Supporting Information

Dynamic Evolution of Atomically Dispersed Cu Species for CO₂ Photoreduction to Solar Fuels

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**Note:** \( m\text{TiO}_2 \) precursor beads were firstly synthesized through the hydrolysis of titanium isopropoxide (TIP) with addition of hexadecylamine (HDA), which possess smooth surfaces (Figure S1a). After solvothermal and calcination treatment, \( m\text{TiO}_2 \) with rough surfaces (Figure S1b) were produced.\(^1\)\(^2\) X-Ray Diffraction (XRD) pattern (Figure S1c) indicates that \( m\text{TiO}_2 \) precursor beads are amorphous.\(^1\) After the solvothermal and calcination treatment, the XRD pattern of \( m\text{TiO}_2 \) spheres shows well-resolved diffraction peaks corresponding to the reflections of anatase TiO\(_2\) (JCPDS file no. 84-1285). No additional crystalline phases for other impurities are detected, suggesting the high phase purity of \( m\text{TiO}_2 \).
Figure S2. (a, b) TEM, (c) HRTEM images and (d) SAED pattern of mTiO$_2$.

Note: The transmission electron microscopy (TEM) images (Figure S2a) show that mTiO$_2$ possesses abundant disordered mesopores (intercrystalline pores) throughout the sphere structure. Figure S2b indicates that mTiO$_2$ is consisted of individual crystals of around 15 nm. High-resolution TEM (HRTEM) image in Figure S2c shows the lattice fringes determined as 0.352 nm, which is corresponding to the (101) phase of anatase TiO$_2$. The distinct selected area electron diffraction (SAED) pattern shows the crystalline anatase phase of the sample (Figure S2d).
Figure S3. Representative N₂ adsorption-desorption isotherms at 77 K for mTiO₂, and insert is the corresponding pore size distribution calculated from BJH adsorption cumulative volume of pores.

Note: The N₂ adsorption-desorption isotherms of mTiO₂ show type IV isotherms with a sharp capillary condensation step at high relative pressures (P/P₀ = 0.8-0.9), and H1 type hysteresis loops, indicating the relatively large pore sizes, which further confirms the mesoporous structure of mTiO₂.²
Figure S4. (a) XRD patterns, (b) DRS and (c) enlarged DRS in the wavelength range of 350-1000 nm for mTiO$_2$ and xCu-mT; inset of (b) is the appearance of the samples, (d) EPR spectra of mTiO$_2$ and xCu-mT catalysts. Experimental parameters: microwave frequency of 9.8655 GHz, microwave power of 6.36 mW; modulation frequency of 100 kHz, modulation amplitude of 1 G, modulation phase of 0, time constant of 10.24 s, sweep time of 41.98 s.

Note: Figure S4a shows the X-Ray diffraction (XRD) patterns of xCu-mT samples, and no characteristic diffraction peaks of Cu species (metal Cu or Cu$_2$O) can be observed, which can be ascribed to the high dispersion or low content of the Cu species. UV-vis diffuse reflectance spectra (DRS) in Figure S4b show that the absorbance intensities of the samples in visible-light region increase with the Cu content increasing, as reflected by the gradually deepened colors of the samples (inset of Figure S4b). Besides the onset absorption of mTiO$_2$ at 400 nm, the absorption shoulders centered at ~450 nm can be ascribed to interfacial charge transfer (IFCT) from the valence band (VB) of TiO$_2$ to Cu species, indicating that the photoexcited electrons from TiO$_2$ are directly transferred to the Cu species upon light irradiation. Another absorption band starting from 580 nm is assigned to the Cu(II) d-d orbital transition (Figure S4c). The electron paramagnetic resonance (EPR) spectrum of mTiO$_2$ displays no EPR signal while xCu-mT catalysts show large signals in the region of 2600-3600 G (Figure S4d), which is attributable to the signal of Cu$^{2+}$, and the signal intensities are strengthened correspondingly with the increase of Cu content.
Note: The energy-dispersive X-ray (EDX) results of 1Cu-mT corresponding to the TEM image in Figure 1b indicate the presence of Ti, O and Cu elements, and the Mo species was detectable because the sample was dispersed on the lacey carbon film with molybdenum grids.
Figure S6. The survey XPS spectra of $m$TiO$_2$ and 1Cu-$m$T.

Note: In the survey XPS spectra (Figure S6), $m$TiO$_2$ shows Ti and O peaks, while 1Cu-$m$T displays Ti, O and Cu elements, suggesting that Cu species have been successfully deposited onto $m$TiO$_2$. 
**Figure S7.** Controlled catalytic experiments: (a) in the absence of light irradiation; (b) in the absence of catalysts; (c) under Ar atmosphere instead of CO\(_2\) with otherwise conditions identical; and (d) normal reaction conditions under CO\(_2\) atmosphere. Reaction conditions: 20 mg of 1Cu-mT catalysts, 0.5 ml of water, under UV-vis light irradiation after 24 h.

**Note:** Controlled experiments have been performed to confirm that the CO\(_2\) reduction reaction is a photocatalytic process (Figure S7). Typically, the absence of light irradiation or catalysts results in the absence of products detection, which confirms that the CO\(_2\) reduction over 1Cu-mT is a characteristic photocatalytic process. Once CO\(_2\) was replaced with Ar, only a trace amount of CO was observed, and thus the suspected carbon-containing products from decomposition of possible carbon residues on photocatalysts, if any, are negligible.
Figure S8. The products evolved rate of CO$_2$ photoreduction with H$_2$O over mTiO$_2$ and xCu-mT within 2 h.

Note: Comparing with bare mTiO$_2$, the products evolution rates are obviously improved on xCu-mT, among which 1Cu-mT achieves the best activity. Further increment in the Cu content leads to a decrease in the reaction rate, and especially for 3Cu-mT, the activity decreased significantly, which is even lower than that of bare mTiO$_2$. This might be because that on one hand, high loading amount of Cu on the surface of mTiO$_2$ can decrease the intensity of light absorbed by mTiO$_2$. This is also called as light “screening effect”, which can be supported by the DRS results that light absorption in the visible region increases with increasing Cu loading amount while that in the UV region decreases. On the other hand, an excessive amount of Cu may act as recombination centers as they, at certain levels, promote recombination of electrons and holes.
Figure S9. (a, b) HAADF STEM images of used 1Cu-\textit{m}T; (c) corresponding intensity profiles for the atomically dispersed Cu species.

Note: The HAADF-STEM images of the used 1Cu-\textit{m}T catalysts confirm that the Cu species still remained well as isolated, which is consistent with the EXAFS result that the as-formed Cu-Cu bonding in the used 1Cu-\textit{m}T catalyst gradually disappeared along with the exposure of the catalysts to air (Figure S10). The results suggest that no obvious aggregation was happened to the Cu species after the CO$_2$ photoreduction reaction, although during which the Cu (II) species has been reduced (Figure 3f) and Cu-Cu bonding was formed (Figure 3g).
Figure S10. EXAFS spectra of used 1Cu-mT, followed by exposure to air.

Note: When exposing the used 1Cu-mT catalysts to air, the as-formed Cu-Cu bonding in the used catalyst during CO$_2$ photoreduction reactions gradually disappeared, which might be ascribed to the re-oxidation of the Cu by oxygen in air.
Figure S11. SEM images of (a) TiO$_2$ and (b) 1Cu-T; (c) XRD and (d) DRS of TiO$_2$ and 1Cu-T.

Note: For comparison, TiO$_2$ nanoparticles and Cu species grafted TiO$_2$ nanoparticles (1Cu-T) have also been prepared. Scanning electron microscopy (SEM) images of TiO$_2$ (Figure S11a) and 1Cu-T (Figure S11b) show that they are composed of aggregated small uniform TiO$_2$ nanoparticles. X-Ray Diffraction (XRD) patterns in Figure S11c suggest that both TiO$_2$ and 1Cu-T show well-resolved diffraction peaks of anatase TiO$_2$. UV-vis diffuse reflectance spectra (DRS) in Figure S11d show the similar phenomenon to that of $m$TiO$_2$ and 1Cu-$m$T. That is, besides the onset absorption of TiO$_2$ at 400 nm, 1Cu-T exhibits two new absorptions centered at $\sim$450 nm and $\sim$580 nm, which can be ascribed to interfacial charge transfer (IFCT) from the valence band (VB) of TiO$_2$ to Cu species$^5-^7$ and the Cu(II) d-d orbital transition$^8-^9$, respectively.
Figure S12. Evolved rate of (a) CH$_4$, (b) CO and (c) H$_2$ over the samples of TiO$_2$, $m$TiO$_2$, 1Cu-T and 1Cu-\textit{m}T. Reaction conditions: 20 mg of catalysts, 0.5 mL of water, under UV-vis light irradiation for 24 h.

Note: Progressively enhanced production for CH$_4$, CO and H$_2$ are observed in the order of TiO$_2 < m$TiO$_2 < 1$Cu-T < 1Cu-\textit{m}T.
Figure S13. Representative N\textsubscript{2} adsorption-desorption isotherms at 77 K for (a) TiO\textsubscript{2} and (b) 1Cu-mT, and inserts are their corresponding pore size distributions calculated from BJH adsorption cumulative volume of pores.

**Note:** The N\textsubscript{2} adsorption-desorption isotherms over TiO\textsubscript{2} nanoparticles show type IV isotherm with H2 type hysteresis (Figure S13a), indicating the mesoporous structure of the TiO\textsubscript{2} sample with relatively small pore sizes,\textsuperscript{3} as reflected in the pore size distribution in the inset of Figure S13a, which is induced by the dense package of the small TiO\textsubscript{2} nanoparticles.\textsuperscript{12} As summarized in Table S1, the surface area and pore volume of TiO\textsubscript{2} nanoparticles are much smaller than those of mTiO\textsubscript{2} spheres. As shown in Figure S13b, the N\textsubscript{2} adsorption-desorption isotherms of 1Cu-mT show type IV isotherms with a sharp capillary condensation step at high relative pressures (P/P\textsubscript{0} = 0.8-0.9), and H1 type hysteresis loops, indicating the relatively large pore sizes inherited from mTiO\textsubscript{2}.
Table S1. Summary of surface area, pore volume, pore size and adsorbed capacity of CO$_2$ over the samples of TiO$_2$, mTiO$_2$ and 1Cu-mT.

<table>
<thead>
<tr>
<th>Samples</th>
<th>$S_{BET}$ (m$^2$/g)$^a$</th>
<th>Total Pore Volume (cm$^3$/g)$^b$</th>
<th>Average Pore Size (nm)$^c$</th>
<th>Adsorbed CO$_2$ (cm$^3$/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$</td>
<td>47</td>
<td>0.09</td>
<td>6.5</td>
<td>10</td>
</tr>
<tr>
<td>mTiO$_2$</td>
<td>100</td>
<td>0.3</td>
<td>13.8</td>
<td>19</td>
</tr>
<tr>
<td>1Cu-mT</td>
<td>99</td>
<td>0.3</td>
<td>13.6</td>
<td>17</td>
</tr>
</tbody>
</table>

$^a$ BET surface area is calculated from the linear part of the BET plot.

$^b$ BJH adsorption cumulative volume of pores.

$^c$ Adsorption average pore width ($4V/A$ by BET).
Figure S14. (a) Mass spectra signals of H$_2$O desorption for the TPD profiles and (b) illuminated OCP over the samples of TiO$_2$, mTiO$_2$ and 1Cu-mT.

Note: As illustrated in Figure S14a, the H$_2$O desorption peaks over mTiO$_2$ and 1Cu-mT show a slight shift from 200 °C to a higher temperature of 220 °C along with an obviously increased peak area, as compared to TiO$_2$, demonstrating the enhanced H$_2$O adsorption ability of the samples in the order of 1Cu-mT > mTiO$_2$ > TiO$_2$.\textsuperscript{13} A measurement of open-circuit photovoltage decay (OCPD) was performed to assess the lifetime of photoelectrons. As shown in Figure S14b, during light illumination, the sample electrodes absorbed the photons and reduced their open-circuit voltage ($V_{OC}$). After equilibration to a steady state, the light was turned off, and subsequent decay of $V_{OC}$ was observed. The decay lifetime of the accumulated electrons can be related to the drop in potential using the following equation\textsuperscript{14-16}:

$$\tau = -\frac{k_B T}{e} \left( \frac{dV_{OC}}{dt} \right)^{-1}$$

where $\tau$ is the potential-dependent photoelectron lifetime, $k_B$ is Boltzmann's constant, $T$ is the temperature, $e$ is the charge of a single electron, and $V_{OC}$ is the open-circuit voltage at time $t$. 

Figure S15. PL emission spectra with an excitation wavelength of 340 nm for the samples of TiO$_2$, mTiO$_2$ and 1Cu-mT.

Note: The steady-state photoluminescence (PL) spectra in Figure S15 show obvious PL quenching over the 1Cu-mT sample, suggesting the establishment of an electron transfer channel in a nonradiative quenching pathway.$^{17}$
Figure S16. (a) Polarization curves, (b) cyclic voltammograms, (c) EIS Nyquist plots, and (d) photocurrent density under UV-vis light irradiation for the samples of TiO$_2$, $m$TiO$_2$ and 1Cu-$m$T.

Note: To gain more insight into the optoelectronic properties of the samples, a series of electrochemical and photoelectrochemical characterizations have been carried out. Figure S16a displays the polarization curves of samples, revealing a higher cathodic current density of $m$TiO$_2$ than TiO$_2$, and that of the 1Cu-$m$T is remarkably enhanced. Considering that the preparation of the electrodes and electrolyte are identical for the measurements, the current density of the electrodes is related to the electron transfer rate of the electrode materials. Therefore, the charge transfer efficiency within the electrode materials increases by a sequence of 1Cu-$m$T $>>$ $m$TiO$_2$ $>$ TiO$_2$. Figure S16b, showing the cyclic voltammograms (CV) with obvious anodic and cathodic peaks for each sample, indicates the same tendency of charge transfer enhancement. Figure S16c shows electrochemical impedance spectroscopy (EIS) Nyquist plots of the samples. Since a smaller semicircle in the Nyquist plot indicates a lower charge-transfer resistance in the hybrid composite that warrants efficient transportation and separation of charge carriers, the charge transfer over 1Cu-$m$T is more efficient than that over $m$TiO$_2$ and TiO$_2$. As shown in Figure S16d, the 1Cu-$m$T displays obviously enhanced photocurrent response as compared to $m$TiO$_2$ and TiO$_2$. Collectively, these results indicate that electron-hole pairs separation efficiency increases by a sequence of 1Cu-$m$T $>>$ $m$TiO$_2$ $>$ TiO$_2$. 
Figure S17. The volumetric ratio of O$_2$/N$_2$ during CO$_2$ photoreduction with H$_2$O on $m$TiO$_2$ and 1Cu-$m$T.

**Note:** The volumetric ratio of O$_2$/N$_2$ was employed to measure the O$_2$ production from H$_2$O oxidation for $m$TiO$_2$ and 1Cu-$m$T catalysts during the CO$_2$ photoreduction experiments. It has been reported that although the photoreactor was purged with CO$_2$ to remove air inside the reactor before reaction, there was always trace amount of background O$_2$ and N$_2$ detected in the reactor even after long-time purge.$^{18-19}$ As shown in **Figure S17**, the O$_2$/N$_2$ ratio increases with the reaction time over $m$TiO$_2$ and 1Cu-$m$T, suggesting the generation of O$_2$ through oxidation of H$_2$O by photogenerated holes (i.e., H$_2$O+h$^+$→2H$^+$+1/2O$_2$). Moreover, the O$_2$/N$_2$ volumetric ratio for 1Cu-$m$T is larger than that for $m$TiO$_2$, indicating that more O$_2$ was produced over 1Cu-$m$T, which corresponds to the enhanced CO$_2$ photoreduction activity of 1Cu-$m$T as compared to $m$TiO$_2$. In addition, the O$_2$ amount experimentally detected is much less than the theoretical O$_2$ evolution amount, which might be because that the O$_2$ and/or O species were readsoorbed or remained on the catalysts surface, or the produced O$_2$ was re-consumed.$^{18-19}$
Figure S18. (a) Schematic illustration and (b) real picture of in situ X-ray absorption experiment setup.
Appendix: Apparent Quantum Yield (AQY) calculation

![Emission profile of the Xe arc lamp used for photocatalysis.](image)

**Figure S19.** Emission profile of the Xe arc lamp used for photocatalysis.

As for the apparent quantum yield (AQY) estimation, the “Number of incident photons” was calculated using a method reported by Bharadwaj et al. The total light intensity incident for the sample was measured using a Thorlabs PM100 optical power and energy meter, placed at the center where the reactor was placed for irradiation, and the emission profile of the lamp was also recorded (Figure S18). Only the incident light intensity in the range of 320-400 nm ($E_m$) was considered for the calculation of quantum yield, based on the UV-Vis absorption of the Cu-mT catalysts and the emission profile of the Xe arc lamp, which was obtained by multiplying the total incident intensity with the ratio of the area in 320-400 nm range to the total area of the emission profile.

Since this is a polychromatic light, energy of a single photon was considered as the weighted average energy ($E_a$) of all the photons in the range of 200-400 nm. For this, contribution of photon of each wavelength $\lambda_i$ (i varying from 200-400 nm) towards the total energy was calculated as

$$E_i(\lambda_i) = \frac{I_{\lambda_i}}{I_{total}} \times \frac{hc}{\lambda_i}$$

where $I_{\lambda_i}$ is the intensity at wavelength $\lambda_i$ and $I_{total}$ is the sum of intensities of all photons in the wavelength range of 320-400 nm obtained from the emission profile of the lamp.

The weighted average energy of single photon ($E_a$) is calculated as
\[ E_a = \sum_{\lambda_i = 200}^{400} E_i(\lambda_i) \]

Total number of incident photons in 200-400 nm range (N) is given by

\[ N = \frac{E_m}{E_a} \]
References


