One-step photodeposition of spatially separated CuOx and MnOx dual cocatalysts on g-C3N4 for enhanced CO2 photoreduction

Fengyu Tian
Yangtze University

Xinyao Wu
Yangtze University

Xuemin Yan
Yangtze University

Guangfu Liao (liaogf@mail2.sysu.edu.cn)  
Fujian Agriculture and Forestry University College of Material Engineering  
https://orcid.org/0000-0003-1299-8106

Research Article

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Abstract

Photocatalytic CO$_2$ conversion into valuable chemicals has been proved to be a promising strategy for relieving energy shortage and environmental pollution. Nevertheless, the rapid recombination of photogenerated carriers of photocatalyst greatly limits their actual application. In this work, dual CuO$_x$ and MnO$_x$ cocatalysts are decorated on g-C$_3$N$_4$ nanosheets via a one-step photodeposition strategy. Benefiting from the repulsion between Cu$^{2+}$ and Mn$^{2+}$ cations, a novel g-C$_3$N$_4$-based heterostructure loaded with spatially separated CuO$_x$ nanoparticles and MnO$_x$ nanosheets dual cocatalysts has been successfully fabricated. The Cu favors the trapping of electrons, while MnO$_x$ tends to collect holes. Moreover, the Cu$_2$O/g-C$_3$N$_4$ p-n heterojunction also accelerates the charge separation. As a result, the photogenerated holes and electrons ow into and out of the photocatalyst, respectively, resulting in enhanced charge separation for achieving efficient CO$_2$ photoreduction over CuO$_x$/g-C$_3$N$_4$/MnO$_x$.

Impressively, the optimized CuO$_x$/g-C$_3$N$_4$/MnO$_x$ exhibits an improved CO production rate of 5.49 µmol g$^{-1}$ h$^{-1}$, which exceeds over 27.5 times than bare g-C$_3$N$_4$. This work designs a promising photocatalyst for CO$_2$ photoreduction and develops a novel one-step photodeposition route for decorating spatially separated dual cocatalysts on a photocatalyst.

1. Introduction

Converting CO$_2$ into useful chemicals is an efficient strategy to solve greenhouse effect (Kondratenko et al. 2013, Liao et al. 2022a, Zhao et al. 2023, Lee et al. 2021). Inspired by the natural photosynthesis, artificial photosynthesis based on semiconductor photocatalysts is considered to be one of the most appealing methods for CO$_2$ conversion because of its distinctive merits such as simplicity, scalability and cost-effectiveness (Feng et al. 2022, Nguyen et al. 2020, Jiang et al. 2020a, Tian et al. 2021, Liao et al. 2022b). To accomplish the photocatalytic CO$_2$ reduction process, a varity of photocatalytic materials have been reported, such as metal oxides (Wang et al. 2019, Zhang et al. 2021, Pathak et al. 2005), metal sulfides (Wang et al. 2017, Li et al. 2019a, Cai et al. 2020, He et al. 2019), and metal-organic frameworks (Li et al. 2020a, Wang et al. 2018a). Nevertheless, these semiconductors exhibit unfulfilling photocatalytic property because of rapid recombination of carriers and wear visible-light absorption. Thus, it is vital that the exploration of highly active and selective CO$_2$ photoreduction catalysts.

In recently years, graphitic carbon nitride (g-C$_3$N$_4$) has achieved increasing interests in CO$_2$ photoreduction because of its low cost and visible-light response features and suitable band structure (Tang et al. 2020, Liao et al. 2019, Liao et al. 2021, Yang et al. 2022). Nevertheless, the photocatalytic activity of g-C$_3$N$_4$ is still greatly limited because of the unsatisfactory separation and migration efficiencies of photogenerated carriers (Cao and Yu 2014, Che et al. 2020). Therefore, it is vital to restrain the recombination of charges and boost their transfer for enhanced photocatalytic performance. To this end, many attempts have been reported for enhancing the photocatalytic efficiency, e.g., element doping (Fu et al. 2017, Yang et al. 2021) and cocatalyst deposition (Jiang et al. 2020b, Chen et al. 2022, Li et al. 2022a). This work designs a promising photocatalyst for CO$_2$ photoreduction and develops a novel one-step photodeposition route for decorating spatially separated dual cocatalysts on a photocatalyst.
A cocatalyst is commonly considered to be an intrinsically inactive material which can enhance the activity, stability and selectivity of single photocatalyst. Generally speaking, a cocatalyst play two important roles in improving the photocatalytic efficiency: i) capturing the photogenerated carriers for restraining the recombination of carriers (Li et al. 2019b); ii) offering more active sites for boosting photocatalytic reactions (Yang et al. 2020). Theoretically, the simultaneous coupling of semiconductor photocatalysts with dual cocatalysts (i.e. oxidation and reduction cocatalysts) is a promising strategy for further enhancing photocatalytic efficiency.

To date, several methods have been conducted to deposit cocatalysts on surfaces of the host semiconductor photocatalysts, such as impregnation (Tian et al. 2018), electrodeposition (Coelho et al. 2020), atomic-layer deposition (ALD) (Ren et al. 2019), and photodeposition (Fageria et al. 2016). Among them, photodeposition is a more promising approach because only light illumination can produce well-defined cocatalyst nanoparticles (Wenderich and Mul 2016, Fernando et al. 2016). For example, Di et al. adopted a two-step photodeposition strategy to load MoS$_2$ and CoO$_x$ dual cocatalysts on CdS nanorods (Di et al. 2022). In this system, MoS$_2$ and CoO$_x$ served as the reduction and oxidation cocatalysts, respectively, obviously restraining the recombination of photogenerated carriers and extending their lifetime for further improving photocatalytic performance. Huang and his co-workers reported that TiO$_2$ photocatalysts, is site-selective loaded with both Pt and CoO$_x$ cocatalysts spatially in two steps, displayed the high conversion efficiency of CO$_2$ to CH$_4$ (Huang et al. 2022). Numerous works have been highly done to load appropriate dual cocatalysts on the surface of the host photocatalyst in unifom distribution. Noteworthily, dual cocatalysts deposited by the two-step method would result in an overlapped of oxidation and reduction cocatalysts, which is not expected in photocatalytic performance improving. Unfortunately, this issue has been seldom solved in report, and it is worthy to further study relevant photocatalytic mechanism.

In general, a repulsive force is always existed between two metal ions with the same positive charges (Fenton et al. 2019). Therefore, they tend to attach to different adsorption sites on the surface of the substrate (Fenton et al. 2018). With the above considerations in mind, the spatial separation of oxidation and reduction cocatalysts can be achieved by the one-step photodeposition using the repulsion between two metal cations. In this work, Cu$^{2+}$ and Mn$^{2+}$ were used as the metal precursors to construct the CuO$_x$/g-C$_3$N$_4$/MnO$_x$ composite structure in which CuO$_x$ and MnO$_x$ are loaded separately on g-C$_3$N$_4$ surface by one-step photo-reduction route (Fig. 1). The optimized CuO$_x$/g-C$_3$N$_4$/MnO$_x$ composite exhibits remarkable enhanced photocatalytic CO$_2$ to CO performance. Further experimental results indicate that the synergistic effect between CuO$_x$ and MnO$_x$ can evidently restrain the recombination of photogenerated carriers and promote the photocatalytic efficiency. This work offers a promising one-step photodeposition method to decorate dual cocatalysts on a photocatalyst.

2. Experimental Section
2.1. Synthesis of samples
Synthesis of g-C$_3$N$_4$

Briefly, a fixed amount of dried urea was put in a crucible with a lid for keeping at 550 °C for 4 h with a heating rate of 15 °C min$^{-1}$ in Muffle oven. After being cooled down to 25 °C, the fluffy porous g-C$_3$N$_4$ powder was obtained.

Synthesis of CuO$_x$/g-C$_3$N$_4$/MnO$_x$ composites

The CuO$_x$/g-C$_3$N$_4$/MnO$_x$ was prepared via a facile photoreduction approach. Typically, 200 mg g-C$_3$N$_4$ was added in 100 mL distilled water with assistance of sonication to get well-dispersed homogenous suspensions. After that, 6.98 mg CuSO$_4$•5H$_2$O and 4.77 mg MnSO$_4$•H$_2$O were quickly added. The mixture was further stirred for 4 h under the irradiation of 300 W Xe lamp. After filtration and washing with distilled water several times, the obtained CuO$_x$/g-C$_3$N$_4$/MnO$_x$ hybrids was dried at 100°C under vacuum for 10 h. The prepared products are named as CuO$_x$/g-C$_3$N$_4$/MnO$_x$-x, where “x” is 0.5, 0.75, 1.0, 3.0 and 5.0, which expresses the weight ratios of both CuO$_x$ and MnO$_x$ to g-C$_3$N$_4$. The samples with 1.0 wt% weight ratio of CuO$_x$ to g-C$_3$N$_4$ and 1.0 wt% weight ratio of MnO$_x$ to g-C$_3$N$_4$ were also prepared, and labeled as CuO$_x$/g-C$_3$N$_4$-1 and MnO$_x$/g-C$_3$N$_4$-1, respectively.

Synthesis of CuO$_x$/(MnO$_x$/g-C$_3$N$_4$)-1 and MnO$_x$/(CuO$_x$/g-C$_3$N$_4$)-1 composites

A two-step photoreduction method was used to synthesis CuO$_x$/(MnO$_x$/g-C$_3$N$_4$)-1 and MnO$_x$/(CuO$_x$/g-C$_3$N$_4$). Typically, 200 mg g-C$_3$N$_4$ was added in 100 mL distilled water with assistance of sonication to get well-dispersed homogenous suspensions. And then a certain amount of CuSO$_4$•5H$_2$O was added. The mixture was further stirred for 4 h under the irradiation of 300 W Xe lamp. After filtration and washing with distilled water several times, the CuO$_x$/g-C$_3$N$_4$ hybrid can be obtained after drying at 100°C under vacuum for 10 h. Then, the obtained CuO$_x$/g-C$_3$N$_4$ was dispersed in 100 mL distilled water and subsequently a certain amount of MnSO$_4$•H$_2$O was added into the solution. After the same 4 h photoreduction and drying processes, the CuO$_x$/(MnO$_x$/g-C$_3$N$_4$)-1 was obtained. Similarly, MnO$_x$/(CuO$_x$/g-C$_3$N$_4$)-1 sample was prepared using the above procedure by switching the addition of CuSO$_4$•5H$_2$O and MnSO$_4$•H$_2$O.

3. Results And Discussion

XRD measurements were conducted to characterize the crystal structures of the obtained samples. As displayed in Fig. 2a, the XRD pattern of g-C$_3$N$_4$ displayed a weak peak at 13.1°, attributing to (100) peak originated from the in-plane ordering of tri-s-triazine units. The strong diffraction peak at 27.4° was assigned to the dense interlayer-stacking (002) peak of aromatic segment (Tian et al. 2018). Notably, no peaks of CuO$_x$ or MnO$_x$ were detected in the XRD patterns of CuO$_x$/g-C$_3$N$_4$/MnO$_x$ composites, attributing to the low content, high dispersion and amorphous structures of CuO$_x$ and MnO$_x$ (Xiang et al. 2021).
Moreover, the diffraction peaks also displayed no obviously changes after the modification with CuO\textsubscript{x} and MnO\textsubscript{x}, indicating that g-C\textsubscript{3}N\textsubscript{4} maintained a good stability during the photodeposition reaction.

Scanning electron microscope (SEM) and transmission electron microscope (TEM) measurements were utilized for studying the morphology and structural feature of the obtained samples. As the SEM image shown in Fig. 2b and 2c, it is clear that both g-C\textsubscript{3}N\textsubscript{4} and CuO\textsubscript{x}/g-C\textsubscript{3}N\textsubscript{4}/MnO\textsubscript{x}-1 exhibit graphite-like layered structure with curled and wrinkled surfaces, indicating that the g-C\textsubscript{3}N\textsubscript{4} morphology was almost unchanged after being modified with cocatalysts. High-resolution TEM (HRTEM) were conducted to investigate the distribution of CuO\textsubscript{x} and MnO\textsubscript{x}. It can be seen that the spatially separated CuO\textsubscript{x} nanoparticles and MnO\textsubscript{x} nanosheets were successfully deposited on the bare g-C\textsubscript{3}N\textsubscript{4} layers (Fig. 2d and e). In addition, no fringes belong to CuO\textsubscript{x} or MnO\textsubscript{x} are observed in the HRTEM image because of their amorphous structures, which was in accordance with the XRD results. Moreover, the related elemental mapping analysis also displays the homogeneous dispersion of Cu, Mn and O elements, indicating the high dispersions of CuO\textsubscript{x} nanoparticles and MnO\textsubscript{x} nanosheets on the g-C\textsubscript{3}N\textsubscript{4} surfaces (Fig. 2f).

XPS measurements were further conducted to investigate the surface compositions of the obtained samples. The high-resolution C 1s spectra of g-C\textsubscript{3}N\textsubscript{4} can be divided into three peaks at 284.5, 285.3 and 287.8 eV (Fig. 3), attributing to the the adventitious carbon, sp\textsuperscript{3}-bonded carbon species from defects and sp\textsuperscript{2}-bonded carbons in the N-containing aromatic structure (N-C = N), respectively (Tian et al. 2018). The N 1s peaks of g-C\textsubscript{3}N\textsubscript{4} (Fig. 3b) at 397.9, 398.8 and 400.1 eV correspond to pyridinic N (C-N = C), pyrrolic N (N-(C)\textsubscript{3}) and amino groups, respectively (Li et al. 2019c, Yang et al. 2023). In addition, the weak peak at 403.8 eV belongs to the π-π* interaction within the g-C\textsubscript{3}N\textsubscript{4} graphite-like layer structure (Li et al. 2020c). It is worth to mention that the binding energies of C 1s and N 1s for CuO\textsubscript{x}/g-C\textsubscript{3}N\textsubscript{4}/MnO\textsubscript{x}-1 composite exhibit positive shifts compared with bare g-C\textsubscript{3}N\textsubscript{4}, suggesting a nonnegligible electron migration from g-C\textsubscript{3}N\textsubscript{4} to CuO\textsubscript{x} and MnO\textsubscript{x} (Xu et al. 2020). Moreover, The Mn 2p XPS signals at 642.3 and 653.2 eV were the Mn 2p\textsubscript{3/2} and Mn 2p\textsubscript{1/2} peaks, respectively (Fig. 3c). The Mn 2p\textsubscript{3/2} spectrum can be separated into three characteristic peaks, which are attributed to Mn\textsuperscript{2+} in MnO, Mn\textsuperscript{3+} in Mn\textsubscript{2}O\textsubscript{3} and Mn\textsuperscript{4+} in MnO\textsubscript{2}, revealing that MnO\textsubscript{x} in the CuO\textsubscript{x}/g-C\textsubscript{3}N\textsubscript{4}/MnO\textsubscript{x}-1 nanocomposite was a mixture of MnO, Mn\textsubscript{2}O\textsubscript{3}, and MnO\textsubscript{2}. As reported, the Mn\textsuperscript{3+} species plays a significant role in photoinduced holes quenching, thus enhancing the photocatalytic performance (Zhang et al. 2020). The spectrum of Cu 2p is revealed in Fig. 3c, where two peaks at 932.5 and 951.9 eV are assigned to Cu\textsuperscript{0}, while the two peaks at 933.3 and 953.5 eV are considered to Cu\textsuperscript{+}, confirming that CuO\textsubscript{x} in the CuO\textsubscript{x}/g-C\textsubscript{3}N\textsubscript{4}/MnO\textsubscript{x}-1 nanocomposite was a mixture of Cu and Cu\textsubscript{2}O (Wang et al. 2022). Generally, Cu can act as the photoinduced electrons acceptors, which can improve the separation of photogenerated carriers (Cui et al. 2021).

UV-vis diffuse reflectance spectra (DRS) were utilized for exploring the optical features of the photocatalysts. From Fig. 3d, it is seen that the pristine g-C\textsubscript{3}N\textsubscript{4} display a distinct absorption at about ~470 nm. Notably, the photoabsorption edges of CuO\textsubscript{x}/g-C\textsubscript{3}N\textsubscript{4}/MnO\textsubscript{x} exhibits a clear red-shift in
comparison to pure g-C$_3$N$_4$, indicating that visible light absorption range of the CuO$_x$/g-C$_3$N$_4$/MnO$_x$ photocatalysts were enhanced with increasing CuO$_x$ and MnO$_x$ content. This could be attributed to the existence of the CuO$_x$ and MnO$_x$ cocatalysts which triggered the notably high scattering over long-wavelength range. The band gap energy values of all sample were determined through the formula below (Yuan et al. 2021):

$$(\alpha h\nu)^{n/2} = A(h\nu - E_g)$$

In which $\alpha$, $h$, $\nu$, $A$, and $E_g$ are the absorption coefficient, Planck constant, light frequency, a constant, and band gap energy, respectively. Accordingly, the band gap can be measured from the intercept of the tangent of the curve of $(\alpha h\nu)^{1/2}$ against the radiant energy $h\nu$. As shown in Fig. 3e, the band gap of g-C$_3$N$_4$ is calculated to be 2.64 V and the band gaps of CuO$_x$/g-C$_3$N$_4$/MnO$_x$-1, CuO$_x$/g-C$_3$N$_4$/MnO$_x$-3 and CuO$_x$/g-C$_3$N$_4$/MnO$_x$-5 composites are 2.53, 2.47 and 2.36, respectively (Fig. 3e). These results confirm the improved light harvesting efficiency in the visible light region.

Generally, the higher photocurrent density implies more efficient photogenerated electron-hole pairs separation and transport across interface (Wang et al. 2018b). Therefore, the improved charge separation of the obtained g-C$_3$N$_4$-based composites can be further verified by photocurrent measurements under visible irradiation. As shown in Fig. 3f, the CuO$_x$/g-C$_3$N$_4$/MnO$_x$-1 composite shows the highest photocurrent density than bare g-C$_3$N$_4$, CuO$_x$/g-C$_3$N$_4$-1 and MnO$_x$/g-C$_3$N$_4$-1, implying that photogenerated charge carrier separation efficiency is significantly enhanced by dual cocatalysts modification.

The photocatalytic CO$_2$ reduction activities of the obtained nanocomposites were evaluated under visible light illumination (> 420 nm) in the gas-solid system. As shown in Fig. 4a, g-C$_3$N$_4$ nanosheets exhibited relatively lower CO evolution with a rate of 0.2 µmol g$^{-1}$ h$^{-1}$, resulting from its rapid charge recombination. Notably, the CO productions were greatly improved with the increased loading of CuO$_x$ and MnO$_x$ cocatalysts, and the production of CO achieved the highest rate (5.49 µmol g$^{-1}$ h$^{-1}$) over CuO$_x$/g-C$_3$N$_4$/MnO$_x$-1, exceeding approximately 27.5 times that of bare g-C$_3$N$_4$. Additionally, the apparent quantum efficiency of CuO$_x$/g-C$_3$N$_4$/MnO$_x$-1 at 420 nm is calculated to be 0.9%. While further increasing CuO$_x$ and MnO$_x$ amounts would be detrimental to the photocatalytic performance, attributing to the fact that the overloading of CuO$_x$ and MnO$_x$ could obscure active sites. Recycled of CuO$_x$/g-C$_3$N$_4$/MnO$_x$-1 still maintained approximately 81% of its initial activity after four cycling runs (each run for 4 h), indicating a good stability (Fig. 4c).

To unveil the electron transfer path and the mechanism of the CuO$_x$ and MnO$_x$ as dual cocatalysts for photocatalytic CO$_2$ reduction, a series of comparative experiments have been conducted. As shown in Fig. 4b, the CO yield of ternary CuO$_x$/g-C$_3$N$_4$/MnO$_x$-1 photocatalyst was even higher than the sum of that of MnO$_x$/g-C$_3$N$_4$-1 and CuO$_x$/g-C$_3$N$_4$-1. This result can be attributed to the dual cocatalysts possessing a
synergistic effect on suppressing the photogenerated charges recombination and furnishing the photocatalytic reaction with more active sites. Notably, the CO production rates of the catalysts with CuO\textsubscript{x} or MnO\textsubscript{x} follow the same orders of MnO\textsubscript{x}/g-C\textsubscript{3}N\textsubscript{4}-1 CuO\textsubscript{x}/g-C\textsubscript{3}N\textsubscript{4}-1, indicating that the oxidation cocatalyst MnO\textsubscript{x} has more to do with the CO\textsubscript{2} reduction than the reduction cocatalyst CuO\textsubscript{x}. This result could be attributed to the fact that MnO\textsubscript{x} can collect photoinduced holes to accelerate the H\textsubscript{2}O oxidization reactions, thus promoting the photocatalytic CO\textsubscript{2} reduction process. Additionally, the photocatalytic activity of CuO\textsubscript{x}/g-C\textsubscript{3}N\textsubscript{4}/MnO\textsubscript{x}-1 was also higher than MnO\textsubscript{x}/(CuO\textsubscript{x}/g-C\textsubscript{3}N\textsubscript{4}) and CuO\textsubscript{x}/(MnO\textsubscript{x}/g-C\textsubscript{3}N\textsubscript{4}), demonstrating the spatially separated dual cocatalysts are more conducive to improving the separation efficiency of photoinduced carriers.

In-situ FTIR spectroscopy was performed to explore the photocatalytic mechanism by investigating the key reaction intermediate products of the reduction of CO\textsubscript{2} and H\textsubscript{2}O toward CO. The spectra were recorded every 5 min. As presented in Fig. 5a, with the illumination time from 0 to 30 min, the intensities of some new peaks that appeared in the in-situ FTIR results of CuO\textsubscript{x}/g-C\textsubscript{3}N\textsubscript{4}/MnO\textsubscript{x}-1 gradually increased. The absorption peaks at 1283 and 1440 cm\textsuperscript{-1} are assigned to bicarbonate (HCO\textsubscript{3}\textsuperscript{-}) (Ban et al. 2022, Zhang et al. 2018), and the peaks at 1354 and 1497 cm\textsuperscript{-1} are assigned to monodentate carbonate (m-CO\textsubscript{3}\textsuperscript{2-}) (Wang et al. 2019, Li et al. 2020b). The peak at 1555 and 1693 cm\textsuperscript{-1} are matched with bidentate carbonate (b-CO\textsubscript{3}\textsuperscript{2-}) and •CO\textsubscript{2}\textsuperscript{-} species, respectively (Wang et al. 2019). Meanwhile, the intensity of the peak increased with the prolonged illumination time at 1593 cm\textsuperscript{-1} could be attributed to COOH\textsuperscript{*}, which has been proved to be a crucial intermediate for multi-step reduction of •CO\textsubscript{2} to produce CO (Ban et al. 2022). No peak belongs to linearly adsorbed and bridging CO (CO\textsuperscript{*}) has been observed at ~ 2000 cm\textsuperscript{-1}, indicating that the CO\textsuperscript{*} is easily desorbed on the CuO\textsubscript{x}/g-C\textsubscript{3}N\textsubscript{4}/MnO\textsubscript{x}-1 surface and turns into the final CO product. According to the in-situ FTIR results, the possible reaction path for CO\textsubscript{2} photoreduction over CuO\textsubscript{x}/g-C\textsubscript{3}N\textsubscript{4}/MnO\textsubscript{x} composites is proposed as follows (the asterisks denote catalytically active sites):

\[
\text{CO}_2(\text{g}) + \text{H}_2\text{O} \rightarrow 2\text{H}^+ + \text{CO}_3^{2-}
\]

1

\[
\ast + \text{CO}_2(\text{g}) \rightarrow \ast\text{CO}_2^-, \text{ or } \ast + 2\text{H}^+ + \text{CO}_3^{2-} \rightarrow \text{H}_2\text{O} + \ast\text{CO}_2^-(2)
\]

\[
\ast\text{CO}_2 + e^- + \text{H}^+ \rightarrow \text{COOH}^*
\]

3

\[
\text{COOH}^* + e^- + \text{H}^+ \rightarrow \text{CO}^* + \text{H}_2\text{O}
\]

4

\[
\text{CO}^* \rightarrow \text{CO(}\text{g}) + *
\]
In order to investigate the photogenerated charges transfer behavior during the photocatalytic process, Mott-Schottky plots were performed for investigating the influence of CuO\textsubscript{x} and MnO\textsubscript{x} cocatalyst on band structure g-C\textsubscript{3}N\textsubscript{4}, as well as the semiconductor types. As shown in Fig. 5b, the positive curve slope unveils that the introduction of CuO\textsubscript{x} and MnO\textsubscript{x} did not change the n-type properties of g-C\textsubscript{3}N\textsubscript{4} (Tian et al. 2018). Moreover, the flat band potential can be determined via the Mott-Schottky equation (Qiao et al. 2018):

\[ \frac{1}{C^2} = \left( \frac{2}{\epsilon \epsilon_0 N} \right) \left[ (E - E_{fb}) - \frac{kT}{e} \right] \]

In which \( C \), \( e \), \( \epsilon \), \( \epsilon_0 \) and \( N \) represent the capacitance of the space charge region, electron charge, dielectric constant, vacuum permittivity and the carrier density of samples, respectively. \( E \) represents the electrode applied potential and \( E_{fb} \) is the flat band potential. \( T \) and \( k \) represent the absolute temperature and Boltzmann constant, respectively. The \( kT/e \) term can be neglected at room temperature because of the extremely small vaule (25.693 meV). Accordingly, the \( E_{fb} \) of g-C\textsubscript{3}N\textsubscript{4} is measured to be -0.90 V (vs. SCE). The CB potential of g-C\textsubscript{3}N\textsubscript{4} is estimated to be -0.67 V (vs. NHE), and the VB level is 1.97 V (vs. NHE) based on to the equation (Qiao et al. 2018): \( E_{VB} = E_{CB} + E_g \). Notably, the \( E_{fb} \) of MnO\textsubscript{x}/g-C\textsubscript{3}N\textsubscript{4-1} exhibited the same \( E_{fb} \) when compared with pure g-C\textsubscript{3}N\textsubscript{4}, while the CuO\textsubscript{x}/g-C\textsubscript{3}N\textsubscript{4-1} and CuO\textsubscript{x}/g-C\textsubscript{3}N\textsubscript{4}/MnO\textsubscript{x-1} displayed the same \( E_{fb} \) of -0.86 V (vs. SCE), indicating that only the introduction of CuO\textsubscript{x} can affect the \( E_{fb} \) of g-C\textsubscript{3}N\textsubscript{4}. According to reports in the literature (Cui et al. 2021), the Fermi level of n-type g-C\textsubscript{3}N\textsubscript{4} is higher than p-type CuO\textsubscript{x}. Therefore, the change in \( E_{fb} \) could be attributed to the feasibility of electrons spontaneously migrating from g-C\textsubscript{3}N\textsubscript{4} to CuO\textsubscript{x} in terms of thermodynamics. Such electron transfer caused the construction of the internal electric field at the CuO\textsubscript{x}/g-C\textsubscript{3}N\textsubscript{4} interfaces pointing from CuO\textsubscript{x} to g-C\textsubscript{3}N\textsubscript{4}, facilitating the formation of p-n heterojunction, which would efficiently separate the charge carriers and thus promote the CO\textsubscript{2} photoreduction performance (Zhao et al. 2021).

Given the above results, a probable mechanism of CuO\textsubscript{x}/g-C\textsubscript{3}N\textsubscript{4}/MnO\textsubscript{x} composite for CO\textsubscript{2} photoreduction to CO has been proposed. As shown in Fig. 5c, when CuO\textsubscript{x} nanoparticles are attached on g-C\textsubscript{3}N\textsubscript{4}, a Cu\textsubscript{2}O/g-C\textsubscript{3}N\textsubscript{4} p-n junction is formed at the interface. Meanwhile, the difference in Fermi levels of Cu\textsubscript{2}O and g-C\textsubscript{3}N\textsubscript{4} induced the interfacial charge redistribution, and thus led to the fabrication of an internal electric field across the interface. Under visible light illumination, the photogenerated electrons on Cu\textsubscript{2}O will spontaneously transfer to the CB of g-C\textsubscript{3}N\textsubscript{4} driven via the internal electric field, and holes on the VB of g-C\textsubscript{3}N\textsubscript{4} slid toward the VB of Cu\textsubscript{2}O simultaneously. Moreover, Cu and MnO\textsubscript{x} can effectively capture photogenerated electrons and holes, respectively, and further facilitate their separation efficiency (Raziq et al. 2018, Bai et al. 2016). Since the CuO\textsubscript{x} and MnO\textsubscript{x} cocatalysts are spatially separated, the recombination of electron-hole pairs is evidently inhibited. As an outcome, the activated CO\textsubscript{2} would transform into CO via a photogenerated electron-induced multistep reduction process. The synergistic effect between the spatially separated CuO\textsubscript{x} nanoparticles and MnO\textsubscript{x} nanosheets can effectively accelerate the photoreduction of CO\textsubscript{2} to CO.
4. Conclusions

In summary, we have prepared various CuO$_x$/g-C$_3$N$_4$/MnO$_x$ heterostructures through a simple one-step photodeposition approach. When CuO$_x$/g-C$_3$N$_4$/MnO$_x$ was illuminated by light, the photogenerated electrons were migrated from the CB of g-C$_3$N$_4$ to Cu species for the reduction of CO$_2$, and the related holes were captured via MnO$_x$ nanoparticles to oxidize water. Besides, the Cu$_2$O/g-C$_3$N$_4$ p-n heterojunction also accelerates the charge separation. As an outcome, the spatially separated CuO$_x$ and MnO$_x$ dual cocatalysts greatly restrain the recombination rate of photogenerated carriers and facilitate the CO$_2$ conversion kinetically, resulting in the enhanced CO$_2$-to-CO photoreduction performance. This work not only provides a high-performance photocatalyst for CO$_2$ reduction, but also develops a novel strategy for decorating spatially separated dual cocatalysts on a photocatalyst.

Declarations

Declaration of competing interest

The authors declare no competing financial interests.

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References

of CO$_2$ with almost complete CO selectivity. Mater Today 35:25–33


Figures
Figure 1

Schematic diagram of the superiority of one-step photoreduction method.
Figure 2

(a) XRD patterns of g-C₃N₄ and CuOₓ/ g-C₃N₄/ MnOₓ composites; SEM images of (b) g-C₃N₄ and (c) CuOₓ/ g-C₃N₄/ MnOₓ-1; (d) TEM image, (e) HRTEM image and (f) HADDF-STEM image and corresponding elemental mapping images of CuOₓ/ g-C₃N₄/ MnOₓ-1.

Figure 3

(a) C 1s and (b) N 1s XPS spectra of g-C₃N₄ and CuOₓ/ g-C₃N₄/ MnOₓ-1; (c) Cu 2p and Mn 2p XPS spectra of CuOₓ/ g-C₃N₄/ MnOₓ-1; (d) UV-vis diffuse reflectance spectra and (e) the corresponding plots of (ahv)⁴/² vs. hv of g-C₃N₄ and CuOₓ/ g-C₃N₄/ MnOₓ composites; (f) Transient photocurrent response curves of g-C₃N₄, CuOₓ/ g-C₃N₄-1 and MnOₓ/ g-C₃N₄-1.
Figure 4

(a-b) Photocatalytic CO\textsubscript{2} reduction activities of different samples. (c) The recycling test of CO production over CuO\textsubscript{x}/g-C\textsubscript{3}N\textsubscript{4}/MnO\textsubscript{x}-1.

Figure 5

(a) In-situ FTIR spectra of CO\textsubscript{2} reduction on CuO\textsubscript{x}/g-C\textsubscript{3}N\textsubscript{4}/MnO\textsubscript{x}-1 at different illumination times; (b) Mott-Schottky plots; (c) Photocatalytic CO\textsubscript{2} reduction mechanism proposed on the surface of CuO\textsubscript{x}/g-C\textsubscript{3}N\textsubscript{4}/MnO\textsubscript{x} composite.

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