Photocatalytic conversion of CO₂ into methanol: Significant enhancement of the methanol yield over Bi₂S₃/CdS photocatalyst

M. Rahim Uddin, Maksudur R. Khan *, M. Wasikur
Rahman, Chin Kui Cheng
Faculty of Chemical and Natural Resources Engineering, Universiti Malaysia Pahang, 26300 Gambang, Pahang, Malaysia
mrkhancep@yahoo.com

Abu Yousuf
Faculty of Engineering Technology, Universiti Malaysia Pahang, 26300 Gambang, Pahang, Malaysia

ABSTRACT The present work is a significant approach to explore the photo-conversion of carbon dioxide (CO₂) into methanol on Bi₂S₃/CdS photocatalyst under visible light irradiation. In this perspective, Bi₂S₃ nanoparticles have been successfully synthesized via corresponding salt and thiourea assisted sol–gel method. An innovative hetero-system Bi₂S₃/CdS has been proposed to achieve methanol photo evolution and its photocatalytic activities have been investigated. The photocatalysts are characterized by X-ray diffraction (XRD), ultraviolet-visible spectroscopy (UV-Vis) instruments. Results show that the photocatalytic activity and visible light response of commercial CdS loaded Bi₂S₃ is higher than that of synthesized CdS. The photocatalytic activity of Bi₂S₃/CdS photocatalyst was enhanced and the highest yield of methanol was 590 μmol/g when the weight proportion of Bi₂S₃ to CdS was (2:1).

Key Words: CO₂ reduction Photocatalyst, Bi₂S₃/CdS, Visible light; Methanol

I. INTRODUCTION

The continuous increase in atmospheric CO₂ leads to climate change, which is one of the major threats of times. The rapid consumption of fuel resources and the underlying concerns over the emissions of CO₂ have prompted research efforts on the conversion of CO₂. It is urgent to reduce the accumulation of CO₂ in the atmosphere. There are three effective ways to reduce CO₂ emissions: reducing the amount of the produced CO₂, using CO₂ and storing CO₂, where transformation of CO₂ into chemicals is an attractive option and fulfills the recycle use of CO₂ [1, 2]. Photocatalytic process for CO₂ reduction provides a suitable approach for clean and environmentally friendly production of hydrocarbon by visible light. However, in order to harness sunlight to produce hydrocarbons from CO₂ conversion, there are different fundamental requirements that must be satisfied [3-8]. Firstly, light must be efficiently absorbed to generate electron-hole pairs for the electron transfer from one conduction band to another. Secondly, either the recombination of the photo-generated electron-hole pairs like to be prevented for the CO₂ adsorption on catalyst surface. Thirdly, undesirable reactions or products, such as photo-corrosion or degradation of the photocatalyst, as well as environmental unfriendly products, must be prohibited by adjusting the pH before suspending the catalyst onto reaction medium. To develop suitable photocatalysts, these fundamental key factors and the aims of photocatalytic reduction of CO₂ need to be satisfied [3, 9-11].

As for photocatalytic conversion of CO₂ to methanol, CdS is the most popular photocatalyst due to its excellent stability, innocuity and low price. In addition, due to its larger surface and regular structure has also been brought to much attention in the field of photocatalytic conversion of CO₂ [12, 13]. The band-gaps of CdS and Bi₂S₃ were narrower and their conduction bands were more negative than those of other photocatalysts [12, 13], therefore, CdS and Bi₂S₃ have been hugely used to the photocatalytic conversion of CO₂. CO₂ bubbled in water was converted to HCHO, HCOOH and CH₃OH over various semiconductor photocatalysts, such as CuFe₂O₄, CdS, TiO₂, ZnO, GaP and SiC under photo irradiation of their suitable reaction medium maintaining required pH value [3, 6, 9, 14-19].

In this study, Bi₂S₃ was modified by CdS and the obtained Bi₂S₃/CdS was used for the photocatalytic conversion of CO₂ with water under visible light irradiation. The Bi₂S₃/CdS photocatalyst was characterized by X-ray diffraction (XRD), ultraviolet visible (UV-Vis) spectroscopy. The photocatalytic activities of Bi₂S₃/CdS photocatalyst for the conversion of CO₂ to CH₃OH under visible light irradiation have been investigated.

II. MATERIALS AND METHODS

2.1. Materials

The Bi(NO₃)₃·5H₂O, thiourea and CdS were obtained from R&M Chemicals. All chemicals used in this work were laboratory standard and used as purchased.

2.2. Preparation of photocatalyst

Bi₂S₃ was synthesized by the reactions between the corresponding salt and thiourea. 3.05 g Bi(NO₃)₃·5H₂O and 0.71 g thiourea was dissolved in 400 ml water and retained for 3 h under continuous stirring at room temperature [13]. The solution was then heated under stirring at 95°C for 3 h. When cooled and settled down, the precipitate was filtered off, and washed with distilled water and dried in vacuum at 60 °C overnight. At last, Bi₂S₃ was heat treated at 250 °C for 3 h. To prepare the hetero-system Bi₂S₃/CdS photocatalyst, the mass ratio of Bi₂S₃ to commercial CdS was taken 1:0.5. The starting materials were mixed randomly after grinding them and the system was heated at 250 °C for 3 h in tubular furnace under N₂ atmosphere.

2.3. Characterization
the range of 200–800 nm was measured with a Daqin UV-2550PC diffuse reflectance spectroscope. The liquid products were analyzed by using gas chromatography-flame ionization detector (GC-FID), and the analysis was performed with Shimadzu, GC-14B series gas chromatograph equipped with FID detector and the capillary column DB-WAX (60 m × 0.25 mm, 0.25 μm). The carrier gas was nitrogen at a flow rate of 1 mL/min. The reactor and detector temperature were maintained at 250 and 260°C, respectively; consisting of split less.

2.4. Photocatalytic activity

Photocatalytic conversion of CO₂ into methanol is a process in which photons are absorbed with higher energies than its band-gap energy (Eₚ) to create electron-hole pairs. The photogenerated electrons (e⁻) and holes (h⁺) participate in various photoreduction processes to produce final products [20]. However, if the electrons fail to find any trapped species (e.g., CO₂) on the semiconductor surface or their energy band-gap is too small, then they recombine immediately and release unproductive energy as heat[21, 22]. Photocatalytic absorption of photons creates photoelectrons in the conduction band (CB) and holes in the valence band (VB) of the semiconductor, as schematically depicted in Figure 1a. In the Figure 1b, the photogenerated electron-hole pairs must separate and migrate to the surface (paths a and b in Figure 1b) competing effectively with the electron-hole recombination process (path c in Figure 1b) that consumes the photo charges generating heat. The photo-induced electrons and holes reduce and oxidize adsorbed CO₂ to hydrocarbons [13, 20, 23, 24]. The photo reaction was performed in a continuous-flow reactor system as shown in Figure 2 [12]. A 500 W Xe lamp located in the quartz cool trap was the irradiation source. The catalyst concentration of the prepared Bi₂S₃/CdS photocatalyst was maintained at 1 gL⁻¹. The pH was adjusted to the desired value by adding KOH (1.2 gm), 2.0 M sodium nitrite, and absolute sodium sulphite (3.78 gm) was dissolved in 300 mL distilled water. This solution was then put into a photocatalytic reactor. Before irradiation, ultrapure CO₂ was bubbled through the solution in the reactor for at least 1 h to ensure that all dissolved oxygen was eliminated, then, 300 mg of catalyst powder was added into 300 mL of prepared solution, and the irradiation process was started. The CO₂ was continuously bubbled through the solution in the reactor during the whole irradiation (6 h). The liquid sample was analyzed by the GC-FID and UV method described above [12, 21].

3. RESULTS AND DISCUSSION

3.1. XRD analysis

The XRD pattern of the Bi₂S₃/CdS photocatalyst is showed in Figure 3. It was observed from Figure 3. According to the XRD diffraction peaks of CdS, these three significant peaks were consistent with the peak positions of CdS as the XRD patterns were obtained at room temperature using Rigaku Miniflex II. The UV-Vis diffuse reflectance spectrum (DRS) in spinel-type (JCPDS 111, 220, 311) respectively. It can be seen from the XRD patterns of the Bi₂S₃ in Figure 3, that sharp peaks were in good matching with the standard diffraction peaks of Bi₂S₃ corresponded with the crystal planes of (JCPDS 130, 211, 221, 431, 351) phase Bi₂S₃, respectively.

3.2. UV-Vis spectroscopy analysis

The UV-Vis DRS of the as-prepared Bi₂S₃/CdS has been presented in Figure 4. As shown in Figure 4, the photo absorption of the Bi₂S₃/CdS photocatalyst was clearly higher than that of CdS and increased with the proportion of Bi₂S₃ in the photocatalysts. This proves that the addition of CdS can effectively enhance the absorbance of Bi₂S₃ under visible light. Therefore, it clearly shows the Bi₂S₃/CdS photocatalyst is more suitable for applying under visible light. A band gap of 1.72 eV was obtained from UV-Vis DRS analysis (Figure 4). The required wavelength to make the photocatalyst active can be calculated using the following equation [25]:

$$\text{Wavelength} = \frac{1240}{\text{band gap of semiconductor (eV)}}$$

3.3. Photocatalytic conversion of CO₂

The mechanism of photocatalytic conversion of CO₂ with H₂O to CH₃OH is shown in figure 1, and the experimental set up is shown in figure 2. The formation of CO₂ photocatalytic conversion products was examined over a period of 6 h on Bi₂S₃/CdS photocatalyst. The evolution products were obtained as the functions of the irradiation time for the Bi₂S₃/CdS (2:1) catalyst. The yield of methanol is higher than that of any other hydrocarbons. The yield of methanol was measured for the 50% commercial CdS loaded Bi₂S₃ catalyst under visible light irradiation. The photo-reactivity of Bi₂S₃/CdS increases with the increase of time, when the active sites of the catalyst decrease the production of methanol was stopped. The yields of methanol production in the photocatalytic conversion of CO₂ over Bi₂S₃/CdS photocatalysts under visible light irradiation are shown in Fig. 3. The highest methanol yield (590μmol/L) was obtained for CdS loaded Bi₂S₃ (2:1) catalyst.

IV. CONCLUSIONS

The photocatalytic conversion of CO₂ into methanol on Bi₂S₃/CdS catalyst surface under visible light has been carried out quite effectively. The Bi₂S₃/CdS photocatalyst for CO₂ conversion has been studied but for the commercial CdS has not been studied yet. The activity is attributed to the increased active site on the surface area of Bi₂S₃/CdS. The modification of Bi₂S₃ with commercial CdS can increase its photocatalytic activity and visible light response. The highest methanol yield was found over Bi₂S₃/CdS photocatalyst and the yield was 590μmol/L, that proved the loading of commercial CdS on Bi₂S₃ cause the significant increase in methanol yield respectively.
V. ACKNOWLEDGMENTS

We would like to thank the Malaysian Ministry of Education under the Fundamental Research Grant Scheme (RDUI20112) and Universiti Malaysia Pahang for funding this research (GRS140330), and providing all the facilities for our research work.

REFERENCES


4. Izumi Y. Recent advances in the photocatalytic conversion of carbon dioxide to fuels with water and/or hydrogen using solar energy and beyond. Coordination Chemistry Reviews 2013; 257:171-186.


*University of South Florida, 2005.*

Fig. 1. Photocatalytic water splitting: (a) photoelectron excitation in the photocatalyst-generating electron hole pairs and (b) processes occurring on photocatalyst for CO$_2$ reduction.

Fig. 2. Schematic presentation of experimental setup for photoreduction of CO$_2$ through splitting of H$_2$O [12]
Fig. 3. XRD patterns of the Bi₂S₃/CdS photocatalyst prepared via sol–gel approach and calcined at 240°C.

Fig. 4. The UV–Vis DRS of the as-fabricated Bi₂S₃/CdS, Bi₂S₅ photocatalyst at CdS loading ratio 2:1.

Fig. 5. The methanol yield in the photocatalytic conversion of CO₂ over Bi₂S₃/CdS (2:1) photocatalyst under visible light irradiation (6 h).