

Supporting Information

Surface Plasmon Resonance Enhanced Photoelectrochemical Water Splitting from Au Nanoparticle-Decorated 3D TiO₂ Nanorod Architectures

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Author Contributions

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

	sample			
Sputtering time (s)	1	3	5	10
Au wt%	3.06±0.19	4.04±0.13	5.67±0.21	11.75±0.27

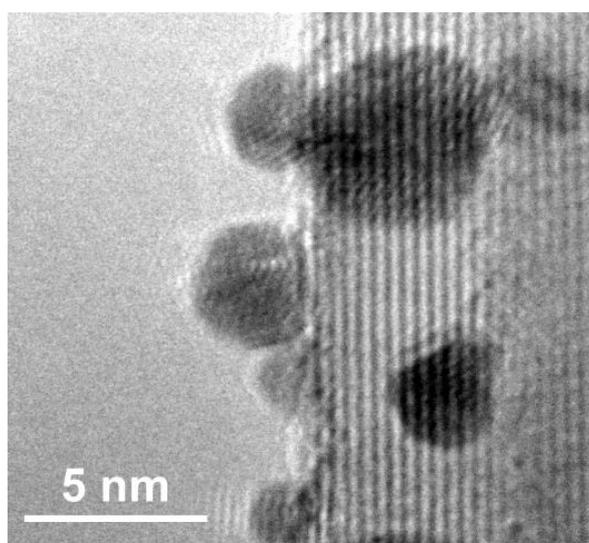


Figure S1. HRTEM image of a single TiO₂ NR decorated with Au NPs. A sharp interface between Au NPs and TiO₂ NRs can be observed.

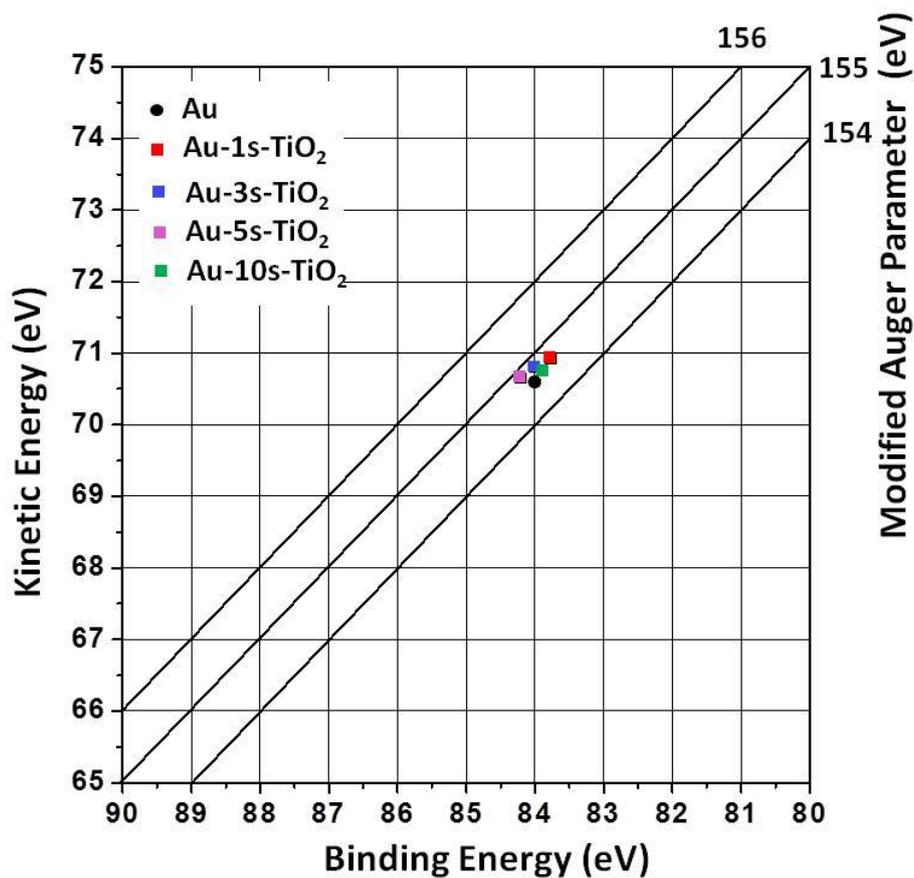


Figure S2. Wagner plot showing the modified auger parameters of Au in all Au NP-3D branched TiO₂ NR architectures. The Au chemical states in Au-TiO₂ composites lie almost at the same position of metallic Au¹ (black dot).

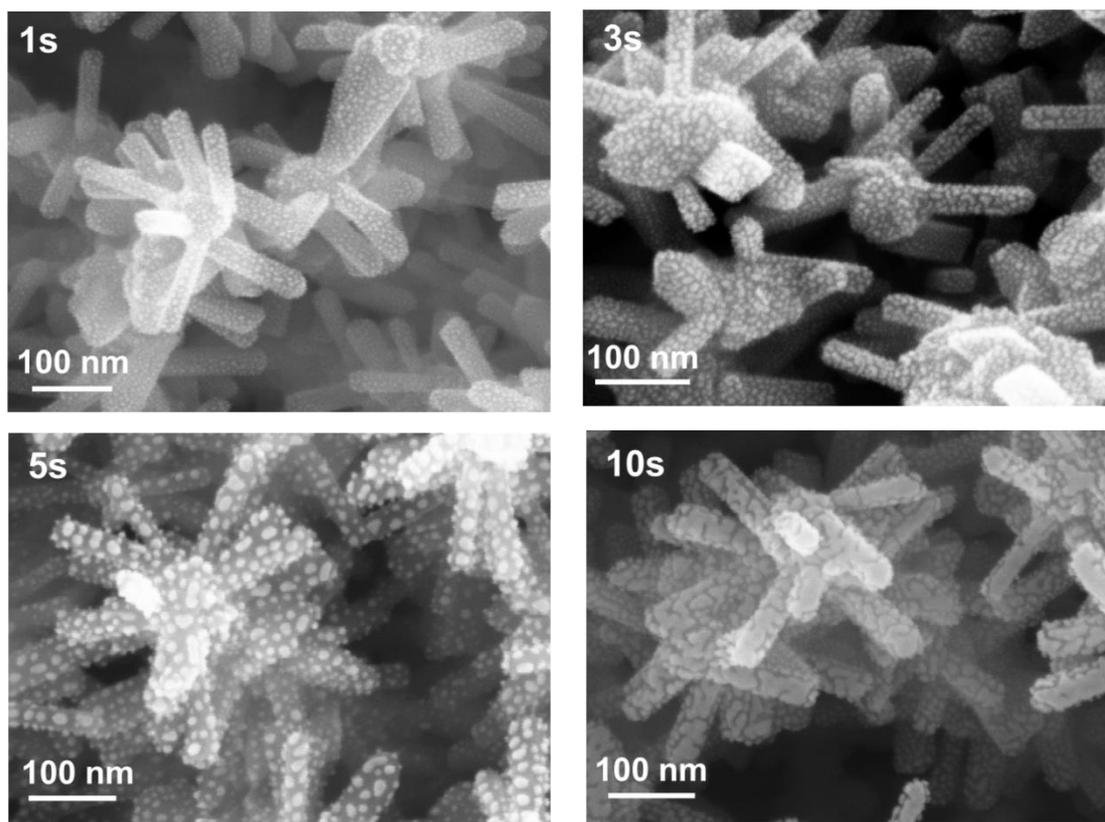


Figure S3. Top-view SEM images of Au NP-3D branched TiO₂ NR architectures with different sputtering time.

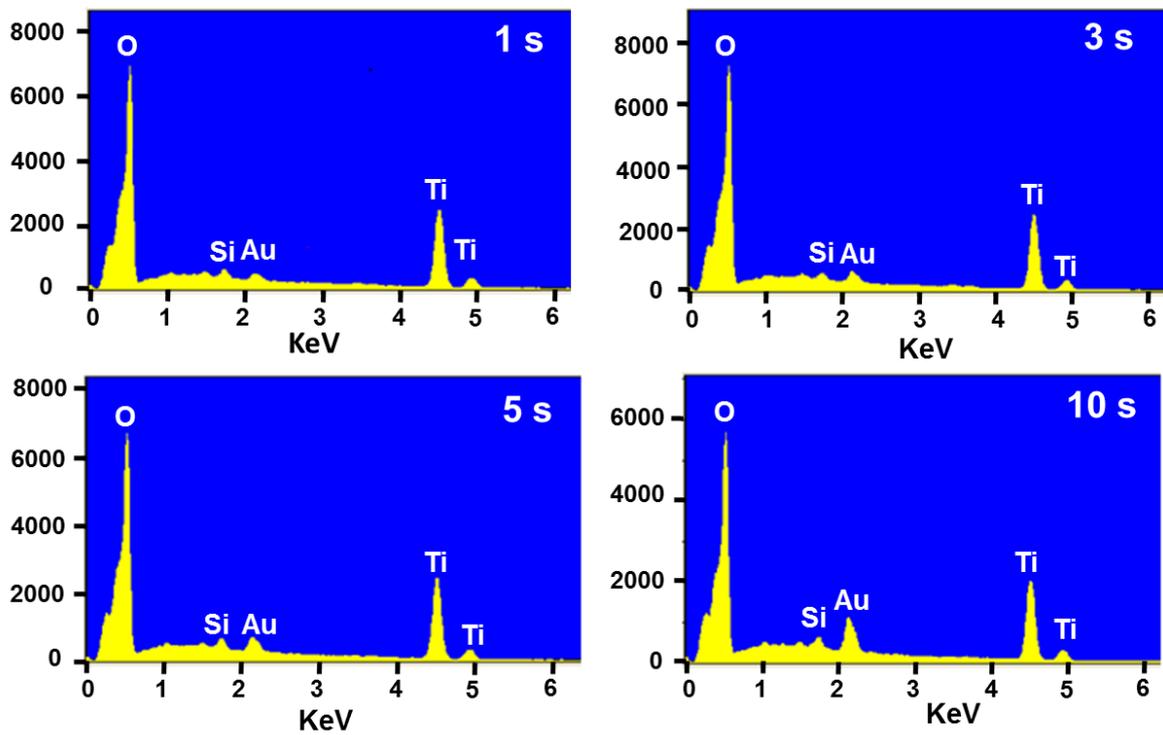


Figure S4. EDS spectra of Au NP-3D branched TiO₂ NR architectures with different sputtering time.

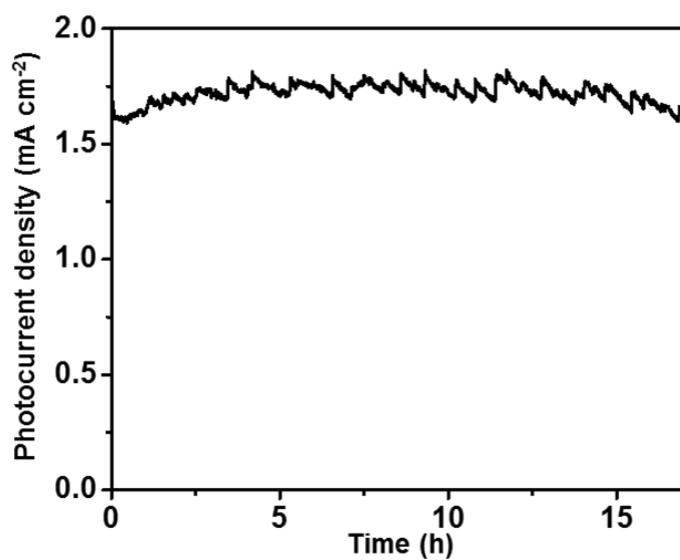


Figure S5. Stability evaluation of pristine 3D TiO₂ NR photoelectrode measured in 1 M NaOH solution with AM 1.5G illumination.

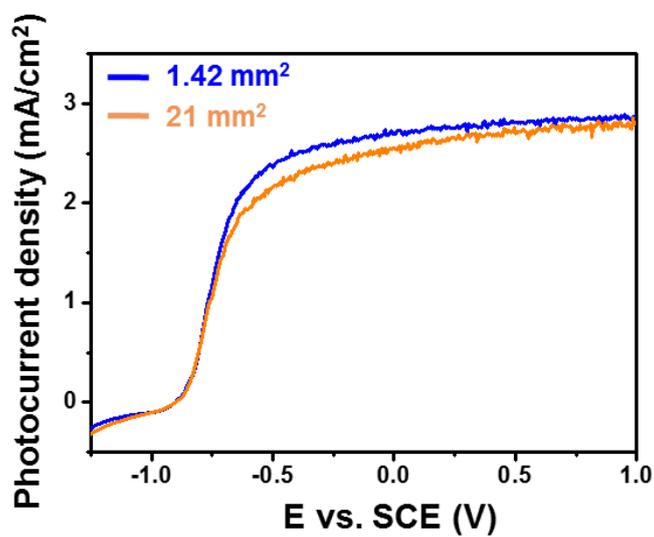


Figure S6. J_{ph} -V curves of of TiO₂-3s Au samples with 1.42 mm² and 21 mm² active areas obtained under AM 1.5G illuminations. Very similar PEC behavior was observed.

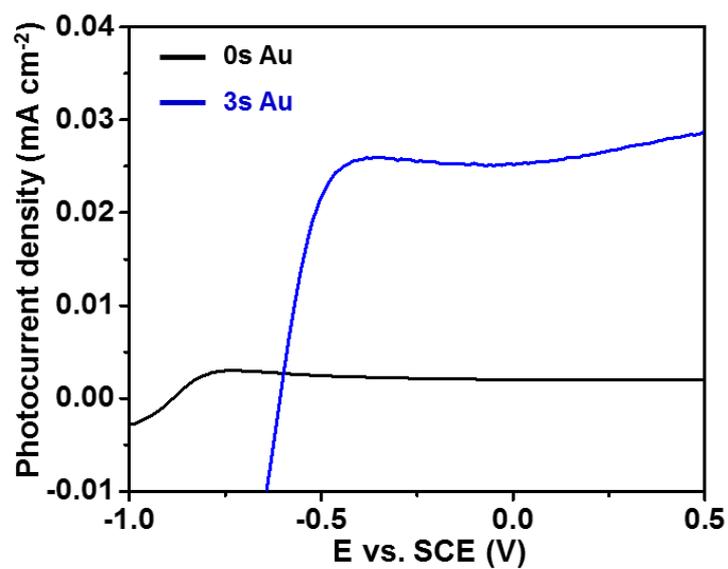


Figure S7. J_{ph} - V curves of pristine TiO_2 and TiO_2 -3s Au photoanodes recorded in 1 M NaOH solution with 430 nm light filter.

S8: Analysis of electron transfer efficiency, rate and number

1) Electron transfer efficiency from Au to TiO₂

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

$$\eta\% = \left[J_{ph} (E_{rev}^0 - |E_{bias} - E_{aoc}|) \frac{100}{I_0} \right]$$

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).

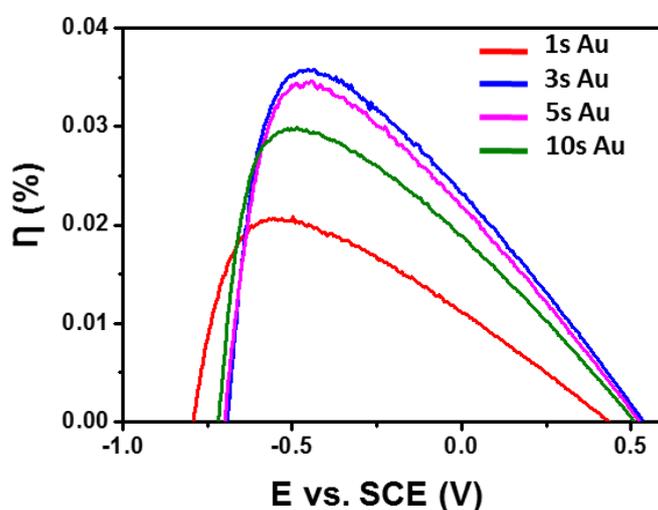


Figure S8. Calculated efficiencies of Au-X-TiO₂ NR photoanodes measured under visible light illumination.

Table S2. Maximal PEC Efficiency of Au-X-TiO₂ NR Architectures Measured under visible light.

Sputtering Time (s)	1	3	5	10
η (%)	0.021±1.9E-4	0.036±2.1E-4	0.034±2.2E-4	0.029±2.0E-4

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 .

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

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 $t_0 = 0$ s, $Q_0 = 0$ C, $V_0 = V_{oc}$, $J_0 = 0$ 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 (σ (C cm^{-2})) can be obtained. One electron has the

charge 1.6×10^{-19} C. Therefore, the number of transferred electrons through the unit photoanode surface:

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

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

3) The calculation results

Based on Figure 2c and the above equations (4) and (5), the calculated electron transfer rate from Au to TiO₂ of four Au-TiO₂ photoanodes under visible light are compared in Table S3

Table S3. The calculated electron transfer rate from Au to TiO₂ of four Au-TiO₂ photoanodes under visible light.

Sputtering Time (s)	1	3	5	10
v_{et} (/S-cm ²)	1.319×10^{14}	2.306×10^{14}	2.196×10^{14}	1.942×10^{14}

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 $t = t_1 - t_0$.

Sputtering Time (s)	0	1	3	5	10
N_e (/cm ²) AM1.5G	3.661×10^{17}	4.698×10^{17}	5.659×10^{17}	5.471×10^{17}	4.821×10^{17}

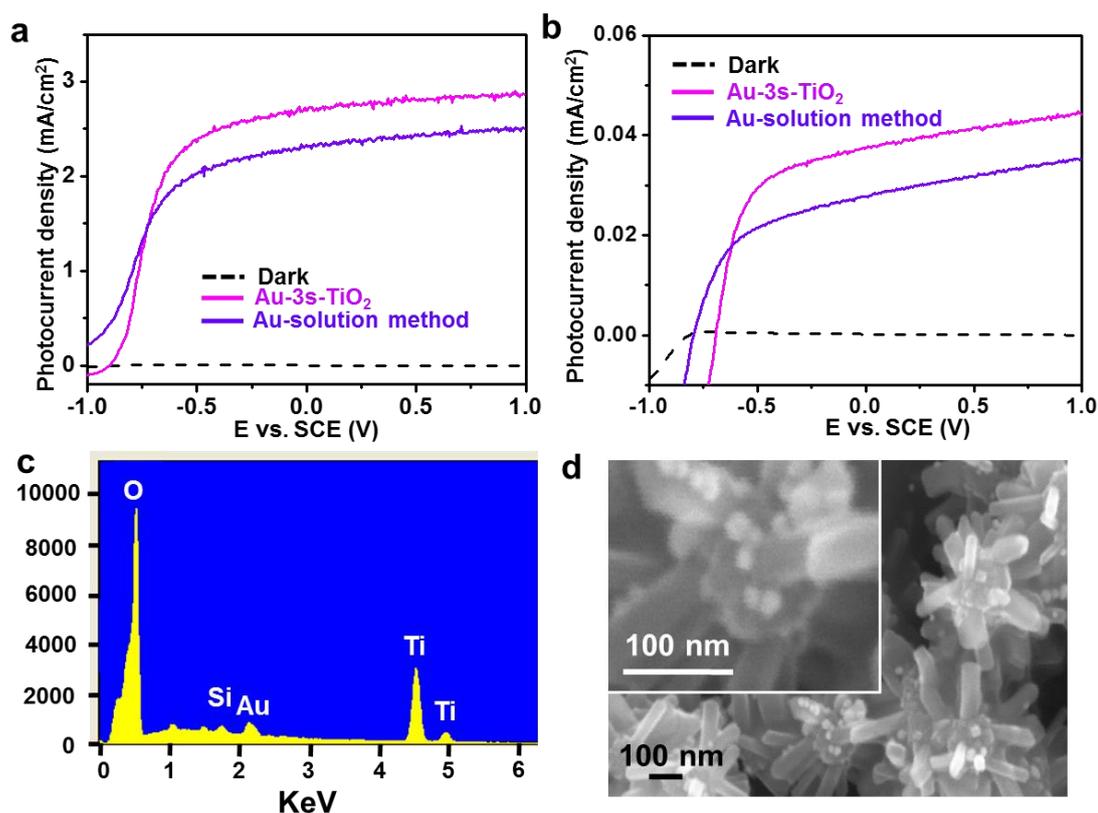


Figure S9. **a.**, **b.** J_{ph} - V curves for Au NP-decorated 3D TiO₂ NR architectures made from 3s sputtering (pink) and Au colloidal solution method (purple). The photocurrent was recorded under dark, AM 1.5G illuminations **a.** and visible light illumination **b.** **c.** EDS spectra of Au NP-3D branched TiO₂ 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 TiO₂ 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.

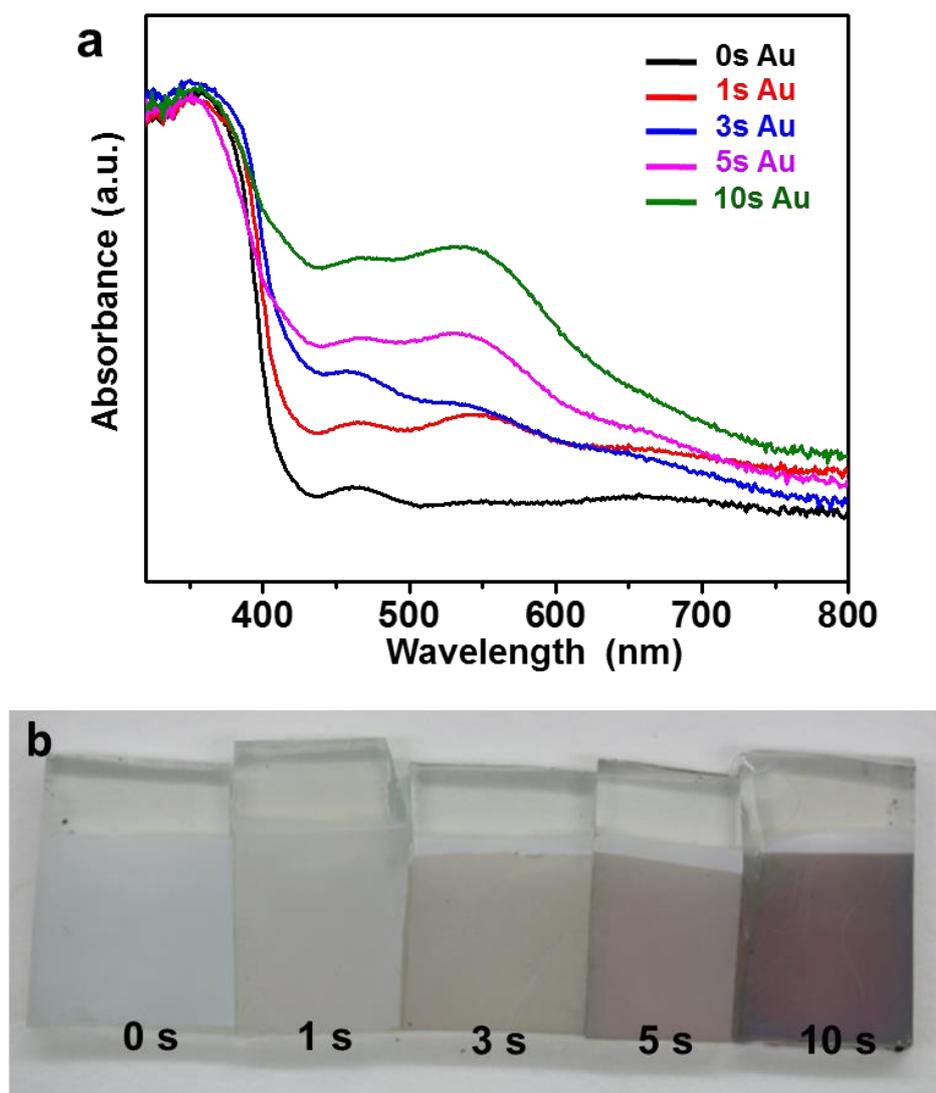


Figure S10. a. Diffuse reflectance UV-visible absorption spectra of the Au NP-3D branched TiO₂ NR samples with different sputtering times. **b.** Digital photo of the Au

NP-3D branched TiO₂ NR samples with different sputtering times showing different color in air.

References:

(1) John F. Moulder; William F. Stickle; Peter E. Sobol; Kenneth D. Bomben. Handbook of X-ray Photoelectron Spectroscopy, Physical Electronics, Inc., USA, **1992**.

(2) Li, Z.; Yao, C.; Yu, Y.; Cai, Z.; Wang, X. Highly Efficient Capillary Photoelectrochemical Water Splitting Using Cellulose Nanofiber-Templated TiO₂ Photoanodes. *Adv Mater* **2014**, *26*, 2262-2267.