**Supplementary Information** 

# A solar-driven photocatalytic fuel cell with dual photoelectrode for simultaneous wastewater treatment and hydrogen production

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#### **Pretreatment of FTO**

FTO sheets, cut into samples of size 1.5 cm  $\cdot$  5 cm, were degreased by immersed into piranha solution for 30 min. Then rinsed by deionized water and dried in the air.

## Preparation of TiO<sub>2</sub> NTs/Ti

Ti sheets, cut into samples of size 1.5cm \* 5cm, were degreased by sonicating in acetone, ethanol, deionized water in turn after polished, then dried in the air. The Ti sheets sample was etched in the HCl (SCRC, AR, 36.0-38.0%) solution (6mol L<sup>-1</sup>) for 20 min then electrochemical anodized by using a DC power supply (Sovotek, E5200-3) to control the experimental voltage and current. The anodization was divided into 2 steps. The first is to anodize in 0.5wt% HF (SCRC, AR,  $\geq$ 40.0%) solution using a platinum foil counter electrode at room temperature and a voltage of 20V for 1h. The second is to anodize in the glycol solution (NH<sub>4</sub>F (SCRC, AR,  $\geq$ 96%): H<sub>2</sub>O: Et(OH)<sub>2</sub> (SCRC, AR,  $\geq$ 99.7%)=1:4:400,wt%) at the same conditions for 2h. After that, it was annealed in air atmosphere for 3h with the heating and cooling rates of 5°Cmin<sup>-1</sup>.

#### **Preparation of CdSe NPs/FTO**

Electrodeposition was carried out in a three-electrode configuration with FTO, Platinum wire and Hg/HgCl<sub>2</sub>, as working electrode, counter electrode and reference electrode, respectively. The electrodeposition bath solution contained 0.1 mol L<sup>-1</sup> CdSO<sub>4</sub> (SCRC, AR,  $\geq$ 99.0%), 0.1 mmol L<sup>-1</sup> SeO<sub>2</sub> (SCRC, AR), and 0.1 mol L<sup>-1</sup> Na<sub>2</sub>SO<sub>4</sub> (Aladdin, AR, 99.0%). The applied potential was -1.1V vs SCE and the deposition time is 2 h. The CdSe NPs/FTO were rinsed thoroughly and annealed at 300 °C in N<sub>2</sub> atmosphere for 3 h.

# Preparation of CdS NPs/FTO

Electrodeposition was carried out in a three-electrode configuration with FTO, Platinum wire and Hg/HgCl<sub>2</sub>, as working electrode, counter electrode and reference

electrode, respectively. The electrodeposition bath solution contained 0.2 mol L<sup>-1</sup> CdCl<sub>2</sub> (Aladdin, AR,  $\geq$ 99.0%) and 0.05 mol L<sup>-1</sup> Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> (Enox, AR,  $\geq$ 99.0%) with adjusting the pH value to 2.1 by HCl solution (0.1 mol L<sup>-1</sup>). The electrochemical configuration was placed in a thermostatted bath where the temperature was 70 °C. The applied potential was -0.65 V vs SCE and the deposition time is 1000 s. Then the CdS NPs/FTO were rinsed and annealed at 500 °C in N<sub>2</sub> atmosphere for 6 h with the heating and cooling rates of 5°C min<sup>-1</sup>.

### Preparation of Cu<sub>2</sub>O NPs/FTO

A standard three-electrode system was used for Cu<sub>2</sub>O nanoparticles deposition. An Ag/AgCl electrode in a saturated KCl (SCRC, AR,  $\geq$ 99.5%) solution was used as a reference electrode, a FTO as a work electrode and a platinum coil as a counter electrode. The electrolyte solution consisted of 0.4 mol L<sup>-1</sup> cupric sulfate (SCRC, AR,  $\geq$ 99.0%) and 3 mol L<sup>-1</sup> lactic acid (Aladdin, AR,  $\geq$ 85.0%), then its pH was adjusted 9.0 by 4 mol L<sup>-1</sup> NaOH (Aladdin, AR, 96.0%) solution with continuous stirring. The electrochemical deposition was performed potentiostatically with a potential of –0.3 V (versus Ag/AgCl) for 30 min and the temperature of the electrolyte was kept at 60°C by water bath.



Fig. S1 The reactor of the PFC.



Fig. S2 The SEM image, TEM image of TiO<sub>2</sub> NRS/FTO (A1-A3); Cu<sub>2</sub>O

NWAs/Cu mesh (B1-B3) and C/ Cu<sub>2</sub>O NWAs/Cu mesh (C1-C3).



Fig. S3 The UV-Vis absorption spectra of the C/Cu<sub>2</sub>O/Cu and TiO<sub>2</sub> NRs/FTO



Fig. S4 Variation of the  $J_{SC}$  of TiO<sub>2</sub> NRs/FTO-C/Cu<sub>2</sub>O/Cu PFC in 8 h.



Fig. S5 The IPCE of the TiO<sub>2</sub> NRs/FTO-C/Cu<sub>2</sub>O/Cu PFC.



Fig. S6 The gas-chromatography spectra of standard  $H_2$  peak.