Supporting Information

Brookite TiO$_2$ mesocrystals with enhanced lithium-ion intercalation properties

Weifeng Zhang,$^{a,b}$ Deli Shen,$^{a,b}$ Zhenwei Liu,$^{a,b}$ Nae-Lih Wu,$^c$ Mingdeng Wei,*$^{a,b}$

$^a$ State Key Laboratory of Photocatalysis on Energy and Environment, Fuzhou University, Fuzhou, Fujian 350002, China
$^b$ Institute of Advanced Energy Materials, Fuzhou University, Fuzhou, Fujian 350002, China
$^c$ Department of Chemical Engineering, Taiwan University, Taipei 106, Taiwan

*Corresponding author: Mingdeng Wei

E-mail address: wei-mingdeng@fzu.edu.cn
Experimental Section

Synthesis of titanate precursor: titanate precursor was obtained optionally by hydrothermal reaction. First, 0.5 g of TiO₂ (P25) was dispersed in a 50 mL of 10 M KOH solution (H₂O: EtOH v/v=1:1). After stirring for 20 min, the resulting suspension was transferred into a Teflon-lined stainless steel autoclave with a capacity of 100 mL. The autoclave was kept at 180 °C for 24 h and then naturally cooled to room temperature. The resulting white precipitate was washed with 0.1 M HCl solution repeated until pH 1-2 was reached, and then kept stirring for 24 h. The final product was collected by centrifugation and dried at 70 °C for 12 h in air.

Synthesis of brookite TiO₂ mesocrystals: In the typical preparation, 3 g of oxalic acid was dissolved firstly in 50 mL of 0.2 M of HCl solution with vigorous stirring. Afterwards, 200 mg of titanate precursor was added into the solution under stirring for 20 min. The final solution was transferred into a 100 mL Teflon-lined stainless autoclave and maintained at 180 °C for 14 h. After cooling down, the final products were obtained by separation and washed with DI water and ethanol for several times and then dried at 70 °C for 12 h.

Materials Characterization: Crystal structure of the as-prepared materials was analyzed by powder XRD on a Rigaku Ultima IV using CuKα radiation (40 kV, 40 mA) and Raman spectroscopy (Invia Reflex with a laser wavelength of 532 nm). Morphology and microstructure of the as-prepared materials were investigated by scanning electron microscopy (SEM, S4800 instrument) and Transmission electron microscopy (TEM, FEI F20 S-TWIN instrument). Chemical composition of the samples was analyzed by X-ray photoelectron spectroscopy (XPS) measurements (ISCALAB 250). Nitrogen adsorption-desorption isotherms were obtained via an ASAP 2020 Accelerated Surface Area and Porosimetry instrument.

Electrochemical Measurements: The working electrodes were fabricated by coating a slurry containing 70 wt% active materials (brookite phase TiO₂), 20 wt% acetylene black, and 10 wt% polyvinylidene fluoride (PVDF) dissolved in N-methyl-2-pyrrolidone (NMP). The mixture was coated uniformly on a copper foil with roughly 1.2 mg cm⁻² mass loading, and then dried at 110 °C under vacuum for 12 h before pressing. The cells were assembled in a glove box filled with highly pure argon gas (O₂ and H₂O levels < 0.1 ppm). The electrolyte solution was composed by 1 M LiPF₆ in the mixture of ethylene carbonate (EC), ethylene methyl carbonate (EMC), and dimethyl carbonate (DEC) in 1:1:1 (volume ratio). Lithium foil was used as the counter electrode with Celgard 2400 as the separator. The electrochemical experiments were evaluated in CR2025 coin cells. Galvanostatic charge-discharge measurements were performed on an electrochemical workstation (Land CT 2001A, Wuhan, China) within a voltage range of 1 to 3 V (vs. Li⁺/Li) at room temperature, and the specific capacity values were based on the total mass of the active materials. Cyclic voltammetry (CV) was carried out on an electrochemical workstation (Chenhua CHI660c, Shanghai, China). Electrochemical measurements of materials were also performed under the same conditions.
Figure S1  (a) XRD pattern and (b) SEM image of amorphous titanate precursor.
Figure S2 (a) TEM image and (b, c) HRTEM images of bm-TiO₂. The inset in (b) and (c) are the corresponding selected area electron diffraction (SAED) patterns.
Figure S3 (a) XRD pattern, (b) Raman spectrum, (c) high-resolution XPS spectrum of Ti 2p and (d) N$_2$ adsorption-desorption isotherms of bm-TiO$_2$, respectively. The inset in (d) is the corresponding pore size distributions calculated using BJH method.
Table S1 Electrochemical properties of pure brookite phase TiO$_2$ anodes in LiBs.

<table>
<thead>
<tr>
<th>Brookite phase TiO$_2$ anodes</th>
<th>Reversible capacity, mA h g$^{-1}$/cycle, (Current density, A g$^{-1}$)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nanocrystalline brookite TiO$_2$</td>
<td>170/40$^{th}$ (0.1 C)</td>
<td><em>Solid-State Lett.</em>, 2007, 10, 29-31.</td>
</tr>
<tr>
<td>Brookite TiO$_2$ mesocrystals</td>
<td>105.7/500$^{th}$ (5 C)</td>
<td>Our work</td>
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</tbody>
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