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Formation of SnO₂ Hollow Nanospheres Inside Mesoporous Silica Nanoreactors

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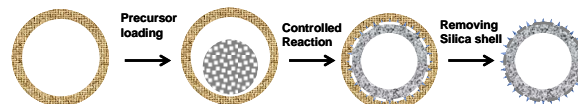
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ABSTRACT: We report an interesting approach for efficient synthesis of SnO₂ hollow spheres inside mesoporous silica “nanoreactors”. The as-prepared products are shown to have a uniform size distribution and good structural stability. When evaluated for their lithium storage properties, these SnO₂ hollow spheres manifest improved capacity retention.

Hollow structures are of great interest due to their characteristics such as low-density, high surface-to-volume ratio and low coefficients of thermal expansion and refractive index compared to their solid counterparts. These outstanding properties render them promising for a spectrum of applications including lithium-ion batteries,¹⁻⁵ catalysis support,^{6,7} drug/gene delivery,⁸⁻¹⁰ and medical imaging/diagnostics.^{11,12}

Procedures for synthesizing hollow nanospheres can be broadly divided into two categories: template-free and templating approaches. Even though template-free techniques generally involve fewer synthetic steps and are thus considered quite facile,^{2,13} templating methods offer important advantages, including narrow-size-distribution products with well-defined structural features.^{14,15} There are nevertheless inherent drawbacks in the template removal process, which limit the utility of the approach. Specifically, if the template core is removed by calcination at high temperature (e.g., to remove carbon or polystyrene spheres), or removed by chemical dissolution (e.g., use of hydrofluoric acid to remove silica templates), collapse of some fraction of the hollow structures is a virtual certainty. It is therefore highly desirable to develop new strategies for synthesizing hollow nanospheres that build on the strengths of both the templating and template-free methods.

In this communication, we report an interesting approach to synthesize metal oxide hollow nanospheres inside mesoporous silica (SiO₂) nanoreactors. We use molten metal salt hydrate (a highly concentrated salt solution with a melting temperature below 100 °C) as precursor, which is able to diffuse into the hollow cavity of the SiO₂ nanoreactors via the mesoporous shell. The excess amount of precursor outside the nanoreactors can be easily washed away thus ensuring exclusive loading of precursor inside the nanoreactors. After controlled thermal annealing, the metal salt is transformed into its corresponding metal oxide *in situ* and, thereby forms a shell on the inner surface of nanoreactors, giving rise to a double-shelled metal oxide@SiO₂ hollow structure. The outer SiO₂ shell is then easily removed by HF etching to obtain metal oxide hollow spheres (caution: HF is highly corrosive, must be handled with



Scheme 1. Schematic formation of SnO₂ hollow spheres inside mesoporous silica nanoreactors.

great care!). In this approach, the SiO₂ mesoporous nanoreactor plays crucial roles by confining and supporting the metal oxide during the thermal treatment. As a result, the metal oxide hollow nanospheres are formed with both uniform size distribution and good structural integrity. The size of as-formed hollow spheres can also be readily tuned by changing the dimensions of the nanoreactor cavity. Here, we choose SnO₂ as an example to simultaneously demonstrate the concept and to prepare hollow nanospheres relevant for applications as an anode material in lithium-ion batteries (LIBs). Compared with SnO₂ solid particles and spheres, the as-prepared SnO₂ hollow nanospheres manifest improved lithium storage properties.

Scheme 1 illustrates the procedure for generating SnO₂ hollow spheres. We first soak the SiO₂ nanoreactors into molten SnCl₂·2H₂O (*T_m* = ~37 °C), which can easily diffuse into the hollow cavity through the mesoporous channels. The excessive precursor remained outside the nanoreactors is removed by rinsing with ethanol then water. After washing, the SiO₂ nanoreactors with precursor loaded are heated at 700 °C in air to obtain SnO₂@SiO₂ double-shelled hollow spheres. Due to this special conformation, the subsequent removal of the outer mesoporous SiO₂ shell by HF etching is more facile than dissolving solid SiO₂ cores,^{1,3,5} and the inner SnO₂ shell is left intact, granting much better structural stability compared to conventional templating approaches.

We first examine the morphology of the SiO₂ mesoporous hollow spheres with field-emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM). From the FESEM image (Figure 1A), it can be clearly observed that the SiO₂ nanoreactors are very uniform with a relatively smooth surface, and a diameter of about 400 nm. The TEM image (Figure 1A, inset) shows that the shell has a thickness of about 30 nm. These mesoporous nanoreactors have a very high surface area of 1300 m² g⁻¹, and an average pore size of 3.08 nm,¹⁶ which is large enough to provide an easy access to the internal void space.¹⁷ The morphology of SnO₂@silica double-shells is shown in Figure 1B, and it can be clearly seen that the dark SnO₂ shell, which is about 50 nm in thickness, is attached on the inner surface of SiO₂ nanoreactors. After removing SiO₂ with a HF solution, the SnO₂ hollow

spheres are obtained with a relatively rough surface (Figure 1 C and D). The outer diameter is about 340 nm, which is consistent with the

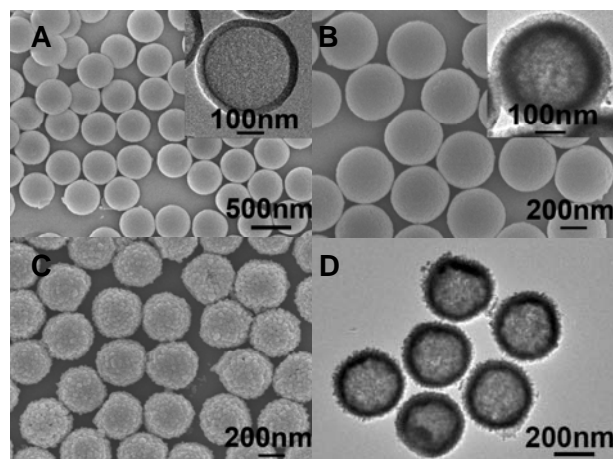


Figure 1. (A) SEM and TEM (inset) images of mesoporous silica hollow spheres with a diameter of 400 nm; (B) SEM and TEM (inset) images of SnO₂@silica double-shells; (C, D) SEM and TEM images of SnO₂ hollow spheres, which are prepared by removing silica with 2 wt% HF solution for 30 min.

cavity size of SiO₂ nanoreactors (Figure 1A). The energy-dispersive X-ray analysis (EDX; see supporting information, Figure S1) shows that the residual SiO₂ is lower than 0.5 wt%, and the atomic ratio of Sn and O elements is about 0.5, which indicates that the hollow spheres are mostly composed of SnO₂. By employing SiO₂ nanoreactors with different cavity sizes, we are able to produce SnO₂ hollow nanospheres with a smaller diameter using the same approach (see supporting information, Figure S2), highlighting the versatility of our method.

In order to further understand the formation mechanism, we carry out some experiment to investigate the effect of annealing temperature. After annealing at a relatively low temperature of 120 °C, the precursor (probably partially hydrolyzed form) appears almost amorphous and exists as a sphere inside each nanoreactor because the melting point of these metal salt hydrates is also quite low (see supporting information, Figure S3). Crystalline SnO₂ starts to form when annealed at 200 °C, and becomes dominant only after annealing at 300 °C. It is thus suggested that the SnO₂ shell formation, from decomposition/oxidation of hydrates, is a result of strong interaction between metal oxide and SiO₂ surface. This might be partly verified by the observation of hairy surface of resulting SnO₂ hollow nanospheres (Figure 1C and D). It is also found that a high annealing temperature of 700 °C is required to obtain structurally robust SnO₂ hollow spheres that can sustain the removal of silica nanoreactors.

The crystal structure of the SnO₂ hollow spheres is determined by X-ray diffraction (XRD), as shown in Figure 2. All the identified peaks can be assigned to tetragonal SnO₂ (JCPDS card no. 41-1445, SG: *P4₂/mmm*, *a_o* = 4.738 Å, *c_o* = 3.187 Å).² The mesoporous structure of the SnO₂ hollow spheres is confirmed by the N₂ adsorption/desorption isotherm (see supporting information, Figure S4), illustrating a type-IV isotherm with a type-H3 hysteresis loop.¹⁸ The narrow pore size distribution (Figure S4, inset) calculated using the Barrett-Joyner-Halenda (BJH) method from both the adsorption and desorption branches of the isotherm indicates that most of the

pores have a diameter in the range of 2 - 5 nm. Such a porous structure leads to a Brunauer-Emmett-Teller (BET) specific surface area of 46 m² g⁻¹.

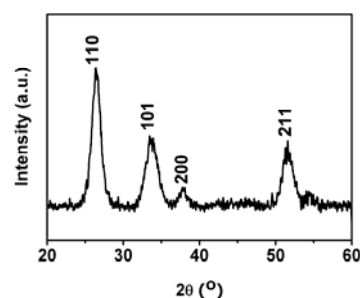


Figure 2. XRD pattern of SnO₂ hollow spheres.

As an n-type wide-bandgap ($E_g = 3.6$ eV) semiconductor, SnO₂ is one of the most widely investigated materials owing to its important technological applications such as gas sensors¹⁹ and lithium-ion batteries (LIBs).² When SnO₂ serves as the active material in a lithium-ion battery, the reaction mechanism can be described as follows: $\text{SnO}_2 + 4\text{Li}^+ + 4\text{e}^- \rightarrow \text{Sn} + 2\text{Li}_2\text{O}$ (1); $\text{Sn} + x\text{Li}^+ + x\text{e}^- \leftrightarrow \text{Li}_x\text{Sn}$ ($0 \leq x \leq 4.4$) (2).^{2,20} SnO₂-based anode materials have attracted much attention due to their theoretical reversible capacity of 790 mA h g⁻¹, which is more than twice that of the currently used graphite (370 mA h g⁻¹).²⁰ However, the practical use of these anode materials is significantly impeded by the poor capacity retention over long term charge-discharge cycling. This problem mainly originates from the large volume change of electrode materials accompanying Li insertion and extraction (reaction (2); the volume change is more than 200% when Sn alloys with Li to form Li_{4.4}Sn), which creates large internal stress, leading to the disintegration of the electrode material, and eventually destroys conduction pathways between neighboring particles.²⁰ To relieve this problem, one effective strategy is to design hollow and/or porous nanostructures, where the concept is to utilize the local empty space, i.e., the pores or the hollow interior, to partially buffer the large volume change,^{2,20,21} thus improve the cyclic capacity retention of the electrode material upon extended cycling.

To reveal the advantage of the hollow structure, we compared the lithium storage properties of the as-prepared SnO₂ hollow nanospheres with other solid counterparts, namely, SnO₂ solid particles and spheres. Figure 3A shows the discharge-charge voltage profiles of the three samples at a constant current density of 160 mA g⁻¹. The voltage profiles are consistent with that of SnO₂-based anodes.^{2,20} It is clear that the SnO₂ hollow nanospheres show the highest discharge capacity of 1571 mA h g⁻¹ among the three samples. A possible reason for the hollow nanospheres to have a higher lithium storage capacity is because of the internal void space, which probably helps to store more lithium.² While both spherical samples are able to deliver a subsequent charge capacity of ~800 mA h g⁻¹, the nanoparticles sample can only have ~700 mA h g⁻¹. This leads to a similar initial irreversible loss in three samples, which is about 40%. This is quite common to SnO₂-based electrode materials,² and such a large initial irreversible loss is attributed to the irreversible reduction of SnO₂ to Sn as described by equation (1) and other possible irreversible processes, such as the formation of solid electrolyte interface (SEI).

The lithium insertion/extraction process in the SnO₂ hollow nanospheres is further characterized with cyclic voltammetry

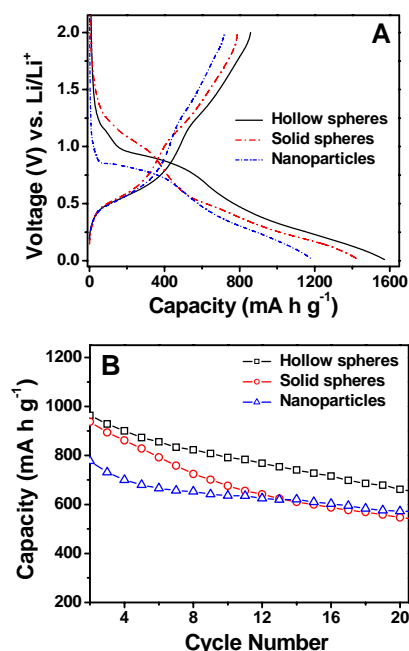


Figure 3. Comparative lithium storage properties of the as-prepared SnO₂ hollow nanospheres, SnO₂ solid spheres, and SnO₂ nanoparticles: (A) Charge-discharge profiles, and (B) Cycling performance. All of the measurements were conducted at a current rate of 160 mA g⁻¹ with a voltage window of 0.01–2.0 V.

(CV). The CV behavior (see supporting information, Figure S5) is generally consistent with previous reports,² indicating a similar electrochemical pathway. The characteristic pair of current peaks is observed at potentials (cathodic/anodic) of 0.05/0.73 V in the first cycle. This is attributed to the alloying (cathodic sweep) and dealloying (anodic sweep) processes that are highly reversible and mainly responsible for the reversible lithium storage capacity. From the second cycle onwards, a broad cathodic band (0.75 – 1.25 V) with a corresponding anodic band (1.25 – 1.9 V) appears pronounced, possibly suggesting partial reversibility of reaction (1).

Figure 3B shows the comparative cycling performance of SnO₂ hollow spheres and the other two solid counterparts with a voltage window of 0.01 – 2 V at a current rate of 160 mA g⁻¹. It is apparent that the as-prepared SnO₂ hollow nanospheres demonstrate much better lithium storage properties compared to the other two samples, in terms of both storage capability and cyclic capacity retention. This is indeed in support of the above concept that the hollow interior will lead to improved lithium storage properties of SnO₂-based anodes. The post-mortem study shows that the hollow structure is somewhat retained after 20 charge-discharge cycles (Figure S6). The cycling performance of the as-prepared SnO₂ hollow nanospheres up to 50 cycles is shown in Figure S5B. Despite of the obvious advantage over the solid counterparts, the as-prepared SnO₂ hollow spheres do not show perfect performance. However, it has been demonstrated that the performance can be significantly improved by coating hollow SnO₂ spheres with a thin layer of carbon materials.⁵

In summary, we have demonstrated a novel and efficient top-down approach to synthesize SnO₂ hollow spheres inside mesoporous silica nanoreactors. The as-prepared SnO₂ hollow

spheres are shown to have a uniform size distribution, good structural stability, and enhanced lithium storage properties. The current strategy for making hollow spheres is new, considering that no conventional template is introduced in the system and the method is quite different from the common one-pot template-free techniques. A perhaps obvious appeal of our approach is that it might be extended to generate other metal oxide hollow nanospheres, such as CuO and Fe_xO_y.

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Supporting Information Available: Detailed experimental procedures, more TEM and SEM images, EDX results, N₂ adsorption-desorption isotherm, XRD patterns, and cyclic voltammograms. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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