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A facile strategy for synthesis of multilayer and conductive organo-silica/polystyrene/polyaniline composite particles

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ABSTRACT

By means of a facilely designed strategy, we successfully fabricated the multilayer and conductive organo-silica/polystyrene/polyaniline (organo-silica/PS/PANi) composite particles. First, organo-silica/PS core/shell composite particles were synthesized by seeded emulsion polymerization and the vinyl groups located on the surface of organo-silica nanoparticles were used to induce in situ polymerization of styrene. The influence of the route of the addition of styrene on the morphology of organo-silica/PS composite particles was investigated. Then, the coating of organo-silica/PS composite particles with PANi was achieved by virtue of the "Swelling–Diffusion–Interfacial-Polymerization Method" (SDIPM). The whole preparation process was monitored by transmission electron microscope, scanning electron microscope, Fourier transform infrared, Raman spectroscopy, dynamic light scattering, and thermogravimetry. As a result, the multilayer and conductive organo-silica/PS/PANi nanocomposites possessed of a uniform size and well-defined morphology, and furthermore, their structure could be well controlled by simply changing the weight ratio of aniline/PS.

1. Introduction

In recent years, considerable attention has been paid to the design and controlled fabrication of core/shell type colloidal nanocomposites with tailored structures and properties [1–5]. Such composite colloids are well known for the advantages of incorporating physical and chemical properties of their respective component counterparts. Therefore, these objects have become one of the most effective sources for advanced materials, and led to interesting applications in the fields of catalysis, chemical and biological sensor, coating, drug storage and controlled release, photo crystals, surface-enhanced spectroscopy, and so on [6–14].

Usually, the core/shell-like colloidal composite particles comprise single layer shell, and the shell components come into being at the core particle surface via surface reaction (e.g. polymerization or precipitation) and the controlled self-assembly. To name only a few, Bourgeat-Lami et al. encapsulated SiOH-functionalized polystyrene (PS) particles with silica shell through surface polymerization of tetraethoxysilane in both aqueous and ethanol/water medium [15,16]. Pich and co-workers have demonstrated that PS particles dispersed in 2-propanol can be coated with ZnO overlayer by direct surface precipitation reaction utilizing β-diketone groups located on the PS particle surface to induce coating [17]. Halas' group reported that gold nanoparticles (NPs) were covalently bound on organosilane-modified silica colloid spheres and even formed homogeneous noble metal shells using a combination of self-assembly technique and colloid reduction chemistry [18,19].

Recently, multilayer core/shell type colloidal hybrid materials have attracted increasing attention and significant progress has been made on the synthesis and characterization of such composite particles [20–26]. The most effective and straightforward strategy is the so-called bottom-up approach, where the core and shells are prepared in an inside-to-outside order. In this approach, the core particles are first synthesized, followed by consecutive coating with desired and different materials. For instance, Chiu et al. and Yang et al. prepared silica/polystyrene/polyaniline and silica/polystyrene/polypyrrole multilayer and conductive composite particles, respectively, by four sequential reactions [20,21]. Yin and co-workers reported that a series of spherical and nonspherical Fe_3O_4/silica/PS composite particles were fabricated by first synthesizing superparamagnetic core, followed by coating with silica and PS in turn [22]. In addition, Wu's group also successfully used the miniemulsion polymerization technique to fabricate the silica/PS/silica and silica/PS/titania multilayer hybrid particles [23,24].

Despite a massive amount of work mentioned above, in general, for the sake of continuous coating, surface functionalizations and modifications of first-order, second-order, third-order or higher-order substrate particles in order to enhance physicochemical or chemistry affinity of substrate particles and the next shell

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component are inevitable. Obviously, time-consuming surface pretreatments complicate the synthetic procedure, even though it could generally improve the deposition architecture of the shell. Therefore, the development of a facile and feasible method for preparing multilayer composite particles remains a great challenge.

In this paper, a facile strategy was exploited intelligently to fabricate the multilayer and conductive organo-silica/polystyrene/polyaniline (organo-silica/PS/PANi) composite particles. After sequentially synthesizing the monodisperse organo-silica NPs and organo-silica/PS core/shell composite particles, we reasonably employed the "Swelling–Diffusion–Interfacial-Polymerization Method" (SDIPM) [27,28] to controllably coat PANi onto the monodisperse organo-silica/PS composite particles and thus to form uniformly multilayer and conductive organo-silica/PS/PANi composite particles.

2. Materials and methods

2.1. Materials

Vinyltriethoxysilane (VTES) was acquired from Liyang Mingtian Chemical Co. Styrene and aniline (AR, Shanghai Chemical Reagent Co.) were purified by distillation under reduced pressure. Potassium persulfate (KPS) and ammonium persulfate (APS) were purified by recrystallization in water. Sodium dodecylbenzene sulfonate (SDBS), ammonia (25 wt.% NH_3 in water) and hydrochloric acid (AR, Nanjing Chemical Reagent Co.) were used as received. Distilled water was applied for all polymerization and treatment processes.

2.2. Synthesis of organo-silica nanoparticles

VTES (8 g), SDBS (0.01 g), and water (60 mL) were mixed and charged into a three-neck round flask, and vigorously stirred for 30 min. Then, ammonia (1 mL) was added dropwise to the mixture, and the reaction mixture was kept at 50 °C for 48 h. Finally, the organo-silica colloidal dispersion was purified by repeated cycles of centrifugation, supernatant removal, and redispersion in water until neutral in order to remove ammonia and by-product ethanol.

2.3. Synthesis of organo-silica/polystyrene composite particles

2.3.1. Route 1

Fourteen gram organo-silica colloidal solution (solid content 10 wt.%) and 60 mL water were first mixed and degassed with nitrogen for 30 min. Then, 10 mL styrene was added, followed by degassing for another 30 min. The temperature of the solution was heated up to 70 °C, and KPS solution (0.1 g/5 mL) was injected to initiate the polymerization. The polymerization was allowed to proceed for 24 h before cooling to ambient temperature.

2.3.2. Route 2

Fourteen gram organo-silica colloidal solution (solid content 10 wt.%) and 60 mL water were first mixed and degassed with nitrogen for 30 min. Then, the temperature of the solution was heated up to 70 °C, and KPS solution (0.1 g/5 mL) was added, followed by the addition of styrene (10 mL), dropwise via syringe. After completing the addition of styrene, the polymerization was allowed to proceed for 24 h before cooling to ambient temperature.

2.4. Synthesis of multilayer and conductive organo-silica/polystyrene/polyaniline composite particles

First, aniline was added to water (15 mL) at 0 °C and under ultrasonic treatment for 15 min, followed by the addition of the organo-silica/PS seed composite particles containing 1.2 g PS component. The mixture was stirred with ultrasonic assistance for 30 min at 0 °C to allow sufficient swell of aniline into PS component inside the composite particles. The dispersion of aniline-swollen composite particles was transferred to a three-necked round-bottom flask in an ice bath. The aqueous solution of APS was added to the dispersion in one batch and the initial oxidant/monomer molar ratio was fixed at 1:1. This was followed by the addition of hydrochloric acid (1 mol/L), also in an equimolar amount relative to aniline, dropwise via syringe. The temperature was maintained at 0 °C for the first 5 h of the polymerization, after which the polymerization was carried out for 18 h at room temperature. The resulting green multilayer composite particles were washed repeatedly by centrifugation until the filtrate became colorless. Finally, the products were dried in a vacuum oven for 48 h at 50 °C.

2.5. Characterization

The morphology of the organo-silica particles, organo-silica/PS composite particles, and organo-silica/PS/PANi multilayer composite particles was observed both by transmission electron microscope (TEM) using a JEM-100 CX (JEOL Co., Japan) microscope at 80 kV and scanning electron microscope (SEM) using S-4800 instrument (Hitachi Co., Japan) operated at an accelerating voltage of 5 kV (samples sputter coated with gold prior to examination). Fourier transform infrared (FTIR) analysis was preformed with a Bruker VECTORTM 22 FTIR spectrometer (Bruker Co., Germany). Raman spectra were measured by use of the Multi-Ram spectrometer (Bruker Co., Germany). A continuous wave Nd:YAG laser working at 1064 nm was employed for Raman excitation. A total of 200 scans were averaged in each spectrum obtained with laser power 10 mW. Particle size and particle size distribution were determined by dynamic light scattering (DLS) on 90PLUS Particle Analyzer (Brookhaven Instruments Co.) with a 500 W helium–neon laser of 660 nm wavelength at 25 °C. Thermogravimetric analysis (TGA) was conducted with a Pyris 1 TGA instrument (PerkinElmer Co., USA) at a heating rate of 20 °C per min in N_2 from room temperature up to 700 °C.

3. Results and discussion

In this work, organo-silica NPs with vinyl groups enriched on the surface were synthesized using a one-step emulsion approach in aqueous solution proposed recently by Meng et al. [29]. A typical TEM image of this sample is shown in Fig. 1. It is evident that the organo-silica NPs have well-defined spherical outline and a

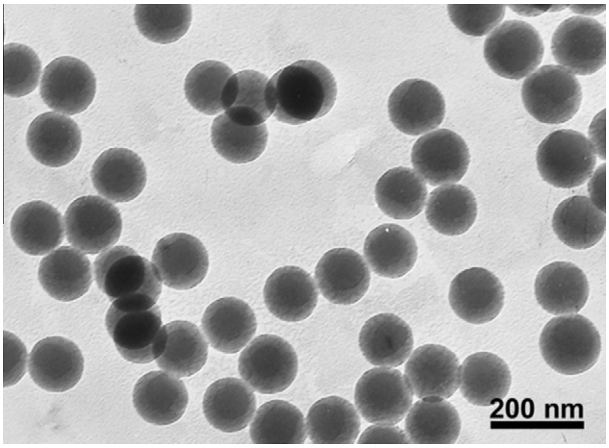

Fig. 1. TEM image of organo-silica nanoparticles.