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Swelling synthesis and modification of Janus composite particles containing natural urushiol

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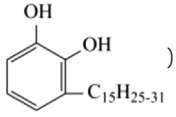
ABSTRACT

Janus materials with anisotropic chemical structure and physical properties have attracted increasing attention due to their diversified potential applications. However, existing organic parts of Janus particles mainly come from synthetic polymer. Urushiol is a kind of natural renewable product. Herein, we described the synthesis and functionalization of urushiol-titanium chelate polymer (UTi)-polystyrene (PS) Janus composite particles. The core@shell composite particles of PS@UTi was obtained through in-situ reaction between sulfonated polystyrene microspheres and UTi. UTi-PS Janus composite particles were synthesized by swelling assisted protrusion. Both of the two knobs of Janus particles could be modified. For example, polyaniline (PANi) could be favorably grown on the PS knob by specific interactions. Results of characterization indicated that the Janus composite particles of UTi-PS containing natural product have been synthesized and modified successfully. The modified product of UTi-PANi Janus composite particles is expected to serve as directional conductive material and heat-resistance polymer material.

1. Introduction

Janus colloids with two different compositions have been attracting interests due to its special physical and chemical properties [1]. To date, it has been applied in biological detection [2], functional solid surfactants [3,4], as well as directional catalysis [5]. However, existing organic parts of Janus particles mainly come from synthetic polymer. As the world is facing tremendous energy and environmental challenges, searching and utilizing alternative raw material to synthesize Janus particles are becoming a hotspot for scientific research.

The natural product of raw lacquer has been used as coating for thousands of years in China [6]. The main component of raw lacquer is urushiol () which is an o-dihydroxybenzene containing an unsaturated side chain. The two adjacent phenolic hydroxyls of urushiol react easily with metal compounds and generated urushiol-metal coordination compounds. The coordination numbers of metal are unsaturated because of the rigidity of phenyl groups and the curl of side chains. Just as the unsaturated coordination of metal, the metal is apt to catalyze the polymerization of the unsaturated side chains in urushiol [7]. As a result, the urushiol-metal chelate polymer forms. The special molecular structure of urushiol-metal chelate polymers provides them with some special properties, such as resistance to acid and alkali, heat resistance and catalytic properties [6,7]. However, nothing has been reported on the urushiol-metal chelate polymer as colloid particles. Then, it is very interesting to introduce the urushiol-metal polymers into Janus structures.

Very recently, emulsion swelling assisted protrusion of Janus colloids has gained increasing interest since it works for a diversity of morphology and compositions [8]. In this paper, urushiol-titanium chelate polymer (UTi) was used as shell and coated on the seeds of polystyrene (PS) microspheres. After swelling assisted protrusion, anisotropic Janus particles were constructed from the core@shell composite particles of PS@UTi. Both the two knobs of Janus particles of UTi-PS could be modified further. Finally, the UTi-polyaniline (PANi) Janus particles with the excellent properties of raw lacquer, titanium and functional groups were synthesized.

2. Experimental

Materials: Chinese lacquer purchased from the Institute of Lacquer, Xi'an, China. Urushiol was obtained after extraction with

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acetone from Chinese lacquer. Styrene (St), tetrabutyl titanate, 2,2′-Azobisisobutyronitrile (AIBN), aniline, ammonium persulfate and sodium dodecyl sulfate (SDS) were purchased from Sinopharm Medicine Holding Co., Ltd. Divinylbenzene (DVB, 80%) was purchased from Aladdin reagent Co., Ltd., China. St and DVB were used after purification by alkaline Al_2O_3 to remove the inhibitor. The aniline was distilled before used.

Characterization: The morphology of the samples was characterized by a JSM-7500F scanning electron microscope (SEM) with operation voltage of 5 kV. Oxford Inca energy-dispersive X-ray (EDX) was used in conjunction with the SEM scans to determine the chemical composition. TEM images were obtained with a JEM-2010 electron microscope. The dried samples were pressed into pellets with potassium bromide and characterized by a Nicolet-5700 Fourier transform infrared spectrometer (USA). X-ray photoelectron spectroscopy (XPS) analyses were carried out with a Thermo Scientific ESCALAB 250 spectrometer using an Al Kα monochromatized source.

Synthesis and modification of the Janus composite particles: The freezed–dried PS microspheres with the average diameter about 230 nm were first dissolved in excess concentrated sulfuric acid at 40 °C water bath for 1 h to derive sulfonated polystyrene (SPS) particles. 1 g of tetrabutyl titanate swollen SPS microspheres prepared according to [9] was added into 5 g of urushiol dissolved in ethanol. The reaction was maintained for 4 h under stirring. The core@shell composite particles of PS@UTi was centrifuged. 0.05 g of dried PS@UTi composite particles was swelled with an emulsion that contained SDS and St under stirring for several minutes. The swelling product was centrifuged, and then was dispersed in 1% SDS mixed emulsion that contained AIBN, DVB and St under stirring in the water bath of 70 °C. After polymerization, the Janus composite particles of UTi-PS were obtained after centrifugation. 0.05*g* of sulfonated UTi-PS Janus composite particles was dispersed in deionized water. 0.1 mol/L ammonium persulfate solution was added into the dispersion solution. After stirring for 30 min, a desired amount of aniline monomer was added and the polymeric reaction was maintained for 24 h. The Janus composite particles of UTi-PANi were centrifuged.

3. Results and discussion

After sulfonation of polystyrene microspheres with concentrated sulfuric acid, sulfonic acid groups were simultaneously derived in the gel shell. With a one step sol–gel process, tetrabutyl titanate was adsorbed in the gel shell. Two adjacent phenolic hydroxyls of urushiol reacted easily with tetrabutyl titanate and generated urushiol-titanium coordination compound. The alkyl chains of urushiol cross-linked at the catalyst of titanium. The average diameter of PS@UTi increased from 230 nm (PS microspheres,

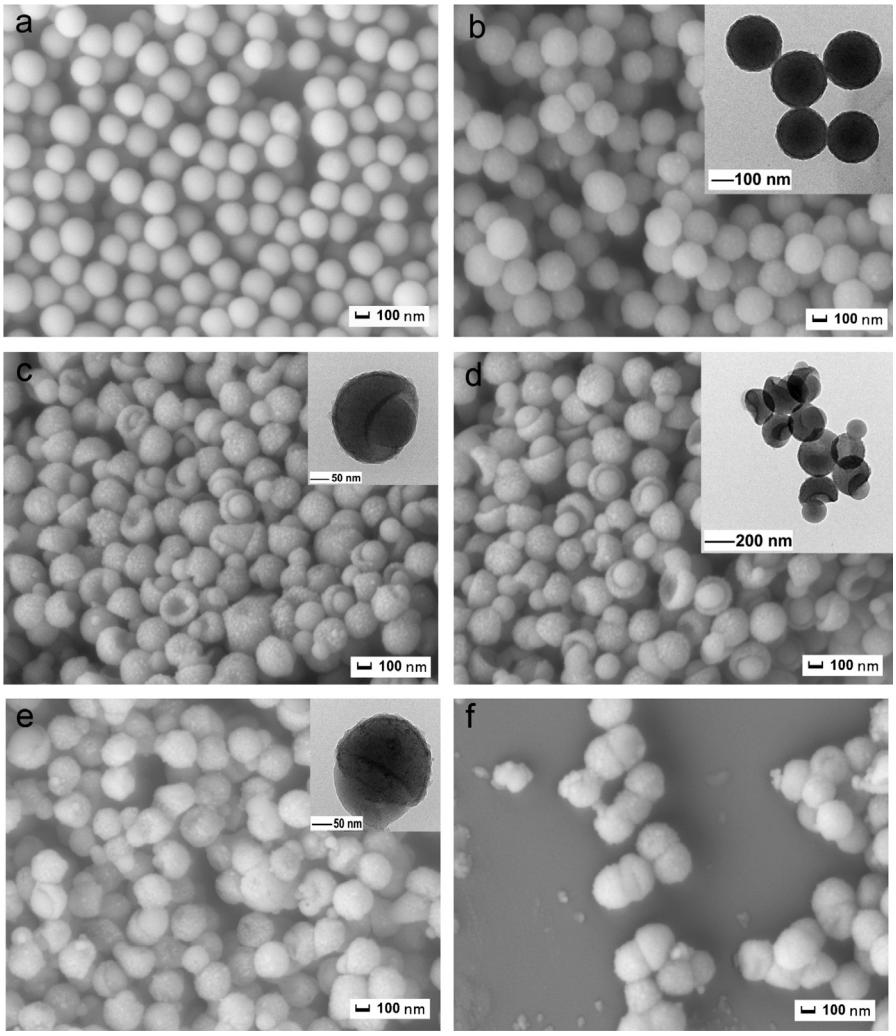

Fig. 1. SEM images and inset TEM images of (a) PS, (b) PS@UTi, (c) UTi-PS Janus composite particles by swelling for 5 min at room temperature, (d) UTi-PS Janus composite particles by swelling for 8 min at room temperature, (e) UTi-PS Janus composite particles by swelling for 10 h in the water bath of 70 °C and (f) UTi-PANi Janus composite particles.