

Electronic Supplementary Information

A simple strategy for engineering heterostructures of AuNPs loaded metal-organic framework nanosheets to achieve plasmon-enhanced photocatalytic CO₂ conversion under visible light

Liyong Chen, Yanxin Wang, Fengyang Yu, Xiaoshuang Shen and Chunying Duan

Experimental Section

Materials and characterization methods

All chemical reagents were used as received. Nafion solution (5 wt% in mixture of water and 2-propanol) was purchased from Sigma Aldrich. Other chemicals and solvents were purchased from Sinopharm Chemical Reagent Co., Ltd, China.

Transmission electron microscopy (TEM), scanning electron microscopy (SEM) and atomic force microscopy (AFM) were conducted on Tecnai F30 operated at 300 kV, HITACHI UHR FE-SEM SU8220 and Park Systems XE-70 with non-contact mode, respectively to characterize morphology and structure of samples. X-ray diffraction (XRD) was performed on a Rigaku D/Max 2400 automatic powder X-ray diffractometer with Cu-K α radiation ($\lambda = 1.5418 \text{ \AA}$). 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 used to analyze surface elemental composition and chemical state on Thermo ESCALAB 250Xi with Al- K α radiation ($h\nu = 1486.6 \text{ eV}$). UV-Vis absorption spectroscopy and photoluminescence (PL) emission spectroscopy were collected on a HITACHI U-4100 spectrometer and a FLS 920 fluorescence spectrometer, respectively. CO₂ adsorption isotherm at 273 K were carried out on an Autosorb-iQ gas sorption analyzer after being degassed in vacuum at 200 °C for 12 h. Cyclic voltammetry (CV), transient photocurrent, and Mott-Schottky (M-S) tests were carried out on a CHI760E electrochemical workstation with a typical three-electrode cell. Electrochemical impedance spectroscopy (EIS) was collected on a ZAHNER ENNIUM electrochemical workstation. Zeta potential were measured by Zetasizer Nano ZS90. Fourier-transform infrared (FTIR) spectroscopy were performed on FTIR EQUINOX 55 spectrometer.

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. ¹H NMR (500 MHz, DMSO) δ 8.87 (s, 8H) δ 8.39 (d, 8H), and δ 8.35 (d, 8H).

Preparation of 5,10,15,20-tetrakis (4-carboxyphenyl) porphyrine (TCPP). The as-synthesized ester (1.95 g) 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 mixutre, 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, wash with water and dried in vacuum at 80 °C for 12 h before being subjected to characterization.

Preparation of electrodes

Photocatalysts (5 mg) were dispersed into the mixture of water and 2-propanol with volume ratio of 1:1 (0.975 mL), and then Nafion solution (0.025 mL, 5 wt%) was added. The final mixture was sonicated in an ultrasonic bath for 20 min to form a well-dispersed electrocatalyst ink.

Prior to utilization, glassy carbon (GC) electrodes (3 mm in diameter) were firstly polished with alumina suspension in deionized water on a Nylon plate; subsequently, the polished GC electrodes were rinsed with deionized water. The resultant electrocatalyst ink (5 μ L) was drop-casted on the surface of a glassy carbon electrode. All electrodes prepared were dried at room temperature in air for 1 h. The GC electrodes loading Photocatalysts were used as the working electrode. Ag/AgCl (3.5 M KCl) and graphite rod were used as the reference electrode and the counter electrode in a three-electron cell, respectively.

To assess photocurrent, photocathode was prepared by dropping of photocatalyst ink (20 μ L) to transparent and conducting indium tin oxide (ITO) electrode.

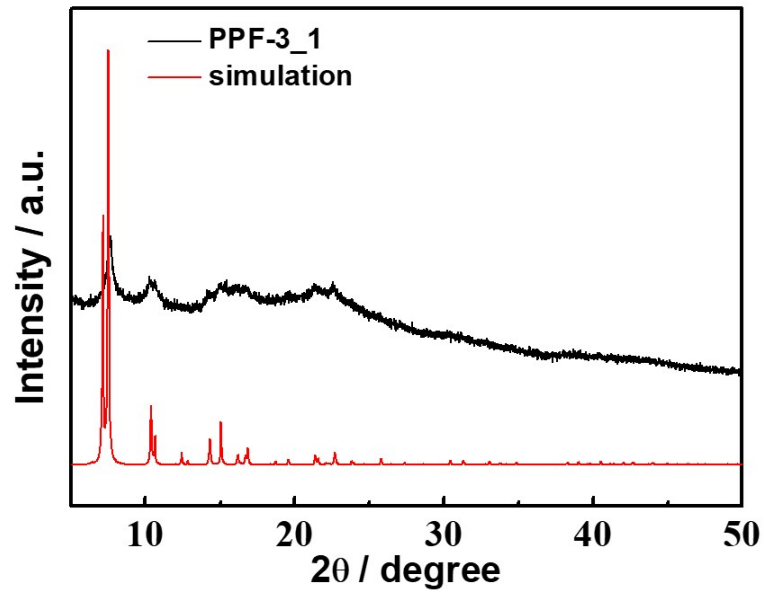


Figure S1. XRD pattern of the as-made PPF-3_1.

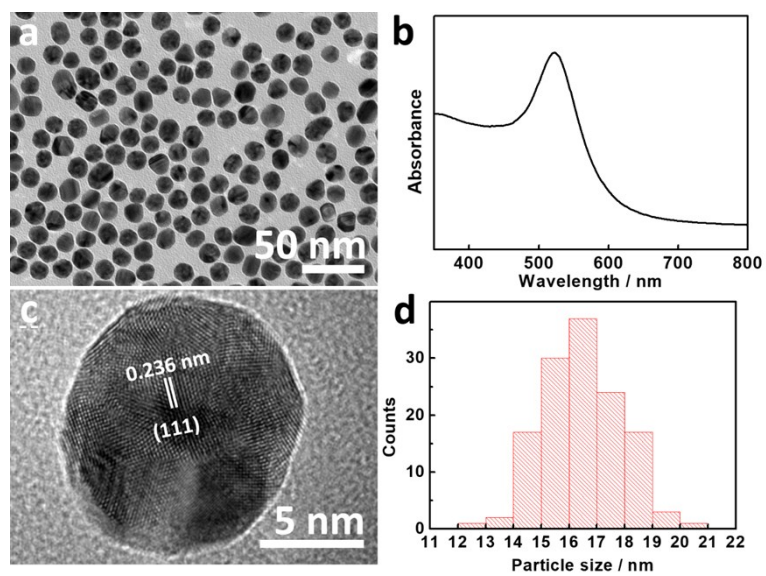


Figure S2. (a) TEM and (c) HRTEM images, (b) UV-Vis absorption spectrum and (d) size distribution of citrate modified AuNPs.

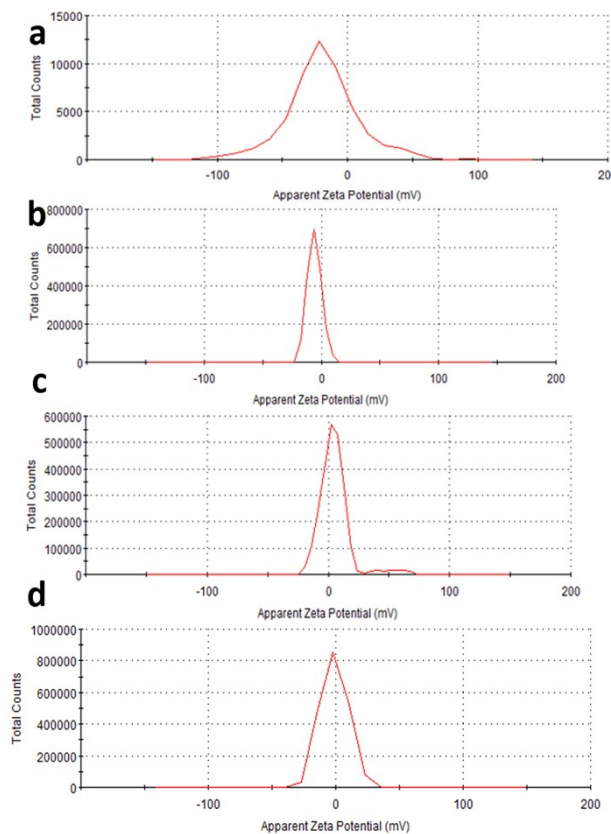


Figure S3. Zeta potential of (a) AuNPs, PPF-3_1 (b) before and (c) after thermal treatment in DMF, and (d) the treated PPF-3_1 re-dispersed into PVP solution in DMF.

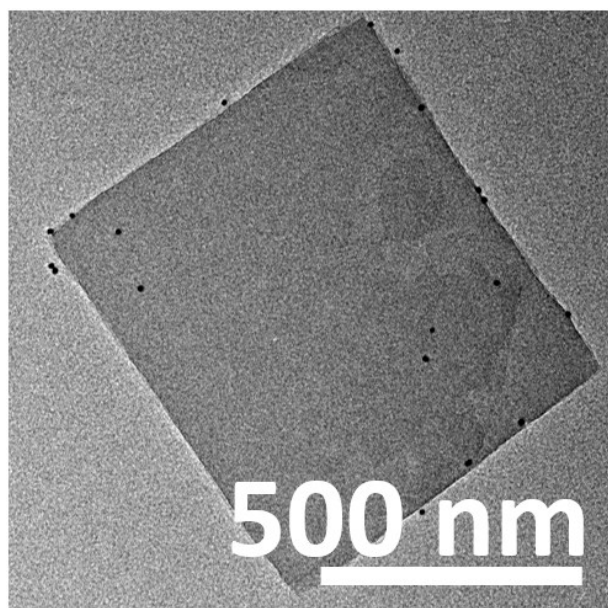


Figure S4. TEM image of PPF-3_1 without treatment and AuNPs.

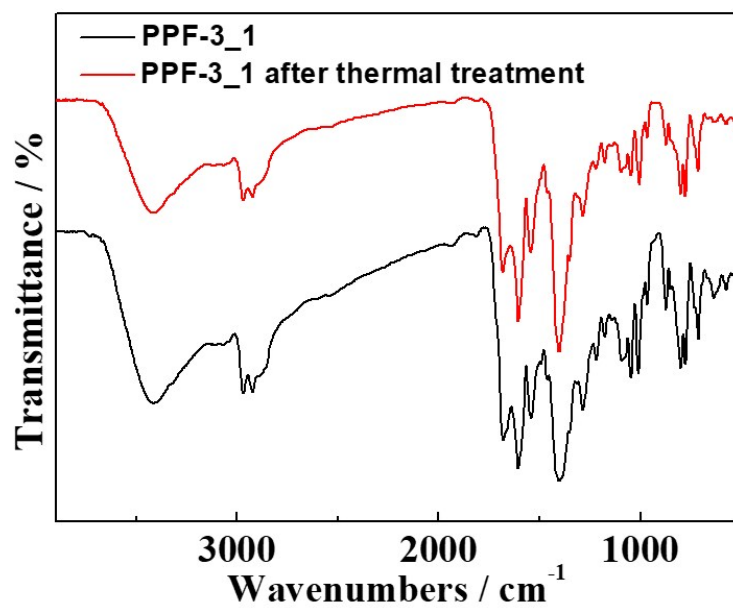


Figure S5. FTIR spectra of PPF-3_1 before and after thermal treatment.

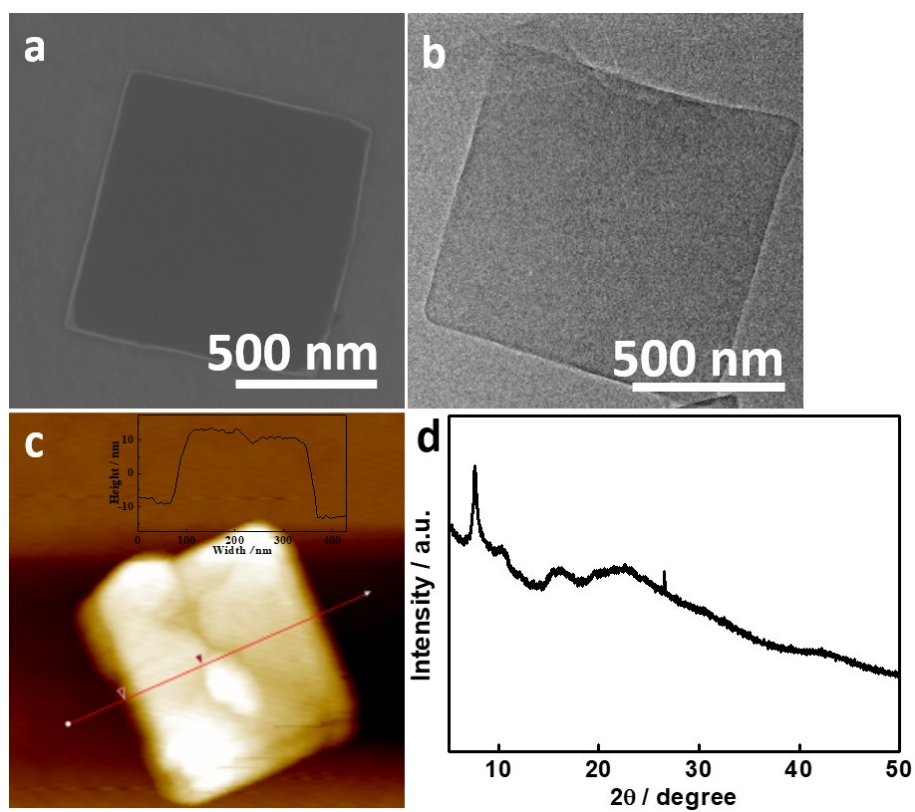


Figure S6. (a) SEM, (b) TEM and (c) AFM images and (d) XRD pattern of PPF-3_1 after thermal treatment at 80 °C in DMF. Inset is the profile of a PPF-3_1 nanosheet.

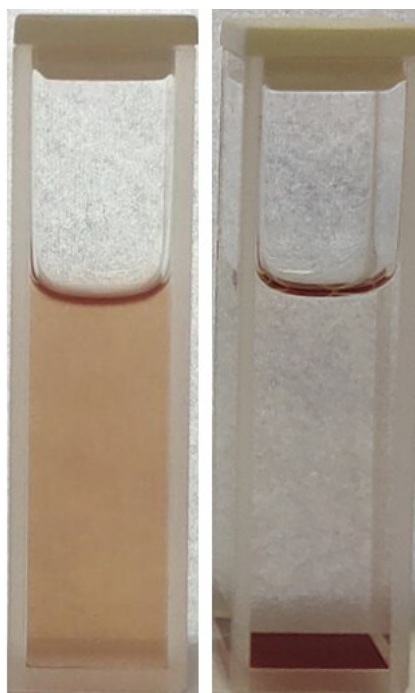


Figure S7. Optical photos of Au and PPF-3_1 (mass ratio: 1:10) suspension in ethanol with gentle stirring for 24 h (left) and then without disturbance for 8 h (right).

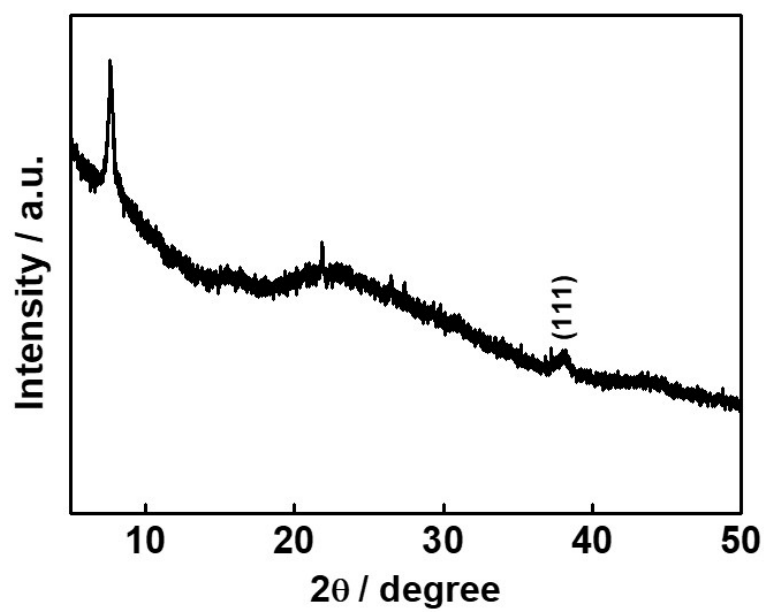


Figure S8. XRD pattern of Au/PPF-3_1A.

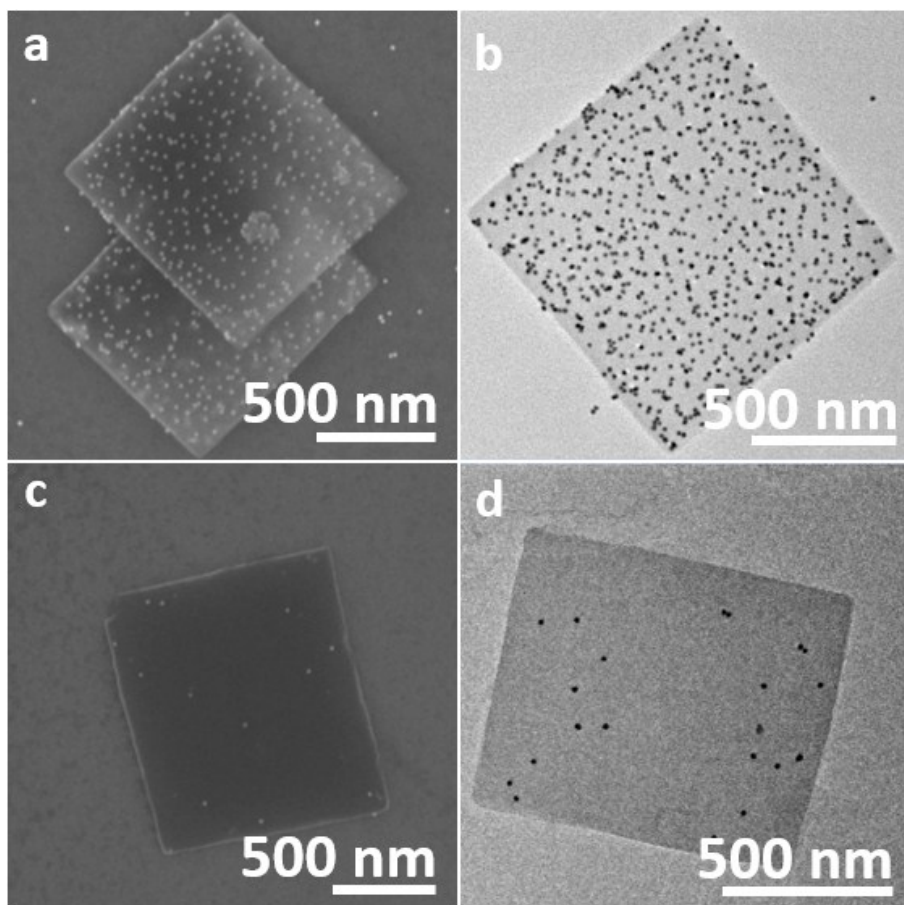


Figure S9. (a, c) SEM and (b, d) TEM images of hybrids of AuNPs loading on PPF-3_1 nanosheets with their mass ratio of 1:1 and 1:50, respectively.

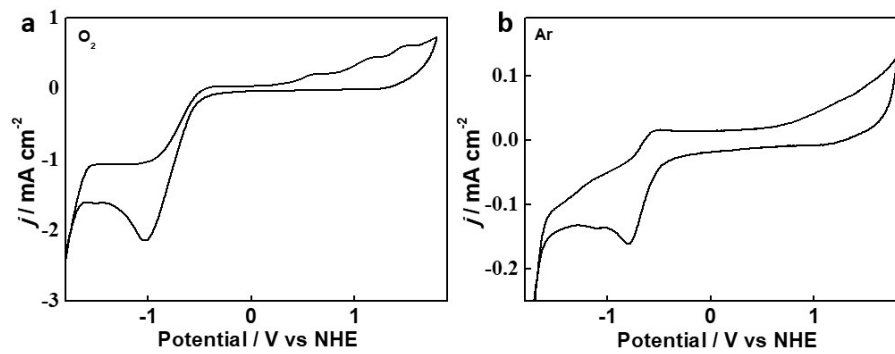


Figure S10. CV curves of treated PPF-3_1 measured in (a) O_2 and (b) Ar.

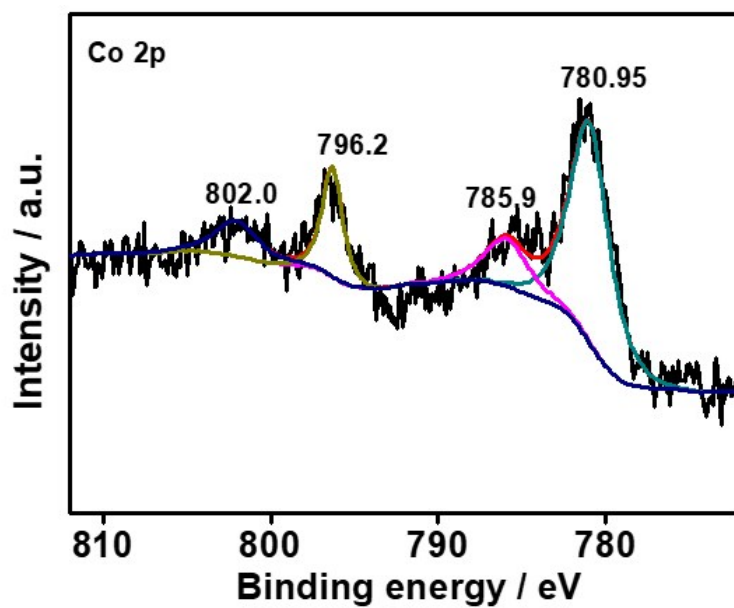


Figure S11. High-resolution Co 2p XPS spectrum of PPF-3_1 without thermal treatment.

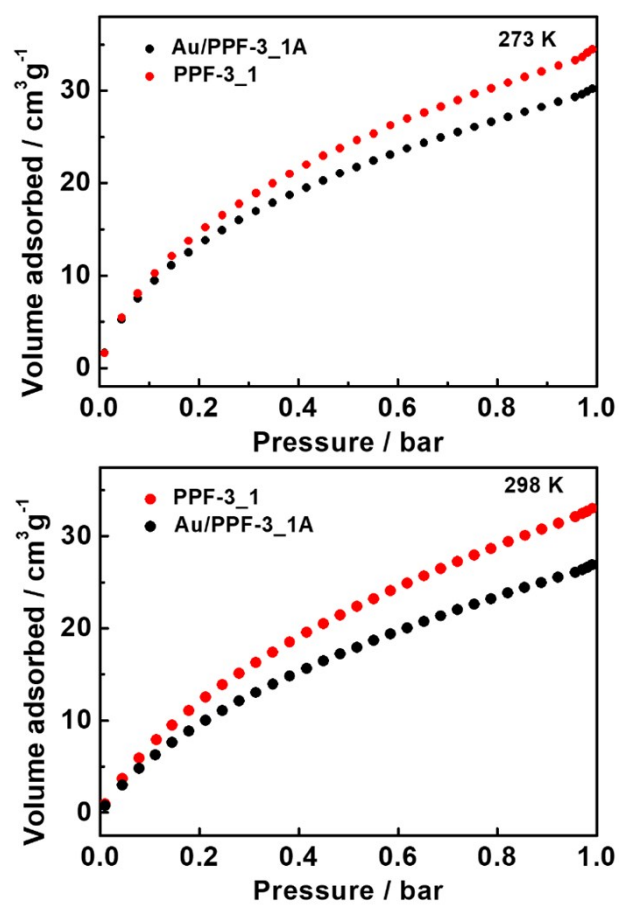


Figure S12. CO₂ adsorption isotherms of treated PPF-3_1 (black) and Au/PPF-3_1A (red) at 273 K (top) and 298 K (bottom), respectively.

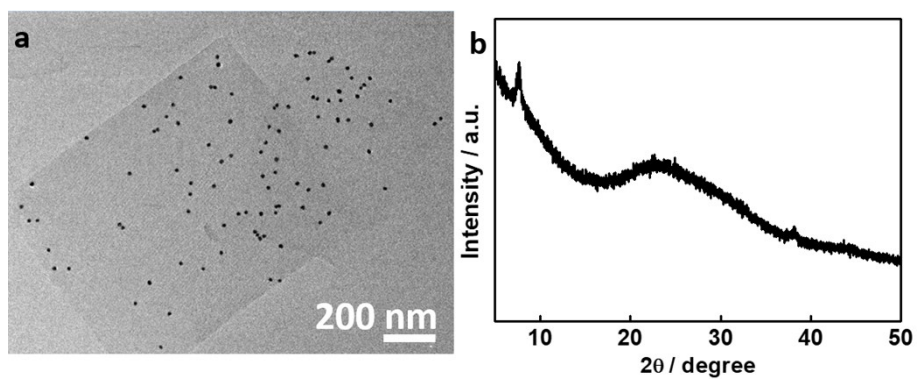


Figure S13. (a) TEM image and (b) XRD pattern of Au/PPF-3_1A after photocatalytic reaction for 12 h.

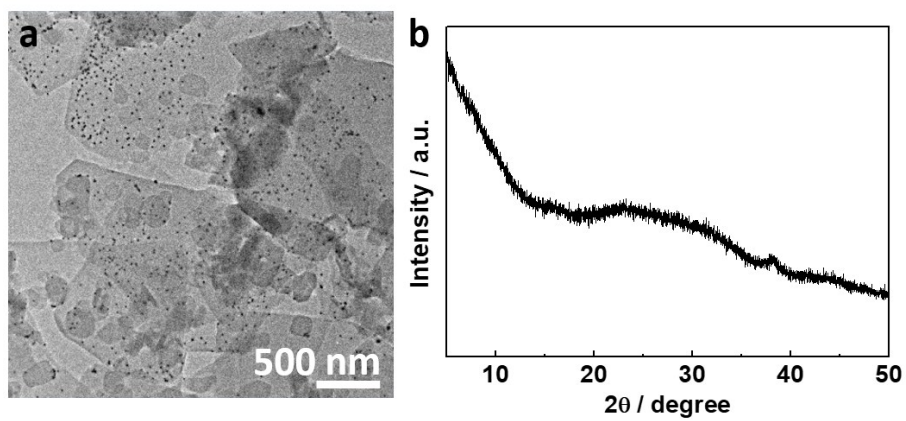


Figure S14. (a) TEM image and (b) XRD pattern of Au/PPF-3_1A after photocatalytic reaction for 24 h.

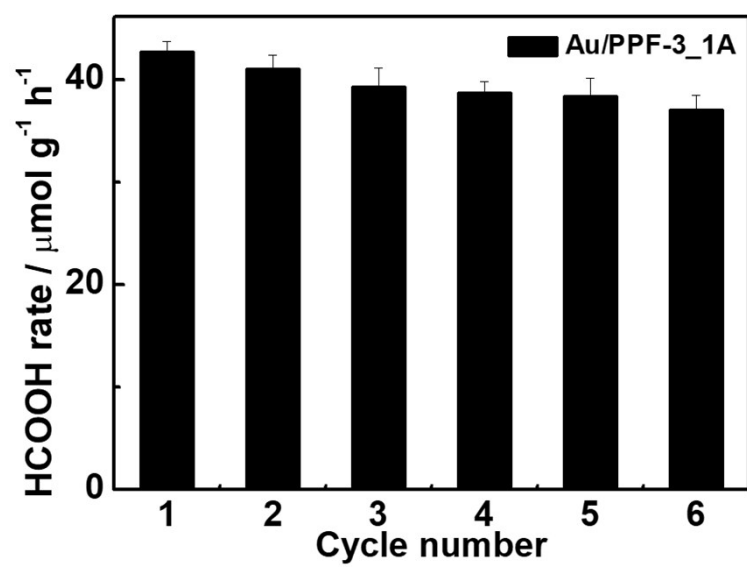


Figure S15. Recyclability of Au/PPF-3_1A for CO₂ conversion via successive 6 photocatalytic runs.

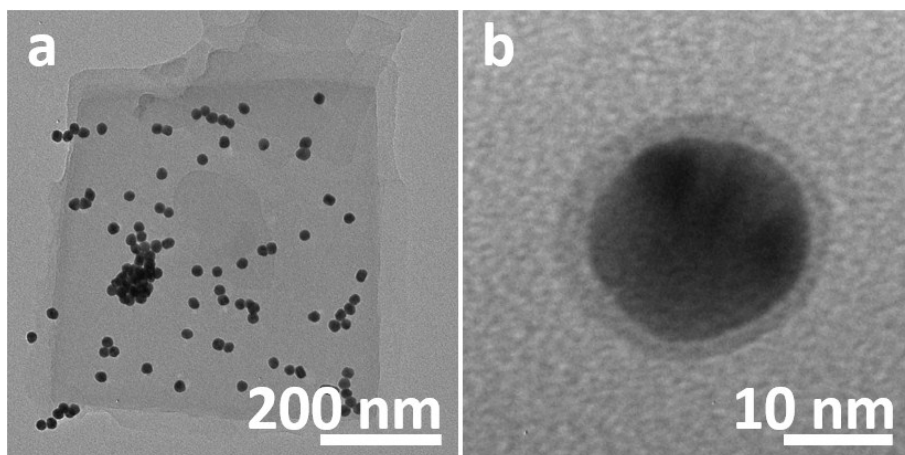


Figure S16. TEM images of (a) Au@SiO₂/PPF-3_1 and (b) Au@SiO₂.

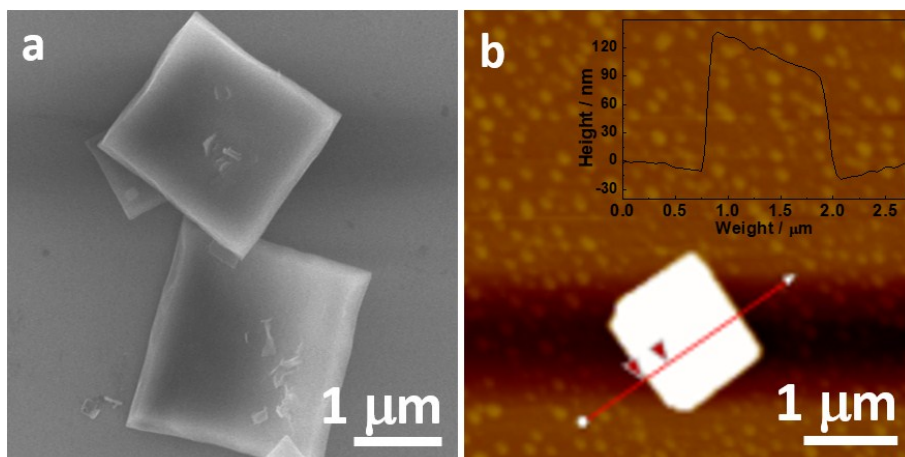


Figure S17. (a) TEM and (b) AFM images of PPF-3_2 without auxiliary of PVP.

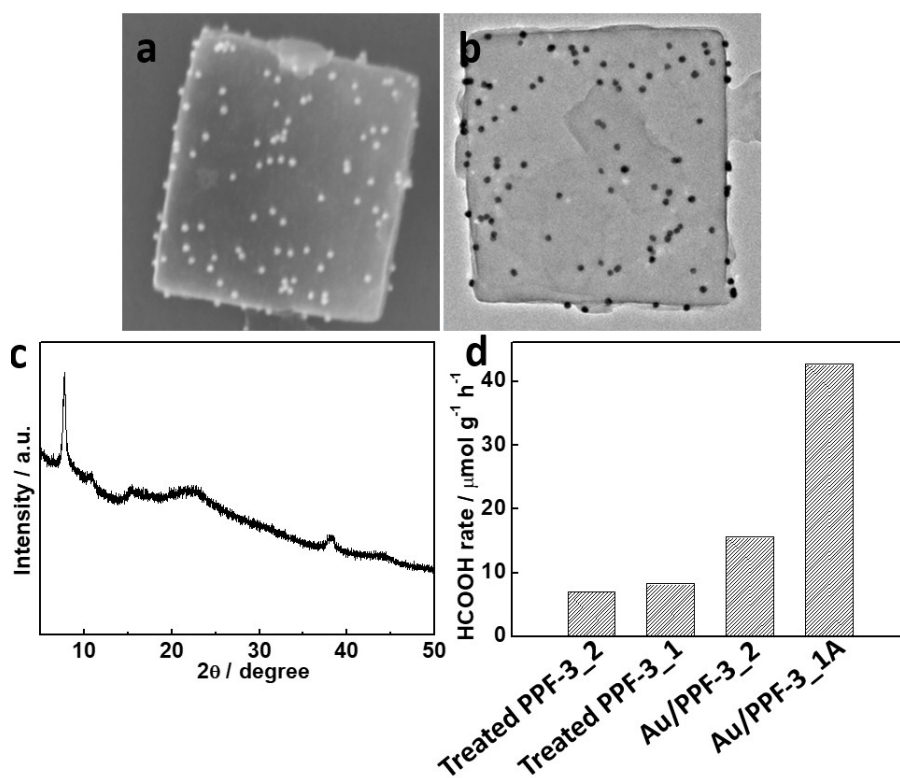


Figure S18. (a) SEM and (b) TEM images, and (c) XRD pattern of Au/PPF-3_2; (d) comparison of photocatalytic activity for CO₂ conversion into HCOOH over different photocatalysts.