Supporting Information

Solution Processable Formation of a Few Nanometers thick-Disordered Overlayer on Surface of Open-Ended TiO₂ Nanotube

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EXPERIMENTAL SECTION

Synthesis of Titanium Dioxide Nanorods: TiO_2 nanorods were fabricated on FTO (fluorine-doped tin oxide) glass via the hydrothermal method.¹ First, FTO glass was ultrasonically cleaned in an ethanol and acetone mixture (volumetric ratio of 1:1) for ten minutes and dried with N₂ gas. Second, 20 mL of deionized (DI) water, 20 mL of concentrated hydrochloric acid (35.0%-37.0% by weight), and 0.5 mL of titanium butoxide (97%, Aldrich) were mixed in a 60-mL Teflon-liner autoclave. Then, the FTO substrates (3×1.5 cm²) were placed in the Teflon liner with the conducting side facing down. Afterwards, the autoclave was heated at 150 °C for 20 hours and cooled for approximately 15 minutes under flowing tap water. After being rinsed with deionized water and drying at room temperature, TiO₂ nanorods were obtained.

Chemically Etching TiO₂ **Nanorods to Nanotubes**: TiO₂ nanotubes were fabricated by chemically etching the TiO₂ nanorods in 75 mL of a 0.17 M HCl and 0.20 M HF aqueous solution for 3 hours at 95 °C.^{2,3} The samples were rinsed with deionized water, dried in ambient air at room temperature and annealed at 500 °C for 2 hours.

Li-EDA Solution Treatment of TiO₂ Nanotubes: The Li-EDA solution was prepared by dissolving lithium metal in anhydrous ethylenediamine (>98%, TCI) at different concentrations. TiO₂ nanotube samples were immersed in a 0.1 M solution for 5, 10, and 20 s, as well as in 0.05, 0.3 and 0.5 M solutions for 10 s. After being removed from the Li-EDA solution, the treated TiO₂ nanotube samples were rinsed in 0.1 M HCl and DI water and dried at room temperature. **Characterization Methods**: The morphologies of the samples were examined by a field-emission scanning electron microscope (FE-SEM, JSM-7001F, Japan) and a transmission electron microscope (HRTEM, JEM-ARM 200F, Japan). X-ray diffraction (XRD, Rigaku Smart Lab) measurements were carried out to observe the crystalline phase using Cu K α radiation (operating voltage: 40 kV, operating current: 200 mA, scan rate: 4°/min). In addition, optical properties were measured using a UV-vis spectrophotometer (Cary 5000). X-ray photoelectron spectroscopy (XPS) measurements were performed using a Thermo VG K-alpha with monochromatic Al K α x-rays at hv = 1486.6 eV.

Photoelectrochemical Measurements: Photocurrent-voltage (J-V) measurements were obtained using an electrochemical workstation (CH Instruments, CHI 608C) with a three-electrode configuration: a Pt wire as a counter electrode, a photoanode as a working electrode and Ag/AgCl as a reference electrode. NaOH (1 M, pH = 14) was used as the electrolyte, and an H-type quartz cell was used as a reactor. The potentials were adjusted as a function of the RHE using the Nernstian relation $E_{RHE} = E_{Ag/AgCl} + 0.059 \text{ pH} + 0.2 \text{ V}$. The photoanodes were placed outside of the reactor in contact with the electrolyte through a hole on the side of the reactor to keep the reaction area fixed. Linear sweep voltammetry (LSV) was conducted at a scan rate of 20 mV/s. The working electrode was illuminated at 100 mW/cm² with a 150-W xenon lamp-based solar simulator (PECCELL, Yokohama, Japan, PEC-L01:100 mW/cm²). The intensity of the light was calibrated using a silicon reference cell (Fraunhofer ISE, certificate no. C-ISE269). Electrochemical impedance measurements were carried out using an Ivium compact stat machine. Mott-Schottky plots were collected over a DC potential range of -1.0 V to -0.4 V vs. Ag/AgCl

and at a frequency of 100 Hz in the dark. Electrochemical impedance spectroscopy (EIS) was performed under a 100-mW/cm² illumination at a potential of 0.2 V vs. Ag/AgCl, an AC potential frequency range of 100 kHz to 1 Hz and an AC modulation amplitude of 5 mV.



Figure S1. Schematic diagram showing the procedure for preparing TiO_2 nanotubes treated in a Li-EDA solution.



Figure S2. TEM image of TiO₂ nanotubes.



Figure S3. SEM images of TiO_2 nanotubes treated in a 0.1 M Li-EDA solution for different durations: 0 s, 5 s, 10 s and 20 s.



Figure S4. SEM images of TiO_2 nanotubes treated in a Li-EDA solution for 10 s at different concentrations: 0.05 M, 0.1 M, 0.3 M and 0.5 M.



Figure S5. TEM images of TiO_2 nanotubes treated in a Li-EDA solution for 10 s at different concentrations: 0.05 M, 0.1 M, 0.3 M and 0.5 M.



Figure S6. Thickness of the disordered layer for each treatment condition.



Figure S7. (a) Linear and (b) chopped photocurrent-potential (J-V) curves of TiO_2 nanotubes with and without treatment in a Li-EDA solution for 10 s at different concentrations: 0.05 M, 0.1 M, 0.3 M and 0.5 M.



Figure S8. Linear photocurrent-potential (J-V) curves of TiO_2 nanotubes and nanorods with and without treatment in a 0.1M Li-EDA solution for 10 s.

Table S1 R_{ct} values for pristine TiO₂ and TiO₂ treated with a 0.1 M Li-EDA solution for 10 s.

Sample	Rct (Ω)
TiO ₂	16,489
R-TiO ₂	9,521

- (1) L. Liu, J. Qian, B. Li, Y. Cui, X. Zhou, X. Guo and W. Ding, *Chem. Commun.*, 2010, 46, 2402.
- (2) E. Bright and D. W. Readey, J. Am. Ceram. Soc., 1987, 70, 900.
- (3) K. Shin and J. H. Park, ACS Appl. Mater. Inter., 2015, 7, 18429.