Linking oxidative and reductive clusters to prepare crystalline porous catalysts for photocatalytic CO₂ reduction with H₂O

Mimicking natural photosynthesis to convert CO₂ with H₂O into value-added fuels achieving overall reaction is a promising way to reduce the atmospheric CO₂ level. Casting the catalyst of two or more catalytic sites with rapid electron transfer and interaction may be an effective strategy for coupling photocatalytic CO₂ reduction and H₂O oxidation. Herein, based on the MOF ∪ COF collaboration, we have carefully designed and synthesized a crystalline hetero-metallic cluster catalyst denoted MCOF-Ti₆Cu₃ with spatial separation and functional cooperation between oxidative and reductive clusters. It utilizes dynamic covalent bonds between clusters to promote photo-induced charge separation and transfer efficiency, to drive both the photocatalytic oxidative and reductive reactions. MCOF-Ti₆Cu₃ exhibits fine activity in the conversion of CO₂ with water into HCOOH (169.8 μmol g⁻¹ h⁻¹). Remarkably, experiments and theoretical calculations reveal that photo-excited electrons are transferred from Ti to Cu, indicating that the Cu cluster is the catalytic reduction center.

Converting CO₂ and H₂O with solar energy into carbon-based fuels is a potential solution that could solve the problems of global warming and energy supply, which is in line with the global green and low-carbon development strategy. However, there is still a long way to realize photocatalytic overall oxidative and reductive reactions, due to the inability of fast photogenerated electron-hole pairs recombination to satisfy both the kinetics of overcoming the high chemical inertness of CO₂ molecules and the slow oxidation of water. In nature, the chlorophyll aggregate P680 of green plants captures light energy for charge separation, then pheophytin pigment rapidly captures electrons to produce the radical cation P680⁺, providing separated electron-hole to complete the conversion of CO₂ and H₂O into carbon-based fuels. Up to date, tremendous efforts have been made to mimic green plants, including type II and Z-scheme heterojunctions for the artificial photosynthesis systems. Therefore, combining two or more catalytic sites to accomplish spatial separation of oxidative and reductive centers, rapid transfer of electrons, and functional interactions may be a promising strategy for realizing the overall photoreaction. Nevertheless, cumbersome synthetic procedures and loss of atomic-scale control are the serious flaws of these strategies, which hinder the understanding of photocatalysis at the atomic level.

The reticular crystalline materials, metal organic frameworks (MOFs) and covalent organic frameworks (COFs), have made great potential in photocatalytic CO₂ conversion, a frontier in the study of structure-property correlations constructed on the atomic level. However, the difficulty to accurately control the structure of the framework material with dual active sites in the in-situ synthesis of crystalline materials may restrict their further development in the conversion of CO₂. Exploring metal clusters or molecular complexes with defined composition and directionality linked with other metal complexes by coordination linkages or even dynamic covalent linkages might be a promising avenue to overcome these shortcomings. To date, the active sites of oxidative or reductive reactions are only...
found on a single species (oxidative or reductive homo-metallic clusters) in the reported examples, which is unfavorable for completing the artificial photosynthetic overall reaction\(^{20-32}\). If the clusters with water oxidative ability and CO\(_2\) reductive ability can be connected, it is possible to realize the overall reaction of artificial photosynthesis without additional photosensitizers and sacrificial agents\(^{33-34}\). Currently, the mainstream methods to achieve the incorporation of dual active sites with different functions in one single material are by integrating photoactive centers into the structure\(^{33}\) or post-synthetic sites with different functions in one single material are by integrating the mainstream methods to achieve the incorporation of dual active individual components and preserving their oxidative and reductive interactions between clusters, without damaging the intrinsic prepared by directed assembly through relatively mild dynamic photocatalytic CO\(_2\) reduction and H\(_2\)O oxidation. MCOF-Ti\(_6\)Cu\(_3\) was intentionally constructed with Ti-O clusters with oxidation ability\(^{40,41}\) and Cu clusters with oxidation ability and CO\(_2\) reductive ability can be connected, it is possible to realize the overall reaction of artificial photosynthesis\(^{35-37}\). Due to the stability and solubility issues of different clusters during synthesis and crystallization, almost no reports have been published to realize the construction of cluster-based crystalline porous catalysts through the linkage by covalent bonds.

With the above in mind, to complete the overall reaction directly, a hetero-metallic cluster catalyst, namely MCOF-Ti\(_6\)Cu\(_3\), has been intentionally constructed with Ti-O clusters with oxidation ability\(^{44,45}\) and Cu clusters with reduction capability\(^{42,43}\) for effective coupling photocatalytic CO\(_2\) reduction and H\(_2\)O oxidation. MCOF-Ti\(_6\)Cu\(_3\) was prepared by directed assembly through relatively mild dynamic covalent linkages, enabling both rapid electron transfer and synergistic interactions between clusters, without damaging the intrinsic individual components and preserving their oxidative and reductive properties. Under simulated sunlight irradiation, MCOF-Ti\(_6\)Cu\(_3\) exhibited excellent photocatalytic activity in the generation of HCOOH with a yield of 20.39 \(\mu\)mol in 12 h with O\(_2\) release, at a high level among the reported non-noble metal photocatalysts with overall reaction. The existence of an internal electric field in MCOF-Ti\(_6\)Cu\(_3\) with the Ti cluster pointing to the Cu cluster was confirmed by X-ray photoelectron spectroscopy (XPS). Notably, the in-situ XPS and density functional theory (DFT) calculations proved that electrons reach to the Cu cluster under light excitation conditions, and finally the reductive reaction occurs at the Cu cluster and the oxidative reaction at the Ti cluster, which is consistent with the oxidative and reductive centers of the pre-designed material. Finally, in-situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) and DFT calculations unambiguously unveiled the intermediates and mechanism of the photoreaction. This work not only provides a rational strategy for constructing hetero-metallic cluster catalyst, but also an insight into photocatalytic overall reaction by using accurate structural models. Overall, our findings may shed light on the application of crystalline materials in the field of photocatalytic overall reaction for CO\(_2\) and H\(_2\)O conversion.

Results and discussion
Two precursors [Ti\(_6\)O\(_6\)(OPr\(_3\))\(_6\)(AB)\(_6\)] (AB = 4-aminobenzoate; Hopr = isopropoxide, denoted Ti\(_6\)\(_{44}\) and [Cu\(_3\) (PyCA)\(_3\)] (1H-PyCA = pyrazolate-4-carboxaldehyde, denoted Cu\(_3\)\(_{32}\) were prepared according to the previously reported methods. The synthesis of MCOF-Ti\(_6\)Cu\(_3\) was carried out from the condensation of Ti\(_6\) and Cu\(_3\) in a mixture of mesitylene and N, N-Dimethylformamide (DMF) under the vacuum solvothermal conditions (Fig. 1a). Fourier-transform infrared (FT-IR) spectra confirmed the condensation reaction between the two starting materials by the obvious disappearance of the C = O (1685 cm\(^{-1}\)) and NH (3200 – 3500 cm\(^{-1}\)) stretching vibration peaks found in Cu\(_3\) and Ti\(_6\) respectively (Fig. 1b). In addition, a new characteristic peak at 1625 cm\(^{-1}\) attributed to the C = N bond was observed, indicating the successful formation of an imine-linked network\(^{38}\). Powder X-ray diffraction (PXRD) pattern of MCOF-Ti\(_6\)Cu\(_3\) displayed the strongest diffraction peak at 28 6.1° corresponding to (110) reflection plane, along with minor peaks at 12.4°, 18.8°, 20.4°, and 25.3° that are attributed to the

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**Fig. 1** The preparation and characterization. a Schematic of the synthesis of MCOF-Ti\(_6\)Cu\(_3\) via the condensation of Ti\(_6\) and Cu\(_3\). b IR spectra of MCOF-Ti\(_6\)Cu\(_3\), Ti\(_6\) and Cu\(_3\). c Experimental and simulated PXRD patterns of MCOF-Ti\(_6\)Cu\(_3\). d Top and e side views of the structure of MCOF-Ti\(_6\)Cu\(_3\). Atomic color: Carbon (gray), Nitrogen (blue), Oxygen (red), Copper (orange), Titanium (silver) and Hydrogen (white).
(220), (330), (502), and (440) crystal planes, respectively (Fig. 1c). To elucidate the crystal structure of MCOF-Ti6Cu3, the staggered stacking model in the $R_3$ and $P_6_3$ space groups corresponding to ABC and AB stacking were built using Materials Studio. The experimental PXRD pattern matches well with the simulated one for the ABC stacking model. Pawley refinement was applied to provide the refined unit cell parameters of $a = b = 29.14 \text{ Å}$, $c = 18.97 \text{ Å}$, with good residual factors of $R_p = 2.36\%$ and $R_wp = 3.10\%$, suggesting the validity of the computational model. The structural information for the AB stacking model is in the Supplementary Information.

These structural analyses reveal that a rhombic channel along c axis with a theoretical pore size of 1.08 nm × 1.72 nm and interlayer distance of 5.6 Å (Fig. 1d, e). The porosity and surface area of MCOF-Ti6Cu3 were examined by N2 adsorption-desorption measurements at 77 K (Fig. 1f). The Brunauer-Emmett-Teller (BET) surface area was calculated to be 215.2 m$^2$ g$^{-1}$. Besides, the pore size distribution (~1.01 and ~1.68 nm) of MCOF-Ti6Cu3 were in good agreement with the results predicted from the theoretical structure model. The crystallinity and structure of MCOF-Ti6Cu3 remained by treating it with various solvents at room temperature, which was confirmed by PXRD analyses (Supplementary Fig. 9). The thermal stability of MCOF-Ti6Cu3 was confirmed by thermogravimetric analysis (TGA) (Supplementary Figs. 10, 11, and 12), which showed no noticeable weight loss up to 300 °C. The morphology of MCOF-Ti6Cu3 was characterized by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The SEM and TEM images of MCOF-Ti6Cu3 shown in Supplementary Figs. 13 and 14 display a sheet-like morphology, which is apparently different from the regular octahedral structure of Ti6 (Supplementary Fig. 15) and the needle-shaped particles of Cu3 (Supplementary Fig. 16). In addition, the high-resolution TEM (HRTEM) image distinctly reveals the high crystallinity of MCOF-Ti6Cu3 (Supplementary Fig. 17). The corresponding energy-dispersive X-ray spectroscopy (EDS) mapping spectra (Supplementary Fig. 18) indicate that Ti and Cu elements are uniformly distributed in MCOF-Ti6Cu3.

In order to conduct a more in-depth study on the hetero-metallic cluster catalyst of MCOF-Ti6Cu3, we also analyzed two monometallic cluster framework materials named MOF901 and FDM-71-ABC as control samples, which were synthesized from Ti6 with p-benzaldehyde and Cu3 with p-phenylenediamine, respectively (Fig. 2a, see Supplementary Information for details). For photocatalytic reduction of CO2, the separation and migration behavior of photogenerated electron-hole pairs is one of the critical factors. The photoelectro-chemical properties of the samples were performed with the combination of transient photocurrent measurements.
measurements, electrochemical impedance spectroscopy (EIS) and photoluminescence (PL) spectra. Figure 2b shows that all samples exhibit obvious photocurrent signals and have an excellent reproducibility of the response intensity in the process of on-off cycles. The transient photocurrent intensity of MCOF-Ti6Cu3 is \( \sim 1.5 \) times that of FDM-71-ABC and much higher than that of MOF901. Moreover, the photocurrent intensity of \( \text{Cu}_3 \) is about three times as high as \( \text{Ti}_6 \), indicating that the \( \text{Cu}_3 \) cluster may have better photosensitivity (Supplementary Fig. 19). The EIS spectra reveal that compared with MOF901 and FDM-71-ABC, MCOF-Ti6Cu3 exhibits a smaller semicircle radius in the high-frequency region in Nyquist plots, suggesting a higher separation and transfer efficiency of charge carriers in MCOF-Ti6Cu3 (Supplementary Fig. 20). As presented in Fig. 2c, the spectral peak position of FDM-71-ABC which originates from \( \text{Cu}_3 \) cluster (Supplementary Fig. 21) is about 400 nm, while that of MOF901 which originates from \( \text{Ti}_6 \) cluster (Supplementary Fig. 22) is about 500 nm. In contrast, MCOF-Ti6Cu3 exhibits two shifted peaks with the weakest PL intensity, indicating the existence of electron transfer and the lowest recombination efficiency of photoinduced electron-hole pairs. Meanwhile, time-resolved fluorescence decay spectra were measured to determine the specific charge carrier dynamics (Fig. 2d). The results showed that the average lifetime of the photogenerated charge carriers in MCOF-Ti6Cu3 was 1.90 ± 0.26 \( \mu \)s, which is comparable to that of FDM-71-ABC (1.67 ± 0.09 \( \mu \)s) and longer than that of MOF901 (1.28 ± 0.15 \( \mu \)s). The difference of fluorescence lifetime between MCOF-Ti6Cu3 and FDM-71-ABC can also be directly evident from the fluorescence decay data (Fig. 2d), which shows that the fluorescence decays with a lower rate in MCOF-Ti6Cu3 compared with those in the other two samples, illustrating that the photo-generated charge carriers survived longer on the surface of MCOF-Ti6Cu3. These results further demonstrate that the spatially separated hetero-metallic cluster structures can effectively capture photogenerated electrons and holes respectively, reduce the change of recombination of charge carriers and facilitate their separation and migration in the framework in favor of the higher photocatalytic activity.

The solid-state UV-vis diffuse reflectance spectra (UV-vis DRS) of the samples were recorded. As shown in Fig. 2e, FDM-71-ABC and MCOF-Ti6Cu3 exhibited considerable absorption in the UV and visible regions, whereas the absorption edge of MOF901 was only located near 650 nm. Evaluated by the Tauc plots, the corresponding band gap energies (\( E_g \)) of MOF901, FDM-71-ABC, and MCOF-Ti6Cu3 were calculated to be 2.5, 2.71, and 2.25 eV, respectively (Supplementary Figs. 23, 24 and 25). Furthermore, Mott-Schottky measurements were performed to elucidate the semiconductor character of the samples (Supplementary Figs. 26, 27 and 28). The flat band potentials of MOF901, FDM-71-ABC, and MCOF-Ti6Cu3 were determined to be −1.06, −1.19, and −0.96 V vs. Ag/AgCl (i.e., −0.86, −0.99, and −0.76 V vs. NHE), respectively, which were equal to their conduction band (CB) potentials \(^{47} \). Based on the equation \( E_g = E_{VB} - E_{CB} \), their valence band (VB) positions were accordingly calculated to be 1.39, 1.51, and 1.95 V vs. NHE, respectively (Fig. 3a). Considering the CB/VB and LUMO/HOMO, the energy of CB/VB is equivalent to the electrochemical potentials, band structure diagram of MOF901, FDM-71-ABC and MCOF-Ti6Cu3. Photocatalysis performances: b The comparison of HCOOH yields for different samples. c The photocatalytic products yields for samples with different morphology and physical mixtures. d Durability measurements (12 h test per cycle). e Time-dependent HCOOH production. f \(^{13} \)C NMR spectra for the photocatalytic reaction solution from \(^{13} \)CO2 atmosphere. The error bar represents the standard deviation of the measurements.

![Fig. 3](https://doi.org/10.1038/s41467-022-32449-z)
energy potentials of LUMO/HOMO. Obviously, they are thermo-dynamically suitable for photocatalytic reduction of CO2 together with oxidation of H2O to various fuels.

The simultaneous completion of CO2 reduction and H2O oxidation is a great challenge. Therefore, the performance of photocatalytic reduction of CO2 with H2O over the samples was systematically investigated under simulated sunlight irradiation. As shown in Fig. 3b, the main product of the CO2 photocatalytic reduction with MCOF-Ti6Cu3 was HCOOH, of which the yield reached 9.25 μmol (77.3 μmol g−1 h−1) after 12 h illumination, while no gaseous products were detected, resulting in a high selectivity. In sharp contrast, MOF901 or FDM-71-ABC showed inactive for CO2 reduction, indicating that neither Ti nor Cu cluster could complete the CO2 reduction coupled with H2O oxidation. In addition, control experiments with Ti6 and Cu3 as the photocatalysts for CO2 reduction have also been evaluated under identical conditions. It could be found that no HCOOH was observed, indicating that neither the precursor nor homo-metallic cluster catalyst can complete the overall reaction alone. The PXRD pattern and FT-IR suggested structural integrity and that no HCOOH was observed, indicating that neither the precursor nor homo-metallic cluster catalyst can complete the overall reaction alone. As shown in Supplementary Fig. 3d, the main product of MCOF-Ti6Cu3 during four consecutive cycles. MCOF-Ti6Cu3 retained the original photocatalytic efficiency after the removal of catalyst from the reaction, further verifying that the carbon source of HCOOH indeed originated from CO2 rather than the photolysis from other carbon-containing species in this photocatalytic system. In order to further confirm the origin of HCOOH, the 13C NMR spectrum gave the corresponding isotopologue H13COOH signal with a peak at 168.4 ppm, and there was no such signal under the same condition as for 13CO2 (Fig. 3f), unambiguously verifying that the carbon source of HCOOH indeed originated from the CO2 reduction. Alternatively, when H2O was replaced with H318O, 18O2 (m/z = 36), 18O16O (m/z = 34) and 16O2 (m/z = 32) were detected after the reaction, confirming that the generated 18O2 or 16O2 was from H218O or H216O (Supplementary Fig. 37).

To investigate the mechanism of the photocatalytic overall reaction XPS and in-situ XPS measurements combined with DFT calculations (method in Supplementary Information) were carried out. The calculation model was constructed based on the finite cluster structure of MCOF-Ti6Cu3. As shown in Supplementary Fig. 38, XPS showed that the observed Ti 2p binding energy at 459.0 eV in Ti6 was consistent with Ti4+, while the Cu 2p binding energy at 932.8 eV and 934.6 eV in Cu3 were assigned to Cu+ and Cu2+, respectively (Fig. 4a, b). Previous studies found that the production of Cu+ was due to the surface oxidation, and the Cu valence could be switched between Cu+ and Cu2+ without altering the backbone of Cu3(pyzrazolate)3 triangular SBUs. For MCOF-Ti6Cu3, the negative shift of the Ti 2p binding energy by 0.4 eV and the positive shift of the Cu 2p binding energy by 0.7 eV indicated a successful covalent-bond connection between the two precursors with the formation of an internal electric field, and the possible migration direction of electrons was from Cu to Ti. This interaction from cluster-to-cluster was conducive to the transfer of electrons. The XPS spectra of C, N and O elements are shown in Supplementary Figs. 39, 40 and 41.

The electron transfer process in the photocatalytic reaction could be distinctly revealed by the valence change using in-situ XPS measurements. As shown in Fig. 4c, d, under irradiation (black and red line), the Ti 2p binding energy increased from 458.46 eV to 458.61 eV. In comparison, the Cu 2p binding energy decreased from 932.94 eV to 932.78 eV, indicating that some electrons returned to Cu cluster with photoexcitation. After CO2 was introduced into the system (red and blue line), the binding energy of Cu 2p increased to 932.94 eV while that of Ti 2p was unchanged, indicating that the transfer direction of the photogenerated electrons was from the Cu cluster to CO2. Consequently, it could be inferred that the active center of the photocatalytic reduction of CO2 to HCOOH over MCOF-Ti6Cu3 was the Cu cluster. Finally, as shown in the Supplementary Figs. 42, 43 and 44, the in-situ XPS and in-situ DRIFTS spectra before and after the reaction were consistent, which proves the good stability of the catalyst. As shown in electrostatic potential (ESP) analyses (Supplementary Fig. 43), the positive charge was concentrated on the Cu-N cluster and benzene moieties, while the negative charge was concentrated on the Ti-O cluster.

The DFT and time-dependent DFT (TD-DFT) calculation results could also prove that the photocatalytic CO2 reduction reaction on the Cu cluster in MCOF-Ti6Cu3. The TD-DFT calculation results (Supplementary Fig. 46) show that the HOMO and LUMO of MCOF-Ti6Cu3 are close to each other and can be excited by the excitation energy of infrared light (1704.16 nm). However, visible and ultraviolet lights correspond to multiple excitation modes. The visible lights with wavelengths of 487.42 nm and 453.25 nm corresponded to the excitation modes of HOMO → LUMO + 27, + 29, + 31, and HOMO → LUMO + 31, + 32, while the wavelengths of 352.79 nm and 351.89 nm in ultraviolet region correspond to the excitation modes of HOMO − 3 → LUMO + 1 and HOMO − 1 → LUMO + 1, respectively. The orbital composition analysis displays that the occupied orbitals of HOMO, − 1, and − 3 are located on the Cu cluster fragments, and the unoccupied orbitals of LUMO, + 27, + 29, + 31, and + 32 are also located on the Cu cluster fragments, other unoccupied orbitals are located on the Ti cluster fragments. It demonstrates that the electron cloud does not transfer in the process of infrared excitation, and indeed transfers from the Cu cluster to the Ti cluster under ultraviolet excitation. The electron cloud is distributed on the Cu cluster under visible excitation, which corresponds to the fact that the Cu cluster receives electrons under optical excitation from the in-situ XPS measurement. To further clarify the reasons for the excellent photocatalytic activity and HCOOH conversion selectivity, in-situ DRIFTS
spectroscopy was performed to probe the intermediates. As shown in Fig. 4e, new peaks obviously appeared and their intensities gradually increased with the illumination time from 0 to 60 min. The absorption peaks located at 1596, 1578, and 1275 cm⁻¹ belong to bidentate carbonate (b-CO$_3^{2-}$), and the peaks at 1541, 1506, 1473, 1351, and 1330 cm⁻¹ are attributed to monodentate carbonate (m-CO$_3^{2-}$). Additionally, the peaks at 1389 and 1403 cm⁻¹ are assigned to polydentate carbonate (p-CO$_3^{2-}$), and the peaks at 1453, 1434, and 1411 cm⁻¹ are ascribed to bicarbonate (HCO$_3^-$). The peak intensities of these carbonates increase significantly, which suggests that MCOF-Ti$_6$Cu$_3$ can chemically adsorb and interact with CO$_2$ and H$_2$O molecules. The peak at 1641 cm⁻¹ and the emerging peaks at 1742, 1761, and 1775 cm⁻¹ might result from a formate, and the peak at 1628 cm⁻¹ could be attributed to carboxylate. Meanwhile, the intensities of the peaks at 1560, 1526, and 1233 cm⁻¹ corresponding to *COOH increased with the prolonged illumination time, which might be possibly caused by the favorable proton capture capability of CO$_2$ radicals. Most importantly, the intensity of the peak at 1709 cm⁻¹ gradually increased with light progresses. The peak is ascribed to *HCOOH which are important intermediates for the formation of HCOOH.

According to the results of in-situ DRIFTS analysis and DFT calculation, the possible mechanism of CO$_2$ reduction and H$_2$O oxidation over the hetero-metallic cluster catalyst MCOF-Ti$_6$Cu$_3$ can be reasonably proposed (Fig. 5a). The specific calculation models are in Supplementary Figs. 47, 48 and 49. We conjectured that the Cu cluster unit could be the active site for CO$_2$ reduction, while the adsorption and activation of H$_2$O were at the Ti cluster (Fig. 5b). To be specific, under irradiation, the photogenerated electrons and holes separated and transferred to the Cu cluster and Ti cluster, respectively. Then reduction and oxidation reactions took place simultaneously on these two clusters (Fig. 5c). On the Cu cluster, the conversion of CO$_2$ to HCOOH requires two consecutive hydrogenation steps. The first step is the formation of 458.61 eV, and then the formed 458.46 eV COOH undergoes a second reaction to generate HCOOH. Correspondingly, the oxidation of H$_2$O at the Ti cluster involves twice the conversion processes of H$_2$O into OH. Finally, when HCOOH is desorbed from the system, the two OH radicals combine with each other to generate O$_2$ and H$_2$O, thus maintaining the charge balance of the catalytic system. As shown in Fig. 5d, the formation of 458.46 eV COOH and 458.61 eV COOH which are important intermediates for the formation of HCOOH.

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overall reaction. In addition, two intermediates, *COOH and HCOO*, are generated in the first hydrogenation reaction. The *COOH is preferentially generated since the energy of the formation of *COOH is lower than that of HCOO*. The energy of *COOH dehydration into CO is much higher than that of *COOH hydrogenation into HCOOH*, accounting for the preferential generation of HCOOH among the reduction products, which is consistent with the experimental results.

In summary, in order to realize an effective coupled photocatalytic oxidative and reductive overall reaction, we have elaborately designed and constructed a hetero-metallic cluster catalyst via linkage of dynamic covalent bonds, namely MCOF-Ti6Cu3, in which functional clusters with reductive and oxidative activities can cooperate for photocatalytic CO2 reduction and water oxidation, respectively. In addition, hetero-metallic cluster catalyst obtained by directed assembly inherits the oxidative and reductive properties of the clusters and achieves spatial separation. Also, the dynamic covalent bonds have more efficient electron transfer, enabling MCOF-Ti6Cu3 to exhibit excellent photocatalytic performance with a high HCOOH yield of 169.8 μmol g⁻¹ h⁻¹ in crystalline materials with only H2O. More importantly, the in-situ tests and DFT calculations prove that the reduction reaction occurs on the Cu cluster and the oxidation reaction on the Ti cluster, which is consistent with our pre-designed oxidative and reductive centers on hetero-metallic cluster catalyst, as well as distinctly reveals the charge transfer path and overall photocatalytic reaction mechanism on the atomic level. This research provides a strategy for the construction of hetero-metallic cluster catalyst from the chemical cooperation of MOF ∪ COF, and offers a significant guideline for the design of the photocatalytic overall reaction systems.

**Methods**

**Materials**
The starting materials for COF syntheses were purchased from Shanghai Tensus Bio-tech Co., Ltd. Other reagents and solvents applied in the synthesis and photocatalysis were purchased from Aladdin and Sigma-Aldrich, and used as received without further pretreatments.

**Synthesis of MCOF-Ti6Cu3**

Ti6 (31.1 mg, 0.02 mmol) and Cu3 (19.8 mg, 0.04 mmol) were mixed in a cylindrical glass tube (20 cm of length, φin = 0.8 cm, φout = 1.0 cm) to which were added mesitylene, DMF and glacial acetic acid (6 M, 9:1:1, v/v/v). Then the mixture was sonicated for 15 min to form a homogeneous dispersion. After degassed by three freeze-pump-thaw cycles, the tube was sealed off and then heated at 120 °C for 3 days. The bright yellow precipitates (turn green in air) were collected by filtration and soaked in DMF for 24 h. The powder was transferred to a Soxhlet extractor and washed with THF (24 h). Finally, the product was evacuated at 120 °C under vacuum overnight to yield the activated sample.

**Photocatalytic experiment**
The photocatalytic experiments were carried out following the reported method. In a quartz reactor (50 mL), the catalyst (10 mg) was dispersed in ultra-pure water (30 mL). This mixture system was bubbled with pure CO2 gas for 20 min. The temperature of the reaction solution was maintained at 25 °C controlled by an outside flow of water during the reaction. Then, the system was irradiated under simulated sunlight using a PLS-SXE300 Xe lamp with an AM 1.5 cut-off filter.

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**Fig. 5 | Mechanism and DFT calculations.** a A proposed reaction pathway for the photocatalytic CO2 reduction over MCOF-Ti6Cu3. b Proposed mechanism of CO2 reduction and H2O oxidation. c Transitions of electron cloud distribution under solar irradiation. d Free-energy profile for the CO2 reduction and H2O oxidation pathway over MCOF-Ti6Cu3.
The liquid products in liquid phase of the reactor were measured using ion chromatography (IC) to analyze HCOOH. The gaseous products were analysed by the gas chromatography. Detailed methods are in the Supplementary Information.

**Electrochemical measurements**

Photocurrent, electrochemical impedance spectroscopy and Mott-Schottky measurements were all tested using the following methods\(^6\). Electrochemical measurements of MOF901 FDM-71-ABC and MCOF-Ti6Cu3 were tested in a three-electrode electrochemical workstation system (CHI 660e) with the ITO glass substrate (1 cm × 1 cm) as the working electrode, the Pt-wire as the auxiliary electrode and Ag/AgCl electrode as the reference electrode. The samples (2 mg) were dispersed into the solution (1 mL) containing Nafion solution (100 µL, 0.5 wt%), water (450 µL), and ethanol (450 µL). After sonication, the spreading aqueous slurries were drop-cast onto the ITO glass substrate. Then, the working electrode was dried spontaneously under ambient temperature. 0.2 M Na2SO4 solution was used as the electrolyte. Irradiation was carried out by using a 300 W xenon lamp with AM 1.5 cut-off in the photocurrent measurement.

**Computational methods**

The calculation model is constructed by a finite cluster structure, and all calculations were performed with the Gaussian 16 software package. The ground state of MCOF-Ti6Cu3 was geometrically optimized by using B3LYP method of DFT with Ti, Cu/LanL2dz, C, H, N, O/6-31 G* basis sets\(^5\). ESP analysis, TD-DFT calculations, and orbital composition were also performed at the same level. In order to obtain the corresponding excited state energies, TD-DFT calculations were performed on the basis of optimized ground state configurations. The energy of [MCOF-Ti6Cu3] is specified as 0.000 eV, and the ΔE (eV) calculations for the other states are shown in Supplementary Tables 6 and 7.

**Data availability**

The data that support the findings of this study are available within the paper and its supplementary information files or are available from the corresponding authors upon reasonable request. Source data are provided with this paper.

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Author contributions
Y.-Q. L. and J. Z. conceived and designed the idea. J. Z. designed the experiments, collected and analyzed the data. Jie L., L. K., Y. C., and Jia. L. assisted with the experiments and characterizations. J. Z. and Y. Y. analyzed the XRD data and performed the crystal structure modeling. J. Z. wrote the manuscript. L. Z., Q. H., Y. Y., and S.-L. L. helped with the manuscript revising and data analysis. J. Z. and Y.-Q. L. discussed the results and prepared the manuscript. All the authors reviewed and contributed to this paper.

Competing interests
The authors declare no competing interests.

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