Ultra-Fast Construction of Novel S-Scheme CuBi$_2$O$_4$/CuO Heterojunction for Selectively Photocatalytic CO$_2$ Conversion to CO

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Abstract: Herein, step-scheme (S-scheme) CuBi$_2$O$_4$/CuO (CBO/CuO) composite films were successfully synthesized on glass substrates by the ultra-fast spraying-calcination method. The photocatalytic activities of the obtained materials for CO$_2$ reduction in the presence of H$_2$O vapor were evaluated under visible light irradiation ($\lambda > 400$ nm). Benefiting from the construction of S-scheme heterojunction, the CO, CH$_4$ and O$_2$ yields of the optimal CBO/CuO composite reached 1599.1, 5.1 and 682.2 µmol/m$^2$ after irradiation for 9 h, and the selectivity of the CO product was notably enhanced from below 18.5% to above 98.5% compared with those of the bare samples. In the sixth cycling experiment, the yields of main products decreased by less than 15%, and a high CO selectivity was still kept. The enhanced photocatalytic performance of CO$_2$ reduction was attributed to the efficient separation of photogenerated charge carriers. Based on the photocatalytic activity, band structure and in situ-XPS results, the S-scheme charge transfer mechanism was confirmed. The study provides an insight into the design of S-scheme photocatalysts for selective CO$_2$ conversion.

Keywords: CO$_2$ reduction; photocatalyst; selectivity; CuBi$_2$O$_4$/Cu$_2$O; S-scheme

1. Introduction

Photocatalytic reduction of CO$_2$ into valuable chemicals utilizing H$_2$O and solar energy is considered to be a promising strategy for addressing energy shortage and greenhouse effect issues. On the basis of that, substantial efforts have been devoted to developing highly efficient photocatalysts, and copper-containing oxide photocatalysts are particularly relevant for CO$_2$ reduction, including CuO, Cu$_2$O, CuBi$_2$O$_4$, CuFe$_2$O$_4$, CuFeO$_2$, CuV$_2$O$_4$, Cu$_3$Nb$_2$O$_8$, CuGaO$_2$, and so on [1]. Among the above encouraging photocatalysts, CuBi$_2$O$_4$ is an attractive candidate in terms of its suitable band gap (1.5–2.0 eV) and relatively negative conduction band edge position [1]. However, the major hurdle for CuBi$_2$O$_4$ lies in its valance band potential, which is more positive than the H$_2$O reduction potential. For instance, CuBi$_2$O$_4$-based composite catalysts with high conversion efficiency and controllable selectivity for photocatalytic CO$_2$ reduction have been reported to boost photocatalytic performances. Our previous work demonstrated that the synthesized S-scheme...
CuBi$_2$O$_4$/Bi$_2$O$_3$ heterojunction exhibited enhanced CO and CH$_4$ yields for CO$_2$ photoreduction in water vapor [2]. We further reported the construction of a S-scheme WO$_3$/CuBi$_2$O$_4$ photocatalyst for a visible-light-driven CO$_2$ reduction with a good photocatalytic activity and stability [12]. As a typical transition metal oxide, CuO has been demonstrated to be feasible for heterojunction construction due to its narrow band gap (1.4–1.8 eV) and suitable band edge position [13], and heterostructures including CuO/TiO$_2$ [14], CuO/ZnO [15], WO$_3$/CuO [16,17], CuO/BiOCl [18], CuO/g-C$_3$N$_4$ [19] and Nb$_2$O$_5$/CuO [20] have been adopted for efficient photocatalytic CO$_2$ photoreduction. For instance, Nogueira et al. reported that compositing Nb$_2$O$_5$ with increased amounts of CuO led to a higher selectivity for CH$_4$ production [20]. Therefore, in view of the above analysis, it is of significance to rationally construct the heterojunction catalyst by combining CuO and CuBi$_2$O$_4$. Recently, CuO/CuBi$_2$O$_4$ heterojunction has been studied for photoelectrocatalysis [21–23], photodegradation [24] and electrochemical detection [25]. However, to date, few studies have been conducted to construct CuO/CuBi$_2$O$_4$ heterojunction for photocatalytic CO$_2$ reduction with H$_2$O vapor, a system in which the limited solubility of CO$_2$ in the solvent or weak CO$_2$ adsorption ability will be overcome.

In this work, a series of CuO/CuBi$_2$O$_4$ heterojunction composites with different molar ratios were synthesized onto glass substrates by ultra-fast spray pyrolysis followed by annealing treatment. The heterojunction catalysts were investigated for photocatalytic CO$_2$ reduction with H$_2$O vapor. The CuO/CuBi$_2$O$_4$ composites exhibited a superior photocatalytic performance than those of the single CuO and CuBi$_2$O$_4$, and the enhanced ratio of CuBi$_2$O$_4$ in the heterojunction benefited the improved product selectivity of CO$_2$ photoreduction into CO. Based on the experimental and theoretical results, the S-scheme charge transfer mechanism was proposed and discussed in detail.

2. Materials and Methods

2.1. Materials Synthesis

In the typical synthesis of the CuBi$_2$O$_4$/CuO sample, 2.6180 g of Cu(NO$_3$)$_2$·3H$_2$O was firstly dissolved into 20 mL of ethanol, and 2.4250 g of Bi(NO$_3$)$_3$·5H$_2$O was dissolved into 4 mL of nitric acid with the subsequent addition of deionized water (16 mL). The precursor solution for spraying was obtained by mixing the above two solutions. The glass substrate (2.1 cm × 2.3 cm) was pre-cleaned in H$_2$O$_2$ solution and irradiated by UV light for 30 min, followed by immobilization onto the heating stage under 280 °C, and then the precursor solution was sprayed on the above substrate with 0.3 MPa N$_2$ pressure. The obtained precursor film was heated at 480 °C for 2 h in air. Finally, the CuBi$_2$O$_4$/CuO composite was obtained and named as 30CBO/CuO (30 represented the ideal molar ratio between CuBi$_2$O$_4$ and CuO). In addition, the other CBO/CuO composites with different ratios of two components were similarly synthesized by spraying the precursor solutions with variations in the contents of Cu(NO$_3$)$_2$·3H$_2$O and Bi(NO$_3$)$_3$·5H$_2$O. For comparison, the bare CuO and CuBi$_2$O$_4$ samples were synthesized based on the stoichiometric molar ratios of Cu and Bi in the precursor solutions. Simultaneously, the 30CBO/CuO-m sample was obtained by mechanically mixing the bare CuO and CuBi$_2$O$_4$ nanoparticles with a molar ratio of 0.3.

2.2. Characterization

The crystal structures of the as-prepared samples were studied by X-ray diffraction (XRD, BRUKER D8 Advance). The morphology and structure were inspected with scanning electron microscopy (SEM, FEI Quanta 250 FEG) and transmission electron microscopy (TEM, FEI Talos F200X). The chemical states were investigated by X-ray photoelectron spectroscopy (XPS, Escalab Xi+, Thermofisher Scientific, Santa Clara, CA, USA). The optical properties of the obtained photocatalysts were obtained on a UV-vis spectrophotometer (Cary 5000, Agilent, Santa Clara, CA, USA). The photocurrent responses and electrochemical impedance spectroscopy were measured by an electrochemical workstation (CHI660E, CH Instruments Ins., Shanghai, China).
2.3. Photocatalytic Performance for CO₂ Reduction

The photocatalytic performance for CO₂ reduction with H₂O vapor was measured in the reactor with a top quartz window. A 300 W Xenon arc lamp (CEL-HXF300, Beijing China Education Au-light Co., Ltd., Beijing, China) with an UV cutoff filter (λ > 400 nm) was utilized as the light source. The glass substrate with the composite catalyst was placed inside the stainless steel cylindrical vessel reactor (CEL-GPRT100, Beijing China Education Au-light Co., Ltd., China). Prior to light irradiation, the reaction setup was purged with high purity CO₂ gas (99.999%) several times. The compressed high-purity CO₂ gas was passed through a water bubbler to generate a mixture of CO₂ and H₂O vapor. After illumination, the gaseous products were quantitatively identified for off-line analysis using the gas chromatograph (GC-7920, Beijing China Education Au-light Co., Ltd., China) equipped with a flame ionized detector (FID) and GC-MS (Agilent 7890A-5975C) with a thermal conductivity detector (TCD), and the equipped columns were TDX-01 and Porapak-Q, respectively. Blank tests were conducted in the absence of photocatalysts and in the dark with catalysts. No products were detected, indicating that the presence of both visible-light irradiation and the photocatalyst were indispensable for the photocatalytic reduction of CO₂ with H₂O vapor. The product selectivity (S) for CO₂ reduction was calculated with the following equations (Equations (1) and (2)):

\[
S_{CO} (%) = \frac{2 \times N_{CO}}{(2 \times N_{CO} + 8 \times N_{CH_4})} \times 100
\]

\[
S_{CH_4} (%) = \frac{2 \times N_{CH_4}}{(2 \times N_{CO} + 8 \times N_{CH_4})} \times 100
\]

N_{CO} and N_{CH_4} represented the yield of detected CO and CH₄ molecules, respectively.

To evaluate the stability, the 30CBO/CuO model sample was refreshed by washing with deionized water, and its photocatalytic performance was reevaluated in the aforementioned conditions.

3. Results and Discussion

3.1. Structure, Composition and Morphology

Figure 1a shows the XRD patterns of the as-prepared samples. Several diffraction peaks were distinctly discovered at 35.5, 38.7, 48.7 and 61.5°, which corresponded to the (−1 1 1), (1 1 1), (−2 0 2) and (−1 1 3) crystal faces of monoclinic CuO (PDF card No. 00-041-0254). Meanwhile, the diffraction peaks of the CuBi₂O₄ sample matched perfectly with those of tetragonal CuBi₂O₄ (PDF card No. 01-072-0493). Simultaneously, the peak intensity of CuBi₂O₄ in the CBO/CuO composites, which was labeled by a green dotted line in Figure 1a, gradually increased with increasing molar ratios of CuBi₂O₄. Except for the diffraction peaks of CuBi₂O₄ and CuO, no other peaks were detected in the composites, which indicated that the CBO/CuO composite was composed of monoclinic CuO and tetragonal CuBi₂O₄. XPS measurements were further conducted to explore the composition of the obtained samples. As shown in Figure S1a, the Cu, Bi, O and C elements existed in the CBO and composite samples, while Cu, O and C elements appeared in the CuO sample. The C element was attributed to the adsorbed CO₂ molecules on the surface. In the high-resolution Cu 2p XPS spectra (Figure 1b) of the CBO/CuO composite, two peaks were observed at binding energies of 933.84 eV for Cu(II) 2p 3/2 and 953.83 eV for Cu(II) 2p 1/2 [26,27]. Furthermore, the conspicuous peaks at binding energies of 158.84 and 164.15 eV in the Bi 4f spectra (Figure 1c) were ascribed to the Bi(III) state of CuBi₂O₄ [28,29]. It was notable that a slight shift of the characteristic peak position appeared for the 30CBO/CuO composite when compared with those of the bare CuBi₂O₄ and CuO samples, which was caused by the formation of a heterojunction between the two components. The O 1s spectrum of CBO/CuO is shown in Figure S1b, and the two peaks at 530.1 and 529.6 eV were ascribed to lattice oxygen of CuO and CuBi₂O₄ materials. Other peaks at 531.2 and 532.5 eV were assigned to intrinsic oxygen defects and surface adsorbed oxygen, respectively [20,24,30].
Furthermore, the conspicuous peaks at binding energies of 158.84 and 164.15 eV in the Bi 4f spectra (Figure 1c) were ascribed to the Bi(III) state of CuBi$_2$O$_4$ [28, 29]. It was notable that a slight shift of the characteristic peak position appeared for the 30CBO/CuO composite when compared with those of the bare CuBi$_2$O$_4$ and CuO samples, which was caused by the formation of a heterojunction between the two components. The O 1 s spectrum of CBO/CuO is shown in Figure S1b, and the two peaks at 530.1 and 529.6 eV were ascribed to lattice oxygen of CuO and CuBi$_2$O$_4$ materials. Other peaks at 531.2 and 532.5 eV were assigned to intrinsic oxygen defects and surface adsorbed oxygen, respectively [20, 24, 30].

Figure 1. XRD patterns (a) and XPS spectra (b) Cu 2p and (c) Bi 4f) of the as-prepared samples.

The morphologies of the as-prepared CuBi$_2$O$_4$, CuO and 30CBO/CuO samples were visualized via SEM and TEM characterizations. The SEM images in Figure 2a–c demonstrated that all the samples exhibited the typical particle morphology. Concurrently, a lot of voids were formed due to piles of particles, leading to large exposed surfaces. TEM measurements were further conducted to determine the accurate sizes of CuO and CuBi$_2$O$_4$ particles, which were obtained from the substrates by ultrasound methods. As shown in Figure S2, the size distribution of CuO and CuBi$_2$O$_4$ nanoparticles basically obeyed the logical normal distribution, and their average particle sizes were about 47.7 and 26.6 nm, respectively. The TEM image of 30CBO/CuO in Figure 2d shows two groups of particles with different sizes. In the HRTEM image (Figure 2e), the distinct lattice spacings of 0.275 and 0.268 nm were indexed to the (1 0 2) and (3 1 0) crystal faces of tetragonal CuBi$_2$O$_4$, and lattice spacings of 0.138, 0.137 and 0.120 nm were also discovered, which were assigned to the (1 1 3), (2 2 0) and (2 0 4) planes of monoclinic CuO. Additionally, the EDX mapping images in Figure 2f showed that the Cu, Bi and O elements were uniformly distributed. The above SEM and TEM observations, combined with the XRD and XPS results, revealed that both monoclinic-phase CuO and tetragonal-phase CuBi$_2$O$_4$ were present and fused at the interface.
Figure 2. SEM images of (a) CuBi$_2$O$_4$, (b) CuO and (c) 30CBO/CuO samples; (d) TEM image, (e) HRTEM image and (f) EDX mapping images of the 30CBO/CuO sample.

To further explore the band structure of heterojunction, the DRS and VB-XPS results were gained and are shown in Figure 3. As shown in Figure 3a, the bare and composite samples showed a strong absorption in the visible light region, indicating the feasibility of a visible-light utilization for photocatalytic CO$_2$ reduction. The band gaps ($E_g$) of the samples were estimated by the plots of $(\alpha h\nu)^n$ versus photo energy ($h\nu$), considering that CuBi$_2$O$_4$
and CuO exhibited band-to-band excitations involving direct and indirect transitions, respectively [20,31]. The \( E_g \) values of CuBi\(_2\)O\(_4\) and CuO were respectively calculated to be 1.87 and 1.60 eV. According to the conventional method, the valence band (VB) positions of the CuBi\(_2\)O\(_4\) and CuO samples (Figure 3b) were determined to be about 0.92 and 1.34 eV, respectively. Hence, their conduction band (CB) positions were calculated to be \(-0.95\) and \(-0.26\) eV, respectively. With the formation of the heterojunction, the alignment of the Fermi levels was assumed at the interfacial phases of the CBO/CuO composite. Accompanied by the movement of the Fermi levels, the CB and VB edge positions for both CuBi\(_2\)O\(_4\) and CuO shifted. In this case, the band offsets of the CBO/CuO heterojunction can be calculated using the XPS core-level alignment method, according to the following equation [24,32]:

\[
\Delta E_{VB} = (E_{Bi 4f 7/2,CBO} - E_{VB,CBO}) - (E_{Cu 2p 3/2,CuO} - E_{VB,CuO}) - (E_{Bi 4f 7/2,CBO/CuO} - E_{Cu 2p 3/2,CBO/CuO})
\]

\[
\Delta E_{CB} = \Delta E_{VB} - \Delta E_{gap,CBO} + \Delta E_{gap,CuO}
\]

where \( E_{x,y} \) was denoted as the binding energy of the core level “\( x \)” or VB for the sample “\( y \)”, and \( \Delta E_{gap,y} \) referred to the values calculated from DRS. According to the above method and relevant data (Table S1), the \( \Delta E_{VB} \) and \( \Delta E_{CB} \) for the CBO/CuO composite were calculated to be about 0.23 and 0.15 eV. The corresponding band structure diagrams (Figure 3c,d) were schemed, and a staggered band alignment heterostructure was constructed.

![Figure 3.](image)

Figure 3. (a) DRS and (b) VB-XPS spectra of the as-prepared samples; and (c,d) schematic diagrams of the band structure for CBO/CuO heterojunction.

### 3.2. Photocatalytic Performance of CO\(_2\) Reduction

The photocatalytic performances for CO\(_2\) reduction were investigated under the mixed atmosphere of CO\(_2\) and H\(_2\)O vapor. Figure 4a shows the production yields after 3 h of visible-light irradiation (>400 nm). The photocatalytic products for the bare CuO catalyst included CO, CH\(_4\) and O\(_2\), while there were no detectable products for bare CuBi\(_2\)O\(_4\). The
CO, CH₄ and O₂ yields of 30CBO/CuO were the highest among the CBO/CuO composites with different ratios. Simultaneously, the CO selectivity was obviously enhanced with the increase of the CuBi₂O₄ content in the composite, reaching about 98% for the 30CBO/CuO catalyst. Compared with the photocatalytic activity of 30CBO/CuO-m (Figure S3), the enhanced yields were caused by the formation of a heterojunction in the 30CBO/CuO composite. CO, CH₄ and O₂ yields respectively reached 561.4, 2.1 and 232.2 μmol/m² after 3 h of visible-light illumination. The yields of the main products rapidly and regularly increased (Figure 4a) when prolonging the illumination time. After 9 h of visible-light illumination, the rate of CO and O₂ yields were still maintained at 177.7 and 75.8 μmol/m²/h, respectively, and the CO selectivity was kept above 98.5%.

The catalytic stability of the photocatalyst was never ignored in the practical application of CO₂ conversion. Figure 5a shows the cycling experiments of photocatalytic CO₂ reduction for the optimal 30CBO/CuO sample. In the sixth cycling experiment, all the product yields were reduced by under 15%, and the CO selectivity still reached over 98.5%. The XRD and XPS results of the used sample after the sixth cycling experiment are shown in Figure 5b–d. In the XRD patterns (Figure 5b), no other new diffraction peaks of the used 30CBO/CuO sample were observed when compared with those of the fresh sample. Similarly, there was no obvious difference between the fresh and used samples in the XPS spectra (Figure 5c,d). It was indicated that the 30CBO/CuO composite exhibited an excellent photocatalytic stability for CO₂ reduction with H₂O vapor.

Figure 4. Photocatalytic activity for different samples under visible-light illumination ((a) A. CBO, B. CuO, C. 10CBO/CuO, D. 20CBO/CuO, E. 30CBO/CuO, F. 40CBO/CuO, G. 50CBO/CuO. (b) 30CBO/CuO as catalyst).

Figure 5. Cont.
Figure 5. Photocatalytic activity (a) of 30CBO/CuO in the cycling experiment; (b) XRD pattern, (c) Bi 4f and (d) Cu 2p XPS spectra of the fresh and used 30CBO/CuO samples after the sixth cycling experiment.

Transient photocurrent responses were recorded for several on-off irradiation cycles to provide more convincing evidence for the separation of photoinduced carriers. As shown in Figure 6a, the photocurrent responses of all the samples reproducibly increased under each irradiation and quickly recovered in the dark. Furthermore, the transient photocurrent of 30CBO/CuO was higher than those of the bare CBO and CuO samples, demonstrating that the composite exhibited a more efficient transfer and separation of photoinduced carriers [27]. Additionally, the EIS Nyquist plots are illustrated in Figure 6b. The semicircles in the high-frequency region correspond to the electron-transfer-limited process, which fit with the interfacial charge transfer resistance (Rct) [33]. The arc radius of 30CBO/CuO (Rct 2875 Ω) was observed to be the smallest when compared with those of bare CBO (Rct 8293 Ω) and CuO (Rct 5610 Ω), indicating the most efficient charge transfer for the composite [11]. The above results proved the positive effect of the heterojunction on the carrier separation.

Figure 6. (a) I-t curves and (b) EIS Nyquist plots of CBO, CuO and 30CBO/CuO samples.

3.3. Possible Photocatalytic Mechanism

Based on the above experimental results and the band energy alignment of the CBO/CuO heterojunction, the enhanced photocatalytic activity for CO2 reduction was deduced as follows. In the CBO/CuO composite, close contact between CBO and CuO caused the formation of a heterojunction, and an inner electrical field was established at the interface. Under visible-light illumination, the VB electrons of both components were excited. If the photoexcited charge carriers transferred following the common double-charge transfer mode (Figure 7a), the accumulated holes in the VB of the CBO component would not be able to oxidize H2O to O2 in thermodynamics, which was due to the VB potential of CBO (1.02 V vs. NHE) being more negative than the standard redox potential E°(O2/H2O) (1.23 V vs. NHE) [33]. Meanwhile, no products were found when using the CBO sample in the photocatalytic experiment. If the S-scheme charge transfer mechanism mode in
Figure 7b was employed, the catalytic sites of H$_2$O oxidization were constructed on the surface of the CuO component. In thermodynamics, the holes on VB of CuO could realize O$_2$ evolution from H$_2$O molecules, and the experimental results also proved that the catalytic process of CO$_2$ reduction and H$_2$O oxidization were realized for the bare CuO sample [34]. In situ-XPS measurements of 30CBO/CuO were conducted for a further demonstration of electron transfer across the heterojunction interface. As shown in Figure 7c,d, two peaks of Bi 4f obviously shifted towards the lower binding energy direction under illumination, and two characteristic peaks of Cu 2p reversely shifted, implying that the photoinduced electrons transferred from CuBi$_2$O$_4$ to CuO [35,36]. Combined with the above analysis, the CBO/CuO composite was a direct S-scheme heterojunction photocatalyst.

Additionally, the conversion of CO$_2$ to CH$_4$ required eight electrons and four protons, while the conversion of CO$_2$ to CO only required two electrons. CO formation was more favorable with a lower surface density of photogenerated electrons, and CH$_4$ formation easily occurred with a higher surface density of photogenerated electrons [37,38]. Moreover, in the hydrogenation of CO$_2$ and CO, H adatoms were obtained from H$_2$O dissociation [37]. To explore the sample’s hydrogen production ability, the photocatalytic activity for water splitting was studied for the CBO/CuO composite. Unfortunately, no product was discovered when using the 30CBO/CuO sample. After Pt loading, the H$_2$ yields for the Pt/CBO/CuO sample reached 12.4 μmol/g$_{cat}$ after 8 h of illumination. Hence, the lack of aggregated electron sites and dissociation of H$_2$O to H adatoms on the CuBi$_2$O$_4$ surface might cause the selectivity of CO formation for CO$_2$ reduction in this study.
4. Conclusions

A series of CuBi$_2$O$_4$/CuO photocatalysts on glass substrates were synthesized by the ultra-fast spraying-calcination method. The optimal CBO/CuO composite exhibited a markedly higher photocatalytic performance of CO$_2$ reduction with H$_2$O vapor than those of bare CuBi$_2$O$_4$ and CuO, and the selectivity of the CO product was observably enhanced from below 18.5% to above 98.5%. After 9 h of visible-light illumination, the CO, CH$_4$ and O$_2$ yields reached 1599.1, 5.1 and 682.2 µmol/m$^2$, respectively. In the sixth cycling experiment, the yields of the main products decreased by less than 15%, and a high CO selectivity was still kept. The enhanced activity of CO$_2$ reduction was attributed to the efficient separation of photogenerated charge carriers that originated from the well-aligned staggered band structure of the CuBi$_2$O$_4$/CuO heterojunction. Based on the photocatalytic activity and in situ-XPS results, the S-scheme charge transfer mechanism was finally proposed. In summary, this study is expected to be useful in developing S-scheme photocatalysts for CO$_2$ reduction and to provide some meaningful information for a deep understanding of how photoinduced electrons transfer across contact interfaces.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/nano12183247/s1, Table S1: Binding energy and band gap of the obtained samples by XPS and DRS measurements; Figure S1: Survey spectra (a) and high resolution O 1s XPS spectra (b) of the CBO, CuO and 30CBO/CuO samples; Figure S2: TEM image of CBO (a) and CuO (b) samples (inset: diameter size distribution); Figure S3: Photocatalytic activity for different samples after 3 h of visible-light illumination.

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