Supporting Information

Probing the Advantageous Photosensitization Effect of Metal Nanoclusters over Plasmonic Metal Nanocrystals in Photoelectrochemical Water Splitting

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Table of Contents

Page No.

Experimental section
Fig. S1. Molecular structure of GSH ligand
Fig. S2. UV-vis absorption, Zeta potential and TEM images of Au _x clustersS8
Fig. S3. Kubelka–Munk function vs. the energy of light for TNTAs and TNTAs-Au _x S9
Fig. S4. XPS spectra of TNTAsS10
Table S1. Chemical bond species vs. B.E. for different photoanodeS11
Fig. S5. FESEM and EDS images of TNTAsS12
Fig. S6. TEM images of TNTAs-Au _x
Fig. S7. I-t results of TNTAs-Au _x by modulating the dipping time and annealing temperatureS14
Fig. S8. The magnified LSV and ABPE results of different photoanodeS15
Table S2. Fitted EIS results of different photoanodes
Fig. S9. DRS spectra of Au _x NCs and Au NPs and photocurrent of TNTAs-Au _x and TNTAs-AuS17
Fig. S10. UV-vis absorption, Zeta potential and TEM images of Au ₂₅ clustersS18
Fig. S11. TEM image of TNTAs-Au ₂₅ and TNTAs-Au with corresponding sample color changeS19
Fig. S12. LSV and I-t results of TNTAs-Au ₂₅ , TNTAs-Au and TNTAsS20
Fig. S13. PL spectra of TNTAs, TNTAs-Au and TNTAs-Au _x S21
Fig. S14. CV curves of Au _x @GSH clusters
References

Experimental section

1.1 Materials

Ethylene glycerol (CH₂OH)₂, Ammonium fluoride (NH₄F), Hydrogen fluoride (HF), Nitric acid (HNO₃), Ethanol absolute (C₂H₅OH), Sodium sulfate (Na₂SO₄), were all obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Gold chloride trihydrate (HAuCl₄ 3H₂O), L-Glutathione (reduced, \geq 98.0%) were obtained from Aladdin Co., Ltd. (Shanghai, China). Titanium sheet (50 mm × 20 mm × 0.1 mm, 99.9%), Deionized water (DI H₂O, Millipore, 18.2 MΩ·cm resistivity), Graphite sheet (50 mm × 20 mm × 0.1 mm, 99.6%. All the chemicals were analytic grade and used as received without further purification.

1.2 Preparation of TNTAs substrate

Ti foil was thoroughly cleaned by sonication in acetone, ethanol and DI H₂O, respectively. Then, Ti sheets were immersed into a mixed solution of HF-HNO₃-H₂O in a volume ratio of 1 : 4 : 5 for 30 s, washed by DI H₂O and dried with a gentle N₂ stream. Anodization was carried out under ambient conditions at 50 V for 2 h with ca. 3 cm separation distance between the working (Ti foil) and counter electrode (graphite). The electrolyte consists of 0.3 wt % of NH₄F (0.6 g) in ethylene glycol (196 mL) and DI H₂O (4 mL). After anodization, surface layer was removed from Ti foil by sonication in ethanol for 5 min. A second anodization was performed at 50 V for 30 min to produce the TNTAs which was also washed by DI H₂O, dried with a N₂ stream and finally calcined at 450 °C for 3 h in air with a heating rate of 5 °C min⁻¹.

1.3 Preparation of Aux@GSH nanoclusters

Au_x@GSH nanoclusters were synthesized by a published method with a slight modification.^{S1} Briefly, gold(III) chloride trihydrate (40 mg) and L-glutathione (GSH, 46 mg) were thoroughly mixed in 50 mL of DI H₂O at

ambient conditions. The mixture was continuously stirred until the appearance of a colorless solution and then heated at 70 °C for 24 h. Subsequently, acetonitrile was added to the cluster solution to purify the clusters followed by washing several times with mixed solution of DI H_2O and acetonitrile (1:3 in volume). Finally, the clusters were re-dissolved in DI H_2O and stored at ambient conditions.

1.4 Preparation of Au₂₅(GSH)₁₈ nanoclusters

Glutathione-protected Au_x nanoclusters was prepared according to the method reported previously with some modifications.^{S2} Briefly, glutathione (reduced form, 1 mmol) was added to methanol (50 mL) containing HAuCl₄·3H₂O (0.25 mmol). Under vigorous stirring, an ice-cold NaBH₄ aqueous solution (0.2 M, 12.5 mL) was added and aged for 1 h. The obtained precipitate was thoroughly washed with methanol and dried in vacuum at room temperature to obtain a mixture of gold clusters. The mixture (4.9 mg) was dissolved in an aqueous solution (7 mL) containing glutathione (130.7 mg) and stirred at 55 °C under air bubbling for 6-9 h to obtain Au₂₅(GSH)₁₈ nanoclusters. To remove excess glutathione, the obtained solution containing the Au₂₅(GSH)₁₈ nanoclusters was loaded into a dialysis membrane (MWCO 8000) and stirred slowly at <10 °C for 12 h. The precipitate formed during the dialysis was removed with a filter (pore size, 0.2 µm). It was confirmed by polyacrylamide gel electrophoresis that the obtained solution contains no other clusters.

1.5 PEC water splitting measurements

Potentials of the electrodes were calibrated against the reversible hydrogen electrode (RHE) based on the formula below:

$$E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.059 \text{pH} + E^{\circ}_{\text{Ag/AgCl}} (E^{\circ}_{\text{Ag/AgCl}} = 0.1976 \text{ V at } 25 \text{ }^{\circ}\text{C})$$

The scan rate for linear sweep voltammogram (LSV) measurements was 5 mV s⁻¹ and photocurrent responses (*i.e.*, I-t) of different electrodes were collected under chopped light irradiation (light on/off cycle:

10 s) at a fixed bias of 0.61 V vs. RHE. Electrochemical impedance spectra (EIS) were measured on an IM6 electrochemical station (Interface 1000E, Gamry, America) with an amplitude of 10 mV in the frequency range of 10^5 to 0.1 Hz. Monochromatic incident photon-to-electron conversion efficiency (IPCE) spectra were collected using a three-electrode configuration under a bias of 0.61 V vs. RHE, for which monochromatic light was provided by a 300 W xenon arc lamp combined with different monochrome filters with wavelength ranging from 365 to 700 nm. Electrolyte for Cyclic voltammogram (CV) measurements was composed of 0.1 M tetraethylammonium perchlorate (TEAP) in acetonitrile (C₂H₃N) and purged with N₂ in a sealed vial for 10 min prior to use. CV measurements were performed using a three-electrode system with glass carbon disk, platinum gauze and Ag/AgCl (0.54 V vs. RHE) as the working, counter and reference electrode, respectively. CV curves were collected by sweeping at 0.1 V s⁻¹ in a mixed C₂H₃N/ TEAP (0.1 M) aqueous solution with adding designated volume (800 and 1000 μ L) of Au_x@GSH clusters aqueous solution.

Scan rate for linear sweep voltammogram (LSV) measurements was 5 mV s⁻¹ and photocurrent responses (*i.e.*, I-t) of different electrodes was collected under chopped light irradiation (light on/off cycle: 10 s) at a fixed bias of 0.61 V *vs*. RHE. Based on the LSV results, applied bias photon-to-current efficiency (ABPE) of the photoelectrodes can be calculated using the following formula:^{S3}

$$\eta$$
 (%)= $I(E_{rev}^{\circ} - V)/J_{light}$

where η is the photoconversion efficiency, *I* is the photocurrent density (mA cm⁻²), *J*_{light} is the incident light irradiance (mW cm⁻²), *E* °_{rev} is the standard reversible potential which is 1.23 V vs. RHE, and V is the applied bias potential vs. RHE. According to Mott-Schottky (M-S) results charge carrier density (N_D) of the photoanodes can be calculated according to the following formula:^{S4}

$$N_d = (2/e\epsilon\epsilon_0) [d(1/C^2)/d(U_s)]^{-1}$$

where N_d is the carrier density, e is the electron charge, ε_0 is the permittivity of vacuum, ε =48 for anatase TiO₂, U_s is the applied potential, and C is the capacitance. As per OCVD results the average electron lifetime (τ_n) can be determined according to the formula below:^{S5}

$$\tau_{\rm n} = -k_{\rm B}T/e \times ({\rm d} {\rm V}_{\rm oc}/{\rm d}t)^{-1}$$

where τ_n represents the electron lifetime, k_B is the Boltzman constant, *T* is the temperature, e is the electron charge, and V_{oc} is the open-circuit voltage. Electrochemical impedance spectra (EIS) were measured on an IM6 electrochemical station (Interface 1000E, Gamry, American) with an amplitude of 10 mV in the frequency range of 10⁵ to 0.1 Hz. Monochromatic incident photon-to-electron conversion efficiency (IPCE) spectra were collected using a three-electrode configuration under a bias of 0.61 V *vs*. RHE, for which monochromatic light was provided by a 300 W Xenon arc lamp combined with different monochrome filters with wavelength ranging from 365 to 700 nm.

IPCE (%)=1240 I/
$$\lambda J_{\text{light}} \times 100\%$$

where I is the photocurrent density (mA cm⁻²), λ is the incident light wavelength (nm), and J_{light} is the incident light intensity (100 mW cm⁻²).^{S6} For determining the predominant active species responsible for the photostability of photoelectrodes, tert-butyl alcohol (C₄H₁₀O, 0.1 M), benzoquinone (C₆H₄O₂, 1 mM), sodium sulfite (Na₂SO₃, 0.05 M), H₂O₂ (30%), ammonium oxalate [(NH₄)₂C₂O₄H₂O, 0.05 M], triethanolamine (C₆H₁₅NO₃, 0.05 M), sodium sulfide (Na₂S₉·H₂O, 0.05 M), lactic acid (C₃H₆O₃, 0.05 M), methanol (CH₃OH, 0.05 M), ammonium formate (HCOONH₄, 0.05 M), ammonium acetate (CH₃COONH₄, 0.05 M) were added in Na₂SO₄ aqueous solution (0.5 M, pH=6.69) for photocurrent measurements.



Fig. S1. Schematic model of Au_x@GSH clusters along with the specific molecular structure of GSH ligand.

Note: GSH ligands capped on $Au_x@GSH$ clusters provide a large number of polar functional groups, e.g. carboxyl (-COOH), amino (-NH₂), and amide (-NH-C=O) groups, among which deprotonated carboxyl groups endows $Au_x@GSH$ clusters with negatively charged surface that is beneficial for its electrostatic deposition on the TNTAs substrate. Consequently, GSH ligand of $Au_x@GSH$ clusters plays an important role in electrostatic self-assembly of TNTAs-Au_x heterogeneous.



Fig. S2. (a) UV-vis absorption spectrum of $Au_x@GSH$ clusters aqueous solution with corresponding photograph in the inset, (b) zeta potential of $Au_x@GSH$ clusters as a function of pH value, and (c) TEM image of $Au_x@GSH$ clusters with corresponding size distribution histogram in the inset.

Note: Zeta potential result indicates the Au_x@GSH clusters are negatively charged, which is mainly ascribed to the deprotonation of carboxylate groups from GSH ligands. In this regard, negatively charged surface of Au_x@GSH renders it suitable building block for self-assembly on the TNTAs substrate. The mean diameter of Au_x@GSH clusters is ca. 1.54 nm. Alternately, it should be emphasized that Au_x@GSH clusters are composed of a few gold-atom cores capped with Au-thiolate shell (1:1 ratio of Au : thiolate, having>29 gold atoms), which is remarkably different from conventional Au nanocrystals in terms of its ultra-small diameter and light-yellow color.



Fig. S3. Transformed plots of based on the Kubelka–Munk function vs. the energy of light for TNTAs and

TNTAs-Au_x.



Fig. S4. (a) Survey spectrum and high-resolution (b) Ti 2p, (c) O 1s, and (d) C 1s spectra of TNTAs substrate.

Element	TNTAs	TNTAs-Au _x	TNTAs-Au	Chemical Bond Species
C 1s A	284.6	284.6	284.6	С-С/С-Н
C 1s B	286.2	285.95	286.78	C-OH/C-O-C ^{S7}
C 1s C	288.1	287.82	288.88	Carboxyl (-COO ⁻) ^{S8}
O 1s A	529.6	529.63	529.69	Lattice Oxygen
O 1s B	531.5	531.28	N.D.	Ti-OH ^{S9}
O 1s C	532.6	533.43	N.D.	O–C–O ^{S10}
Ti 2p3/2	458.4	458.41	458.63	Anatase $(4^+)^{S11}$
Ti 2p _{1/2}	464.1	464.18	464.33	Anatase (4+)
N 1s A	N.D.	399.63	N.D.	-NH ² /-NH ^{-S12}
N 1s B	N.D.	400.88	N.D.	-NH3 ^{+S13}
N 1s C	N.D.	401.63	N.D.	N-C=O ^{S14}
Au 4f7/2A	N.D.	83.83	84.03	Au ^{0S15}
Au 4f7/2B	N.D.	84.60	N.D.	Au ^{+S16}
Au 4f _{5/2} A	N.D.	87.51	87.68	Au^0
Au 4f5/2B	N.D.	88.10	N.D.	Au^+
S 2p A	N.D.	162.48	N.D.	-SH
S 2p B	N.D.	163.83	N.D.	-SH

 Table S1. Chemical bond species vs. B.E. for different photoelectrodes.

N.D.: Not Detected.



Fig. S5. (a-b) Top-view, (c-d) cross-sectional FESEM images and (e-g) elemental mapping & (h) EDS results of TNTAs substrate.

Fig. S6. TEM images of TNTAs-Au $_x$ with different magnification.

Fig. S7. On-off transient photocurrents of TNTAs- Au_x with different (a) dipping time and subjected to different (b) annealing temperature (t=1 h, in air) along with the (c) corresponding photographs of different samples.

Note: It was unveiled in **Fig. S7a** that dipping time considerably influences the photocurrent of TNTAs-Au_x. Specifically, photocurrent of TNTAs-Au_x gradually increases with increasing the dipping time from 15 min to 3 h and subsequently, it no longer increases upon further prolonging the dipping time to 24 h. Obviously, amount of Au_x@GSH clusters deposited on the TNTAs is saturated when TNTAs was dipped into the Au_x@GSH aqueous solution for 3 h. **Fig. S7b** reveals the photocurrent of TNTAs-Au_x decreases with increasing the annealing temperature from 100 to 300 °C, which is attributed to the gradual transformation of Au_x@GSH clusters to Au NPs, retarding the photosensitization effect of Au_x@GSH clusters. This speculation can be corroborated by the color change of the samples (**Fig. S7c**).

Fig. S8. Magnified (a) LSV curves (5 mV s⁻¹) and (b) ABPE results of TNTAs, TNTAs-Au_x and TNTAs-Au heterostructures under visible light irradiation (λ >420 nm). (c) EPR result of TNTAs.

Note: TNTAs-Au_x always demonstrates the optimal photocurrent (**Fig. S8a**) and ABPE (**Fig. S8b**) and they follow the order of TNTAs-Au_x>TNTAs-Au>TNTAs, verifying the advantage of photosensitization effect of Au_x@GSH clusters over plasmonic effect of Au NPs. Note that TNTAs shows weak photocurrent under visible light irradiation and this results from the defect of TNTAs, as evidenced by the EPR signal (**Fig. S8c**).

Photoanodes	R _s /ohm	R _{ct} /ohm	CPE/(×10^-4 F·cm ⁻²)
TNTAs	2.72	13850	2.73
TNTAs-Au _x	3.015	3152	2.57
TNTAs-Au	2.642	6392	2.28

 Table S2. Fitted EIS results of different photoanodes under visible light irradiation based on the equivalent circuit.

Note: As shown in Table S2, R_{ct} values were determined by fitting the EIS results based on the equivalent circuit composed of a series of resistance (Fig. 4d, inset). Apparently, TNTAs-Au_x demonstrated the smallest R_{ct} value in comparison with other counterparts, indicative of its lowest charge transfer resistance in the interfacial region.

Fig. S9. (a) UV-vis absorption spectra of Au_x NCs and Au NPs aqueous solution, (b) photocurrents of TNTAs- Au_x and TNTAs-Au under different wavelength light irradiation.

Fig. S10. (a) UV-vis absorption spectrum, (b) zeta potential and TEM image of $Au_{25}@(GSH)_{18}$ clusters aqueous solution with corresponding size distribution histogram in the inset.

Note: Zeta potential result indicates $Au_{25}@(GSH)_{18}$ clusters are featured by negatively charged surface, which is mainly ascribed to the deprotonation of carboxyl groups from GSH ligands. In this regard, pronounced negatively charged surface of $Au_{25}@GSH$ renders it suitable building block for electrostatic self-assembly on the TNTAs framework.

Fig. S11. TEM image of (a) TNTAs-Au₂₅ and (b) TNTAs-Au along with corresponding (c) sample color change of TNTAs-Au₂₅ before (left) and after (right) thermal treatment.

Note: Au₂₅(GSH)₁₈ clusters in TNTAs-Au₂₅ (Fig. S10a) aggregate to larger metallic Au NPs (ca. 5 nm) (Fig. S10b) after thermal treatment.

Fig. S12. (a) LSV results (5 mV s⁻¹) and (b) on-off transient photocurrent responses (0.61 V vs. RHE) of TNTAs, TNTAs-Au₂₅ and TNTAs-Au photoanodes.

Note: TNTAs-Au₂₅ shows the considerably enhanced photocurrent in comparison with TNTAs-Au and TNTAs, verifying the pronounced photosensitization effect of $Au_{25}(GSH)_{18}$ clusters. Noteworthily, TNTAs-Au exhibits much more improved photocurrent than blank TNTAs under visible light irradiation, implying plasmonic effect of Au NPs plays an important role in producing the hot electrons which boosts the photocurrent enhancement.

Fig. S13. PL spectra of TNTAs, TNTAs-Au and TNTAs-Au_x with an excitation wavelength of 270 nm.

Fig. S14. (a) CV curves of $Au_x@GSH$ clusters with corresponding (b) magnified image. (electrolyte: degassed acetonitrile containing 0.1 mol L⁻¹ TEAP)

Note: Apparently, when the volume of $Au_x@GSH$ clusters increases, an oxidation potential at 1.95 V (vs. NHE) was seen in the CV results (Fig. S14), which is attributed to the HOMO level of Au_x clusters.^{S17}

Fig. S15. Schematic illustration of the (a) plasmon excitation and (b) hot electrons generation process.

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