Bi/BiOCl Nanosheets Enriched with Oxygen Vacancies to Enhance Photocatalytic CO₂ Reduction

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Abstract

BiOCl has been used in the photoreduction of CO₂, but exhibits limited photocatalytic activity. In this study, Bi was in situ reduced and deposited on the surface of (001)-dominated BiOCl nanosheets by NaBH₄ to form Bi/BiOCl nanosheets enriched with oxygen vacancies. The as-prepared Bi/BiOCl nanosheets having low thickness (ca. 10 nm) showed much higher concentration of oxygen vacancies compared to Bi/BiOCl nanoplates having high thickness (ca. 100 nm). Subsequently, the photocatalytic activity of the Bi/BiOCl nanosheets enriched with oxygen vacancies for CO₂ reduction was dramatically enhanced and much higher than that of BiOCl nanoplates, nanosheets, and Bi/BiOCl nanoplates. It showed that the improved photocatalytic activity in the reduction of CO₂ can be attributed to the enhanced separation efficiency of photogenerated electron–hole pairs of the oxygen vacancies on BiOCl nanosheets and Bi metals. This work demonstrated that the in situ reduction of non-noble metals on the surface of BiOCl nanosheets that are enriched with oxygen vacancies is favorable for increasing photocatalytic CO₂ reduction.

Keywords Bi · Oxygen vacancy · BiOCl nanosheets · Photocatalysis · CO₂ reduction

Introduction

With the development of modern economy and society, fossil fuels are extensively used in many sectors. The burning of fossil fuels inevitably leads to the emission of huge amounts of carbon dioxide (CO₂). It is predicted that the global concentration of CO₂ will reach 500 ppm by the end of the twenty-first century and global temperature will increase by 1.9 °C [1]. The increasing temperature will cause global warming, which can cause huge economic losses and threaten human survival [2]. Therefore, reducing

CO₂ emissions is an urgent necessity. Among the numerous strategies developed to reduce CO₂ emission, capturing and utilizing CO₂ to produce other carbon sources is a promising way, which has been demonstrated, to reduce atmospheric CO₂ concentration. Specifically, since the 1980s, photocatalytic conversion of CO₂ has been reported as an important strategy for CO₂ utilization [3]. Until now, various photocatalysts [4–9] have been employed for the process of CO₂ utilization. However, the photocatalytic activities of these photocatalysts are still unsatisfactory.

Bismuth oxychloride (BiOCl), a typical two-dimensional (2D) material with a layered structure, has been used for the photoreduction of CO₂ [10–12]. However, the CO₂ reduction efficiency of BiOCl photocatalysts is usually quite low because of the following reasons: limited light absorption capacity, low efficiency of electron–hole carriers, and fast recombination of photogenerated electron–hole pairs. Various strategies, such as controlling exposed active facets [12–14], forming oxygen vacancies [10, 11, 15, 16], loading metals as cocatalysts [17–19], and constructing heterojunctions [20–23], are used to improve the photocatalytic efficiency of BiOCl catalysts. The strategy of loading metals as cocatalysts onto BiOCl to enhance photocatalytic activity has gained increasing attention because cocatalysts can

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form Schottky barriers as strong electron traps to direct the flow of electrons. Recently, a couple of studies have reported bismuth (Bi) as a cocatalyst loaded on BiOCl (Bi/BiOCl) to show enhanced photocatalytic activity [24–26]. The use of Bi as a cocatalyst is not only due to the low cost, but also because Bi can be easily formed in situ on the surface of BiOCl via reduction reagents. The lattice matching interfaces between Bi and BiOCl can be formed in Bi/BiOCl to achieve better charge transfer compared with other metals [27, 28]. Moreover, the in situ reduction process usually induces oxygen vacancies on the surface of BiOCl [24, 26]. Oxygen vacancies are believed to favor CO₂ adsorption and activation [11, 29, 30]. Therefore, it is possible to develop Bi/BiOCl catalysts that are enriched with oxygen vacancies for photocatalytic CO₂ reduction.

Herein, photocatalytic CO₂ reduction using Bi metal deposited on BiOCl nanosheets that were enriched with oxygen vacancies was studied for the first time. It was found that the concentration of oxygen vacancies on Bi/BiOCl nanosheets with a thickness of ca. 10 nm were much higher than on Bi/BiOCl nanoplates with a thickness of ca. 100 nm. Bi/BiOCl nanosheets with enriched oxygen vacancies showed much higher photocatalytic activity during CO₂ reduction than BiOCl nanoplates, nanosheets, and Bi/BiOCl nanoplates.

Experimental

Chemicals

Polyvinyl pyrrolidone (PVP) was purchased from Sigma Co., Ltd, Shanghai, China. All the other reagents were purchased from Chengdu Kelong Chemical Co., Ltd, Chengdu, China. All chemicals were used without further purification, if not specifically mentioned. Ultrapure water was used throughout the experiment.

Preparation of Photocatalysts

Preparation of BiOCl Nanosheets

Thin BiOCl nanosheets were synthesized using a method similar to the method reported in Ref. [14]. In a typical synthesis procedure, 1.0 mmol Bi(NO₃)₃·5H₂O and 1.0 mmol NaCl were dissolved in a solution containing 30 mL ethylene glycol and 5 mL deionized water with strong stirring. Next, 0.2 g PVP was added into the above suspension. After 30 min of stirring, the mixture was transferred into 50-mL Teflon-lined autoclave and then heated at 160 °C for 8 h. After being naturally cooled down to room temperature under air atmosphere, the resultant precipitate was washed with ethanol and deionized water by centrifugation. Then,

the mixture was stirred for 20 min and frozen at – 80 °C for 2 h. After 48 h of freeze-drying, the powders were ground and obtained. Finally, the products were calcined at 400 °C under air atmosphere for 4 h. The resulting thin BiOCl nanosheets were defined as BiOCl-NS.

Preparation of BiOCl Nanoplates

The BiOCl nanoplates were synthesized using water as solvent and without PVP. The 1.0 mmol Bi(NO₃)₃·5H₂O and 1.0 mmol NaCl were dissolved in 35 mL deionized water with strong stirring. After 30 min of stirring, the mixture was transferred into a 50-mL Teflon-lined autoclave and then heated at 160 °C for 8 h. The BiOCl nanoplate was obtained using the post-processing process for BiOCl-NS, which was defined as BiOCl-NP.

Preparation of Bi/BiOCl Nanocomposite

The Bi/BiOCl nanocomposite was obtained via an in situ reduction process using NaBH₄ solution. In detail, 0.2 g of the as-prepared thin BiOCl nanosheets was added to 30 mL NaBH₄ solution of 4.0 mmol/L and reacted for 8 min under stirring. The resulting products were washed with ethanol and deionized water several times until the impurities were removed. Using the same method, the final Bi/BiOCl nanocomposites were obtained by freeze-drying. The Bi/BiOCl nanocomposite synthesized with various concentrations of NaBH₄ solutions was defined as BiOCl-NS. In addition, Bi/BiOCl-NP meant that 4.0 mmol/L NaBH₄ and BiOCl nanoplates were used during the reduction process.

Characterizations

Powder X-ray diffraction (XRD) patterns were measured on a PANalytical X'pert at 40 kV and 40 mA with Cu K α radiation, and the 2 θ range was measured from 10° to 70° with step width of 0.05°. Scanning electron microscopy (SEM) was conducted using JEOL JSM-7800F. Transmission electron microscopy (TEM) was performed using FEI Tecnai G² F30. The binding environment of the samples and surface chemical composition were investigated using a Thermo ESCALAB250Xi X-ray photoelectron spectroscopy (XPS). Meanwhile, all the binding energies were referenced to the C 1s level at 284.8 eV. UV–Vis diffuse reflectance spectra (DRS) were investigated at room temperature using BaSO₄ as the standard background for reflectance. The photoluminescence (PL) spectra were recorded on Nicolet 6700 with an excitation wavelength of 370 nm. The electron spin-resonance spectroscopy (ESR) was recorded on a JESFA200 spectrometer at room temperature.

Photocatalytic Performance

Photocatalytic reduction of CO₂ was conducted in a closed cylindrical reaction vessel with a volume of 380 mL. 20 mg samples were evenly spread into the culture dish, which had a diameter of 7.5 cm. Then, the dish was put into the reactor and sealed with a stainless steel cover and a quartz window. Next, the reactor was evacuated by a vacuum pump and then high purity Ar gas was introduced. The above steps were repeated for 10 times to eliminate the air in the reactor and to fill the reactor with high purity Ar. 400 ppm of CO₂ was then passed through a two-hole gas wash bottle with 50 mL of ultrapure water. The CO₂ containing water vapor was continuously introduced into the reactor for around 15 min. After unplugging the interface, the reactor was tightly closed. Finally, the mixture of catalyst and CO₂ with water vapor was illuminated using a 300-W Xe lamp as a UV–Vis light. The gas products were detected by a Techcomp GC7900 gas chromatograph (GC). A thermal conductivity detector (TCD) was used to detect H₂ gas, and a flame ionization detector (FID) was used to detect CO and CH₄ gases. The selectivity toward products was calculated using the following equations:

$$\text{CO selectivity (\%)} = 100 \times 2R_{\text{CO}} / (2R_{\text{CO}} + 2R_{\text{H}_2} + 8R_{\text{CH}_4}) \quad (1)$$

$$\text{CH}_4 \text{ selectivity (\%)} = 100 \times 8R_{\text{CH}_4} / (2R_{\text{CO}} + 2R_{\text{H}_2} + 8R_{\text{CH}_4}) \quad (2)$$

$$\text{H}_2 \text{ selectivity (\%)} = 100 \times 2R_{\text{H}_2} / (2R_{\text{CO}} + 2R_{\text{H}_2} + 8R_{\text{CH}_4}) \quad (3)$$

Results and Discussion

Figure 1a shows the XRD spectra of the as-synthesized BiOCl and Bi/BiOCl. Both spectra of BiOCl prepared without reduction were perfectly assigned to tetragonal phase of BiOCl (JCPDS-ICDD card No.06-0249). The diffraction peaks of Bi element (JCPDS-ICDD card No.44-1246) were observed in the samples prepared after NaBH₄ reducing. It is noted that the (001) plane assigned to BiOCl at 11.98° showed obvious decrease of relative intensity, indicating that Bi might be formed on {001} facets. No obvious peak shifts were found in the Bi/BiOCl samples reduced by NaBH₄ (Fig. 1b), indicating that Bi elements were not doped into BiOCl.

The micromorphologies of the as-prepared BiOCl-NS and Bi/BiOCl-NS were characterized using TEM (Fig. 2). The pristine BiOCl-NS using EG as a solvent showed nanosheet-like morphology with the length and width are ca. 100 nm (Fig. 2a, b). The measured thicknesses of these nanosheets were around 8–28 nm (Fig. S1). However, BiOCl-NP prepared using H₂O as a solvent exhibited a thickness of a

Fig. 1 a XRD spectra. b Magnification spectra from 25° to 28°

Fig. 2 TEM images of **a, b** BiOCl-NS, and **d, e** Bi/BiOCl-NS. HRTEM images of **c** BiOCl-NS and **f** Bi/BiOCl-NS

few hundred nanometers (Fig. S2). The HRTEM image of BiOCl-NS clearly shows the lattice fringes with a lattice spacing of 0.275 nm and an angle of 90° (Fig. 2c), well matched with the (110) plane of tetragonal phase BiOCl. This result confirmed the formation of BiOCl nanosheets with the exposed {001} facets in BiOCl-NS sample. Although NaBH_4 reduction destroyed part of the BiOCl-NS surface in the Bi/BiOCl-NS sample, it still maintained nanosheet-like morphology (Fig. 2d and Fig. S3). Besides, uniformly dispersed nanodots on the surface of BiOCl with less than 10 nm in diameter were evident (Fig. 2e). The HRTEM image of Bi/BiOCl-NS sample confirmed that these nanodots are Bi metal with the (012) planes of 0.328 nm (Fig. 2f), consistent with the result of XRD (Fig. 1a). The TEM images and XRD results of the as-prepared samples confirmed the formation of BiOCl nanoplates, BiOCl nanosheets, Bi/BiOCl nanoplates, and Bi/BiOCl nanosheets.

To elucidate the surface chemical properties of Bi/BiOCl nanoplates and nanosheets, the chemical states of Bi/BiOCl-NS and Bi/BiOCl-NP were measured by XPS (Fig. 3). The XPS survey patterns of both samples contain the peaks of Bi, O, C, and Cl (Fig. 3a). Both samples were corrected by C 1s at 284.8 eV. As shown in Fig. 3b, two main peaks assigned to Bi $4f_{7/2}$ and $4f_{5/2}$ were observed in both samples [26, 31, 32]. These two peaks can be further fitted into two pairs of $\text{Bi}^{(3-x)+}$ ($x \geq 0$) and Bi metal. The peaks of Bi $4f$ at 164.4 eV and 159.1 eV in Bi/BiOCl-NP sample were assigned to Bi $4f_{7/2}$ and $4f_{5/2}$ of $\text{Bi}^{(3-x)+}$ ($x \geq 0$), respectively. However, these two peaks shifted to lower binding energies of 164.2 eV and 158.9 eV in Bi/BiOCl-NS sample, indicating a higher electron density around the Bi element due to the appearance of defects in Bi/BiOCl-NS [11, 33]. In addition, another two pairs of peaks at 162.6 eV (Bi $4f_{5/2}$) and 156.9 eV (Bi $4f_{7/2}$)

assigned to the Bi metal showed no obvious shifts, but the relative intensities increased in Bi/BiOCl-NS sample, implying a higher concentration of Bi metal on the surface of Bi/BiOCl-NS than that of Bi/BiOCl-NP.

The O 1s peaks can be fitted into two peaks in both samples (Fig. 3c). The peaks at 530.2 eV in Bi/BiOCl-NS and 529.8 eV in Bi/BiOCl-NP were assigned to the Bi–O bonds [10, 32]. O 1s XPS of Bi/BiOCl-NP sample showed an obvious peak at 531.6 eV assigned to the surface OH groups, which was difficult to be found in Bi/BiOCl-NS sample. The fitted peak at 532.9 eV might be assigned to the oxygen vacancies on the surface [10, 34, 35]. Additionally, for the Bi/BiOCl-NS and Bi/BiOCl-NP, there are two main peaks at 197.7 eV and 199.5 eV belonging to Cl 2p XPS spectra (Fig. 3d) [36].

The ESR spectroscopy was used to verify the presence of oxygen vacancies. The pristine BiOCl-NS showed no signal all over the range, indicating the absence of the non-solitary pair electrons in the sample. However, Bi/BiOCl-NS and Bi/BiOCl-NP samples showed significant signals at $g = 2.001$, which is a classic signal of oxygen vacancies (Fig. 4) [11, 12, 16]. Interestingly, the EPR signal of Bi/BiOCl-NS arising from oxygen vacancy is much stronger than that of Bi/BiOCl-NP, indicating a significantly enhanced oxygen vacancy concentration of Bi/BiOCl-NS. The thickness of BiOCl was reported to be a key factor to control the formation of surface oxygen vacancies and photocatalytic activity for CO_2 reduction. This phenomenon is much obvious when BiOCl exposed {001} facets due to much more oxygen atoms on {001} facets than on other facets [37]. Specifically, the thinner nanosheets with exposed {001} facets would induce oxygen vacancies easier on the BiOCl surface [38]. Therefore, it is reasonable that a thinner BiOCl can induce

Fig. 3 **a** XPS survey pattern of the samples, **b** Bi 4f, **c** O 1s, **d** Cl 2p XPS of Bi/BiOCl-NP and Bi/BiOCl-NS

Fig. 4 EPR spectra of BiOCl-NS, Bi/BiOCl-NS, and Bi/BiOCl-NP at room temperature

higher amount of oxygen vacancies after NaBH₄ reduction to form Bi/BiOCl enriched oxygen vacancies. Generally, a high amount of oxygen vacancies on the surface of catalysts is believed to show better activity due to their involvement in new photoexcitation processes [11, 13, 39].

The optical absorption properties of the as-prepared samples were measured using UV–Vis diffuse reflectance spectra. It can be seen in Fig. 5 that the pristine BiOCl shows absorption edge at around 360 nm, indicating a band gap of 3.4 eV, which is consistent with other reports [25, 26]. Bi/BiOCl-NS sample showed similar absorption edge the pristine BiOCl. However, an absorption tail extended to the whole visible light range. This is attributed to the formation of oxygen vacancies, which is consistent with the results of XPS and EPR (Figs. 3c, 4) [33]. In Bi/BiOCl-NP, the absorption peak centered at 500 nm instead of the absorption tail was found due to the formation of Bi particles with its surface plasmon resonance (SPR) effect. Based on the analysis above, Bi/BiOCl-NS enriched with oxygen vacancies was formed during the reducing process.

Fig. 5 UV-Vis absorbance spectra of BiOCl-NP, BiOCl-NS, Bi/BiOCl-NP, and BiOCl-NS

The photocatalytic activities of CO_2 reduction over the as-prepared samples were carried out in a close system using 300-W Xe lamp as a light source with H_2O vapor. The detected products were H_2 , CO , and CH_4 . As shown in Fig. 6, the pristine BiOCl-NP showed the lowest photocatalytic activities of all the detectable products. However, pristine BiOCl-NS sample showed enhanced photocatalytic activity, which is consistent with Ref. [12]. It is noted that Bi/BiOCl-NS sample showed the highest photocatalytic activity of CO_2 reduction. The formation amounts of CO , CH_4 and H_2 in 8 h are $38 \mu\text{mol/g}$, $3.6 \mu\text{mol/g}$, and $1.9 \mu\text{mol/g}$, respectively, which are 2.7, 5.1, and 1.4 times of pristine BiOCl-NS sample. Bi/BiOCl-NS with thinner BiOCl nanosheets showed much higher activity in all products than Bi/BiOCl-NP with thicker BiOCl nanoplates. The

results also showed that Bi metal on BiOCl showed an overall enhancement of activity compared to bare BiOCl in both nanoplates and nanosheets. Higher oxygen vacancies in Bi/BiOCl-NS showed higher formation rates of CH_4 and CO , while no obvious enhancement of H_2 . It should be noted that the enhancement of photocatalytic activity was not due to the SPR effect because the sample of Bi/BiOCl-NP with Bi SPR peak showed no activity under visible light irradiation ($\lambda > 420 \text{ nm}$).

Compared with some typical photocatalysts that were reported under similar reaction conditions, photocatalysts synthesized in this study showed moderate activity for formations of CO and CH_4 and good activity for suppressing H_2 formation (Table S1). The time for each product in Fig. 6b showed steadily increasing formation of these products during photoirradiation. The photocatalytic activities of Bi/BiOCl during the first two cycles showed a significant decrease, which might be due to the further reduction of BiOCl and/or disappearance of oxygen vacancies. However, stable photocatalytic activities were observed during the third cycle (Fig. S4).

The selectivity of $(\text{CO} + \text{CH}_4)$ was higher than 90%, whereas H_2 selectivity was less than 10% in all cases, indicating that water splitting during the reaction was heavily suppressed. CH_4 selectivity showed enhancement after Bi metal and oxygen vacancies formed on both BiOCl-NP and BiOCl-NS (Fig. S5), which indicated that Bi metal and oxygen vacancies might be beneficial for the formation of CH_4 . CH_4 selectivity was enhanced by 3% over Bi/BiOCl-NP as compared to that over bare BiOCl-NP. This enhancement was increased to $\sim 12\%$ between BiOCl-NS and Bi/BiOCl-NS. Considering that the concentration of oxygen vacancies was much higher in Bi/BiOCl-NS, oxygen vacancy might be the important factor for CH_4 selectivity during photocatalytic CO_2 reduction.

Fig. 6 **a** Generations of CO , CH_4 , and H_2 over BiOCl-NP, Bi/BiOCl-NP, BiOCl-NS, and Bi/BiOCl-NS under UV-Vis irradiation for 8 h. **b** Time-dependent photocatalytic evolution of products over Bi/BiOCl-NS

Five blank tests and an isotopic experiment were performed to confirm the photocatalytic process. The results revealed that BiOCl with Bi as cocatalyst in CO₂ and H₂O atmosphere under photoirradiation can consistently achieve the significant formation of CO, which indicated that the reaction process should be a photocatalytic process (Fig. 7a). The isotopic experiments with ¹³CO₂ and H₂O showed that the ¹³CO and ¹³CH₄ were formed from ¹³CO₂ during the photoirradiation (Fig. 7b). This further confirmed that CO₂ was photocatalytically reduced to carbon sources during the reaction.

The specific surface area should show significant effect when comparing the activity between BiOCl-NP and BiOCl-NS. However, when the NaBH₄ was used to reduce both BiOCl-NP and BiOCl-NS, the enhancement of activities between Bi/BiOCl-NP and Bi/BiOCl-NS was obviously different. Bi/BiOCl-NS showed much higher enhancement than Bi/BiOCl-NP with same reduction concentration of NaBH₄. Specifically, CO formation over Bi/BiOCl-NS was 2.7 times higher than that over BiOCl-NS. However, no obvious enhancement was found over BiOCl-NP and Bi/BiOCl-NP (Fig. 6a). Besides, CH₄ formation over Bi/BiOCl-NS was 5.5 times higher than that over BiOCl-NS. However, the enhancement was only 1.1 over BiOCl-NP and Bi/BiOCl-NP. Therefore, specific surface area should not be the main factor for the enhancement of activity.

PL spectra were acquired to study the generation, transfer, and recombination of electron–hole pairs. Figure 8 shows the PL spectra of as-prepared samples with excitation at 250 nm. BiOCl-NP sample showed the highest PL intensity, indicating highest photogenerated electron–hole pairs recombination rate. Therefore, this sample showed the lowest photocatalytic activity for CO₂ reduction. Significant decrease of PL intensities of Bi/BiOCl-NP and Bi/BiOCl-NS

Fig. 8 PL spectra at room temperature

samples implied that the in situ reduced Bi showed a significant increase in the separation rate of electron–hole pairs. It was reported in our previous works that metal Bi is a good medium for conducting electrons [40, 41]. When metal Bi is loaded on the surface of the BiOCl, it can effectively improve the transfer efficiency of electrons. In turn, more electrons are involved in the reduction reaction. Interestingly, BiOCl-NS showed lower PL intensity than BiOCl-NP. This means that BiOCl-NS enriched with oxygen vacancies showed a better efficiency for separation of electron–hole pairs.

Photocurrent tests were performed to further study the recombination rate of photogenerated charge carriers (Fig. 9). All samples showed reproducible on–off effects

Fig. 7 a Blank tests over Bi/BiOCl-NS. b MS of the CO₂ reduction reactions using ¹³CO₂

Fig. 9 Transient photocurrent responses of BiOCl-NP, BiOCl-NS, Bi/BiOCl-NP, and Bi/BiOCl-NS

with the photoirradiation turned on and off. BiOCl-NP sample showed the lowest photocurrent density, whereas BiOCl-NS showed the enhanced photocurrent density. This indicated that thinner BiOCl could be beneficial for the photogenerated charge mobility, consistent with the photocatalytic activity for CO₂ reduction. It is found that Bi loading on BiOCl showed obvious enhancement of photocurrent density. Among all tested samples, the Bi/BiOCl-NS showed the highest photocurrent density of 0.87 $\mu\text{A}/\text{cm}^2$, which was about 2 times than that of pristine BiOCl-NS (0.37 $\mu\text{A}/\text{cm}^2$) and 47% higher than that of Bi/BiOCl-NP (0.59 $\mu\text{A}/\text{cm}^2$). Note that the trend of photocurrent density is consistent with that of the photocatalytic activity of CO₂ reduction, implying that the separation of charge carriers plays an important role during photocatalysis.

Based on the above characterization and discussion, Bi reduction from BiOCl nanosheets with enriched oxygen

vacancies is believed to play a crucial role in photocatalytic CO₂ reduction. NaBH₄ not only acted as a reductant to form Bi on BiOCl, but also induced the formation of oxygen vacancies. Therefore, the photocatalytic activity for CO₂ reduction was dramatically enhanced compared to the bare BiOCl nanosheets. Bi acts as a metal to effectively enhance the separation of electrons and holes. Such effect could be further enhanced with oxygen vacancies, and therefore, Bi/BiOCl nanosheets showed much higher photocatalytic activity for CO₂ reduction than Bi/BiOCl nanoplates (Scheme 1).

Conclusions

In summary, we fabricated Bi/BiOCl nanosheets enriched with oxygen vacancies to show enhanced photocatalytic activity for CO₂ reduction. Pure BiOCl nanoplates with higher thickness showed the lowest photocatalytic activity, and the enhancement of photocatalytic activity was limited even with the formation of Bi as cocatalysts on BiOCl nanoplates using NaBH₄ as a reductant. On the other hand, such effect of enhancement of photocatalytic activity was dramatically enlarged when Bi metal was formed on lower thickness of BiOCl nanosheets. It is also believed that the enriched oxygen vacancies are a key factor for the further enhancement of photocatalytic activity for CO₂ reduction. This work suggested that the Bi particles enriched with oxygen vacancies on BiOCl nanosheets play crucial roles in converting solar energy into chemical energy.

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Scheme 1 Schematic illustration of the proposed mechanism of photocatalytic CO₂ reduction over Bi/BiOCl

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