Supporting Information

Experimental Section

Synthesis of TiO₂ and TiO₂@C nanosheets

In this work, TiO₂ nanosheets were synthesized by a facile solvothermal method. In a typical synthesis,^[32] titanate butoxide (5 mL) was first added into a 50 mL Teflon-lined autoclave. Then 47% HF solution (0.6 mL) was added dropwise to above solvent under magnetic stirring. After stirring for about 10 min, the autoclave was maintained at 180 °C for 30 h and then cooled to room temperature naturally. The white product was collected by centrifugation and washed with deionized water and ethanol four times, and dried at 60 °C overnight.

To obtain the carbon-coated TiO₂@C, 0.5g of TiO₂ white power as-prepared were submerged in oleic acid for 24 h at room temperature. Then centrifugation it at 5000r/min for 5 minutes to remove the excess oleic acid. The oleic acid treated materials were annealed in the Argon atmosphere for 2 h with a heating rate of 3 °C min⁻¹ at 600 °C, respectively. The black power was the carbon-coated TiO₂.

Material Characterizations

The scanning electron microscopy (SEM) images were taken with a JEOLJSM-6700F field emission scanning electron microscope (15 kV). The transmission electron microscopy (HR-TEM) images were taken on a JEOL 2010 high-resolution transmission electron microscope performed at 200 kV. The specimen of HR-TEM measurement was prepared via spreading a droplet of ethanol suspension onto a copper grid, coated with a thin layer of amorphous carbon film, and allowed to dry in air. The X-ray diffraction (XRD) patterns of the products were recorded with Rigaku D/max Diffraction System using a Cu K α source ($\lambda = 0.15406$ nm). Thermal gravimetric analysis (TGA) was performed to better understand the decomposition of TiO₂@C in oxygen environment with increased temperature. A TG-DTA7300 instrument was used.

Electrochemical properties

The working electrodes were prepared by mixing 80 wt% as-prepared active materials with 10 wt% carbon black and 10 wt% carboxymethylcellulose (CMC) binder in distilled water to form homogeneous slurry, which was uniformly pasted onto copper foil. The prepared working electrodes were dried in a vacuum oven at 80 °C over 12 h and were then ready for assembly in

test cells after pressing. Electrochemical cells (CR2032 coin type) using the active materials (about 1.5 mg per sheet) as working electrode, Li foil as the counter electrode and reference electrode, a microporous polypropylene film as the separator, and 1 M LiPF₆ in a 1:1 (v/v) mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) as the electrolyte were assembled in an Ar-filled glove box (H₂O, O₂ < 0.1 ppm, Mbraun, Unilab, USA). The cells were galvanostatically charged and discharged over a voltage range of 0.02-3 V versus Li/Li⁺ at different constant current densities based on the weight of the samples on a Land CT2001A cycler. Cyclic voltammetry (CV) was performed on an Ametek PARSTAT®2273 electrochemistry workstation.

References:

1 X. G. Han, Q. Kuang, M. S. Jin, Z. X. Xie and L. S. Zheng, *J. Am. Chem. Soc.*, 2009, **131**, 3152-3153.