

Synthesis of sea urchin-like polystyrene/polyaniline microspheres by seeded swelling polymerization and their catalytic application



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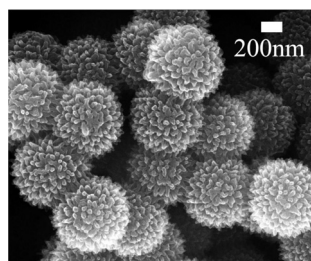
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HIGHLIGHTS

- A simple approach for assembly structures of polyaniline nanofibers.
- Simultaneously form and array of PANI nanofibers on PS microspheres.
- Special morphology with large BET surface area.

GRAPHICAL ABSTRACT

Radial array of PANI nanofibers on PS microspheres.



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ABSTRACT

Polystyrene/polyaniline (PS/PANI) composite microspheres with sea urchin-like morphology, radial array of PANI nanofibers on the surface, are synthesized by seeded swelling polymerization with polystyrene (PS) microspheres as seed. The redox potential of the oxidants and the concentrations of reactants have important influences on the morphology of the obtained composite microspheres. The formation mechanism of the sea urchin-like microspheres has been clearly revealed. When removing the PS template with tetrahydrofuran, the sea urchin-like hollow PANI microspheres are obtained. This approach is simple and can produce these microspheres in bulk. The sea urchin-like PS/PANI composite microspheres display high BET surface areas and can be further used as catalyst supports.

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1. Introduction

PANI has attracted considerable attentions due to its low cost, unique oxidation–reduction chemistry, environmental stability, and excellent optical and electrical properties [1,2]. Colloidal synthesis of PANI, such as microsphere and nanofibers, can overcome its poor processability, while assembly structures of these colloids will further improve its properties and expand its applications [3–5].

In the last decade, PANI nanoparticles and microspheres [6–16] have been widely researched. Armes [6–8] coated the poly(*N*-vinylpyrrolidone) stabilized PS microspheres with various conducting polymers such as polyaniline, polypyrrole. Okubo [9] have employed the chemical oxidative seeded polymerization to prepare various kinds of core–shell composite microspheres. In this method, a monomer has been first dissolved in HCl aqueous solution, and then the polymerization was initiated at the surface of PS microspheres template. Sulfonated PS microspheres have also been utilized to prepare the core–shell composite microspheres [10–14]. Zhu [13] has fabricated the core–shell PS/PANI composite microspheres by chemical oxidative polymerization with the sulfonated PS microspheres as template and ammonium persulfate as oxidant. Wang [15,16] has synthesized the PS/PANI

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composite microspheres by swelling aniline followed by the diffusion and polymerization in the surface of PS microsphere. However, all these obtained microspheres have smooth surface and some preparation methods involve complex procedures.

In another way, a variety of chemical methods have been developed to produce PANI nanofibers, such as template method [17], interfacial polymerization [18,19], and dilute polymerization [20]. Some assembly structures of nanofibers have also been synthesized. Parallel array PANI film and radially aligned dendrites have been obtained with soft template [5,20–22]. Array of PANI nanofibers has also been synthesized by a stepwise electrochemical deposition process or dilute chemical oxidative polymerization [3,23,24]. Some literatures report the assembly of nanofibers into spherical structure [25–28]. Wan has developed “emulsion template” approach to prepare hollow polyaniline spheres in aqueous media using spherical micells composed of a dopant and the monomer as template [2,25,26]. Our group has prepared sea urchin-like PS/PANI using commercial hollow polymer microsphere as template and support [27]. The anilinium salt was first permeated into the cavities of the hollow spheres through the hydrophilic channels, then diffused out and reacted with ferric chloride aqueous solution, and the PANI nanofibers radially construct on the exterior surface of microsphere to form sea urchin-like PS/PANI hollow microspheres. We further explore a simpler method to prepare sea urchin-like PS/PANI composite microspheres by seeded swelling polymerization with PS microsphere seeds and investigate their switchable wettability [28].

In this article, we further investigate the morphology effect factors and the forming mechanism. The effect factors of composite microsphere morphologies, including the oxidant redox potential and the oxidant content, the concentration of aniline monomer, were studied in detail. The forming mechanism was clearly revealed. The composite microspheres with high surface area were further used as support to load homogeneous catalyst.

2. Experimental part

2.1. Materials

Aniline and styrene was distilled under reduced pressure before use. Ammonium persulfate ((NH₄)₂S₂O₈, APS), ferric chloride (FeCl₃), ferric sulfate (Fe₂(SO₄)₃), ferric nitrate ninahydrate (Fe(NO₃)₃·9H₂O), tetrahydrofuran (THF) and ethanol were purchased from Beijing Chemical Reagent Company and used as received.

2.2. Preparation of polystyrene microspheres

Monodisperse PS microspheres were prepared by emulsifier-free emulsion polymerization at 70 °C for 24 h under nitrogen atmosphere in a four-necked round bottom flask as reported in pervious document [29]. The PS microspheres were centrifuged, washed with ethanol and de-ionized water, and then dried under vacuum.

2.3. Preparation of sea urchin-like PS/PANI composite microspheres and PANI hollow microspheres

Sea urchin-like PS/PANI composite microspheres were synthesized by seeded swelling polymerization with PS microsphere seed [28]. An amount of 0.3 g synthesized PS microspheres was dispersed in 20 mL of de-ionized water. The specified amount of aniline was added into the above solution. The solution was stirred for several hours at room temperature. Chemical oxidative polymerization was carried out for 12 h by adding oxidant aqueous solutions into

the above mixtures at room temperature. The product was centrifuged, washed with de-ionized water and ethanol, and finally dried in a dynamic vacuum at room temperature for 24 h.

The PS/PANI composite microspheres were dispersed into THF and immersed for 24 h. The residue was centrifuged and washed with THF, and then PANI hollow microspheres were obtained.

2.4. Preparation of PS/PANI-Mo catalyst and their catalytic properties

For preparation of PS/PANI-Mo, 0.6 g of Mo(O₂)₂O·2DMF (1.86 mmol) was dissolved in ethanol (100 mL) under stirring at room temperature. An amount of 0.5 g the prepared composite microspheres were added to the above solution and remained stirring for 48 h at room temperature. After filtration, the precipitates were washed thoroughly with ethanol until the filtrate was colorless, and then were dried in vacuum at 50 °C for 48 h.

In a typical catalytic epoxidation of *cis*-cyclooctene: 0.46 mL *cis*-cyclooctene (3.5 mmol), 1.20 mL of *tert*-butyl hydroperoxide (22 mmol) and 100 mg of PS/PANI-Mo catalysts was added in 2.5 mL CHCl₃ under stirring for 10 h at 60 °C. A volume of 0.2 mL nitrobenzene was employed as internal standard. Products were quantified by gas chromatography–mass spectrum (GC–MS) with an internal standard technique.

2.5. Characterization

The morphologies of microspheres were observed by scanning electron microscopy (SEM, SUPRA55) and transmission electron microscopy (TEM, JEOL JEM-200CX). Nitrogen adsorption was obtained at 77 K with an AUTOSORB-1C analyzer. FTIR spectra were measured on a Bruker model VECTOR22. Ultraviolet–visible (UV–Vis) absorption spectrum of PS/PANI *m*-cresol solution was recorded on a UV-2401PC spectrometer. Conductivity measurement was performed on compressed pellets of dry powders by a four-probe method on a WR-2B digital multimeter at room temperature. X-ray photo-electron spectrometer was characterized with PHI Quantera SXM. GC–MS was measured on Thermo DSQ.

3. Results and discussion

3.1. Effect of oxidant type on the morphology of PS/PANI composite microspheres

PS microsphere seed has smooth surface with 500 nm in diameter. PS/PANI composite microspheres were obtained by seeded swelling polymerization with PS seed and oxidant ferric salt or APS. When used Fe³⁺ as oxidant, the prepared PS/PANI composite microspheres are uniform and have narrow size distribution as shown in Fig. 1a,c,e. After extraction of PS core, sea urchin-like PANI hollow microspheres are clearly observed (Fig. 1b,d,f), which provides direct evidence for their morphologies. These sea urchin-like hollow microspheres are composed of highly oriented PANI nanofibers, the nanofibers form successive shell, and the length and diameter of the nanofibers depends on the oxidant types used in the reactions. When used Fe₂(SO₄)₃ as oxidant, the microspheres have PANI nanofibers with 10–20 nm in diameter and 100–200 nm in length (Fig. 1a and b), and have high BET surface area (30.97 m² g⁻¹, Table 1). While used Fe(NO₃)₃ as oxidant, the microspheres have PANI nanofibers with 15–30 nm in diameter and 50–150 nm in length (Fig. 1c and d), and the BET surface area is 26.72 m² g⁻¹ (Table 1) [28]. Using FeCl₃, the microspheres have short PANI nanofibers (Fig. 1e and f) and low BET surface area. In contrast, when APS is utilized as oxidant, smooth core–shell PS/PANI composite microspheres with 40 nm in shell thickness are obtained (Fig. 1g and h), which is in conformity with recent reports

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