INTERNATIONAL JOURNAL OF ENGINEERING TECHNOLOGY AND SCIENCES (IJETS) Vol.3 (1) June 2015
DOI: http://dx.doi.org/10.15282/ijets.3.2015.1.4.1021

Photocatalytic conversion of CO_2 into methanol: Significant enhancement of the methanol yield over Bi_2S_3/CdS photocatalyst

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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 photoactivity 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 : CO_2 reduction Photocatalyst,Bi_2S_3/CdS, Visible light; Methanol

I. INTRODUCTION

The continuous increase in atmospheric CO_2 leads to climate change, which is one of the major threats of times. The rapid consumption of fuel resources and the undergoing concerns over the emissions of CO_2 have stimulated research objectives on the conversion of CO_2. It is urgent to reduce the accumulation of CO_2 in the atmosphere. There are three effective ways to reduce CO_2 emissions: reducing the amount of the produced CO_2, using CO_2 and storing CO_2, where transformation of CO_2 into chemicals is an attractive option and fulfils the recycle use of CO_2 [1, 2]. Photocatalytic process for CO_2 reduction provides a suitable approach for clean and environmental friendly production of hydrocarbon by visible light. However, in order to harness sunlight to produce hydrocarbons from CO_2 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 other. Secondly, either the recombination of the photo-generated electron-hole pairs like to be prevented for the CO_2 adsorption on catalyst surface. Thirdly, undesirable reactions or products, such as photocorrosion or degradation of the photocatalyst, as well as environmental unfriendly products, must be prohibited by adjusting the p^H before suspending the catalyst onto reaction medium. To develop suitable photocatalysts, these fundamental key factors and the aims of photocatalytic reduction of CO_2 need to be satisfied [3, 9-11].

As for photocatalytic conversion of CO_2 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 CO_2 [12, 13]. The band-gaps of CdS and Bi_2S_3 were narrower and their conduction bands were more negative than those of other photocatalysts [12, 13], therefore, CdS and Bi_2S_3 have been hugely used to the photocatalytic conversion of CO_2. CO_2 bubbled in water was converted to HCHO, HCOOH and CH_3OH over various semiconductor photocatalysts, such as $CuFe_2O_4$,CdS, TiO_2, ZnO, GaP and SiC under photo irradiation of their suitable reaction medium maintaining required P^H value [3, 6, 9, 14-19].
In this study, Bi_2S_3 was modified by CdS and the obtained Bi_2S_3/CdS was used for the photocatalytic conversion of CO_2 with water under visible light irradiation. The Bi_2S_3/CdS photocatalyst was characterized by X-ray diffraction (XRD), ultraviolet visible (UV-Vis) spectroscopy. The photocatalytic activities of Bi_2S_3/CdS photocatalyst for the conversion of CO_2 to CH_3OH under visible light irradiation have been investigated.

II. MATERIALS AND METHODS

2.1. Materials

The $Bi(NO_3)_3 \cdot 5H_2O$, 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

Bi_2S_3 was synthesized by the reactions between the corresponding salt and thiourea, 3.05 g $Bi(NO_3)_3 \cdot 5H_2O$ 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, Bi_2S_3 was heat treated at 250 ◦C for 3 h. To prepare the hetero-system Bi_2S_3/CdS photocomposite, the mass ratio of Bi_2S_3 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 N_2 atmosphere.

2.3. Characterization

the range of 200−800 nm was measured with a Daojin 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 injector and detector temperature were maintained at 250 and 260°C, respectively; consisting of split less.

2.4. Photocatalytic activity

Photocatalytic conversion of CO_2 into methanol is a process in which photons are absorbed with higher energies than its band-gap energy (E_g) 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. CO_2) 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 CO_2 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 Bi_2S_3/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 CO_2 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 CO_2 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 describe above [12, 21]

III. Results and Discussion

3.1. XRD analysis

The XRD pattern of the Bi_2S_3/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 Bi_2S_3 in Figure 3, that sharp peaks were in good matching with the standard diffraction peaks of Bi_2S_3 corresponded with the crystal planes of (JCPDS 130, 211, 221, 431, 351) phase Bi_2S_3, respectively.

3.2. UV-Vis spectroscopy analysis

The UV–Vis DRS of the as-prepared Bi_2S_3/CdS has been presented in Figure 4. As shown in Figure 4, the photo absorption of the Bi_2S_3/CdS photocatalyst was clearly higher than that of CdS and increased with the proportion of Bi_2S_3 in the photocatalysts. This proves that the addition of CdS can effectively enhance the absorbance of Bi_2S_3 under visible light. Therefore, it clearly shows the Bi_2S_3/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]:

$$\text{Wavelength},\lambda(\text{nm}) \leq \frac{1240}{Band\ gap\ of\ semiconductor\ (eV)}$$

3.3. Photocatalytic conversion of CO_2

The mechanism of photocatalytic conversion of CO_2 with H_2O to CH_3OH is shown in figure 1, and the experimental set up is shown in figure 2. The formation of CO_2 photocatalytic conversion products was examined over a period of 6 h on Bi_2S_3/CdS photocatalyst. The evolution products were obtained as the functions of the irradiation time for the Bi_2S_3/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 Bi_2S_3 catalyst during 6 h irradiation. The photo-reactivity of Bi_2S_3/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 CO_2 over Bi_2S_3/CdS photocatalysts under visible light irradiation are shown in Fig. 5. The highest methanol yield (590µmol/g) obtained for CdS loaded Bi_2S_3 (2:1) catalyst

IV. Conclusions

The photocatalytic conversion of CO_2 into methanol on Bi_2S_3/CdS catalyst surface under visible light has been carried out quite effectively. The Bi_2S_3/CdS photocatalyst for CO_2 conversion has been studied but for the commercial CdS has not been studied yet. The activity is attributed due to the increased active site on the surface area of Bi_2S_3/CdS. The modification of Bi_2S_3 with commercial CdS can increase its photocatalytic activity and visible light response. The highest methanol yields was found over Bi_2S_3/CdS photocatalyst and the yield was 590µmol/g_{cat} that proved the loading of commercial CdS on Bi_2S_3 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 (RDU120112) and Universiti Malaysia Pahang for funding this research (GRS140330), and providing all the facilities for our research work.

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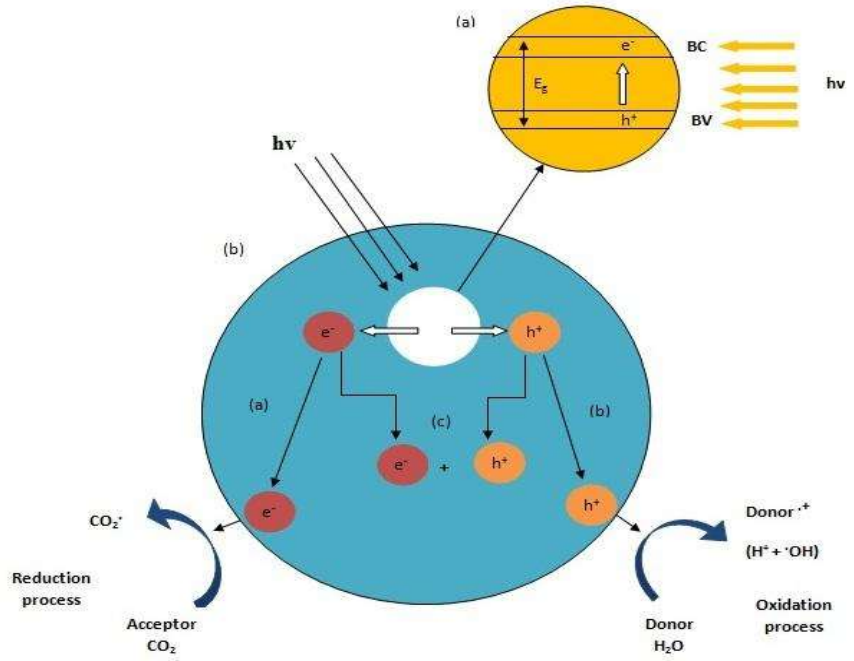

Fig. 1. Photocatalytic water splitting: (a) photoelectron excitation in the photocatalyst-generating electron hole pairs and (b) processes occurring on photocatalyst for CO_2 reduction.

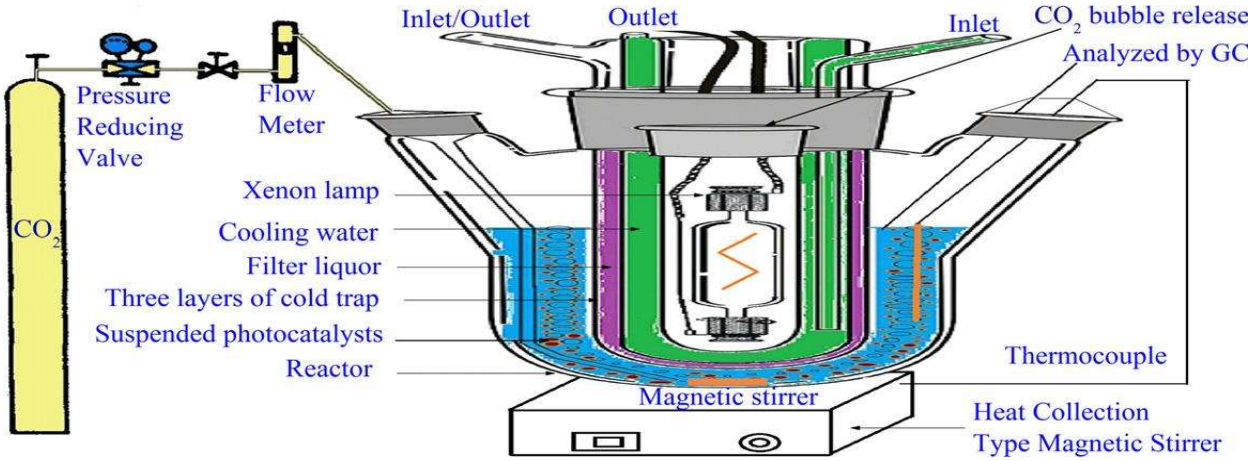

Fig. 2. Schematic presentation of experimental setup for photoreduction of CO_2 through splitting of H_2O [12]

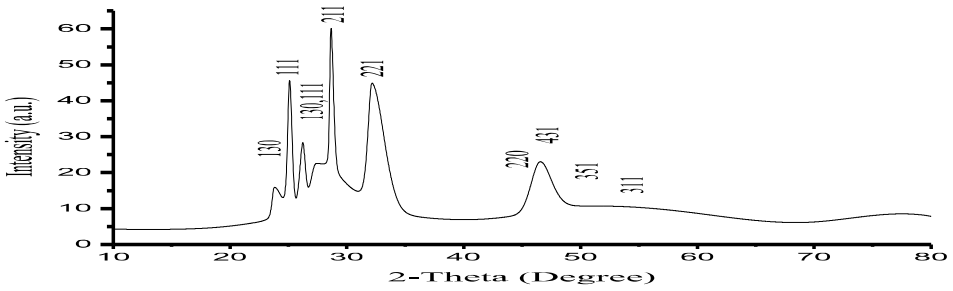

Fig. 3. XRD patterns of the Bi_2S_3/CdS photocatalyst prepared via sol–gel approach and calcined at 240°C

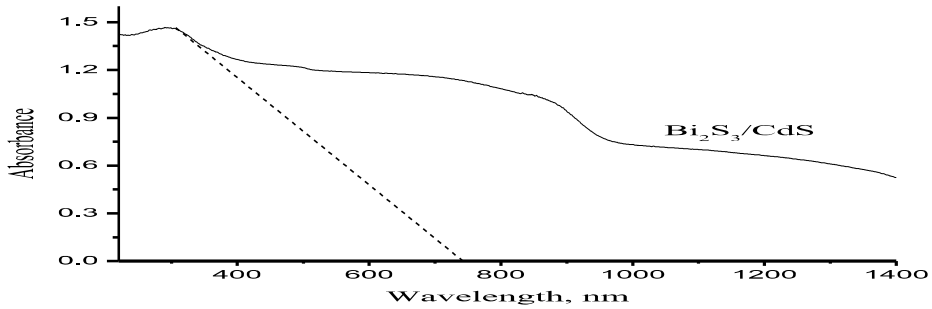

Fig. 4. The UV–Vis DRS of the as-fabricated Bi_2S_3/CdS, Bi_2S_3 photocatalyst at CdS loading ratio 2:1.

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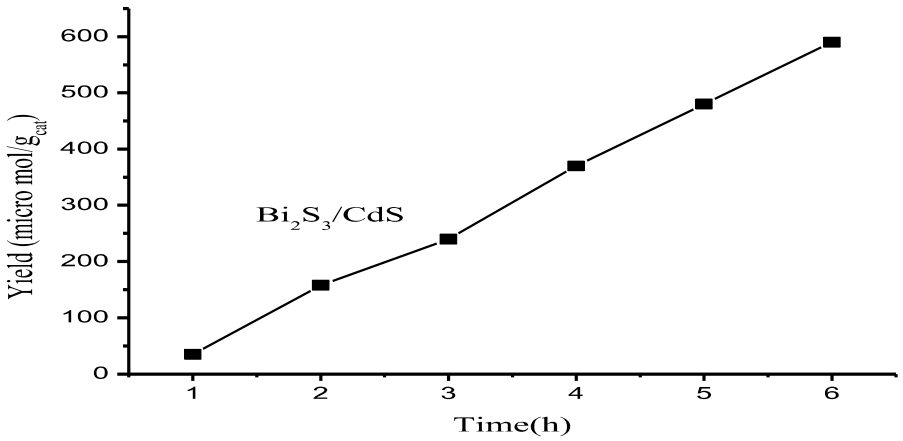

Fig. 5. The methanol yield in the photocatalytic conversion of CO_2 over Bi_2S_3/CdS (2:1) photocatalyst under visible light irradiation (6 h).