

## Electronic Supplementary Information

### **Lithium ion intercalation of 3-D vertical hierarchical TiO<sub>2</sub> nanotubes on titanium mesh for efficient photoelectrochemical water splitting†**

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#### **Experimental Section**

**Chemicals and Materials.** Titanium mesh (99.6%, 100 mesh, Strem Chemicals) was cut into pieces of 25 × 10 mm<sup>2</sup>. Ethylene glycol (EG), ammonia fluoride (NH<sub>4</sub>F), lithium sulfate (Li<sub>2</sub>SO<sub>4</sub>), potassium hydroxide (KOH) were purchased from Macklin Chemical and used as received. All aqueous solutions were prepared using deionized water (DI) with a resistivity of 18.2 MΩ cm.

**Preparation of hierarchical TiO<sub>2</sub> NTs/mesh.** The TiO<sub>2</sub> nanotubes (TiO<sub>2</sub> NTs) were fabricated by a two-step anodization process. Prior to anodization, the Ti meshes were first degreased by sonicating in ethanol and room-temperature DI water, followed by drying in pure nitrogen stream. The anodization was carried out using a conventional two-electrode system with the Ti mesh as an anode and a Pt gauze (Aldrich, 100 mesh) as a cathode respectively. All electrolytes consisted of

0.5 wt%  $\text{NH}_4\text{F}$  in EG solution with 2 vol% water. All the anodization was carried out at room temperature. In the first-step anodization, the Ti mesh was anodized at 60 V for 60 min, and then the as-grown nanotube layer was ultrasonically removed in DI water. The same Ti mesh then underwent the second anodization at 20 V for 60 min. After the two-step anodization, the prepared  $\text{TiO}_2$  NT/mesh samples were cleaned with DI water and dried off with  $\text{N}_2$  gas. The as-anodized  $\text{TiO}_2$  NTs/mesh were annealed in air at 450 °C for 1 h with a heating rate of 5 °C/min.

**Intercalation of lithium ions.** The electrochemical intercalation of  $\text{Li}^+$  was conducted in a typical three-electrode system, with  $\text{TiO}_2$  NTs/mesh, Ag/AgCl electrode, and Pt mesh as working electrode, reference electrode, and counter electrode, respectively, in 1 M  $\text{Li}_2\text{SO}_4$  aqueous solution. The  $\text{TiO}_2$  NTs/mesh was then subject to the electrochemical reduction and ion intercalation process under negative potentials of -0.4 V vs RHE (reversible hydrogen electrode). The thus prepared Li/ $\text{TiO}_2$  NTs/mesh was finally cleaned with DI water and dried off with  $\text{N}_2$  gas.

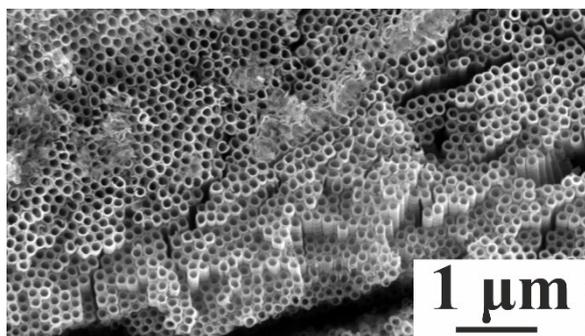
**Characterization of Li/ $\text{TiO}_2$  NTs/mesh.** The morphologies of Li/ $\text{TiO}_2$  NTs/mesh was determined by field-emission scanning electron microscope (FESEM, Hitachi S4800). The crystalline structure of the samples was analyzed by X-ray diffraction (XRD, Bruker D8 Discover diffractometer, using Cu  $K\alpha$  radiation,  $\lambda = 1.540598 \text{ \AA}$ ). Photoelectron Spectroscopy (XPS) data were collected by an Axis Ultra instrument (Kratos Analytical) under ultrahigh vacuum ( $<10^{-8}$  torr) and using a monochromatic Al  $K\alpha$  X-ray source operating at 150 W. The survey and high-resolution spectra were collected at fixed analyzer pass energies of 160 and 20 eV, respectively. Binding energies were referenced to the C 1s binding energy of adventitious carbon contamination which was taken to be 285.0 eV.

**Photoelectrochemical performance of TiO<sub>2</sub> NTs/mesh and Li/TiO<sub>2</sub> NTs/mesh.** The photoelectrochemical (PEC) performances of the TiO<sub>2</sub> NTs/mesh and Li/TiO<sub>2</sub> NTs/mesh were evaluated using a three-electrode configuration. The supporting electrolyte used was 1 M KOH solution. The potential of the photoelectrodes were controlled by a potentiostat and were reported against the reversible hydrogen electrode (RHE) following the equation below:

$$E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.059\text{pH} + E^{\circ}_{\text{Ag/AgCl}} \text{ with}$$

$$E^{\circ}_{\text{Ag/AgCl}} = 0.1976 \text{ V at } 25 \text{ }^{\circ}\text{C} \quad (1)$$

The scan rate for the linear sweep voltammetry (LSV) was 5 mV s<sup>-1</sup>. The photocurrent was measured under an irradiation from a 300 W Xe lamp (PLS-SXE300, PE300BF). The intensity of the light source was calibrated with a Si diode (Model 818, Newport) to simulate AM 1.5 illumination (100 mW cm<sup>-2</sup>). The electrochemical impedance spectra (EIS) were measured using a PGSTAT302N Autolab Potentiostat/Galvanostat (Metrohm) equipped with a frequency analyzer module (FRA2) with an excitation signal of 10 mV amplitude. The impedance vs frequency spectra were acquired at the open circular potential of the system under illumination condition. Afterward, impedance vs potential measurement at a fixed frequency was performed to determine the carrier density. The IPCE were obtained under illumination through monochromatic system, composed of a monochromator (Model: 74125, Newport) and light source (Model 73404, Newport).



**Fig. S1** SEM image of 1-step anodized TiO<sub>2</sub> NTs.

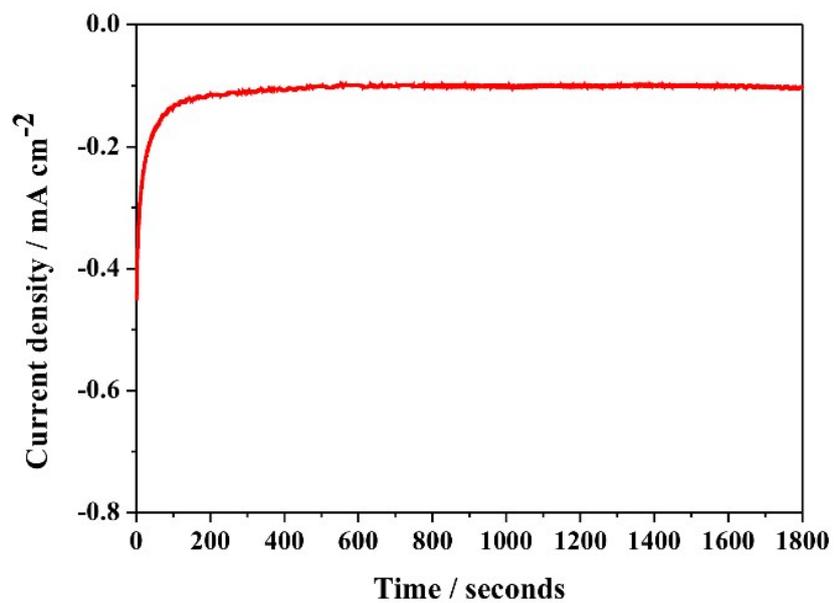


Fig. S2 Li<sup>+</sup> intercalation of TiO<sub>2</sub> NTs/mesh.

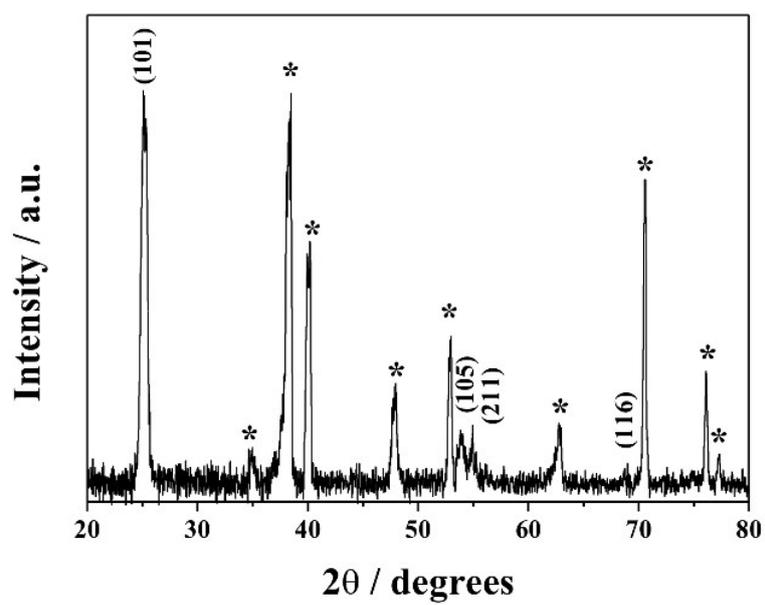
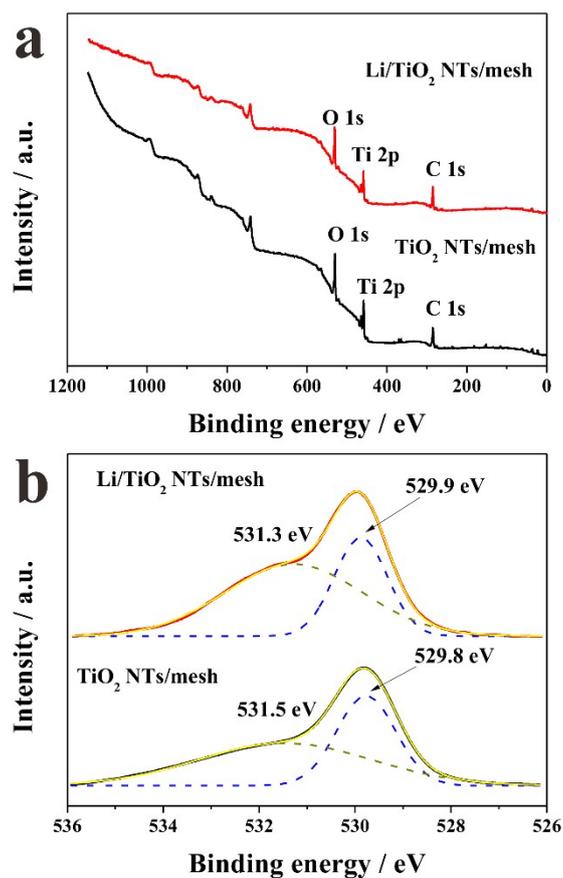
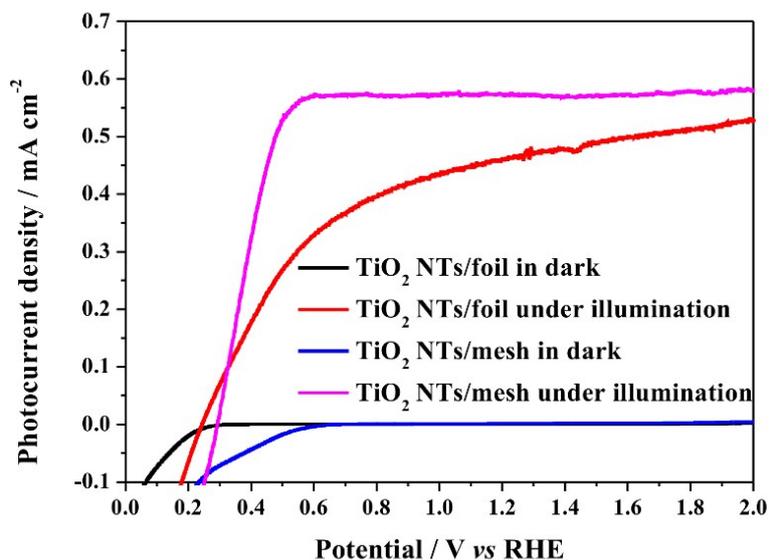


Fig. S3 XRD patterns of Li/TiO<sub>2</sub> NTs/mesh.



**Fig. S4** (a) XPS survey and (b) core-level XPS of O 1s of TiO<sub>2</sub> NTs/mesh and Li/TiO<sub>2</sub> NTs/mesh.



**Fig. S5** Linear sweep voltammograms collected from the TiO<sub>2</sub> NTs/foil and TiO<sub>2</sub> NTs/mesh.