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Synthesis of hollow ellipsoidal silica nanostructures using a wet-chemical etching approach

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ABSTRACT

We have utilized wet-chemical etching of ellipsoidal silica nanoparticles (ESNs) to form silica nanoshells of a range of elliptical morphologies, with the thicknesses of the ellipsoidal silica nanoshells (ESSs) controlled through variation of synthesis conditions. A mechanism has been proposed to explain how the nanoshells are formed, and we demonstrate that the porosity of the silica ellipsoid plays a role in generating silica shells. Our self-templated, wet-etching approach is an attractive alternate procedure to the approaches presently in existence for the following reasons: (i) it is a facile, one-step process that directly produces ellipsoidal silica nanoshells, while overcoming barriers (such as requirement of removing a solid-core template seed) utilized in many reported chemical etching studies; (ii) it results in ellipsoidal silica nanostructures with dimension less than 100 nm; (iii) with an appropriate etchant, the roughness of the silica shells can be well-controlled; and (iv) it results in tunable, uniform size particles with controllable shell thicknesses. Moreover, the silica materials with the unique structures might be adjusted to meet practical application requirements.

1. Introduction

A wide range of silica materials have proven interesting from a basic science perspective as well as because of crucial roles such materials play in everyday commercial applications, such as energy storage, chem- and bio-sensors, food processing, drug delivery, and catalysis systems [1–6]. In particular, silica colloids (because of the ease of surface functionalization) have proven to be useful absorbent materials in composite structures for enabling controlled porosity, solvent compatibility, and processability [7–9].

Morphologically different silica materials have been created using a broad spectrum of synthesis protocols, including such approaches as soft/hard-templating and the Kirkendall effect [10–15]. The synthesis of spherical silica particles has been the primary focus; the main reason for the present state of affairs is undoubtedly that self-assembled spherical shapes are kinetically favored to occur for most homogeneous synthesis processes. However, unsymmetrical template-assisted approaches may facilitate the formation of uniform, morphologically controllable, nonspherical silica materials [16–18]. It is to be noted that recently, ellipsoidal silica colloidal particles have garnered a great deal of attention because of their use as photonic crystals. In particular, α-Fe_2O_3 spindles have been utilized as templates for fabricating silica ellipsoids, which in turn have been used to form photonic crystals [19]. Also, α-Fe_2O_3/SiO_2 core–shell particles have been converted, through a chemical etching approach, to yolk–shell structures [20,21]. For this latter more complex yolk–shell structure, a shell-by-shell deposition of polycrystalline SnO_2 onto α-Fe_2O_3/SiO_2 templates has been developed, which resulted in double-walled SnO_2 nano-cocoons [19]. To date, however, although synthesis approaches for formation of unsymmetrical silica particles have been developed, practical applications of such materials are severely limited, largely due to the complexities of preparation processes and the compositional variabilities of the cores.

Another approach to control the morphology of silica particles involves the use of wet-chemical etching. For example, Zhang et al. [21] have reported a spontaneous dissolution-regrowth process for fabricating hollow silica spheres. The approach allows the control of surface porosity, as well as minimizes coalescence of nanoparticles, while, because of the porosity, permitting the reactivity of encapsulated catalytic agents to be maintained [21,22]. Chen et al. [23] have used a controllable structural difference-based selective etching strategy to produce nanosized hollow/rattle-type mesoporous silica structures. While Du and He [24] have prepared surface-roughened silica nanoparticles by a self-templating etching route for superhydrophobic coating formation. And, recently, Fang et al. [25] have developed a cationic surface assisted selective etching strategy (CSASE) to produce hollow spherical silica particles with either wormhole-like or oriented mesoporous shells. Generally, in a wet-chemical etching approach, it is found that etching of silica particles leads to the decomposition of the silica and forma-

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tion of silicate species; the redeposition of silicate species at the interior surface of the initial silica particles results in retention of overall shape and, as a result of Ostwald ripening, leads to the formation of hollow silica nanostructures [26].

In the present paper, we utilize a chemical etching approach on prior synthesized ESNs [27] in order to fabricate unique ellipsoidal silica shells with dimension less than 100 nm. Compared with prior studies, some of which generated ellipsoidal silica nanoshells (ESSs) using α-Fe_2O_3 templates, our self-templated, wet-etching approach is an attractive alternate procedure for the following reasons: (i) it is a facile, one-step process that directly produces ellipsoidal silica nanoshells, while overcoming barriers (such as requirement of removing a solid-core template seed) utilized in many reported chemical etching studies; (ii) it results in ellipsoidal silica nanostructures with dimension less than 100 nm; (iii) with an appropriate etchant (e.g., sodium borohydride ($NaBH_4$)), the roughness of the silica shells can be well-controlled, and (iv) results in tunable, uniform size particles with controllable shell thicknesses.

2. Experimental

2.1. Materials and methods

2.1.1. Synthesis of ellipsoidal silica nanoparticles

The detailed information concerning the synthesis of ellipsoidal silica nanoparticles has been discussed previously [27]. A typical synthesis process was the following: Deionized water and ethylene glycol (Sigma–Aldrich, ReagentPlus® ⩾99%) solution was prepared; CTAB (Alfa Aesar, 99+ %) was dissolved in the prepared solvent; then, 1 M ammonium hydroxide (Pharmco Products, Inc.) was added. After slow addition of TEOS (Acros Organics, 98%), the reaction was held at room temperature with stirring. Following the reaction, the white precipitate was filtered, washed with ethyl alcohol (Decon Labs, Inc., 190 proof), then dried overnight in air at ~60 °C. The final product was calcination for 8 h at ~580 °C to remove any residual CTAB. The molar ratio of CTAB/NH_4OH/TEOS/ethylene glycol/water was 1:1.2:77.1:381.4:1246.

2.1.2. Synthesis of ellipsoidal silica nanoshells

0.03 g of prior prepared ellipsoidal silica nanoparticles and 0.025 g PVP K29-32 (Acros Organics, M.W. 58,000) were added to a preheated aqueous solvent (50 °C, IKA® ETS-D5) and mixed by mechanical stirring (1200 rpm) until clear; 0.06 g $NaBH_4$ (Fisher Scientific) was then added to initiate etching, with vigorously stirring for 6 h. Following the reaction, the silica nanoshells were centrifuged (8500 rpm) and washed three times with ethyl alcohol. Finally, after drying in air at ~40 °C overnight, the resultant white powder was collected.

2.2. Characterization

Transmission electron microscopy (TEM, Zeiss EM 902) was performed to observe the sizes and morphologies of silica nanoparticles/nanoshells. To prepare the TEM samples, calcined silica white powders were dispersed in ethyl alcohol. A 10 μL aliquot of the silica–alcohol solution was dropped onto a carbon-coated copper grid. After evaporation of the alcohol, the sample was characterized by TEM at an acceleration voltage of 80 kV. The same preparation as above was used for scanning electron microscopy (SEM) and energy dispersive X-ray spectrometry (EDS) measurements (using a SEM, Zeiss Supra 55 VP). For the SEM analysis, the voltage was 5 kV, and the working distance was between 2 and 5 nm. For the EDS analysis, the voltage was 15 kV, and working distance was 8.5 nm.

Fourier-transform infrared (FTIR) spectra were obtained, in the range of 400–5500 cm^{-1}, using a Varian 7000 spectrometer with a resolution of 2 cm^{-1}. A MIRacle single horizontal reflection Attenuated Total Reflectance (ATR) accessory was used in most studies.

Nitrogen adsorption isotherms were measured using an ASAP 2010 analyzer (Micromeritics, Norcross, GA, USA) at −196 °C. Before the experiment, the sample was degassed at 120 °C to a constant pressure of 10^{-4} Torr. The isotherms were used to calculate the specific surface area (S_{BET}), micropore volume (V_{mic}), mesopore volume (V_{mes}), and total pore volume (V_t). Pore size distributions (PSDs) were determined using BJH method.

3. Results and discussion

As indicated in the literature, the usual approach for making monodispersed solid and mesoporous silica spheres of tunable sizes involve the Stöber et al. [28] and "modified Stöber" methods [29], respectively. Starting with these basic approaches, and, additionally, by variation of the water/oil (w/o) reaction solution, it has been shown to be possible to vary the shapes of silica particles and make them spherical, ellipsoidal, rodlike, or cubic; also the size of silica particles have been tuned in the range from nano- to microsize [18,27].

In this work, meso/microporous silica ellipsoids have been synthesized by controlling the anisotropic surface tension of the reaction solution, and then using chemical etching to morphologically convert nanoparticles to nanoshells. Typical TEM images show that the resultant silica nanoparticles (see Fig. 1a) and silica nanoshells (see Fig. 1b) are elliptical in shape. Moreover, the outer dimensions of the nanoshells have been found to be essentially the same as that of their precursor ellipsoidal nanoparticles. Measurements of particles shown in Fig. 1a reveal that a typical ellipsoidal silica nanoparticle has a long axis dimension of ~100 nm and an aspect ratio of approximately 4:3. Additionally, we have found that ESSs exhibit a much denser packing than the silica precursors, as indicated by nitrogen adsorption measurements, suggesting the existence of enhanced attractive forces between the nanoshell particles. Specifically, after etching, for the porous structure of the shells, a steep increase in nitrogen adsorption at the relative pressure close to one has been observed (as shown in Fig. 1c), indicating that nitrogen is prevented from entering the inner-shell surface due to dense packing, which is consistent with the observation of Fig. 1b. It is also to be noted that the changes in morphologies of silica particles and shells are indicated by changed porosities (see Table 1). Brunauer–Emmett–Teller (BET) measurements of adsorption on our silica samples after etching indicates a decrease in surface area and pore volume, which is due to the removal of silica matrix. Also, the increase in average pore sizes upon conversion of silica particles to shells (~3 nm before etching, ~30 nm after etching), as estimated using the BJH method, demonstrates that the micro-mesoporous structure of the initial silica nanoparticles is changed to shells that contain mesoporous and inter-particular spaces (see Fig. S1).

The molecular structural change of silica ellipsoids before and after chemical etching was also investigated using FTIR-ATR spectroscopy. The intense band at ca. 1086 cm^{-1} (see Fig. 1d), which is attributed to the transverse-optical mode of the Si–O–Si lattice, and the band at ca. 810 cm^{-1}, generally attributed to the Si–O–Si symmetric stretching vibration band, can provide qualitative information on the distance between Si and O atoms [30]. In Fig. 1d, FTIR spectra indicates that, the band at 1086 cm^{-1} experiences a red shift of ca. 7 cm^{-1}, from 1086 to 1079 cm^{-1}, while the 801 cm^{-1} band experiences a ca. 10 cm^{-1} red shift, from 811 to 801 cm^{-1}, suggesting that upon formation of silica nanoshells a more open network (Si–O–Si bond) results [31].