Enhancing the durability of Au clusters in CO₂ photoreduction via

encapsulation in Cu-based metal-organic frameworks

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Experimental Procedures

Materials.

All reagents and solvents were used as received without further purification. Gold(III) chloride tetrahydrate (HAuCl₄·4H₂O, \geq 99.9%), sodium hydroxide (NaOH, AR), sodium borohydride (NaBH₄), dimethylformamide (DMF, AR), acetic acid (AcOH, \geq 99%) and acetonitrile (CH₃CN, AR) were purchased from Sinopharm Chemical Reagent Co., Ltd. 4-Mercaptobenzoic acid (*p*-MBA, \geq 90%), benzene tricarboxylic acid (HBTC, \geq 98%) and cuprous oxide (Cu₂O, \geq 99%) were purchased from Aladdin Reagent Inc. 1,3-dimethyl-2-phenyl-2,3-dihydro-1*H*-benzo[d]imidazole (BIH, 98%) was purchased from Energy Chemical Reagent Inc.

Synthesis of Au₂₅(p-MBA)₁₈ clusters.

Au₂₅(p-MBA)₁₈ nanoclusters (NCs) were synthesized by modifying a protocol reported by Chen al.⁵¹ First, HAuCl₄ aqueous solution (2.2 mM, 21 mL) was kept for 10 min under a N₂ atmosphere, and then *p*-MBA aqueous solution (15.4 mg *p*-MBA dissolved in 2 mL of 150 mM NaOH) was added dropwise and stirred at 500 rpm for 30 min. Then, the pH of this mixture solution was adjusted to 11.5 by 1 M NaOH solution. Subsequently, 1.56 mL of fresh NaBH₄ solution (1 mM aqueous solution) was quickly injected into the above reaction solution, and stirred at 1,000 rpm for 1 min. Then the magnetic stirrer was switched off, and the reactants were kept under a N₂ atmosphere for another 89 min. The nanoclusters were purified by adding 90 mL of ethanol to 10 mL of the asprepared Au₂₅(p-MBA)₁₈ solution. This solution was mixed well and centrifuged at 12,000 rpm for 40 min. Finally, the supernatant was discarded, and the remaining crystals were washed three times with a mixture of deionized water and ethanol (1:9 volume ratio). The purified Au₂₅(p-MBA)₁₈ was dried under vacuum at room temperature for further use.

Synthesis of encapsulated Au₂₅@Cu-BTC composites.

The encapsulation of $Au_{25}(p-MBA)_{18}$ in $Cu_3(BTC)_2$ matrix was carried out by an in-situ growth method. First, 22.4 mg HBTC was dissolved in 7.5 mL DMF in a 50 mL round-bottom flask. $Au_{25}(p-MBA)_{18}$ aqueous solution (5 mg in 15 mL ultrapure water) was added to the above solution under 500 rpm stirring at room temperature. Then Cu_2O suspension (7.2 mg in 7.5 mL DMF) and 0.5 mL acetic acid were added into the above round-bottom flask, and the temperature was elevated to 45 °C and kept for 29 h. The obtained solid samples were collected by centrifuging, washing with ethanol three times and drying at 40 °C overnight. To remove the residual ligands and/or adsorbed

solvent molecules in the $Cu_3(BTC)_2$ channels, the composite was activated at 120 °C for 6 h under vacuum.

Synthesis of physically mixed Au₂₅/Cu-BTC composites.

As a reference sample, the physically mixed Au_{25}/Cu -BTC composite was prepared via the ultrasonic dispersion method. Typically, $Au_{25}(p-MBA)_{18}$ solution (5 mg in 5 mL DMF) was dropwise added into a pristine $Cu_3(BTC)_2$ suspension (7.2 mg in 15 mL DMF) under vigorous stirring, and then the stock solution was ultrasonically oscillated for 12 h at room temperature. The obtained solid samples were collected by centrifuging and then washing with DMF and ethanol three times. The obtained Au_{25}/Cu -BTC composite was collected and activated through the same process as the $Au_{25}@Cu$ -BTC composite.

Sample characterizations.

Powder X-ray diffraction (PXRD) patterns were recorded with a diffractometer (SmartLab 9kw) using Cu Ka (k = 0.15406 nm) radiation with a Nickel filter operating at 40 kV and 10 mA at a scanning rate of 20°-min⁻¹. Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images were taken on a Talos F200S-G2 field-emission high-resolution transmission electron microscope operated at 200 kV. Prior to electron microscopy characterizations, a drop of the ethanol suspension of particles was placed on a piece of carbon-coated copper grid and dried under ambient conditions. The size of Au nanoclusters was measured from HRTEM images and the average particle diameter was calculated from the mean diameter frequency distribution with the formula: $d = \sum n_i d_i / \sum n_i$, where n_i is the number of particles with a particle diameter (d_i) in a certain range. X-ray photoelectron spectra (XPS) were collected on an ESCALab 250 X-ray photoelectron spectrometer, using monochromatized Al–K α X-ray as the excitation source. CO₂ sorption studies were performed in a Micromeritics ASAP 2020 adsorption apparatus at 298 K and 1 bar. Prior to sorption measurements, all samples were degassed at 100 °C for 6 h. Fourier transform infrared (FT-IR) spectra (KBr pellets) were collected on a PerkinElmer Spectrum 100 FT-IR spectrometer with 2 cm⁻¹ resolution over a range of 400–4000 cm⁻¹. ESI mass spectra were measured on a Shimadzu (LCMS9030) Q-TOF ESI time-of-flight system operating in negative ion mode. (sample injection rate 30 μ L·min⁻¹; capillary voltage 4 kV; nebulizer 1.5 bar; dry gas 4 L·min⁻¹ at 160 °C; and m/z 2000–4500). The amount of Au in Au₂₅@Cu-BTC composite were measured with a PerkinElmer

Optima 8300 inductively-coupled plasma atomic emission spectrometry (ICP-AES).

CO₂ photoreduction measurements.

The CO₂ photoreduction measurements were performed in a gas–solid reactor (LabSolar6A, Perfect Light, China) under visible-light irradiation coupled with a gas chromatograph (GC) (Fig. S4). The reactor was wetted with 0.1 mL deionized water. 5 mg of photocatalysts and 2 mg of BIH were ultrasonically dispersed into 2 mL of CH₃CN, and then the stock solution was carefully coated on a quartz wafer (12.6 cm⁻²) and placed into the moist reactor. The entire reaction setup was vacuum degassed, and then high-purity CO₂ gas or 10% CO₂ (Ar as the diluent) was filled into the reaction setup to reach a pressure of 0.8 bar. A 300 W xenon lamp (PLS-SXE300+, China) with a 420 nm longwave pass cut-off filter (i.e., $\lambda > 420$ nm) was used to illuminate the quartz lid of the reactor. The incident light intensity was measured to be 250 mW cm⁻². The amounts of CO and H₂ evolved were determined using a GC (FULI, GC-9790II, China) equipped with a TDX-01 packed column. H₂ was detected using a thermal conductivity detector (TCD) with Ar as the carrier gas. CO was passed through a methanation reactor and then analyzed by a flame ionization detector (FID). CH₄ and C₂H₄ were directly analyzed by an FID. For the durability testing, equal amounts of new BIH solution and deionized water were added to each cycle.

The selectivity of reduction products was evaluated based on the required electrons using the following equation: Selectivity $(H_2)\% = [2v(H_2)]/[2v(H_2) + 2v(CO) +8v(CH_4) + 12v(C_2H_4)] \times 100$; Selectivity $(CO)\% = [2v(CO)]/[2v(H_2) + 2v(CO) +8v(CH_4) + 12v(C_2H_4)] \times 100$; Selectivity $(CH_4)\% = [8v(CH_4)]/[2v(H_2) + 2v(CO) +8v(CH_4) + 12v(C_2H_4)] \times 100$, and Selectivity $(C_2H_4)\% = [8v(C_2H_4)]/[2v(H_2) + 2v(CO) +8v(CH_4) + 12v(C_2H_4)] \times 100$, where $v(H_2)$, v(CO), $v(CH_4)$ and $v(C_2H_4)$ stand for the production rates for H_2 , CO, CH₄ and C_2H_4 , respectively.

Electrochemical measurements.

All electrochemical measurements were carried out on a CHI 660E workstation in a conventional three-electrode system. Platinum foil was used as a counter electrode, and the reference electrode was a nonaqueous Ag/Ag⁺ electrode with a ferrocene/ferrocenium (Fc/Fc⁺) couple as an internal potential reference. 0.1 M acetonitrile solution of tetrabutylammonium hexafluorophosphate was used as a supporting electrolyte. As the Ag/Ag⁺ electrode is not a standard reference for a nonaqueous system, the recorded potentials vs Ag/Ag⁺ were converted to the ones vs Fc/Fc⁺ by the following equation: $E(vs Fc/Fc^+) = E(vs Ag/Ag^+) - E(Fc/Fc^+)$, where the Fc/Fc⁺ potential vs Ag/Ag⁺ is measured as 0.19 V in acetonitrile.^{S2}

Photocurrent was recorded in a quartz electrolytic cell with an initial potential of 0.21 V (vs Fc/Fc⁺) under 300 W xenon lamp irradiation with a 420 nm longwave-pass cut-off filter. The power density was measured to be 250 mW·cm⁻². The working electrode was prepared as follows: 5 mg photocatalysts were dispersed in a mixed solution of 980 μ L methanol and 20 μ L Nafion D-520 dispersion to generate a homogeneous slurry. This slurry was transferred and coated on indiumtin oxide (ITO) glass plates (1 cm × 2 cm) and then dried at room temperature. Linear sweep voltammetry (LSV) measurements were performed in a N₂ or CO₂-saturated electrolyte at a scan rate of 1 mV s⁻¹ under ambient conditions. The Ohmic drop between the working electrode and the reference electrode was tested at open circuit voltage between 0.01 Hz and 100 kHz in 0.1 M tetrabutylammonium hexafluorophosphate acetonitrile solution. The resistance was determined by fitting the Nyquist plot curve through equivalent circuit with the software of ZView 2.0. The working electrodes for LSV and Nyquist plot measurements were prepared as follows: 2 mg photocatalysts were dispersed in a mixed solution of 980 μ L methanol and 20 μ L Nafion D-520 dispersion to generate a homogeneous slurry. Subsequently, 20 μ L of slurry was transferred and coated on a glassy carbon electrode (6 mm) and then dried at room temperature.





Fig. S1 (a) UV–vis absorption spectrum of $Au_{25}(p-MBA)_{18}$ nanoclusters in aqueous solution, (b) TEM image, and ESI mass spectrum of $Au_{25}(p-MBA)_{18}$ nanoclusters.

The UV–vis absorption spectrum (Fig. S1a) shows the characteristic absorption bands at 430, 467 and 697 nm, which are the spectroscopic fingerprints for $Au_{25}(p-MBA)_{18}$ nanoclusters ^{S1}. HRTEM image (Fig. S1b) reveals that the $Au_{25}(p-MBA)_{18}$ NCs have an average size of *ca*. 1.3 nm. ESI time-of-flight mass spectrometry is further employed to confirm the core nature of the Au_{25} NCs. As shown in Fig. S1c, the two sets of major peaks at m/z around 2559 and 3839 can be ascribed to $[Au_{25}(SR)_{18}]^{-}$. ^{S1} These results demonstrates that the Au_{25} NCs have been successfully synthesized.



Fig. S2 (a) PXRD patterns and (b) their local amplifications of commercial Cu₂O nanoparticles, simulated Cu₃(BTC)₂, and Au₂₅@Cu-BTC composites with different etching times (4 h, 11 h, 24 h, and 29 h). (c) Photographs of as used Cu₂O raw materials and as prepared Cu₃(BTC)₂ and Au₂₅@Cu-BTC samples.



Fig. S3 FT-IR spectra of Cu₃(BTC)₂, Au NCs, Au₂₅@Cu-BTC and Au₂₅/Cu-BTC.

FT-IR spectroscopy was employed to confirm the interaction between embedded Au NCs and coated $Cu_2(BTC)_3$. As shown in Fig. S3, the characteristic peak at 1646 cm⁻¹ can be ascribed to asymmetric stretching vibrations of carboxylate groups in the BTC linker, and symmetric stretching vibrations were found around 1374 cm⁻¹. These peaks around 1448 and 730 cm⁻¹ can be assigned to the C–C stretching vibration in the aromatic ring and the C–H bending vibration, respectively. All these characteristic peaks are related to $Cu_2(BTC)_3$ and labelled with black dotted lines.⁵³ Other characteristic peaks at 1587 and 1534 cm⁻¹ can be assigned to Au–S vibrations in Au NCs. Both the characteristic peaks of $Cu_2(BTC)_3$ (black dotted lines) and Au NCs (orange dotted lines) can be found in Au_{25} @Cu-BTC and Au_{25}/Cu -BTC, confirming that they are constituted with $Cu_2(BTC)_3$ and Au NCs. Interestingly, a new peak at 1105 cm⁻¹ appears only in the Au_{25} @Cu-BTC composite, which can be assigned to the C–O stretching vibration of primary alcohols. Most likely, the carboxyl groups of implanted Au NCs are coordinated with Cu^{2+} in a monodentate fashion and then are protonated into primary alcohols, which is confirmed by the stronger C=O vibration (at 1641 cm⁻¹) and slight redshift (ca. 6 cm⁻¹). These results demonstrate that Au NCs are connected with Cu nodes through chemical bonds.



Fig. S4 High-resolution XPS spectra of (a) O 1s in Au NCs, $Cu_3(BTC)_2$ and $Au_{25}@Cu-BTC$, (b) S 2p and (c) Au 4f in Au NCs and $Au_{25}@Cu-BTC$. (d) Cu LMM and (e) Cu 2p in $Cu_3(BTC)_2$ and $Au_{25}@Cu-BTC$.

Upon forming the hierarchical structure, we further investigated the interaction between the embedded Au NCs and the coated Cu₂(BTC)₃ shell using X-ray photoelectron spectroscopy (XPS) and FT-IR spectroscopy. The high-resolution O1s XPS spectra (Fig. S4a) reveal that Au NCs, Cu₃(BTC)₂ and Au₂₅@Cu-BTC give the most distinct difference in both the existing forms and chemical shifts. The characteristic peaks around 532.5 eV and 531.7 eV can be assigned to hydroxide (H–C–O bonding) and carbonate (C–O bonding), respectively.⁵⁴ H–C–O bonding is dominant in the Au NCs, which can be assigned to the uncoordinated carboxyl groups in p-MBA. When the Au NCs are incorporated into Cu₃(BTC)₂, C–O bonding becomes dominant in Au₂₅@Cu-BTC, which can be attributed to the coordination of carboxyl groups of p-MBA with Cu nodes of Cu₃(BTC)₂ during in situ coating. This argument is confirmed by the shift of the O 1s (Fig. S4a), S 2p (Fig. S4b) and Au 4f (Fig. S4c) characteristic peaks for Au₂₅@Cu-BTC toward higher binding energy compared with the pristine Au NCs. This shift is caused by the coordination of carboxyl groups of Au NCs with Cu²⁺, reducing the electron densities of the p-MBA ligands. In the meantime, the

characteristic peaks of Cu in the Cu LMM spectrum of $Au_{25}@Cu-BTC$ shift toward lower binding energy compared to bare $Cu_3(BTC)_2$ (Fig. S4d), as the electron donation by O in the carboxyl of the Au NCs can increase the electron density of the Cu nodes in $Cu_3(BTC)_2$. These results demonstrate that the embedded Au NCs are directly connected with the Cu sites of coated $Cu_3(BTC)_2$ through coordination bonds, which is also confirmed by FT-IR (Fig. S3), providing a good foundation for charge transfer between Au NCs and $Cu_3(BTC)_2$.

No new Cu species (Fig. S4d and Fig. S4e) was found on $Au_{25}@Cu-BTC$ in comparation with the bare $Cu_3(BTC)_2$ except bigger chemical shifts was observed on Cu LMM spectra compared to Cu 2p. So, it can be conclusion that the chemical environment of Cu sites in $Au_{25}@Cu-BTC$ and $Cu_3(BTC)_2$ is not significantly change after Au NCs inserting, which provides a good basis for studying other mechanisms, such as, charge transfer and separation.



Fig. S5 (a) Nitrogen sorption isotherms of $Cu_3(BTC)_2$ and $Au_{25}@Cu-BTC$ at 77 K, and (b) corresponding pore size distribution plot.

Fig. S5a shows the representative N₂ adsorption–desorption isotherms for the bare Cu₃(BTC)₂ and Au₂₅@Cu-BTC core-shell composites. Au₂₅@Cu-BTC shows similar isotherms (type I) with Cu₃(BTC)₂, suggesting it is still a microporous material.⁵⁵ The BET surface area (S_{BET}) of is determined to 810 m² g⁻¹, while the S_{BET} value of Au₂₅@Cu-BTC based on the total weight is relatively low (538 m² g⁻¹). Nevertheless, the decrease in S_{BET} after Au NCs inserting is reasonable, as the Au NC core account for about 18.1 % of the total weight and do not have as large a surface area as the MOF structure. Thus, the S_{BET} of coated Cu₃(BTC)₂ component can be calculated to be approximately 657 cm³·g⁻¹, which is comparable to that of bare Cu₃(BTC)₂. In addition, the pore size distribution (Fig. S5b) of bare Cu₃(BTC)₂ and Au₂₅@Cu-BTC analyzed via a BJH method is nearly identical. These results indicate that the pore structures of Cu₃(BTC)₂ shell are not significant change during encapsulation Au NCs.



Fig. S6 Photographs of the gas–solid reactor for CO_2 photoreduction.



Fig. S7 The FID-detected GC spectra of the gaseous products including CH_4 , CO and C_2H_4 in the CO_2 photoreduction system of Au_{25} @Cu-BTC photocatalyst from 2 h to 8 h.



Fig. S8 TEM images of Au_{25} @Cu-BTC after 32-hour photocatalytic CO₂ reduction.

After the 32-hour CO_2 photoreduction, the $Cu_3(BTC)_2$ coating is well maintained as indicated by TEM (Fig. S8).



Fig. S9 Durability test for CO_2 photoreduction over Au_{25}/Cu -BTC. Each cycle took 8 h.

As shown in the Fig. S9, Au_{25}/Cu -BTC shows obviously weakened catalytic activity after 2 successive cycles. When it reaches to the sixth cycle, the photoactivity (determined by the rate of electron consumption for reduction products) has been decayed to ca. 15% that of initial performance, indicating its poor durability for CO₂ photoreduction.



Fig. S10 TEM images of Au_{25}/Cu -BTC after 48-hour CO_2 photoreduction.

TEM characterization (Fig. S10) reveals that the Au NCs loaded on $Cu_3(BTC)_2$ have been aggregated and grown from 1.34 nm up to Au nanoparticles with an average diameter of ca. 4.5 nm after the 6 cycles.

References

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