

Electronic Supplementary Information
for
Water Splitting Using a Three-dimensional
Plasmonic Photoanode with Titanium Dioxide Nano-
tunnels

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1. Au-NPs deposited on the thin film TiO₂

TiO₂ thin films were prepared onto silica glass substrates with a size of 10 × 10 × 0.5 mm³ (Pier Optics, Japan) using hot-wall flow-type atomic layer deposition ALD reactor (SUNALETM R series, Picosun, Finland) by reported procedure.¹ The deposition procedure involved alternating exposure of TiCl₄ and deionized water vapor at a process temperature of 300 °C with N₂ as a precursor carrier and purge gas at a pressure of 1.6 kPa. The pulse and purge times for the precursors were 0.1 and 4 s, respectively. The thickness of deposited TiO₂ film was ca. 230 nm. Au-NPs were deposited in the same way written in the experimental section of the main text using HAu(OH)₄ as a precursor. The reduction cycle (immersion into the precursor solution, NaBH₄ solution and pure water) was varied from 3 to 10 cycles.

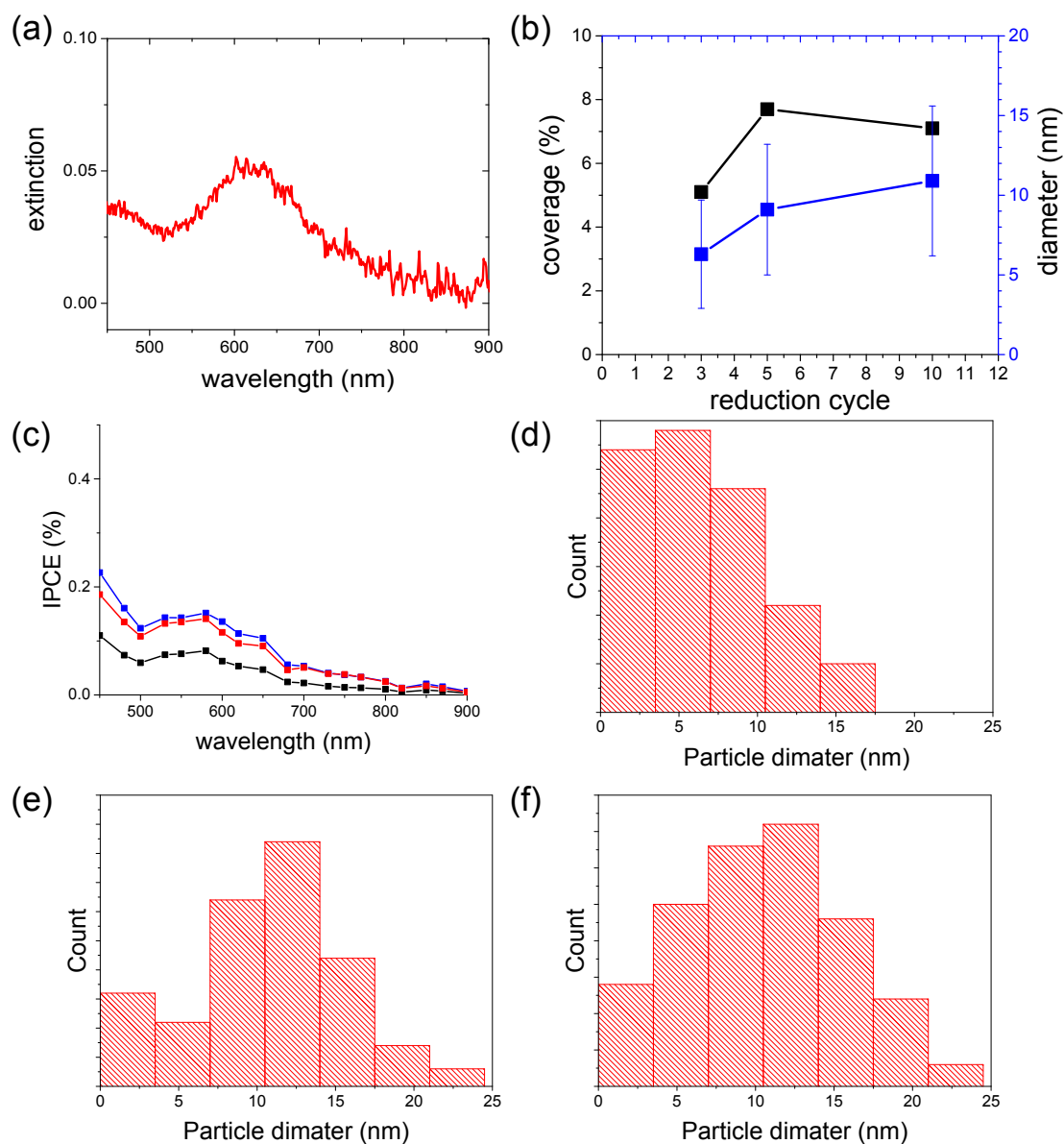


Figure S1. (a) The extinction spectrum of Au-NPs on TiO₂ with 10 reduction cycles. (b) The reduction cycle dependencies of the coverage of TiO₂ substrate with gold and diameter of Au-NPs. (c) The IPCE action spectra of Au-NPs on TiO₂ with different reduction cycles; 3 cycles (black), 5 cycles (blue) and 10 cycles (red). (d-e) The particle size distribution of Au-NPs on TiO₂ with 3 (d), 5 (e), 10 (f) reduction cycles.

2. Synthesis of HAu(OH)_4 and $\text{Au(en)}_2\text{Cl}_3$

HAu(OH)_4 : 2 mL of an aqueous solution of $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$ (10 mol dm^{-3}) and 1.4 mL of NaOH aqueous solution (pH 13) was mixed to the volume ratio of 1.0:0.7. Then, 16.6 mL of NaOH aqueous solution (pH 10) was added into the solution. After standing 24 h, the solution was used for the deposition.

$\text{Au(en)}_2\text{Cl}_3$: $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$ 1.0 g (2.4 mmol) was dissolved in 10 mL of ultrapure water. 0.45 mL of ethylenediamine (8.3 mmol) was poured into the solution under the stirring. After stirring for 30 min, the mixed solution was poured into 70 mL of ethanol to form precipitate. The precipitate was corrected by the filtering and dried under vacuum at r.t. to give 0.61 g (1.5 mmol, 61%) of $\text{Au(en)}_2\text{Cl}_3$ as a white solid. 2 mL an aqueous solution of $\text{Au(en)}_2\text{Cl}_3$ (10 mol dm^{-3}), 4.5 mL of NaOH aqueous solution (pH 13) and 16.6 mL of NaOH aqueous solution (pH 10) were mixed to use the deposition.

3. Statistical analysis of the Au-NPs deposited on the wall of TNTs

Figure S2a shows a cross-sectional STEM image of the Au-NPs/TNTs prepared from HAuCl_4 . Cross-sectional STEM images of the Au-NPs/TNTs shown in Figure 5 and Figure S2a were used for statistical analysis based on the usage of free software ImageJ (<http://rsb.info.nih.gov/ij/>). Figure S2 b and c depicts The particle size distribution of Au-NPs on TNTs. Table S1 depicts average diameter of Au-NPs, standard deviation of the diameters of Au-NPs, and the coverage of TNT surface by Au-NPs.

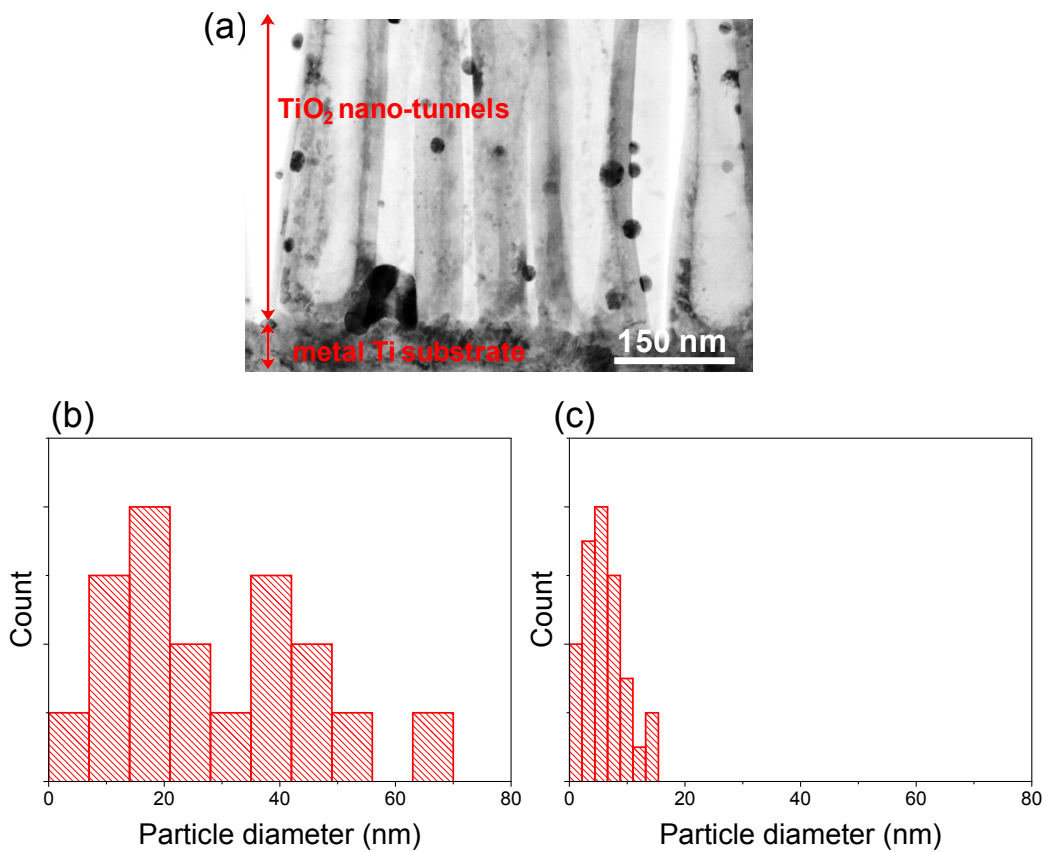


Figure S2. (a) A cross-sectional STEM image of the Au-NPs/TNTs prepared from HAuCl_4 . (b, c) The particle size distribution of Au-NPs on TNTs prepared from HAuCl_4 (b) and HAu(OH)_4 (c).

Table S1. Statics parameters of Au-NPs deposited on the wall of TNTs

Precursor	Average diameter of Au-NPs (nm)	Standard deviation of the diameters (nm)	Coverage of TNT surface by Au-NPs (%)
HAuCl ₄	28.5	17.0	13.3
HAu(OH) ₄	6.3	2.9	6.3

4. A numerical simulation using a finite-difference time-domain (FDTD) method

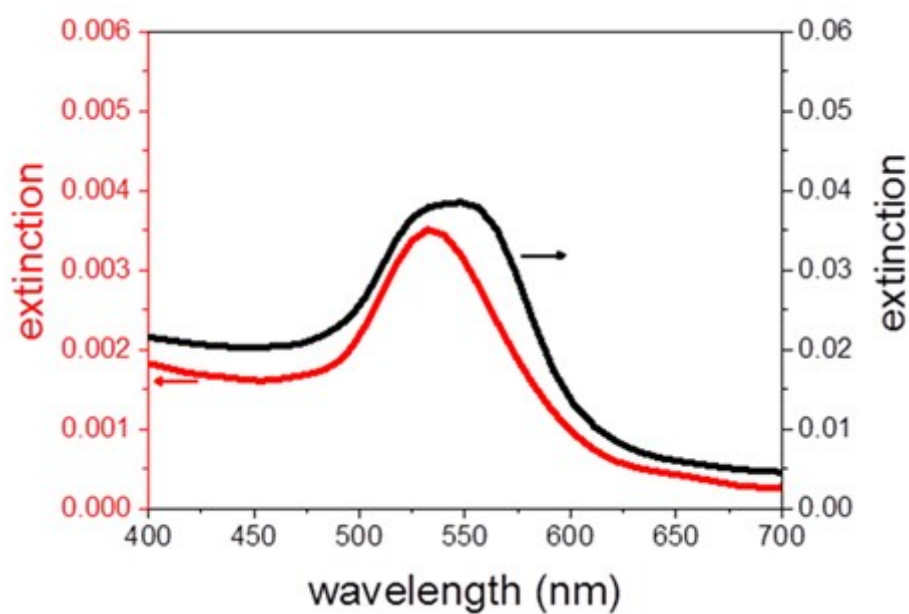


Figure S3. The extinction spectra of Au-NPs on TiO₂ substrate calculated by the FDTD numerical simulations. The lines in black and red indicate Au-NPs with the diameters of 28.5 nm and 6.3 nm, respectively

5. Statistical analysis of the Au-NPs deposited on the wall of TNTs

The photoelectrochemical reaction was promoted by the use of aqueous solution of 0.1 mol dm⁻³ KClO₄ including 7% of H₂¹⁸O. The evolved O₂ was identified by GC-mass spectrometry.

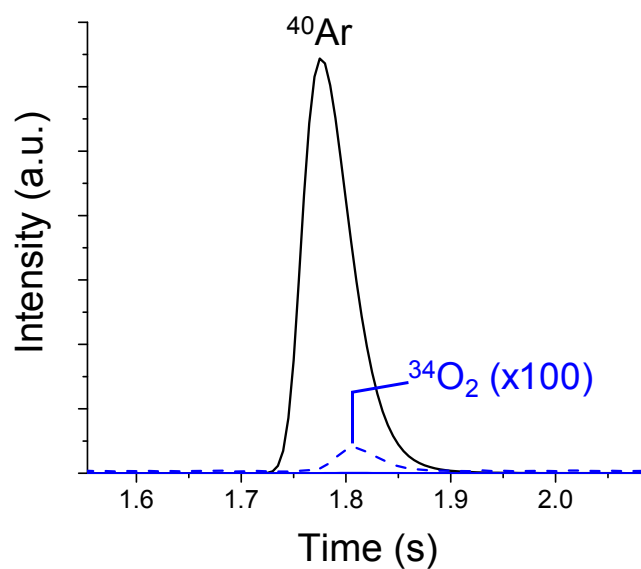


Figure S4. GC-MS chromatograph of the sample after 1 h of irradiation time (black: $m/z = 40$, and blue: $m/z = 34$).

6. Stability check of the photoanode

The stability was checked by accumulating electricity during the photoreaction using two electrode system as shown in Figure S5. Also, number of Au atoms can be calculated as 1.8 nmol from following parameters, and the value is much smaller than that of evolved oxygen molecules. Surface area of TNTs :4.24 cm², cross-sectional area of Au: 0.267 cm², average diameter of Au-NP: 6.3 x10⁻⁷ cm, number of Au-NPs: 8.57 x10¹¹, volume of an Au-NP (approximated as hemisphere): 2.08 x10⁻²⁰ cm³, volume of net Au-NPs 1.78 x10⁻⁸ cm³

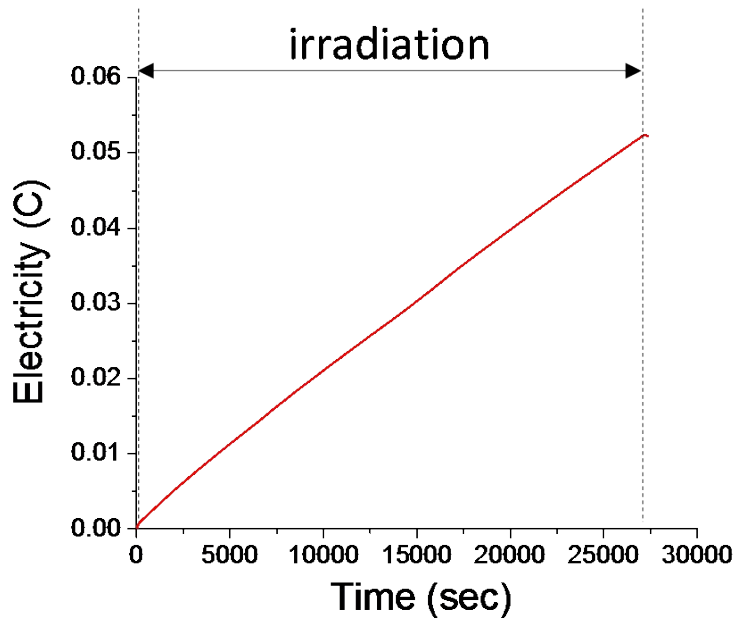


Figure S5. The accumulative electricity during the irradiation to Au-NPs/TNTs. The bias for the measurement was 0 V between two electrodes, and an AM 1.5 G solar simulator was used as the light source.

References

1. X. Shi, K. Ueno, T. Oshikiri and H. Misawa, *J. Phys. Chem. C*, 2013, **117**, 24733-24739.