Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information for

Preparation of ZnO/two-layer Self-doped Black TiO_2 Nanotube Arrays and its Enhanced Photochemical Properties

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Experimental section

Fabrication of TiO_2 nanotubes

The TiO_2 nanotubes were fabricated by two-step anodic oxidation on Ti substrate in Scheme 1. Briefly, the Ti foils (99.99% purity, 0.2 mm thickness) were used as the anode in the experiments. Before anodization, the Ti foils were cleaned with deionized water, acetone and ethanol in an ultrasonic cleaner and dried in nitrogen atmosphere, respectively. The anodization process was performed in a 100ml two-electrode system with the Ti foil and a Graphite sheet for the anode and cathode at room temperature. The solution consists of 90 ml of ethylene glycol, mixed with 0.3 wt% Ammonium fluoride (NH_4F) and 2 vol% H_2O. In the first anodization, the TiO_2 nanotubes were formed at the applied voltage of 60 V for 2 h and then the as-grown nanotube layer was ultrasonically removed in the deionized water for 30 min. The same thus-obtained Ti foil immersed in the new solution for the second-step anodization at 60 V for 30 min. After the two-step anodization, the prepared samples were cleaned with ethanol and deionized water and dried off with N_2 gas. Finally, the samples were calcined at 450 °C in an ambient atmosphere for 2 h to transform the amorphous phase. In addition, an as-prepared TiO_2 nanotube sample by one-step anodic oxidation at 60 V for 30 min was fabricated for comparison with the same preparation process.

Characterization

Field emission scanning electron microscope (Hitachi, SU-8010) was used to characterize the microscopic morphology of the samples. The crystal structure was

characterized by X-ray diffraction (Rigaku, D/MAX-2400). The surface chemical analysis was investigated by X-ray Photoelectron Spectroscopy (Thermo Scientific, ESCALAB Xi+).

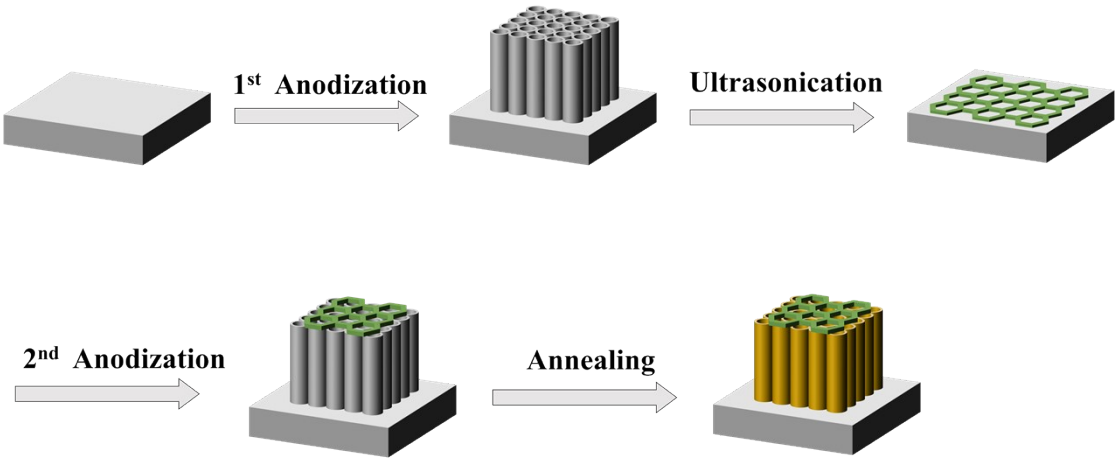
Photoelectrochemical Measurement

All electrochemical measurements were performed by a CHI660E electrochemical system using a three-electrode configuration with the as-prepared samples, Ag/AgCl electrode and Pt wire as working, reference and counter electrode, respectively. An aqueous solution of 0.1 M Na_2SO_4 was used as the electrolyte. The potential of the photoelectrodes should be converted to a standard value which is reported against RHE by the following the equation below:

$E_{RHE} = E_{Ag/AgCl} + 0.059\ pH + E_{Ag/AgCl}^{0}$ with

$E_{Ag/AgCl}^{0} = 0.197V$ at 25 ℃

The linear sweep voltammetry (LSV) was measured at the scan rate of 5 mV s^{-1}. The transient photocurrent responses were evaluated under chopped light irradiation without the bias voltage. The incident-photon-to-current-conversion efficiency (IPCE) measurements, electrochemical impedance spectroscopic(EIS) and Mott−Schottky plots were performed at the open circuit voltage. EIS was performed between 100 kHz and 0.01Hz in dark with a scan rate of 5 mV s^{-1}. Mott−Schottky plots were collected in the dark at a frequency of 1kHz.



Scheme S1. Schematic illustration of for construction of the TiO_2 nanotubes.

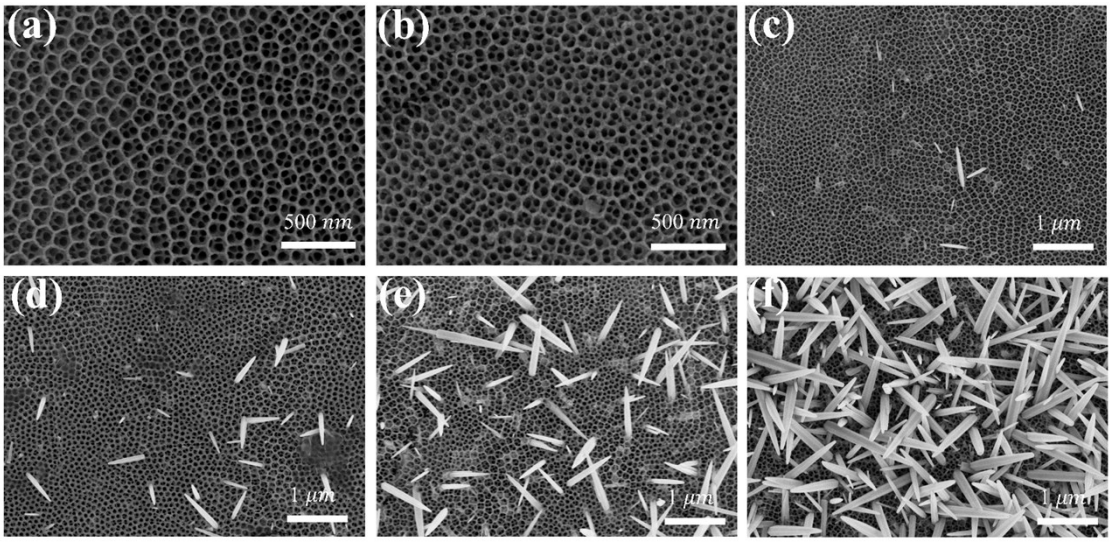


Figure S1. FESEM images of (a) 2-TNTs and the ZnO/2-TNTs with different hydrothermal concentration of (b) 0.01, (c) 0.03, (d) 0.05, (e) 0.07, (f) 0.09 mol/L for growing ZnO.

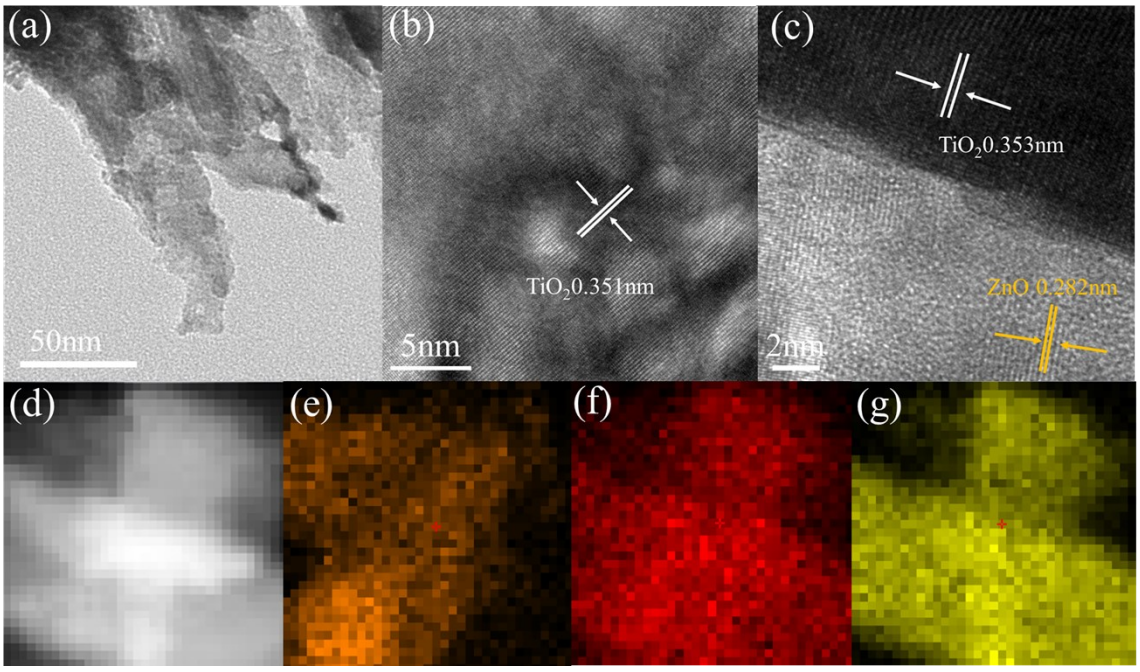


Figure S2 (a-c) TEM and HRTEM images of the ZnO/2-B-TNTs; (d) with corresponding mapping results for (e) Ti, (f) O, (g) Zn.

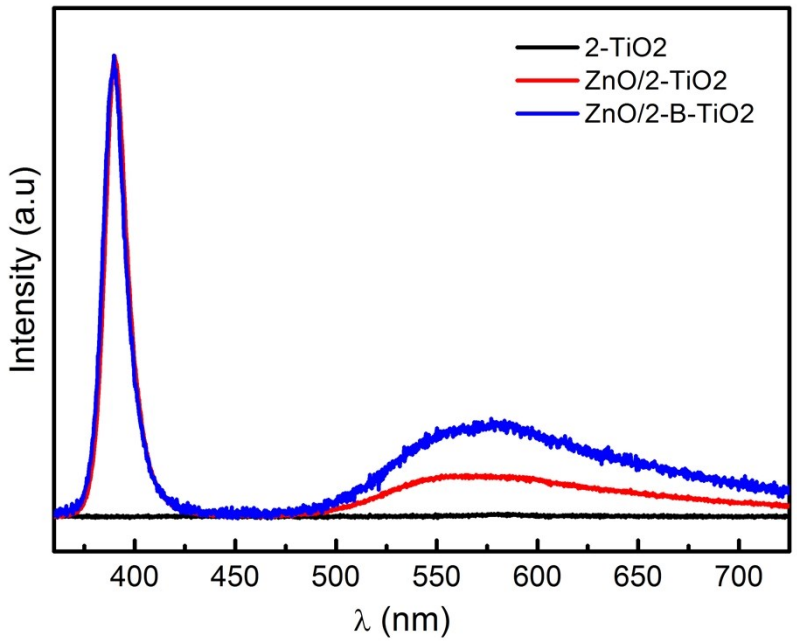


Figure S3 PL spectra of 2-TNTs, 2-B-TNTs, ZnO/2-TNTs

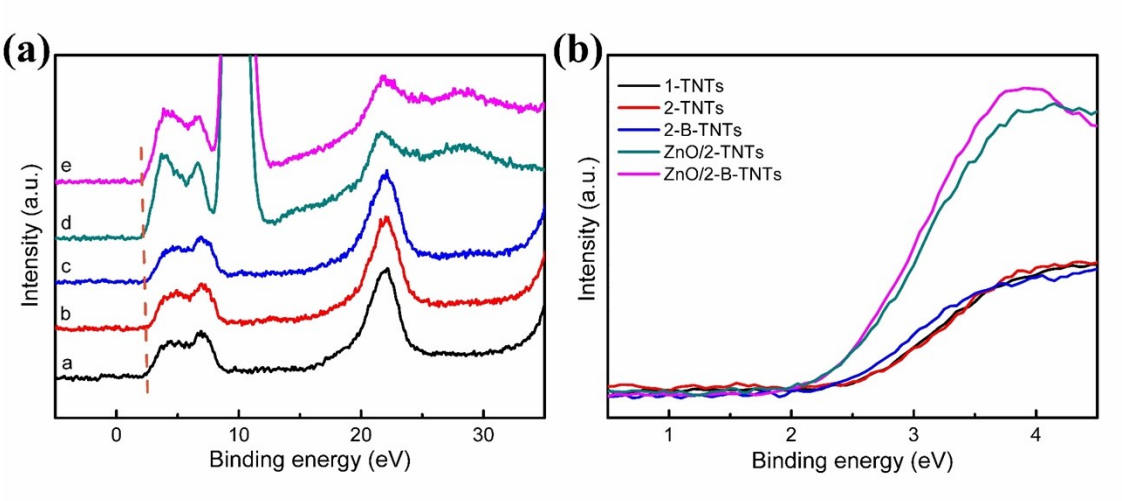


Figure S4 (a) XPS valence band spectra of 1-TNTs, 2-TNTs, 2-B-TNTs, ZnO/2-TNTs, ZnO/2-B-TNTs; (b) Enlarged XPS valence band spectra.

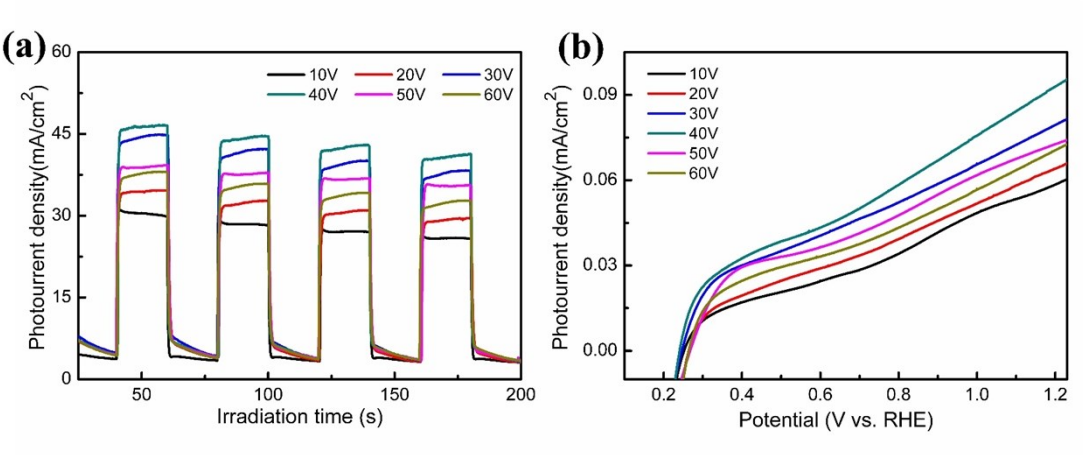


Figure S5 (a) Transient photocurrent responses and (b) Linear-sweep voltammograms of the different applied potential for the electrochemical reduction.

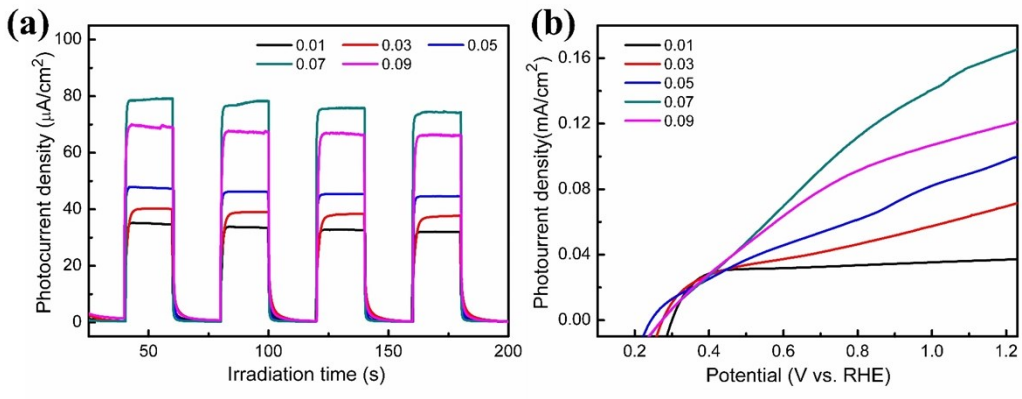


Figure S6 (a) Transient photocurrent responses and (b) Linear-sweep voltammograms of the ZnO/2-TNTs with different hydrothermal concentration for gowing ZnO.

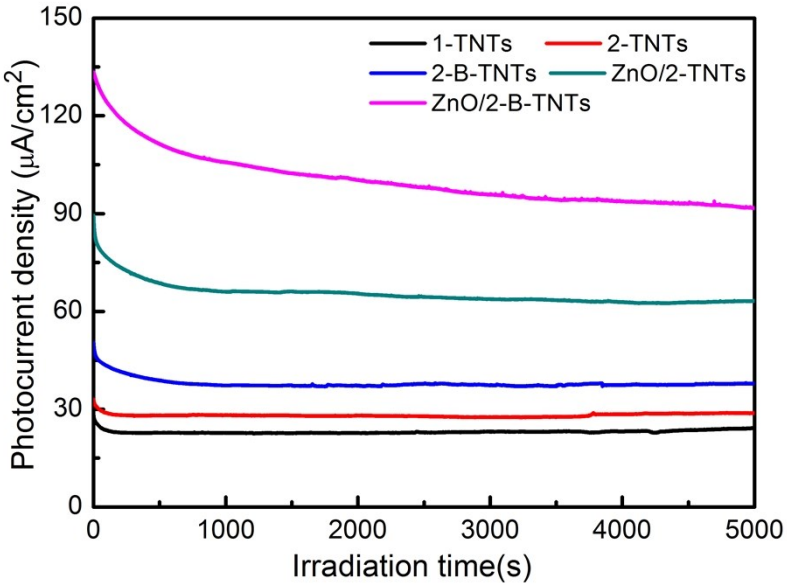


Figure S7 Photocurrent densities of 1-TNTs, 2-TNTs, 2-B-TNTs, ZnO/2-TNTs, ZnO/2-B-TNTs running for 5000s.