MOF-based Ternary Nanocomposites for Better CO$_2$ Photoreduction: Roles of Heterojunction and Coordinatively Unsaturated Metal Sites

Xiang He and Wei-Ning Wang*

Department of Mechanical and Nuclear Engineering, Virginia Commonwealth University, Richmond, Virginia 23219, United States

*Corresponding Author
Wei-Ning Wang: Tel: 1-(804) 827-4306; Fax: 1-(804) 827-7030; Email: wnwang@vcu.edu
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S1. Characterization of TiO$_2$ and Cu$_2$O

The commercial P25 nanoparticles have an irregular shape with an average diameter of 25 nm (Figure S1A) and mainly exist as anatase phase with a trace of rutile phase (Figure S1B). As shown in Figure S1C, the as-synthesized Cu$_2$O has a cubic shape and has an average diameter of 42 nm. The Cu$_2$O phase has also been confirmed in Figure S1D with the reference (JCPDS 01-071-3645). The Cu$_2$O nanocubes exhibit broad light absorption from 350 nm to around 500 nm (Figure S1E).
S2. Low-magnification SEM Images of As-prepared Samples

Figure S2. SEM images of (A) sprayed TiO$_2$, (B) TiO$_2$/Cu$_2$O and (C) TiO$_2$/Cu$_2$O/Cu$_3$(BTC)$_2$. Scale bars: 2 μm.

S3. CO$_2$ Uptake Analysis

Figure S3. CO$_2$ uptake analysis by quantifying the area of the characteristic IR peak of adsorbed CO$_2$ as a function of time during the adsorption process.

The CO$_2$ adsorption kinetics can be assessed by using DRIFTS, as detailed in our previous studies.$^{1,2}$ In brief, adsorbed CO$_2$ has characteristic IR peaks in the range of 2280 to 2400 cm$^{-1}$. The peak areas increase with increased amount of adsorbed CO$_2$. Thus, CO$_2$ adsorption kinetics can be obtained by measuring the peak areas from the continuous recorded IR spectra during the CO$_2$ adsorption process. The CO$_2$ adsorption results were shown in Figure S3, which shows similar CO$_2$ uptake properties of these three samples, eliminating the effects of CO$_2$ uptake on the photoreduction efficiency.
S4. Determination of Component Ratios in the Ternary Composite

The component ratios in the ternary composite were determined based on the quantities of the precursors (i.e., TiO$_2$ and Cu$_2$O) used for the synthesis and the XPS data of as-prepared ternary composite. To be specific, the molar ratio of TiO$_2$ to Cu$_2$O in TiO$_2$/Cu$_2$O composite is assumed to be consistent with the precursor TiO$_2$/Cu$_2$O molar ratio (i.e., 20:1) used for the synthesis of the binary composite. The binary composite was then used as precursor for the ternary composite after partial conversion of Cu$_2$O to Cu$_3$(BTC)$_2$. The percentage of Cu$_2$O converted to Cu$_3$(BTC)$_2$ was determined from the XPS analysis of Cu 2p$_{3/2}$, where a standard Shirley background and the Gaussian (80%)-Lorentzian (20%) profile were used. As shown in Figure 1N, the Cu 2p$_{3/2}$ was further deconvoluted into two peaks centered 932.2 eV and 933.8 eV, originating from Cu$^+$ in Cu$_2$O and Cu$^{2+}$ in Cu$_3$(BTC)$_2$, respectively.$^{3,4}$ From the peak areas, the molar ratio of Cu$^+$ to Cu$^{2+}$ was determined to be 1.22:1, indicating that Cu$_2$O/Cu$_3$(BTC)$_2$ ratio is 1.22:1. Given that the molar ratio of Ti to total Cu is 20:1, the molar ratio of TiO$_2$, Cu$_2$O, Cu$_3$(BTC)$_2$ was determined to be 20: 0.55: 0.45.
S5. CO₂ Photoreduction Analysis

**Figure S4.** Gas chromatograms attained with samples illuminated at He/water atmosphere (A-E) and CO₂/water atmosphere (F-H). A: Pristine TiO₂; B: Pristine Cu₂O; C and F: Sprayed TiO₂; D and G: TiO₂/Cu₂O; E and H: TiO₂/Cu₂O/Cu₃(BTC)₂.

All samples were first subjected to control measurements under helium/water atmosphere to rule out the possibilities of carbon contamination (**Figures S4A-E**), where no CO nor CH₄ peaks are observed for the samples involved, indicating that these samples are carbon contamination-free. Once the CO₂/H₂O mixture was used as the precursor, CO and CH₄ were observed as the major products (**Figures S4F-H**).
In addition, pure Cu$_3$(BTC)$_2$ was synthesized and subjected to CO$_2$ photoreduction process in order to determine the role of Cu$_3$(BTC)$_2$ during the photocatalysis process. The pure Cu$_3$(BTC)$_2$ was synthesized through the following process. Copper nitrate trihydrate (1.432 g) and trimesic acid (0.842 g) were firstly dissolved in 20 mL dimethylformamide (DMF). The solution was then placed in an oven (80 °C) for 24 hours. After that, the powders were collected by centrifugation, and washed with DMF twice and then methanol twice. Finally, the powder samples were dried overnight in a vacuum oven at 50 °C.

As shown in Figure S5A, the as-prepared pure Cu$_3$(BTC)$_2$ exhibits the characteristic octahedron shape. And the crystal structure of the as-prepared sample was consistent with the simulated pattern of HKUST-1 (Figure S5B). Both the SEM and XRD analysis demonstrate that pure Cu$_3$(BTC)$_2$ crystals have been successfully synthesized. Subsequently, pure Cu$_3$(BTC)$_2$ was used as the photocatalyst for CO$_2$ reduction. However, no discernible products were observed (Figure S5C) due to the fact that pure Cu$_3$(BTC)$_2$ is unfavorable for charge separation and can’t serve as the photocatalyst for CO$_2$ reduction. This result is consistent with our previous study$^2$ and the prior work done by Xiong et al.$^5$

**Figure S5.** SEM image (A) and XRD pattern (B) of as-prepared pure Cu$_3$(BTC)$_2$; Gas chromatogram attained with as-prepared pure Cu$_3$(BTC)$_2$ at CO$_2$/water atmosphere (C).
S6. Analysis of Cu Valence States after Photocatalysis

Figure S6. Cu2p XPS spectra of TiO2/Cu2O/Cu3(BTC)2 composite after photocatalysis

S7. Photoluminescence Analysis of ·OH Formation

Figure S7. Mechanism of ·OH detection by using coumarin as a probe molecule. (A) Reaction pathway; (B) Emission spectra of various samples. (Concentration of coumarin and 7-hydroxycoumarin: 0.15 μmol/L; Excitation wavelength: 350 nm)

The formation of ·OH, a product from the reaction of holes with water molecules, can be used to monitor the electron/hole pairs generated by the catalysts. The mechanism of ·OH by using coumarin as a probe was illustrated in Figure S7. Specifically, coumarin reacts with ·OH to generate 7-hydroxycoumarin (Figure S7A), which is highly fluorescent and has a characteristic luminescent emission peak around 455 nm when excited at 350 nm (Figure S7B). On the other hand, pure coumarin does not possess any fluorescent properties, as indicated from the identical emission spectra of coumarin and DI water. The emission peak at 397 nm was observed for all the three samples, which is attributed to the Raman scattering of water.7
Figure S8. Calibration of PL intensity versus ·OH concentration. (A) Spectra of 7-hydroxycoumarin with various concentrations (μmol/L) (Excitation wavelength: 350 nm); (B) Linear fitting of the experimental data.

Calibration was carried out to quantify the ·OH formation by the photoluminescence peak intensity. In brief, 7-hydroxycoumarin solutions with various concentrations were prepared, and their corresponding emission spectra were obtained at the excitation wavelength of 350 nm (Figure S8A). Subsequently, the calibration curve was obtained by correlating the peak intensities with the concentrations (Figure S8B). Based on the equation derived from Figure S8B, the photogenerated ·OH by TiO$_2$, TiO$_2$/Cu$_2$O and TiO$_2$/Cu$_2$O/Cu$_3$(BTC)$_2$ were quantified to be 0.032, 0.067 and 0.105 μmol/(g-h), respectively. The amount of electron/hole pairs is expected to be the same as that of ·OH because of their stoichiometric relationship. From the information above, the photo-generated electron/hole pairs by TiO$_2$/Cu$_2$O and TiO$_2$/Cu$_2$O/Cu$_3$(BTC)$_2$ were calculated to be 2.09 and 3.28 times of those by TiO$_2$. 

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Figure S9. Emission spectra of photo-generated 7-hydroxycoumarin obtained from various samples (Excitation wavelength: 350 nm).
S8. Water Adsorption Analysis

Figure S10. DRIFTS spectra in the range of 2500 to 3800 cm\(^{-1}\) obtained during the adsorption of CO\(_2\)/water mixture on (A) TiO\(_2\), (B) TiO\(_2\)/Cu\(_2\)O and (C) TiO\(_2\)/Cu\(_2\)O/Cu\(_3\)(BTC)\(_2\).

Figure S10 shows the DRIFTS spectra (2500 to 3800 cm\(^{-1}\)) obtained during the adsorption of CO\(_2\)/H\(_2\)O mixture on the surfaces of the catalysts. In the beginning, no obvious peaks were observed within this range. With prolonged adsorption time, four apparent peaks show up at 3600, 3626, 3705 and 3727 cm\(^{-1}\), which can all be assigned to hydroxyl groups, demonstrating the existence of dissociatively chemisorbed water on these three catalysts. Protons, as another product from the dissociation of water, should also exist on the catalyst surface. These protons can react with carbonates to form formate species, which further enhance the photoreduction efficiency.
REFERENCES

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