Single site anchored BiOBr nanosheets for visible-light-driven CO₂ Reduction

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Abstract. Carbon dioxide (CO₂) reduction is important for environmental protection, reducing climate warming trends and energy conversion and storage. Photocatalytic CO₂ reduction reaction (CO₂RR) in visible light is a highly important green route for this target. The variation of active sites on various semiconductor have been extensively studied. Exploring new routes for CO₂RR is highly desired. Herein, we successfully loaded single tungsten atomic oxide (STAO) on BiOBr substrate. A visible-light-driven photocatalytic CO₂RR is achieved by STAO/BiOBr, and the stability has been realized. The CO production of STAO/BiOBr was more than one time larger than that of bare BiOBr and CH₄ is also realized. The photo-electric performance of STAO/BiOBr is much different with that of bare BiOBr. By investigating the active sites on single site anchored BiOBr base, the single sites of tungsten played as reductive active sites for CO₂ to replace Bi atoms on bare BiOBr. This study sheds lights for photocatalytic CO₂RR by single atomic sites through single metallic atom oxides.

Keywords: CO₂ Reduction, Single atomic site, Visible-light-driven, Photocatalytic, BiOBr.

1. Introduction
Since the beginning of this century, greenhouse effect caused by excessive CO₂ emission has become a huge problem affecting human living environment [1-3]. Due to the rapid growth of population, it brings huge energy consumption and CO₂ emissions. Solving the energy and environmental problems caused by CO₂ is both a challenge and an opportunity [4-6]. Unfortunately, CO₂ reduction reaction (CO₂RR) is still not widely used to solve the problem in our daily life because of the low reaction efficiency and high cost [7-9]. One important reason is that we don't understand the mechanism of reaction site clearly, so that we can't precisely control the separation and transport of photogenerated carriers [10-12]. Hence, the study of single reaction site is particularly significant.

The study of single site catalysis has attracted extensive interest. He et al reported a universal preparation method to fabricate single atom catalysts, which has high chemical selectivity for hydrogenation [13]. Hejazi et al successfully loaded single site Pt on anatase TiO₂ for hydrogen evolution reaction (HER) [14]. Meanwhile, Liu et al achieved efficient oxygen evolution reaction (OER) with single site Co on brookite TiO₂ [15]. Zhang et al made a microscopic analysis of the structural sites,
concluded that the single atomic site is cation vacancy substitution [16]. Our group also had a certain foundation for the study of tungsten single site [17, 18]. Wang et al developed the preparation and characterization methods for homogeneous single tungsten atomic oxide (STAO), which raised the efficiency of organic pollutants degradation by more than two orders of magnitude [17]. Although the research on single atom site is very popular, a suitable visible-light-driven substrate is still need for loading single site to achieve high-performance and environment-friendly CO$_2$RR photocatalytic application.

Among the many substrates, BiOBr has attracted much attention because of its excellent visible-light-driven photocatalytic ability and efficient photogenerated electron-hole separation behavior [19-21]. BiOBr nanostructured materials of oxygen vacancies has been proved to be a good choice for nitrogen fixation [22, 23]. The change of electron-hole separation ability caused by different exposure facets of BiOBr has been widely studied and recognized [24, 25]. Meanwhile, the application of BiOBr in the field of CO$_2$RR is also concerned by people [26, 27]. Di et al studied the excellent CO evolution properties driven by solar light of Co single site supported by Bi$_3$O$_4$Br [27]. Moreover, visible-light-driven photocatalytic reaction is more conducive to practical application. Thus, it is challenging to control the band structure of materials while maintaining the improvement of properties.

Herein, in this work, we successfully loaded single tungsten atomic oxide on BiOBr substrate (STAO/BiOBr) through a simple preparation process. Compared with pure BiOBr, the CO production of STAO/BiOBr had been improved more than one time. At the same time, CH$_4$ products that was not detected before also appeared. In order to study the single site structure, the cs-corrected TEM was carried out to take pictures of atoms, XRD and EPR were used to study the structural information, XPS was used to characterize the chemical state. For the photocatalytic test, 300W Xe lamp with 420 nm UV filter was used as light sources, and gas chromatography was used to detect gas products. For the understanding of reaction mechanism, UV-Vis and PL measurement were carried out.

2. Results and Discussion

![Figure 1](image)

**Figure 1.** (a) STEM-HADDF image of STAO/BiOBr nanosheets. (b) EDX elemental mapping analysis of the STAO/BiOBr. The same region of figure 1a. (c) High magnification STEM-HADDF image of STAO/BiOBr nanosheets. (d) High contrast image of figure 1c.
Figure 1a shows the cs-corrected scanning transmission electron microscopy high-angle annular dark field (STEM-HAADF) of the STAO/BiOBr, the as prepared BiOBr nanosheets could be seen to be evenly dispersed on the carbon support lacey films.

The elemental mapping analysis confirms that bismuth (Bi), oxygen (O), bromine (Br) and tungsten (W) are evenly dispersed (Figure 1b). The image of the atoms could be clearly seen in the high magnification STEM-HADDF image (Figure 1c). By optimizing the contrast of figure 1c, some brighter atoms can be observed, like those circled in red circles, indicate that the single tungsten atomic oxide (STAO) is successfully loaded on the BiOBr nanosheets substrate.

In order to further explore the structure-activity relationship of the single site, Other structural characterizations were also carried out. X-ray diffraction (XRD) results show that the lattice of the substrate did not change before and after the single site loading (Figure 2a), also proved that the single site not formed a long-range ordered structure, but was monodispersed. Low temperature electron paramagnetic resonance (EPR) (Figure 2a) shown a stronger vibration in at g value = 2.01, indicates that more oxygen vacancies appeared with the loading of single site [23]. These points can also be obtained by XPS analysis of the samples (Figure 2c-g). O 1s spectra (Figure 2e) can clearly see that the amount of oxygen vacancy at 531 eV was greatly increased [26]. Meanwhile, Bi 4f spectra (Figure 2f) can also found out a slightly peak shift to lower energy after the loading, demonstrating that more +3 oxidation state has appeared [23]. Figure 2g show that some W5+ appeared in the sample, but the main part is still W6+.

Through a series of characterizations of the single site, STAO loaded oxygen vacancies riched BiOBr can be clearly recognized. The CO2 reduction reaction (CO2RR) performance of STAO/BiOBr is the focus of concern. Driven by Xe lamp with 420 nm UV filter, visible-light-driven photocatalytic CO2 reduction performance of STAO/BiOBr was been researched. Over time, pure BiOBr did not produce any methane (Figure 3a). This is because the thermodynamic barrier had not been reached. However, the introduction of STAO changed the band structure of the active site, resulting in the emergence of more valuable CH4 products, indicates that single site had stronger hydrogenation ability. More surprisingly, the original carbon monoxide evolution had been enhanced more than one time (Figure 3b). The statistics of photocatalytic performance are shown in Figure 3c. The evolution yields of CH4 and CO have been increased to 0.31 μmol/g/h and 9.52 μmol/g/h. It is proved that that STAO/BiOBr
site accelerate the CO$_2$RR reaction both in thermodynamics and kinetics, which provides a new possibility for the application of CO$_2$RR.

![Figure 3](image1.png)

**Figure 3.** Visible-light-driven photocatalytic CO$_2$ reduction performance. Time-varying gas evolution of a. CH$_4$ and b. CO. (c) 5-hours’ statistical average performance. 420 nm UV cut filter was used for the test.

In order to better understand the reaction mechanism of single site, UV–vis absorption spectra had been carried out (Figure 4a). We can see that BiOBr substrate is a very good visible light response material. With the loading of the single sites, the absorption of visible light increased slightly. The bandgap of the as-prepared BiOBr and STAO/BiOBr was estimated to be 2.38 and 2.32 eV (Figure 4b). The single site also brings the change of energy band structure, which improves the absorption capacity of visible-light and makes the photocatalytic reaction more conducive to occur. Figure 4c shows the transformation of photoluminescence (PL), demonstrate that the separation ability of photogenerated carriers was enhanced with the introduction of single site. The enhancement of optical absorption and the separation of photo generated carrier are beneficial to improve the efficiency of CO$_2$ reduction reaction.

![Figure 4](image2.png)

**Figure 4.** (a) UV–vis absorption spectra of the STAO/BiOBr and BiOBr. (b) Tauc plots of the STAO/BiOBr and BiOBr. (c) PL spectra of the STAO/BiOBr and BiOBr.

In summary, STAO was successfully loaded on BiOBr substrate, and a large number of oxygen vacancies were introduced. The single site was proved to be favorable for the occurrence of CO$_2$RR. This point has been proved from the point of view of dynamics and thermodynamics. This study provides a new idea for people to explore the structure-activity relationship of active sites in CO$_2$RR, especially the relationship between single site and the efficiency.

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