

**Au nanorods modified PCN-222(Cu) for H<sub>2</sub> evolution from HCOOH  
dehydrogenation by photothermal enhanced photocatalysis**

Yao Wang, Xiaohua Wang, Haiyue Lu, Zhizhi Gu and Liyong Chen\*

## Experimental Section

### Materials and characterization methods

All chemical reagents were used as received. Nafion solution (5 wt% in mixture of water and 2-propanol), tetra-*n*-butylammonium hexafluorophosphate were purchased from Sigma Aldrich, and other chemicals and solvents, including copper(II) chloride ( $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ ), zirconium chloride ( $\text{ZrCl}_4$ ), chloroauric acid ( $\text{HAuCl}_4$ ), benzoic acid, methyl *p*-formylbenzoate, propionic acid, pyrrole, methanol, ethanol, ethyl acetate, tetrahydrofuran (THF), *N,N*-dimethylformamide (DMF), *N,N*-Diethylformylamide (DEF), potassium hydroxide (KOH), hexadecyl trimethyl ammonium bromide (CTAB), and hydrochloric acid (HCl), were purchased from Sinopharm Chemical Reagent Co., Ltd, China.

Transmission electron microscopy (TEM) and scanning electron microscopy (SEM) were performed for microstructural and morphological characterization on Tecnai F30, and HITACHI UHR FE-SEM SU8220, respectively. X-ray diffraction (XRD) was conducted in a Rigaku D/Max 2400 automatic powder X-ray diffractometer with  $\text{Cu-K}\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ). Cyclic voltammetry (CV), Mott Schottky (M-S) and transient photocurrent measurements were carried out by a CHI760E electrochemical workstation with a typical three-electrode cell. UV-vis absorption spectrum was collected by a HITACHI U-4100 spectrometer.  $\text{N}_2$  sorption isotherm at 77 K were recorded by a Micromeritics 3Flex Surface Characterization Analyzer. Gas chromatograph (GC7900 Techcomp) was performed on analyzing the gas products. The temperature of reaction were collected on Fluke TiS20<sup>+</sup> thermal imager. Bruker AC-400FT spectrometer (400 MHz) was performed for  $^1\text{H}$ NMR of the liquid phase products. The content of metal elements was evaluated by inductively coupled plasma atomic emission spectroscopy (ICP-AES) on Optima 2000DV. X-ray photoelectron spectroscopy (XPS) was performed on Thermo ESCALAB 250Xi with  $\text{Al-K}\alpha$  radiation ( $h\nu = 1486.6 \text{ eV}$ ).

### Materials synthesis

#### Preparation of 5,10,15,20-Tetrakis(4-methoxycarbonylphenyl)porphyrin.

In a typical synthetic procedure, methyl *p*-formylbenzoate (6.9 g, 0.042 mol) was added in a 250-mL round-bottom flask containing propionic acid (100 mL). Pyrrole (3 mL, 0.043 mol) was added dropwise to the solution. The resultant mixture was refluxed for 12 h at 140 °C. Afterwards, the flask was cooled down to room temperature, and then the purple precipitate was collected by suction filtration before washing with methanol, ethyl acetate, and THF in sequence. The final product was dried in vacuum at 80 °C for 12 h before being subjected to characterization.  $^1\text{H}$  NMR (500 MHz, DMSO)  $\delta$  8.87 (s, 8H)  $\delta$  8.39 (d, 8H), and  $\delta$  8.35 (d, 8H).

#### Preparation of [5,10,15,20-tetrakis (4-carboxyphenyl) porphyrine]-Cu (Cu-TCPP).

The as synthesized ester (1.95 g) and  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  (2.2 g, 12.8 mmol) in 100 mL of DMF was refluxed for 6 h. After the mixture was cooled to room temperature, 150 mL of  $\text{H}_2\text{O}$  was added. The red precipitate was collected by suction filtration before washing with ethyl acetate and THF in sequence. The final product was dried in vacuum

at 80 °C for 12 h before being subjected to characterization. The obtained ester was dispersed into a round-bottom flask containing a mixture solvent of THF and methanol (120 mL, V:V = 1:1) with stirring. An aqueous solution of KOH (6.28 g, in 60 mL of water) was introduced to the aforementioned flask. The resultant mixture was refluxed for 12 h at 60 °C before cooling down to room temperature. Methanol and THF were evaporated from the mixture, and then additional water was added until the solid was completely dissolved. Afterwards, the aqueous solution was acidified with HCl (1 M) until no precipitate was further produced. The final purple product was collected by suction filtration, washed with water and dried in vacuum at 80 °C for 12 h before being subjected to characterization.

#### **Synthesis of PCN-222(Cu).**

PCN-222(Cu) was synthesized by a typical solvothermal reaction. ZrCl<sub>4</sub> (70 mg), Cu-TCPP (60 mg) and benzoic acid (2700 mg) in 8 mL of DEF were ultrasonically dissolved in a 15 mL Teflon-lined stainless autoclave and heated at 120 °C for 48 h. After cooling down to room temperature, red-colored products were collected by centrifugation at 8000 g for 5 min, and then washed several times with DEF and ethanol, and dried under vacuum at 80 °C for 24 h.

#### **Synthesis of Au/PCN-222(Cu).**

Firstly, Au seeds were prepared by quickly adding NaBH<sub>4</sub> ice-cold aqueous solution (180 μL, 10 mM) to HAuCl<sub>4</sub> (3 mL, 0.25 mM) solution prepared in CTAB solution (0.1 M) under vigorously stirring for 10 min. The mixture was kept at room temperature for another 1 h. PCN-222(Cu) (20 mg) was dispersed in CTAB solution (5 mL, 0.1 M) by sonication, and the seed solution (100 μL) was added with stirring for 30 min to form Au seeds modified PCN-222(Cu). CTAB solution in water (14 mL, 0.1 M) and AgNO<sub>3</sub> solution (0.6 mL, 10 mM) were added in 25-mL conical flask followed by HAuCl<sub>4</sub> solution (2 mL, 10 mM). Ascorbic acid solution (0.22 mL, 0.1 M) was added into conical flask with gently shaking. Finally, Au seeds modified PCN-222(Cu) (60 μL) were added. The resulting solution was kept at room temperature in the darkness without disturbing overnight. The material were collected by centrifugation at 8000 g for 5 min and then washed several times with water and ethanol, and dried under vacuum at 80 °C for 24 h.

To control the amount of Au NRs loaded on the surfaces of PCN-222(Cu), the volume of Au seed solution was adjusted from 50 μL to 200 μL.

#### **Photocatalytic reaction**

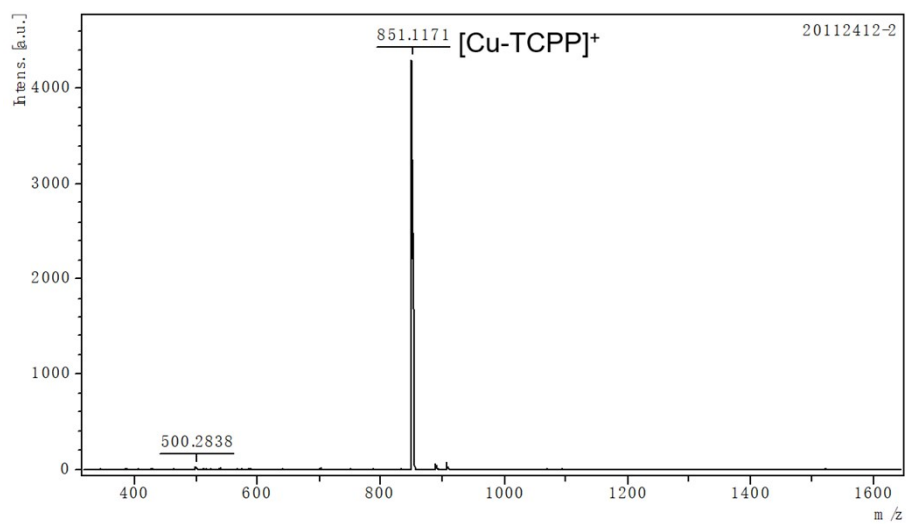
The photocatalytic experiment was carried out in a custom-made quartz glass (20 mL, Perfectlight, China). The photocatalyst powder (5 mg) was dispersed into 5 mL of the mixed aqueous solution of HCOOH (1 M) and HCOONa (1 M). The reaction setup was purged by Ar for 20 min to remove all the impurities. The photocatalytic reaction was irradiated with visible light by a 300 W Xe-arc lamp with UV cutoff filter ( $\lambda > 400$  nm, 10 mW cm<sup>-2</sup>) under magnetic stirring gently at room temperature. The gas products were analyzed by using a gas chromatograph (GC7900 Techcomp) and liquid products were determined by a nuclear magnetic resonance (NMR) spectrometer (Bruker AC-400FT).

The photocatalyst powder of PCN-222(Cu) (5 mg) was dispersed into deionized water (5 mL) with sonication for 10 min. The resultant mixture was transferred to a custom-made quartz glass, and CO<sub>2</sub> was constantly purged into the quartz reactor for 20 min to remove all impurities. The photocatalytic reaction was irradiated with visible light by a 300 W Xe-arc lamp with UV cutoff filter ( $\lambda > 400$  nm, 10 mW cm<sup>-2</sup>) under magnetic stirring gently at room temperature for 4 h. Gas products were detected by gas chromatography (GC 7900), and liquid products were detected and quantified by ion chromatography (IC, DIONEX ICS-1100). According to the data of IC, the rate of photocatalytic reduction CO<sub>2</sub> to formic acid was estimated to be about 10  $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$ .

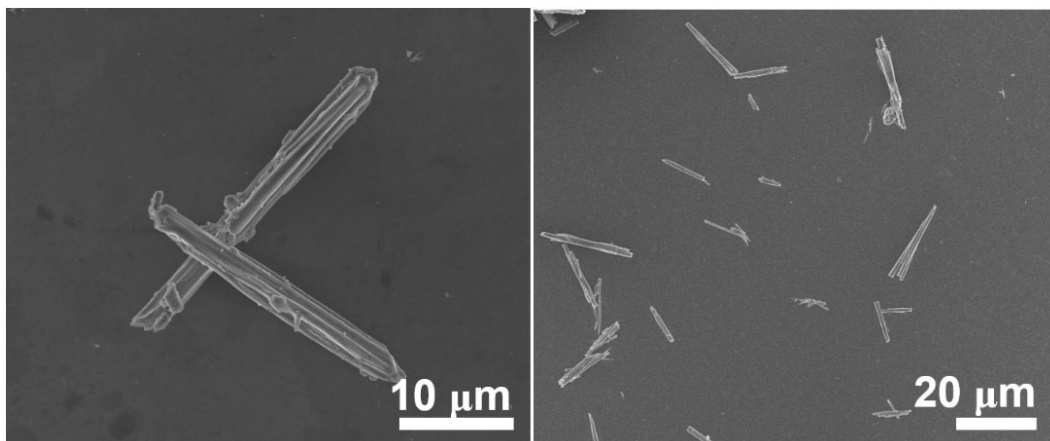
The flat-band potential was determined in accordance to the equation:

$$\frac{1}{C^2} = \frac{2}{q\epsilon\epsilon_0N_d} \left( E - E_{fb} - \frac{k_bT}{q} \right), \quad 1$$

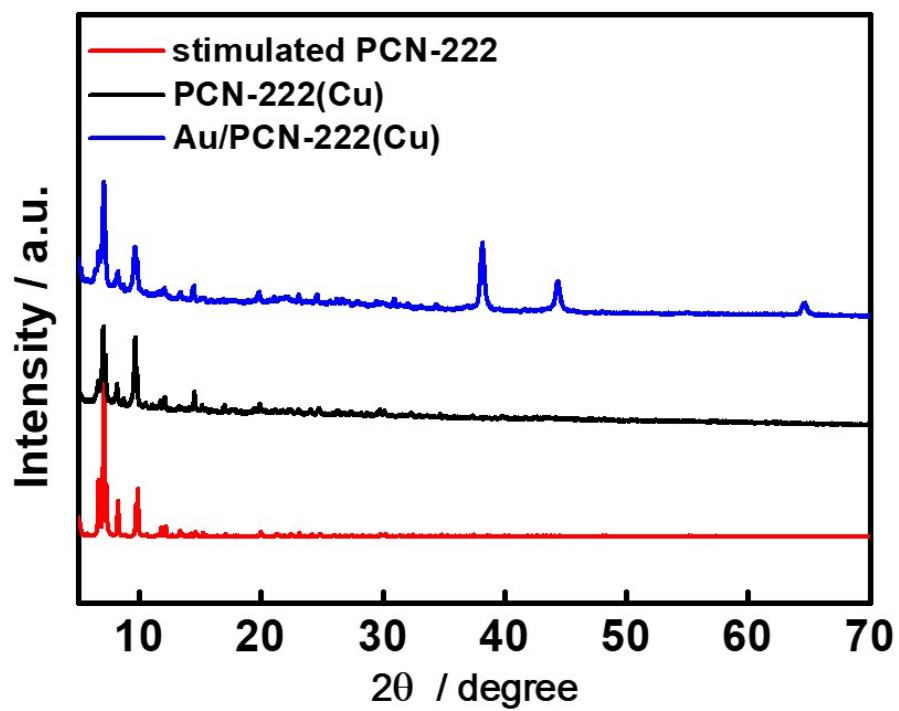
where  $C$ ,  $k_b$ ,  $T$ ,  $E$ ,  $E_{fb}$ ,  $N_d$ , and  $q$  represent space charge capacitance, Boltzmann's constant, absolute temperature, applied potential, flat-band potential, carrier concentration, and electronic charge respectively;  $\epsilon$ ,  $\epsilon_0$  are dielectric constant of semiconductor and permittivity in vacuum, respectively.



**Figure S1.** Mass spectrum of Cu-TCPP.

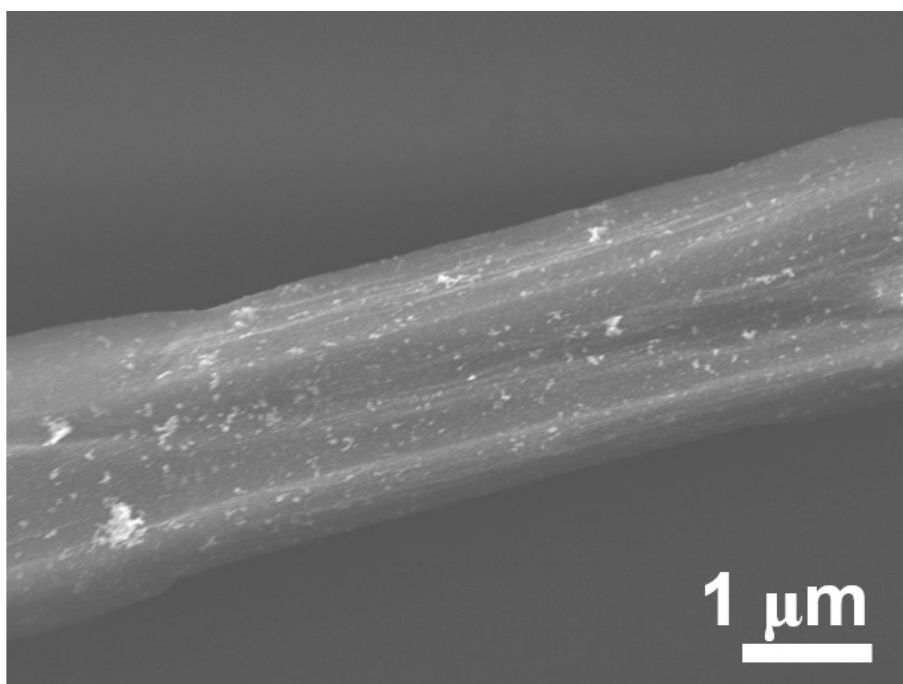


**Figure S2.** TEM images of PCN-222(Cu) with different magnification.

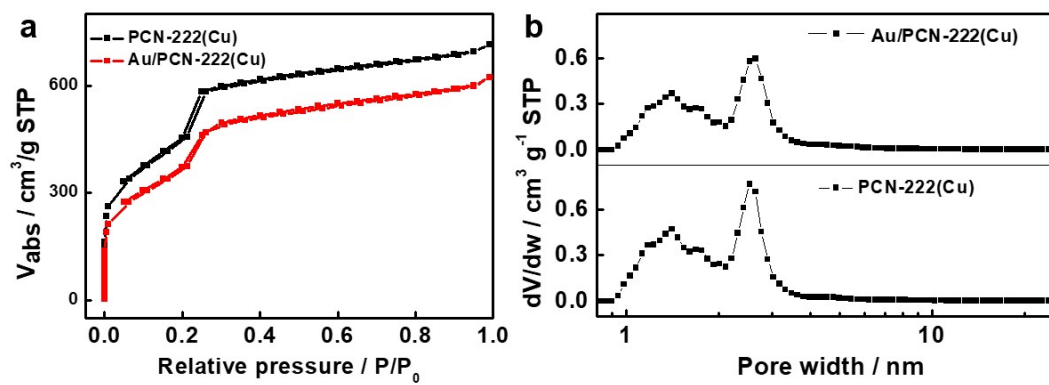


**Figure S3.** XRD patterns of PCN-222(Cu) and Au/PCN-222(Cu).

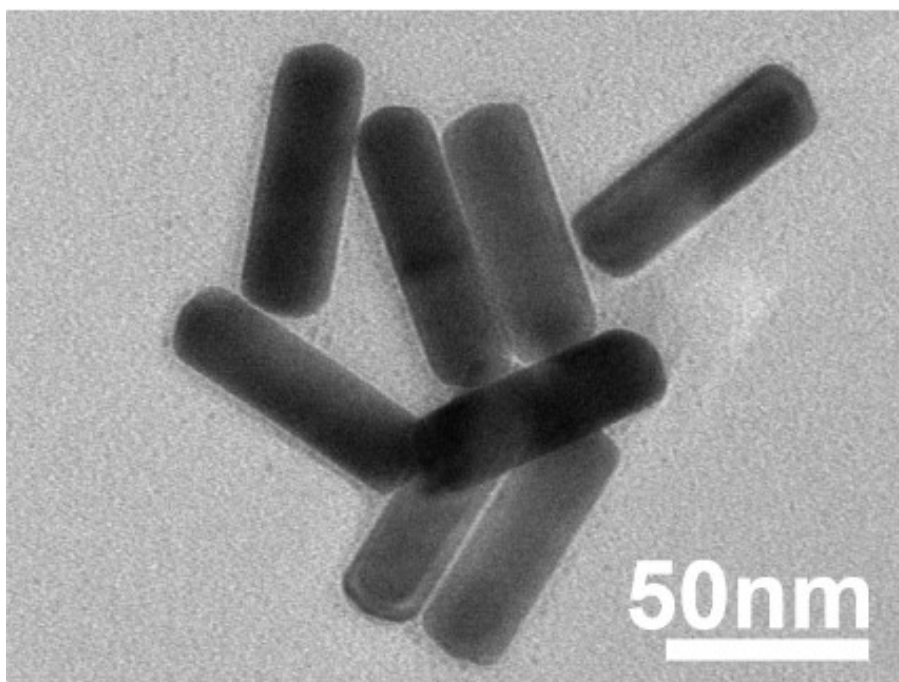




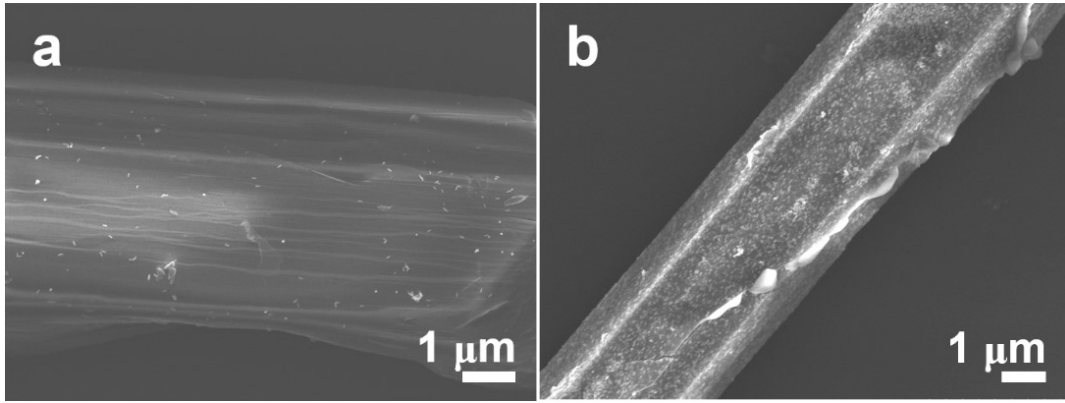
**Figure S4.** SEM image of Au/PCN-222(Cu).



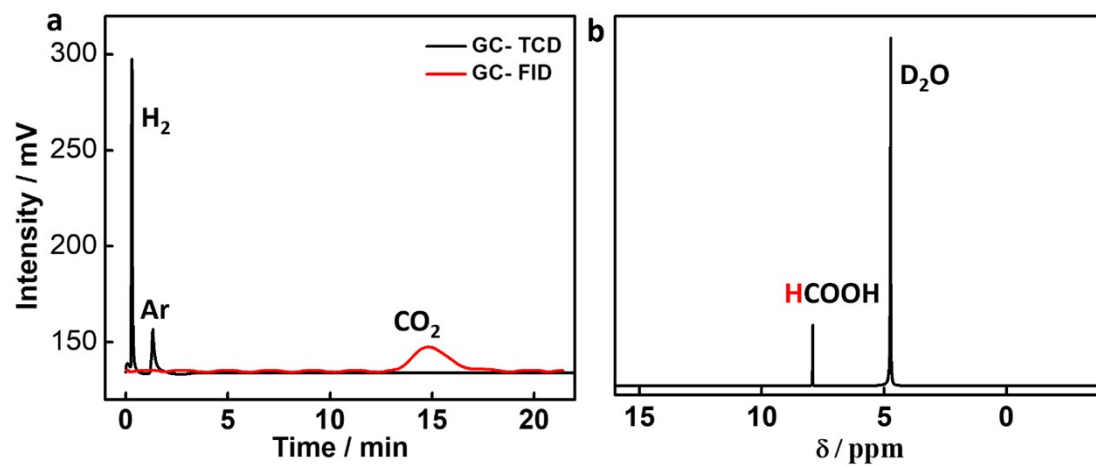
**Figure S5.** (a)  $\text{N}_2$  physisorption isotherms at 77 K and (b) pore size distribution of PCN-222(Cu) and Au/PCN-222(Cu).



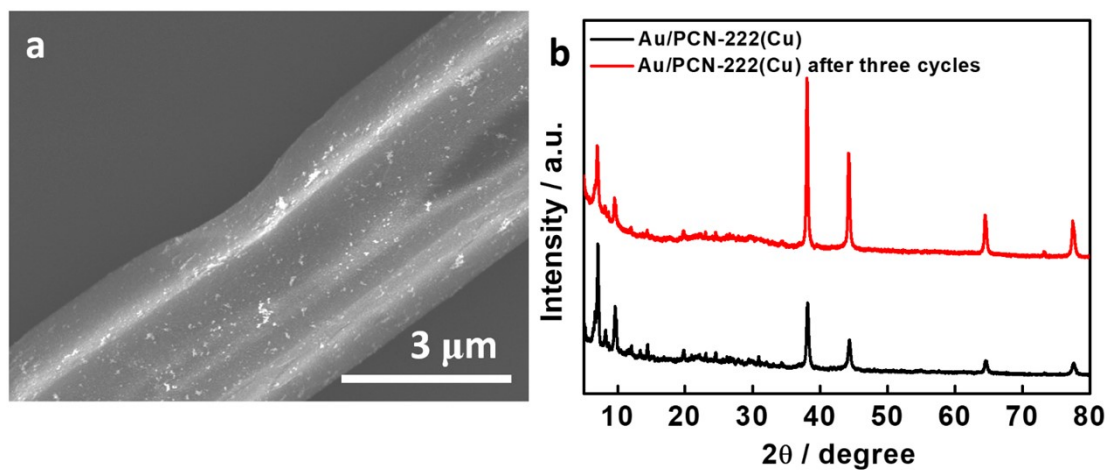
**Figure S6.** TEM image of Au NRs prepared by direct use of seeds.



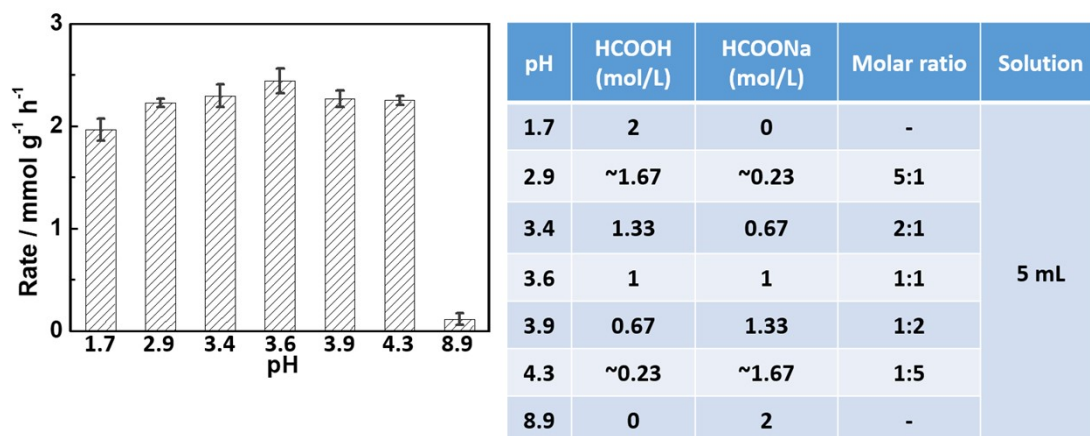
**Figure S7.** SEM image of composites of Au NRs loaded PCN-222 while the amount of seeds is (a) 50  $\mu\text{L}$  and (b) 200  $\mu\text{L}$ , respectively.



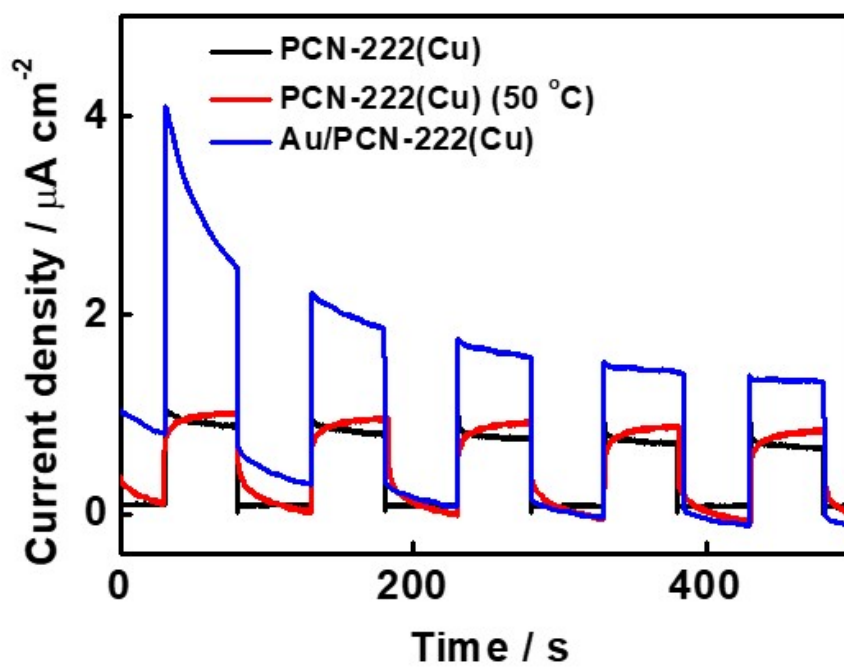
**Figure S8.** (a) GC and (b) NMR analysis of gas products and liquid products from photocatalytic dehydrogenation of HCOOH over Au/PCN-222(Cu).



**Figure S9.** (a) SEM image and (b) XRD pattern of Au/PCN-222(Cu) after three-cycle photocatalytic HCOOH dehydrogenation and the as-synthesized Au/PCN-222(Cu).

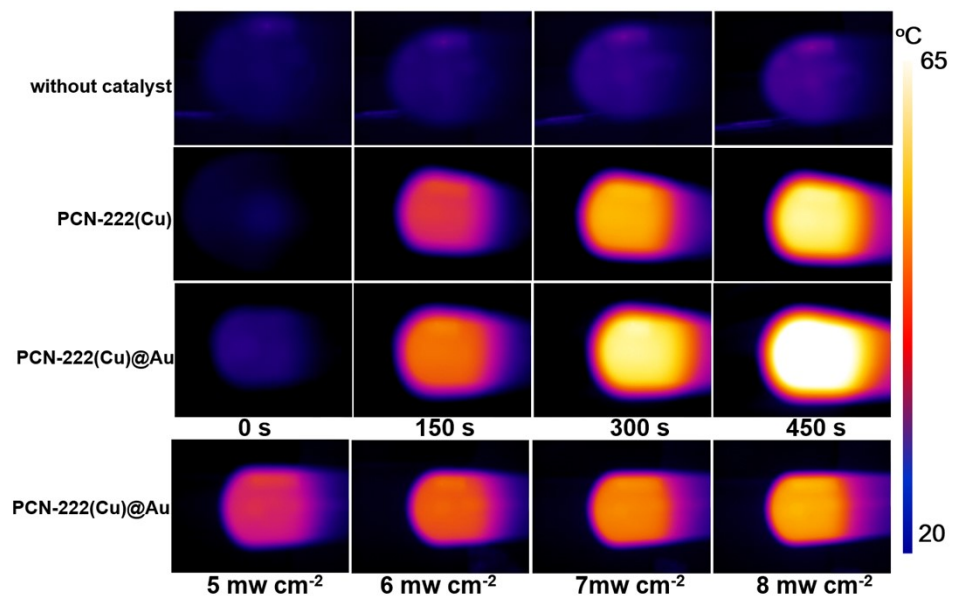


**Figure S10.** Photocatalytic activity of Au/PCN-222(Cu) under different pH upon visible light irradiation ( $10 \text{ mW cm}^{-2}$ )

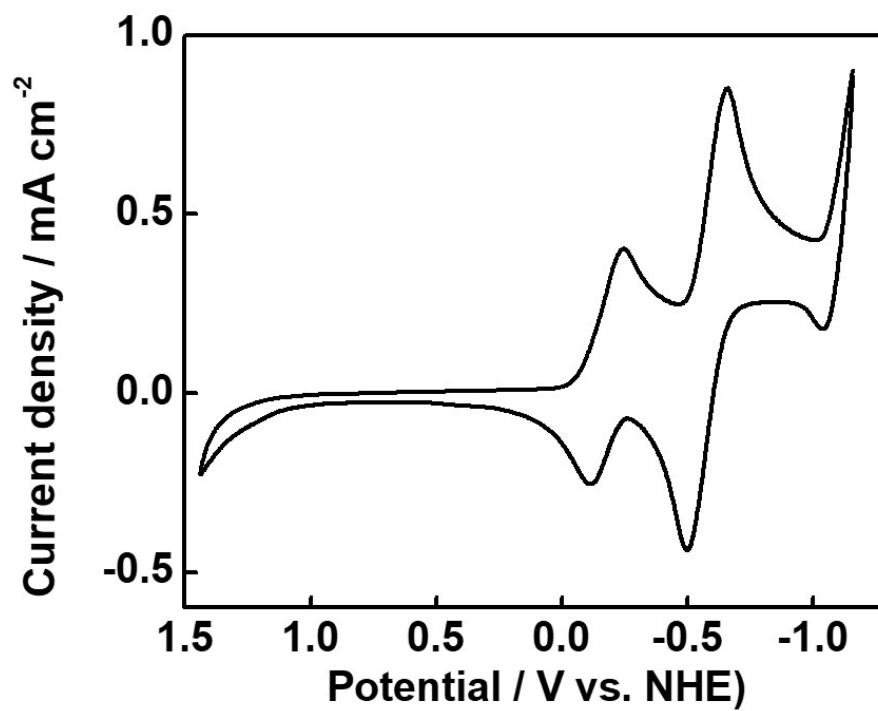


**Figure S11.** Photocurrents of PCN-222(Cu) and Au/PCN-222(Cu) measured at room temperature and 50 °C.

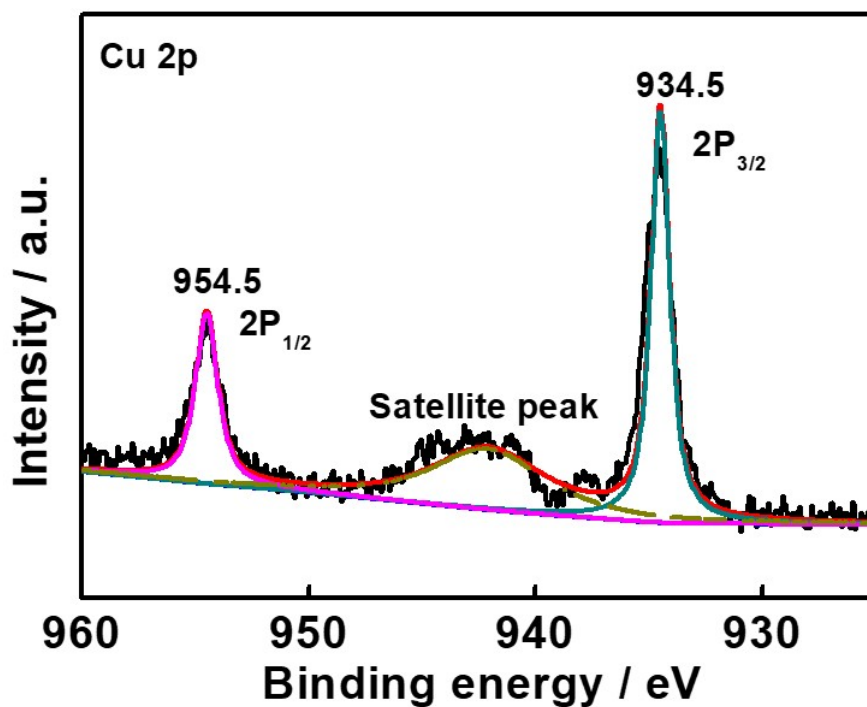




**Figure S12.** IR images of photocatalytic system with and without photocatalysts upon irradiation of visible light ( $10 \text{ mW cm}^{-2}$ ) from 0 to 15 min and upon irradiation of visible light with different output power for 15 min.

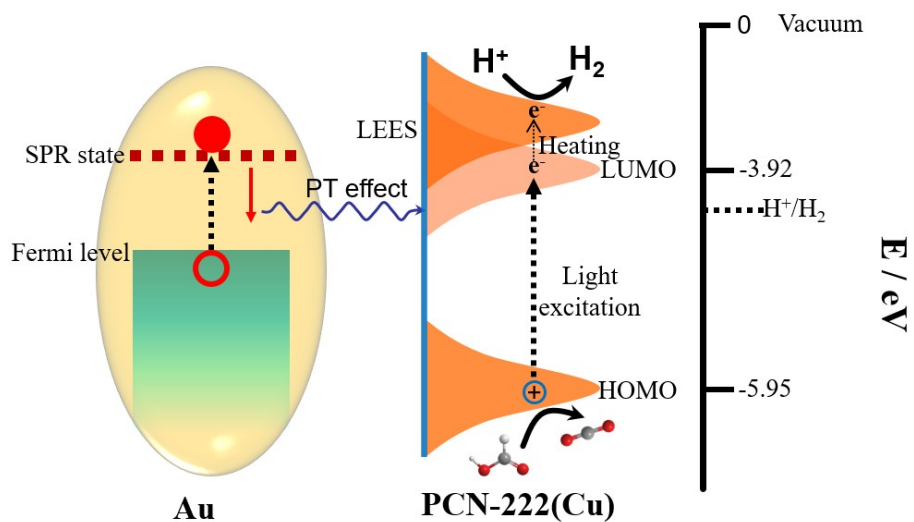


**Figure S13.** CV of Cu-TCPP in DMF with TBAPF<sub>6</sub> (0.1 M) at 100 mV/s scan rates.

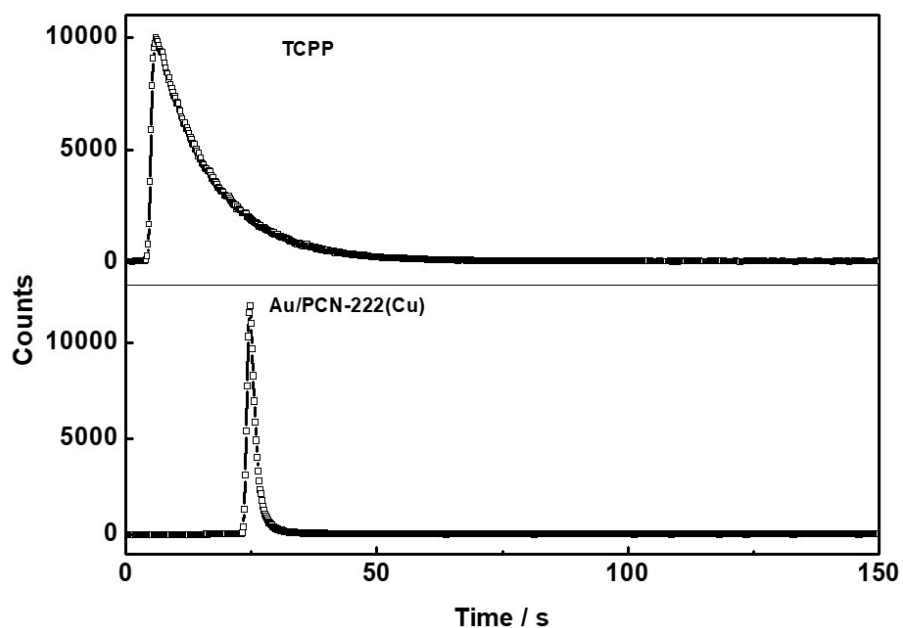


**Figure S14.** Cu 2p core level XPS spectrum of Au/PCN-222(Cu).

The peaks assigned to Cu  $2P_{3/2}$  and  $2P_{1/2}$  core levels were captured at 934.5 and 954.5 eV, accompanied with satellite peaks at higher binding energy side, further revealing the presence of Cu(II) species.

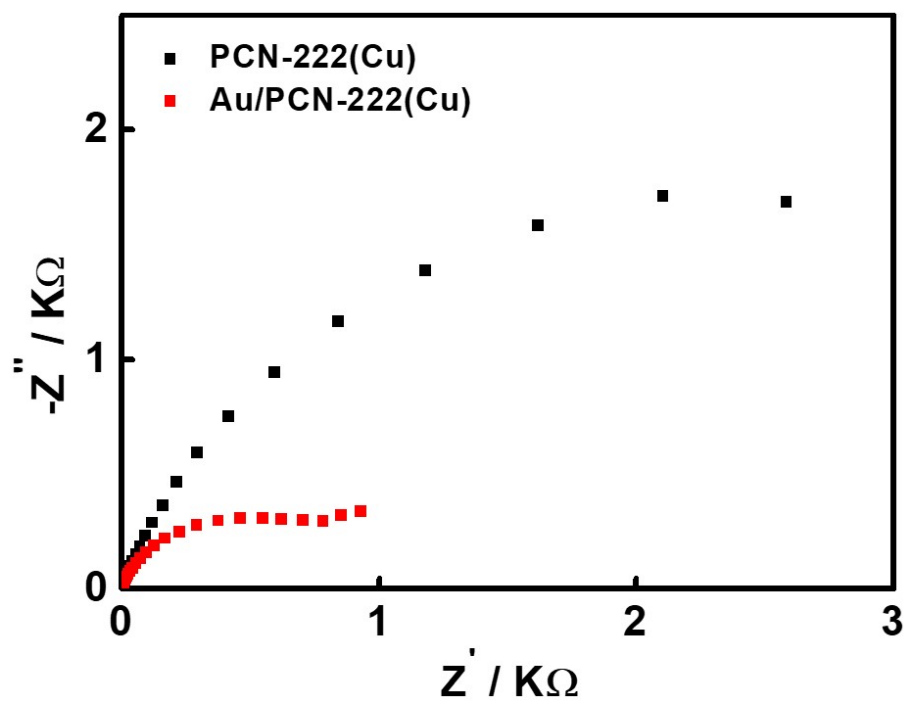


**Figure S15.** (a) Schematic illustrating the mechanism for photothermal effect enhanced photocatalytic activity of Au/PCN-222(Cu) towards HCOOH dehydrogenation.



**Figure S16.** Time-resolved PL spectra of TCPP and Au/PCN-222(Cu).

Time-resolved emission spectra of TCPP and Au/PCN-222(Cu) in DMF (N,N-dimethylformamide) at 650 nm were conducted under excitation of 515 nm laser. The excited-state lifetime of TCPP is about 11.2 ns according to single-exponential fitting equation of  $A + B_1 \exp(-t/\tau)$ . Interestingly, time-resolved emission spectrum of Au/PCN-222(Cu) shows biexponential PL decays by the fitting equation of  $A + B_1 \exp(-t/\tau_1) + B_2 \exp(-t/\tau_2)$ , and the average excited-state lifetime is estimated to 7.0 ns based on  $\tau_1 = 1.09$  ns (39%) and  $\tau_2 = 10.81$  ns (61%).



**Figure S17.** Nyquist plots of PCN-222(Cu) and Au/PCN-222(Cu) measured at 1.0 V vs Ag/AgCl.

**Table 1.** Comparison of the photocatalytic activity of different photocatalysts towards H<sub>2</sub> evolution.

Photocatalyst	Incident light (light intensity)	Catalytic medium	H <sub>2</sub> evolution rate (mmol g <sup>-1</sup> h <sup>-1</sup> )	Quantum efficiency (%@wavelength)	Reference
QD-MPA/CoCl <sub>2</sub>	Newport Oriel (100 mW·cm <sup>-2</sup> )	FA- HCOONa- H <sub>2</sub> O	116±14	21.2±2.7@460 nm	1
Pt/CdS	400 W Hg lamp (-)	FA-H <sub>2</sub> O	4	13.9@420 nm	2
Ru-CdS/ZnS	350 W Xe lamp (-)	FA-H <sub>2</sub> O	4.8	20%	3
CdS/P/MoS <sub>2</sub>	300 W Xe lamp (-)	FA-H <sub>2</sub> O	68.89	6.39%@420 nm,	4
Cu-TiO <sub>2</sub>	300 W Xe lamp (80 mW·cm <sup>-2</sup> )	FA-H <sub>2</sub> O	0.83	-	5
CdS	500 W halogen lamp(-)	FA-H <sub>2</sub> O	0.036	1.9%	6
AuPd-TiO <sub>2</sub> NW	300 W Xe lamp (80 mW·cm <sup>-2</sup> )	FA-H <sub>2</sub> O	17.7	15.6%@365 nm	7
CdS-TNT + WO <sub>3</sub>	150 W CDM- TD(-)	FA-H <sub>2</sub> O	0.619	-	8
Pt/g-C <sub>3</sub> N <sub>4</sub>	300 W Xe lamp (70 mW·cm <sup>-2</sup> )	FA-H <sub>2</sub> O	1.59	-	9
Cu <sub>2</sub> O	Halogen lamp (280 mW·cm <sup>-2</sup> )	FA-NaOH	0.07	-	10
Pt-Cu <sub>2</sub> O	Halogen lamp (280 mW·cm <sup>-2</sup> )	FA-NaOH	0.155	-	10
FHS	San-Ei Electric (100 mW·cm <sup>-2</sup> )	FA-H <sub>2</sub> O	0.47	-	11
Pt(0.5%)/P <sub>25</sub> TiO <sub>2</sub>	250 W Hg lamp (70 mW·cm <sup>-2</sup> )	FA-H <sub>2</sub> O	1.15	-	12
Cu <sub>2</sub> O/TiO <sub>2</sub>	300 W Xe lamp (100 mW·cm <sup>-2</sup> )	FA-H <sub>2</sub> O	2.36	2.21%@365 nm	13
0.25wt% MoP/ZIS6	300 W Xe lamp (-)	FA-H <sub>2</sub> O	0.93	6.4%@400±10 nm	14
MoS <sub>2</sub> /Zn <sub>3</sub> In <sub>2</sub> S <sub>6</sub>	300 W Xe lamp (-)	FA-H <sub>2</sub> O	0.74	-	15
Au/PCN- 222(Cu)	300 W Xe lamp (70 mW·cm <sup>-2</sup> )	HCOOH- HCOONa	2.33±0.12	2.7±0.14 %	This work

1. M. F. Kuehnel, D. W. Wakerley, K. L. Orchard and E. Reisner, *Angew. Chem. Int. Ed.*, 2015, **54**, 9627-9631.
2. Y. Li, Y. Hu, S. Peng, G. Lu and S. Li, *J. Phys. Chem. C*, 2009, **113**, 9352-9358.

3. X. Wang, W.-c. Peng and X.-y. Li, *Int. J. Hydrog. Energ.*, 2014, **39**, 13454-13461.
4. J. Liu, H. Huang, C. Ge, Z. Wang, X. Zhou and Y. Fang, *Nanomaterials*, 2022, **12**, 10.3390/nano12030561.
5. V. Lanese, D. Spasiano, R. Marotta, I. Di Somma, L. Lisi, S. Cimino and R. Andreozzi, *Int. J. Hydrog. Energ.*, 2013, **38**, 9644-9654.
6. A. I. Nedoluzhko, I. A. Shumilin and V. V. Nikandrov, *J. Phys. Chem.*, 1996, **100**, 17544-17550.
7. Z. Zhang, S.-W. Cao, Y. Liao and C. Xue, *Appl. Catal. B-Environ.*, 2015, **162**, 204-209.
8. H. M. Yeh, S. L. Lo, M. J. Chen and H. Y. Chen, *Water Sci. Technol.*, 2014, **69**, 1676-1681.
9. J. Wang, X. Wang, L. Qiu, H. Wang, L. Duan, Z. Kang and J. Liu, *Nanotechnology*, 2021, **32**, 275404.
10. S. Kakuta and T. Abe, *ACS Appl. Mater. Interfaces*, 2009, **1**, 2707-2710.
11. H. El-Hosainy, R. Tahawy, M. Esmat, M. El-Kemary and Y. Ide, *Front. Energy Res.*, 2021, **9**, 630535.
12. Y. X. Li, G. X. Lu and S. B. Li, *Chemosphere*, 2003, **52**, 843-850.
13. Z. Zhang, K. Liu, Y. Bao and B. Dong, *Appl. Catal. B-Environ.*, 2017, **203**, 599-606.
14. S. Duan, S. Zhang, S. Chang, S. Meng, Y. Fan, X. Zheng and S. Chen, *Int. J. Hydrog. Energ.*, 2019, **44**, 21803-21820.
15. S. Zhang, S. Duan, G. Chen, S. Meng, X. Zheng, Y. Fan, X. Fu and S. Chen, *Chinese J. Catal.*, 2021, **42**, 193-204.