

Supporting Materials

Ligands engineering of Au nanoclusters with multifunctional metalloporphyrin for photocatalytic H₂O₂ production

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1. Materials

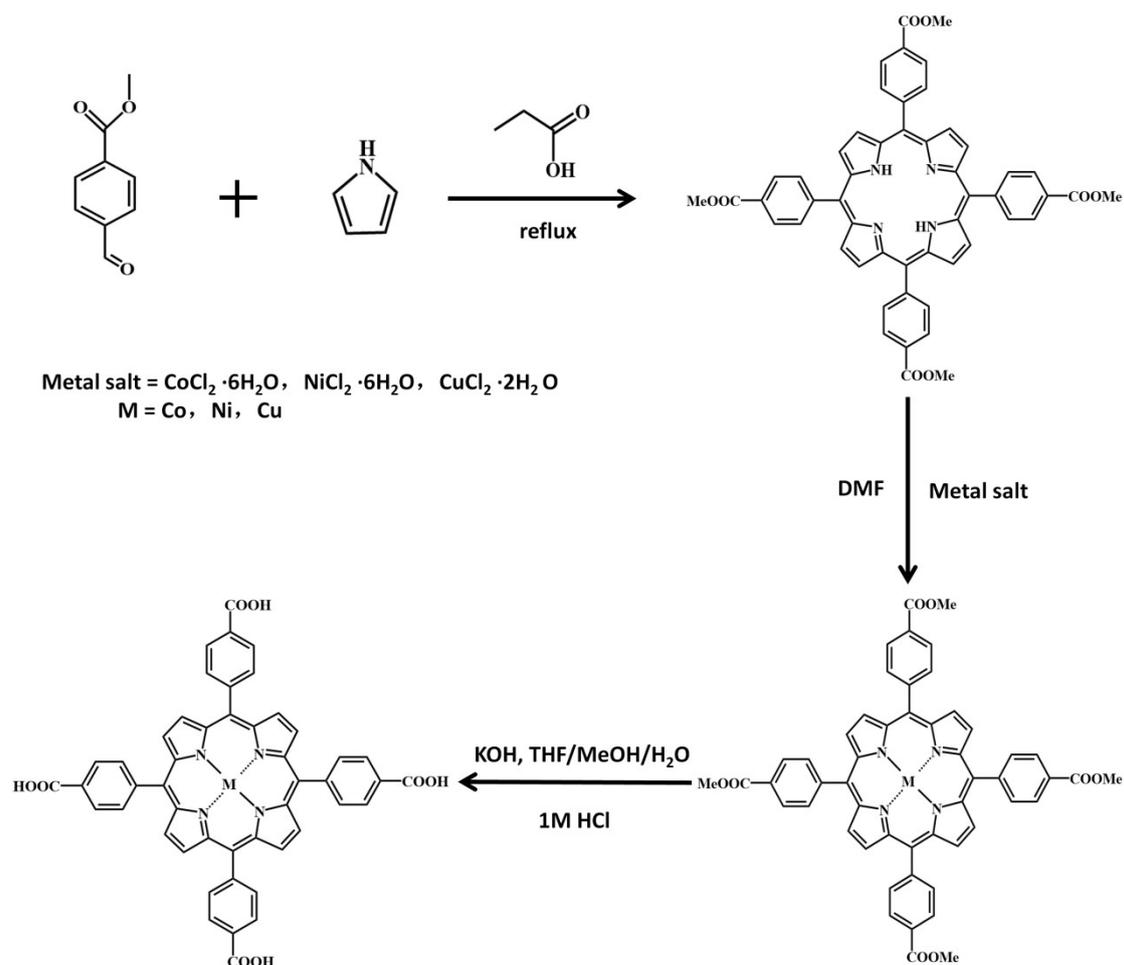
Ultrapure water (18.2 MΩ cm) was used in the whole experiment. Gold chloride trihydrate (HAuCl₄·3H₂O, ≥ 99.9%) from Sima-Aldrich; Deuterated oxide (D₂O) L-glutathione reduced (GSH, ≥ 98%), 2-(N-morpholino) ethane sulfonic hydrochloride (MES, ≥ 99%), N-hydroxysuccinimide (NHS, ≥ 98%) and perchloric acid (HClO₄) from Aladdin Reagent Inc.; Sodium bicarbonate (NaHCO₃, ≥ 98%), trichloromethane (CHCl₃), sodium hydroxide (NaOH, ≥ 99%), sodium borohydride (NaBH₄, ≥ 98%), potassium hydroxide (KOH, ≥ 99%), anhydrous magnesium sulfate (MgSO₄, ≥ 98%), cobalt (II) chloride hexahydrate (CoCl₂·6H₂O), N, N-dimethylformamine (DMF), tetrahydrofuran (THF), methanol (MeOH), hydrochloric acid (HCl), propanoic acid, ethanol and acetonitrile from Sinopharm Chemical Reagent Co., Ltd; Pyrrole and methyl p-formylbenzoate from Yuanye Biotechnology Co., Ltd; (Sodium 3-[1-[(phenylamino)-carbonyl] 3,4-tetrazolium]-bis (4-methoxy-6-nitro) benzene-sulfonic acid hydrate) (XTT) from Kulaibo Technology Co., Ltd.; Tetrakis (4-carboxyphenyl) porphyrin (2H-TCPP) from Shanghai Bidder Pharmaceutical Technology Co., Ltd., were all received without further refinement.

2. Instruments

The UV-visible absorption and UV-visible diffuse reflectance (UV-vis DRS) spectra were recorded on a Shimadzu UV-1800 photospectrometer and a U-3900 spectrophotometer with an integration sphere, respectively. Fourier transform infrared (FTIR) spectra were gained from a VERTEX 70 spectrometer. The steady-state photoluminescence (PL) spectra were collected on a PerkinElmer FL-8500 fluorescence spectrometer with an excitation wavelength of 412 nm. The PL decay results were collected on a photoluminescence spectrometer (FLS-1000, Edinburgh Instruments Ltd.). The X-ray photoelectron spectroscopy (XPS) analysis was carried out on an AXIS SUPRA spectrometer using a standard Al K α X-ray source. All binding energies were referenced to the binding energy of adventitious carbon at 284.8 eV. The electrospray ionization mass spectra (ESI-MS) of Au NCs were acquired on a Bruker Impact-II Q-TOF system. Transmission electron microscope (TEM) images were acquired on a JEOL JEM 2100F microscope. Electron spin resonance (ESR) measurements were carried out on a Bruker EMX PLUS spectrometer. H-nuclear Nuclear magnetic resonance (^1H NMR) spectra were obtained on a Bruker 400 spectrometer.

3. Synthesis of tetrakis-(4-carboxyphenyl) porphyrin cobalt (M-TCPP)

M-TCPP was synthesized according to the method reported by Zhou et al.¹, which includes three steps as follows:



Scheme S1. The synthetic route of the M-TCPP.

(1) Synthesis of 5, 10, 15, 20-tetrakis (4-methoxycarbonylphenyl) porphyrin (TPPCOOMe)

Pyrrole (3.0 g, 0.043 mol) and methyl p-formylbenzoate (6.9 g, 0.042 mol) were added into a 300 mL flask containing 100 mL propionic acid, and the obtained solution was refluxed in darkness for 12 h. After that, the mixture was filtered to collect purple crystals.

(2) Synthesis of 5, 10, 15, 20-tetrakis (4-methoxycarbonylphenyl) porphyrin-M (M-TPPCOOMe)

Synthesis of Co-TCPPCOOMe: The TPPCOOMe (0.854 g, 1.0 mmol) and $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (3.1 g, 12.8 mmol) were added into a 300 mL flask containing 100 mL DMF solution, which was then refluxed for 6 h. After cooling to room temperature, 150 mL H_2O was introduced into the solution, and the precipitates were centrifuged and subsequently washed with 50 mL H_2O two times. The

obtained solids were dissolved into CHCl_3 , followed by washing three times with 1 M HCl and two times with water. The organic layer was then dried over anhydrous magnesium sulfate and evaporated to obtain the final red crystals.

Synthesis of Ni-TCPPCOOMe: The TPP-COOMe (0.854 g, 1.0 mmol) and $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (3.1 g, 12.8 mmol) were added into a 300 mL flask containing 100 mL DMF solution, which was then refluxed for 6 h. After cooling to room temperature, 150 mL H_2O was introduced into the solution, and the precipitates were centrifuged and subsequently washed with 50 mL H_2O two times. The obtained solids were dissolved into CHCl_3 , followed by washing three times with 1 M HCl and two times with water. The organic layer was then dried over anhydrous magnesium sulfate and evaporated to obtain the final quantitative crimson crystals.

Synthesis of Cu-TCPPCOOMe: The TPP-COOMe (0.854 g, 1.0 mmol) and $\text{CuCl}_2 \cdot 6\text{H}_2\text{O}$ (2.2 g, 12.8 mmol) were added into a 300 mL flask containing 100 mL DMF solution, which was then refluxed for 6 h. After cooling to room temperature, 150 mL H_2O was introduced into the solution, and the precipitates were centrifuged and subsequently washed with 50 mL H_2O two times. The obtained solids were dissolved into CHCl_3 , followed by washing three with water. The organic layer was then dried over anhydrous magnesium sulfate and evaporated to obtain the final dark red crystals.

(3) Synthesis of [5,10,15,20-Tetrakis(4-carboxyphenyl)porphyrinato]-M (M-TCPP, M=Co, Ni and Cu)

Synthesis of Co-TCPP: The obtained Co-TPPCOOMe (0.75 g) was added to a 150 mL flask containing a mixture of 25 mL THF and 25 mL MeOH, followed by introducing a solution of KOH (2.63 g) in H_2O (25 mL). The mixed solution was refluxed for 12 h. After cooling to room temperature, THF and MeOH were evaporated. Additional water was then added and heated until the solid was completely dissolved. After that, the resulting solution was acidified with 1 M HCl until no further precipitate was generated, which was then filtered and washed with water and dried under vacuum to obtain the final red solid. FTIR: $\nu = 3423$ (m), 2950 (w), 2840 (w), 1719 (s), 1605 (s), 1546 (m), 1458 (m), 1394 (s), 1351 (m), 1276 (s), 1177 (w), 1112 (s), 1002 (s), 868 (w), 833 (m), 798 (s), and 716 (m) cm^{-1} .

Synthesis of Ni-TCPP: The obtained Ni-TPPCOOMe (0.75 g) was added to a 150 mL flask containing a mixture of 25 mL THF and 25 mL MeOH, followed by introducing a solution of

KOH (2.63 g) in H₂O (25 mL). The mixed solution was refluxed for 12 h. After cooling to room temperature, THF and MeOH were evaporated. Additional water was then added and heated until the solid was completely dissolved. After that, the resulting solution was acidified with 1 M HCl until no further precipitate was generated, which was then filtered and washed with water and dried under vacuum to obtain the final crimson solid.

Synthesis of Cu-TCPP: The obtained Cu-TPPCOOMe (0.75 g) was added to a 150 mL flask containing a mixture of 25 mL THF and 25 mL MeOH, followed by introducing a solution of KOH (2.63 g) in H₂O (25 mL). The mixed solution was refluxed for 12 h. After cooling to room temperature, THF and MeOH were evaporated. Additional water was then added and heated until the solid was completely dissolved. After that, the resulting solution was acidified with 1 M HCl until no further precipitate was generated, which was then filtered and washed with water and dried under vacuum to obtain the final dark red solid.

4. Synthesis of highly luminescent GSH-protected Au NCs

The Au NCs were synthesized according to a previously reported procedure¹. In brief, freshly prepared aqueous solutions of GSH (20 mM, 15 mL) and HAuCl₄ (20 mM, 10 mL) were mixed with 25 mL H₂O, followed by stirring at room temperature to colorless. After that, the homogeneous solution was heated at 70 °C for 24 h to obtain highly luminescent Au NCs. The obtained Au NCs were purified by centrifuging the mixture (Au NCs: acetonitrile = 1:3 at volume ratio) at 8000 rpm for 5 min. The obtained solids of Au NCs were redissolved in 10 mL H₂O for further use.

5. Synthesis of non-luminescent GSH-protected Au₂₅(SG)₁₈ NCs

Non-luminescent Au₂₅(SG)₁₈ NCs were synthesized by the NaOH-mediated NaBH₄ reduction method.³ In a typical synthesis of Au₂₅(SG)₁₈ NCs, aqueous solutions of HAuCl₄ (20 mM, 250 μL) were mixed in water (1.15 mL) and ethanol (3 mL). An aqueous NaOH solution (1 M, 0.3 mL) was then introduced into the reaction mixture, followed by the addition of 0.1 mL of NaBH₄ solution (prepared by dissolving 43 mg of NaBH₄ powder in 10 mL of 0.2 M NaOH solution). The

Au₂₅(SG)₁₈ NCs were collected after 3 h.

6. Synthesis of the Co-TCPP grafted Au NCs (Au-Co-TCPP)

1 mL of Co-TCPP solution (600 $\mu\text{g}\cdot\text{mL}^{-1}$) was added in a 20 mL round-bottomed flask containing 5 mL of MES buffer (3.9 $\text{mg}\cdot\text{mL}^{-1}$). Subsequently, 6 mg of EDC and 1.6 mg of NHS were separately added to the solution, which was then heated to 65 °C. After stirring for 30 min, 5 mL of Au NCs (1 $\text{mg}\cdot\text{mL}^{-1}$) was introduced into the reaction system, followed by heating at 65 °C for 6 h. After cooling to room temperature, the reaction solution was washed with 50 mL acetonitrile and then centrifuged for 15 min at 12000 rpm to obtain Au-Co-TCPP. The grafting amount of Co-TCPP on the surface of Au NCs could be controlled by adjusting the concentration of Co-TCPP (e.g., 200 $\mu\text{g}\cdot\text{mL}^{-1}$, 400 $\mu\text{g}\cdot\text{mL}^{-1}$, and 800 $\mu\text{g}\cdot\text{mL}^{-1}$).

7. Synthesis of other M-TCPP (M=Ni, Cu and 2H) grafted Au NCs (Au-M-TCPP)

Au-Ni-TCPP, Au-Cu-TCPP, and Au-2H-TCPP photocatalysts were prepared by the same preparation procedure as for Au-Co-TCPP except for the replacement of the Co-TCPP with Ni-TCPP, Cu-TCPP, and 2H-TCPP, respectively.

8. Photocatalytic H₂O₂ production over the photocatalyst

5 mL Au-Co-TCPP photocatalyst was added in a quartz glass reactor, followed by bubbling O₂ into solution in dark for 30 min to ensure the formation of saturated O₂ atmosphere. After that, the solution was exposed to a 300 W Xe lamp ($\lambda \geq 400$ nm) with a power density of 100 $\text{mW}\cdot\text{cm}^{-2}$. 100 μL of the reaction solution was pipetted at given irradiation time intervals (0, 15, 30, 45, and 60 min) to determine the concentration of H₂O₂, which was quantified using the Quantitative Peroxide Assay Kit (*aqueous*) (see more details in Figure S3 or instructions). In addition, XTT was added to the reaction solution as a superoxide radical trapping agent to investigate the H₂O₂ formation route. The pH of the reaction system was adjusted to 2–7 with HClO₄ or NaOH. The H₂O₂ decomposition behavior (initial concentration: 500 mM L^{-1}) was performed in the presence

of different photocatalysts, including pristine Co-TCPP, pristine Au NCs, and the Au-Co-TCPP, under light irradiation ($\lambda \geq 400$ nm) for 60 min.

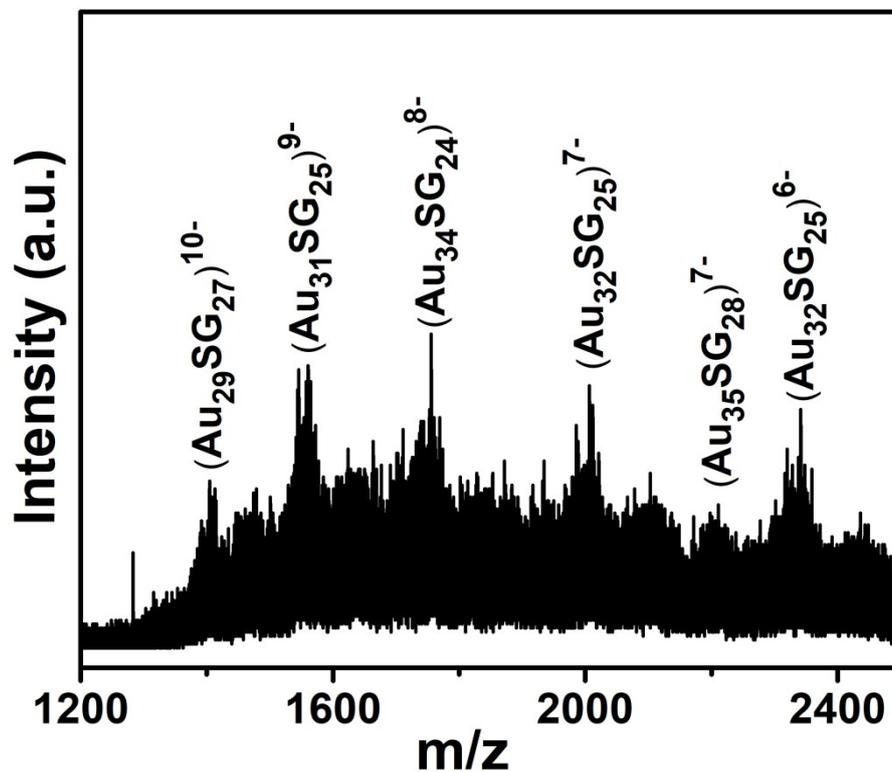


Figure S1. ESI-MS spectrum of the GSH-protected Au NCs.

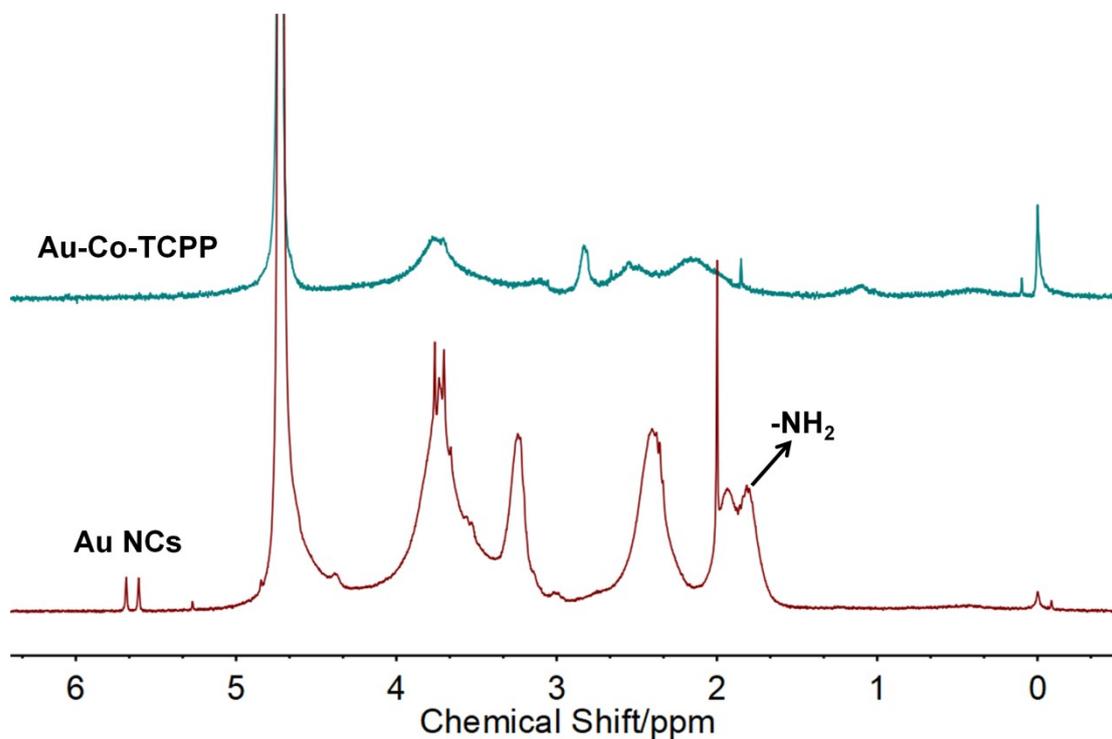


Figure S2. ^1H NMR spectra of Au-Co-TCPP (upper) and Au NCs (lower).

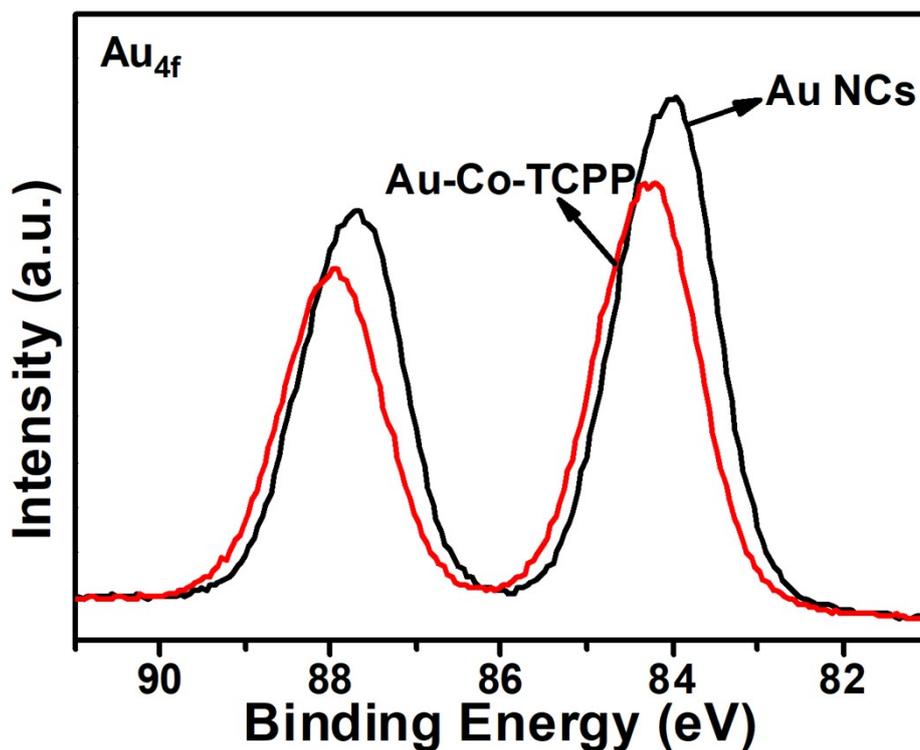


Figure S3. High-resolution XPS spectra of Au_{4f} in the Au-Co-TCPP sample and pristine Au NCs.

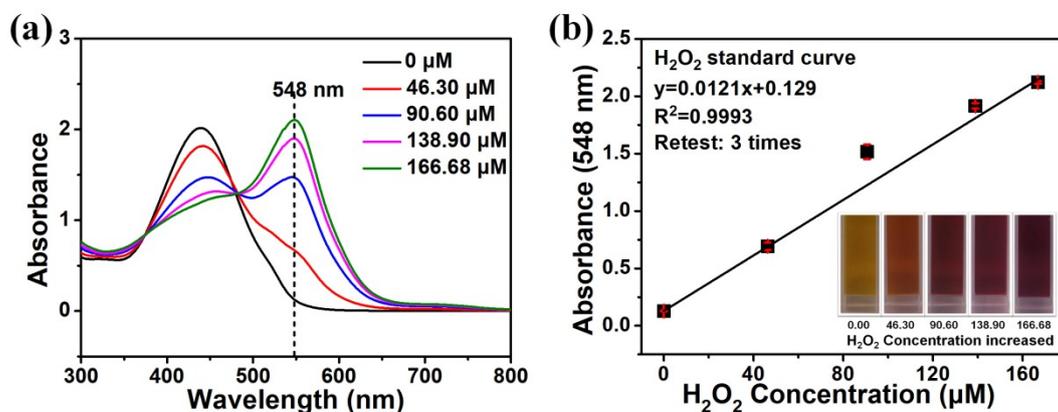


Figure S4. H₂O₂ concentrations were quantified using the quantitative peroxide assay kit. (a) UV-visible absorption spectra of the solutions of peroxide assay reagents in the presence of different concentrations of H₂O₂ after incubation of 20 min at room temperature. (b) The standard calibration curve of H₂O₂ concentration by measuring the absorbance of the solutions at 548 nm ($R^2 = 0.9993$, data are presented as the mean \pm SD ($n = 3$)). The inset in (b) shows the color change of the solutions with the increased H₂O₂ concentrations.

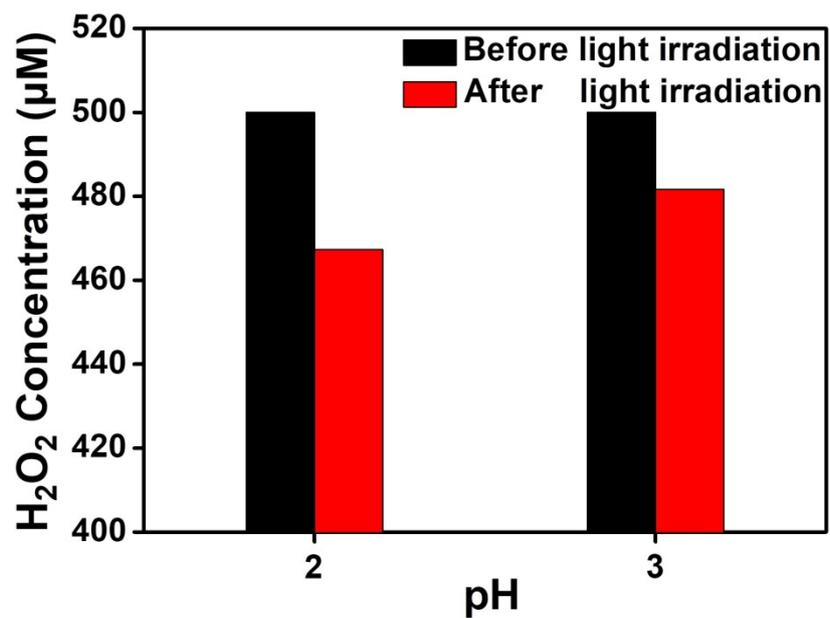


Figure S5. Decomposition efficiency of Au-Co-TCPP for H₂O₂ (500 µM) after visible light irradiation for 1h at different pH (in Ar-saturated suspension).

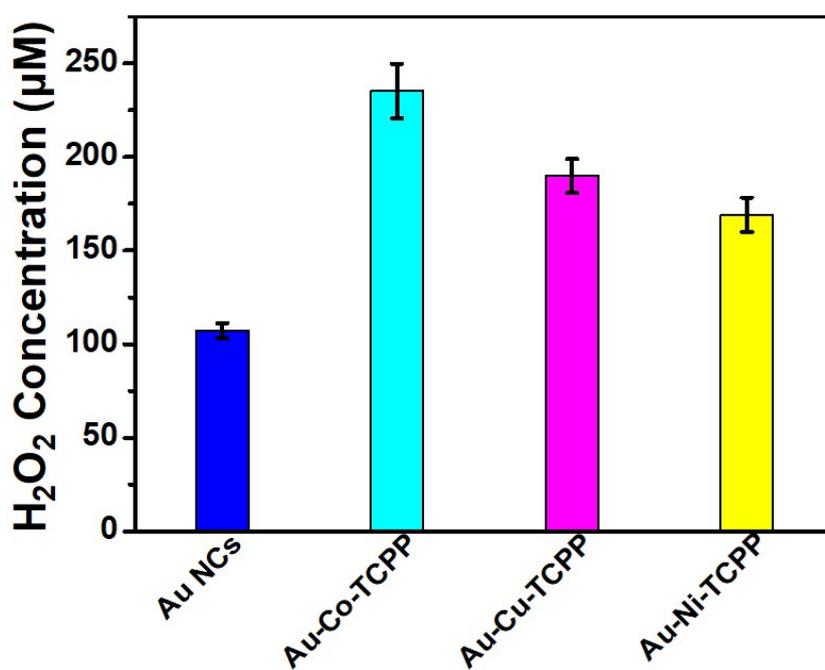


Figure S6. Photocatalytic production of H₂O₂ over Au NCS, Au-Co-TCPP, Au-Cu-TCPP, and Au-Ni-TCPP.

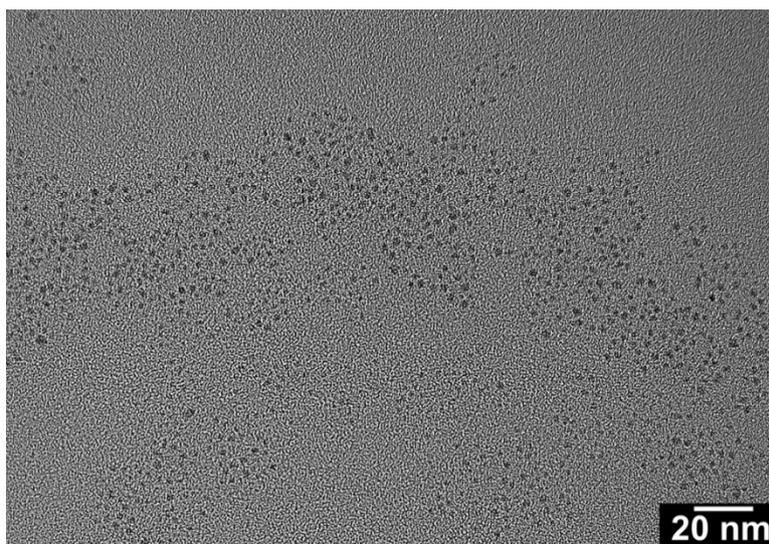


Figure S7. TEM image of the Au-Co-TCPP after 1 h photocatalytic test.

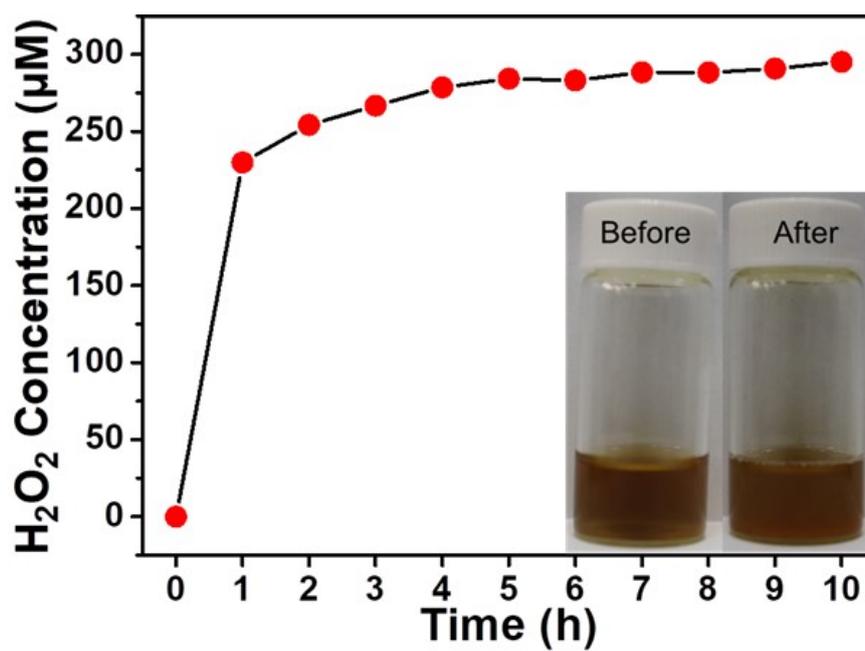


Figure S8. Long-term photocatalytic H₂O₂ production (10 h) over the Au-Co-TCPP. The inset shows digital photos of the Au-Co-TCPP solution before and after the photocatalytic reaction.

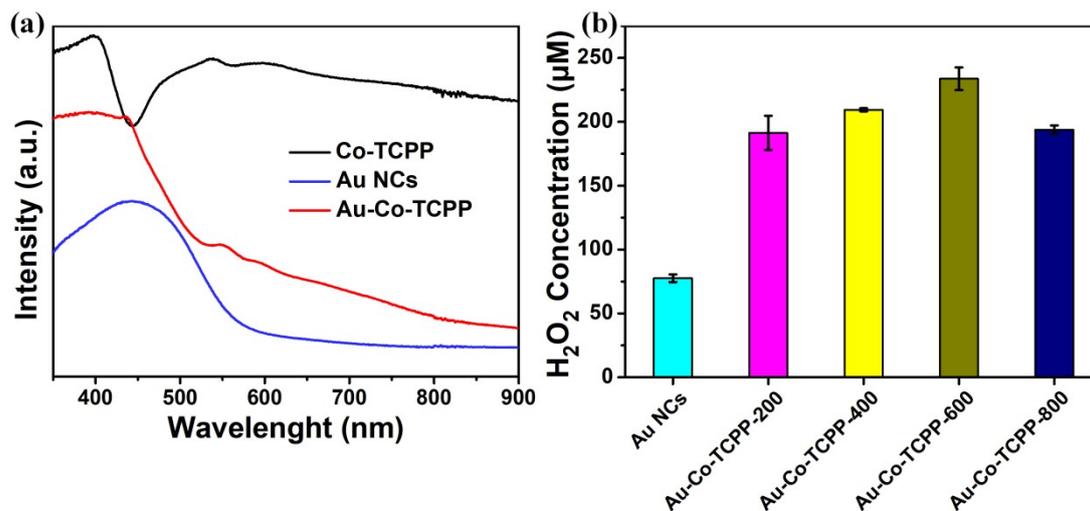


Figure S9. (a) UV-visible DRS spectra of pristine Au NCs, pristine Co-TCPP, and the Au-Co-TCPP. (b) The H₂O₂ production over five Au-Co-TCPP samples with different grafting amounts of Co-TCPP.

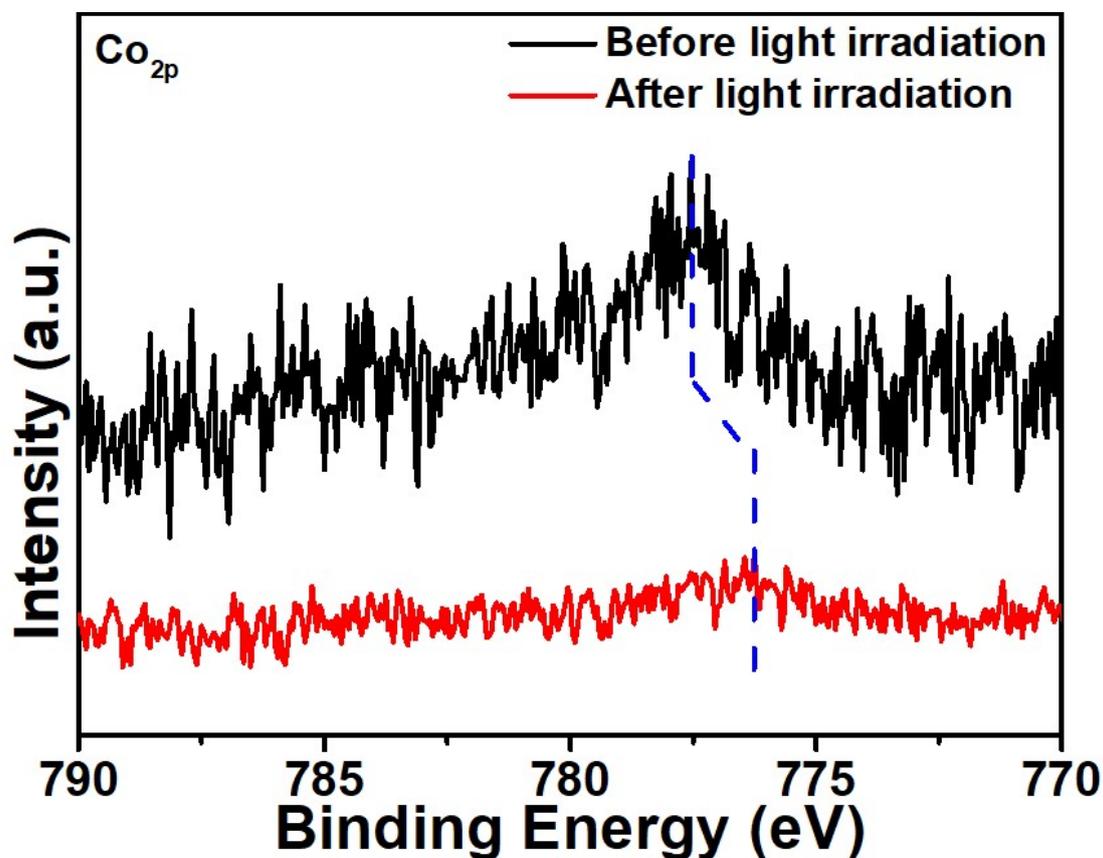


Figure S10. High-resolution XPS spectra of Co_{2p} in the Au-Co-TCPP before and after the recycled reaction.

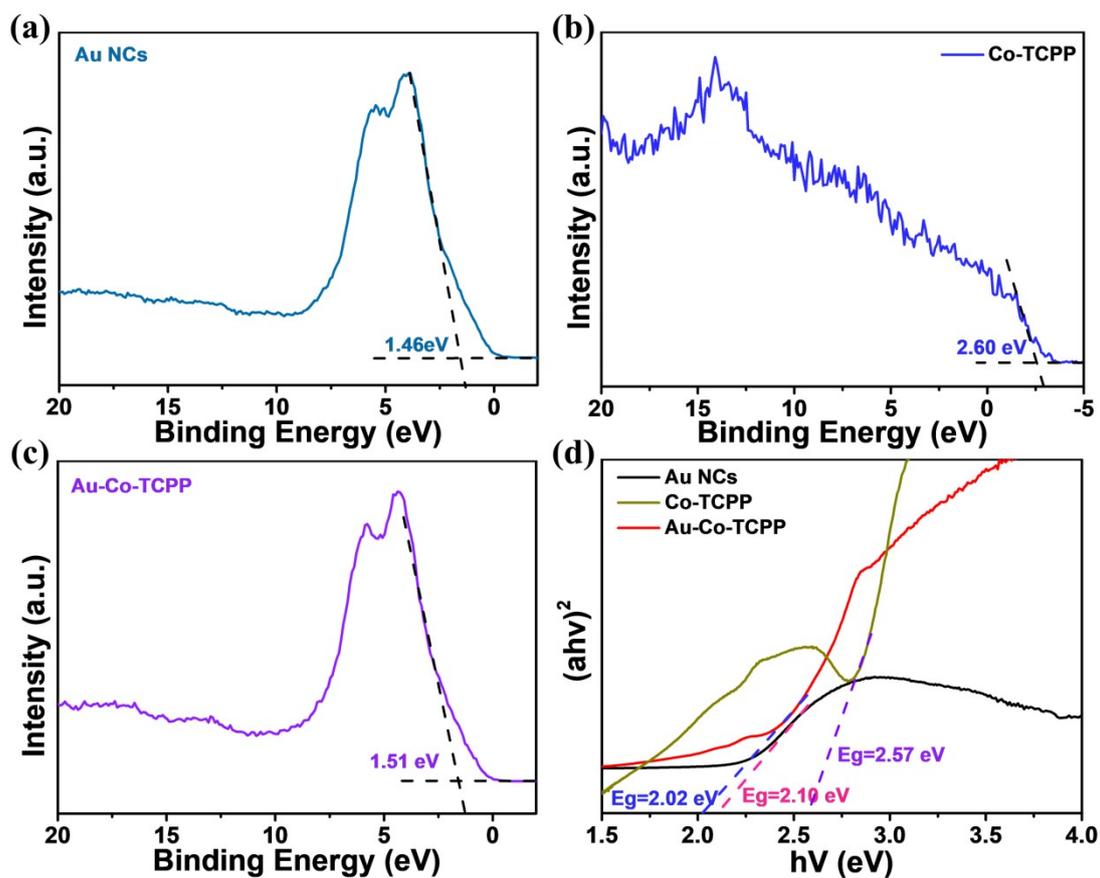


Figure S11. VB-XPS curves of (a) pristine Au NCs (b) Co-TCPP and (c) the Au-Co-TCPP. (d) The calculated energy gap (E_g) of pristine Au NCs, Co-TCPP and the Au-Co-TCPP photocatalysts according to their corresponding UV-visible DRS.

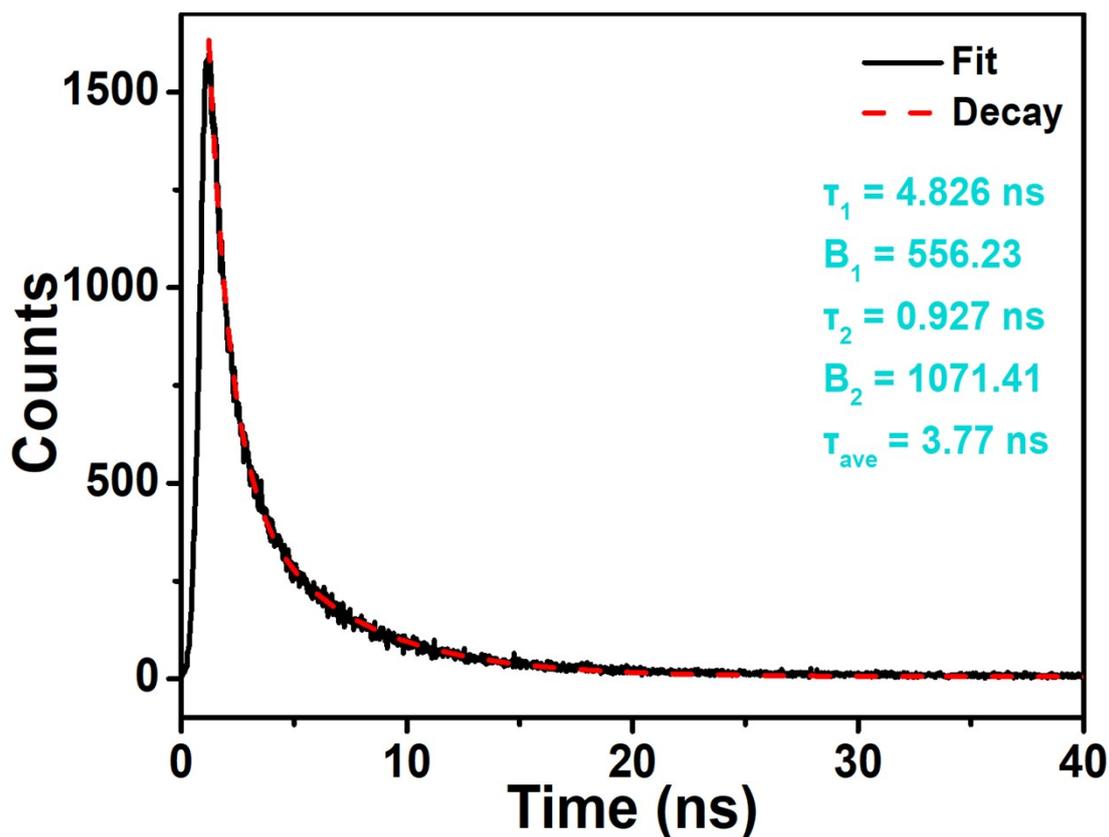


Figure S12. Luminescence decay profile of Co-TCPP.

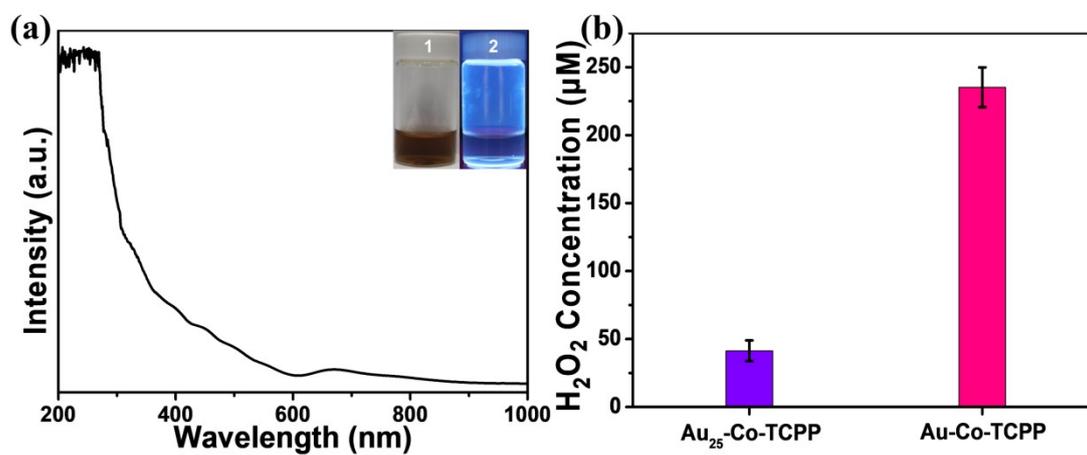


Figure S13. (a) UV-visible absorption of the as-synthesized Au₂₅(SG)₁₈ NCs. The inset shows digital photos of the Au₂₅(SG)₁₈ NCs solution under visible (1) and UV (2) light irradiation. (b) Comparison of Au₂₅-Co-TCPP and Au-Co-TCPP in photocatalytic production of H₂O₂.

Table S1. Comparison in the photocatalytic H₂O₂ production of the Au-Co-TCPP with other semiconductor photocatalysts reported in the literature.

Photocatalyst	Dosage (g · L ⁻¹)	Light wavelength	Reaction solution	Yield (μM g ⁻¹ h ⁻¹)	Ref.
Ag Au/TiO ₂	1	λ > 280 nm	EtOH/Water	25.00	[4]
MnO@C ₃ N ₄	1	λ ≥ 420 nm	Water	42.00	[5]
CN/rGO@BPQDS	1	λ ≥ 420 nm	Water	60.56	[6]
CoP/g-C ₃ N ₄	1	λ ≥ 420 nm	Water	70.00	[7]
DCN	0.83	λ ≥ 420 nm	IPA/water	96.80	[8]
OCN-500	1	λ ≥ 420 nm	Water	106.00	[9]
SN-GQD/TiO ₂	0.5	λ ≥ 420 nm	IPA/water	110.4	[10]
K ₂ HPO ₄ /g-C ₃ N ₄	1	λ ≥ 420 nm	EtOH/water	114.00	[11]
Ti ₃ C ₂ /g-C ₃ N ₄	1	λ ≥ 420 nm	IPA/water	131.70	[12]
Au/MoS ₂	1	λ ≥ 420 nm	water	131.95	[13]
Pd/APTMS/TiO ₂	1	AM = 1.5 G	Water	150.00	[14]
AkMT	1	AM = 1.5 G	EtOH/water	175.00	[15]
AQ/g-C ₃ N ₄	1	AM = 1.5 G	IPA/water	180.00	[16]
TAPD-(Me) ₂ COF	4	λ = 420 – 700 nm	IPA/water	234.52	[17]
Sb-SAPC15	2	λ ≥ 420 nm	water	470.00	[18]
Au-Co-TCPP	1	λ ≥ 400 nm	Water	235.93	This work

Table S2. The fitting parameters for the luminescence decay curves of the Au-Co-TCPP at different atmospheres. The average luminescent lifetime (τ_{ave}) can be calculated from the following $\tau_{ave} = (B_1 \tau_1^2 + B_2 \tau_2^2) / (B_1 \tau_1 + B_2 \tau_2)$.

Gas	τ_1 (μs)	B ₁	τ_2 (μs)	B ₂	τ_{ave} (μs)
O ₂	9.22	24088.02	2.23	74428.55	6.17
Air	2.44	73591.67	9.70	32970.11	7.00
Ar	9.75	38215.23	2.40	81901.02	7.19

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