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Enhancing the durability of Au clusters in CO₂ photoreduction *via* encapsulation in Cu-based metal–organic frameworks†

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Here, we report the encapsulation of Au₂₅ nanoclusters in a Cu₃(BTC)₂ metal–organic framework (Au₂₅@Cu-BTC), which can achieve CO₂ photoreduction for selective CO production in a gas–solid reaction system at low-concentration CO₂ atmospheres (even to 0.1%), with remarkably enhanced durability up to at least 48 h.

Light-driven CO₂ reduction has continuously received attention.^{1–3} To this end, various photocatalytic materials have been explored for achieving this promising reaction. Very recently, atomically precise metal nanoclusters (NCs) with highly tunable numbers of atoms have emerged as a new class of catalytic materials.^{4–7} In particular, their subnanometer sizes (~ 1 nm), approaching the de Broglie wavelength, result in discrete electronic structures, which makes their light absorption readily tuned.^{8,9} Moreover, the ultrasmall sizes and high conductivity of metal NCs are beneficial for the transfer of photogenerated electrons to their surface.^{10–12} These characteristics endow the metal NCs with the capability of working for light-driven catalytic reactions. In practical applications, the light-driven catalysts based on metal nanoclusters still typically suffer from two limitations. First of all, metal nanoclusters more readily aggregate into nanoparticles under heating or light illumination due to their extremely high surface energy, leading to the decay of their specific photochemical properties.¹³ In the other limitation, the tightly capped ligands on the metal surface, as well as the lack of catalytically active sites, hinder the photogenerated electrons from participating in surface reactions, limiting the catalytic activity.⁶

To prevent aggregation, metal oxides,¹⁴ polymers¹⁵ and covalent organic frameworks¹⁶ can serve as surface coatings. However, these approaches often involve complicated processes and/or can hardly provide effective active sites. Ideally, a surface coating material should not only improve the stability of metal NCs but also offer catalytically active sites for enhancing their catalytic performance. Metal–organic frameworks (MOFs) are crystalline porous materials that can be prepared under mild conditions, and their abundant metal nodes may work as active sites for targeted catalytic applications.^{16,17} For this reason, the encapsulation of nanomaterials in MOFs has been intensively studied in recent years.^{18,19} However, it remains a great challenge to accomplish surface coating with MOFs because of the lattice mismatch between the guest materials and the MOFs.²⁰ The abundant surface functional groups and ultrasmall sizes of metal NCs offer the possibility of packaging them in the cavities of a MOF without affecting the framework. Such promising features would make the MOF material an ideal candidate for encapsulating metal NCs to enhance CO₂ photoreduction performance.

Herein, we report a facile process for encapsulating atomically precise Au₂₅(*p*-MBA)₁₈ (*p*-MBA = 4-mercaptopbenzoic acid) clusters in MOFs to enhance the durability of the catalyst in the selective photoreduction of CO₂ to CO. In our designed scheme, the MOFs are expected to introduce multiple advantages for CO₂ photoreduction, *i.e.*, confining Au NCs to prevent aggregation, offering active sites for CO₂ reduction, and capturing CO₂ to facilitate the conversion process. Inspired by these considerations, Cu₃(BTC)₂ (BTC = benzene-1,3,5-tricarboxylate) is selected as the MOF model, as it can provide a framework for CO₂ capture and Cu sites for CO₂ activation as demonstrated by our previous studies.^{21,22}

Fig. 1a schematically illustrates the synthetic procedure of Cu₃(BTC)₂-encapsulated Au₂₅(*p*-MBA)₁₈ (denoted as Au₂₅@Cu-BTC). Water-soluble Au₂₅(*p*-MBA)₁₈ was synthesized according to the method reported by Chen *et al.*²³ The successful preparation of Au₂₅(*p*-MBA)₁₈ was confirmed by UV-vis absorption spectroscopy and ESI mass spectrum (Fig. S1, ESI†). Of particular note is that we selected Au₂₅(*p*-MBA)₁₈ as the model cluster on account of its good

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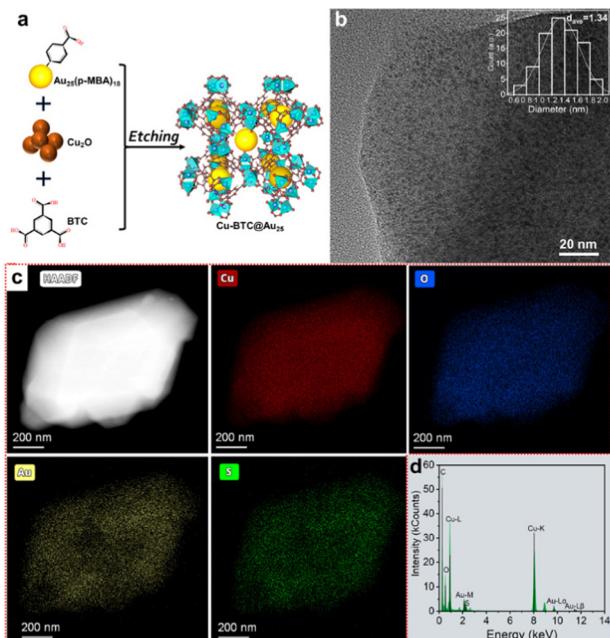


Fig. 1 (a) Schematic illustration of the preparation process of the Au_{25} @Cu-BTC composite. (b) HRTEM image, (c) STEM image and corresponding EDS elemental mapping images and (d) EDS spectrum of Au_{25} @Cu-BTC.

visible light response and facile synthesis. More importantly, the protected ligand of *p*-MBA has a similar structure to the BTC ligand of MOFs, and as such, its carboxyl group can directly be coordinated with the Cu nodes, which will facilitate electron transfer from the Au NCs to Cu sites in MOFs.

Unlike harsh synthesis conditions (*i.e.*, solvo/hydrothermal methods), we assembled such a hierarchical composite through a mild one-pot solution-phase method to avoid altering the properties of the Au_{25} NCs. In our synthesis, Cu_2O nanoparticles rather than Cu^{2+} ions were used as the Cu precursor for $\text{Cu}_3(\text{BTC})_2$, as we found that directly adding Cu^{2+} inevitably induced Au NC aggregation. The Cu_2O nanoparticles can be etched by the protons of carboxyl to slowly release Cu^+ and then oxidized to Cu^{2+} by dissolved oxygen, which will coordinate with the carboxyl of BTC and *p*-MBA to *in situ* form the encapsulated Au_{25} @Cu-BTC.²² As displayed in the powder X-ray diffraction (PXRD) pattern (Fig. S2, ESI†), the characteristic peak of Cu_2O at $2\theta = 36.6^\circ$ (PDF#05-0667) decreased in intensity by prolonging the etching time. When it proceeded to 29 h, this characteristic peak faded thoroughly while the diffraction pattern is consistent with the simulated $\text{Cu}_3(\text{BTC})_2$, indicating that Cu_2O had been completely converted into $\text{Cu}_3(\text{BTC})_2$. No characteristic peak of Au NCs was found in the PXRD pattern of the Au_{25} @Cu-BTC composite, most likely due to the ultrasmall sizes of the Au NCs.

To investigate the structure, high-resolution transmission electron microscopy (HRTEM) was employed to examine Au_{25} @Cu-BTC, as shown in Fig. 1b. Au NCs are clearly observed in the HRTEM image and uniformly dispersed in $\text{Cu}_3(\text{BTC})_2$ with an average diameter of 1.34 nm (Fig. 1b inset). The size is consistent with that of the pristine Au NCs (Fig. S1b, ESI†), confirming that

the Au NCs were well maintained during encapsulation. $\text{Cu}_3(\text{BTC})_2$ was reported to have cavities with 1.33 nm size and 3D connected channels with 1.8 nm windows,²⁴ so ultrasmall Au NCs can be confined in the cavities of $\text{Cu}_3(\text{BTC})_2$ and/or implanted into their channels, preventing the aggregation of the Au NCs. The formation of Au_{25} @Cu-BTC was further verified by scanning transmission electron microscopy (STEM) and corresponding energy-dispersive X-ray spectroscopy (EDS) elemental analysis (Fig. 1c and d). The EDS mapping images illustrate that Cu, Au, C, O and S are uniformly distributed, and the good coincidence relation between Cu and O as well as Au and S further confirms that the hierarchical structure has been successfully constructed. The amount of Au in the Au_{25} @Cu-BTC composite is determined to be 11.6 wt% by ICP-AES, and the content of Au NCs in this composite is roughly calculated to be 18.1 wt% based on the molecular formula of $\text{Au}_{25}(p\text{-MBA})_{18}$.

Upon forming the hierarchical structure, we further investigated the interaction between the embedded Au NCs and the coated $\text{Cu}_3(\text{BTC})_3$ shell using X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared (FT-IR) spectroscopy. The high-resolution O1s XPS spectra (Fig. S4a, ESI†) reveal that Au NCs, $\text{Cu}_3(\text{BTC})_2$ and Au_{25} @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. 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 $\text{Cu}_3(\text{BTC})_2$, C-O bonding becomes dominant in Au_{25} @Cu-BTC, which can be attributed to the coordination of carboxyl groups of *p*-MBA with Cu nodes of $\text{Cu}_3(\text{BTC})_2$ during *in situ* coating. This argument is confirmed by the shift of the O 1s (Fig. S4a, ESI†), S 2p (Fig. S4b, ESI†) and Au 4f (Fig. S4c, ESI†) characteristic peaks for Au_{25} @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 Cu^{2+} , 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 $\text{Cu}_3(\text{BTC})_2$ (Fig. S4d, ESI†), as the electron donation by O in the carboxyl of the Au NCs can increase the electron density of the Cu nodes in $\text{Cu}_3(\text{BTC})_2$. These results demonstrate that the embedded Au NCs are directly connected with the Cu sites of coated $\text{Cu}_3(\text{BTC})_2$ through coordination bonds, which is also confirmed by FT-IR (Fig. S3, ESI†), providing a good foundation for charge transfer between Au NCs and $\text{Cu}_3(\text{BTC})_2$. No new Cu species are found on Au_{25} @Cu-BTC (Fig. S4d, ESI† and Fig. S4, ESI†).

Upon acquiring the structural characteristics of Au_{25} @Cu-BTC, we further examined its performance for CO_2 capture and activation. $\text{Cu}_3(\text{BTC})_2$ has been well demonstrated to have excellent selective sorption for CO_2 .²⁵ The CO_2 uptake capacity of Au_{25} @Cu-BTC was evaluated by comparing the CO_2 sorption isotherms with $\text{Cu}_3(\text{BTC})_2$ under ambient conditions. As revealed by the adsorption and desorption isotherms (Fig. 2a), the CO_2 uptake capacity of $\text{Cu}_3(\text{BTC})_2$ and Au_{25} @Cu-BTC was determined to be 100.63 and $62.17 \text{ cm}^3 \text{ g}^{-1}$, respectively, based on the total weight. Given that Au NCs are not a characteristic

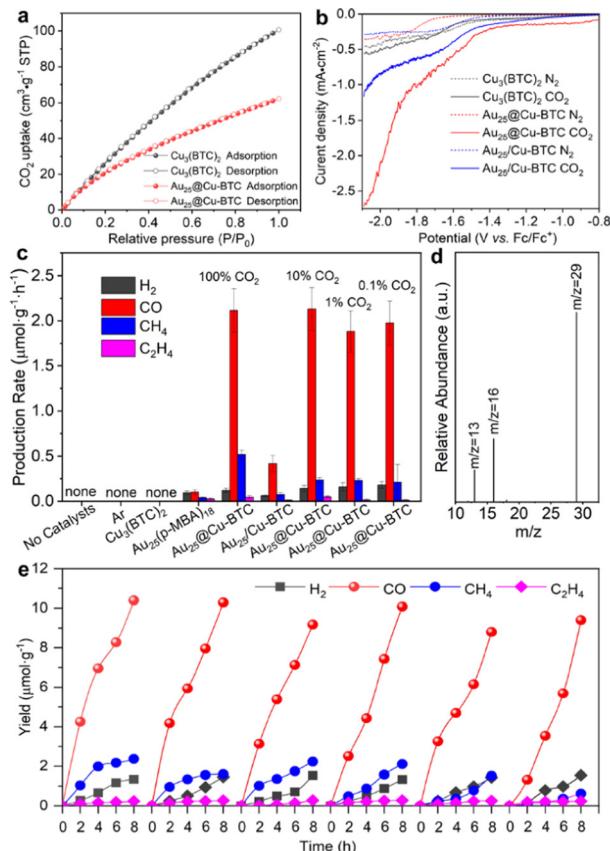


Fig. 2 (a) CO₂ adsorption behavior for Au₂₅@Cu-BTC and bare Cu₃(BTC)₂. (b) LSV curves of pristine Cu₃(BTC)₂, Au₂₅@Cu-BTC and mechanically mixed Au₂₅/Cu-BTC in 0.1 M TBAHFP solution saturated with N₂ or CO₂. (c) Average production rates of H₂, CO, CH₄ and C₂H₄ in photoreduction CO₂ by Au₂₅@Cu-BTC in the first 2 h under visible-light ($\lambda > 420$ nm) irradiation, in comparison with those by Cu₃(BTC)₂, Au₂₅(p-MBA)₁₈, Au₂₅/Cu-BTC and other control experiments under the same conditions. All measurements were performed on a gas–solid reactor in the presence of BIH and a trace amount of H₂O. (d) GC–MS analysis of ¹³CO ($m/z = 29$) produced over Au₂₅@Cu-BTC in light-driven reduction of ¹³CO₂. (e) Light-driven catalytic durability over Au₂₅@Cu-BTC. Each cycle takes 8 h.

material for CO₂ adsorption, the CO₂ uptake of the coated Cu₃(BTC)₂ component is calculated to be approximately 75.91 cm³ g⁻¹, which is comparable to that of Cu₃(BTC)₂, indicating that the incorporation of Au NCs does not significantly block the channels of Cu₃(BTC)₂ for CO₂ capture and mass transfer. This result is confirmed by N₂ sorption measurements (Fig. S5, ESI[†]). The CO₂ activation ability of the Cu₃(BTC)₂-based samples was examined by electrochemical linear sweep voltammetry (LSV) measurements in 0.1 M tetrabutylammonium hexafluorophosphate (TBAHFP) purged with CO₂ or N₂. As the reference sample, Cu₃(BTC)₂-loaded Au₂₅(p-MBA)₁₈ (denoted as Au₂₅/Cu-BTC) was prepared *via* a mechanical mixing method. As shown in Fig. 2b, all the samples exhibit higher current density in the CO₂ atmosphere than that in an inert atmosphere, indicating that all of them have the ability to activate CO₂ under a reduction potential. Obviously, the Au₂₅@Cu-BTC composite offers the largest increase of current density in the presence of CO₂, which may be attributed to the improvement of electrical conductivity by embedding Au NCs into the framework of Cu₃(BTC)₂.

Given the excellent performance for CO₂ capture and activation, we are now in a position to examine the performance of Au₂₅@Cu-BTC as a light-driven catalyst for CO₂ reduction. To fully take advantage of the outstanding CO₂ uptake capability, the light-driven catalytic performance was assessed in a gas–solid reactor (Fig. S6, ESI[†]) under visible-light irradiation using a trace amount (100 μL) of H₂O as a proton source and 1,3-dimethyl-2-phenyl-2,3-dihydro-1H-benz[*d*]imidazole (BIH) as a sacrificial agent to consume photogenerated holes. As shown in Fig. 2c, no reduction products were detected in the absence of catalysts and CO₂, suggesting its strong dependence on both catalysts and CO₂. Consistent with our previous study,¹⁸ pristine Cu₃(BTC)₂ did not exhibit catalytic activity for CO₂ reduction because it lacks photo-excited electrons for the reduction reaction. Meanwhile, bare Au NCs also presented negligible photoreduction activity and lower selectivity for carbon products (84.1%), which should be due to their lack of active sites for catalyzing reactions.¹⁵ In sharp contrast, when Au NCs were embedded into the Cu₃(BTC)₂ matrix, the photoreduction activity of Au₂₅@Cu-BTC was greatly improved (Fig. 2c and Fig. S7, ESI[†]). It turned out that the production rate of 2.13 μmol g⁻¹ h⁻¹ for CO is over 21 times that of bare Au NCs (0.102 μmol g⁻¹ h⁻¹), and the selectivity of the carbon products was increased up to 97.6% (Fig. 2c). This enhanced efficiency was achieved through the complementary roles of the two components, with Au NCs serving as a light-harvesting center and Cu₃(BTC)₂ providing catalytic sites. It has been well verified that Cu sites can suppress the side reaction of hydrogen evolution in photocatalytic and electrocatalytic CO₂ reduction.²¹ However, it is difficult to accomplish such an effect by the simply mixed Au₂₅/Cu-BTC, which yielded CO at a production rate of only 0.515 μmol g⁻¹ h⁻¹ (Fig. 2c). This indicates that the connection mode between them is the key for their efficient integration.

Considering the excellent CO₂ capture capability of the Cu₃(BTC)₂ shell, we evaluated the photoreduction performance of Au₂₅@Cu-BTC in a lower concentration CO₂ (10%, 1%, and 0.1%) atmosphere (diluted with argon) under identical reaction conditions. Interestingly, our designed Au₂₅@Cu-BTC gives roughly comparable photocatalytic performance in pure and diluted CO₂ atmospheres (Fig. 2c), demonstrating that it has broad application potential in a low-concentration CO₂ atmosphere. To determine the carbon source of the detected CO, isotopic ¹³CO₂ was used as the reactant to carry out the light-driven catalytic reaction under the same conditions, and the product was analysed by gas chromatography–mass spectrometry (GC–MS) (Fig. 2d). The peak appearing at $m/z = 29$ in MS can be ascribed to ¹³CO, confirming that CO is indeed produced from the photoreduction of CO₂.

To examine the durability of our catalysts, we performed a test in 6 successive cycles, each of which took 8 h. As shown in Fig. 2e, the catalytic performance of Au₂₅@Cu-BTC remained steady for at least 48 h, indicating its excellent durability. HRTEM analysis confirms no distinct size change for the Au NCs confined in the Cu₃(BTC)₂ matrix (Fig. S8, ESI[†]). In contrast, bare Au NCs and physically mixed Au₂₅/Cu-BTC can hardly maintain their catalytic activity for 2 successive cycles (Fig. S9, ESI[†]), as the Au NCs tend to be aggregated into Au nanoparticles (*ca.* 4.5 nm) (Fig. S10, ESI[†]). These results fully prove that the good durability of

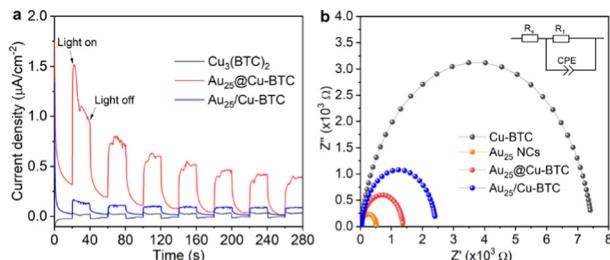


Fig. 3 (a) Photocurrents and (b) Nyquist plots of Cu₃(BTC)₂, Au NCs, Au₂₅@Cu-BTC and Au₂₅/Cu-BTC. The inset in (b) is the equivalent circuit for fitting.

Au₂₅@Cu-BTC in CO₂ photoreduction is attributed to the confinement effect of Cu₃(BTC)₂ encapsulation.

To gain a deeper understanding on the enhanced performance of Au₂₅@Cu-BTC, we collected the photocurrent response on our catalysts, which has been widely used to reveal the charge separation efficiency. As shown in Fig. 3a, Au₂₅@Cu-BTC exhibits about 4 times higher photocurrent density than Au₂₅/Cu-BTC and 8 times that of bare Cu₃(BTC)₂, indicating the superiority of our designed composites for photogenerated charge separation. To find out the reason behind this improvement, Mott–Schottky measurements were applied to examine the charge transfer capability by comparing their resistance. As displayed in Fig. 3b, the charge transfer resistance R_1 drops sharply from 7449 Ω of Cu₃(BTC)₂ to 2405 Ω of Au₂₅/Cu-BTC and 1349 Ω of Au₂₅@Cu-BTC, manifesting the smallest internal resistance of Au₂₅@Cu-BTC for its efficient charge transfer. In combining the results of TEM, XPS and FT-IR with the preparation procedure of Au₂₅@Cu-BTC, we can conclude that the efficient charge transfer and separation of Au₂₅@Cu-BTC can be attributed to the following advantages compared with simple mixed Au₂₅/Cu-BTC: (i) the high conductivity Au NCs (Fig. 3b), implanted in the Cu₃(BTC)₂ matrix, can improve the overall conductivity for fast transport of photogenerated charges; (ii) the *in situ* implanted Au NCs in Cu₃(BTC)₂ are directly connected with Cu sites through chemical bonds between the carboxyl of *p*-MBA and Cu nodes (Fig. S4, ESI†), offering more efficient transfer of photogenerated electrons than the Au₂₅/Cu-BTC through physical contact; (iii) the photogenerated electrons on the embedded Au NCs have shorter migration distances to the Cu sites in the Cu₃(BTC)₂ channels than for Au₂₅/Cu-BTC, which can greatly reduce the possibility of charge recombination during travelling to the Cu sites; (iv) more internal Cu sites can be utilized for efficient catalysis in the Au₂₅@Cu-BTC system than in the counterpart of Au₂₅/Cu-BTC.

In summary, we have developed a mild strategy for *in situ* encapsulating ultrasmall Au₂₅ nanoclusters in a Cu-based MOF for CO₂ photoreduction, in which the embedded Au NCs produce photoexcited charges while the coated microporous shells capture CO₂ and provide active sites. Remarkably, the light-driven catalytic performance, particularly the durability, was enhanced by our designed Au₂₅@Cu-BTC composite, in stark contrast to bare Au NCs and mechanically mixed Au₂₅/Cu-BTC. The spectroscopic and

morphological characterizations have proven that the performance enhancement is attributed to the direct chemical connection of Au NCs with the Cu sites of MOFs promoting charge transfer and the well-matched size between the Au NCs and MOF channels offering a strong confinement effect. This work highlights the importance of ligand and size matching in designing hierarchical photocatalytic materials based on molecular units.

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Conflicts of interest

There are no conflicts to declare.

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