Supporting Information

Higher charge/discharge rates of lithium-ions across engineered TiO₂ surfaces leads to enhanced battery performance[†]

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Materials Preparation. Anatase TiO₂ single crystals with large percentage of (001) surface was prepared by using hydrofluoric acid (HF) as capping agent, which was firstly developed by Yang et al.¹ In a typically synthesis, 5 mL of titanate isopropoxide or tetrabutyl titanate and $0.4 \sim 0.6$ mL of HF (48 % w/w) were put into a Teflon-lined stainless steel autoclaves with a capacity of 30 ~ 50 mL, and then kept at 180 °C for 24 h.²⁻⁴ After reactions, the anatase TiO₂ single crystals were harvested by centrifugation, washed with ethanol and deionized water 3 times, respectively, and then dried in vacuum overnight.

To prepare anatase TiO₂ single crystals with low percentage of (001) surface, in a typical experiment, titanium tetrachloride aqueous solution (5.33 mM) and hydrochloric acid (HCl, 10% w/w, 0.73 mL in 30 mL of TiCl₄ aqueous solution) were used as the anatase TiO₂ precursor and the crystallographic controlling agent, respectively. The reaction was carried out in a Teflon-lined autoclave at 180 °C for 14 h. The synthesized products are well-facetted anatase nanocrystals with 100% pure anatase phase which was confirmed by X-ray diffraction (XRD) (Figure S1). The percentages of the (001) surface can only reach 2.18% even though the elimination of some (001) surfaces caused by the oriented attachment of primary octahedral bipyramidal units is neglected.

Materials Characterization. The shape and crystal structure of the resulting anatase TiO_2 were investigated by X-ray spectroscopy (XRD, Bruker D8 Advanced Diffractometer, Cu-K α radiation, 40 kV) and transmission electron microscopy (TEM, Philips Tecnai T30F FEG Cryo AEM). Nitrogen sorption isotherms were obtained with a Quadrasorb analyzer (Quantachrome) at 77 K and all the samples were degassed at 120 °C for 12 h under vacuum before any measurements were taken.

Theoretical Calculations. Spin-polarized DFT calculations were performed using the CASTEP (Cambridge Serial Total Energy Package) code, ⁵ in which the Kohn-Sham approach was employed to calculate the fundamental eigenvalues.⁶ In order to reduce the basis set of plane wave functions used to describe the real electronic functions, the pseudopotential approximation was introduced, where the nucleus and the core electrons were replaced by an effective potential.⁷ Pseudoatomic calculation for Ti, O and Li were respectively performed by {3p4s3d}, {2s2p} and {2s}. Exchange and correlation were treated in the generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof (PBE).⁸ Based on our tests, we have set the energy cut off at 380 eV, and the number of k-points at $7 \times 7 \times 1$. For the SCF process, the convergence criteria were set to (1) energy tolerance of 5 $\times 10^{-6}$ eV/atom, (2) force tolerance of 1.0×10^{-2} eV/atom, (3) maximum displacement tolerance of 5.0×10^{-3} . TiO₂ is modeled by a 1×1 slab model with 12-15 atomic layers. Over the surface, a vacuum of 15 Å was employed to separate the slab from each other. Transition states were calculated using the complete linear synchronous transit and quadratic synchronous transit (LST/QST) method.9

Electrochemical Measurements. The electrochemical tests were performed using two-electrode Swagelok-type cells with lithium serving as both the counter and reference electrodes under ambient temperature. The working electrode was composed of 70 wt % of active material (e.g., TiO_2 single crystals), 20 wt % of conductivity agent (carbon black, Super-P-Li), and 10 wt % of binder (polyvinylidene difluoride, PVDF, Aldrich). The electrolyte used was 1 M LiPF₆ in a 50:50 (w/w) mixture of ethylene carbonate and diethyl carbonate. Cell assembly was carried out in an Argon-filled glovebox with both moisture and

oxygen contents below 1 ppm. Cyclic voltammetry (CV, 1 V – 3 V, 0.1 mV/sec) was performed using an electrochemical workstation (CHI 660C). Galvanostatic charge/discharge was conducted using a battery tester (NEWAER) with voltage window 1 V – 3 V at different current rates of 1 C, 4 C, 10 C and 20 C where 1 C = 167.5 mAg⁻¹.

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Fig. S1 Original HRTEM images of anatase TiO_2 with dominant {001} (a) and {101} (b) facets.



Fig. S2 Cycling performance at different rates by using anatase TiO_2 with dominant {001} (blue) and {101} (red) facets.



Fig. S3 TEM image of TiO_2 nanosheets after 50 charge/discharge cycles at 1 C.