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Here, we report the encapsulation of  $\text{Au}_{25}$  nanoclusters in a  $\text{Cu}_3(\text{BTC})_2$  metal–organic framework ( $\text{Au}_{25}@\text{Cu-BTC}$ ), which can achieve  $\text{CO}_2$  photoreduction for selective CO production in a gas–solid reaction system at low-concentration  $\text{CO}_2$  atmospheres (even to 0.1%), with remarkably enhanced durability up to at least 48 h.

Light-driven  $\text{CO}_2$  reduction has continuously received attention.<sup>1–3</sup> 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.<sup>4–7</sup> In particular, their subnanometer sizes ( $\sim 1$  nm), approaching the de Broglie wavelength, result in discrete electronic structures, which makes their light absorption readily tuned.<sup>8,9</sup> Moreover, the ultrasmall sizes and high conductivity of metal NCs are beneficial for the transfer of photogenerated electrons to their surface.<sup>10–12</sup> 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.<sup>13</sup> 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.<sup>6</sup>

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## Enhancing the durability of Au clusters in $\text{CO}_2$ photoreduction via encapsulation in Cu-based metal–organic frameworks†

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To prevent aggregation, metal oxides,<sup>14</sup> polymers<sup>15</sup> and covalent organic frameworks<sup>16</sup> 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.<sup>16,17</sup> For this reason, the encapsulation of nanomaterials in MOFs has been intensively studied in recent years.<sup>18,19</sup> However, it remains a great challenge to accomplish surface coating with MOFs because of the lattice mismatch between the guest materials and the MOFs.<sup>20</sup> 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  $\text{CO}_2$  photoreduction performance.

Herein, we report a facile process for encapsulating atomically precise  $\text{Au}_{25}(p\text{-MBA})_{18}$  ( $p\text{-MBA}$  = 4-mercaptopbenzoic acid) clusters in MOFs to enhance the durability of the catalyst in the selective photoreduction of  $\text{CO}_2$  to CO. In our designed scheme, the MOFs are expected to introduce multiple advantages for  $\text{CO}_2$  photoreduction, *i.e.*, confining Au NCs to prevent aggregation, offering active sites for  $\text{CO}_2$  reduction, and capturing  $\text{CO}_2$  to facilitate the conversion process. Inspired by these considerations,  $\text{Cu}_3(\text{BTC})_2$  ( $\text{BTC}$  = benzene-1,3,5-tricarboxylate) is selected as the MOF model, as it can provide a framework for  $\text{CO}_2$  capture and Cu sites for  $\text{CO}_2$  activation as demonstrated by our previous studies.<sup>21,22</sup>

Fig. 1a schematically illustrates the synthetic procedure of  $\text{Cu}_3(\text{BTC})_2$ -encapsulated  $\text{Au}_{25}(p\text{-MBA})_{18}$  (denoted as  $\text{Au}_{25}@\text{Cu-BTC}$ ). Water-soluble  $\text{Au}_{25}(p\text{-MBA})_{18}$  was synthesized according to the method reported by Chen *et al.*<sup>23</sup> The successful preparation of  $\text{Au}_{25}(p\text{-MBA})_{18}$  was confirmed by UV-vis absorption spectroscopy and ESI mass spectrum (Fig. S1, ESI†). Of particular note is that we selected  $\text{Au}_{25}(p\text{-MBA})_{18}$  as the model cluster on account of its good

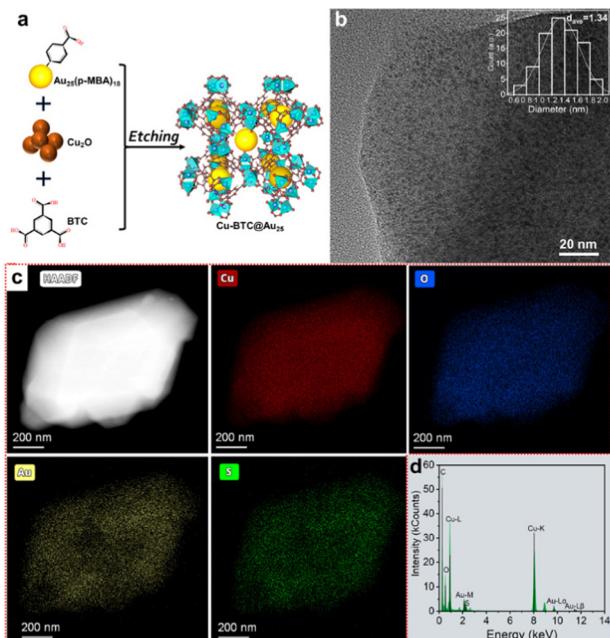


Fig. 1 (a) Schematic illustration of the preparation process of the  $\text{Au}_{25}$ @Cu-BTC composite. (b) HRTEM image, (c) STEM image and corresponding EDS elemental mapping images and (d) EDS spectrum of  $\text{Au}_{25}$ @Cu-BTC.

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  $\text{Au}_{25}$  NCs. In our synthesis,  $\text{Cu}_2\text{O}$  nanoparticles rather than  $\text{Cu}^{2+}$  ions were used as the Cu precursor for  $\text{Cu}_3(\text{BTC})_2$ , as we found that directly adding  $\text{Cu}^{2+}$  inevitably induced Au NC aggregation. The  $\text{Cu}_2\text{O}$  nanoparticles can be etched by the protons of carboxyl to slowly release  $\text{Cu}^+$  and then oxidized to  $\text{Cu}^{2+}$  by dissolved oxygen, which will coordinate with the carboxyl of BTC and *p*-MBA to *in situ* form the encapsulated  $\text{Au}_{25}$ @Cu-BTC.<sup>22</sup> As displayed in the powder X-ray diffraction (PXRD) pattern (Fig. S2, ESI†), the characteristic peak of  $\text{Cu}_2\text{O}$  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  $\text{Cu}_2\text{O}$  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  $\text{Au}_{25}$ @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  $\text{Au}_{25}$ @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,<sup>24</sup> 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  $\text{Au}_{25}$ @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  $\text{Au}_{25}$ @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  $\text{Au}_{25}$ @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  $\text{Au}_{25}$ @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  $\text{Au}_{25}$ @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  $\text{Cu}^{2+}$ , reducing the electron densities of the *p*-MBA ligands. In the meantime, the characteristic peaks of Cu in the Cu LMM spectrum of  $\text{Au}_{25}$ @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  $\text{Au}_{25}$ @Cu-BTC (Fig. S4d, ESI† and Fig. S4, ESI†).

Upon acquiring the structural characteristics of  $\text{Au}_{25}$ @Cu-BTC, we further examined its performance for  $\text{CO}_2$  capture and activation.  $\text{Cu}_3(\text{BTC})_2$  has been well demonstrated to have excellent selective sorption for  $\text{CO}_2$ .<sup>25</sup> The  $\text{CO}_2$  uptake capacity of  $\text{Au}_{25}$ @Cu-BTC was evaluated by comparing the  $\text{CO}_2$  sorption isotherms with  $\text{Cu}_3(\text{BTC})_2$  under ambient conditions. As revealed by the adsorption and desorption isotherms (Fig. 2a), the  $\text{CO}_2$  uptake capacity of  $\text{Cu}_3(\text{BTC})_2$  and  $\text{Au}_{25}$ @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

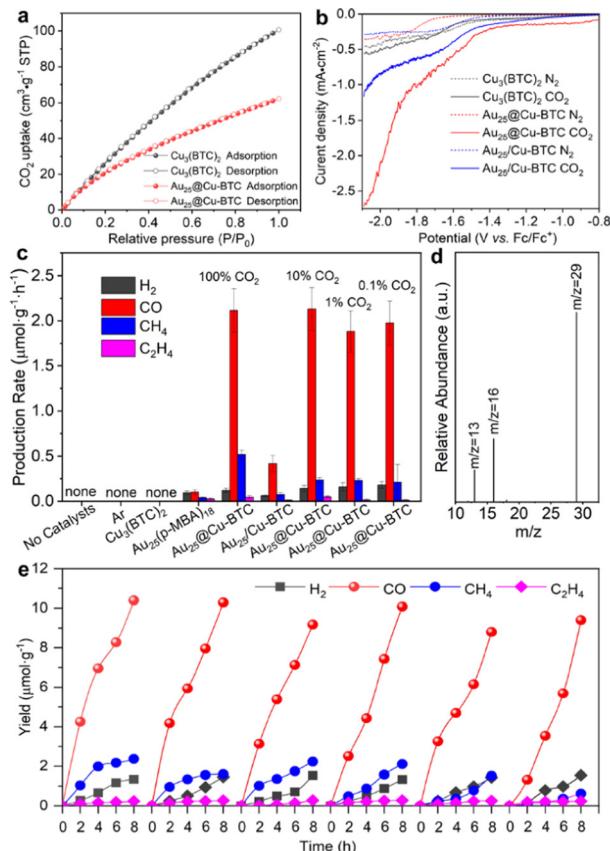


Fig. 2 (a) CO<sub>2</sub> adsorption behavior for Au<sub>25</sub>@Cu-BTC and bare Cu<sub>3</sub>(BTC)<sub>2</sub>. (b) LSV curves of pristine Cu<sub>3</sub>(BTC)<sub>2</sub>, Au<sub>25</sub>@Cu-BTC and mechanically mixed Au<sub>25</sub>/Cu-BTC in 0.1 M TBAHFP solution saturated with N<sub>2</sub> or CO<sub>2</sub>. (c) Average production rates of H<sub>2</sub>, CO, CH<sub>4</sub> and C<sub>2</sub>H<sub>4</sub> in photoreduction CO<sub>2</sub> by Au<sub>25</sub>@Cu-BTC in the first 2 h under visible-light ( $\lambda > 420$  nm) irradiation, in comparison with those by Cu<sub>3</sub>(BTC)<sub>2</sub>, Au<sub>25</sub>(p-MBA)<sub>18</sub>, Au<sub>25</sub>/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 H<sub>2</sub>O. (d) GC–MS analysis of <sup>13</sup>CO ( $m/z = 29$ ) produced over Au<sub>25</sub>@Cu-BTC in light-driven reduction of <sup>13</sup>CO<sub>2</sub>. (e) Light-driven catalytic durability over Au<sub>25</sub>@Cu-BTC. Each cycle takes 8 h.

material for CO<sub>2</sub> adsorption, the CO<sub>2</sub> uptake of the coated Cu<sub>3</sub>(BTC)<sub>2</sub> component is calculated to be approximately 75.91 cm<sup>3</sup> g<sup>-1</sup>, which is comparable to that of Cu<sub>3</sub>(BTC)<sub>2</sub>, indicating that the incorporation of Au NCs does not significantly block the channels of Cu<sub>3</sub>(BTC)<sub>2</sub> for CO<sub>2</sub> capture and mass transfer. This result is confirmed by N<sub>2</sub> sorption measurements (Fig. S5, ESI<sup>†</sup>). The CO<sub>2</sub> activation ability of the Cu<sub>3</sub>(BTC)<sub>2</sub>-based samples was examined by electrochemical linear sweep voltammetry (LSV) measurements in 0.1 M tetrabutylammonium hexafluorophosphate (TBAHFP) purged with CO<sub>2</sub> or N<sub>2</sub>. As the reference sample, Cu<sub>3</sub>(BTC)<sub>2</sub>-loaded Au<sub>25</sub>(p-MBA)<sub>18</sub> (denoted as Au<sub>25</sub>/Cu-BTC) was prepared *via* a mechanical mixing method. As shown in Fig. 2b, all the samples exhibit higher current density in the CO<sub>2</sub> atmosphere than that in an inert atmosphere, indicating that all of them have the ability to activate CO<sub>2</sub> under a reduction potential. Obviously, the Au<sub>25</sub>@Cu-BTC composite offers the largest increase of current density in the presence of CO<sub>2</sub>, which may be attributed to the improvement of electrical conductivity by embedding Au NCs into the framework of Cu<sub>3</sub>(BTC)<sub>2</sub>.

Given the excellent performance for CO<sub>2</sub> capture and activation, we are now in a position to examine the performance of Au<sub>25</sub>@Cu-BTC as a light-driven catalyst for CO<sub>2</sub> reduction. To fully take advantage of the outstanding CO<sub>2</sub> uptake capability, the light-driven catalytic performance was assessed in a gas–solid reactor (Fig. S6, ESI<sup>†</sup>) under visible-light irradiation using a trace amount (100  $\mu$ L) of H<sub>2</sub>O 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 CO<sub>2</sub>, suggesting its strong dependence on both catalysts and CO<sub>2</sub>. Consistent with our previous study,<sup>18</sup> pristine Cu<sub>3</sub>(BTC)<sub>2</sub> did not exhibit catalytic activity for CO<sub>2</sub> 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.<sup>15</sup> In sharp contrast, when Au NCs were embedded into the Cu<sub>3</sub>(BTC)<sub>2</sub> matrix, the photoreduction activity of Au<sub>25</sub>@Cu-BTC was greatly improved (Fig. 2c and Fig. S7, ESI<sup>†</sup>). It turned out that the production rate of 2.13  $\mu$ mol g<sup>-1</sup> h<sup>-1</sup> for CO is over 21 times that of bare Au NCs (0.102  $\mu$ mol g<sup>-1</sup> h<sup>-1</sup>), 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 Cu<sub>3</sub>(BTC)<sub>2</sub> providing catalytic sites. It has been well verified that Cu sites can suppress the side reaction of hydrogen evolution in photocatalytic and electrocatalytic CO<sub>2</sub> reduction.<sup>21</sup> However, it is difficult to accomplish such an effect by the simply mixed Au<sub>25</sub>/Cu-BTC, which yielded CO at a production rate of only 0.515  $\mu$ mol g<sup>-1</sup> h<sup>-1</sup> (Fig. 2c). This indicates that the connection mode between them is the key for their efficient integration.

Considering the excellent CO<sub>2</sub> capture capability of the Cu<sub>3</sub>(BTC)<sub>2</sub> shell, we evaluated the photoreduction performance of Au<sub>25</sub>@Cu-BTC in a lower concentration CO<sub>2</sub> (10%, 1%, and 0.1%) atmosphere (diluted with argon) under identical reaction conditions. Interestingly, our designed Au<sub>25</sub>@Cu-BTC gives roughly comparable photocatalytic performance in pure and diluted CO<sub>2</sub> atmospheres (Fig. 2c), demonstrating that it has broad application potential in a low-concentration CO<sub>2</sub> atmosphere. To determine the carbon source of the detected CO, isotopic <sup>13</sup>CO<sub>2</sub> 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 <sup>13</sup>CO, confirming that CO is indeed produced from the photoreduction of CO<sub>2</sub>.

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 Au<sub>25</sub>@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 Cu<sub>3</sub>(BTC)<sub>2</sub> matrix (Fig. S8, ESI<sup>†</sup>). In contrast, bare Au NCs and physically mixed Au<sub>25</sub>/Cu-BTC can hardly maintain their catalytic activity for 2 successive cycles (Fig. S9, ESI<sup>†</sup>), as the Au NCs tend to be aggregated into Au nanoparticles (*ca.* 4.5 nm) (Fig. S10, ESI<sup>†</sup>). These results fully prove that the good durability of

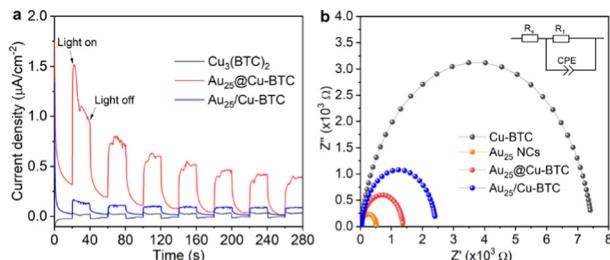


Fig. 3 (a) Photocurrents and (b) Nyquist plots of Cu<sub>3</sub>(BTC)<sub>2</sub>, Au NCs, Au<sub>25</sub>@Cu-BTC and Au<sub>25</sub>/Cu-BTC. The inset in (b) is the equivalent circuit for fitting.

Au<sub>25</sub>@Cu-BTC in CO<sub>2</sub> photoreduction is attributed to the confinement effect of Cu<sub>3</sub>(BTC)<sub>2</sub> encapsulation.

To gain a deeper understanding on the enhanced performance of Au<sub>25</sub>@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, Au<sub>25</sub>@Cu-BTC exhibits about 4 times higher photocurrent density than Au<sub>25</sub>/Cu-BTC and 8 times that of bare Cu<sub>3</sub>(BTC)<sub>2</sub>, 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 Cu<sub>3</sub>(BTC)<sub>2</sub> to 2405 Ω of Au<sub>25</sub>/Cu-BTC and 1349 Ω of Au<sub>25</sub>@Cu-BTC, manifesting the smallest internal resistance of Au<sub>25</sub>@Cu-BTC for its efficient charge transfer. In combining the results of TEM, XPS and FT-IR with the preparation procedure of Au<sub>25</sub>@Cu-BTC, we can conclude that the efficient charge transfer and separation of Au<sub>25</sub>@Cu-BTC can be attributed to the following advantages compared with simple mixed Au<sub>25</sub>/Cu-BTC: (i) the high conductivity Au NCs (Fig. 3b), implanted in the Cu<sub>3</sub>(BTC)<sub>2</sub> matrix, can improve the overall conductivity for fast transport of photogenerated charges; (ii) the *in situ* implanted Au NCs in Cu<sub>3</sub>(BTC)<sub>2</sub> 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 Au<sub>25</sub>/Cu-BTC through physical contact; (iii) the photogenerated electrons on the embedded Au NCs have shorter migration distances to the Cu sites in the Cu<sub>3</sub>(BTC)<sub>2</sub> channels than for Au<sub>25</sub>/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 Au<sub>25</sub>@Cu-BTC system than in the counterpart of Au<sub>25</sub>/Cu-BTC.

In summary, we have developed a mild strategy for *in situ* encapsulating ultrasmall Au<sub>25</sub> nanoclusters in a Cu-based MOF for CO<sub>2</sub> photoreduction, in which the embedded Au NCs produce photoexcited charges while the coated microporous shells capture CO<sub>2</sub> and provide active sites. Remarkably, the light-driven catalytic performance, particularly the durability, was enhanced by our designed Au<sub>25</sub>@Cu-BTC composite, in stark contrast to bare Au NCs and mechanically mixed Au<sub>25</sub>/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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