Supplementary Information (SI) for Inorganic Chemistry Frontiers.
This journal is © the Partner Organisations 2025

Supporting Information

Atomically precise metal nanocluster sandwich heterojunction for robust and efficient photocatalytic CO_2 reduction to methanol

Rui Lu#, Aimin Yao#, Yali Dai, Haijiao Yin, Chengqi Li, Yuanxin Du*, Manzhou Zhu*

Department of Materials Science and Engineering, Centre for Atomic Engineering of Advanced Materials, Key Laboratory of Structure and Functional Regulation of Hybrid Materials of Ministry of Education, Key Laboratory of Functional Inorganic Material Chemistry of Anhui Province, Anhui University, Hefei 230601, China

E-mail: duyuanxin@ahu.edu.cn, zmz@ahu.edu.cn

1.1 Characterization

The crystal structures were analyzed by using an XRD with Cu Kα radiation (λ= 0.15418 nm) (Smart Lab 9 kW, Japan). The TEM images were obtained from a transmission electron microscope (JEM F200 JEOL). XPS data spectra were recorded on the EscaLab 250Xi X-ray photoelectron spectrometer. Using $BaSO_4$ as reference material, the UV-Vis diffuse reflectance spectroscopy (DRS) was determined by Hitachi U-3900 UV-Vis spectrophotometer. CO_2 adsorption test was measured on automatic microporous gas adsorption analyzer ASAP 2460 respectively. Photoluminescence spectroscopy was performed on fluorescence spectrophotometer (Hitachi, F-4600). Time-resolved transient PL decay curves were obtained by using ultra-fast time-resolved fluorescence spectrometer (Horiba Fluoro max plus). Thermo Fisher Scientific TSQ8000EVO gas chromatography-mass spectrometry (GC-MS) was used to detect ^{13}C and ^{12}C labeled products. In situ FT-IR spectroscopy was detected by using a Perkin Elmer FT-IR spectrometer (Perkin Elmer, USA). Photoelectrochemical measurements were conducted on an electrochemical workstation (CHI 760C, Chenhua Instrument, China). Platinum foil and Ag/AgCl (saturated potassium chloride) was used as counter and reference electrode, respectively. Na_2SO_4 (0.5 M, pH = 7) was used as electrolyte. In the transient photocurrent test, the catalyst was coated on doped indium tin oxide (ITO) as the working electrode. Electrochemical impedance spectroscopy (EIS) test was carried out at open circuit potential from 10^5 to 1 Hz. Mott–Schottky test was conducted from 500 to 1500 Hz, maintaining AC amplitude of 10 mV at each of the potentials.

1.2 In situ attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) measurement

In situ ATR-FTIR spectra were obtained by using a temperature-controlled Perkin Elmer instrument equipped with a MCT detector cooled by liquid nitrogen and PIKE VeeMAX optical accessories. The catalyst was evenly smeared onto the silicon single crystal substrate, and sodium bicarbonate solution (64 mg/ml) was added into the reactor. The dark adsorption process involved placing the reactor in the dark and purging it with argon gas to remove impurities from the sample surface. After 30 min, record the spectra as dark adsorption curve. The photocatalytic CO_2 conversion process involved repeating the dark adsorption process and then turning on the xenon lamp and injecting high-purity CO_2, followed by recording spectra at regular intervals.

1.3 Photocatalytic CO_2 reduction test

Photocatalytic CO_2 reduction was carried out in a closed container with a 300 W xenon lamp with a 420 nm filter as the light source. In simple terms, 20 mg catalyst was dispersed into 10 mL sodium bicarbonate solution (64 mg/mL). The content of Au in the M-A/C is determined to be ~ 2.167 wt. % by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES). After sufficient dispersion, the suspension was transferred to the reactor. Then, high purity carbon dioxide (99.999%) gas was injected into the system. The suspension was placed under light irradiation and the pressure of carbon dioxide in the reactor was (80 Kpa). After the reaction, the gas and liquid product was quantified by online GC and ^1H NMR, respectively. The leaching test is conducted as following procedures: Collect the solution from the photocatalytic reactor, then recover the catalyst by centrifugation and vacuum dry it before using it in the next recycle experiment. In addition, the Au content of the M-A/C after the reaction is also tested by ICP-OES (2.143 wt. %), indicating its stability after continuous 7 runs recycling tests.

1.4 The calculation of apparent quantum yield (AQY)

The apparent quantum yield (AQY) can be calculated by the following equation:

$$\text{AQY (\%)} = \frac{N_e}{N_p} \times 100\% = \frac{M_{methanol} \times 6 \times N_A \times h \times c}{P \times S \times t \times \lambda} \times 100\%$$

N_e, N_p, and $M_{methanol}$, represent the number of electrons required for the reaction product, the number of incident photons, and the Molar amount of generated CH_3OH, respectively.

N_A: Avogadro constant; h: Planck's constant; c: speed of light;

P: light intensity (150 mW/cm^2); S: irradiated area 12.56 cm^2; t: exposure time; λ: wavelength (350 nm).

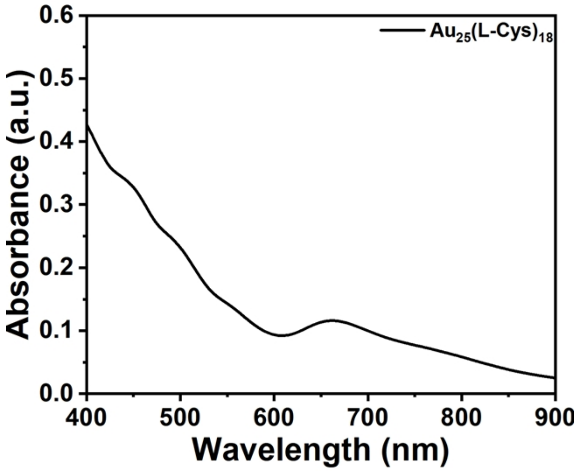

Fig. S1 UV–Vis absorption spectrum of $Au_{25}(L\text{-}Cys)_{18}$ NC.

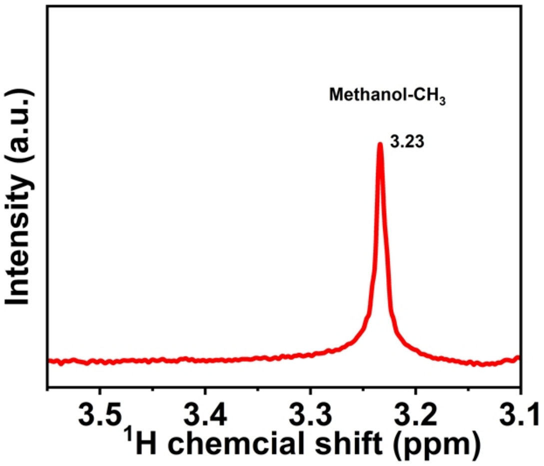

Fig. S2 ^{1}H NMR spectrum of the generated liquid product.

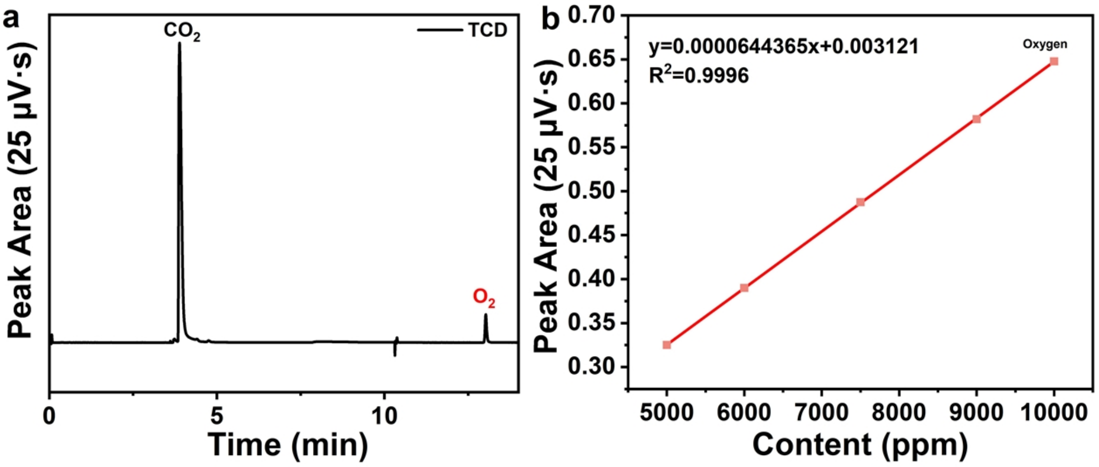

Fig. S3 (a) Online GC curve measured on TCD detector of the generated gas product. (b) The quantitative standard curve of O_2.

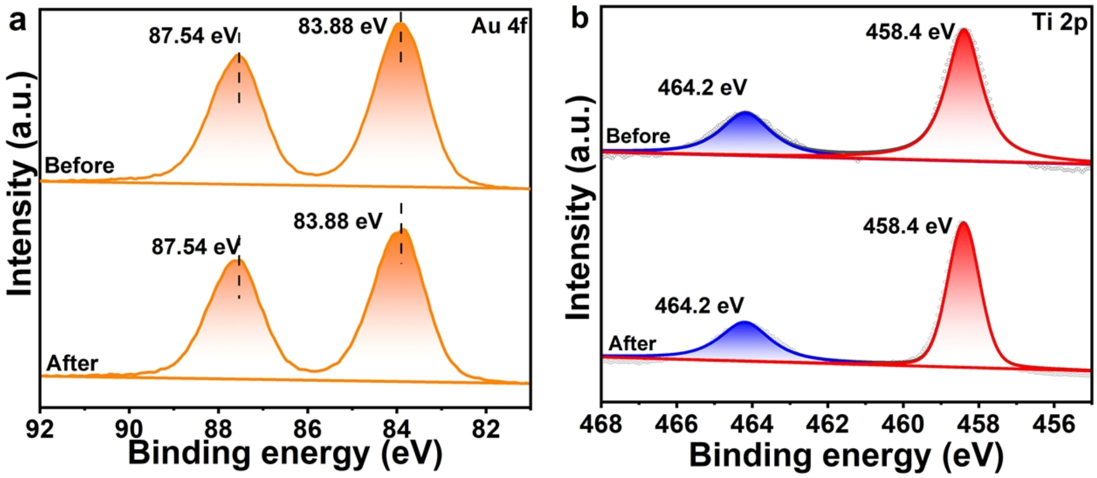

Fig. S4 (a) Au 4f and (b) Ti 2p XPS spectra of M-A/C before and after CO_2RR.

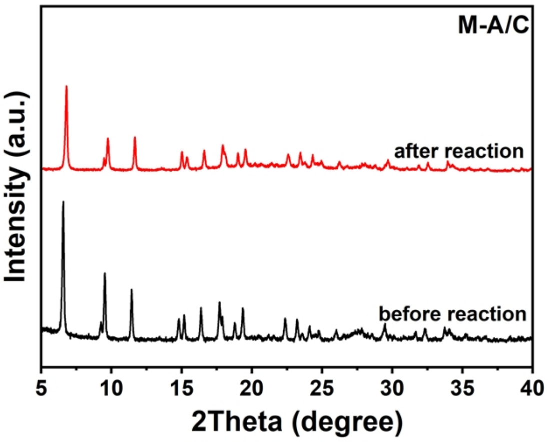

Fig. S5 XRD pattern of M-A/C before and after CO_2RR.

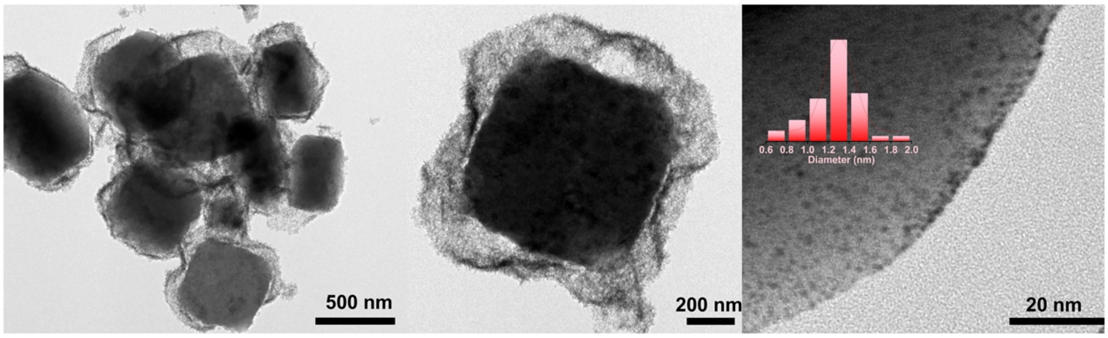

Fig. S6 TEM images of M-A/C before and after CO_2RR. The inset is the cluster size distribution.

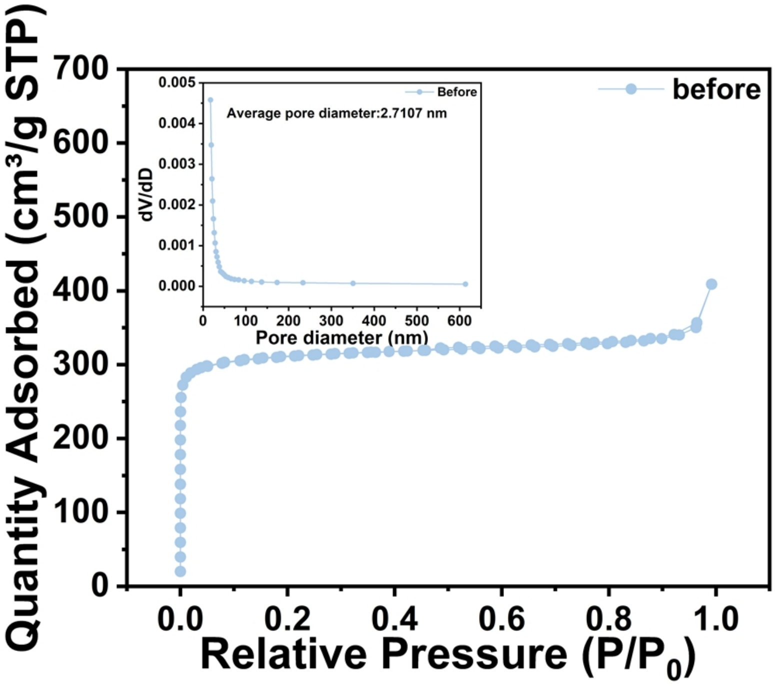

Fig. S7 The N_2 adsorption-desorption isotherm and the pore size distribution of the fresh M-A/C.

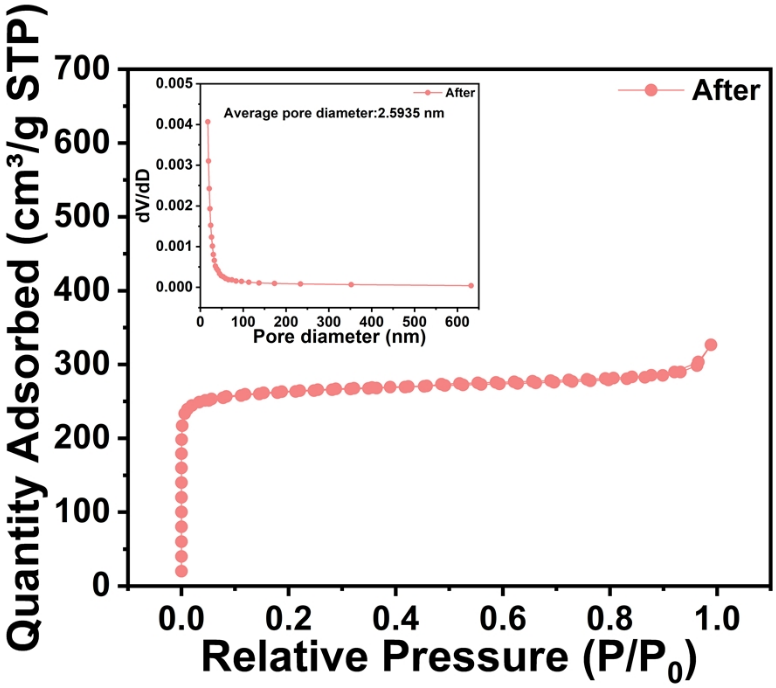

Fig. S8 The N_2 adsorption-desorption isotherm and the pore size distribution of the spent M-A/C.

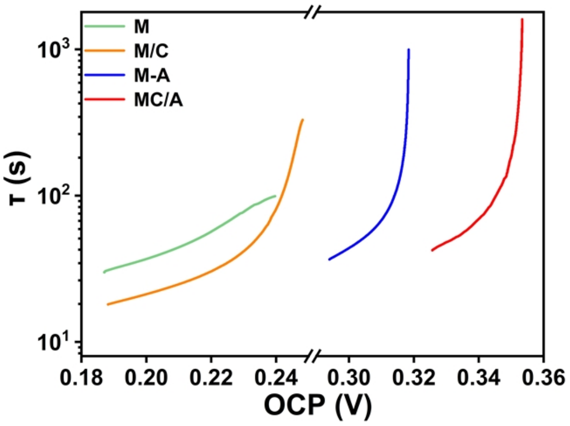

Fig. S9 The OCVD curves of different samples.

Table S1. The comparsion of photocatalytic CO_2RR performance with the reported catalysts.

Catalyst	Light source	Condition	Products and yields/μmol·g_{Cat}^{-1}·h^{-1}		TOF/h^{-1}	References
Co/g-C_3N_4-0.2 SAC	300 W Xe lamp	CO_2 and water	CH_3OH	235.475	0.056	Appl. Catal. B Environ. 2022, 300, 120695
Au@UiO-67-bpy-Cu	300 W Xe lamp (λ > 400 nm)	CO_2 and water	CH_3OH	118.4	0.668	Adv. Energy Mater. 2024, 14, 2401887
g-C_3N_4/UiO-66(Zr/Ce)	300 W Xe lamp	DMF and water	CH_3OH	54.71	0.032	ACS Catal. 2023, 13, 4597
Cu SAs/UiO-66-NH_2	300 W Xe lamp (λ > 400 nm)	0.1% TEOA and water	CH_3OH	5.33	0.008	J. Am. Chem. Soc. 2020, 142, 19339
$Zn_xCd_{1-x}S$/Au@g-C_3N_4	300 W Xe lamp (λ > 420 nm)	CO_2 and water	CH_3OH	1.31	0.026	Appl. Catal. B Environ. 2021, 282, 119600
Pd-Cu/TiO_2	300 W Xe lamp	CO_2 and water	CH_3OH	71.84	0.402	Chem. Eng. J. 2023, 456, 140805
M-A/C	300 W Xe lamp (λ > 420 nm)	CO_2,$NaHCO_3$ and water	CH_3OH	200.2	1.972	This work

Table S2. The production rate of the generated product during photocatalytic CO_2RR.

Photocatalysts	Methanol (μmol g^{-1} h^{-1})	Oxygen (μmol g^{-1} h^{-1})	O_2/CH_3OH Ratio
M/C	38.2	55.6	1.455
M-A	48.9	65.4	1.337
M-A/C	200.2	275.3	1.375