Electronic supplementary information

Hierarchical TiO_2 nanowires/microflowers photoanode modified with Au nanoparticles for efficient photoelectrochemical water splitting

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1. The specific measurement and calculation processes of ECAS.

First, we measured *CV* in a range of 0 V to 0.17 V vs. Ag/AgCl (1 M KOH solution) at different scan rates (5, 10, 20, 50, 100, 150, and 200 mV s^{-1}). Under each scan rate, the measurements were repeated four cycles to reduce errors. Fig. S1 present the measured CV results of each photoanode (one cycle). **Second,** the double-layer capacitance Cdl was estimated by plotting the Δj (Y-axis in Fig. 6) = ($ja - jc$) at 0.1 V (where *jc* and *ja* are the cathodic and anodic current densities, respectively) against the scan rate (X-axis in Fig. 6) for each photoanode, in which the slope was twice that of Cdl. **Third,** the roughness factor Rf was estimated from the ratio of Cdl for the working electrode and the corresponding selected smooth metal electrode (a constant), that is, R_f = *Cdl*/(the constant). **Fourth,** based on the formula: ECSA = R_f*S = S**Cdl*/(the constant), that is the slope in the $\Delta j - \upsilon$ plot directly proportional to the ECSA. As observed from Fig. 6 that the sample possesses the biggest slope when the volume of introduced TTIP is 1 mL, and thus it has the highest ECSA.

2. The synthesis process of Pt/H-TiO_2.

The synthesis process of Pt/H-TiO_2 is similar with that of Au/H-TiO_2. Typically, EG (0.5 mL) was diluted with water (20 mL) in a beaker (50 mL) and stirred for 10 min. Then, the EG solution was mixed with different volumes 10 μL of $H_2PtCI_6 \cdot 6H_2O$ (0.019 mol/L). After stirring for another 20 min, H-TiO_2 electrodes were put into the above solution with the conducting side facing up. The solution was subjected to UV irradiation. UV treatment was conducted with a LED-lamp of 365 nm (Au Light, Beijing, CEL-LED100) at an operation current of 3.5 A. The FTO substrates were cleaned extensively for 10 min. The samples were then heated at 350 °C for another 4 h in air to deposit Pt NPs on H-TiO_2 surface.

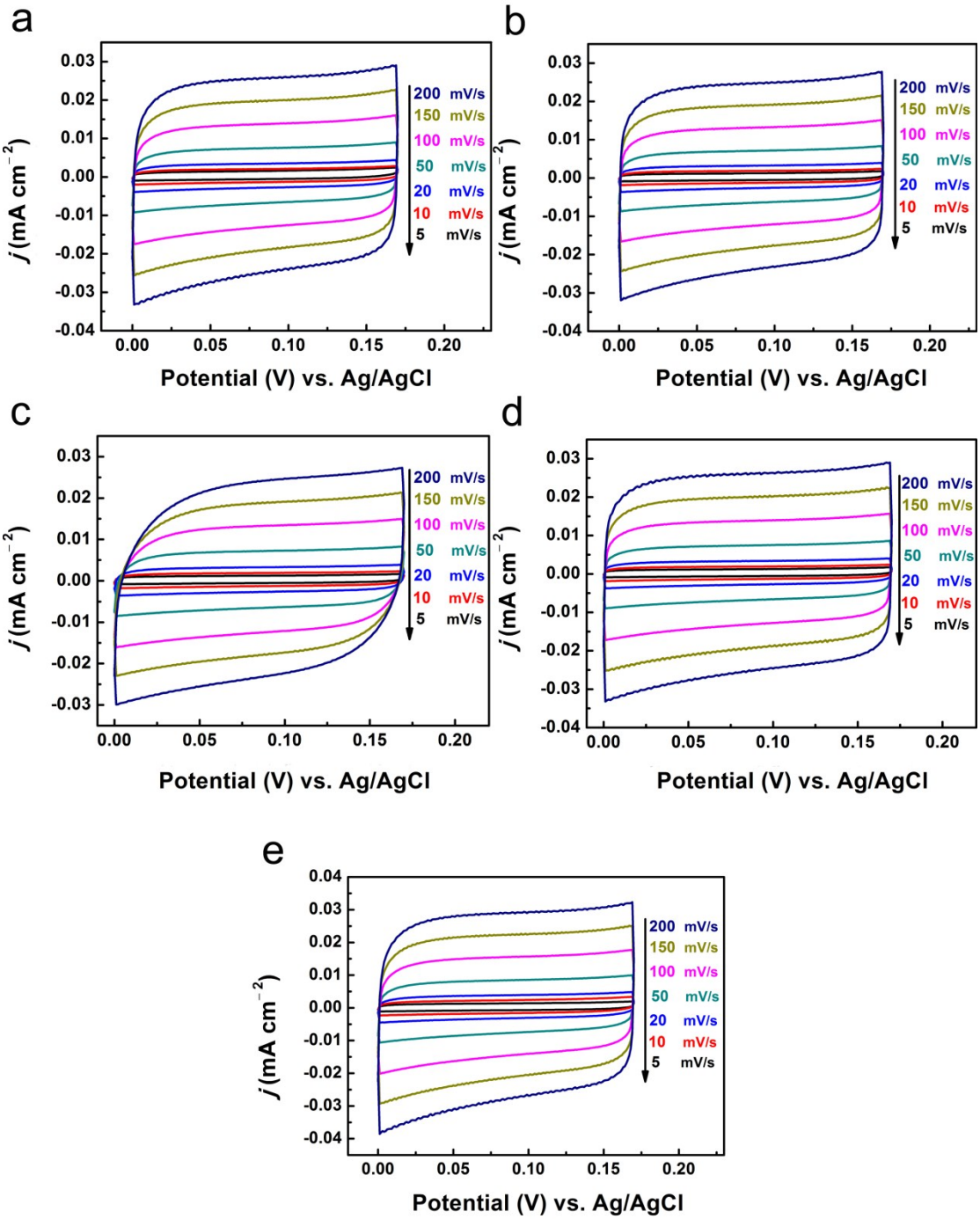

Fig. S1 The CV response versus different υ when adding different volumes of TTIP. (a) 0.6, (b) 0.7 mL, (c) 0.8 mL, (d) 0.9 mL, and (e) 1 mL, υ are 5 mV s^{-1}, 10 mV s^{-1}, 20 mV s^{-1}, 50 mV s^{-1}, 100 mV s^{-1}, 150 mV s^{-1}, and 200 mV s^{-1}.

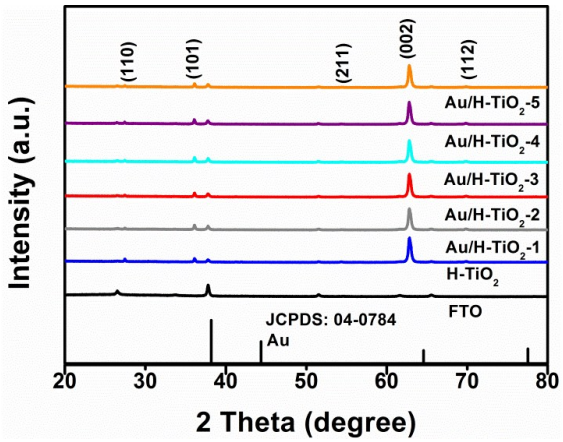

Fig. S2 The XRD spectra of H-TiO_2 and Au/H-TiO_2-X, XRD spectrum of FTO substrate is also presented here as a reference.

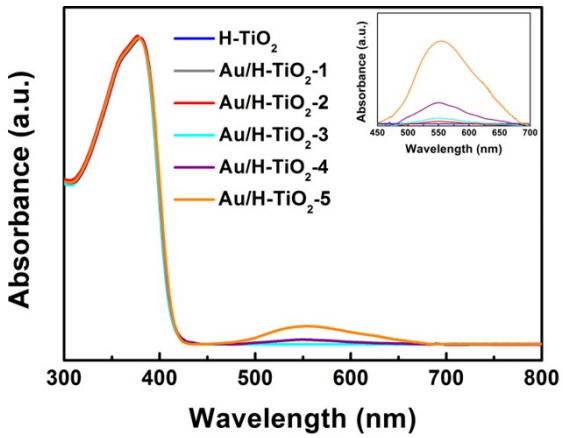

Fig. S3 UV-vis DRS of H-TiO_2 and Au/H-TiO_2-X photoelectrodes.

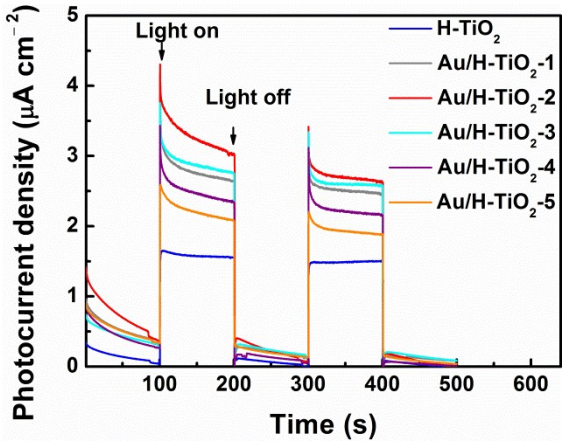

Fig. S4 Chronoamperomertic *I*–*t* curves collected at 1.23 V vs. RHE for H-TiO_2 and Au/H-TiO_2-X electrodes under visible-light illumination.

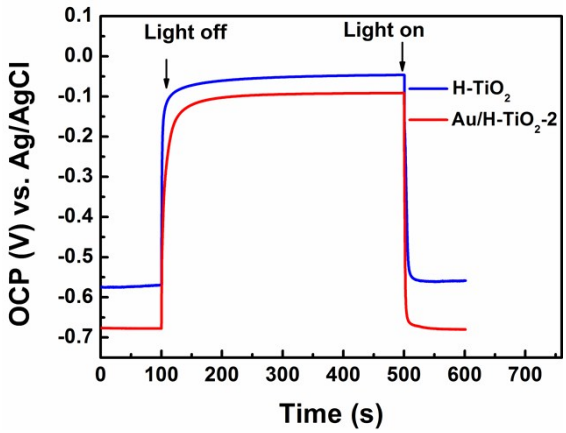

Fig. S5 OCP versus time profile of H-TiO_2 and Au/H-TiO_2-2 electrodes.

Table S1 Elements weight ratio of Au/H-TiO_2-X nanostructures in SEM EDS analysis.

Samples	Ti (weight %)	Au (weight %)	Au/Ti (%)
Au/H-TiO_2-1	54.65	0.085	0.155
Au/H-TiO_2-2	57.33	0.15	0.261
Au/H-TiO_2-3	56.31	0.31	0.553
Au/H-TiO_2-4	52.62	0.41	0.779
Au/H-TiO_2-5	55.85	0.46	0.82