Supporting Information

Surface Plasmon Resonance Enhanced Photoelectrochemical Water Splitting from Au Nanoparticle-Decorated 3D TiO$_2$ Nanorod Architectures

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Author Contributions

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Table S1. The wt % of Au corresponding to different sputtering times.

<table>
<thead>
<tr>
<th>Sputtering time (s)</th>
<th>1</th>
<th>3</th>
<th>5</th>
<th>10</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au wt%</td>
<td>3.06±0.19</td>
<td>4.04±0.13</td>
<td>5.67±0.21</td>
<td>11.75±0.27</td>
</tr>
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</table>

Figure S1. HRTEM image of a single TiO$_2$ NR decorated with Au NPs. A sharp interface between Au NPs and TiO$_2$ NRs can be observed.
Figure S2. Wagner plot showing the modified auger parameters of Au in all Au NP-3D branched TiO$_2$ NR architectures. The Au chemical states in Au-TiO$_2$ composites lie almost at the same position of metallic Au$^1$ (black dot).
**Figure S3.** Top-view SEM images of Au NP-3D branched TiO$_2$ NR architectures with different sputtering time.
Figure S4. EDS spectra of Au NP-3D branched TiO$_2$ NR architectures with different sputtering time.
Figure S5. Stability evaluation of pristine 3D TiO$_2$ NR photoelectrode measured in 1 M NaOH solution with AM 1.5G illumination.

Figure S6. $J_{ph}$-V curves of TiO$_2$-3s Au samples with 1.42 mm$^2$ and 21 mm$^2$ active areas obtained under AM 1.5G illuminations. Very similar PEC behavior was observed.
Figure S7. $J_{ph}-V$ curves of pristine TiO$_2$ and TiO$_2$-3s Au photoanodes recorded in 1 M NaOH solution with 430 nm light filter.

S8: Analysis of electron transfer efficiency, rate and number
1) **Electron transfer efficiency from Au to TiO\textsubscript{2}**

The corresponding electron transfer efficiencies can be determined by the solar to hydrogen (STH) efficiency which were estimated using following equation \(^2\):

\[
\eta \%= \left[ \frac{I_{ph}}{J_0} \right] \left( E_{rev}^0 - |E_{bias} - E_{aoc}| \right) \times 100
\]

where \(E_{bias}\) is the bias potential, \(E_{rev}^0 = 1.23\ V\) is the standard state reversible potential for water-splitting reactions, and \(E_{aoc} = V_{oc}\) is the open circuit voltage (vs. SCE).

![Graph showing efficiency vs. voltage](image)

**Figure S8.** Calculated efficiencies of Au-X-TiO\textsubscript{2} NR photoanodes measured under visible light illumination.

**Table S2.** Maximal PEC Efficiency of Au-X-TiO\textsubscript{2} NR Architectures Measured under visible light.

<table>
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</tr>
</thead>
<tbody>
<tr>
<td>(\eta %)</td>
<td>0.021±1.9E-4</td>
<td>0.036±2.1E-4</td>
<td>0.034±2.2E-4</td>
<td>0.029±2.0E-4</td>
</tr>
</tbody>
</table>

2) **The calculation of electron transfer rate and transfer number**
From the $J$-$V$ curve, the positive current density started at $V_{oc}$ represents the beginning of water oxidation in which a number of charges passed through the active surface of photoanode. Under the visible light, the water oxidation reaction was only induced by the electrons which were produced on the Au and transferred to TiO$_2$.

Because: 
\[
J(t) = \frac{I(t)}{A} = \frac{1}{A} \frac{dQ}{dt}
\]

Where $J$ is the measured current density, $A$ is the exposed active area of photoanode, and $Q$ is the charges transferred through the active surface.

Thus, the transferred charge through the unit photoanode surface for water oxidation is:

\[
\sigma = \frac{Q}{A} = \frac{1}{A} \int_{Q_0}^{Q_1} dQ = \frac{1}{A} \int_{t_0}^{t_1} J(t) dt
\]

Where the $Q_0$ and $Q_1$ are the charges transfer through the active surface corresponding to $t_0$ and $t_1$, respectively.

Read data $(V_0, J_0)$ at $t_0$ and $(V_1, J_1)$ at $t_1$ on the $J$-$V$ curve. The water oxidation just started at $t_0$. Thus, let $t_0 = 0 \text{ s}$, $Q_0 = 0 \text{ C}$, $V_0 = V_{oc}$, $J_0 = 0 \text{ mA cm}^{-2}$.

When the potential scans to $V_1$, the $t_1$ can be achieved by $(V_1-V_0)/S$. $S$ is the potential scan speed (0.05V/s) of our $J$-$V$ measurement. In order to make the comparison of each electrode, the $t_1$ was kept as a constant.

By putting the above quantity values into equation (3), the transferred charges through the unit photoanode surface ($\sigma \text{ (C cm}^{-2})$) can be obtained. One electron has the
charge $1.6 \times 10^{-19}$ C. Therefore, the number of transferred electrons through the unit photoanode surface:

$$N_e = \sigma/(1.6 \times 10^{-19})$$  \hspace{1cm} (4)

Let $t = t_1 - t_0$, finally, the electron transfer rate: $v_{et} = N_e / t$. (/s·cm$^2$) \hspace{1cm} (5)

3) The calculation results

Based on Figure 2c and the above equations (4) and (5), the calculated electron transfer rate from Au to TiO$_2$ of four Au-TiO$_2$ photoanodes under visible light are compared in Table S3

**Table S3.** The calculated electron transfer rate from Au to TiO$_2$ of four Au-TiO$_2$ photoanodes under visible light.

<table>
<thead>
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</tr>
</thead>
<tbody>
<tr>
<td>$v_{et}$ (/S·cm$^2$)</td>
<td>1.319×10$^{14}$</td>
<td>2.306×10$^{14}$</td>
<td>2.196×10$^{14}$</td>
<td>1.942×10$^{14}$</td>
</tr>
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</table>

In addition, the total electron transfer number through the unit photoanode surface in the potential scan duration $t = t_1 - t_0$ were calculated by using the data from Figure 2b (AM 1.5 G illumination), Figure 2c (visible light illumination) and equation (4). The results are compared in Table S4.

**Table S4.** The total electron transfer number through the unit photoanode surface in the potential scan duration $t = t_1 - t_0$.

<table>
<thead>
<tr>
<th>Sputtering Time (s)</th>
<th>0</th>
<th>1</th>
<th>3</th>
<th>5</th>
<th>10</th>
</tr>
</thead>
<tbody>
<tr>
<td>$N_e$ (/cm$^2$) AM1.5G</td>
<td>3.661×10$^{17}$</td>
<td>4.698×10$^{17}$</td>
<td>5.659×10$^{17}$</td>
<td>5.471×10$^{17}$</td>
<td>4.821×10$^{17}$</td>
</tr>
</tbody>
</table>
Figure S9. a., b. \(J_{ph-V}\) curves for Au NP-decorated 3D TiO\(_2\) NR architectures made from 3s sputtering (pink) and Au colloidal solution method (purple). The photocurrent was recorded under dark, AM 1.5G illuminations a. and visible light illumination b.. c. EDS spectra of Au NP-3D branched TiO\(_2\) NR architecture prepared by colloidal solution method. The amount of decorated Au NPs was 3.97±0.26 wt%. d. Top-view SEM images of Au NP-3D branched TiO\(_2\) NR architecture prepared by colloidal
solution method. Inset is a high magnification SEM image showing the distribution of Au NPs. The size of Au NP prepared by the colloidal solution method was about 8 nm, which was the same as that prepared by 3s Au sputtering.

**Figure S10.** a. Diffuse reflectance UV-visible absorption spectra of the Au NP-3D branched TiO₂ NR samples with different sputtering times. b. Digital photo of the Au
NP-3D branched TiO$_2$ NR samples with different sputtering times showing different color in air.

References:
