

## Supporting information

### **Double-walled TiO<sub>2</sub> nanotubes prepared with NH<sub>4</sub>BF<sub>4</sub> based electrolyte and their photoelectrochemical performance**

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**Preparation of TiO<sub>2</sub> nanotube arrays.** A common two-electrode electrochemical cell, with the working electrode of Ti foil (1.0 mm thick) and the counter electrode of Pt foil, was used for the preparation of TiO<sub>2</sub> NTs. The distance between two electrodes was measured to be 4 cm. Two-step anodization methods were adopted. The titanium substrates were firstly anodized in the ethylene glycol (EG) electrolyte containing 0.5 wt% NH<sub>4</sub>F and 2 vol% deionized water under 60 V (supplied by a DC power) for 2 h. Then the as-formed TiO<sub>2</sub> layer was peeled off by ultrasonication in deionized water to expose the underneath substrate. Subsequently, the well-textured titanium foils were subjected to the second anodization in EG electrolyte containing 0.5 wt% NH<sub>4</sub>BF<sub>4</sub> and 5 vol% deionized water at different voltages. Finally, the as-anodized TiO<sub>2</sub> NTs were annealed at 450 °C for 2 h with a heating and cooling rate of 5 °C/min to transform the amorphous TiO<sub>2</sub> into crystalline photoactive

anatase phase. All the electrochemical anodization experiments were carried out at the ambient temperature (25 °C).

**Characterization.** The morphologies of the samples were characterized by field-emission scanning electron microscopy (FE-SEM) (NOVA NANOSEM 430, Holland) at an acceleration voltage of 15KV. The transmission electron microscopy (TEM) (Hitachi H-7650, Japan) was used to observe the morphology details of individual tube. X-ray diffraction (XRD) patterns were obtained on an X-ray diffractometer (Bruker D8 ADVANCE, Germany) using Cu K $\alpha$  radiation and operating at 40 kV/40 mA. X-ray photoelectron spectrometry (XPS, Kratos Axis Ultra DLD, UK) was used to detect the chemical composition of TiO<sub>2</sub> NTs. The UV-vis light absorption spectra were obtained from a Hitachi UV-3010 spectrophotometer (Japan) equipped with an integrating sphere assembly and using BaSO<sub>4</sub> as reference to measure all the samples. Photoluminescence (PL) spectra were obtained using a fluorescence spectrometer (Hitachi F-7000).

**Photoelectrochemical test.** Photoelectrochemical water splitting measurements were carried out in 1 M KOH electrolyte with a standard three-electrode cell of TiO<sub>2</sub> NTs, platinum foil and Ag/AgCl as the working, counter and reference electrode, respectively. The potential and photocurrent of the photoelectrode were controlled by a potentiostat and were reported against the reversible hydrogen electrode (RHE):

$$E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.059 \text{ pH} + E_{\text{Ag/AgCl}}^{\circ} \text{ with } E_{\text{Ag/AgCl}}^{\circ} = 0.1976 \text{ V at } 25 \text{ }^{\circ}\text{C}$$

The samples were illuminated by a stimulated solar light (AM1.5, 100 mW/cm<sup>2</sup>) provided by a PLS-SXE300UV Xe lamp (Changtuo, China).