**RESEARCH ARTICLE** 



# Ultra-Thin Carbon-Doped Bi<sub>2</sub>WO<sub>6</sub> Nanosheets for Enhanced Photocatalytic CO<sub>2</sub> Reduction

Han Li<sup>1</sup> · Junchao Zhang<sup>1</sup> · Jiaguo Yu<sup>1</sup> · Shaowen Cao<sup>1</sup>

Received: 24 March 2021 / Revised: 11 April 2021 / Accepted: 23 April 2021 / Published online: 20 May 2021 © The Author(s) 2021

#### Abstract

The photocatalytic reduction of  $CO_2$  is a promising strategy to generate chemical fuels. However, this reaction usually suffers from low photoactivity because of insufficient light absorption and rapid charge recombination. Defect engineering has become an effective approach to improve the photocatalytic activity. Herein, ultra-thin (~4.1 nm) carbon-doped Bi<sub>2</sub>WO<sub>6</sub> nanosheets were prepared via hydrothermal treatment followed by calcination. The ultra-thin nanosheet structure of the catalyst not only provides more active sites but also shortens the diffusion distance of charge carriers, thereby suppressing charge recombination. Moreover, carbon doping could successfully extend the light absorption range of the catalyst and remarkably promote charge separation, thus inhibiting recombination. As a result, the as-prepared Bi<sub>2</sub>WO<sub>6</sub> photocatalyst with ultra-thin nanosheet structure and carbon doping exhibits enhanced photocatalytic CO<sub>2</sub> reduction performance, which is twice that of pristine ultra-thin Bi<sub>2</sub>WO<sub>6</sub> nanosheet. This study highlights the importance of defect engineering in photocatalytic energy conversion and provides new insights for fabricating efficient photocatalysts.

Keyword Defect engineering  $\cdot$  Bi<sub>2</sub>WO<sub>6</sub> nanosheet  $\cdot$  Charge separation  $\cdot$  Light absorption

# Introduction

The massive consumption of fossil fuels over the last several decades has led to the energy crisis and global warming [1, 2]. The photocatalytic conversion of  $CO_2$  into chemical fuels is widely believed to be a very promising approach to solve energy and environmental problems [3–8]. Although several photocatalysts, including CdS [9], TiO<sub>2</sub> [10], ZnIn<sub>2</sub>S<sub>4</sub> [11], and polymeric carbon nitride [12, 13], have been explored, the serious recombination of photogenerated charge carriers in these materials limits their photocatalytic efficiency [14, 15].

Bismuth tungstate ( $Bi_2WO_6$ ), the simplest among the Aurivillius oxides, has attracted great attention on account of its layered structure, non-toxicity, and chemical stability [16, 17]. Despite these advantages, however, pristine  $Bi_2WO_6$  exhibits only moderate photocatalytic  $CO_2$  activity because of extensive charge recombination. Therefore,

various strategies, including morphology design [18], heteroatom doping [19, 20], heterojunction construction [21, 22], and coupling with cocatalysts [23], have been developed to enhance the photocatalytic  $CO_2$  reduction activity. Studies have confirmed that heteroatom doping is an effective approach to enhance the photocatalytic performance of Bi<sub>2</sub>WO<sub>6</sub>.

Herein, we propose a facile hydrothermal and calcination method to prepare ultra-thin carbon-doped  $Bi_2WO_6$ nanosheets ( $Bi_2WO_6s$ ) with improved photocatalytic  $CO_2$ reduction activity. The thickness of the C-doped  $Bi_2WO_6$ nanosheets ( $C-Bi_2WO_6s$ ) is within ~4.1 nm. Carbon doping not only successfully extended the light absorption range of the nanosheet but also greatly promoted charge separation, thereby inhibited recombination. The ultra-thin  $Bi_2WO_6$ nanosheet exhibited relatively high  $CO_2$  photoreduction performance as a result of its increased active sites and excellent charge separation.

Shaowen Cao swcao@whut.edu.cn

<sup>&</sup>lt;sup>1</sup> State Key Laboratory of Advanced Technology for Materials Synthesis and Processing, Wuhan University of Technology, Wuhan 430070, China

#### Experimental

#### Preparation of C-Bi<sub>2</sub>WO<sub>6</sub>s

C-Bi<sub>2</sub>WO<sub>6</sub>s were prepared by a facile hydrothermal and calcination method. In brief, 0.5 mmol of Na<sub>2</sub>WO<sub>4</sub>·2H<sub>2</sub>O and 0.025 g of hexadecyltrimethylammonium bromide (CTAB) were added to 40 mL of deionized water and mixed to obtain a solution. Then, 1 mmol of  $Bi(NO_3)_3 \cdot 5H_2O$  was added to the above solution, and the suspension was magnetically stirred for 60 min. The suspension was poured into a 50 mL Teflon-lined autoclave and hydrothermally treated at 120 °C for 24 h. The reactor was cooled to room temperature naturally, and the obtained sample was collected, washed three times with deionized water, and then dried at 60 °C in a vacuum oven for 12 h. The dry powder was placed in a tube furnace and calcined in a nitrogen gas atmosphere at 350 °C for 1 h with a heating rate of 3 °C/min. Finally, the obtained powder was denoted as C-Bi<sub>2</sub>WO<sub>6</sub>s. Carbon doping was



Fig. 1 XRD patterns of bulk Bi<sub>2</sub>WO<sub>6</sub>, Bi<sub>2</sub>WO<sub>6</sub>s, and C-Bi<sub>2</sub>WO<sub>6</sub>s

realized by the carbonization of long carbon links in the residual CTAB.

## **Results and Discussion**

## **Structure and Morphology**

The X-ray diffraction (XRD) patterns of bulk  $Bi_2WO_6$ , pristine  $Bi_2WO_6s$ , and C- $Bi_2WO_6s$  are shown in Fig. 1. The diffraction peaks of the samples could be indexed to those of orthorhombic  $Bi_2WO_6$  (JCPDS Card No. 73–2020) [16]. No diffraction peaks assigned to carbon were observed in the XRD patterns, thus suggesting the high dispersibility of the element [24]. Compared with those of bulk  $Bi_2WO_6$  and  $Bi_2WO_6s$ , the diffraction angles of C- $Bi_2WO_6s$  showed no changes, thereby indicating that carbon doping does not change the crystalline phase of  $Bi_2WO_6$  [25]. The XRD peaks of  $Bi_2WO_6s$  and  $C-Bi_2WO_6s$  were weaker and broader compared with those of bulk  $Bi_2WO_6$ . [23]. According to the Scherrer equation, a smaller grain size results in broader XRD peaks.

Field emission scanning electron microscopy (Fig. 2) and transmission electron microscopy (TEM; Fig. 3) were performed to investigate the microstructures of the samples. Interestingly, compared with bulk Bi<sub>2</sub>WO<sub>6</sub>, both Bi<sub>2</sub>WO<sub>6</sub>s and C-Bi<sub>2</sub>WO<sub>6</sub>s showed ultra-thin nanosheet structures, but the latter has small deformation, which could be attributed to the calcination treatment. Furthermore, this nanosheet-like structure of the samples was further confirmed by TEM and atomic force microscopy (AFM). The TEM micrographs in Fig. 3a and b reveal nearly transparent features, which suggests an ultra-thin nanosheet structure. The high-resolution TEM micrographs also demonstrated marked interplanar spacings of (200) and (020) planes, which correspond to the orientation of the Bi<sub>2</sub>WO<sub>6</sub> nanosheet along the [001] projection [17]. The AFM image of C-Bi<sub>2</sub>WO<sub>6</sub>s shown in Fig. 3c reveals an average nanosheet thickness of ~4.1 nm,



Fig. 2 Field emission scanning electron micrographs of a bulk Bi<sub>2</sub>WO<sub>6</sub>, b Bi<sub>2</sub>WO<sub>6</sub>s, and c C-Bi<sub>2</sub>WO<sub>6</sub>s



Fig. 3 Transmission electron and high-resolution transmission electron micrographs of a  $Bi_2WO_6s$  and b C- $Bi_2WO_6s$ . c Atomic force microscopic image of C- $Bi_2WO_6s$ 

which corresponds to approximately three layers of  $Bi_2WO_6$ . These results demonstrate the intercalation of CTAB during the formation of the ultra-thin  $Bi_2WO_6$  nanosheets. As a long carbon chain surfactant, CTAB could intercalate into the interlayers of  $Bi_2WO_6$ , thereby inducing the formation of ultra-thin  $Bi_2WO_6$  nanosheets. Such an ultra-thin nanosheet structure could increase the availability of active sites and shorten the migration distance of charge carriers, thereby achieving effective charge separation [16, 26].

Energy-dispersive spectrometry (EDS) and elemental mapping were conducted to clarify the elemental composition of the C-Bi<sub>2</sub>WO<sub>6</sub>s catalyst. The EDS spectrum provided in Fig. 4 demonstrates that the elements Bi, W, C, and O are uniformly distributed in the C-Bi<sub>2</sub>WO<sub>6</sub>s catalyst. To further clarify the carbon content in the C-Bi<sub>2</sub>WO<sub>6</sub>s catalyst, C

elemental analysis was carried out using an elemental analyzer. The elemental analysis result revealed that the atomic composition of C was about 0.36%.

## X-Ray Photoelectron Spectroscopic Analysis

X-ray photoelectron spectroscopy (XPS) was performed on  $Bi_2WO_6s$  and  $C-Bi_2WO_6s$ , as shown in Fig. 5, to confirm the successful doping of carbon into  $Bi_2WO_6s$ . The survey XPS spectra confirmed the existence of Bi, W, O, and C in  $Bi_2WO_6s$  and  $C-Bi_2WO_6s$ . The high-resolution spectrum of Bi could be fitted to two peaks at 164.26 and 158.96 eV, which, respectively, correspond to Bi  $4f_{5/2}$ and Bi  $4f_{7/2}$  in  $Bi^{3+}$  [27]. After carbon doping, the binding energy of Bi shifted toward higher energy, thereby



Fig. 4 a Field emission scanning electron micrograph and b corresponding EDS spectrum of C-Bi<sub>2</sub>WO<sub>6</sub>s. Elemental mappings of C-Bi<sub>2</sub>WO<sub>6</sub>s: c Bi, d W, e C, and f O

Fig. 5 a X-ray photoelectron survey (XPS) spectra of  $Bi_2WO_6s$  and C- $Bi_2WO_6s$ . High-resolution XPS spectra of **b** Bi 4f, **c** W 4f, **d** O 1 s, and **e** C1s of  $Bi_2WO_6s$  and C- $Bi_2WO_6s$ 



indicating the presence of Bi-C interactions. The binding energies of W at 37.36 and 35.26 eV in the XPS spectrum of  $Bi_2WO_6s$  correspond to the W<sup>6+</sup> oxidation state. The binding energy of W also shifted toward higher binding energy, thus suggesting the successful doping of C. The binding energy of O in Bi<sub>2</sub>WO<sub>6</sub>s could be fitted to two peaks at 529.9 and 531.51 eV, which correspond to Bi-O and W-O, respectively. The binding energy of O 1s in C-Bi<sub>2</sub>WO<sub>6</sub>s slightly shifted, and the peak at 533.06 eV could be attributed to physically adsorbed water. The binding energy shifts of Bi, W, and O reflect strong interactions between Bi<sub>2</sub>WO<sub>6</sub> and C [27, 28]. The binding energies of C 1s centered at 284.8, 286.3, and 288.8 eV could be assigned to C-C sp<sup>2</sup>-hybridized carbon on surface, C-O, and COO bonds, respectively, thus indicating that carbon was successfully doped into the Bi<sub>2</sub>WO<sub>6</sub> nanosheets.

#### N<sub>2</sub> Adsorption–Desorption Isotherms

The curves of all  $Bi_2WO_6$  samples were classified as type IV isotherms according to the Brunauer–Deming–Deming–Teller classification (Fig. 6) [29]. Moreover, the curves of all  $Bi_2WO_6$  samples showed a type H3 hysteresis loop, suggests that slit-like pores formed due to the stacking and aggregation of plate-like particles, which is in agreement with the sheet-like morphology of  $Bi_2WO_6$ . The pore size distribution curves confirm the presence of mesopores and macropores in the  $Bi_2WO_6$  samples. The Brunauer–Emmett–Teller (BET) surface areas of bulk  $Bi_2WO_6$ ,  $Bi_2WO_6$ s, and C- $Bi_2WO_6$ s were measured to be 15.5, 43.8, and 42.7 m<sup>2</sup>/g, respectively. Compared with that of  $Bi_2WO_6$ s, the specific surface area of C- $Bi_2WO_6$ s showed no obvious change, thus suggesting that the microstructure of  $Bi_2WO_6$ s is well preserved after carbon doping by thermal



Fig. 6  $N_2$  adsorption-desorption isotherms of bulk  $Bi_2WO_6$ ,  $Bi_2WO_6$ s, and C- $Bi_2WO_6$ s and the corresponding pore-size distribution curves

treatment. These results collectively confirm the formation of ultra-thin nanosheet structures, which increase the BET surface area of the material and provide more active sites for greater photocatalytic activity.

### CO<sub>2</sub> Adsorption

The CO<sub>2</sub> adsorption curves of the samples were measured and are shown in Fig. 7.  $Bi_2WO_6s$  and  $C-Bi_2WO_6s$  show similar CO<sub>2</sub> adsorption performance, which is 4 times higher than that of the bulk  $Bi_2WO_6$ . This enhanced CO<sub>2</sub> adsorption ability is mainly attributed to large specific surface area [16, 30]. The comparable CO<sub>2</sub> adsorption capacity of the two nanosheet samples indicated that carbon doping does



Fig.7 CO2 adsorption isotherms of bulk  $\rm Bi_2WO_6,~Bi_2WO_6s,~and~C\text{-}Bi_2WO_6s$ 

not significantly change the catalyst microstructure, which is consistent with the  $N_2$  adsorption–desorption results. Enhancements in  $CO_2$  adsorption capacity can reinforce the photocatalytic  $CO_2$  reduction activity of the prepared materials [31].

## **UV–Visible Diffuse Reflectance Spectra**

Figure 8 shows the UV–Vis absorption spectra of bulk Bi<sub>2</sub>WO<sub>6</sub>, Bi<sub>2</sub>WO<sub>6</sub>s, and C-Bi<sub>2</sub>WO<sub>6</sub>s. The absorption edge of bulk Bi<sub>2</sub>WO<sub>6</sub> was approximately 430 nm, which corresponds to a band gap of 2.88 eV. Moreover, the absorption edge of Bi<sub>2</sub>WO<sub>6</sub>s was blue-shifted compared with that of bulk  $Bi_2WO_6$  because of the quantum size effect [32]. Compared with that of Bi<sub>2</sub>WO<sub>6</sub>s, the absorption edge of C-Bi<sub>2</sub>WO<sub>6</sub>s was red-shifted, thereby indicating uniform carbon doping. Extension of the absorption tail was also observed in C-Bi<sub>2</sub>WO<sub>6</sub>s, which suggests that doping-related mid-gap states are generated and that these states regulate the band structure of Bi<sub>2</sub>WO<sub>6</sub>s. C-Bi<sub>2</sub>WO<sub>6</sub>s showed enhanced light absorption in the full-range visible-light region, which implies that, besides the lattice, carbon is also doped on the surface of Bi<sub>2</sub>WO<sub>6</sub>. These results indicate that carbon doping could reduce the band gap of Bi<sub>2</sub>WO<sub>6</sub> nanosheets and enhance their light absorption [33].

#### Mott–Schottky Curves and Band Structure

Mott–Schottky plots were constructed, as shown in Fig. 9a–c, to confirm the band structures of the samples. All of the samples are typical n-type semiconductors, as evidenced by their positive slopes [34]. The flat-band potentials of bulk  $Bi_2WO_6$ ,  $Bi_2WO_6s$ , and  $C-Bi_2WO_6s$  were – 1.08, – 1.30, and – 1.11 V (vs. Ag/AgCl, pH=7),



Fig. 8 UV-Vis absorption spectra of the prepared samples





Fig. 10 Photocatalytic CO<sub>2</sub> reduction performance of bulk  $Bi_2WO_6$ ,  $Bi_2WO_6s$ , and C- $Bi_2WO_6s$ 

respectively. A more negative conduction band (CB) compared with that of bulk  $Bi_2WO_6$  implies that the reduction ability of electrons is enhanced [35]. The more positive CB potential of C-Bi<sub>2</sub>WO<sub>6</sub>s compared with that of  $Bi_2WO_6$ s may be attributed to carbon doping [36]. The corresponding band structures of bulk  $Bi_2WO_6$ ,  $Bi_2WO_6$ s, and C-Bi<sub>2</sub>WO<sub>6</sub>s are shown in Fig. 9d. The CB of the  $Bi_2WO_6$  photocatalyst was more negative than the potential of the CO<sub>2</sub>/reduced-product redox couple and, thus, could provide sufficient driving force for CO<sub>2</sub> reduction [33, 37, 38].

Photocatalytic CO<sub>2</sub> Reduction and *In-Situ* FTIR Analysis

The photocatalytic  $CO_2$  reduction performance of all samples was measured under full-spectrum irradiation. As shown in Fig. 10, the generation rates of CH<sub>3</sub>OH and C<sub>2</sub>H<sub>5</sub>OH for Bi<sub>2</sub>WO<sub>6</sub>s were remarkably enhanced by approximately 4.7 and 3.0 times, respectively, compared with those of bulk Bi<sub>2</sub>WO<sub>6</sub>. Compared with that of Bi<sub>2</sub>WO<sub>6</sub>s, the photocatalytic CO<sub>2</sub> reduction activity of C-Bi<sub>2</sub>WO<sub>6</sub>s was further improved, and the corresponding generation rates of CH<sub>3</sub>OH and C<sub>2</sub>H<sub>5</sub>OH were 1.15 and 0.65 µmol/(g·h), respectively.



Fig. 11 In-situ FTIR spectra of C-Bi<sub>2</sub>WO<sub>6</sub>s





This photocatalytic performance is comparable with those of other bismuth-based photocatalysts (Table S1).

The photocatalytic reduction of CO<sub>2</sub> over C-Bi<sub>2</sub>WO<sub>6</sub>s was investigated by in-situ Fourier transform infrared (FTIR) spectroscopy. As shown in Fig. 11, the peak at 1648 cm<sup>-1</sup> can be attributed to  $H_2O$  [39]. The peaks at 1684, 1670, 1662, 1575, 1559, and 1256  $cm^{-1}$  can be attributed to carboxylate  $(CO_2^-)$  [39–42]. The peaks at 1696, 1636, 1623, 1617, 1458, 1449, 1436, 1406, 1397, and 1227 cm<sup>-1</sup> are ascribed to bicarbonate (HCO<sub>2</sub>) [39, 40, 42–46]. The peaks at 1654, 1361, 1340, and 1318  $cm^{-1}$ refer to bidentate carbonate  $(b-CO_3^{2-})$  [40, 43, 46]. The peaks at 1569, 1541, 1532, 1522, 1508, 1498, 1488, 1474, 1466, and 1388 cm<sup>-1</sup> are attributed to monodentate carbonate (m-CO<sub>3</sub><sup>2-</sup>) [39–41, 43, 47–49]. After light irradiation, a number of new peaks were observed. The peaks at 1375 and 1318  $\text{cm}^{-1}$  are assigned to formate [50]. The peak at 1419  $\text{cm}^{-1}$  is related to formaldehyde (HCHO) [35], and the peak at 1162  $\text{cm}^{-1}$  is ascribed to methoxyl groups ( $CH_3OH$ ) [31, 51]. The presence of these peaks, which indicate intermediate products, reveals that CO<sub>2</sub> conversion over C-Bi<sub>2</sub>WO<sub>6</sub>s is a multi-electron reduction process.

## Mechanism of Photocatalytic Performance Enhancement

The charge transfer and separation dynamics of bulk  $Bi_2WO_6$ ,  $Bi_2WO_6s$ , and  $C-Bi_2WO_6s$  were studied by transient photocurrent response analysis and electrochemical impedance spectroscopy (EIS). The photocurrent intensity of  $C-Bi_2WO_6s$  was larger than those of bulk  $Bi_2WO_6$  and  $Bi_2WO_6s$  (Fig. 12a), suggesting the best electron transfer efficiency and lowest charge carrier recombination rate of  $C-Bi_2WO_6s$  sample [52]. Anodic spikes were observed in all samples when the light was switched on because of the separation of photogenerated electrons and holes at the interface

of  $Bi_2WO_6$ /electrolyte. A decrease in photocurrent was subsequently observed, because photogenerated holes tend to recombine with electrons instead of undergoing capture by reduced species in the electrolyte. The EIS Nyquist plots of all samples were also obtained, as shown in Fig. 12b. A smaller semicircular radius usually indicates lower chargetransfer resistance. Among the samples studied, C-Bi<sub>2</sub>WO<sub>6</sub>s showed the smallest arc radius, which suggests that charge transfer occurs fastest in this sample.

# Conclusions

In summary, ultra-thin (~4.1 nm) carbon-doped  $Bi_2WO_6$ nanosheets were prepared by a simple hydrothermal treatment and calcination method. The prepared  $Bi_2WO_6$ nanosheets exhibited twofold enhanced photocatalytic activity for  $CO_2$  reduction compared with that of pristine ultrathin  $Bi_2WO_6$  nanosheets. This enhancement was attributed to the ultra-thin nanosheet structure and carbon doping. An ultra-thin nanosheet structure provides more active sites and shortens the diffusion distance of charge carriers, thereby suppressing charge recombination. Carbon doping extends the light absorption ability of the catalyst and promotes charge separation. This work highlights the importance of defect engineering in photocatalytic energy conversion and provides new insights for fabricating efficient two-dimensional photocatalysts.

Supplementary Information The online version contains supplementary material available at https://doi.org/10.1007/s12209-021-00289-5.

Acknowledgements The authors acknowledge the financial support from the National Key Research and Development Program of China (No. 2018YFB1502001), the National Natural Science Foundation of China (Nos. 51922081, 21773179, 51961135303, 51932007 and U1705251).

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Shaowen Cao (State Key Laboratory of Advanced Technology for Materials Synthesis and Processing, Wuhan University of Technology) received his B.S. in Geochemistry in 2005 from the University of Science and Technology of China, and his Ph.D. in Materials Chemistry & Physics in 2010 from the Shanghai Institute of Ceramics, Chinese Academy of Sciences. He then worked as a Research Fellow at the School of Materials Science and Engineering, Nanyang Technological University until Feb

2014. He is now a professor at State Key Laboratory of Advanced Technology for Materials Synthesis and Processing, Wuhan University of Technology. From Mar 2018 to Feb 2020, he was a Visiting Scientist at Max Planck Institute of Colloids and Interfaces. His current research interests include the design and fabrication of photocatalytic materials for energy and environmental applications. He is the author or co-author of more than 100 peer-reviewed scientific papers published on Chem. Soc. Rev., Joule, Adv. Mater., Angew. Chem. Int. Ed., Chinese J. Catal. etc., with over 12000 citations, an H-index 57 and 19 ESI highly cited papers. He is also one of the "Highly Cited Researchers" from 2018 to 2020 awarded by Clarivate Analytics.