Supporting Information

Micelles directed self-assembly to single-crystal-like mesoporous stoichiometric oxides for high-performance lithium storage

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Experimental section

Chemicals. Titanium isopropoxide (Ti(OCH(CH₃)₃)₄, TIPO, ≥ 97 %) was purchased from Fluka. Poly(ethylene oxide)-block-poly(propylene oxide)-block-poly(ethylene oxide) triblock copolymer Pluronic F127 (Mw = 12600, PEO₁₀₆-PPO₇₀-PEO₁₀₆) was purchased from Aldrich. Tetraethyl orthosilicate (Si(OC₂H₅)₄, TEOS, ≥96 wt%), citric acid monohydrate (C₆H₈O₇·H₂O, AR), hydrogen chloride (HCl, AR), and ethanol (AR) were purchased from Sino–Pharm Chemical Reagent Co. Ltd. Lithium nitrate (LiNO₃, AR) was purchased from Aladdin. All the chemicals were used without further purification. Deionized water was used for all experiments.

Synthesis of Stoichiometric Ti⁴⁺/Li⁺-Citrate Chelate Precursor. The stoichiometric Ti⁴⁺/Li⁺-citrate chelate precursor (SCP) was synthesized according to our previous method.¹ For a typical preparation, citric acid (21.0 g, 100 mmol) was dissolved in 100 mL of ethanol (solution A), titanium isoproxide (28.4 g, 100 mmol) was dissolved in 50 mL of ethanol (solution B), and lithium nitrate (13.8 g, 200 mmol) was dissolved in 50 mL of ethanol (solution C). Solution A was dropped into solution B slowly and heated with stirring at 50 °C for 3 h (solution D). Then, solution C was dropped into solution D and heated with stirring for another 3 h. Ethanol was distilled off under vacuum at 45 °C. The obtained gel was then re-dissolved in water to obtain a 1.0 M stoichiometric Ti⁴⁺/Li⁺-Citrate chelate precursor (SCP) solution.

Synthesis of Single-Crystal-Like Mesoporous Li₂TiSiO₅. The single-crystal-like mesoporous Li₂TiSiO₅ was synthesized via the micelles-directed step-crystallization strategy. In a typical synthesis, 1.5 g of triblock copolymer Pluronic F127, 0.83 g of TEOS, and 4.0 mL of 1.0 M SCP solution were dissolved in an ethanol/water mixture (10 mL, 4:1 v/v). After stirring for 3 h at room temperature, the obtained light yellow homogenous solution was poured into Petri dishes to evaporate the solvents at 40 °C for 8 h, followed by sequential solidifying the samples at 100 °C for 20 h in an oven to remove the solvents completely, leading to the formation of the as-made F127/Ti⁴⁺/Si⁴⁺/Li⁺/Citrate composites (denoted as as-made sample). Then the as-made
sample was pyrolyzed at 900 °C for 3 h with a ramp of 2 °C min⁻¹ in N₂ atmospheres, resulting in the mesoporous Li₂TiSiO₅.

**Characterization.** Small-angle X-ray scattering (SAXS) measurements were taken on a Nanostar U small-angle X-ray scattering system (Bruker, Germany) using Cu Kα radiation (40 kV, 35 mA). X-ray diffraction (XRD) patterns were obtained from a Bruker D4 diffractometer within 20 range from 10 to 90°, by using a Cu Kα radiation source (40 kV, 40 mA). Nitrogen adsorption–desorption isotherms were measured at 77 K with a Micromeritics Tristar 2420 analyzer (USA). Before measurements, the samples were degassed in a vacuum at 190 °C for 10 h. The Brunauer–Emmett–Teller (BET) method was utilized to calculate the specific surface areas. By using the Barrett–Joyner–Halenda (BJH) model, the pore volumes and pore size distributions were derived from the adsorption branches of isotherms, and the total pore volumes were estimated from the adsorbed amount at a relative pressure $P/P_0$ of 0.992. Transmission electron microscopy (TEM) measurements were conducted on a JEM-2100 F microscope (JEOL, Japan) operated at 200 kV. The atomic resolution HAADF-STEM imaging was conducted with a field-emission transmission electron microscope (Themis Z, Thermo Fisher Scientific) equipped with double aberration correctors (SCORR probe corrector and CETCOR image corrector, CEOS GmbH). The microscope was operated at 300 kV. For STEM-HAADF imaging, the semi-convergent angle of the probe forming lens was set to 21.4 mrad, and the semi-collection angle of the annular dark field detector is from 79 mrad to 200 mrad. The samples for the TEM measurements were suspended in ethanol and supported onto a holey carbon film on a Cu grid. Field-emission scanning electron microscopy (FESEM) images were taken on a Hitachi S-4800 microscope. The dried samples were directly used for the observation without any treatment. X-ray photoelectron spectroscopy (XPS) was recorded on an AXIS ULTRA DLD XPS System with MONO Al source (Shimadzu Corp). Photoelectron spectrometer was recorded by using monochromatic Al KR radiation under vacuum at $5 \times 10^{-9}$ Pa. All calibrations were referenced to the surface adventitious carbon (C1s = 284.6 eV). Elemental analysis experiments were carried out using an Elementar Vario EL III microanalyzer.
Raman spectra were recorded with a Dilor LabRam-1 B microscopic Raman spectrometer, using a He−Ne laser with an excitation wavelength of 632.8 nm.

**Cell assembly and electrochemical measurements.** The electrodes were fabricated by mixing the active material, conductive agent Super P, and polymer binder (Carboxymethylcellulose sodium, CMC) at a weight ratio of 8:1:1. This mixture was dispersed in deionized water to form a slurry and then cast on the Cu foil. Then, the electrodes were dried at 80 °C in a vacuum oven overnight. The average mass loading was about 1.5 mg cm\(^{-2}\). 2025 coin-type lithium-ion cells were assembled in an argon-filled glovebox with moisture and oxygen concentration below 1.0 ppm for electrochemical characterization. 1.0 M LiPF\(_6\) in a 1:1:1 volume ratio of ethyl methyl carbonate (EMC), dimethyl carbonate (DMC), and ethylene carbonate (EC) was used as the electrolyte. Li metal foils were used as counter electrodes for electrochemical measurement. Cyclic voltammograms (CV) were obtained using a CHI660e electrochemical workstation at a sweep rate of 0.1 mV s\(^{-1}\) within a range from 0.1–3.0 V. The charge/discharge tests were performed on NEWARE Battery Test System (CT-4008, Shenzhen, China) within a voltage range of 0.1–3.0 V vs. Li/Li\(^+\) at room temperature. For the high-rate testing, the charge/discharge current gradually increased from 0.02 to 0.05, 0.1, 0.2, 0.5, 1.0, 2.0 and 5.0 A g\(^{-1}\), then decreased to 0.02 A g\(^{-1}\). The cycle performance at high current density (0.2 and 2.0 A g\(^{-1}\)) was activated at 0.02 A g\(^{-1}\) for five cycles. Electrochemical impedance spectroscopy (EIS) spectra were collected from 100 kHz to 100 MHz at room temperature (25 °C).
Figure S1. TEM image of the spherical F127/SCP/SiO$_2$ composite micelles.
Figure S2. (a) The XPS survey spectrum and (b-d) XPS core-level spectra of Ti 2p, Si 2p, and Li 1s of the mesoporous Li$_2$TiSiO$_5$ prepared by the micelles-directed self-assembly and step-crystallization strategy after the pyrolysis at 900 °C in N$_2$. 
Figure S3. (a-c) HAADF-STEM images of single-crystal-like mesoporous Li$_2$TiSiO$_5$. 
Figure S4. The EDX spectrum of the mesoporous \( \text{Li}_2\text{TiSiO}_5 \) obtained after the pyrolysis at 900 °C in \( \text{N}_2 \).
Figure S5. Size distribution of the samples after pyrolysis at different temperatures.
Figure S6. SAXS pattern (a), TEM image (b) of the as-made sample. TEM image (c) and corresponding SAED pattern (d), and XRD pattern (e) of bulk Li$_2$TiSiO$_5$ after pyrolysis at 900 °C in N$_2$ prepared without the addition of Pluronic F127 in the synthesis.
Figure S7. SAXS (a) and XRD (b) patterns of samples obtained after heat-treatment at 100 and 500 °C prepared by using TIPO and LiNO₃ as precursors, respectively.
Figure S8. TEM image (a), HRTEM image (b), XRD pattern (c), Nitrogen-sorption isotherms and pore size distribution curves (b) of the sample obtained after pyrolysis at 900 °C in N₂ prepared by using TIPO and LiNO₃ as precursors, respectively.
Figure S9. TEM, HRTEM, and corresponding SAED pattern of the sample obtained after pyrolysis at 500 °C (a, b) and 900 °C (c, d) in N₂, respectively, prepared without the addition of silica precursors in the synthesis system.
Figure S10. XRD pattern (a), nitrogen-sorption isotherms (b), and the corresponding pore size distribution curves (c) of the sample obtained after pyrolysis at 500 and 900 °C in N₂, respectively, prepared without the addition of silica precursors in the synthesis system.
Figure S11. CV curves of the mesoporous Li$_2$TiSiO$_5$ for the initial three cycles at a scan rate of 0.1 mV s$^{-1}$. 
Figure S12. Charge-discharge curves of the bulk Li$_2$TiSiO$_5$ at (a) initial three cycles and (b) different current densities.
Figure S13. Charge-discharge curves of the bulk Li$_2$TiSiO$_5$ at (a) initial three cycles and (b) different current densities.
Figure S14. Charge-discharge curves of different cycles at 0.2 A g\textsuperscript{-1} of (a) mesoporous Li\textsubscript{2}TiSiO\textsubscript{5} and (b) bulk Li\textsubscript{2}TiSiO\textsubscript{5}. Charge-discharge curves of different cycles at 2.0 A g\textsuperscript{-1} of (c) mesoporous Li\textsubscript{2}TiSiO\textsubscript{5}. 
Figure S15. (a) CV curves, (b) Charge-discharge curves, (c) Rate performance, and (d) Charge-discharge curves at different current densities of the Li$_2$TiSiO$_5$ sample obtained after pyrolysis at 690 °C.
Table S1. The lithium storage performance of the reported Li$_2$TiSiO$_5$ materials.

<table>
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<tr>
<th>Material</th>
<th>Potential range (V vs Li/Li$^+$)</th>
<th>Specific capacity (mAh g$^{-1}$/A g$^{-1}$)</th>
<th>Rate capacity (mAh g$^{-1}$/A g$^{-1}$)</th>
<th>Cycling stability (mAh g$^{-1}$/Cycles/A g$^{-1}$)</th>
<th>Ref.</th>
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<tr>
<td>Fibrous Li$_2$TiSiO$_5$/C</td>
<td>0.1–3.0</td>
<td>265.9/0.1</td>
<td>151.2/5.0</td>
<td>~180/1000/0.5</td>
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<td>TiO$_2$- Li$_2$TiSiO$_5$</td>
<td>0.1–3.0</td>
<td>325/0.1</td>
<td>150/1.0</td>
<td>~160/2000/5</td>
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<tr>
<td>Li$_2$TiSiO$_5$/N-C@C</td>
<td>0.01–3.0</td>
<td>332.6/0.05</td>
<td>108.3/4.0</td>
<td>240.6/500/1.0</td>
<td>[4]</td>
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<tr>
<td>Li$_2$TiSiO$_5$/CNT</td>
<td>0–3.0</td>
<td>430/0.16</td>
<td>125/3.15</td>
<td>~125/1500/3.15</td>
<td>[5]</td>
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<tr>
<td>3DC@ Li$_2$TiSiO$_5$</td>
<td>0–3.0</td>
<td>280/0.2</td>
<td>80/4.0</td>
<td>~80/3000/2.0</td>
<td>[6]</td>
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<tr>
<td>Li$_2$TiSiO$_5$</td>
<td>0–3.0</td>
<td>~300/0.02</td>
<td>~200/1.0</td>
<td>~160/1000/0.5</td>
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<tr>
<td>G- Li$_2$TiSiO$_5$</td>
<td>0.1–3.0</td>
<td>242.3/0.03</td>
<td>100/4.5</td>
<td>200/50/0.3</td>
<td>[8]</td>
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<td>Single-crystal-like</td>
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<td>mesoporous Li$_2$TiSiO$_5$</td>
<td>0.1–3.0</td>
<td>393/0.02</td>
<td>148/5.0</td>
<td>201/1400/0.2</td>
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References


