

Supporting Information

Tuning Atomically Precise Metal Nanoclusters Mediated Photoelectrocatalysis via Non-Conjugated Polymer

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Experimental Section

1. Materials

Fluorine-doped tin oxide glass (FTO, 50 mm × 10 mm × 20 mm, 99.9%), deionized water (DI H₂O, Millipore, 18.2 MΩ·cm resistivity), titanium butoxide (C₁₆H₃₆O₄Ti), hydrochloric acid (HCl), silver nitrate (AgNO₃), L-glutathione (GSH), ammonium oxalate ((NH₄)₂C₂O₄), sodium chloride (NaCl), sodium borohydride (NaBH₄), sodium hydroxide (NaOH), hydrogen peroxide (H₂O₂), L-glutathione (GSH) and poly(diallyl-dimethyl-ammonium chloride) solution (PDDA, average Mw 200.000-350.000) were obtained from Sigma-Aldrich. All the materials above were used directly without further purification.

2. Preparation of TiO₂ nanorod arrays (TNRAs)

Firstly, 15ml ultrapure water and 15ml concentrated hydrochloric acid (36.5%-38% by weight) were poured into 50ml inner lining and stirred at 1000r/min for 5 min. Then 0.45ml titanium butoxide as titanium source was added into the reactor and stirred for 15 min. The cleaned FTO substrate is added to the substrate, and the conductive surface is placed downward, just completely immersed in the solution. The inner lining was put into the reactor and heated in an electric oven at 150 °C for 12 h. The FTO substrate was taken out, cleaned with deionized water and dried with N₂, then heated to 500 °C in muffle furnace and kept for 1 h.

3. Preparation of Ag_x@GSH NCs

Firstly, 12.5 mL of 20 mM AgNO₃ and 7.5 mL of 50 mM reduced-glutathione (GSH) were added to a 500 mL flask containing 200 mL of ultrapure water. Stirring the white precipitates for 2 min, and then changing the pH of the reaction mixture to 11 by adding a 1 M NaOH solution. Subsequently, heating this solution at 90 °C for 1 h under stirring at 500 rpm. After the solution was naturally cooled to room temperature, the pH was changed again to 3.75 by adding 1 M HCl. Finally, the NC solution was aged for 24 h at room temperature, and all precipitates appeared during this period were removed via centrifugation.

4. Preparation of GSH-capped Ag₉(SG)₆, Ag₁₆(SG)₉ and Ag₃₁(SG)₁₉ NCs

Ag₉(SG)₆, Ag₁₆(SG)₉ NCs were prepared by referring to the previous work of Xun.^{S1} Ag₃₁(SG)₁₉ NCs were prepared by referring to the previous work of Franck.^{S2}

(1) Preparation of Ag₉(SG)₆ and Ag₁₆(SG)₉ NCs

Aqueous solutions of AgNO₃ (20 mM) and GSH (50 mM) were prepared with ultrapure water. An aqueous solution of NaBH₄ (112 mM) was freshly prepared by dissolving 43 mg of NaBH₄ in 2 ml of 1 M

NaOH solution, followed by the addition of 8 ml of ultrapure water. The addition of a certain amount of NaOH to the NaBH₄ solution was used to improve the stability of borohydride ions against hydrolysis. In a typical experiment to synthesize Ag₉(SG)₆ and Ag₁₆(SG)₉ NCs, aqueous solutions of AgNO₃ (125 μl, 20 mM) and GSH (150 μl, 50 mM) were first mixed in water (4.85 ml) under vigorous stirring to form thiolate-Ag complexes, followed by the addition of an aqueous solution of NaBH₄ (50 μl, 112 mM). A deep-red solution of Ag NCs (~5ml) was collected after 5 min. This Ag NC solution was then incubated at room temperature for 3h, and the deep-red solution gradually decomposed into a colorless solution, leading to the formation of thiolate-Ag complexes. Subsequently, a certain amount of 112 mM NaBH₄ (50 μl for the synthesis of Ag₁₆(SG)₉ or 250 μl for Ag₉(SG)₆ NCs) was introduced into this colorless solution under vigorous stirring, leading to the formation of a light-brown Ag NC solution after 15 min. Without stirring, this light-brown Ag NC solution was incubated at room temperature for a certain period of time (8 h for Ag₁₆(SG)₉ and 48 h for Ag₉(SG)₆). A strong red or green emission was then observed in the aqueous phase. The Ag₁₆(SG)₉ or Ag₉(SG)₆ NCs were collected without purification and stored at 4 °C for further characterization.

(2) Preparation of Ag₃₁(SG)₁₉ NCs

To an ice-cold solution of glutathione (200 mg GSH in 35 ml of H₂O) was added drop by drop 1 ml of AgNO₃ solution (55 mg ml⁻¹). A white precipitate appeared that was dispersed by adding 0.8 ml of 1 M NaOH solution (final pH≈6-7). Then 36 mg of NaBH₄ in 1 ml of ice-cold water was quickly added and the solution was left under strong agitation. After 1 h 30 min, 0.3 ml of H₂O₂ (33%) was added to the dark brown solution. 30 min later, additional amounts of AgNO₃ (0.14 ml at 100 mg ml⁻¹) and GSH (50 mg per powder) were added and after 5 min, 0.5 ml of an ice-cold solution of NaBH₄ (20 mg ml⁻¹) was added. The reaction mixture was kept stirring vigorously for 1 h 30 min.

5. Preparation of TNRAs/(Ag_x@GSH NCs)₄ and TNRAs/(PDDA)₄ photoanodes

TNRAs substrate was first dipped into a Ag_x@GSH NCs aqueous solution (0.19 mg/ml, pH=3.75) for 5 min, and then washed with deionized water (DI H₂O). We define the above preparation process as TNRAs/(Ag_x@GSH)₁. TNRAs were first dipped into a PDDA aqueous solution (0.5 mg/mL, 0.5 M NaCl, pH=10) for 5 min, and then washed with deionized water (DI H₂O). We define the above preparation process as TNRAs/(PDDA)₁. We can repeat the above synthesis steps to prepare multilayer TNRAs/(Ag_x@GSH NCs)₄ and TNRAs/(PDDA)₄ photoanodes.

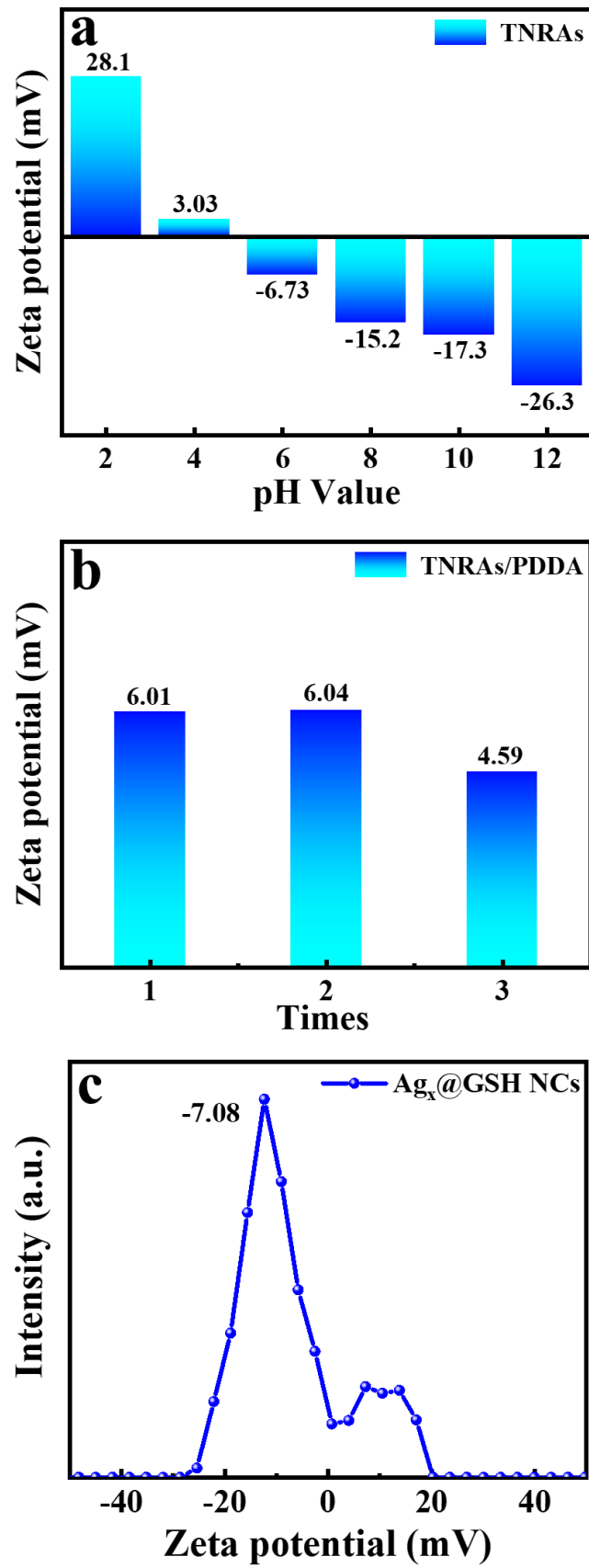


Fig. S1. Zeta potentials of (a) TNRAs, (b) TNRAs/PDDA and (c) Ag_x@GSH NCs.

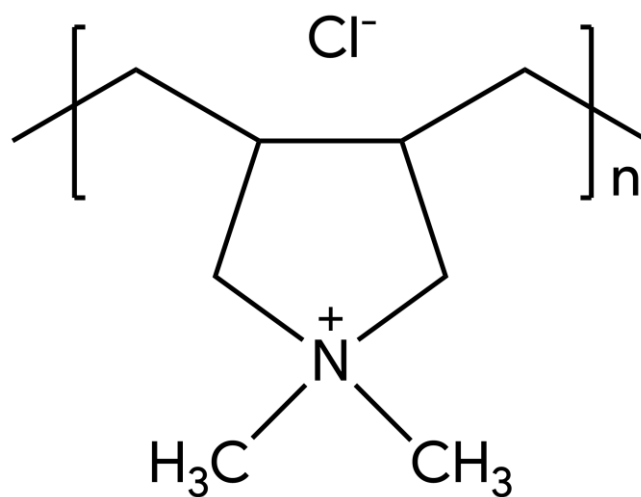


Fig. S2. Molecular structure of PDDA.

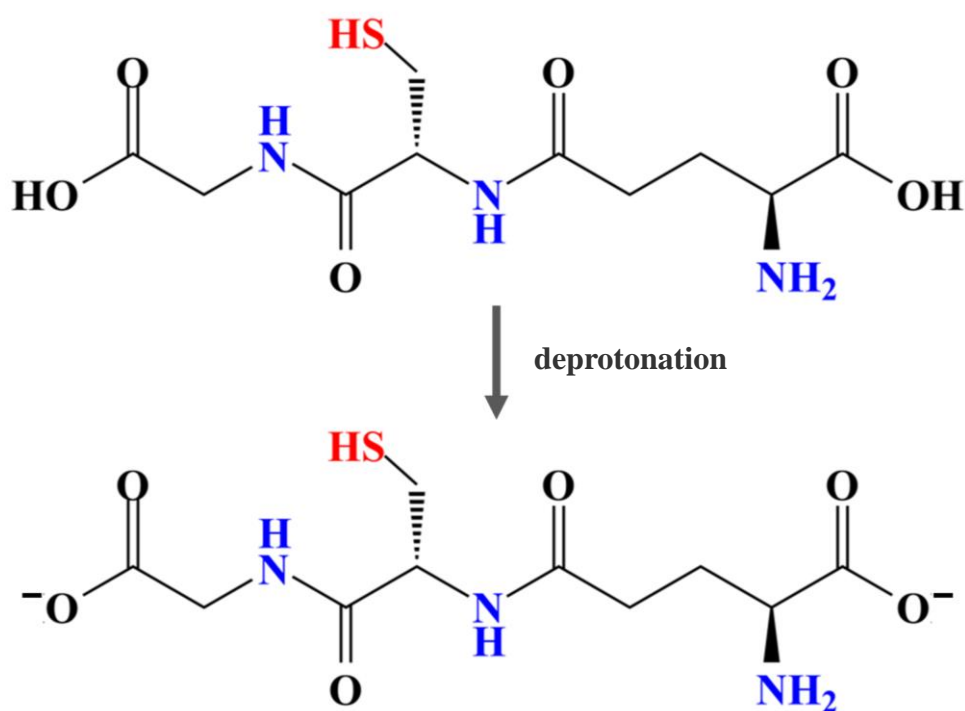


Fig. S3. Molecular structure of GSH ligand along with deprotonation process.

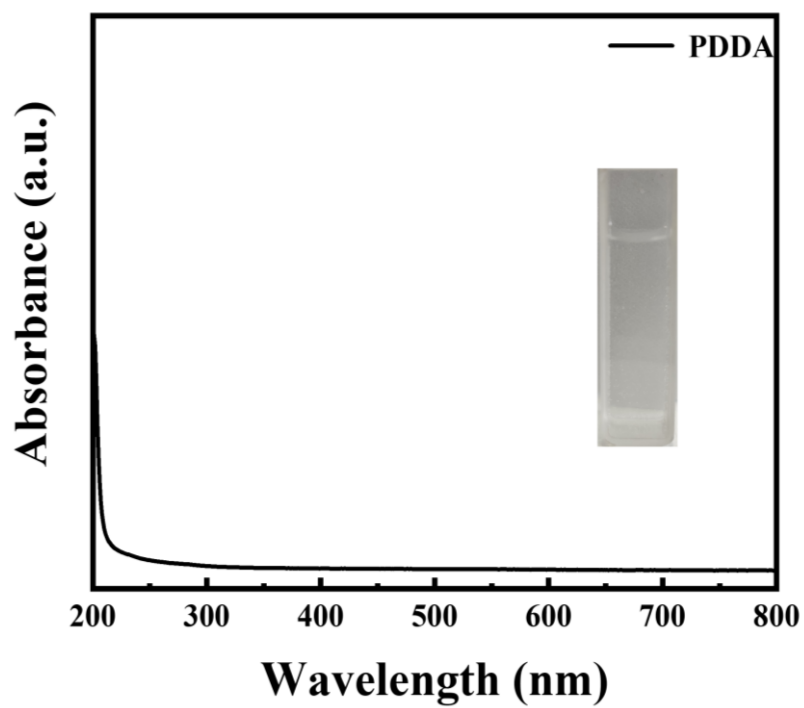


Fig. S4. UV-vis absorption spectrum of PDDA aqueous solution.

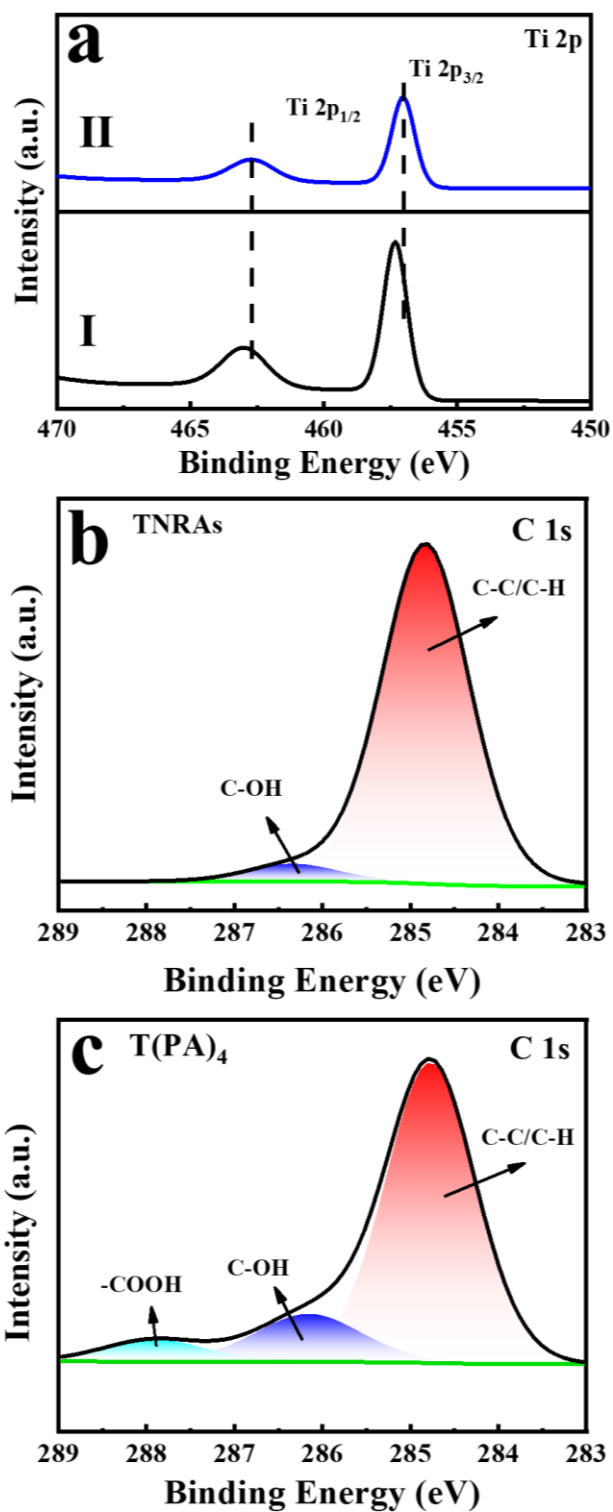


Fig. S5. High-resolution (a) Ti 2d of (I) TNRAs and (II) T(PA)₄, and C 1s spectra of (b) TNRAs and (c) T(PA)₄.

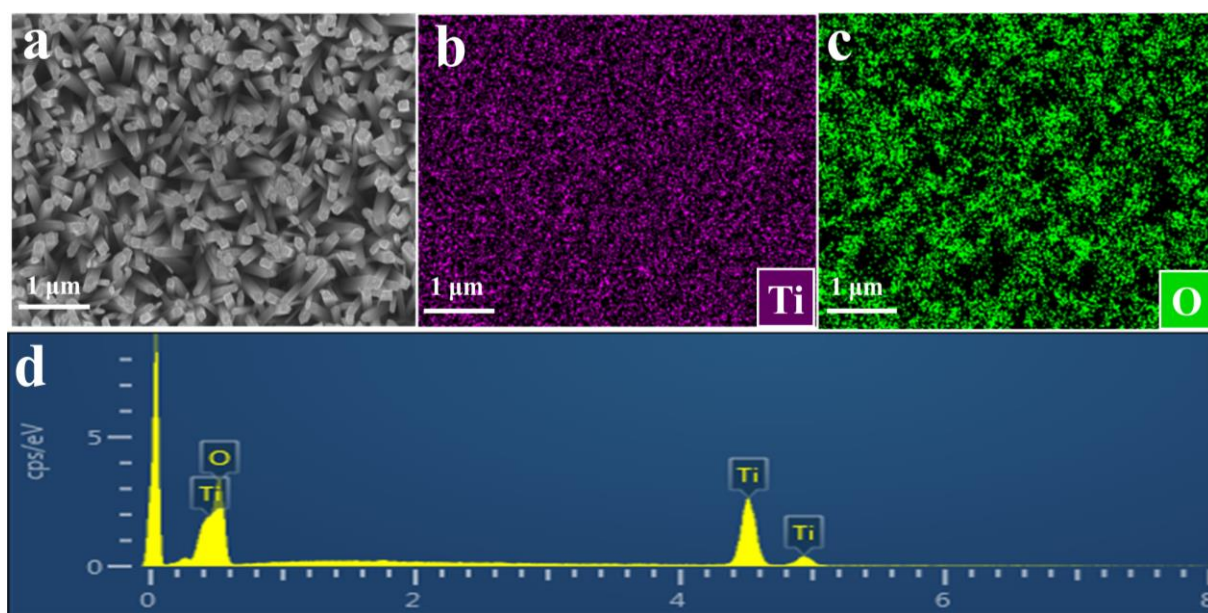


Fig. S6. (a) Top-view FESEM image of TNRAs with (b & c) elemental mapping and (d) EDS results.

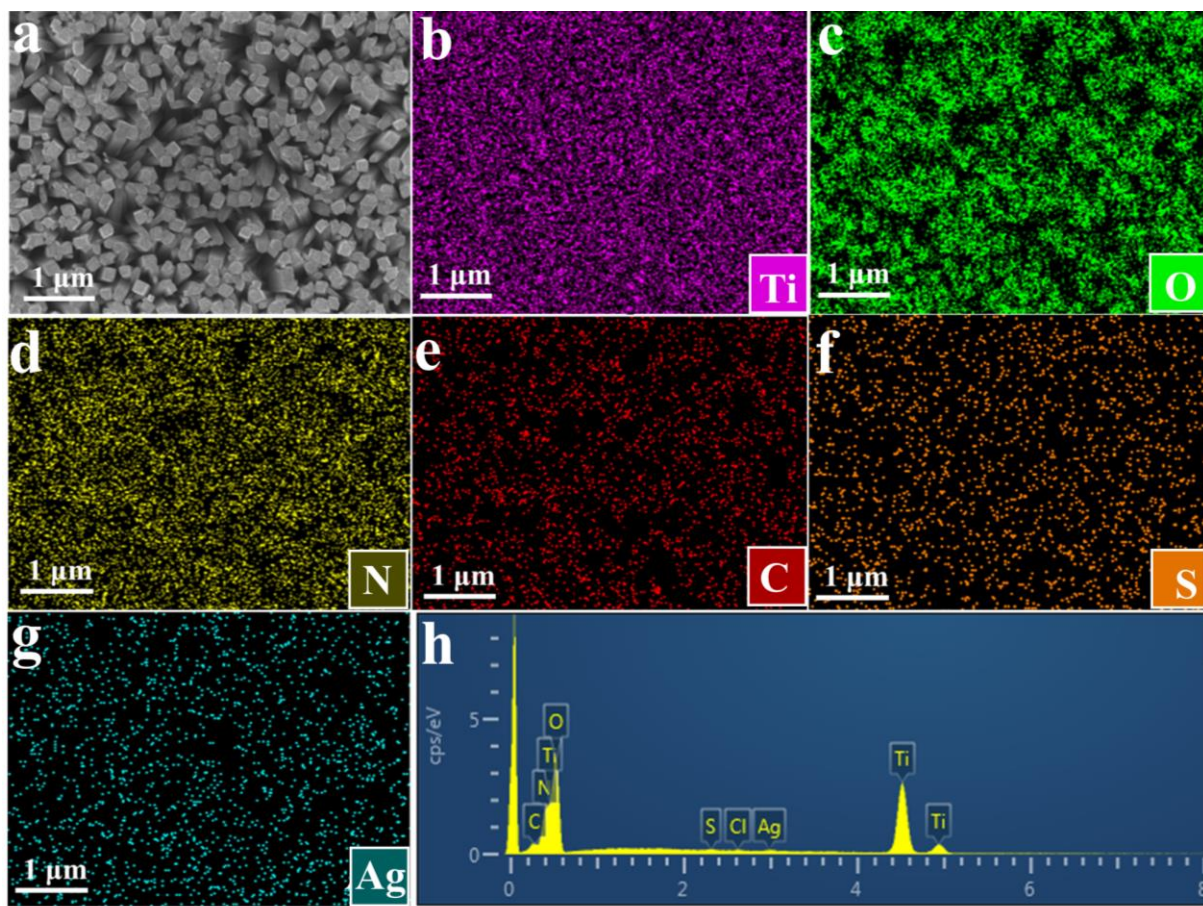


Fig. S7. (a) Top-view FESEM image of T(PA)₄ with (b-g) elemental mapping and (h) EDS results.

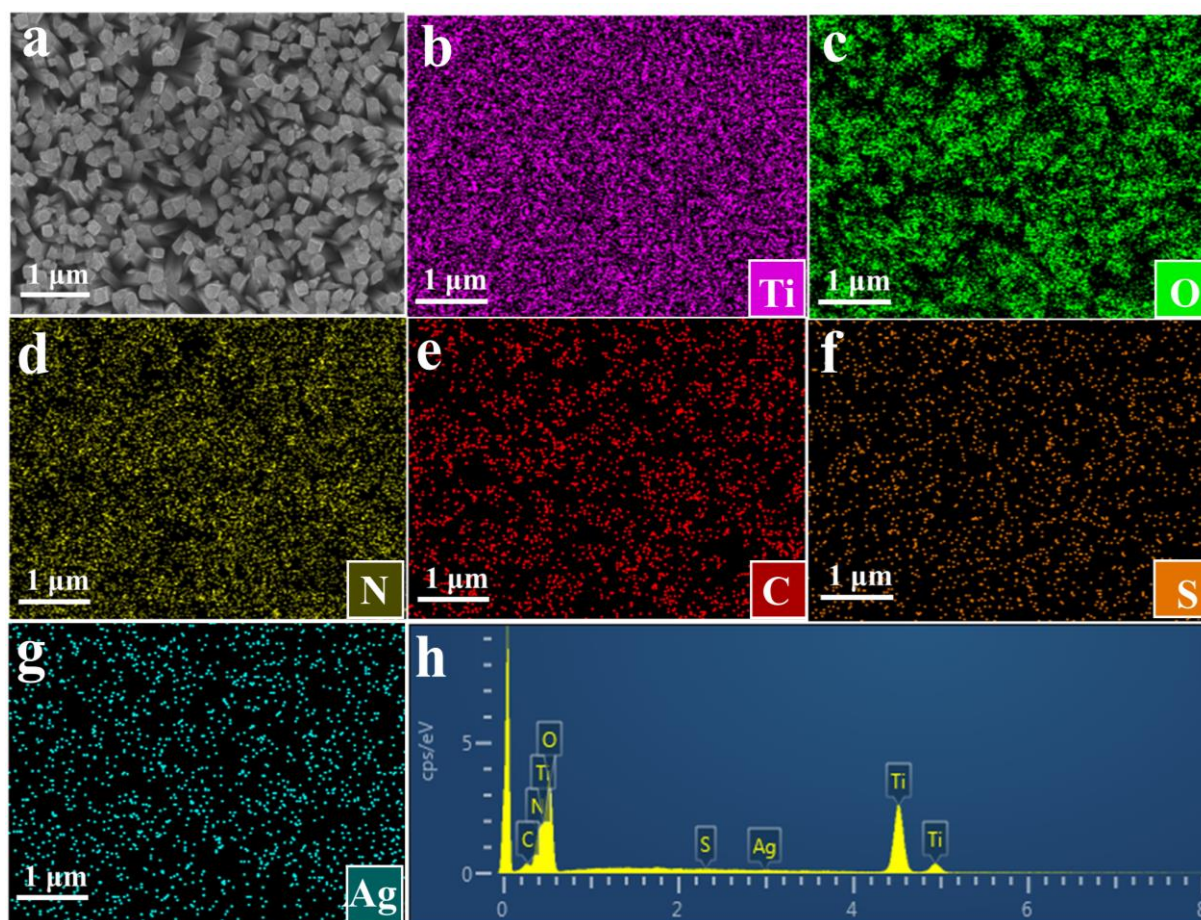


Fig. S8. (a) Top-view FESEM image of TA₄ with (b-g) elemental mapping and (h) EDS results.

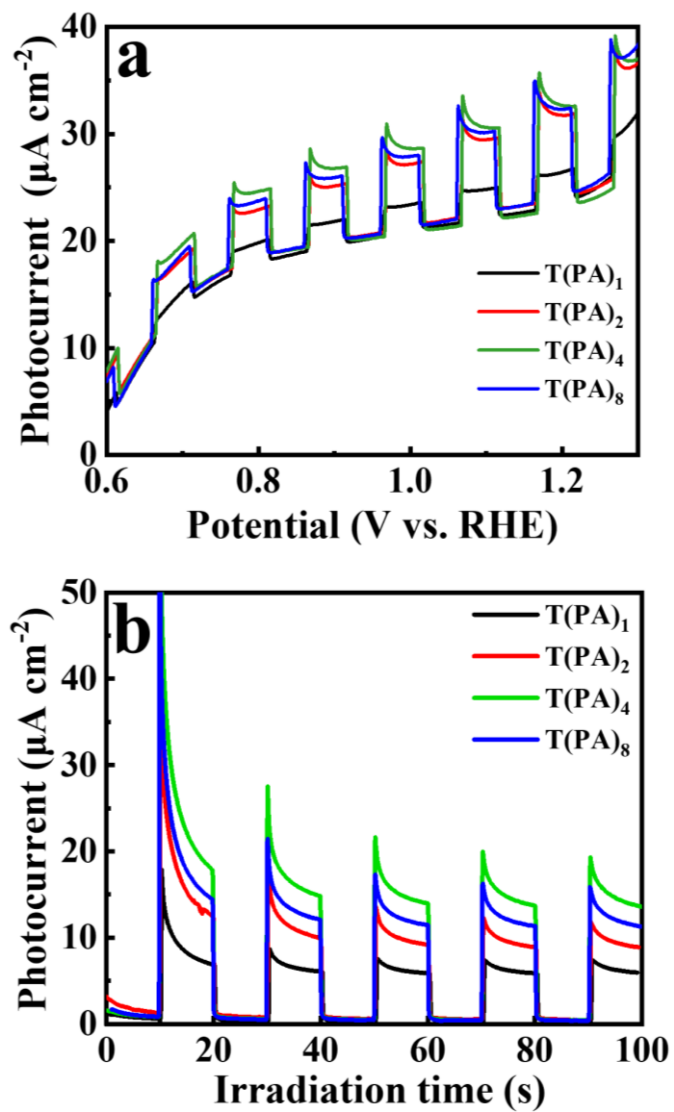


Fig. S9. (a) LSV curves and (b) transient photocurrent responses of T(PA)₁, T(PA)₂, T(PA)₄, and T(PA)₈.

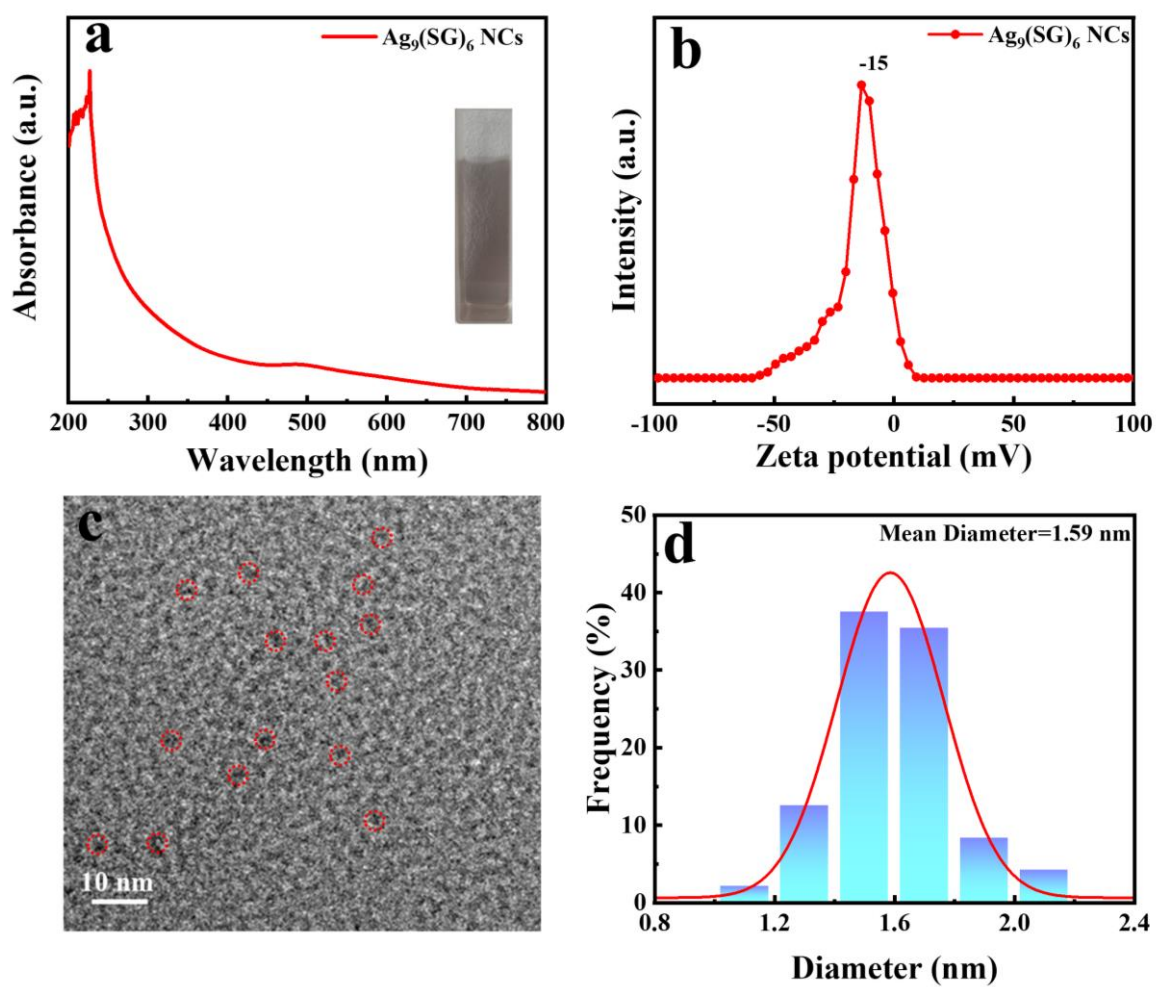


Fig. S10. (a) UV-vis absorption spectrum, (b) Zeta potential, (c) TEM image and (d) size distribution histogram of $\text{Ag}_9(\text{SG})_6$ NCs.

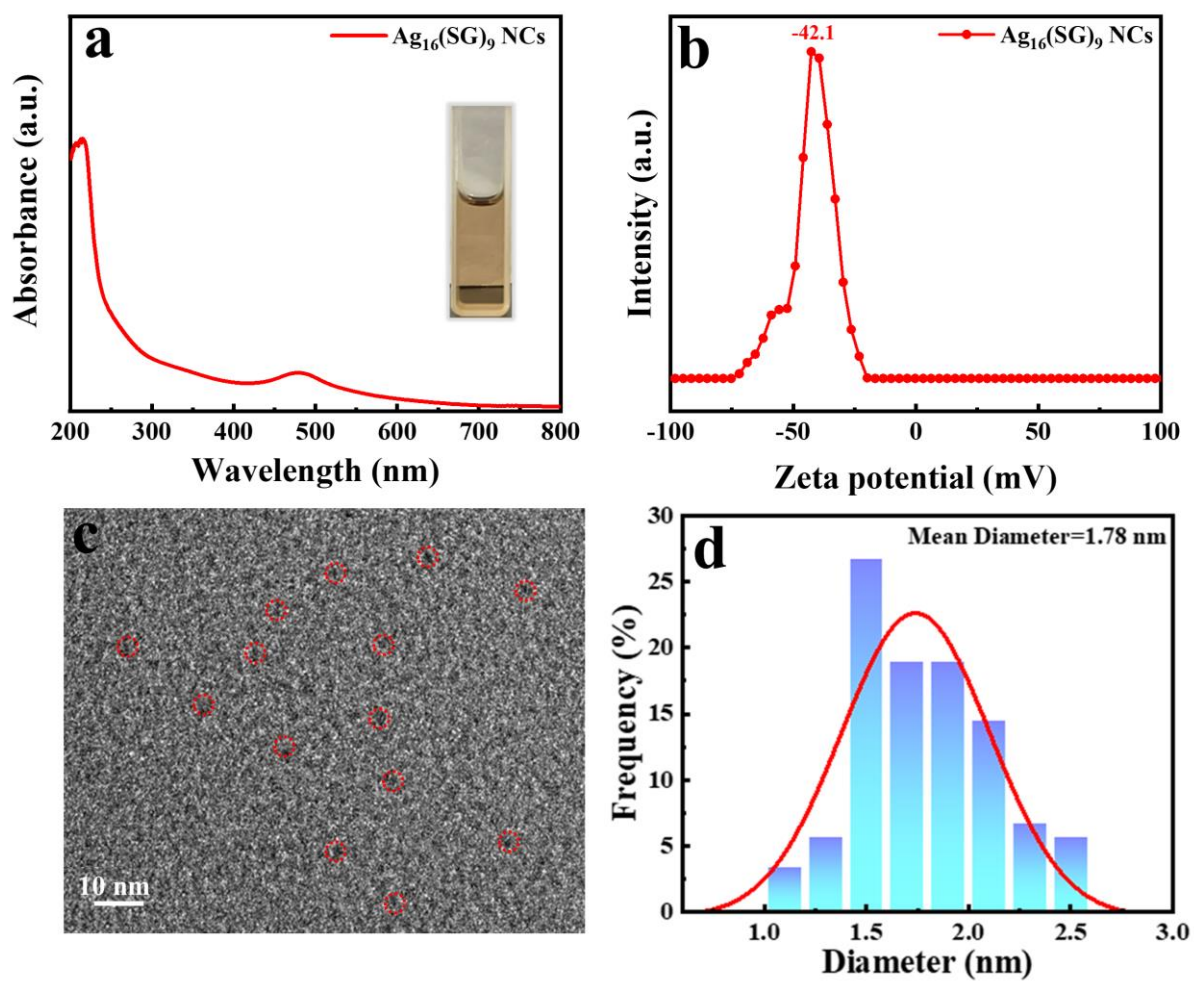


Fig. S11. (a) UV-vis absorption spectrum, (b) Zeta potential, (c) TEM image, and (d) size distribution histogram of $\text{Ag}_{16}(\text{SG})_9$ NCs.

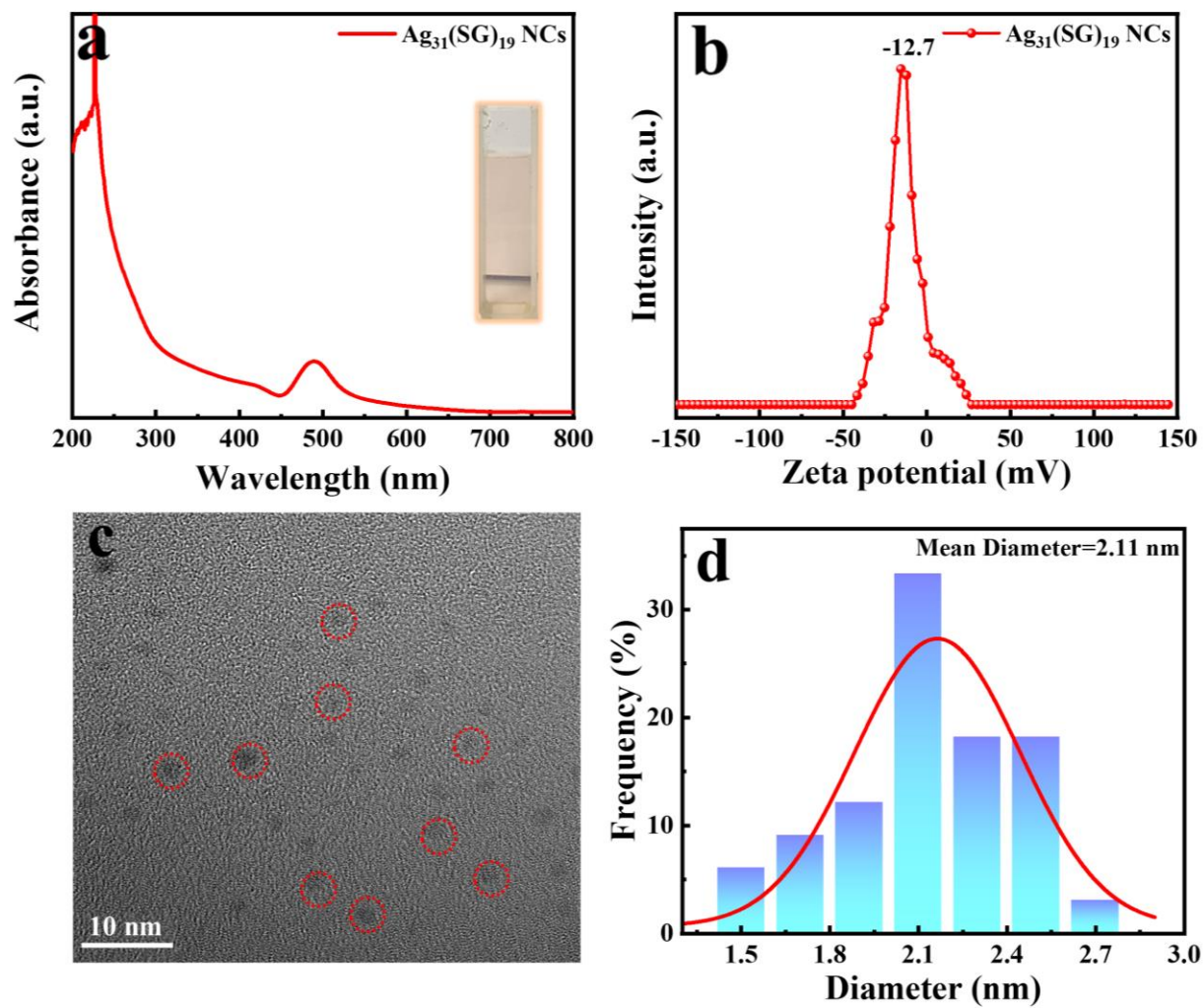


Fig. S12. (a) UV-vis absorption spectrum, (b) Zeta potential, (c) TEM image and (d) size distribution histogram of $\text{Ag}_{31}(\text{SG})_{19}$ NCs.

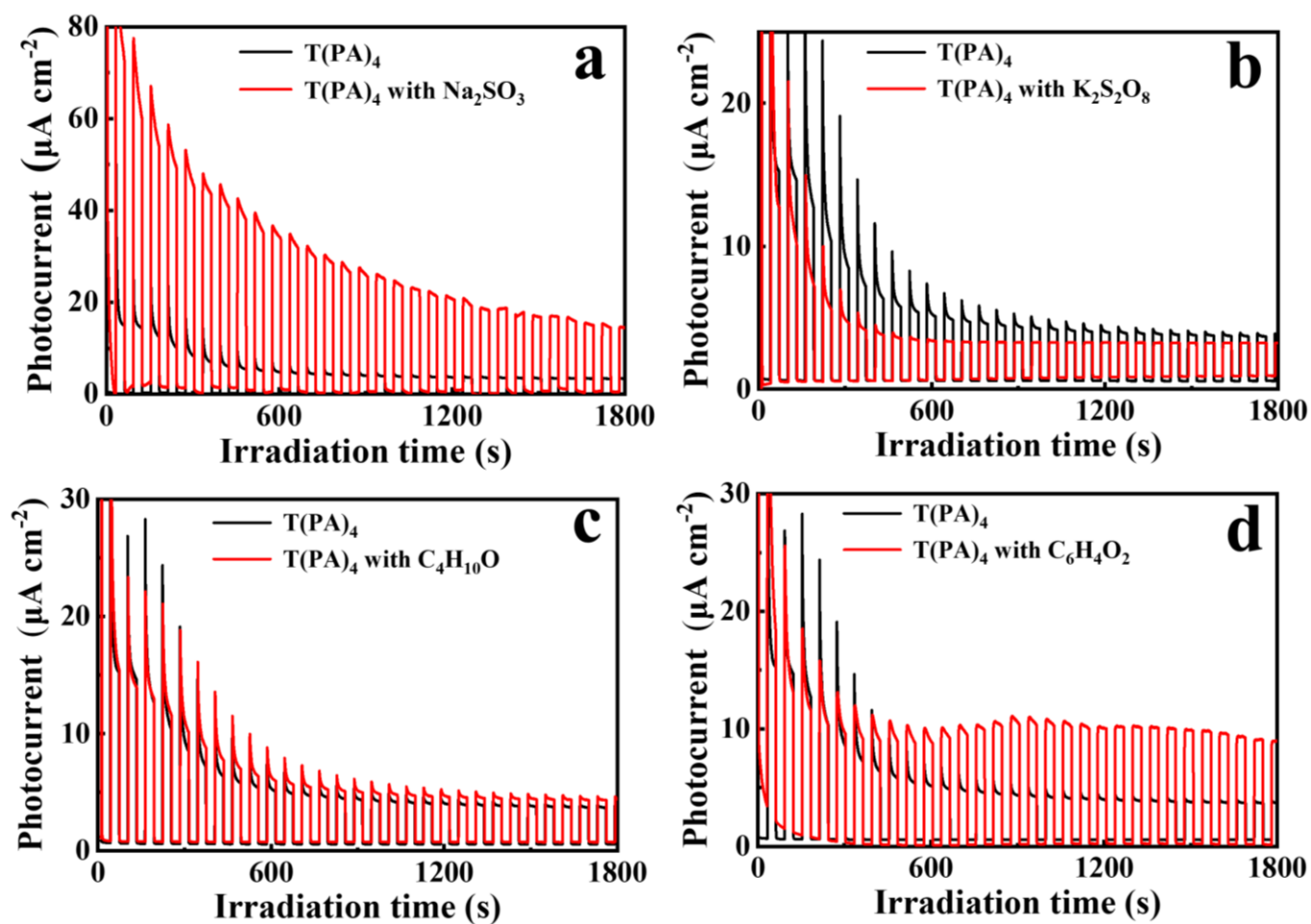


Fig. S13. Transient photocurrent responses of T(PA)₄ in Na₂SO₄ aqueous solution with adding (a) Na₂SO₃ (50 mM), (b) K₂S₂O₈ (50 mM), (c) C₄H₁₀O (50 mM), and (d) C₆H₄O₂ (50 mM) under continuous visible light irradiation ($\lambda > 420$ nm) for 0.5 h (pH=7, bias: 1.0 V vs. RHE).

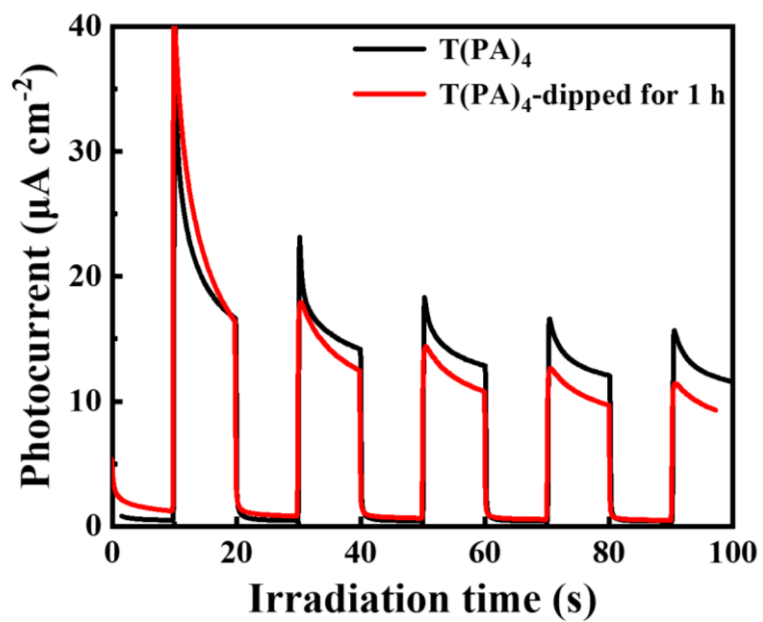


Fig. S14. Transient photocurrent responses of T(PA)₄ before and after dipping in Na₂SO₄ aqueous solution (pH=6.69) for 1 h under visible light ($\lambda > 420$ nm) irradiation (bias: 1.0 V vs. RHE).

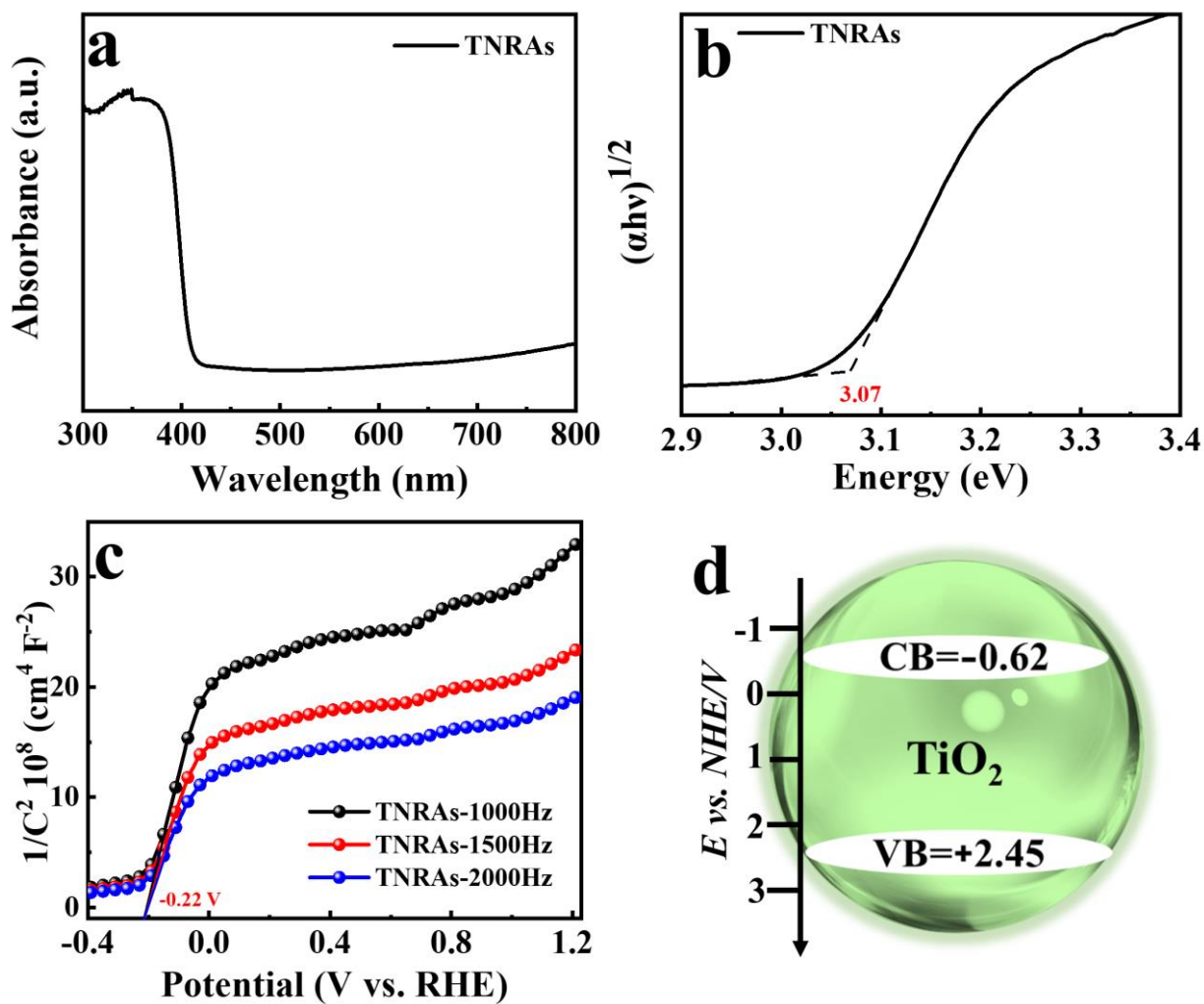


Fig. S15. (a) DRS results with corresponding (b) bandgap determination, (c) Mott-Schottky plots and (d) energy band structure of TNRAs substrate.

Table S1. Peak position with corresponding functional groups for all photoanodes.

<i>Peak position (cm⁻¹)</i>	<i>TNRAs</i>	<i>TP₄</i>	<i>TA₄</i>	<i>T(PA)₄</i>
3463 ^{S3}	VO-H	VO-H, VN-H	VO-H, VN-H	VO-H, VN-H
2975&2913 ^{S4}	Not Detected	VC-H	VC-H	VC-H
1111	Not Detected	VC-N	VC-N	VC-N
1633 ^{S3, S5}	$\delta_{\text{O-H}}$	$\delta_{\text{O-H}}, \delta_{\text{N-H}}$	$\delta_{\text{O-H}}, \delta_{\text{N-H}}, \delta_{\text{C=O}}$	$\delta_{\text{O-H}}, \delta_{\text{N-H}}, \delta_{\text{C=O}}$
653, 640, 638&615 ^{S6}	$\delta_{\text{Ti-O}}$	$\delta_{\text{Ti-O}}$	$\delta_{\text{Ti-O}}$	$\delta_{\text{Ti-O}}$

Table S2. Chemical bond species for different photoelectrodes.

<i>Element</i>	<i>TNRAs (eV)</i>	<i>T(PA)₄ (eV)</i>	<i>Chemical Bond Specie</i>
C 1s a	284.80	284.80	C-C/C-H
C 1s b	286.32	286.16	C-OH ^{S7}
C 1s a	Not Detected	287.92	-COOH ^{S7}
Ti 2p_{1/2}	463.00	462.76	Monoclinic (Ti ⁴⁺) ^{S6}
Ti 2p_{3/2}	457.30	457.06	Monoclinic (Ti ⁴⁺) ^{S6}
O 1s a	528.60	528.25	Lattice Oxygen ^{S6}
O 1s b	531.16	530.72	Ti-OH ^{S8}
N 1s a	Not Detected	399.69	-NH ₂ /-NH- ^{S8}
N 1s b	Not Detected	402.48	NH ₄ ⁺ ^{S8}
Ag 3d_{3/2}	Not Detected	367.92	Ag ⁰ ^{S9, S10}
Ag 3d_{3/2}	Not Detected	368.32	Ag ⁺ ^{S9, S10}
Ag 3d_{5/2}	Not Detected	373.92	Ag ⁰ ^{S9, S10}
Ag 3d_{5/2}	Not Detected	374.24	Ag ⁺ ^{S9, S10}

Table S3. Fitted EIS results of photoanodes under visible-light irradiation based on the equivalent circuit.

<i>Photoanode</i>	<i>R_s/ohm</i>	<i>R_{ct}/ohm</i>	<i>CPE/(F cm⁻²)</i>	<i>Z_w</i>
T(PA)₄	27.44	4098	0.00005645	0.0007106
TA₄	8.929	6581	0.000166	0.001564
TP₄	8.835	10970	0.0001343	0.001081
TNRAs	11.21	12480	0.0001246	0.0009721

Note: T(PA)₄ demonstrates the smallest R_{ct} in comparison with other counterparts under visible light irradiation ($\lambda > 420$ nm), indicative of its lowest interfacial charge transfer resistance.

Table S4. HOMO, LUMO levels and bandgap of Ag_x@GSH, Ag₉(SG)₆, Ag₁₆(SG)₉ and Ag₃₁(SG)₁₉NCs.

<i>Metal NCs</i>	<i>HOMO (V vs. NHE)</i>	<i>LUMO (V vs. NHE)</i>	<i>Bandgap (eV)</i>
Ag _x @GSH NCs	1.45	-1.09	2.54
Ag ₉ (SG) ₆ NCs	0.83	-1.76	2.59
Ag ₁₆ (SG) ₉ NCs	0.78	-1.8	2.58
Ag ₃₁ (SG) ₁₉ NCs	1.0	-1.53	2.53

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