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One-pot synthesis of hierarchical SnO\textsubscript{2} hollow nanospindles self-assembled from nanorods and their lithium storage properties

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**One-pot synthesis of hierarchical SnO\textsubscript{2} hollow nanospindles self-assembled from nanorods and their lithium storage properties**

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Novel hierarchical SnO\textsubscript{2} hollow nanospindles self-assembled from nanorods have been successfully synthesized via a templating approach under hydrothermal conditions. The influence of the reactant concentration on SnO\textsubscript{2} products is investigated in detail. It is found that the interplay of the acidic etching of Fe\textsubscript{2}O\textsubscript{3} templates and controlled hydrolysis of SnCl\textsubscript{2} is significant for the formation of the hierarchical SnO\textsubscript{2} hollow nanostructures. The evolution process and formation mechanism of the hollow structures with nanorods are analyzed from the angle of nucleation and morphology. Moreover, the electrochemical properties of the hollow structures are also studied by charge–discharge cycling, the result displays that the hierarchical SnO\textsubscript{2} hollow nanostructure exhibits much better lithium storage properties with higher reversible capacities and enhanced cyclic capacity retention than the commercial SnO\textsubscript{2} nanoparticles.

**Introduction**

SnO\textsubscript{2} is one of the most intensively investigated materials owing to its widespread applications in lithium-ion batteries,\textsuperscript{1} gas sensors,\textsuperscript{2} photocatalysts,\textsuperscript{3} and optoelectronic devices.\textsuperscript{4} So far, numerous efforts have been devoted to synthesizing various nanostructures of SnO\textsubscript{2}, such as nanoparticles,\textsuperscript{5} nanorods,\textsuperscript{6} nanowires,\textsuperscript{7} nanobelts,\textsuperscript{8} nanotubes,\textsuperscript{9} nanosheets,\textsuperscript{10} hollow structures,\textsuperscript{11–15} and mesoporous structures.$^{16–18}$

In recent years, hollow structures have attracted considerable attention due to high surface area, low density, well-defined interior voids, and surface permeability.$^{19}$ Controlled synthesis strategies for hollow structures have involved the use of templating or template-free methods. The template-free formation of hollow structures is usually based on the oriented attachment and inside-out Ostwald ripening.$^{11,12,20}$ However, the morphological uniformity and interior complexity of hollow products are less controllable by this strategy. Although templating methods generally include multiple steps, they have been considered as the most representative and effective approach for the preparation of hollow structures with a narrow size distribution and well-defined shape.$^{21}$ The controlled assembling of the designed materials on various removable templates, such as monodisperse silica/polymer latex spheres,$^{22,23}$ emulsion micelles,$^{24}$ and even gas bubbles,$^{25}$ has been widely investigated.

Nevertheless, the geometry of hollow structures obtained from template-engaged approaches is mostly spherical. While the preparation of non-spherical hollow structures still suffer from many difficulties in uniform coating around high-curvature surfaces and the paucity of non-spherical templates available.$^{19}$ In this regard, several novel approaches in combination with sacrificial templates have been developed to synthesize various hollow structures on the basis of different formation mechanisms, including the Kirkendall effect,$^{26}$ galvanic replacement,$^{27}$ chemical etching,$^{28}$ thermal decomposition,$^{29}$ etc. The sacrificial templates can directly determine the shape and cavity size of the resultant hollow structures by involving themselves as the consumable reactants for shell construction. Recently, Lou and co-workers have demonstrated the fast formation of SnO\textsubscript{2} nanoboxes with uniform morphology, good structural stability and tunable interior volume by template-engaged coordinating etching of pregrown Cu\textsubscript{2}O nanocubes at room temperature.$^{30}$

Shortly after that, uniform polycrystalline SnO\textsubscript{2} hollow nanostructures with various shapes have also been synthesized by templating against shape-controlled α-Fe\textsubscript{2}O\textsubscript{3} crystals under hydrothermal conditions.$^{31}$

To date, the research for SnO\textsubscript{2} hollow structures mainly focuses on the control of the shape and hollow interior by engineering the templates, while tailoring of the outer shell structure remains a great challenge. Generally, the shells of SnO\textsubscript{2} hollow structures are comprised of zero-dimensional polycrystalline nanoparticles.$^{11–15,30,31}$ However, constructing SnO\textsubscript{2} hollow nanostructures from building blocks of single-crystalline nanorods were rarely studied. Herein, we present one-step synthesis of hierarchical SnO\textsubscript{2} hollow nanospindles self-assembled from single-crystalline nanorods by utilizing α-Fe\textsubscript{2}O\textsubscript{3} nanocrystals with non-spherical shapes as the sacrificial templates under hydrothermal conditions. The effects of the reactant concentration and reaction time on SnO\textsubscript{2} products are analyzed, and the formation mechanism of the hierarchical SnO\textsubscript{2} hollow nanostructure is discussed from the angle nucleation and morphology. Moreover, we also evaluate the electrochemical characteristics of the SnO\textsubscript{2} hollow nanospindles as lithium storage anodes for secondary lithium batteries.
Experimental

Material synthesis

The $\alpha$-Fe$_2$O$_3$ nanospindles were synthesized by treating an aqueous of 20 mM FeCl$_3$, 6H$_2$O and 0.35 mM Na$_2$HPO$_4$ at 105 °C for 48 h. In a typical synthesis process of SnO$_2$ hollow nanospindles, 0.02 g of $\alpha$-Fe$_2$O$_3$ nanospindles was dispersed in 30 ml of an aqueous solution containing a 0.45 M HCl by ultrasonication for 10 min, followed by successively adding 0.05 g of SnCl$_2$·2H$_2$O powder under mild magnetic stirring for 10 min. Then the suspension was transferred into a 50 ml Teflon-lined stainless steel autoclave. The reaction was conducted at 180 °C for 20 h. Subsequently, the resulting products were centrifuged, and washed with deionized water and ethanol several times before being dried at 60 °C in air.

Characterization and electrochemical measurement

X-ray power diffraction (XRD) analysis was conducted on a Rigaku D/max-2500 X-ray diffractometer with Cu Kα radiation (λ=1.5418 Å). Field emission scanning electron microscopic (FESEM) images were performed on a JEOL JEM-6700F microscope operating at 5 KV. Transmission electron microscope (TEM) and high-resolution TEM (HRTEM) observations were carried out with a JEOL JEM-2100 microscope operated at 200 KV. The Brunauer–Emmett–Teller (BET) surface area was determined by N$_2$ adsorption-desorption at 77 K using a BELSORP-max surface area analyzer. The electrochemical measurements were conducted by using two-electrode Swagelok-type cells with pure lithium foil as the counter and reference electrode at room temperature. The working electrode consisted of SnO$_2$ hollow nanospindles, conductivity agent (carbon black, Super-P-Li), and polyvinylidene difluoride (PVDF) in a weight ratio of 70:20:10. The electrolyte was 1.0 M LiPF$_6$ in a 50:50 (w/w) mixture of ethylene carbonate and diethyl carbonate. Cell assembly was carried out in an Ar-filled glovebox with concentrations of moisture and oxygen below 1.0 ppm. The galvanostatic charge−discharge tests were performed with a NEWARE battery tester at different current densities within a cutoff voltage window of 0.01−1.2 V. 1 C is equivalent to 782 mA g$^{-1}$, corresponding to 4.4 Li atoms per SnO$_2$ molecule.

Results and Discussion

Fig. 1 XRD pattern of the SnO$_2$ hollow nanospindles.

To investigate the effect of the reactant concentration, we first changed the concentration of HCl while keeping the content of SnCl$_2$ (0.05 g). Fig. 3 displays the morphologies of the synthesized products at different reaction concentrations. When the concentration of HCl is 0.15 M, the Fe$_2$O$_3$ templates are not dissolved due to a lower concentration of HCl. Large quantities of SnO$_2$ nanoparticles (3–6 nm in diameter) are formed on the surface or outside of Fe$_2$O$_3$ nanospindles, as shown in Fig. 3a. When the HCl concentration is increased to 0.25 M, the continuous shells consisting of SnO$_2$ nanoparticles (2–3 nm in diameter) are formed around the scaffold of Fe$_2$O$_3$ nanospindles while the Fe$_2$O$_3$ cores are partially dissolved (Fig. 3b). As the HCl concentration is adding to 0.35 M, the Fe$_2$O$_3$ templates are almost eliminated and the SnO$_2$ hollow nanospindles are obtained. It can

Fig. 2 (a and b) FESEM and TEM images of SnO$_2$ hollow nanospindles. 
(c) high-magnification TEM image recorded around the edge of a SnO$_2$ hollow nanospindle with vertical nanorods. (d) high-resolution TEM image of a single nanorod.
be obviously observed that the shells of these hollow nanospindles are comprised of nanorod arrays with ~13 nm in length (Fig. 3c). By further increasing the HCl concentration, these vertical nanorods gradually grow up (Fig. 2). Once the HCl concentration is increased to 0.55 M, imperfect hollow nanospindles are obtained, as displayed in Fig. 3d. This may be attributed to the fast dissolution of the Fe$_2$O$_3$ templates due to a higher HCl concentration, leading to forming large amounts of unordered nanorods. Moreover, we also changed the content of SnCl$_2$ while keeping the HCl concentration (0.45 M). At a low content of SnCl$_2$ (0.02 g), the SnO$_2$ hollow nanospindles are built from smaller nanorods with lengths of ~22 nm, as shown in Fig. 3e. When the content of SnCl$_2$ is added to 0.08 g, the building blocks of hollow nanospindles are not one-dimensional nanorods but some irregular nanoparticles (Fig. 3f). This possible reason will be described below.

To understand the formation process of the SnO$_2$ hollow nanospindles comprised of vertical nanorods, the products were synthesized at different reaction times. Fig. 4 shows the evolution of the SnO$_2$ hollow nanospindles as a function of reaction time. TEM observation of the product, which aged 180 °C for 0.5 h, reveals that SnO$_2$ nanoparticles with ~2 nm in diameter are formed on the surface of Fe$_2$O$_3$ templates which are not almost changed (Fig. 4a). As the reaction time is prolonged to 3 h, the Fe$_2$O$_3$ templates are partially dissolved by HCl etching and the shells formed around the scaffold of Fe$_2$O$_3$ templates are comprised of SnO$_2$ nanoparticles and small nanorods (~8 nm in length and ~3 nm in diameter), as displayed in Fig. 4b. Upon prolonging the reaction time, the size of the nanorods obviously increase while the nanoparticles disappear (Fig. 4c), which indicates that the nanoparticles are only an intermediate and will gradually form nanorods with increasing the reaction time. After reaction for 12 h, the Fe$_2$O$_3$ templates are almost removed (Fig. 4d) and the SnO$_2$ hollow nanospindles with perpendicular nanorods are achieved after 20 h (Fig. 2). The effect of longer reaction times, up to 30 h, was also investigated. Results show that the reaction time exceeding 20 h will not bring about evident morphological modifications.

On the basis of the experimental results mentioned above, the following chemical reactions may take place during the formation of the SnO$_2$ hollow nanospindles with nanorods:

\[ 2\text{Sn}^{2+} + 2\text{H}_2\text{O} + \text{O}_2 → 2\text{SnO}_2 + 4\text{H}^+ \]  

(1)

\[ \text{Fe}_2\text{O}_3 + 6\text{H}^+ → 2\text{Fe}^{3+} + 3\text{H}_2\text{O} \]  

(2)

In this reaction, Sn$^{2+}$ reacts with oxygen in the solution under the hydrothermal conditions to yield insoluble SnO$_2$ (Eq. 1). At the early stage of the reaction, SnO$_2$ will nucleate on the surface of Fe$_2$O$_3$ templates due to the mutual crystallographic compatibility. Subsequently, the SnO$_2$ nuclei grow duratively and further evolve a precipitation layer. Meanwhile, the Fe$_2$O$_3$ templates are gradually dissolved in the acidic solution (Eq. 2). The SnO$_2$ hollow nanostructures are ultimately formed after entire etching of the Fe$_2$O$_3$ templates. In the reaction solution, HCl plays a key role in the formation of the SnO$_2$ hollow nanospindles covered by nanorods, because it can kinetically control the hydrolysis of Sn$^{2+}$ and the dissolution of Fe$_2$O$_3$ templates. Moreover, at a given content of Sn$^{2+}$, a higher concentration of HCl is beneficial to the

![Fig. 3](a-d) TEM images of the products obtained with different HCl concentrations: (a) 0.15 M, (b) 0.25 M, (c) 0.35 M, and (d) 0.55 M. (e and f) TEM images of the products obtained with various SnCl$_2$ contents: (e) 0.02 g, and (f) 0.08 g.

![Fig. 4](a) TEM images of the products prepared at different reaction times: (a) 0.5 h, (b) 3 h, (c) 8 h, and (d) 12 h.

![Fig. 5](a) Schematic sketch of the formation process of SnO$_2$ hollow nanospindles with nanorods: (a) heterogeneous nucleation of SnO$_2$ grains; (b) growth of SnO$_2$ nanorods and simultaneous dissolution of Fe$_2$O$_3$ cores by HCl etching; and (c)...

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formation of SnO2 hollow nanospindles with nanorods after complete consumption of Fe2O3 crystals. The formation of SnO2 nanorods, which is because Cl− may absorb preferentially on (110) crystal faces of SnO2 and prevent the growth rate of these surfaces. However, at a higher Sn2+ concentration, the more SnO2 nuclei appear simultaneously at beginning of the reaction and congregate easily under hydrothermal conditions, which will attenuate the influence of Cl− on retarding the growth rate of SnO2 (110) crystal faces, leading to the formation of irregular SnO2 nanoparticles. The formation process of SnO2 hollow nanospindles with nanorods can be schematically summarized in Fig. 5.

Fig. 6a displays representative discharge–charge voltage profiles of SnO2 hollow nanospindles in the range of 0.01−1.2 V at 0.2 C. The voltage window of 0.01−1.2 V was chosen in order to partly prevent the surface reaction between Sn and Li₂O which occurs at higher voltage and minimize solid electrolyte interface (SEI) formation on Sn. The initial discharge and charge capacities are 1850 and 602 mA h g⁻¹, respectively. Such a large capacity loss in the first cycle is often ascribed to the irreversible reduction of SnO2 (Eq. 3), and other irreversible processes such as trapping of some lithium in the lattice and inevitable formation of SEI layer. Fig. 6b depicts the cycling performance of SnO2 hollow nanospindles and commercial SnO2 nanoparticles up to 35 cycles. In view of the initial irreversible loss, there is a large drop in capacity of the 2nd cycle for both samples. It is found that SnO2 hollow nanospindles exhibit a high discharge capacity of 516 mA h g⁻¹ after 35 cycles, which is much higher than the theoretical capacity of graphite (372 mA h g⁻¹). From the fourth cycle onward, the SnO2 hollow nanospindles display a high Coulombic efficiency of about 95%. However, the discharge capacity decays rapidly to less than 300 mA h g⁻¹ after 15 cycles for the commercial SnO2 nanoparticles. It is suggested that such SnO2 hierarchical structure could prevent dense aggregation of the nanorod building blocks and provide a more stable porous structure. The pores and void space between nanorods could effectively alleviate the so-called pulverization problem and enhance the kinetics and structural stability for lithium storage.

SnO2 has been intensively investigated as a promising anode material for the next generation lithium-ion batteries. The lithium storage mechanism of SnO2 can be described by the following two reactions:

\[ \text{SnO}_2 + 4\text{Li}^+ + 4e^- \rightarrow \text{Sn} + 2\text{Li}_2\text{O} \]  

\[ \text{Sn} + x\text{Li}^+ + xe^- \leftrightarrow \text{Li}_x\text{Sn} \quad (0 \leq x \leq 4.4) \]  

The lithium storage capability of SnO2 is dependent on the reversible alloying-dealloying processes between lithium and metallic Sn nanocrystals (Eq. 4) which are generated from the initial irreversible reduction of SnO2 (Eq. 3). Although SnO2 has an attractive theoretical capacity of ~781 mA h g⁻¹, a major hindrance against the commercial use of SnO2-based anode materials in lithium-ion batteries is large volume and uneven changes during the lithium alloying and dealloying processes, which leads to poor cycling capability. Recently, increasing evidence has indicated that use of hollow structures could effectively alleviate the so-called pulverization problem and enhance the kinetics and structural stability for lithium storage. Motivated by this interest, we have carried out preliminary electrochemical characterization using the SnO2 hollow nanospindles as anode materials for lithium-ion batteries.
electrode was discharged and charged at various current rates, as shown in Fig. 6c. The specific capacity slightly decreases with an increase in the current rate, and it still displays a discharge capacity of above 490 mA h g\(^{-1}\) at 1 C. When the current rate is returned to 0.2 C, the capacity of about 585 mA h g\(^{-1}\) can be resumed.

**Conclusions**

In summary, we have been successfully synthesized uniform hierarchical SnO\(_2\) hollow nanospindles self-assembled from nanorods by templating against \(\alpha\)-Fe\(_2\)O\(_3\) nanocrystals under hydrothermal conditions. The fine-tuned interaction between the acidic etching of Fe\(_2\)O\(_3\) templates and hydrolysis of SnCl\(_2\) is crucial for the formation of this novel SnO\(_2\) hollow nanostructure. The evolution process and formation mechanism of the SnO\(_2\) hollow nanospindles are discussed from the angle of nucleation and morphology. When evaluated for their lithium storage properties, the SnO\(_2\) hollow nanospindles manifest higher specific discharge capacity and better cycling ability compared to the commercial SnO\(_2\) nanoparticles. The enhanced electrochemical properties may be due to the unique nanostructure which provides good structural stability and improve Li\(^+\) ion transfer rate. It is believed that such hierarchical SnO\(_2\) hollow structures are also promising in other applications such as photocatalysis, gas sensors, and dye-sensitized solar cells.

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**Notes and references**