Z-Scheme Heterojunction of SnS$_2$/Bi$_2$WO$_6$ for Photoreduction of CO$_2$ to 100% Alcohol Products by Promoting the Separation of Photogenerated Charges

Yong Xu, Juanjuan Yu, Jianfei Long, Lingxiao Tu, Weili Dai * and Lixia Yang

Key Laboratory of Jiangxi Province for Persistent Pollutants Control and Resources Recycle, School of Environmental and Chemical Engineering, Nanchang Hangkong University, Nanchang 330063, China; xu_yong001@163.com (Y.X.); qddxshhh_1@sina.com (J.Y.); 15007047545@139.com (J.L.); 20202085700109@stu.nchu.edu.cn (L.T.); zgay20080808@126.com (L.Y.)

* Correspondence: wldai81@126.com

Abstract: Using sunlight to convert CO$_2$ into solar fuel is an ideal solution to both global warming and the energy crisis. The construction of direct Z-scheme heterojunctions is an effective method to overcome the shortcomings of single-component or conventional heterogeneous photocatalysts for photocatalytic CO$_2$ (carbon dioxide) reduction. In this work, a composite photocatalyst of narrow-gap SnS$_2$ and stable oxide Bi$_2$WO$_6$ were prepared by a simple hydrothermal method. The combination of Bi$_2$WO$_6$ and SnS$_2$ narrows the bandgap, thereby broadening the absorption edge and increasing the absorption intensity of visible light. Photoluminescence, transient photocurrent, and electrochemical impedance showed that the coupling of SnS$_2$ and Bi$_2$WO$_6$ enhances the efficiency of photogenerated charge separation. The experimental results show that the electron transfer in the Z-scheme heterojunction of SnS$_2$/Bi$_2$WO$_6$ enables the CO$_2$ reduction reactions to take place. The photocatalytic reduction of CO$_2$ is carried out in pure water phase without electron donor, and the products are only methanol and ethanol. By constructing a Z-scheme heterojunction, the photocatalytic activity of the SnS$_2$/Bi$_2$WO$_6$ composite was improved to 3.3 times that of pure SnS$_2$.

Keywords: Bi$_2$WO$_6$; SnS$_2$; photocatalytic CO$_2$ reduction; charge separation; liquid phase products

1. Introduction

The fossil fuels dilemma has become a serious issue that must be confronted and tried to solve, especially for the demand of industrial development in today’s society [1–3]. Inspired by natural photosynthesis, the conversion of CO$_2$ into renewable energy driven by light is widely claimed to be the most promising and environmentally friendly way to deal with the global greenhouse effect [4–6]. Although a great deal of effort has been made to transform CO$_2$ into valuable chemicals, it is rarely reported that the reduction products are alcohol products with high selectivity [5,7]. More importantly, C2 hydrocarbons are hard to form because it is difficult for C-C coupling reaction to occur and more electrons and protons are needed to participate in the reaction. Another important issue is that semiconductor catalysts suffer from the sluggish charge separation efficiency ascribing to the fast recombination of photogenerated electrons and holes during the photoreaction process [8–10].

In order to improve the efficiency of charge separation as well as the durability of photocatalysts, a great many measures have been taken including adding cocatalysts, manufacturing defects or doping elements in the bulk materials, forming heterojunction, and so on [11–14]. The construction of heterojunction can not only improve the light absorption capacity but also enhance the separation efficiency of photogenerated charge. For example, Guo et al. constructed a Z-scheme NiTiO$_3$/g-C$_3$N$_4$ (NT/GCN) photocatalyst by a facile calcination method. In the absence of any sacrificial agent and cocatalyst, the
optimized NT/GCN40 can obtain the highest CH$_3$OH yield (13.74 μmol·g$^{-1}$·h$^{-1}$), which is almost 3.29 times that of g-C$_3$N$_4$ [15]. Wang et al. designed and fabricated 0D/2D direct Z-scheme heterojunction involving carbonized polymer dots and Bi$_4$O$_5$Br$_2$ nanosheets (CPDs/Bi$_4$O$_5$Br$_2$), which effectively facilitate migration and separation efficiency of photogenerated carriers and retain more negative electron reduction potential of CPDs and more positive hole production potential of Bi$_4$O$_5$Br$_2$. The 8 wt% CPDs/Bi$_4$O$_5$Br$_2$ exhibits the maximal CO production of 132.42 μmol h$^{-1}$g$^{-1}$ under Xe lamp irradiation, 5.43-fold higher than that of Bi$_4$O$_5$Br$_2$ nanosheets [16].

SnS$_2$, as a narrow bandgap semiconductor, is nontoxic and has a bandgap value of 2.2–2.4 eV, which can absorb visible light efficiently. It has a CdI$_2$-type layered structure, and the force between the layers is the weak van der Waals force. SnS$_2$ has good chemical thermal stability and oxidation resistance in acidic and neutral solutions, so it has been favored by researchers as a new type of visible light response photocatalyst in recent years [17]. Wu et al. successfully fabricated the SnS-SnS$_2$ Z-scheme heterostructure with nanosheet framework by post-annealing in a specified atmosphere to partially convert the SnS$_2$ matrix into SnS. The converted SnS possesses CO$_2$ adsorption sites with significantly reduced activation energy, which can be used to drive the rate-determining step for efficient CO$_2$ conversion. The final Z-scheme SnS-SnS$_2$ heterostructure enhances the photocatalytic activity of CO$_2$ conversion to C2 and C3 hydrocarbons [18]. Wu et al. constructed a novel direct Z-scheme g-C$_3$N$_4$/SnS$_2$ heterojunction by in situ deposition of SnS$_2$ quantum dots onto the g-C$_3$N$_4$ surface by a simple one-step hydrothermal method. The transfer of electrons from g-C$_3$N$_4$ to SnS$_2$ results in the formation of an intra-interface electric field (IEF) between the two semiconductors. Compared with g-C$_3$N$_4$ and SnS$_2$ alone, the g-C$_3$N$_4$/SnS$_2$ hybrid showed better performance of photocatalytic CO$_2$ reduction [19]. Bi$_2$WO$_6$ is a semiconductor multi-element oxide with the bandgap of 2.75 eV, which has a certain response under visible light. Bi$_2$WO$_6$ is a direct bandgap semiconductor, the photogenerated electrons and holes generated by illumination have a high probability of direct recombination. So, the photon quantum efficiency is low. In addition, the Bi$_2$WO$_6$ material also has a small specific surface area, and the photogenerated charges are easily recombined in the bulk phase, which limits its practical application. According to the energy band matching theory, the energy band positions of SnS$_2$ and Bi$_2$WO$_6$ match each other, and the combination of SnS$_2$ and Bi$_2$WO$_6$ can effectively reduce the recombination of photogenerated electron-hole pairs, thereby achieving the purpose of improving the photocatalytic efficiency. Here, we constructed stable Bi$_2$WO$_6$ oxide semiconductors and SnS$_2$ narrow-bandgap semiconductors as Z-scheme heterojunctions to improve the separation efficiency of photogenerated electrons and holes, thereby enhancing the photocatalytic activity. We also expanded the application of SnS$_2$/Bi$_2$WO$_6$ in photocatalytic reduction of CO$_2$ and obtained 100% alcohol.

2. Materials and Methods

2.1. Sample Preparation

2.1.1. Preparation of Flower-like SnS$_2$

SnCl$_4$·5H$_2$O (0.525 g) was dissolved into ethylene glycol (80 mL), and then CH$_4$N$_2$S (thiourea, 0.609 g) was added. The above solution was stirred until dissolved, and dispersed uniformly by ultrasonic wave. Then the mixture was transferred into 100 mL of autoclave and the temperature was kept at 180 °C for 18 h. Finally, the product was washed with ethanol and distilled water.

2.1.2. Preparation of SnS$_2$/Bi$_2$WO$_6$

Bi(NO$_3$)$_3$·5H$_2$O (0.485 g) and Na$_2$WO$_4$·2H$_2$O (0.165 g) were dissolved in 10 mL of ethylene glycol solution, respectively. After dissolving, the two solutions were mixed and dispersed by ultrasonic treatment. SnS$_2$ was dissolved in ethylene glycol (60 mL) solution and sonicated for 30 min, then slowly added dropwise to the above solution. The obtained yellow mixture was transferred into a 100 mL of autoclave, and the temperature was kept...
at 160 °C for 24 h. The product was washed three times with ethanol and distilled water, respectively. The mass ratio of SnS$_2$: Bi$_2$WO$_6$ was 0.025:1, 0.05:1, 0.1:1, and 0.15:1, thus the composites were named as SnS$_2$/Bi$_2$WO$_6$-2.5, SnS$_2$/Bi$_2$WO$_6$-5, SnS$_2$/Bi$_2$WO$_6$-10, and SnS$_2$/Bi$_2$WO$_6$-15, respectively.

2.2. Characterization

X-ray diffraction (XRD) patterns of prepared samples were determined on a D/max-3 X-ray diffractometer (Bruker, Germany) using Cu K$_\alpha$ radiation ($\lambda = 0.154056$ Å). The detailed surface morphology of catalysts was characterized by employing a Nova Nano SEM450 (FEI, Hillsboro, OR, USA) field-emission scanning electron microscope (SEM) and transmission electron microscopy (TEM) images were obtained with JEOL JEM-2100F (Hitachi, Japan) operated at 200 kV. X-ray photoelectron spectroscopy (XPS) analysis was carried out by a Kratos Axis Ultra DLD spectrometer (VERTEX 70, Bruker, Germany) with a monochromatic Al K$_\alpha$ X-ray source. The property about light absorption of catalysts were determined with a UV-vis spectrophotometer (Hitachi U-3900H, Tokyo, Japan). Photoluminescence (PL) spectra were obtained using a fluorescence spectrophotometer (Hitachi F-7000, Tokyo, Japan). Transient spectra of the testing samples were recorded with time-resolved fluorescence spectroscopy (Edinburgh, Scotland, FS5).

2.3. Photoelectrochemical Measurements

The transient photocurrent response, EIS and Mott–Schottky curves were carried out on the electrochemical workstation (CHI660E, Shanghai) in a standard three-electrode system with the Pt mesh as the counter electrode, the Ag/AgCl (saturated KCl) as the reference electrode, and the sample loaded photocathode as the working electrode in 0.1 M Na$_2$SO$_4$ aqueous solution (electrolyte solution) at room temperature. The distance between the counter electrode and the working electrode is 2 cm. Indium tin oxide (ITO) with a 1 cm × 1 cm area photocatalyst was used as the working electrode. The photocurrent measurement of the photocatalyst is measured by several switching cycles of light irradiated by a 300 W xenon lamp (using a 420 nm cut-off filter).

The photoelectrode in this system is prepared as follows: 10 mg of powder sample was dispersed in 0.2 mL of a mixed solution of ethanol and H$_2$O (H$_2$O:ethanol = 1:1 v/v), then 5 µL of Nafion solution was added, and the mixture was sonicated for several minutes. Finally, the obtained slurry was coated on an ITO glass substrate in an area of 1 × 1 cm.

2.4. Photocatalytic CO$_2$ Reduction

Light-driven reduction of CO$_2$ was performed in a closed 200 mL quartz glass reactor containing 50 mL of ultrapure water and 0.05 g of photocatalyst at atmospheric pressure. A 300 W Xe arc lamp (PLS-SXE300, Beijing, China) with a 420 nm cut-off filter was positioned 5 cm above the reactor as a visible light source. Before irradiation, high purity CO$_2$ gas (99.995%) was bubbled into above suspension for 30 min to expel air and dissolved oxygen. During the whole catalytic process, CO$_2$ gas was bubbled into the solution at a rate of 50 mL per minute. Since the efficiency in photocatalytic reduction of CO$_2$ is dependent on both the solubility in water and reaction temperature, 4 °C is optimal for this reaction by considering the trade-off between solubility and temperature. The yields of obtained alcohols were determined by sampling the suspension (1 mL) every hour and filtering it with a specific membrane to remove the solid catalysts. The aimed products such as methanol and ethanol were quantitatively monitored with Agilent Technologies 7890A gas chromatography (Shanghai China, FID detector, DB-WAX column). The detailed diagram of the catalytic reaction device is shown in Figure S1.

3. Results

3.1. Characterization of Materials

Figure 1 shows the XRD patterns of pure SnS$_2$, Bi$_2$WO$_6$ and the composite materials with different mass ratios. The pattern of unmodified Bi$_2$WO$_6$ suggests all the diffraction
peaks are indexed to the orthorhombic phase (JCPDS No. 39-0256). The main diffraction peaks at 28.3°, 32.8°, 47.0°, and 55.9° correspond to the crystal planes of (131), (200), (260), and (133), respectively. Bi$_2$WO$_6$ has a larger half-width value, and it can be inferred that Bi$_2$WO$_6$ has a small grain size, which can provide more reactive sites. The pure phase of SnS$_2$ mainly has six diffraction peaks, which are consistent with the (001), (100), (101), (102), (110), and (111) planes of the standard card (No. 23-0677). With the increase of the molar ratio of SnS$_2$, the diffraction peaks of (101) and (111) crystal planes of SnS$_2$ gradually appeared. Since the diffraction peak of SnS$_2$ in the composite material is not obvious, the amount of SnS$_2$ was increased to 50%, and the obtained XRD patterns are shown in Figure S2. The diffraction peaks of the material with 50% content of SnS$_2$ become relatively obvious, especially the diffraction peaks around 15° and 50°. This is due to the different degree of crystallization of materials SnS$_2$ and Bi$_2$WO$_6$, which leads to the obvious difference in the intensity of their diffraction peaks. When the two are combined, the diffraction peaks belonging to SnS$_2$ will be easily masked by Bi$_2$WO$_6$, especially the peaks near the strong diffraction peaks at 28.3° and 32.6°. Therefore, this leads to masking of the two strongest diffraction peaks near these positions in SnS$_2$. The half-peak width of (131) composite is slightly larger than that of pure Bi$_2$WO$_6$ (Figure 1). This phenomenon shows that during the hydrothermal process, due to the interaction between the two materials, the single material will be less likely to aggregate, resulting in a slight decrease in the crystallinity of the material [20]. The BET test in Figure S3 shows that the specific surface areas of Bi$_2$WO$_6$ and SnS$_2$/Bi$_2$WO$_6$-10 are 25.70 and 37.13 m$^2$/g, respectively, which indicates that the specific surface area of the composite is significantly increased, while the pore size is slightly reduced.

![XRD patterns of prepared materials.](image)

The flower-like SnS$_2$ spheres were prepared by hydrothermal method, as shown in Figure 2a, the diameter distribution ranges from 2 µm to 5 µm. According to Figure 2b, it can be seen more clearly that the spherical SnS$_2$ is formed by self-assembly with regular two-dimensional nanosheets. Moreover, the reaction process may be due to the adsorption of ethylene glycol on the precursors of SnS$_2$, then the intermolecular force as well as crystal growth orientation make the nanosheets self-assemble into the flower-like spheres. The thickness of nanosheets is about 50 nm, besides there are large pores between the nanosheets, which is conducive to the adsorption of CO$_2$. This unique porous structure can provide a large number of catalytic active sites and charge transport channels, therefore, the flower-like SnS$_2$ has higher photocatalytic activity than that of SnS$_2$ synthesized by traditional method. Figure 2c,d shows the SEM images of the composite SnS$_2$/Bi$_2$WO$_6$-10 obtained by the hydrothermal reaction, while the morphology of nanospheres has no obvious change because of the high dispersion of Bi$_2$WO$_6$. As can be seen from the TEM image (Figure 2e), the SnS$_2$ spheres consist of staggered nanosheets. Two different lattice distances of 0.278 and 0.315 nm can be observed in the high-resolution TEM (HRTEM) image (Figure 2f), corresponding to the (101) plane of SnS$_2$ and the (131) plane of Bi$_2$WO$_6$. 


Nanomaterials 2022, 12, x FOR PEER REVIEW 5 of 12

10 obtained by the hydrothermal reaction, while the morphology of nanospheres has no

ages of SnS2/Bi2WO6-10, red arrows and red lines indicate the lattice spacings.

Figure 2. (a,b) SEM images of flower-like SnS2, (c,d) SEM images of SnS2/Bi2WO6-10, (e,f) TEM images of SnS2/Bi2WO6-10, red arrows and red lines indicate the lattice spacings.

As shown in Figure 3a, an obvious redshift occurs from SnS2 to SnS2/Bi2WO6-10, which is beneficial to absorb visible light. The combination of SnS2 and Bi2WO6 makes the bandgap narrow, thus broadening the absorption edges and improving the absorption intensity of visible light. The bandgaps are determined using the Tauc/Davis–Mott model described by the equation: \((a\nu)^{1/n} = A(\nu - E_g)\) [21]. The exponent \(n\) denotes the natural properties of the material, and the value of \(n\) is 0.5 for the direct bandgap. The fitting results (Figure 3b) suggest that the bandgaps of SnS2, Bi2WO6, and SnS2/Bi2WO6-10 are 2.14, 2.75, and 2.26 eV, respectively.

XPS studies were carried out to investigate the surface elemental compositions and chemical states. As depicted in Figure S6, the XPS survey spectrum of SnS2/Bi2WO6-10 indicates that elements of Bi, W, O, Sn, and S exist in the sample. The Bi 4f spectrum of SnS2/Bi2WO6-10 can be deconvoluted into two peaks with spin orbits of Bi 4f7/2 and Bi 4f5/2, and the binding energies locate at 158.74 and 164.07 eV assigning to the Bi3+ species in Bi2WO6 lattice [22]. The peaks located at 34.95 and 37.12 eV are assigned to W 4f7/2 and W 4f5/2 (Figure 4b), respectively, indicating the oxidation state of W6+ in SnS2/Bi2WO6-10 composite [23]. Figure 4c displays the high-resolution spectra of Sn 3d, and two characteristic peaks at 486.77 and 495.19 eV ascribe to the inner electrons of Sn 3d5/2 and Sn 3d3/2 in SnS2, demonstrating the feature of Sn4+ species in SnS2/Bi2WO6-10 [24].
The peaks located at 161.67 and 162.53 eV are assigned to S 2p3/2 and S 2p1/2 (Figure 4d), respectively, indicating the oxidation state of S^{2-} in SnS_{2}/Bi_{2}WO_{6}-10 composite. According to the high-resolution XPS spectra, the binding energies of Bi 4f and W 4f move to the direction of lower binding energy in SnS_{2}/Bi_{2}WO_{6}-10, while the peaks of Sn 3d shift to the direction of larger binding energy. The result suggests that the electron density of Bi and W increases, while the electron density of Sn is reduced, which indicates that there is a strong interaction between Bi_{2}WO_{6} and SnS_{2}, giving rise to the formation of heterojunction.

**Figure 3.** (a) Ultraviolet-visible diffuse reflectance spectra, (b) corresponding plots of (αhν)^2 versus energy (hν) for the bandgap energies.

**Figure 4.** High-resolution XPS spectra of (a) Bi 4f, (b) W 4f, (c) Sn 3d, and (d) S 2p.

### 3.2. Improvement of Photogenerated Charge Separation

Photoluminescence (PL) is an effective as well as simple method to evaluate the probability of photogenerated electron-hole recombination. Figure 5a shows the fluorescence spectra of SnS_{2}, Bi_{2}WO_{6}, and SnS_{2}/Bi_{2}WO_{6}-10 composite catalysts with different mass ratios, SnS_{2} and SnS_{2}/Bi_{2}WO_{6} with different ratios having similar main peak positions under 300 nm laser excitation. Compared with SnS_{2} and Bi_{2}WO_{6} material, the PL intensity of composite materials is significantly reduced due to suppressing the recombination of electron-hole pairs. Therefore, more photoexcited electrons can participate in the reaction of CO_{2} reduction. In addition, the time-resolved PL decay spectra of Bi_{2}WO_{6} and SnS_{2}/Bi_{2}WO_{6}-10 are shown in Figure 5b, and the average lifetimes are 1.75 and 0.78 ns,
respectively. This indicates that the addition of SnS$_2$ will endow the material with effective charge separation, proving the formation of Z-scheme heterojunction between SnS$_2$ and Bi$_2$WO$_6$.

![Figure 5. (a) Photoluminescence spectra, (b) time-resolved PL decay spectra, (c) transient photocurrent response, (d) EIS Nyquist plots.](image)

The photocurrent response spectra were tested using a three-electrode system in the electrolyte of 0.5 M Na$_2$SO$_4$. As can be seen in Figure 5c, in the continuous on-off conversion of visible light, the samples show a relatively stable photocurrent curve, indicating the photogenerated electrons are effectively captured by the photoelectrochemical system. The catalyst with the largest photocurrent is SnS$_2$/Bi$_2$WO$_6$-10, which is about four times that of pure phase SnS$_2$. The composite material of SnS$_2$/Bi$_2$WO$_6$ can effectively accelerate the migration of electrons and prolong the lifetime of photogenerated electrons, thus benefitting for improving the efficiency of photocatalytic reduction of CO$_2$. Electrochemical impedance spectroscopy (EIS) is presented in Figure 5d, the smaller the radius, the faster the charge transfer on the surface of electrode [25]. From the photocurrent response and EIS spectra, we can see that the Z-scheme heterojunction interface formed by an appropriate amount of SnS$_2$ and Bi$_2$WO$_6$ will facilitate the separation and transport of photogenerated charges. However, when the content of SnS$_2$ is further increased, the sheet-like morphology of SnS$_2$ will cover Bi$_2$WO$_6$ nanoparticles, resulting in poor light absorption. In addition, SnS$_2$ is prone to recombination of photogenerated electrons and holes due to its narrow bandgap. Therefore, the photocurrent of SnS$_2$/Bi$_2$WO$_6$-15 is lower than that of SnS$_2$/Bi$_2$WO$_6$-10. While the impedance of SnS$_2$/Bi$_2$WO$_6$-15 is higher than that of SnS$_2$/Bi$_2$WO$_6$-10. It can be seen that the radius of SnS$_2$/Bi$_2$WO$_6$-10 in all materials is the smallest, which confirms that SnS$_2$/Bi$_2$WO$_6$-10 possesses an interface that can accelerate the charge transfer, in accordance with the results of PL and photocurrent. At the same time, the Z-scheme heterojunction interface formed with an appropriate amount of SnS$_2$ and Bi$_2$WO$_6$ will facilitate the separation and transport of photogenerated charges. However, when the content of SnS$_2$ is further increased, the sheet-like morphology of SnS$_2$ will cover Bi$_2$WO$_6$ nanoparticles, resulting in poor light absorption. In addition, SnS$_2$ is prone to recombination of photogenerated electrons and holes due to its narrow bandgap.
3.3. Photochemical Reduction of CO$_2$

Photoreduction of CO$_2$ was performed in a closed 200 mL quartz glass reactor containing 50 mL of ultrapure water saturated with CO$_2$ and 50 mg of prepared photocatalysts under the irradiation of visible light. After 4 h of photoreaction, only methanol and ethanol were detected as the final products. As presented in Figure 6, with the increase of SnS$_2$ in the composites, the yields of methanol and ethanol first increase and then decrease. When the amount of SnS$_2$ reaches 10%, the composite photocatalyst shows the highest catalytic activity. The production rate of methanol and ethanol is 50.2 $\mu$mol g$^{-1}$ and 19.7 $\mu$mol g$^{-1}$ in 4 h respectively, which is nearly 3.3 times that of pure SnS$_2$, according to the number of transferred electrons. The yields of methanol and ethanol are shown in Table 1. Moreover, the photocatalytic performance of SnS$_2$/Bi$_2$WO$_6$-10 is superior to that of similar photocatalysts reported in other literature (Table S1). The photocatalytic performance starts to decline with further increase in the amount of SnS$_2$, this conclusion is in line with the results of PL, photocurrent, and EIS. When the amount of SnS$_2$ reaches a certain level, the catalytic ability drops suddenly, which implies that the excessive SnS$_2$ is not conducive to the timely transfer of photogenerated electrons to Bi$_2$WO$_6$ through Z-scheme heterojunction. In addition, it is worth mentioning that the conduction band (CB) reduction potential of Bi$_2$WO$_6$ is theoretically insufficient to directly reduce CO$_2$ to alcohols. However, after CO$_2$ is dissolved into water to form CO$_3^{2-}$ and other species, the reduction potential is sufficient to reduce carbonate species to alcohols [26].

![Figure 6](image-url)

**Figure 6.** Time dependence of yields of (a) methanol and (b) ethanol during photoreduction of CO$_2$.

| Sample        | Yield of Methanol ($\mu$mol g$^{-1}$) | Yield of Ethanol ($\mu$mol g$^{-1}$) |
|---------------|---------------------------------------|--------------------------------------|
| Bi$_2$WO$_6$  | 14.11                                 | 9.00                                 |
| SnS$_2$       | 10.55                                 | 8.18                                 |
| SnS$_2$/Bi$_2$WO$_6$-2.5 | 24.97                             | 14.76                                 |
| SnS$_2$/Bi$_2$WO$_6$-5  | 32.18                             | 13.94                                 |
| SnS$_2$/Bi$_2$WO$_6$-10 | 50.20                             | 19.70                                 |
| SnS$_2$/Bi$_2$WO$_6$-15 | 37.58                             | 16.82                                 |

The control experiments showed that the products of methanol and ethanol were not detected in the dark or without catalyst, indicating that the light source and catalyst are essential factors for photochemical reduction of CO$_2$. No carbon-containing product was detected when CO$_2$ was replaced by N$_2$, suggesting CO$_2$ is also a necessary condition for CO$_2$ photosplitting. In other words, the element of C in the products is derived from the reactant CO$_2$. In order to investigate the stability of SnS$_2$/Bi$_2$WO$_6$-10, the cycling experiment was carried out. At the end of each cycle, the reaction suspension was centrifuged, after washing with distilled water for several times, it was dried in vacuum at 60 °C for next
run. As shown in Figure S7, the catalytic performance of SnS2/Bi2WO6-10 shows a slight decrease after four consecutive cycles. Figure S8 is the XRD pattern of SnS2/Bi2WO6-10 after four cycles, which is consistent with fresh one, further proving its good stability.

Figure 7a shows the Mott–Schottky plots of flower-like SnS2 and Bi2WO6 at voltages from −1.0 to 1.0 V. Classified according to the conductive properties of semiconductors, flower-shaped spherical SnS2 and Bi2WO6 nanoparticle materials belong to n-type semiconductors. The flat band potential (Vfb) of SnS2 is −0.44 V vs. SCE (saturated calomel electrode), which is equivalent to −0.20 V vs. NHE (normal hydrogen electrode), so the CB potential (Vcb) of flower-shaped spherical SnS2 can be calculated to be −0.40 V. The Vfb of Bi2WO6 is −0.32 V vs. SCE, which is equivalent to −0.080 V vs. NHE, so the Vcb of Bi2WO6 can be calculated to be -0.280 V. According to the photocatalytic theory [27], the potentials for photocatalytic reduction of CO2 to methanol and ethanol are −0.38 V and −0.33 V (vs. NHE, pH = 7.00), respectively. Therefore, the Z-scheme heterojunction composed of SnS2 and Bi2WO6 has sufficient reduction ability to reduce CO2 to methanol and ethanol. In addition, the surface photovoltage test (Figure 7b) further shows that the SnS2/Bi2WO6-10 has higher surface photovoltage after photoexcitation, thus more photogenerated electrons will transfer to the surface active sites, and the photoreduction efficiency of CO2 is significantly improved compared to pure phase of SnS2 and Bi2WO6.

Figure 7. Mott–Schottky plot of (a) Bi2WO6 and SnS2, (b) surface photovoltage spectra.

Based on the above experimental results and discussion, the possible reaction mechanism is as follows: electrons (e−) in the valence bands (VBs) of SnS2 and Bi2WO6 are excited and transfer to the CBs under sunlight irradiation, thus leaving the same number of holes (h+) in the VBs of SnS2 and Bi2WO6. Then, the photogenerated electrons on the CB of Bi2WO6 are transferred to the VB of SnS2, subsequently the electrons are excited to the CB of SnS2. Therefore, the photogenerated electrons and holes of the SnS2/Bi2WO6 photocatalyst are effectively separated by constructing Z-scheme heterojunction. Based on Equations (1)–(3) [28], the electrons on the CB of SnS2 have enough reduction ability to reduce the CO2 to methanol and ethanol. This is further demonstrated by Pt photodeposition experiment on SnS2/Bi2WO6-10 (Figure S9). In addition, the Bi2WO6 sphere is composed of intricate nanosheets, so some intermediates (−CH3, OCH3) may not be converted into methanol immediately, and the dimerization reaction takes place, and finally ethanol can be formed (Figure 8).

\[
\begin{align*}
\text{CO}_2 + 6\text{H}^+ + 6\text{e}^- & \rightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O} - 0.38 \text{ V} \\
2\text{CO}_2 + 12\text{H}^+ + 12\text{e}^- & \rightarrow \text{C}_2\text{H}_5\text{OH} + \text{H}_2\text{O} - 0.33 \text{ V} \\
\text{H}_2\text{O} + 4\text{h}^+ & \rightarrow \text{O}_2 + 4\text{H}^+ 0.82 \text{ V}
\end{align*}
\]
4. Conclusions

Here, flower-like SnS$_2$ microspheres were successfully prepared by hydrothermal method, and SnS$_2$/Bi$_2$WO$_6$ composites with different mass ratios were synthesized. Among them, SnS$_2$/Bi$_2$WO$_6$-10 exhibited the highest catalytic activity in the photochemical reduction of CO$_2$ without sacrificial agent, and only methanol and ethanol were detected as reduction products. The improvement of catalytic activity is attributed to the formation of Z-scheme heterojunction between SnS$_2$ and Bi$_2$WO$_6$. Under sunlight irradiation, the photogenerated electrons on the CB of Bi$_2$WO$_6$ will be transferred to the VB of SnS$_2$. Therefore, the photogenerated electrons and holes of the SnS$_2$/Bi$_2$WO$_6$ photocatalyst are effectively separated, which effectively inhibits the recombination of photogenerated electron-hole pairs and expands the light absorption range. Finally, the yield of CO$_2$ photoreduction to alcohol products was 3.3 times higher than that of SnS$_2$ in pure water.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/nano12122030/s1. Figure S1: Reaction device diagram. Figure S2: XRD spectra of SnS$_2$/Bi$_2$WO$_6$. Figure S3: (a) N$_2$ adsorption-desorption isotherms, and (b) pore size distribution profiles of Bi$_2$WO$_6$ and SnS$_2$/Bi$_2$WO$_6$-10. Figure S4: HRTEM spectra of SnS$_2$/Bi$_2$WO$_6$-10. Figure S5: EDX spectrum of SnS$_2$/Bi$_2$WO$_6$-10. Figure S6: XPS survey spectra of Bi$_2$WO$_6$ and SnS$_2$/Bi$_2$WO$_6$-10. Figure S7: Cycling tests with catalyst SnS$_2$/Bi$_2$WO$_6$-10 for 4 h irradiation. Figure S8: XRD patterns before and after recycling. Figure S9: HRTEM spectra of 1%Pt-SnS$_2$/Bi$_2$WO$_6$-10. Table S1: The comparison of CO$_2$ photoreduction performance. References [29–35] are cited in the supplementary materials.

Author Contributions: Conceptualization, W.D.; methodology, Y.X.; validation, J.Y. and J.L.; formal analysis, L.T.; investigation, L.Y.; resources, W.D.; data curation, Y.X.; writing—original draft preparation, Y.X.; writing—review and editing, J.L.; visualization, J.Y.; supervision, J.L.; project administration, L.T.; funding acquisition, W.D. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the National Natural Science Foundation of China (Grants 52072165, 51662031, 51720105001, 51938007 and 51868051), and the project funded by China Postdoctoral Science Foundation (2019M653583). We are grateful for the financial support received for the project.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.
27. Li, K.; Peng, B.S.; Peng, T.Y. Recent advances in heterogeneous photocatalytic CO\textsubscript{2} conversion to solar fuels. *ACS Catal.* 2016, 6, 7485–7527. [CrossRef]

28. Dai, W.L.; Long, J.F.; Yang, L.X.; Zhang, S.Q.; Xu, Y.; Luo, X.B.; Zou, J.P.; Luo, S.L. Oxygen migration triggering molybdenum exposure in oxygen vacancy-rich ultra-thin Bi\textsubscript{2}MoO\textsubscript{6} nanoflakes: Dual binding sites governing selective CO\textsubscript{2} reduction into liquid hydrocarbons. *J. Energy Chem.* 2021, 61, 281–289. [CrossRef]

29. Dai, W.L.; Yu, J.J.; Xu, H.; Hu, X.; Luo, X.B.; Yang, L.X.; Tu, X.M. Synthesis of hierarchical flower-like Bi\textsubscript{2}MoO\textsubscript{6} microspheres as efficient photocatalyst for photoreduction of CO\textsubscript{2} into solar fuels under visible light. *CrystEngComm* 2016, 18, 3472–3480. [CrossRef]

30. Xu, F.; Zhu, B.; Cheng, B.; Yu, J.G.; Xu, J.S. 1D/2D TiO\textsubscript{2}/MoS\textsubscript{2} hybrid nanostructures for enhanced photocatalytic CO\textsubscript{2} reduction. *Adv. Opt. Mater.* 2018, 6, 1800911. [CrossRef]

31. Yang, G.; Chen, D.; Ding, H.; Feng, J.; Zhang, J.Z.; Zhu, Y.; Hamid, S.; Bahnemann, D.W. Well-designed 3D ZnIn\textsubscript{2}S\textsubscript{4} nanosheets/TiO\textsubscript{2} nanobelts as direct Z-scheme photocatalysts for CO\textsubscript{2} photoreduction into renewable hydrocarbon fuel with high efficiency. *Appl. Catal. B* 2017, 219, 611–618. [CrossRef]

32. Yan, Y.; Yu, Y.; Huang, S.; Yang, Y.; Yang, X.; Yin, S.; Cao, Y. Adjustment and matching of energy band of TiO\textsubscript{2}-based photocatalysts by metal ions (Pd, Cu, Mn) for photoreduction of CO\textsubscript{2} into CH\textsubscript{4}. *J. Phys. Chem. C* 2017, 121, 1089–1098. [CrossRef]

33. Dai, W.L.; Xu, H.; Yu, J.J.; Hu, X.; Luo, X.B.; Tu, X.M.; Yang, L.X. Photocatalytic reduction of CO\textsubscript{2} into methanol and ethanol over conducting polymers modified Bi\textsubscript{2}WO\textsubscript{6} microspheres under visible light. *Appl. Surf. Sci.* 2015, 367, 798, 173–180. [CrossRef]

34. Al-Mhyawi, S.R.; Salam, M.A. Enhancement of photocatalytic activity of Gd(OH)\textsubscript{3} nanoparticles by Pd deposition for reduction of CO\textsubscript{2} to methanol. *J. Photoch. Photobio. A* 2018, 367, 89–93. [CrossRef]

35. Abdullah, H.; Khan, M.R.; Pudukudy, M.; Yaakob, Z.; Ismail, N.A. CeO\textsubscript{2}-TiO\textsubscript{2} as a visible light active catalyst for the photoreduction of CO\textsubscript{2} to methanol. *J. Rare Earth.* 2015, 11, 1155–1161. [CrossRef]