Supporting Information

Effect of band structure on the hot-electron transfer over Au photosensitized brookite TiO$_2$

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Experiment Section

Synthesis of facet optimized brookite TiO$_2$

{121} facet exposed TiO$_2$ nanorods (T$_{121}$) and {211} facet exposed TiO$_2$ nanocubes (T$_{211}$) were prepared by our previously reported method.$^{[1]}$ Typically, 10 mmol of tetrabutyl titanate (TBOT) was firstly added into 25 mL of deionized water dropletly. Then, 2 g of urea and 2.5 mL of sodium lactate liquor (60%) were dissolved in the above solution with agitation. After stirring for 30 min, the above solution was adjust to pH 7 or 14 by 1 M of NaOH solution for the preparation of T$_{121}$ and T$_{211}$, respectively. After reaction at 200 °C for 12 h, the final products could be obtained.

Synthesis of Au@TiO$_2$ nanocomposites

Au@TiO$_2$ plasmonic photocatalysts were fabricated by using HAuCl$_4$ and hydrazine monohydrate (N$_2$H$_4$ˑH$_2$O) as precursor and reductant, respectively. Typically, 1% wt of HAuCl$_4$ aqueous solution was slowly added into 12 mL of deionized water with 200 mg of brookite TiO$_2$ samples, then 1 mL of N$_2$H$_4$ˑH$_2$O (80%) was added in the above suspension. After reaction at 120 °C for 1.5 h, the final Au@TiO$_2$ nanocomposites could be obtained.

Preparation of Au@TiO$_2$ films

The Au@TiO$_2$ films used for the electrochemical test were prepared via a spin-coating method. 5 mg of Au@TiO$_2$ samples were firstly dispersed into 3 mL of ethanol solvent by ultrasonic treatment for 30 min, then spin-coated on the ITO substrate layer by layer. In the procedure of spin coating, every drop of the Au@TiO$_2$ suspension was about 0.05 mL, and 3 drops of suspension in total was dripped on the ITO substrate in each cycle. The spin speed and time were 200 rpm for 10 s followed with 600 rpm for 30 s. Finally, the coated films were heated to 300 °C at a rate of 1 °C/min and kept at this temperature for 2 h.

Characterizations
XRD patterns were recorded by a powder X-ray diffractometer (Cu Kα radiation source, D8 Advanced, Bruker, Germany). The morphology of the samples were observed with a transmission electron microscopy (TEM, Tecnai G2 F20, FEI, USA.) operated at 200 KV. The UV-visible diffuse reflection spectra were conducted on a UV-visible spectrophotometer (UV-2700, Shimazu, Japan). Steady state and dynamic photoluminescence test were carried out using an excitation wavelength of 455 nm and a 455 nm diode laser, respectively, on a Fluorolog-3 spectrofluorometer (Horiba Jobin Yvon).

**Theoretical calculations**

The surface structures of brookite TiO$_2$ covered {121} or {211} surface were obtained as our previous report.$^{[1]}$ In detail, the surfaces were modeled using periodic slabs with thicknesses over 17 Å, constructed from an optimized unit cell. The repeated slabs in the z direction were separated by a 12 Å wide vacuum region, which can sufficiently suppress the interaction between adjacent slabs. Both {121} and {211} surface cells consist of 144 atoms. Atomic positions were optimized with fixed cell lattices until the force was converged to less than 0.03 eV·Å$^{-1}$.$^{[1]}$ Then, the band structures were calculated on the basis of density functional theory (DFT), as implemented in the CASTEP code. The electronic exchange-correlation energy was treated by the generalized-gradient approximation as parameterized by Perdew, Burke and Ernzerhof (GGA-PBE). The energy cutoff for the plane-wave basis set was 400 eV. The self-consistent filed (SCF) tolerance was 5.0×10$^{-7}$ eV/atom. The Ti 3d$^2$4s$^2$ and O 2s$^2$2p$^4$ were treated as valence electrons. The interactions between valence and core electrons were treated via ultrasoft pseudopotentials. The $k$-point spacing is less than 0.015 Å$^{-1}$ in the Brillouin zone for all cells.
Photocatalytic test

The photocatalytic H₂ evolution test was carried out in a glass reactor with closed gas circulation system. The 50 mg of 1 wt % of Au@TiO₂ plasmonic photocatalyst without any cocatalyst was dispersed in an aqueous methanol solution (50 mL methanol and 220 mL H₂O). The light source was a 300 W Xe lamp equipped with a L42 cutoff filter to remove the UV light. The evolved gas was detected by an online gas chromatograph (GC-2014 with TCD, Shimadzu).

The apparent quantum efficiency (AQE) at each wavelength of incident light were calculated by the equation: \( AQE = 2 \times \frac{n(\text{the molar number of evolved } H_2)}{n(\text{the number of incident photons})} \times 100\% \). Band-pass filters (425±12 nm, 448±18 nm, 478±18 nm, 512±25 nm, 527±25 nm, 549±25 nm, and 600±30 nm) in addition with a L42 cutoff filter were used to obtain the incident light with fixed wavelength region. The light intensities were measured via spectroradiometer (Avasolar-1, USA).

**Fig. S1** Surface structures of the {121} (a) and {211} (b) surfaces of brookite TiO₂.
Table S1 The light intensities of the visible light ($\lambda > 400$ nm) and the monochromatic light centered at various wavelength region used in the AQE test.

<table>
<thead>
<tr>
<th>Wavelength (nm)</th>
<th>$&gt;400$</th>
<th>425</th>
<th>448</th>
<th>478</th>
<th>512</th>
<th>527</th>
<th>549</th>
<th>600</th>
</tr>
</thead>
<tbody>
<tr>
<td>Light intensity (mW·cm$^{-2}$)</td>
<td>338</td>
<td>1.8</td>
<td>3.2</td>
<td>11.9</td>
<td>8.3</td>
<td>16.6</td>
<td>17.6</td>
<td>20.0</td>
</tr>
</tbody>
</table>

**Photoelectrochemical measurements**

The photoelectrochemical properties were investigated in a three-electrode cell (Au@TiO$_2$ anode: working electrode; Pt foil: counter-electrode; Ag/AgCl electrode: reference electrode) by using a CHI electrochemical station (ALS/CH model 660E) with 0.1 M Na$_2$SO$_4$ aqueous solution as electrolyte. A 500 W Xe arc lamp equipped with a L42 cutoff filter was utilized as light source. Mott-Schottky plots were converted from the Impedance-Potential test at 100 Hz. Electrochemical impedance spectra were measured at an applied potential of 0.3 V over the frequency range of 1 MHz to 0.01 Hz.
Fig. S3 Points of measured flat band potentials with error bars were constructed using the standard deviation to the average of three repeated experiments.

Fig. S4 TEM images of Au@T_{121} (a) and Au@T_{211} (b).

References