

## Supporting Information

### **Thin-film Silicon based Photocathode with Hydrogen doping TiO<sub>2</sub> Protection Layer for Solar Hydrogen Evolution**

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## Determining work function

The flat potential ( $V_{fb}$ ) can be deduced by the difference between the Fermi level ( $E_F$ ) of semiconductor and the electrochemical potential of electrolyte ( $E_{redox}$ ). It should be noted that whilst the redox potential of an electrolyte is usually quoted against the standard hydrogen electrode scale (SHE), the Fermi level of a semiconductor is typically given with reference to the electron energy in absolute vacuum level (AVL). Thus, in order to calculate the work function of the pristine TiO<sub>2</sub> and HTO, the AVL, SHE and reversible hydrogen electrode (RHE) should be clarified by follow equations firstly:

$$E_{AVL} = -4.5 - E_{SHE} \quad (1)$$

$$E_{RHE} = E_{SHE} + 0.0591 \times PH \quad (2)$$

Secondly, when a semiconductor is immersed in an electrolyte, the transferred charges form an electrical double layer comprising of a compact Helmholtz layer and a diffuse Gouy-Chapman layer during the equilibrium process. There is a potential drop between the inner and outer Helmholtz layers, called Helmholtz double layer voltage ( $V_H$ ) which depends on the PH of the electrolyte. The  $V_H$  can be determined by the equation as follow

$$V_H = 0.059 \times (PH_{PZZP} - PH) \quad (3)$$

Where  $PH_{PZZP}$  is the PH of the point of zero zeta potential. The flat band potential can be expressed in the following

$$E_{fb} = |E_F - E_{redox}(vs \cdot AVL)| + V_H \quad (4)$$

The  $E_{fb}$  is a property of the interface between the semiconductor and electrolyte and thus the band positions of the semiconductor will also depend on the PH. In conclusion, both of the redox electrochemical potential and  $E_F$  depend on the PH via the Nernst equation. In order to determine the  $E_F$  of semiconductor without contacting electrolyte, the  $V_H$  can be ignored. So the  $E_{fb}$  can be determined by the following

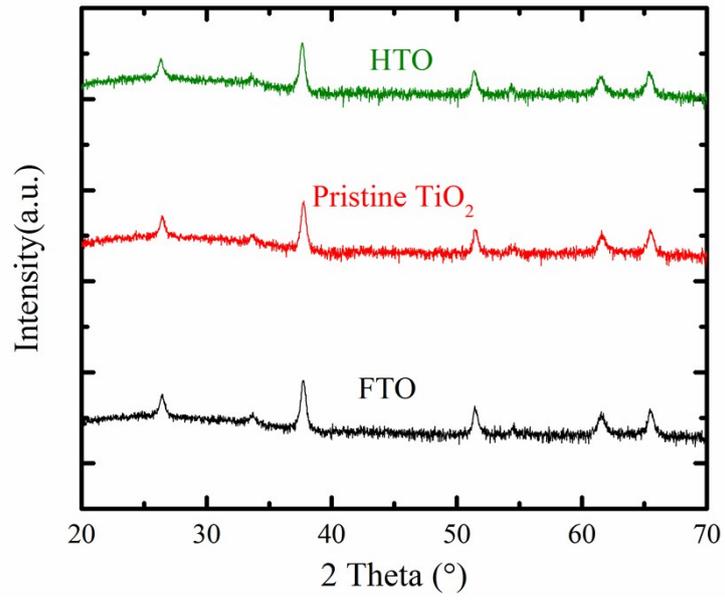
$$|E_{fb}| = |E_F - E_{redox}(vs \cdot AVL)| \quad (5)$$

Where the  $E_{redox}$  can be calculated as -5.115 eV vs. AVL. The  $E_{fb}$  can be obtained by Mott-Schottky plots and converted into the potential vs. SHE. So the Fermi level of the pristine TiO<sub>2</sub> and HTO are -

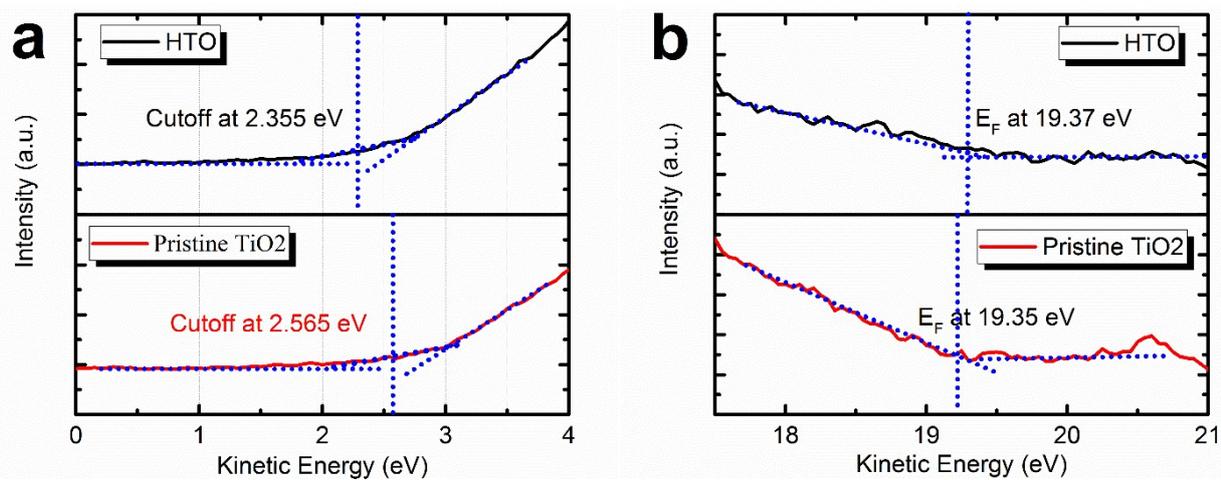
4.432 eV and -4.192 eV vs. AVL respectively. The Fermi level of HTO shifts 0.24 eV upwardly comparing to pristine TiO<sub>2</sub>.

**Discussions about sharp spikes:**

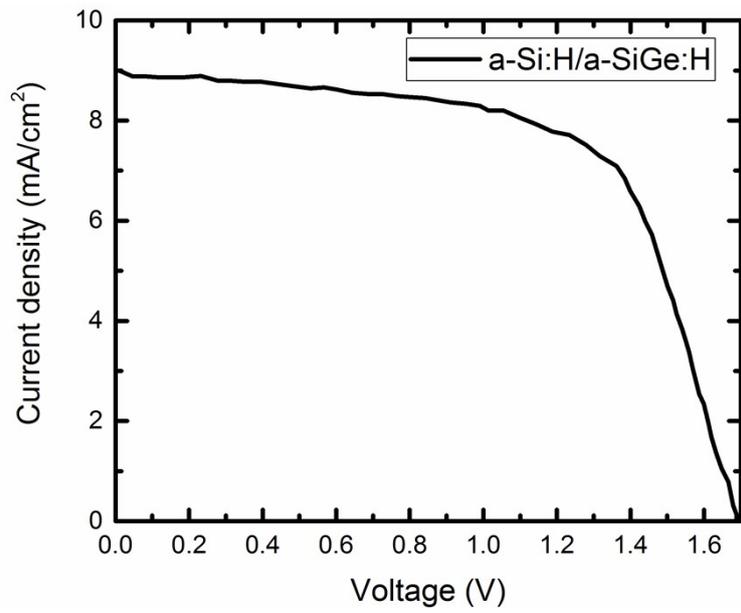
The high sharp spikes are mainly attributed to the poor gas desorption rate. Comparing to the pristine TiO<sub>2</sub> protected sample, HTO protected sample can transport much more electrons to the interface of SLJ when the sample is illuminated. At first, a large amount of photogenerated electrons transfer across the semiconductor/electrolyte interface to drive the hydrogen evolution reaction (HER) and produce adsorptive hydrogen gas with a high rate, and this results in higher photocurrent density. With time going on, more and more hydrogen gas is adsorbed on the surface of the sample. The transfer rate of electrons and corresponding photocurrent density will be reduced extremely. Within a few minutes, the adsorption rate is greater than the desorption rate, thus the photocurrent density continues to decline and a high spike can be seen. Similarly, the pristine TiO<sub>2</sub> protected sample owns lower photocurrent density and presents a low spike. As time passes by, the adsorption rate and desorption rate gradually achieve balance and tends toward stability. The photocurrent density will remain unchanged.



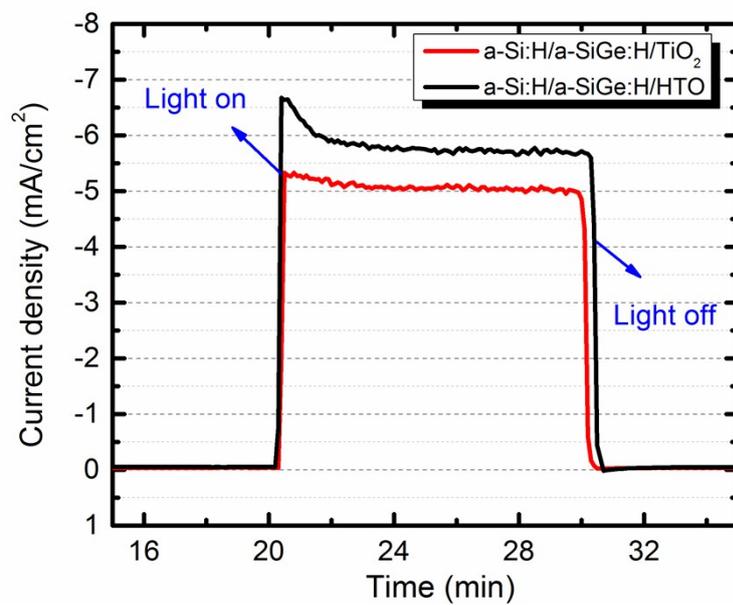
**Fig. S1** XRD patterns of the bare FTO substrate, pristine TiO<sub>2</sub> and HTO films deposited on FTO glass substrate.



**Fig. S2** The detailed spectrum of typical He I UPS for pristine TiO<sub>2</sub> and HTO taken with -8.000 V bias applied to the samples. (a) The inelastic cutoff region and the cutoff energy is shown with a vertical bar. (b) The Fermi edge region and the Fermi edge energy is also shown with a vertical bar.



**Fig. S3** The I-V curve of a-Si:H/a-SiGe:H tandem solar cell.



**Fig. S4** The magnified view of the chronoamperometry J-t curves of the HTO and pristine TiO<sub>2</sub> protected a-Si:H/a-SiGe:H tandem photocathodes measured at 0 V vs. RHE.