Hierarchical TiO$_2$/SnO$_2$ Hollow Spheres Coated with Graphitized Carbon for High-Performance Electrochemical Li-Ion Storage

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A self-templated strategy is developed to fabricate hierarchical TiO$_2$/SnO$_2$ hollow spheres coated with graphitized carbon (HTSO/GC-HSs) by combined sol–gel processes with hydrothermal treatment and calcination. The as-prepared mesoporous HTSO/GC-HSs present an approximate yolk-double–shell structure, with high specific area and small nanocrystals of TiO$_2$ and SnO$_2$, and thus exhibit superior electrochemical reactivity and stability when used as anode materials for Li-ion batteries. A high reversible specific capacity of about 310 mAh g$^{-1}$ at a high current density of 5 A g$^{-1}$ can be achieved over 500 cycles indicating very good cycle stability and rate performance.

1. Introduction

It is well known that rechargeable Li-ion batteries (LIBs) are regarded as promising power sources for portable electronic devices and electric vehicles due to the advantage of their high energy density compared to other rechargeable systems.[1–4] The challenge is how to develop outstanding electrode materials with high energy capacity, high rate capability, long cycle life, and safety. On this perspective, SnO$_2$ as one of the most extensively investigated anode materials displays high specific capacity (782 mAh g$^{-1}$ theoretically). Unfortunately, its poor cycle stability due to large volume expansion (up to 250%) and subsequent pulverization during Li-ion insertion/extraction processes have negative impact on its application as anode materials.[5–9] In contrast, TiO$_2$ polymorphs exhibit negligible structure expansion (<4%), and stable physicochemical properties, while its performance is limited by the low specific capacity.[10–13]

Considering that SnO$_2$ and TiO$_2$ possess complementary characteristics in Li-ion batteries, and similar Ti$^{4+}$ (60.5 pm) and Sn$^{4+}$ (69 pm) radius as well as lattice matching of rutile TiO$_2$ and SnO$_2$,[14] various SnO$_2$/TiO$_2$ nano-heterostructures have been recently prepared to overcome their respective demerits to a certain degree.[15–19] However, owing to their low electronic conductivity, SnO$_2$/TiO$_2$ heterostructures generally display poor rate performance and disappointing long-term cycling property as anode materials for LIBs. Conductive carbon materials, such as carbon nanotubes, graphene, electronic conductivity can improve the rate capability of the SnO$_2$/TiO$_2$ composite materials, but simple loading with SnO$_2$ and TiO$_2$ cannot completely work out the deteriorating cyclical stability owing to unavoidable volume changes.[20–23]

Accordingly, it still remains challenge for carbon how to work with SnO$_2$ and TiO$_2$ to efficiently improve the rate and cycling performances.[24–26]

In this paper, we design and synthesize hierarchical TiO$_2$/SnO$_2$ hollow spheres coated with graphitic carbon (HTSO/GC-HSs) through a self-templated strategy. Compared to the previously reported methods,[27–31] this self-templated process is quite simple and facile, by combining sol–gel processes with hydrothermal treatment in glucose solution and calcination. And because of the robust mesoporous hollow structure with ultrafine solid solution of rutile TiO$_2$ and SnO$_2$ and anatase TiO$_2$ embedded in carbon, the obtained HTSO/GC-HSs-based anode for LIBs manifests exceptional cycling stability and rate performance. A stable and reversible specific capacity of about 310 mAh g$^{-1}$ even at a high current density of 5 A g$^{-1}$ can be achieved over...
500 cycles, which is considerably higher than the previously reported TiO₂/SnO₂-based electrodes for LIBs.

2. Results and Discussion

The synthesis route of the HTSO/GC-HSs is schematically illustrated in Scheme 1. Titanate–silicone gel particles were obtained by our previous report[32] and showed monodispersed spherical structure (Figure S1a, Supporting Information). These particles firstly reacted with anhydrous SnCl₂ via a sol–gel process, to produce spiky spheres with core–shell structures (Figure S1b, inset, Supporting Information). Polysaccharides were then coated around the composite spheres by hydrothermal treatment in glucose aqueous solution, which could be carbonized at a relatively low temperature in an inert atmosphere.[33] From the field emission scanning electron microscopy (FESEM) and transmission electron microscope (TEM) images in Figure S1c, inset in the Supporting Information the hydrothermal treated composite spheres exhibited a yolk–shell structure. After calcination and etching by hydrofluoric acid (HF) solution, the HTSO/GC-HSs were obtained.

As shown in Figure 1a,b, the HTSO/GC-HSs exhibit an approximate yolk-double–shell hollow structure with porous shell, which can be further confirmed by the FESEM images of the man-made broken spheres (Figure S2, Supporting Information). The X-ray diffraction (XRD) pattern in Figure 1c reveals that rutile phase (instructed by red rhombus), and anatase TiO₂ are both existing in the composite spheres. This rutile phase is attributed to neither rutile TiO₂ nor SnO₂ according to PDF standard cards, which is instead from the formation of solid solution of TiO₂ and SnO₂.[34]

The broadened diffraction peaks indicate that nanocrystals are small in size. Based on Scherrer equation, the average crystallite size is calculated to be less than 10 nm. The marked lattice spacings of about 0.33 and 0.35 nm can belong to the solid solution of rutile SnO₂ and TiO₂ and anatase TiO₂ respectively, as shown by the high resolution transmission electron microscopy (HRTEM) (Figure 1d). The selected area electron diffraction (SAED) pattern in the upper inset of Figure 1d indicates polycrystalline structure which can be indexed to anatase TiO₂, while the diffraction rings of the solid solution cannot be clearly seen from the SAED pattern, probably because of its similar lattice parameters to the anatase TiO₂, low crystallinity, and small size of the nanocrystals. Besides, the graphitized carbon is wrapping on these small nanocrystals indicated by red arrows (Figure 1d and Figure S3a, Supporting Information), which is believed to enhance electrical conductivity and interfacial stability for good rate performance and cycling stability.[35] Lower calcination temperature such as 350 °C would cause the hierarchical TiO₂/SnO₂ hollow spheres with more disordered carbon wrapping on the surfaces (denoted as HTSO/DC-HSs, Figure S3b, Supporting Information). Elemental mapping spectrum (EDS) of the HTSO/GC-HSs displays that Sn, Ti, and O species are well distributed in the double shell and yolk of the hierarchical hollow structure (Figure 1e), in which carbon is not only distributed in both shell and yolk, but also coated exterior...
inhibited but reacts with the titanate and silicone in the gel,
temperature.

D/ is lower than that of the HTSO/DC-HSs (I
D/ and G-band of the HTSO/GC-HSs (I
G ratio of 0.84) is lower than that of the HTSO/DC-HSs (I
G ratio of 1.0), confirming better graphitization by calcination at higher
temperature.36] Furthermore, two bands at about 1346 cm
1 (D band) and 1592 cm
1 (G band) for the graphitized structures are also observed in the Raman pattern (Figure S5b, Supporting
Information), indicating that the shallow sub-
surface of the hollow spheres mainly contains the solid solu-
tion.37] The formation of such hierarchical HTSO/GC-HSs could
be explained as shown in Scheme 1. Under the acidic condi-
tion, the hydrolytic reaction of anhydrous Tin(II) chloride is
inhibited but reacts with the titanate and silicone in the gel
the Line scan spectrum of sol–gel products after reaction
for 3 h (Figure S6, Supporting Information), Ti is enriched
toward the surface with Sn counterpart uniformly distrib-
uted in the whole sphere, indicating the diffusion effect of
titanate from the inside to outside and the penetration of tin
through the composite spheres. Silicone is gathered toward
the core because of the hydrophobicity of hexadecylsilan-
etriol (C16TS) oligomers, yielding a core–shell structure
(Figure S7a, Supporting Information). After hydrothermal
treatment in glucose aqueous solution, yolk–shell structure
(Figure S7b, Supporting Information). The yolk of the com-
posite spheres takes similar core–shell structures to the sol–
gel products (Figure S7c, Supporting Information). Because
of the low density of the C16TS oligomers,[40] the inside part
of the yolk contains almost all of the silicone and a portion of
tin–titanate compositions is shrinking more apparently
than the outside-part, which results in approximate yolk-
double–shell structures after calcination (Figure 1). Silica
of the resulted products could be removed by dilute HF
aqueous solution.

Nitrogen absorption–desorption isotherm measurement
of the HTSO/GC-HSs presents typical type IV hysteresis
loop, which is characteristic of mesoporous structures
(Figure S8, Supporting Information). Their Brunauer–Emmett–
Teller surface area and pore volume are 210.9 m2 g
−1 and 0.39 m3 g
−1. The pore size distribution curve based on the BJH method shows average pore size of about 3.75 nm. Such
a mesoporous structure could also be beneficial for Li
electrolyte passing through the shells efficiently, giving high usage
ratio of active materials.

XPS was conducted to evaluate the chemical bonding
environments of Ti, Sn, C, O within this unique structure. Obvious peaks of Sn 3d, Ti 2p, O 1s, C 1s can be detected in
the full spectra of HTSO/GC-HSs (Figure S9a, Supporting
Information). The core level XPS spectra of Sn 3d and
Ti 2p are displayed in Figure 2. The binding energy peaks of
Sn 3d
3/2 and Sn 3d
5/2 are located at 495.7 and 487.3 eV,
suggesting the formation of Sn4+ in the composite spheres.[41]
For the Ti 2p core level XPS spectrum, Ti 2p
1/2, and Ti 2p
3/2 peaks centered at 465.3 and 459.5 eV are observed, which
are about 1 eV higher than those of typical TiO2, indicating
that the electron of Ti is inclined toward Sn, and showing the
intimate interaction of TiO2 and SnO2.[42] In addition, four
fitted peaks positioned at 284.3, 285.3, 286.7, and 289.3 eV
in the high resolution spectra of C 1s can be assigned to
the graphitized, disordered carbon, some hydroxyl and
carboxyl groups (Figure S9b, Supporting Information), respectively.[24,43]

The electrochemical performance of the HTSO/GC-HSs
as anode material for LIBs was investigated. As shown in
Figure 3a for the cyclic voltammetry (CV) at a scan rate of
0.1 mV s
−1 in the voltage range from 0.005 to 3.0 V,
two redox peaks recorded at 1.7 and 2.0 V (vs Li+/Li) are
respectively attributed to characteristic Lithium
ion insertion/extraction reaction of anatase TiO2 (see
Equation (1)).44,45] Meanwhile, irreversible cathodic peaks
are at about 0.64, 1.40, and 1.07 V in the first cycle may be
due to the decomposition of electrolyte for the forma-
tion of surface electrolyte interface (SEI), Li+ inserting
into rutile TiO2 within the solid solution, and reduction
of SnO2 to Sn and Li2O as described in Equation (2),46,47] whereas a couple of peaks at 0.07 and 0.54 V are origin-
ated from alloying/dealloying reaction of Sn with lithium
ion (see Equation (3)), which are highly reversible in

![Figure 2. Core level XPS spectra of a) Sn 3d for the HTSO/GC-HSs and b) Ti 2p for the HTSO/GC-HSs and TiO2.](image-url)
substantial cycles.\textsuperscript{[48,49]} With increasing scan rate of cyclic voltammetry, the peak intensity attributed to alloying/dealloying reaction of Sn is becoming stronger than that of insertion/extraction reaction of anatase TiO\textsubscript{2} (Figure 3b). The relation ($i = a v^b$, where $a$ and $b$ are suitable values) between current ($i$) and voltage ($v$) obeys power law.\textsuperscript{[50,51]} The electrochemical reactions between diffusion controlled insertion of Li\textsuperscript{+} and capacitive processes can be distinguished from the $b$ value. As shown from Figure 3c, the anodic $b$ values attributed to the dealloying reaction of Sn (peaks $a$) and the desertion process of anatase TiO\textsubscript{2} (peaks $b$) are 0.76 and 0.5, respectively, indicating that Sn alloying/dealloying process contributes more capacity at high rates. This may be ascribed to the formation of small-size solid solution nanocrystals embedded in graphitized carbon, which would not only alleviate the pulverization and drastic volume change of Sn, but also contribute to the electrochemically active Sn/Sn–Ti–O bilayer with improving electronic conductivity:\textsuperscript{[52,53]}

\[
\text{TiO}_2 + x\text{Li}^+ + xe^- \leftrightarrow \text{Li}_x\text{TiO}_2 \quad (0 \leq x \leq 1) \quad (1)
\]

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

\[
\text{Sn} + y\text{Li}^+ + ye^- \leftrightarrow \text{Li}_y\text{Sn} \quad (0 \leq y \leq 4.4) \quad (3)
\]

Galvanostatic technique is utilized to evaluate the charge/discharge cycling performance of the HTSO/GC-HSs-based anode at a current density of 0.1 A g\textsuperscript{-1} in the voltage range of 0.005–3.0 V. The first discharge and charge specific capacities of the composite spheres are 1353.5 and 644.7 mAh g\textsuperscript{-1}, respectively, showing coulombic efficiency of 47.6\% (Figure 4a). Capacity fade is mainly located between 1.5 and 0.5 V due to irreversible reaction of SnO\textsubscript{2} and rutile TiO\textsubscript{2} with Li\textsuperscript{+}, and the formation of SEI on the surfaces of mesoporous HTSO/GC-HSs. A stable SEI layer is essential for long cycle performance as for anode material with
large volume change. Upon further cycling, shapes of the discharge and charge curves do not change obviously, indicating reversible reaction with Li⁺. Reversible specific capacity of about 590 mA h g⁻¹ can be obtained after 50th cycle (Figure 4b), which is a little higher than the theoretical specific capacity of the composite spheres. This may be ascribed to the surface charge storage mechanism because of such hierarchical structure with high specific area and small nanocrystals of the HTSO/GC-HSs. As a control, the TiO₂ hollow spheres coated with carbon (TO/C-HSs)- and the SnO₂ hollow spheres coated with carbon (SO/C-HSs)-based electrodes are fabricated via a hard template method (Figure S10, Supporting Information). Although the first discharge capacity of the SO/C-HSs is higher than the HTSO/GC-HSs, the capacity fades apparently to only 284.8 mA h g⁻¹ after 50th cycles, while the TO/C-HSs exhibit much lower reversible capacity of about 230 mA h g⁻¹ than that of the HTSO/GC-HSs (Figure 1b).

The rate performances of the HTSO/GC-HSs at various specific current densities in the range of 0.1 and 5 A g⁻¹ are shown in Figure 4c, inset. When cycled at the current density of 0.1 A g⁻¹, the specific discharge capacity gradually fades to near 610 mA h g⁻¹ after ten cycles. During the subsequent cycles, average specific discharge capacities of 572, 507, 440, and 355 mA h g⁻¹ at current densities of 0.2, 0.5, 1.0, and 2.0 A g⁻¹ are achieved, respectively. Even at a high current density of 5 A g⁻¹, a specific discharge capacity of 218 mA h g⁻¹ is delivered. When the current density is set back to 0.1 A g⁻¹, the specific discharge capacity goes up to 710 mA h g⁻¹. Subsequent cycling at the high current density of 5 A g⁻¹ achieves reversible specific capacity of 310 mA h g⁻¹ with excellent stability and coulombic efficiency close to 100% after 600 cycles. In the contrast, the HTSO/DC-HSs deliver lower capacity at high current densities (Figure 4c, inset) indicating that graphitized carbon coating could efficiently improve the rate capability of the electrode materials. Moreover, the cycling performance of the HTSO/GC-HSs at a galvanostatic current density of 1.0 A g⁻¹ also indicates a stable specific discharge capacity of about 680 mA h g⁻¹ over 500 repeated cycles (Figure S11, Supporting Information). This electrochemical performance is considerably higher than those of the previously reported TiO₂/SnO₂-based electrodes for LIBs (Table S1, Supporting Information). From the above electrochemical tests, the capacity fluctuation acts as the common case during cycling processes for the HTSO/GC-HSs as the electrode materials. This may be resulted from the following a couple of factors: (1) Lithiation can induce reconstruction of the electrode structure and optimization of stable SEI layer. (2) The volume change during the electrochemical reactions of Sn expands the mesopores within the TiO₂ and conformal carbon, facilitating more and more internal particles in the shell and yolk of the HTSO/GC-HSs to be exposed and activated. After 500 charge/discharge cycles at current density of 1.0 A g⁻¹, the hierarchical architectures are still kept well with small nanocrystals encapsulated within the spheres (Figure S12, Supporting Information), indicating that the HTSO/GC-HSs are stable to sustain the repeated expansion/shrinkage during the electrochemical reactions with Lithium ion.

This superior electrochemical performance of the HTSO/GC-HSs may be attributed to the hierarchical hollow structure with synergistic effects of SnO₂, TiO₂, and graphitized carbon: First, the mesoporous yolk-double–shell structure with high specific area (210.9 m² g⁻¹) and large pore size (≈3.75 nm) could efficiently facilitate electrolyte diffusion and accommodate the severe Sn volume change during charge/discharge processes; Second, the formation of the solid solution through intimate interaction between SnO₂ and stable TiO₂ nanocrystals could depress the volume expansion of Sn in the processes of cycling. Third, TiO₂ and SnO₂ nanocrystals with small size of less than 10 nm within the mesoporous shell and yolk could shorten Li⁺ diffusion pathway, greatly enhancing the diffusion dynamics of Li⁺. Fourth, carbon layers with good graphitization could not only increase electronic conductivity, but also suppress the strain derived from the volume change of the wrapped TiO₂ and SnO₂. In addition, more capacitive capacities originated from the alloying/dealloying process of Sn contribute to the high rate performance of the HTSO/GC-HSs. In a word, such unique structures of the HTSO/GC-HSs can improve the electrochemical performance, by providing excellent cycling stability and good rate capability.

3. Conclusion

In summary, rationally designed HTSO/GC-HSs with mesoporous structures synthesized via a self-templated method combining sol–gel processes with hydrothermal treatment in glucose solution and calcination are demonstrated. Owing to the robust mesoporous hollow structure with ultrafine solid solution of rutile TiO₂ and SnO₂ and anatase TiO₂ embedded in carbon, these HTSO/GC-HSs exhibit very good electrochemical reactivity and stability as anode material for Li-ion battery, with a high and reversible specific capacity of about 310 mA h g⁻¹ at a current density of 5 A g⁻¹. This work is expected to be favored for the development of high performance anode materials for Li-ion batteries.

4. Experimental Section

Synthesis of Titanate–Silicone Gel Particles: Synthesis of titinate–silicone gel particles was conducted as follows: Typically, Ti(OiPr)₄ (1.40 g, 5.0 mmol) was dissolved in hexane (7.0 mL) and heated to 60 °C, and added by C₁₆TS oligomers (0.25 g, =1.0 mmol) in 2.5 mL tetrahydrofuran under stirring. This mixture was held at the same temperature for 1 h. After that, the solvent and resultant isopropyl alcohol were fractionated off continuously under vacuum until no gas bubbles came out, producing the composite precursors which were then cooled down and kept sealed.

The composite precursors (1.0 g) were dissolved in hexane (1.89 mL), then added into a flask charged with anhydrous ethanol (100 mL) and concentrated ammonia solution (0.78 mL, 28 wt%), and the reaction was allowed to proceed at 60 °C for 18 h under continuously vigorous stirring. This product was centrifuged at 5000 r min⁻¹ and washed with ethanol for three times, redispersed in ethanol (8 mL) for further use.
Preparation of HTSO/6C-HSs: The dispersion of titane–silicone gel particles in ethanol (4 mL) was mixed with deionized water (20 mL), followed by a sol–gel reaction after addition of thiglycolic acid (0.24 mg), concentrated hydrochloric acid (0.2 mL), anhydrous SnCl₂ (0.3 g), and urea (0.3 g) successively with continuous stirring for 5 min and kept at 80 °C in oil bath for 3 h. Then the yellow product was washed three times with ethanol and redispersed in glucose aqueous solution (0.20 M), and sealed in Teflon reactor at 180 °C for 18 h. The dark brown precipitation was washed several times with ethanol and dried at 80 °C overnight, then calcined at 500 °C for 2 h at a heating rate of 2 °C min⁻¹ in Ar. As for HTSO/DC-HSs, the temperature of calcination was 350 °C. To remove small amount of SiO₂, the resulted powder was dispersed in HF (0.6% in water) for 1 h, then washed with deionized water for three times and dried at 80 °C overnight for use. The controls, TO/C-HSs and SO/C-HSs were prepared through typical hard-template method.

Characterization: The surface morphology of the as-prepared samples was observed by FESEM (Zeiss, Ultra 55, 3 kV), and their microstructures was observed by TEM (FEI, Tecnai G2 20 TWIN, 200 kV) and HRTEM (JEOL JEM-2010). Crystallographic information was collected using powder XRD. Cu KR radiation (λ = 1.5406 Å). The Raman spectra were measured on a micro Raman spectroscopy (Horiba Jobin Yvon, XploRA, the excitation wavelength of 532 nm). The surface area of the samples was measured using a Quantachrome Instruments Quadrasorb evo instrument. TGA was carried out under a flow of air with a temperature ramp of 10 °C min⁻¹. Element contents were determined by the inductively coupled plasma atomic emission spectroscopy (ICP-AES, ICAP 7400 ICP-OES).

Electrochemical Properties: The electrodes for half-cell tests were prepared by homogeneously mixing the active materials (80 wt%) with super-P carbon (10 wt%) and polyvinylidene fluoride (10 wt%) in N-methyl-2-pyrrolidone. And the mass loading of the electrodes was controlled within the range of 0.4–1.0 mg cm⁻². The specific capacity was calculated based on the mass of the active materials. The resulting slurries were applied to the Cu foil. After being heated at 120 °C for 12 h, the sheet was pressed and punched into 14 mm diameter electrodes. The anode was tested using CR2032-type coin cells, where Li metal was used as both the counter and reference electrodes, and 1.0 M LiPF₆ in ethylene carbonate/dimethyl carbonate/ethyl methyl carbonate (EC/ DMC/EMC, 1:1:1 volume ratio) as electrolyte. CR2032-type coin cells were assembled in a glovebox for electrochemical characterization. The CV measurements were conducted on a CHI 660B electrochemical workstation (Shanghai CH Instrument Company, China). Cycle-life measurements for the half-cell were carried out on a battery test system (Land CT2001A model, Wuhan Land Electronics. Ltd.).

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

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