



Using silane coupling agents to prepare raspberry-shaped polyaniline hollow microspheres with tunable nanoshell thickness

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ABSTRACT

In this paper, we present the facile preparation of polyaniline (PANI) hollow spheres by using a silane coupling agent, *N*-[3-(trimethoxysilyl) propyl]aniline (PAPTMS), as a precursor. The PANI hollow spheres exhibit tunable shell thickness. PAPTMS was used to prepare aniline-modified silica microparticles, ~550 nm in diameter, by the Stöber process. PANI-coated silica core-shell microcapsules (SiO₂@PANI) were subsequently obtained by performing chemically oxidative polymerization of a specific aniline monomer loading in the presence of the core-shell particles. PANI hollow spheres with tunable PANI shell thicknesses were eventually obtained by immersing the as-prepared core-shell particles in 5 wt% HF aqueous solutions to simultaneously remove the silica cores and further dope the PANI shells. The as-prepared core-shell particles and PANI hollow spheres were characterized using Fourier-transform infrared (FTIR) and ²⁹Si nuclear magnetic resonance (NMR) spectroscopies. The surface morphologies of the core-shell particles and PANI hollow spheres were investigated using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The electrical conductivities and optical absorption spectra of the as-prepared core-shell microparticles and the PANI hollow spheres were measured using the standard four-point probe method and ultraviolet–visual (UV–Vis) absorption spectroscopy, respectively.

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1. Introduction

The impetus for the intense research into production of uniformly sized hollow capsules, typically of spherical geometry, emanates from their scientific and technological interest. Nanosized and microsized hollow spheres constitute an important class of materials that are used in a diverse range of applications. For example, hollow spheres are used for the encapsulation and controlled release of various substances (e.g., drugs, cosmetics, dyes, and inks), for catalysis, and for medicinal purposes. For the development of piezoelectric transducers and electronic components, hollow spheres are applied in light-weight composites and low-dielectric-constant fillers toward the manufacture of advanced materials [1–5].

Recently, microscale and/or nanoscale hollow spheres of conducting polymers have attracted a great amount of attention because of their potential use in encapsulation applications, confined reaction vessels, controlled release and delivery mechanisms, separation systems, and biosensors [6–8]. The century-old

polyaniline (PANI) is of particular interest because of its good environmental stability [9], controllable electrical conductivity [10–12], and ability to exist in a number of intrinsic redox states [13]. The unique physicochemical and solution-processable properties of the aniline polymers make them potentially useful for application in energy storage devices [14], optoelectronic devices [15], display devices [16], electrodes and sensors [17,18], corrosion protection of metals [19], electrorheological fluid [20–27], and biomedical engineering [28]. Accordingly, the preparation of PANI hollow spheres is of interest and is important.

Obviously, the simplest method of fabricating hollow particles is to coat a sacrificial core particle with a shell and then to remove the core. Hollow spheres are usually prepared from spherical hard templates such as polystyrene beads [29,30] or silica colloids [31–33] followed by removal of the sacrificial core through calcination and solvent etching. For example, many studies propose a general method of synthesizing composite hollow spheres with robust hollow spheres sulfonated polystyrene gel as templates. The gel hollow spheres are highly cross-linked to well-preserve the spherical contours during template synthesis. Sulfonated polystyrene gel shells are infiltrative, enabling precursors to diffuse and be favorably absorbed within the whole shell by specific interaction. This

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is followed by growth of the desired materials, thereby forming composite shells. The compositions of the materials including metals and oxides, inorganic materials, and organic polymers and their composites can be tuned [34–42]. Preparation of PANI hollow spheres on silica templates has rarely been reported. Fu and Kang reported that the atom transfer radical polymerization (ATRP) initiator trichloro(4-chloromethylphenyl)silane was immobilized on the surface of about-25-nm-diameter SiO₂ nanoparticles. Silica nanoparticles with a surface-grafted polymer of 4-vinylaniline were prepared using surface-initiated ATRP of 4-vinylaniline (VAn). Subsequent surface oxidative graft copolymerization of aniline, using the aniline moieties of PVAn as the anchoring sites, and removal of the silica cores with HF etching produced well-defined P(VAn-graft-PANI) hollow nanospheres with a conductive shell about 15–40 nm thick and a core void about 25 nm in diameter [43].

In this report, a simple one-step hydrolytic co-condensation process replaces the multistage surface-grafted polymerization, and the shell thickness can be controlled by changing the number of monomers applied. There has recently been considerable interest in the development of organic/inorganic hybrid materials in the fields of chemistry and physics. The most common approach to developing ormosil and silsesquioxane particles [44–46] has involved using a sol–gel synthesis route to graft the organic groups of pre-synthesized Stöber silica particles with certain silane coupling agents [47–49]. This method enables the synthesis of uniform polymer shells with predictable thicknesses. Herein, we describe a method of fabricating 60- and 120-nm-thick PANI hollow particles with highly monodisperse hard templates in the 600-nm range. The monodisperse SiO₂@PANI core–shell particles were produced using chemical oxidation polymerization. The SiO₂ templates were removed using HF etching to produce monodisperse hollow PANI particles. The walls of the hollow structures could readily be tuned to be either 60 or 120 nm thick, and the 120-nm-thick walls exhibit strong electrical activity and conductivity.

2. Experimental details

2.1. Materials

The silsesquioxane *N*-[3-(trimethoxysilyl)propyl]aniline ((CH₃O)₃SiCH₂CH₂CH₂NHC₆H₅, PAPTMS) used in this work was purchased from Aldrich. The stabilizer and co-precursor used were poly(ethylene glycol) (PEG, *M_w* = 600 and 1500, Aldrich) and tetraethyl orthosilicate (TEOS, Fluka, ≥98.0%), respectively. Hydrochloric acid (HCl, 37%) was acquired from Riedel-de Haën as a 1 N aqueous solution. Both ammonium hydroxide solution (NH₃, 25%) and ammonium peroxodisulfate ((NH₄)₂S₂O₈, APS, ≥98.0%) were obtained from Fluka. Aniline (Riedel-de Haën, ≥99.5%) was purified using distillation under reduced pressure.

2.2. Synthesis of aniline-hang-silica particles

The following synthesis procedure is typically used. The amount of stabilizer required to prepare the co-hydrolysate of PAPTMS and TEOS was dissolved in deionized water containing ammonium hydroxide solution for the hydrolysis and condensation of the organic siloxanes. After the stabilizer was completely dissolved, the mixtures of PAPTMS and TEOS were gradually added to 50 g of aqueous medium and were moderately stirred with a magnetic stirrer. The reaction then progressed for 12 h at room temperature. The molar ratio of PAPTMS to TEOS in the emulsion was maintained at 4:1. The resulting precipitate was centrifuged and washed repeatedly with ethanol to remove the surfactant. Silica microspheres functionalized by aniline groups were also fabricated

by adding PAPTMS to initiate the sol–gel reaction, and the hydrophobic white particles were observed to be of a narrow size distribution in the range 500–1000 nm.

2.3. Preparation of SiO₂@PANI core–shell capsules

The white particles were directly dispersed in a stirred 1 N HCl aqueous solution containing 0.1 g of HCl by dry weight; 1 mmol (or 2 mmol) of aniline monomer was added to the mixture, and the mixture was vigorously stirred. An aqueous solution of APS (1:4 molar ratio of APS to aniline) was poured into the mixture, and the reaction was allowed to proceed for 6 h. After 6 h, the solution was centrifuged, and the precipitate was washed with ethanol several times. The final green powders were dried in a vacuum at 40 °C for 24 h.

2.4. Preparation of conducting PANI hollow spheres

The PANI-coated SiO₂ particles were treated with a 5 wt% HF solution for one week to produce hollow PANI spheres. Removal of the silica cores produced well-defined conductive shells about 60 or 120 nm thick and core voids about 600 nm in diameter.

2.5. Characterization

A JEOL JEM-1400 transmission electron microscope operating at an acceleration voltage of 120 kV and a Hitachi S-4100 field-emission scanning electron microscope operating at a voltage of 15 kV were used to observe the SiO₂@PANI capsules and hollow spheres. Fourier-transform infrared (FTIR) spectra were recorded on a JASCO 4200 spectrometer with KBr disks. High-resolution solid-state nuclear magnetic resonance (NMR) spectra were recorded on a Varian Infinityplus-500 NMR spectrometer; the Larmor frequency for ²⁹Si nuclei is 99.3 MHz. Ultraviolet–visual (UV–Vis) spectra were measured for *N*-methyl-2-pyrrolidinone (NMP) solutions of the SiO₂@PANI capsules and hollow spheres on a JASCO V-530 UV–Vis spectrometer. The molecular weights of the polymers were determined using a Waters GPC-150 CV viscometer, a differential refractometer detector, and a Styragel[®] HR column with NMP as the eluent and monodispersed polystyrenes as calibration standards. Conducting measurements on compressed pieces of dry powder (pellets pressed using a 15-ton hydraulic press, PIKE Technology CrushIRTM) were performed using a standard four-point probe method at room temperature. Cyclic voltammograms were obtained for the hollow spheres that were spread onto a platinum electrode and for a platinum counter electrode. The electrodes were placed in 50 mL of 1.0 M aqueous H₂SO₄ and were swept between operating potentials of –0.2 and 0.8 V at 1 mV/s before the electrochemical cyclic voltammetry measurements were performed.

3. Results and discussion

As shown in Scheme 1, the core particles were prepared by chemical reacting pre-synthesized Stöber silica particles with certain silane coupling agents [47,50]. Well-established hydrolysis and condensation reactions of monomeric alkoxysilane precursors in an aqueous solvent system are widely used to develop such materials. The approach involves the Stöber synthesis of silica particles starting from a mixture of tetraalkoxysilane (TAOS) and organotrialkoxysilane precursors with the general formula RSi(OR')₃, where R = methyl, vinyl, phenyl, aminopropyl, etc. groups, and R' = methyl or ethyl groups. The silica-based particles were generated by co-condensation of droplets in water. The one-step method of preparing monodispersed hybrid silica

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