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Carbon Dioxide Photoreduction on the $\text{Bi}_2\text{S}_3/\text{MoS}_2$ Catalyst

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Received: 8 November 2019; Accepted: 25 November 2019; Published: 27 November 2019

Abstract: The photocatalytic activity of a material is contingent on efficient light absorption, fast electron excitation, and control of the recombination rate by effective charge separation. Inorganic materials manufactured in unique shapes via controlled synthesis can exhibit significantly improved properties. Here, n-type Bi_2S_3 nanorods (with good optical activity) were wrapped with two-dimensional (2D) p-type MoS_2 sheets, which have good light absorption properties. The designed p-n junction $\text{Bi}_2\text{S}_3/\text{MoS}_2$ composite exhibited enhanced light absorption over the entire wavelength range, and higher carbon dioxide adsorption capacity and photocurrent density compared to the single catalysts. Consequently, the activity of the $1\text{Bi}_2\text{S}_3/1\text{MoS}_2$ composite catalyst for the photocatalytic reduction of carbon dioxide was more than 20 times higher than that of the single catalysts under visible-light irradiation at ≤ 400 nm, with partial selectivity for CO conversion. This is attributed to the p-n heterojunction $\text{Bi}_2\text{S}_3/\text{MoS}_2$ composite designed in this study, the high light absorption of n- Bi_2S_3 , accelerated electron excitation, and the electron affinity of the 2D sheet-p- MoS_2 , which quickly absorbed excited electrons, resulting in effective charge separation. This ultimately improved the catalytic performance by continuously supplying catalytically active sites to the heterojunction interfaces.

Keywords: CO_2 photoreduction; effective charge separation; p-n heterojunction $\text{Bi}_2\text{S}_3/\text{MoS}_2$ composite; Selective CO production

1. Introduction

The greatest challenge for an eco-friendly CO_2 -to-fuel system, which produces fuel by photocatalytically reducing carbon dioxide under visible light, is the development of stable and highly efficient photocatalysts. Chalcogenides are currently highly topical as candidate materials for this purpose and extensive studies of these materials have been conducted. Chalcogenides are an attractive research theme because their physicochemical properties vary with their unique shape and size. Furthermore, the shape and size of these materials can be easily controlled by the synthesis methods [1,2]. In particular, chalcogenides have small band-gaps and large extinction coefficients, and can be utilized in various applications such as batteries [3], gas sensors [4], and photodetectors [5]. In recent years, due to their wide light absorption ability, the application of chalcogenides as photocatalysts that are active under visible-light irradiation has been actively studied.

Chalcogen compounds, such as CdS [6], ZnS [7], SnS_2 [8], NiS [9], Bi_2S_3 [10], CuS [11], and MoS_2 [12], can be used for water decomposition or CO_2 conversion, and these have produced quite reliable results. Specifically, CdS has been evaluated as one of the most promising catalyst candidates for water decomposition under visible light, which is thermodynamically advantageous, as the positions of the valence and conduction bands overlap with the oxidation and reduction potentials of

water [13,14]. However, CdS suffers from the inherent disadvantage of low efficiency due to inefficient charge separation between the electrons and holes generated by the absorption of photons, and is self-decomposing due to its structural instability in water [15]. Therefore, the catalytic performance varies widely depending on the degree of overlap between the redox potential of the selected chemical reaction and the band-gap of the catalyst. Thus, designing a stable and highly active chalcogen photocatalyst for a given reaction is a very attractive challenge. Additionally, by controlling the morphology of chalcogenides, significantly improved properties can be derived from the unique shapes generated at various stages of synthesis.

Here, p-type MoS₂ with excellent light absorption ability is prepared as 2D-structured nanosheets, and n-type Bi₂S₃ with excellent optical activity and a nanorod morphology is also prepared. A heterojunction comprising the two types of particles is designed to create a heterojunction composite system. Weng and coworkers suggested that the use of MoS₂ nanosheets to coat the surface of Bi₂S₃ discoids by a facile anion-exchange strategy accelerates the light-harvesting efficiency and charge separation, and helps faster charge transport and collection, leading to higher activity in the photocatalytic reduction of Cr(VI) under visible-light irradiation ($\lambda > 400$ nm) [16]. As another example, Ke and coworkers reported that a prepared Bi₂O₃/Bi₂S₃/MoS₂ nanocomposite exhibits improved photocatalytic activity for water oxidation ($529.1 \mu\text{mol h}^{-1} \text{g}^{-1}_{\text{cat}}$), with a value that is 1.5 and 12.5 times higher than that of pure Bi₂O₃ and MoS₂, respectively, under simulated solar-light irradiation [17]. Ultimately, in this study, we propose that p-type MoS₂ particles, which lack electrons, will easily accept electrons excited by n-type Bi₂S₃ particles that have a narrow band-gap (which facilitates excitation of the electrons by the absorbed visible light [18]). Consequently, it was expected that the cycle of electron flow would proceed smoothly and separation between the electrons and holes would progress effectively. Furthermore, we anticipated that sulfur deficient sites [19] would be formed at the new interfaces between the two particles, which would eventually act as reaction sites, leading to enhanced catalytic activity.

2. Results and Discussion

2.1. Physical Properties of Catalysts

Figure 1 shows the X-ray diffraction patterns of the as-synthesized Bi₂S₃, MoS₂, 1Bi₂S₃/1MoS₂, 2Bi₂S₃/1MoS₂, and 1Bi₂S₃/2MoS₂ particles. The XRD (X-ray diffraction) pattern of as-synthesized Bi₂S₃ indicated the formation of orthorhombic phase Bi₂S₃ (JCPDS No. 002-0391) [20]. No other crystalline phases were detected in the product. The XRD patterns show that the sample was mainly composed of rhombohedral MoS₂, and the diffraction peaks at $2\theta = 14.5^\circ$, 33° , 40° , and 58° are ascribed to the (002), (100), (103), and (110) lattice planes of crystalline MoS₂ (JCPDS card No. 037-1492) [21]. Extremely broad reflection peaks were observed in the profile of the MoS₂ particles, which indicated that the obtained MoS₂ sample was nano-sized. The XRD profile of the heterojunction Bi₂S₃/MoS₂ catalysts clearly showed the characteristic peaks of Bi₂S₃, but the peak assigned to the (002) plane of MoS₂ was hardly visible. The expanded spacing of the MoS₂ (002) plane resulted from the synthesis conditions. The spacing usually increases in the alkali solution, and in addition, the environmental temperature also has a critical effect. In particular, the expanding becomes large in both the alkali environment and the low temperature. At this time, it is reported that the new shifted peak ($2\theta = 9.3^\circ$) associated with the expanded (002) d-spacing was observed [22]. However, at temperatures higher than 220 °C, the spacing of the (002) plane of MoS₂ did not be expanded [23]. In this study, perhaps both the alkali environment and the low temperature (180 °C) caused the expansion of the (002) plane of MoS₂ in Bi₂S₃/MoS₂ heterojunction materials. Furthermore, in the 1Bi₂S₃/2MoS₂ sample, a new peak associated with the expanded (002) plane was also seen at $2\theta = 9.3^\circ$. The intensity of the characteristic peaks of the Bi₂S₃ particles increased in proportion to the concentration added during the synthesis step. However, the crystallite sizes obtained from the Scherrer equation [24] based on the (111) plane, which is the characteristic peak of Bi₂S₃ nanoparticles, decreased slightly with increasing addition of MoS₂.

The crystallite sizes were 10, 9, 8, and 7 nm, respectively, for Bi_2S_3 , $1\text{Bi}_2\text{S}_3/1\text{MoS}_2$, $2\text{Bi}_2\text{S}_3/1\text{MoS}_2$, and $1\text{Bi}_2\text{S}_3/2\text{MoS}_2$. From these results, we predicted that the crystallite sizes of Bi_2S_3 in the $\text{Bi}_2\text{S}_3/\text{MoS}_2$ heterojunction composites did not change and the shape was maintained, even when different amounts of Bi_2S_3 and MoS_2 were incorporated into the heterocapsulated catalysts.

Figure 1. XRD patterns of all of catalysts.

The Bi_2S_3 particles comprising 50–60 nm wide and 100–150 nm long rods are shown in the TEM (Transmission Electron Microscope) image in Figure 2. The MoS_2 sample had a wide and thin sheet morphology. In the heterojunction $\text{Bi}_2\text{S}_3/\text{MoS}_2$ samples, the rod-shaped Bi_2S_3 was wrapped by a thin sheet of MoS_2 . Increasing the amount of MoS_2 led to complete wrapping of the Bi_2S_3 particles by MoS_2 . From these results, it was deduced that the two particles were uniformly structured and aligned for wrapping by electrostatic attraction during heterojunction formation.

Figure 2. TEM images of all of catalysts.

HRTEM (High-resolution transmission electron microscope) (Figure 3A), selected area electron diffraction (SAED) (Figure 3B), and element mapping analysis (Figure 3C) were performed for $1\text{Bi}_2\text{S}_3/1\text{MoS}_2$ as a prototype of the heterojunction catalysts, and the results are shown in Figure 3. The fringe spacing parallel to the nanorod was estimated to be 3.55 and 6.34 Å in Bi_2S_3 and MoS_2 , which indicates that crystal growth occurred preferentially in the (111) and (002) directions, respectively. Additionally, some of the characteristic peaks identified in the XRD pattern could be seen in this figure. The SAED pattern of Bi_2S_3 recorded for the regularly spaced orthorhombic phase exhibited diffraction rings, thereby indicating that the orthorhombic phase was polycrystalline and could be readily indexed as the Bi_2S_3 phase. A circle attributed to the (002) plane was also observed, which also corresponds to the rhombohedral MoS_2 nanosheet. Based on these results, we deduced that each of the crystallized particles, $1\text{Bi}_2\text{S}_3$ and 1MoS_2 , existed stably in the $1\text{Bi}_2\text{S}_3/1\text{MoS}_2$ heterojunction particle with no crystal change. However, element mapping by TEM confirmed that all components ($1\text{Bi}_2\text{S}_3$ or 1MoS_2) of the catalyst were uniformly dispersed in the catalyst; particularly, it was confirmed that MoS_2 uniformly wrapped Bi_2S_3 as an outer layer. Moreover, there were almost no impurities such as C and O.

Figure 3. HRTEM image (A) of 1Bi₂S₃/1MoS₂ catalyst, selected area electron diffraction (SAED) pattern (B), and element mapping images (C) of each element.

The EDS (Energy Dispersive X-ray Spectroscopy) spectrum in Figure 4 showed the presence of only Bi and S on the surface of Bi₂S₃, and the atomic ratio of Bi:S was close to the stoichiometric value of 2:3, as shown in the inset table. In the EDS spectrum of the MoS₂ particles, only Mo and S components were observed, and no other impurities were found. The ratio of Mo:S, as shown in the inset table (Figure 4), was about 1:2. The atomic ratio of Bi₂S₃ and MoS₂ once again suggested reliability of the synthesis. These ratios were almost the same as the theoretical values used in the synthesis step. On the other hand, all the components of the Bi₂S₃/MoS₂ heterojunction particles were detected in the EDS spectrum, and the intensities of the peaks were proportional to the contents. The theoretical metal/S ratio of the 1Bi₂S₃/1MoS₂ particles is 1:1.68. However, the actual surface ratio of Mo + Bi/S was 1:1.73, where the sulfur content was relatively high. In the 2Bi₂S₃/1MoS₂ heterojunction particle, the theoretical ratio of Mo + Bi/S is 1:1.6, but the actual surface ratio was 1:1.9. For the 1Bi₂S₃/2MoS₂ heterojunction particles, the theoretical ratio of Mo + Bi/S is 1:1.75, but the surface composition ratio of Mo + Bi/S was 1:1.99. This result suggests that more elemental sulfur is exposed on the surface of the Bi₂S₃/MoS₂ heterojunction particles than on the surfaces of the pure particles. Ultimately, this result is also related to the disulfide peaks observed in the XPS (X-ray Photoelectron Spectroscopy) profile and may be responsible for defects in the edges of the heterojunction particles.

Figure 4. EDS patterns for all of catalysts and their compositional ratios.

Typical high-resolution quantitative Bi 4f, Mo 3d, and S 2p in Bi₂S₃, MoS₂, and 1Bi₂S₃/1MoS₂ XPS spectra are presented in Figure 5. The characteristic orbital peaks occurred at different positions in the full scan for each sample (Figure 5a). The highest intensity peaks for the Mo 3d, Bi 4f, and S 2p states are presented in Figure 5b. The deconvoluted peaks of the Mo 3d_{5/2} and Mo 3d_{3/2} states, located at binding energies of 229.1 and 232.4 eV, respectively, are attributed to Mo⁴⁺ in the MoS₂ sample [25]. A small peak due to Mo⁶⁺ [26] was observed at 235.5 eV, but this peak was negligibly small. The Mo 3d_{5/2} peak located at the lower binding energy of 228.4 eV in the profile of the 1Bi₂S₃/1MoS₂ sample corresponds to the reduced Mo atoms due to sulfur vacancies [27]. Moreover, an overlapping peak of Mo⁶⁺ and a singlet S 1s peak was observed at 225.7 eV due to sulfur defects [27]. Additionally, Kwok and coworkers reported the presence of edge S-defect sites (S 2p) in MoS₂ nanosheets within a mesoporous silica shell [28], such as Mo_V=O sites that are comparable to molybdenum oxysulfides (MoO_xS_y), bridging disulfides (S–S)_{br}^{2–}, shared disulfides (S–S)_{sh}^{2–}, and terminal disulfides (S–S)_t^{2–}. Notably, the disulfide ligands at these defect sites can be easily removed to expose unsaturated Mo⁴⁺ sites, and have been suggested as the active sites. In this study, the O 1s and S 2p peaks were also observed in the full range spectrum of MoS₂ (Figure 5a). This result means that Mo present in the 1Bi₂S₃/1MoS₂ heterojunction catalyst is not present as MoS₂, but as MoO_xS_y. Eventually, this results in more defects in MoS₂, which are believed to act as catalytically active sites. Two peaks respectively corresponding to the Bi 4f_{5/2} and Bi 4f_{7/2} states of Bi³⁺ appeared at 163.8 and 158.4 eV in the profile of the Bi₂S₃ sample (Figure 5b). Bi₂S₃ remain unchanged after the formation of Bi₂S₃/MoS₂ heterojunction. The peaks at 161 and 162.3 eV could be assigned to the S 2p state, and the S 2s XPS peak at the higher binding energy of 225.7 eV is consistent with the Bi–S species [29]. From these results, we confirmed that after heterojunction formation, there was no significant change in the Bi₂S₃ crystal, but the oxidation state of Mo in the MoS₂ crystal was lowered. Ultimately, this is believed to lead to the formation of S defects and to increase the capacity for carbon dioxide adsorption.

Figure 5. XPS curves at full range (A) and binding energy curves (B) for Mo 3d, Bi 4f, and S 2s.

2.2. Carbon Dioxide Photoreduction on Catalysts

Before entering the full-scale CO_2 photoreduction experiment, an isotopic experiment using $^{13}\text{CO}_2$ as the substrate was performed under the same photocatalytic reaction conditions to further verify the source of the generated CO, and the products were analyzed by gas chromatography and mass spectrometry. The peak at $m/z = 29$ could be assigned to ^{13}CO , indicating that the carbon source for the formation of CO was the CO_2 used. When the CO_2 was replaced with N_2 , no detectable products were formed. When CO_2 was subsequently added to the reaction mixture with the clean photocatalyst (Ar gas/ H_2O /catalyst/ CO_2 gas/light on), the product formation yield increased, providing strong evidence of product formation from CO_2 . This means that the final carbon compounds produced were exclusively generated by the reduction of externally injected CO_2 , which was the only

carbon source in this study. Additionally, isotopic study of $1\text{Bi}_2\text{S}_3/1\text{MoS}_2$ in the presence of moist $^{13}\text{CO}_2$ was performed, as shown in Figure 6. Various signals of isotopic carbon compounds, ^{13}C , $^{13}\text{CH}_2$, $^{13}\text{CH}_3$, $^{13}\text{CH}_4$, ^{13}CO , $^{13}\text{CH}_3\text{OH}$, and H^{13}COOH were observed at $m/z = 13, 15, 16, 17, 29, 33$, and 47, respectively, and the $^{13}\text{CO}_2$ carbon source was detected at $m/z = 45$. Generally, the overall photoreduction reaction of CO_2 to CH_4 is a very complicated process that includes the transfer of eight electrons and eight protons, breaking of C–O bonds, and the formation of C–H bonds. There are two pathways, and both pathways preferentially follow the two-electron mechanism. Here, the formaldehyde pathway (fast hydrogenation pathway) follows the path $\text{CO}_2 \rightarrow \text{HCOOH} \rightarrow \text{HCHO} \rightarrow \text{CH}_3\text{OH} \rightarrow \text{CH}_4$, which is thermodynamically feasible [30]. However, no HCHO was detected in the GC-MS analysis. The favorable production of HCOOH as an intermediate increases CO production, and the favorable production of HCHO increases CH_4 production. Mass analysis showed that the $1\text{Bi}_2\text{S}_3/1\text{MoS}_2$ catalyst produced slightly more CH_3OH than CH_4 . Overall, the production of CH_4 from the complete reduction of CO_2 in the presence of the $1\text{Bi}_2\text{S}_3/1\text{MoS}_2$ heterojunction catalysts seems to be unfavorable.

Figure 6. Product distributions observed in ^{13}C -mass spectrum during CO_2 photoconversion over $\text{Bi}_2\text{S}_3/\text{MoS}_2$ heterojunction catalyst.

CO_2 reduction was conducted under visible-light irradiation. As illustrated in Figure 7, the amount of CO generated increased almost linearly with the irradiation time for all of the catalysts. However, the amount of CO generated with the pure MoS_2 and Bi_2S_3 catalysts was minimal, whereas the conversion to CO in the presence of the heterojunctioned $\text{Bi}_2\text{S}_3/\text{MoS}_2$ catalysts increased surprisingly. There was no selectivity for CH_4 when only Bi_2S_3 was used, whereas the heterojunctioned catalysts exhibited selectivity. The total amount of CO and CH_4 generated from CO_2 was similar for the $2\text{Bi}_2\text{S}_3/1\text{MoS}_2$ and $1\text{Bi}_2\text{S}_3/2\text{MoS}_2$ catalysts after 10 h. However, a high CO evolution of $40 \mu\text{mol g}^{-1}$ ($42.5 \mu\text{mol g}^{-1}$ for total amounts of CO and CH_4) was achieved with the $1\text{Bi}_2\text{S}_3/1\text{MoS}_2$ catalyst, having a junction comprising 1:1 Bi_2S_3 and MoS_2 , under photo-illumination for 10 h. These results reveal that the activity of $1\text{Bi}_2\text{S}_3/1\text{MoS}_2$ for CO_2 reduction was comparable to that of other catalysts. The total yield obtained with the $1\text{Bi}_2\text{S}_3/1\text{MoS}_2$ composite did not change significantly after five cycles (1 cycle

corresponds to 10 h of reaction), as shown in Figure 7B), indicating the excellent stability of the $1\text{Bi}_2\text{S}_3/1\text{MoS}_2$ heterojunction catalyst.

Figure 7. Carbon dioxide photoconversion in the presence of catalysts under visible-light (A) and recycling test for $\text{Bi}_2\text{S}_3/\text{MoS}_2$ heterojunction catalyst (B).

2.3. Optical Properties of $\text{Bi}_2\text{S}_3/\text{MoS}_2$ Catalysts

The UV-vis diffuse reflectance spectra were used to analyze the light absorption and energy band features of the $\text{Bi}_2\text{S}_3/\text{MoS}_2$ catalysts, as illustrated in Figure 8a. The absorption edge of Bi_2S_3 was close to 970 nm; thus, the compound exhibited a photo-response from the visible to near-infrared region. In comparison, the pure MoS_2 nanosheets also presented a broad absorption band around 670 nm, which indicates that they can absorb photons over almost all of the visible region. Furthermore,

the Bi₂S₃/MoS₂ heterojunction catalysts absorbed light over the full spectral region due to the transition of MoS₂ and Bi₂S₃. Other factors affect the observed photocatalytic efficiency, such as the optical range, containment of the charge transfer, specific surface area, and the suppression of the recombination of electron–hole pairs in the MoS₂/Bi₂S₃ heterojunction. Nevertheless, the highest absorbance point was around 670 nm. To determine the relative band-gap and the energy levels of all the catalysts, the band-gap energy (E_g) was determined by applying the following formula based on the differential reflectance spectroscopy (DRS) data [31]: the hetero-junction particles are direct band-gap semiconductors. The reflectance data can be converted to absorption according to the Kubelka–Munk (K-M) theory: $F(R_\infty) = (1 - R_\infty)^2 / 2R_\infty$, where, R_∞ is reflectance and $F(R_\infty)$ is the K-M function [32]. The band gap of the samples can be estimated by using Tauc plot: $(\alpha h\nu)^{1/n} = A(h\nu - E_g)$, where, α , $h\nu$, A , and E_g are the absorption coefficient, incident light frequency, proportionality constant, and band gap, respectively. The value of exponent n determines the nature of electronic transition; $n = 1/2$ for direct transition and $n = 2$ for indirect transition. The linear extrapolation of $(\alpha h\nu)^{1/n}$ to zero give the band gap energies of the samples. According to Tauc's relation, the plotting of $(\alpha h\nu)^{1/2}$ versus the photon energy ($h\nu$) gives a straight line in a certain region. The extrapolation of this straight line will intercept the $(h\nu)$ -axis to give the value of the indirect optical energy gap (E_g). From the Tauc plots presented in Figure 8B, the E_g s of Bi₂S₃ and MoS₂ (determined from the plot of $(\alpha h\nu)^2$ versus $(h\nu)$) were found to be 1.32 and 1.58 eV, respectively. The band-gap of the heterogeneous catalysts was intermediate between the band-gap of these two particles.

To determine the valence band (VB) and conduction band (CB) edge potential of the semiconductors, the VB positions were determined from XPS, as shown in Figure 9a; the VBs of MoS₂ and Bi₂S₃ were 0.4 and 1.05 eV, respectively. Thus, by combining the XPS spectral data and band-gaps in Figure 8, the CB position was determined by applying the following equation, $E_g = CB - VB$ [33]. In conclusion, the conductance bands of MoS₂ and Bi₂S₃ were −0.62 and −0.88 eV, respectively, as illustrated in Figure 9b. Based on these findings, it can be seen that the Bi₂S₃ rod and MoS₂ sheet can form a perfect heterojunction.

To understand the charge carrier transfer behavior in the catalysts, photocurrent experiments were carried out and the photocurrent responses are shown in Figure 10. For the photocurrent density cycle, the analytical samples were prepared as pastes and coated on the cell-type FTO (Fluorine doped tin oxide) glass. This cell was used as the working electrode, and the Pt-coated FTO glass was used as the counter-electrode. The two electrodes were connected to form a single system. An iodolyte electrolyte (AN-50, Solaronix) was used and sufficiently immersed in the electrode, and a potential of 0 V was applied. The current was measured under one-sun illumination with a 2000 Solar Simulator (IVIUM STAT, ABET Technologies). After the initial 1 min stabilization period, the current was measured during periodic irradiation at intervals of 30 s. The cell area (0.4 cm²) was divided by the measured current, and the current density was calculated. The photocurrent was 30 nA for Bi₂S₃ and 1185 nA for MoS₂. When the amount of MoS₂ in the heterojunction catalyst was increased, the photocurrent increased with the active photoirradiation (light on) time; when the amount of Bi₂S₃ was increased, the current was small but stable during active photoirradiation. The 1Bi₂S₃/1MoS₂ heterojunction showed the best photocurrent response, which was 1.5 and 58 times that of pristine MoS₂ and Bi₂S₃, respectively. This result confirms slower recombination of the charge carriers in the 1Bi₂S₃/1MoS₂ heterojunction, indicating significant improvement of the photocatalytic performance. Moreover, the steady and reproducible photocurrent response after several cycles suggests that the 1Bi₂S₃/1MoS₂ heterojunction possessed good photostability.

Figure 8. DR (Diffuse Reflectance)-UV-Visible spectra (A) and Tauc plots (B) for all catalysts. Differential reflectance spectroscopy (DRS).

Figure 9. Valence band (VB) locations recorded by XPS (A) and energy diagrams for pure Bi_2S_3 and MoS_2 particles (B).

Figure 10. Photocurrent density cycles of all catalysts.

2.4. Catalytic Mechanism for 1Bi₂S₃/1MoS₂

Figure 11 shows the CO₂ gas adsorption capacity (CO₂-TPD (Temperature programmed desorption) curve) of the Bi₂S₃, MoS₂, and 1Bi₂S₃/1MoS₂ particles. In order to remove impurities, the particles were treated at 300 °C for 30 min, and CO₂ gas was adsorbed at 50 °C for 2 h.

Figure 11. CO₂-TPD curves of Bi₂S₃, MoS₂, and Bi₂S₃/MoS₂ heterojunction catalysts.

The temperature was increased to 550 °C at a rate of 5 °C min⁻¹ to determine the desorption temperature and curves in order to determine the amount of CO₂ gas adsorbed on the catalysts. The results indicated that CO₂ gas was desorbed above 300 °C; the amount of CO₂ desorbed was

small, but the desorption temperature was high in the case of Bi_2S_3 . The CO_2 desorption curves were separated into peaks at 324.2 and 484.4 °C for the MoS_2 sample, and the amount of CO_2 gas desorbed by the MoS_2 sample was significantly greater than that desorbed by Bi_2S_3 . As noted above, this was attributed to the amount of sulfur vacancies in MoS_2 , as shown in the XPS profile. CO_2 is expected to be adsorbed in the vacant sulfur sites, and therefore, more sulfur vacancies lead to stronger attraction between CO_2 gas and the particles. However, in the case of $1\text{Bi}_2\text{S}_3/1\text{MoS}_2$, desorption occurred at lower temperatures and the highest desorption was achieved at 392.6 °C. However, the desorption amount decreased relative to that achieved with the single MoS_2 catalyst. This is because the amount of MoS_2 present per unit weight was reduced. Nevertheless, the amount of CO_2 adsorbed was high enough to react with water. Moreover, the lower CO_2 desorption temperature suggests that the adsorbed CO_2 can easily be converted in the next step. This also means that even after conversion to the product by the reaction with water, the product was easily desorbed, resulting in less coking on the catalyst. This in turn extended the catalytic performance.

To comprehend the method of transfer of the photo-induced charge, a possible mechanism for photocatalysis by the $\text{Bi}_2\text{S}_3/\text{MoS}_2$ heterojunction was proposed, as shown in Scheme 1.

Scheme 1. Plausible mechanism for carbon dioxide photo-conversion on $\text{Bi}_2\text{S}_3/\text{MoS}_2$ heterojunction catalysts. Conduction band (CB).

When the $\text{Bi}_2\text{S}_3/\text{MoS}_2$ heterojunction is excited by visible light, the electrons move from the CB of the Bi_2S_3 rods to the CB of the MoS_2 nanosheets. The holes are then transferred from the VB of MoS_2 to the VB of Bi_2S_3 . Excited electrons naturally flow through the CB surface of Bi_2S_3 to the CB of MoS_2 at lower potential (-0.62 eV vs. NHE (Normal Hydrogen Electrode)); thus, the density of electrons at the interface of these two particles will plausibly increase. Finally, CO_2 gas is adsorbed on the electron-rich junction surface or the VB surface of MoS_2 based on the gas adsorption data presented in Figure 11, and these electrons can reduce CO_2 to produce CO. This leads to efficient separation between the electrons and holes in this $\text{Bi}_2\text{S}_3/\text{MoS}_2$ heterojunction catalytic system. In theory, the photo-induced electrons in the VB of Bi_2S_3 (0.4 eV vs. NHE) are not effective for the decomposition of water to produce H^+ ions; thus, the CB of Bi_2S_3 cannot participate in reduction to yield H radicals or H_2 gas. This reduces the possibility of interaction of the CO intermediate with hydrogen, which in turn leads to lower CH_4 yields. Overall, the yield of CO was increased and the yield of CH_4 was very low.

3. Materials and Methods

3.1. Preparation of Catalysts

As shown in Scheme 2, the catalysts were prepared by a hydrothermal method.

Scheme 2. Preparation of Bi₂S₃/MoS₂ heterojunction catalyst using the hydrothermal method.

Bi₂S₃ was synthesized as follows: 0.25 g (3.28 mmol) of thiourea (SC(NH₂)₂, $M_W = 76.12 \text{ g mol}^{-1}$, Aldrich) was dissolved by stirring in 50 mL of deionized (DI) water; 0.61 g (1.26 mmol) of bismuth nitrate pentahydrate (Bi(NO₃)₃·5H₂O, $M_W = 485.07 \text{ g mol}^{-1}$, Aldrich) was slowly added to this solution. The homogenous solution was stirred for 4 h, then transferred to a Teflon-lined autoclave, heated to 140 °C at a rate of 10 °C min^{−1}, and maintained for 10 h. The solution was then slowly cooled at room temperature to obtain a precipitate that was separated by centrifugation and washed several times with absolute ethanol. The washed sample was dried at 70 °C for 8 h to obtain the final compound. MoS₂ was synthesized in the following order: 0.41 g (5.4 mmol) of thiourea was uniformly dissolved in 35 mL of DI water with stirring. Hexaammonium heptamolybdate tetrahydrate ((NH₄)₆Mo₇O₂₄·4H₂O, $M_W = 1235.9 \text{ g mol}^{-1}$, Aldrich) was slowly added to the above solution and stirred for 4 h. This solution was transferred to a Teflon-lined autoclave, heated to 220 °C at a rate of 10 °C min^{−1}, and then held for 18 h. At the end of the reaction, the autoclave was cooled to room temperature, and the precipitate obtained was centrifuged and washed several times with anhydrous ethanol. The compound was dried at 70 °C for 8 h to obtain the final product. Finally, heterojunction Bi₂S₃/MoS₂ catalysts were synthesized in the following manner: thiourea was dissolved in 35 mL of DI (Deionized) water. To this solution, the appropriate amounts of (NH₄)₆Mo₇O₂₄·4H₂O and Bi(NO₃)₃·5H₂O were slowly added and then stirred for 4 h for homogenization. The solution was transferred to a Teflon-lined autoclave, heated to 180 °C at a rate of 10 °C min^{−1}, and held for 14 h. After the reaction, the autoclave was cooled to room temperature, and the precipitate obtained by centrifugation was washed several times with anhydrous ethanol. Finally, the compound was dried at 70 °C for 8 h to obtain the final product. The molar ratios of Bi₂S₃:MoS₂ in the obtained samples, were 1:1, 2:1, and 1:2. In total, five types of catalysts, Bi₂S₃, MoS₂, 1Bi₂S₃/1MoS₂, 2Bi₂S₃/1MoS₂, and 1Bi₂S₃/2MoS₂, were synthesized and their optical properties and activities were investigated.

3.2. Characterization

Powder XRD patterns of the prepared catalysts were collected with an XPert Pro MPD PANalytical 2-circle diffractometer using Cu-K α radiation ($\lambda = 1.5406 \text{ \AA}$), a working voltage of 30 kV, and a current of 15 mA in the angle of diffraction (2θ) range 10–80°. The morphologies and compositions

of the as-prepared samples were characterized by transmission electron microscopy (TEM, H-7600, Hitachi, operating at 200 kV, Japan), energy dispersive spectrometric element mapping (EDS, EX-250, Horiba), and high-resolution transmission electron microscopy (HRTEM, JEM-2100 F, Jeol). The optical properties were confirmed from the UV-visible diffuse reflectance spectra collected on a Neosys-2000 (UV-vis, Scinco Co. Korea) spectrometer using BaSO₄ as the reference sample, photoluminescence spectroscopy (PL, Perkin Elmer, He–Cd laser source, wavelength of 300 nm), and a photocurrent–time response system (IVIUM STAT, ABET Technologies). A 150 W Xe lamp was used as the light source. A saturated calomel electrode (SCE), and saturated 0.1 M Na₂SO₄ solution were used as the counter-electrode and electrolyte, respectively. The working electrode was prepared via a dip-coating method. Time-dependent photocurrent curves were constructed by the *i*–*t* curve method.

3.3. Photocatalytic Carbon Dioxide Conversion Reaction

The photoreduction of CO₂ in the presence of the synthesized Bi₂S₃, MoS₂, 1Bi₂S₃/1MoS₂, 2Bi₂S₃/1MoS₂, and 1Bi₂S₃/2MoS₂ particles with H₂O was performed in a closed cylinder-type quartz vessel (length: 15.0 cm; diameter: 1.0 cm; total volume: 12.50 mL). A schematic diagram of the photoreactor is provided in a previous report [34]. Here, 0.2 g of the catalyst and 40.0 L of distilled water were placed in the photoreactor. High-purity CO₂ gas (99.99%) was used as the reactant. The chamber was purged with the CO₂ gas before irradiation. The water was injected and the reactor was sealed; the outside of the reactor was wrapped with a heat tape and kept at 80 °C for 30 min to vaporize the water in the reactor. The reaction was performed after cooling the reactor to 25–30 °C. At this time, the pressure in the reactor was close to atmospheric pressure. Here, in general, the activity of a photocatalyst that decomposes organic molecules in a solution shows a tendency to increase steadily up to a reaction temperature of 60 °C, but decreases above it [35]. When the temperature is increased, it causes the bubbles formation in the solution which results in the generation of free radicals. Additionally, the increase in temperature helps the degradation reaction to overcome electron-hole recombination. In addition to that, the increasing temperature may enhance the oxidation rate of organic molecules at the interface. Zhang et al. also reported [36] when temperature increased from 323 K to 343 K, the yield of the photocatalytic reaction increased by two times. Although raising temperature is an effective strategy to obtain higher yields, the photoreduction of carbon dioxide has been reported to have the best performance at the low reaction temperature of 25 °C in some researches [37]. Thus, there is always an optimum temperature range to get the best. Here, the photoreactor in this study was an open system in which a one sun lamp illuminates a quartz photoreactor from above, with a diameter of up to 10 cm × 10 cm radiated from one sun. The distance from the end of one sun lamp to the reactor was 1.0 cm and the inner diameter of the reactor was 1.0 cm, thus the distance between the lamp and the photocatalyst sample was 2.0 cm. Moreover, the laboratory was maintained at 18 °C by the air conditioner to suppress the photoreactor temperature from rising above 25 °C by the one sun lamp. The reactor chamber was then closed and the lamp was switched on. A natural solar simulator (a xenon lamp, 150 mW cm^{−2}, 620 nm, 2000 Solar Simulator, ABET Tech) was used as the irradiation source. The solar light intensity of the solar simulator was calculated with a digital lux meter and the average light intensity was determined as approximately 1,200,000 Lux. Photoreduction was carried out at room temperature and atmospheric pressure. The product gases were analyzed using a gas chromatography (GC; Master GC, Scinco, Korea) instrument. Hydrocarbons such as methane, ethane, and propane were quantified by flame ionization detection (FID), and quantitative analysis of CO, H₂, O₂, CH₃OH, etc., was performed with thermal conductivity detectors (TCD). The minimum detection limit of the GC was 1.5 pg carbon/s for FID, 2.5 ng mL^{−1} (standard), and 400 pg mL^{−1} (μ-TCD) for TCD. The product selectivity was calculated using the following equation: $C_i (\%) = C_i \text{ moles of the product} / \text{total moles of C produced} \times 100\%$. Furthermore, trace amounts of gases that are difficult to analyze by GC were analyzed by using a mass spectrometer (BELMASS, BEL Japan Inc., Japan).

When the catalyst is repeatedly done to run-off rather than continuously running the reaction for a long time, the catalyst structure is more damaged and so the activity of the catalyst is lowered. That is,

more important than the lifetime of the catalyst is to confirm the recycling of the catalyst. Generally, in the thermal catalyst system, a catalyst used in the reaction is calcined at a high temperature, and a regeneration method for removing carbon coking accumulated on the catalyst surface is performed. However, a general regeneration method is not standardized in the photocatalyst system. Therefore, some researchers, including us, choose their own special regeneration method. In this study, the recycling experiment was carried out in the following manner: After each run of photocatalysis reactions for 10 h, the light was switched off, the reactor was disassembled, and then the photocatalyst was separated from reactor. The used catalyst was washed with distilled water for three times, filtered and dried at 60 °C. It was then thermal-treated for 2 h under N₂ at 150 °C. The catalyst was then stored in the dark for 24 h to minimize contact with external light until it was repacked into the photoreactor. This is to ensure that all regenerated catalysts are in the same environment as much as possible. The reactor was again installed, and then the gas inside the reactor was ejected. The stored catalyst was again fixed in the reactor, and the reactor was purged with CO₂ to displace the air inside the reactor. At this time, the reactor valve is closed/opened and repeated three times while purging CO₂ into the reactor. After ejecting all the air gas inside the reactor, both valves of the reactor are closed, water was injected in, vaporized it, and the reaction was initiated by switching on the light source. This experiment was repeated five times.

4. Conclusions

Bi₂S₃/MoS₂ heterojunction catalysts comprising Bi₂S₃ rods wrapped with MoS₂ nanosheets were prepared via a hydrothermal method. The optimal photocatalytic performance was achieved with the 1Bi₂S₃/1MoS₂ heterojunction, for which CO₂ reduction to CO after 10 h was almost 40 and 16 times higher than that achieved with pure MoS₂ and Bi₂S₃, respectively. The novelty of this study is that CO was generated with sufficiently high selectivity to preclude the need for secondary gas separation. Additionally, the enhanced photocatalytic efficiency could be attributed to the combination of Bi₂S₃ and MoS₂, which extends the light absorption ability and formation of the Bi₂S₃/MoS₂ heterojunction with a tight face-to-face connection and a good energy band match between MoS₂ and Bi₂S₃. The interfacial interaction between MoS₂ and Bi₂S₃ can accelerate the separation of the photo-induced carriers and increase the sulfur defects.

Author Contributions: Conceptualization, M.K.; Data curation, R.K. and J.Y.D.; Formal analysis, R.K., J.K. and J.Y.D.; Investigation, R.K. and J.K.; Methodology, M.W.S. and J.Y.D.; Writing—original draft, M.K.

Funding: This research was funded by a Yeungnam University research grant 2019 (Grant No. 219A345005).

Conflicts of Interest: The authors declare no conflict of interest.

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