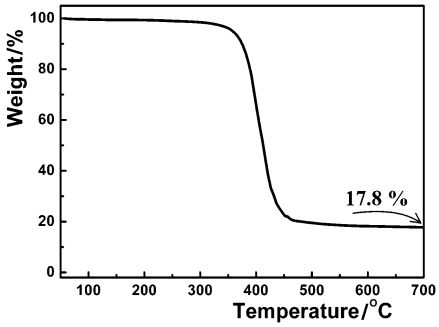

Figure 4. TGA curve of Janus microspheres.

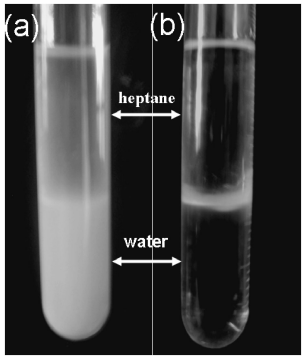

Figure 5. Optical pictures of the Janus microspheres showing the amphiphilic properties. Locations of Janus microspheres added to a water–heptane dual-phase system. a) Sonification for 15 min after adding heptane to the water dispersion. b) Janus microspheres accumulated at the boundary of water–heptane after standing for 10 min.

PS particles. By the hydrolysis–condensation reaction under basic conditions, TEOS phase turned into silica and constituted one hemisphere of Janus microspheres, which was joined with the other polymeric hemisphere by silane couplers.[7] Compared with organic polymer, inorganic silica show a darker brightness under the same determination conditions. As shown in Figure 2a and the inset, the darker hemispheres and the brighter hemispheres of the hybrid Janus microspheres represented the inorganic silica and polymer, respectively. The morphology of the resulted microspheres was quite different from that of the recently reported work via miniemulsion polymerization.[5] By using an oil-soluble initiator, the compressed TEOS phase was extruded out of PS particles, which resulted in the formation of dimer particles. However, we controlled phase separation within polymeric microspheres successfully by using water-soluble initiator, which led to the fabrication of Janus microspheres after TEOS phase turned into silica. The size distribution of Janus microspheres determined by DLS measurement is shown in Figure 2b.

FT-IR is generally used to identify the chemical structure of silica/polymer nanocomposite particles and widely used to prove the formation of nanocomposites. FT-IR spectrum of Janus microspheres is shown in Figure 3. It could be seen that an absorption band characteristic for the Si–O–C group (1084 cm^{-1}) and absorptions at 2925, 1718, and 1635 cm^{-1}, corresponding to the stretching vibration of the $–CH_3$, C=O, and C=C groups of MPS.[8] Because the redundant MPS was eliminated by rinsing three times with hot ethanol, the result confirmed the formation of silica and also indicated that there existed chemical interaction between MPS and silica, not single physical absorption.

The TGA curve of the prepared hybrid microspheres is shown in Figure 4. The weight loss corresponded to the degradation of the polymer backbones at about 400 °C. The SiO_2 content in the hybrid particles was about 17.8%, which was consistent with the value of theoretical calculation from the synthesis formulation.

Figure 5 shows the photographs of the Janus microspheres suspended in a dual-phase mixture of water and heptane. Because the polymerization of St was initiated by water-soluble initiator, the sulfate ions generated from KPS were mainly on the surface of polymeric hemisphere. Meanwhile, the other silica hemispheres were made hydrophobic by the hydrolysis and polycondensation of TEOS and MPS.[9] Although most of the emulsifier in the dispersion medium was removed, hybrid microspheres were dispersed well in water, which was stabilized by the sulfates ions on the surface of polymeric hemispheres. After heptane was added to the aqueous suspension (Figure 5a), the amphiphilic hybrid Janus microspheres spontaneously assembled at the water–heptane boundary as seen in Figure 5b.

In summary, hybrid Janus microspheres were prepared successfully in one step via miniemulsion polymerization. By using a water-soluble initiator, the phase separation between TEOS and the growing polymer particles resulted in the formation of inorganic/organic Janus microspheres. The method makes possible the production of various composite asymmetric particles of different chemical composition.

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