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Synthesis of Janus composite particles by the template of dumbbell-like silica/polystyrene

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ABSTRACT

Janus particles possess promising performances. It is challenging to develop new methods to control composition and microstructure of the particles. In this report, we describe a general template synthesis of several non-spherical Janus composite particles by the template of dumbbell-like silica/polystyrene (PS) Janus particles. Both PS and silica can be modified to introduce desired functional groups respectively, or induce crystallization of other materials on the particle surface. Especially, by favorable growth of materials within the sulfonated PS gel forming the core–shell structure at the polymer part, several new Janus hollow particles are obtained after removal of the PS core.

1. Introduction

Anisotropic particles with different structure or/and surface chemistry integrated together, are attracting much attention for both theoretical and practical application considerations [1–8]. They can be used as artificial molecules to mimic stacking behavior of building units in condensed matter physics. Many new complex superstructures form by directionally induced assembly from the anisotropic particles as building blocks. In biomedical field, they can serve as multifunctional carriers or probes. Especially, Janus particles with two distinct different structures or components integrated together can be used as nanomotors or colloidal surfactants [9,10].

It is important to develop synthesis methods to prepare anisotropic particles with sizes from nanometers to micrometers [11–22]. Micron-sized Janus polymer particles have been massively synthesized using microfluidic techniques by solidifying two fluids [15,16,23,24]. Based on self-assembly of triblock copolymers, Janus micelle, disc and cylinder can be obtained. The PS/polymethyl methacrylate Janus particles are prepared by phase separation induced by solvent evaporation [26]. Compared with the above mentioned methods, the surface protection and de-protection, valid for both planar and three-dimensional interface, is usually employed in preparing Janus particles. That is, when a particle is partially embedded into a matrix, modification of the exposed part would make the particle with two different surfaces. Recently, Liu et al. reported a new interesting non-spherical dumbbell-like organic–inorganic (PS/SiO_2) Janus colloids based on Pickering emulsion [27]. A surface modified SiO_2 colloid with vinyl group is partially embedded at the interface of a solid wax/water Pickering emulsion. After selectively etching the exposed part towards the aqueous phase, a fresh silica surface is generated. By a selective polymerization of styrene monomer onto the surface of unetched part with vinyl groups, PS/SiO_2 Janus colloids are derived. However, all the Janus particles are solid rather than hollow ones. We are interested in Janus hollow particles since some desired materials can be loaded into the hollow cargoes [28], which can interact directionally with their targets.

Herein, we report the synthesis of Janus hollow particles with a dumbbell-like shape using the PS/SiO_2 Janus particles as templates. The PS part is firstly sulfonated to form a gel layer, which can induce a favorable growth of other materials within the gel layer. Then, a hollow structure is obtained after the PS core is removed.

2. Experimental

2.1. Materials

Aniline, ethanol, tetrabutyl titanate (TBT), styrene, sulfuric acid (H_2SO_4), ammonium persulfate ($(NH_4)_2S_2O_8$), $AgNO_3$ and N,N-dimethylfomamide (DMF) were purchased from Sinopharm Medicine Holding Co., Ltd. Aminopropyltriethoxysilane (APTES) was purchased from Aladdin reagent (China) Co., Ltd.

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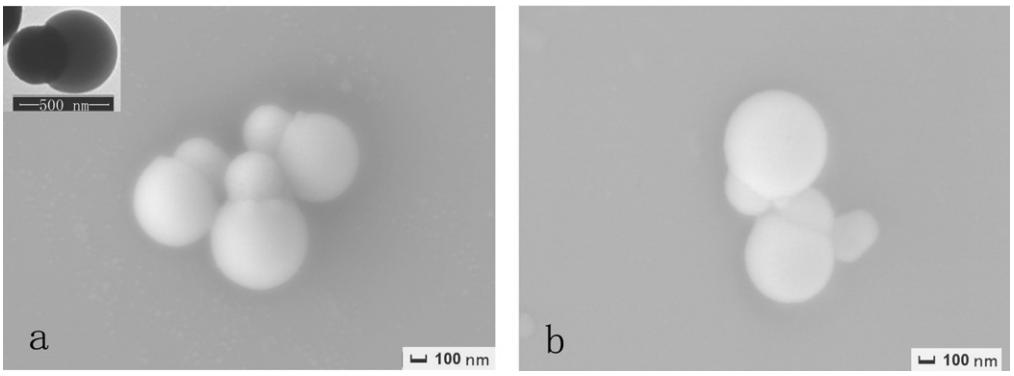

Fig. 1. (a) SEM and inset TEM images of the Janus template particles. (b) SEM image of the sulfonated PS gel/SiO_2 Janus particles.

2.2. Synthesis of sulfonated PS/SiO_2 Janus particles

PS/SiO_2 Janus particles with a diameter ranging from 700 to 800 nm were prepared according to the reported method [27]. The obtained PS/SiO_2 particles were dried, and then dispersed into concentrated sulfuric acid under stirring for 4 h at 40 °C. Accordingly, the outer layer of the PS part was converted into sulfonated PS gel. The particles were thoroughly washed with water and ethanol.

2.3. Synthesis of silica/titania Janus hollow particles

Dried sulfonated PS/SiO_2 Janus particles (0.1 g) were dispersed into 5 mL of tetrabutyl titanate (TBT) and alcohol mixture (V_{TBT}:$V_{alcohol}$ = 1:1) with ultrasonic agitation for 1 h. The particles swelled by TBT were separated by centrifugation and washed with ethanol, and then were re-dispersed into ethanol (5 mL). 5 mL of water was added to the dispersion under stirring. After hydrolyzed for 4 h, PS–TiO_2/SiO_2 Janus particles were obtained after centrifugation. After the PS core was calcined at 450 °C for 2 h, the resultant TiO_2/SiO_2 Janus hollow particles were prepared.

2.4. Synthesis of silica/polyaniline Janus hollow particles

0.1 g of dried sulfonated PS/SiO_2 Janus particles were immersed in 20 mL of water containing aniline monomer (0.1 g) under stirring for 24 h. Then, aqueous ammonium persulfate (5 mL, $M_{ammonium\ persulfate}$:$M_{aniline}$ = 1:1) was added to initiate the oxidative polymerization at room temperature for 24 h. After the resultant composite particles were treated with DMF to remove the PS core, polyaniline/silica Janus hollow particles were obtained.

2.5. Synthesis of silica/polystyrene–silver Janus composite particles

0.1 g of dried sulfonated PS/SiO_2 Janus particles was immersed in aqueous silver nitrate (50 mL, 0.1 M) for 24 h. The particles were separated by centrifugation and washed with water. After re-dispersed in 5 mL of water, 2 mL of hydrazine hydrate aqueous solution (50 wt%) was added to deoxidize silver ion to form the SiO_2/PS–Ag Janus particles.

2.6. Synthesis of silica/polystyrene–palladium Janus composite particles

0.1 g of dried sulfonated PS/SiO_2 Janus particles was dispersed in 5 mL of aqueous solution containing 0.2 g of palladium chloride under stirring in nitrogen for 12 h. After centrifugation, the particles were washed with water. Then they were re-dispersed in 5 mL of water, into which 1 mL of hydrazine hydrate was dropped under stirring. A reductive reaction of Pd^{2+} was run for 0.5 h at ambient temperature, leading to the formation of the SiO_2/PS–Pd Janus particles.

2.7. Preparation of silica–silver/polystyrene Janus composite particles

The PS/SiO_2 template particles were immersed into 50 mL of ethanol containing 1 mL of APTES under stirring for 24 h. The modified Janus particles were thoroughly washed with ethanol. They were re-dispersed in ethanol (10 mL). Then 70 mL of Ag nanoparticle dispersion (synthesized according to Zhang et al. [29]) and 70 mL of citrate solution (0.01 M) were added orderly under stirring. After 24 h, the Janus particles coated with Ag nanoparticles onto the silica surface were collected by centrifugation.

2.8. Characterization

The Janus particles were characterized by a JEOL JEM-200CX transmission electron microscopy (TEM) operated at an accelerating voltage of 5 kV. The morphology and the composition of the samples were performed by using a JSM-7500F scanning electron microscope (SEM) equipped with an Oxford Inca energy-dispersive X-ray (EDX) analyzer at an accelerating voltage of 25 kV. The X-ray diffraction (XRD) patterns of the samples were taken on a Philip-X' Pert diffract meter with a Cu Kα radiation. The Infrared spectrum was analysed by a Nicolet-5700 Fourier transform infrared spectrometer (USA) using KBr pellets. Pyrolysis was done using a CDS 5150 pyroprobe by heating samples to 600 °C for 5 s. The resulting pyrolysis products were swept by a stream of helium gas into a Thermo Trace GC ULTRA gas chromatograph. The separation was carried out on a 30 m × 0.25 mm column with a 0.25 μm film programmed from 50 °C to 250 °C at 10 °C min^{-1} with approximately 30:1 split ratio. The Thermo DSQ mass spectrometer was scanned over a range of m/z 50–650.

3. Results and discussion

3.1. Sulfonated PS/SiO_2 Janus particles

As shown in Fig. 1a, the typical PS/SiO_2 template particles have a silica part about 350 nm in diameter and a PS part about 550 nm in diameter, respectively. After the PS/SiO_2 Janus particles were sulfonated in concentrated sulfuric acid at low temperature for the given time, the whole shape remains intact (Fig. 1b). The diameter of the PS part increases slightly to 600 nm, suggesting that the outer layer of the PS part has been sulfonated and coated with a thin gel layer.

In order to further confirm the formation of the sulfonated PS gel layer, a FT-IR measurement was preformed (Fig. 2). The characteristic bands at 1093 cm^{-1}, 799 cm^{-1} and 467 cm^{-1} are assigned to the Si–O–Si stretching vibration. The characteristic peaks at 1601 cm^{-1} and 1492 cm^{-1} (the C=C stretching of benzene-rings) and 755 cm^{-1} and 700 cm^{-1} (the out-of-plane bending of C–H of mono-substituted benzene-ring) reveal the presence of PS. The new absorption bands at 670 cm^{-1} and 1242 cm^{-1} are attributed to the vibration of the –SO_3H group in the curve of sulfonated PS/SiO_2

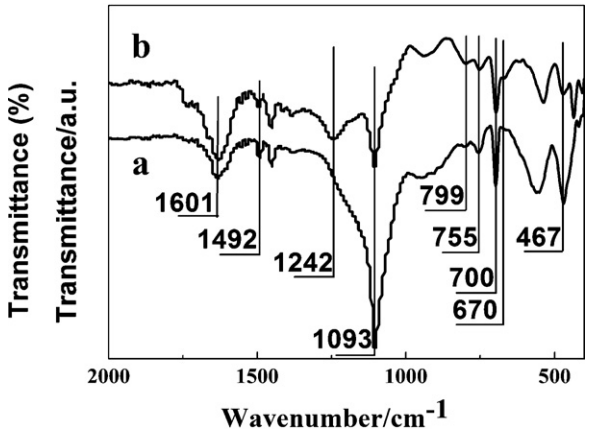

Fig. 2. FT-IR spectra of (a) the template of PS/SiO_2 Janus particles and (b) the sulfonated PS/SiO_2 Janus particles.