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Preparation and Characterization of Photocatalyst for the Conversion of Carbon Dioxide to Methanol

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***Abstract*—**Carbon dioxide (CO_2) emission to the environment is inevitable which is responsible for global warming. Photocatalytic reduction of CO_2 to fuel, such as methanol, methane etc. is a promising way to reduce greenhouse gas CO_2 emission. In the present work, Bi_2S_3/CdS was synthesized as an effective visible light responsive photocatalyst for CO_2 reduction into methanol. The Bi_2S_3/CdS photocatalyst was prepared by hydrothermal reaction. The catalyst was characterized by X-ray diffraction (XRD) instrument. The photocatalytic activity of the catalyst has been investigated for methanol production as a function of time. Gas chromatograph flame ionization detector (GC-FID) was employed to analyze the product. The yield of methanol was found to increase with higher CdS concentration in Bi_2S_3/CdS and the maximum yield was obtained for 45 wt% of Bi_2S_3/CdS under visible light irradiation was 20 μmole/g. The result establishes that Bi_2S_3/CdS is favorable catalyst to reduce CO_2 to methanol.

***Keywords*—**Photocatalyst, Carbon dioxide reduction, visible light, Irradiation.

I. Introduction

DUE to the reliance of the world on fossil fuels as a major source of energy, the carbon dioxide (CO_2) emission to the environment is inevitable which is responsible for global warming. Photocatalytic reduction of CO_2 to fuel, such as methanol, methane etc. is a promising way to reduce greenhouse gas CO_2 emission and energy crisis [12]. UV light covers only 3% and visible light 44% of the solar light spectrum [10] hence visible light active photocatalyst for CO_2 conversion is important.

Threats of global warming and energy crisis had accelerated the rush for new renewable energy resources. In order to reduce carbon dioxide emission and to produce maintainable fuels, recycling the greenhouse gases such as carbon dioxide seems eminently potential. Due to the increasing levels of carbon dioxide emissions from fossil fuels consumption, the problem of global warming has aroused into public concern [2]. One of the biggest challenges are to seek a renewable energy which not only meet the increasing energy demand, but also to replace the traditional chemicals fuels and environmentally friendly. One of the prospective way to reuse hydrocarbon resources is the photocatalytic reduction of CO_2 with H_2O utilizing the solar energy [12]. By using this way, carbon dioxide emissions can be reduced and energy crisis can be solved.

The most popular photocatalytic material with an excellent stability, innocuity and low price [6], three-dimensional, larger surface and regular structure [5] is titanium dioxide (TiO_2). However, TiO_2 have low quantum efficiency, which increase the combining ratio of electrons and holes. It can only absorb 5% sunlight in the ultraviolet region since it is a wide band gap semiconductor (3.0-3.2 eV) [11]. The ideal photocatalyst with a gap of 1.5 eV is well approximated by narrow band gap semiconductor material and highly stable electrodes may be produced by appropriate surface modification in order to enhance the photocatalytic activity and visible light response. CdS is a classical photocatalyst shows high activity under ultraviolet (UV) light irradiation. It is well known that the band gaps of CdS and Bi_2S_3 are narrower, active under visible light irradiation and the potentials of conduction bands are more negative compare to other photocatalysts [9], [13]. The CdS and Bi_2S_3 have higher quantum efficiency, which decrease the combining ratio of electrons and holes.

The photocatalytic reduction of CO_2 with H_2O to reusable hydrocarbon resources such as methanol is found to be one of the prospective ways to reduce CO_2 emissions and resolve the energy crisis. The process of water-splitting is a highly endothermic process ($\Delta H > 0$). The minimum potential difference (voltage) needed to split water is 1.23V at 0 pH [2], [8]. Since the minimum band gap for successful water splitting at pH=0 is 1.23 eV, corresponding to light of 1008 nm, the electrochemical requirements can theoretically reach down into infrared light, albeit with negligible catalytic activity.

Inoue et al. 1979 [7] first reported that CO_2 bubbled in water was reduced to HCHO, HCOOH and CH_3OH over various photocatalysts, such as CdS, TiO_2, ZnO, GaP and SiC under photo-irradiation of their aqueous suspension. In addition, the catalytic effect of Bi_2S_3 and CdS was examined for CO2 reduction in presence of H_2S and found comparable products [1]. Similar works were also reported in the literatures and they obtained various hydrocarbon products using aqueous CdS or ZnS colloids [3], [4]. These photocatalytic reductions of CO_2over CdS and Bi_2S_3had been carried out under UV light irradiation or by other reductants, and they have not been used for photocatalytic reduction of CO2tomethanol with water as reductant under visible light irradiation. However, photocatalyst with excellent stability,

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efficient, cost-effective and active in visible light region for the conversion of CO_2 into methanol still suffers from lacking. In this study, a hetero-junction of Bi_2S_3 and CdS was synthesized as an effective visible light responsive photocatalyst following effective hydrothermal method. In addition, the catalytic activity of the Bi_2S_3/CdS photocatalyst was investigated for CO_2 conversion into methanol.

II. Materials and Methods

A. Chemicals

The chemical reagents used in this experiment were thio-urea, cadmium nitrate tetrahydrate, cadmium sulfide (CdS) powder, bismuth III nitrate pentahydrate, sodium nitrite, potassium hydroxide and sodium sulphite. All chemicals were ~99% purity obtained from Sigma, USA.

B. Preparation of Photocatalysts

The Bi_2S_3/CdS catalyst was prepared by following direct hydrothermal method. $Cd(NO_3)_2.4H_2O$, $Bi(NO_3)_3.5H_2O$ and thio-urea of different compositions such as 6, 3 and 2.25 g, respectively were considered for the preparation followed by hydrolysis with 600 mL of deionized water in an autoclave at 90-100℃ for 6 h. Then cooled down to room temperature and successively the precipitate was filtered off, washed with distilled water and dried in an oven at 60℃ overnight. The catalyst was grinded with mortar before calcined at 250℃ for 3 h. Similarly, the weight proportions of Bi_2S_3 to CdS were 15%, 30% and 45% were prepared with the same method.

C. XRD Experiment

The XRD patterns were obtained at room temperature using MSAL-XD2 diffractometer with CuK_α radiation (operated at 36 kV and 30 mA, λ = 0.15406 nm).

D. Photocatalytic Experiment

The photocatalytic experiment was performed in a photochemical reactor equipped with a magnetic stirrer, a quartz cool trap and a condensation tube. A 500 W Xe lamp was located in the quartz cool trap as illuminant. The UV light was removed by 1.0 M sodium nitrite solution. Sodium nitrite, potassium hydroxide and sodium sulphite of corresponding quantities 0.7, 1.2 and 3.7 g were dissolved in 300 mL of ultra-filtered water. The solution was then put into the photochemical reactor. Ultrapure CO_2 was bubbled through the solution in the reactor before irradiation for 30 min to ensure that all dissolved oxygen was eliminated. 0.2 g of catalyst powder was added into the solution and the irradiation lamp was turned on to start the photoreaction. The temperature with the range of 30-35℃ was observed for every 1 h to avoid the loss of methanol into the air. Ultrapure CO_2 was continuously bubbled through the solution during the whole irradiation for 6 h. A needle-type probe was inserted into the solution of the reactor with the aid of vacuum pump to withdraw a small amount of liquid samples for 1 h interval up to 6 h (Fig. 1). The concentrations of methanol in the samples were analyzed using a gas chromatograph flame ionization detector (GC-FID).

III. Results and Discussion

A. XRD Analysis

The XRD pattern of pure CdS is shown in the Fig. 2 (2θ=3-80◦), was used as a reference for the structural analysis of prepared Bi_2S_3/CdS photocatalysts. XRD patterns of various as-prepared photocatalysts are shown in Fig. 3 corresponding to (a) Bi_2S_3/CdS (b) Bi_2S_3/CdS (15%) (c) Bi_2S_3/CdS (30%) (d) Bi_2S_3/CdS (45%).

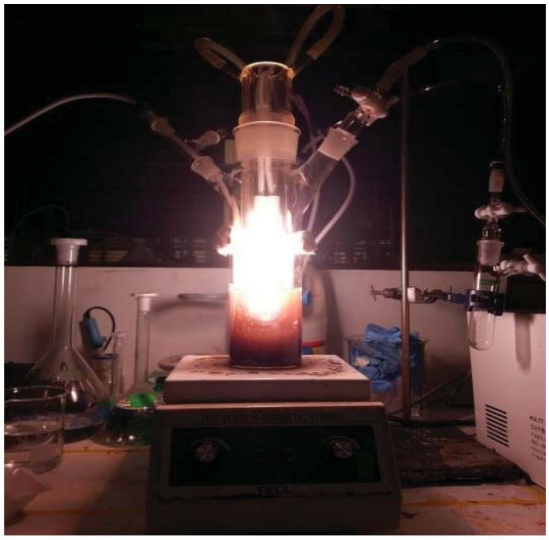

Fig. 1 Experimental Setup

The XRD patterns of the catalysts were recorded in the range of diffracting angles of 2θ=3-80◦ but shown only 2θ=15-50◦, the most significant portion. The XRD study reveals that CdS (15-45 wt%) incorporation in Bi_2S_3 takes place and gradual changes in the crystallographic parameters are detected. It was observed from the XRD analysis that there are mainly two types of crystallite structures e.g., orthorhombic Bi_2S_3 and cubic CdS. Using Scherrer formula for the full width at half maximum (FWHM) of the main peaks, the average crystallite size of the CdS and Bi_2S_3 were found to be 5-30 nm and 30-50 nm, respectively. It has been noticed that the crystallite size of Bi_2S_3 increased with CdS loading. According to the standard diffraction peaks of cubic CdS (JCPDS # 89-0440), the sharp peaks were consistent with the peak positions of CdS (100, 002, 101) (Fig. 2).

It can be seen from the XRD spectrum of the Bi_2S_3 in Fig. 3 that the peaks were in good agreement with the standard diffraction peaks of orthorhombic Bi_2S_3 (JCPDS # 17-0320). Five peaks with 2θ values of 25.1°, 28.78°, 31.94°, 46.62° and 53.72° in Bi_2S_3/CdS correspond to the crystal panes of (130), (211), (221), (351) and (431) of orthorhombic phase Bi_2S_3, respectively.

The lattice parameters are estimated for orthorhombic structure of Bi2S3 and found to be a_0=10.84 Å (standard a_0=11.49 Å), b_0=11.38 Å (standard b_0=11.30 Å) and c_0=3.97 Å (standard c_0=3.981 Å). Hence, it is confirmed that the Bi2S3 structure is orthorhombic. Moreover, the peaks of all the Bi_2S_3/CdS photocatalysts in Fig. 3 suggesting that all the

Bi_2S_3/CdS photocatalysts are all composed of the two crystallite phases and there are no unknown phases proved that they do not react each other and make a hetero-junction to show catalytic activities.

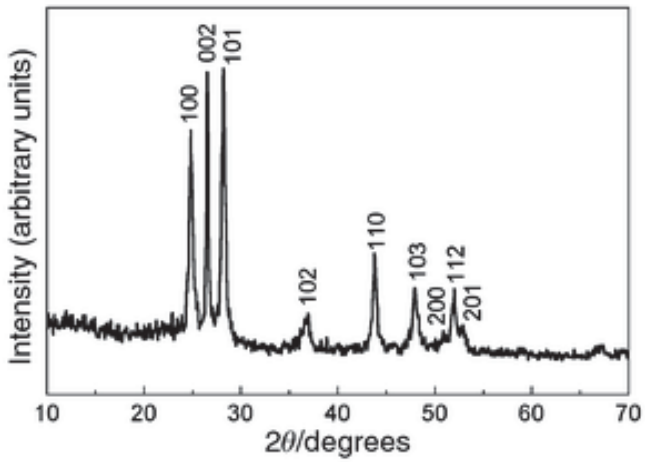

Fig. 2 XRD pattern of CdS shown as a reference

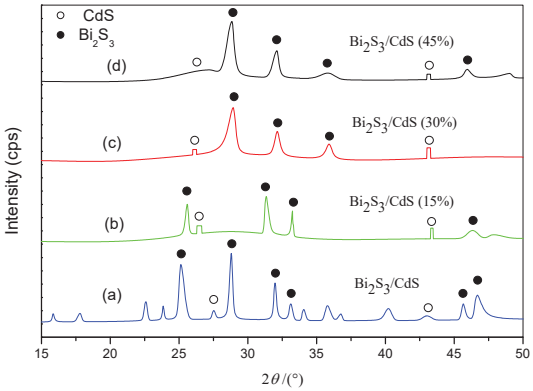

Fig. 3 XRD patterns of various photocatalysts (a) Bi_2S_3/CdS (b) Bi_2S_3/CdS (15%) (c) Bi_2S_3/CdS (30%) (d) Bi_2S_3/CdS (45%)

B. Photocatalytic Activity

The yields of CH_3OH in the photocatalytic reduction of CO_2 with H_2O on various photocatalysts under visible light irradiation are shown in Fig. 4. The presence of CH_3OH in the final samples is shown in Fig. 5. From Fig. 4, it can be seen that the generation rates of CH_3OH over the Bi_2S_3/CdS were significantly higher when the concentration of CdS was increased. The highest yield of methanol over Bi_2S_3/CdS was 20 μmole/g when the weight proportion of Bi_2S_3 to CdS was 45%. This may be due to doping Bi_2S_3 to CdS could form hetero-junction structures which improves the separation of electrons and holes, prevents the charge-carrier recombination and prolongs the lifetime of photo-carriers in Bi_2S_3/CdS photocatalyst. In addition, the spread of belt-shaped Bi_2S_3 on the surface of CdS particles was better when the weight proportion of Bi_2S_3 to CdS was 45%. The mechanism of photocatalytic reduction of CO_2 with H_2O to CH_3OH is shown in Fig. 5. It can be seen from Fig. 5 that both Bi_2S_3 and CdS can be used as photocatalyst for reducing CO_2 to CH_3OH under visible light.

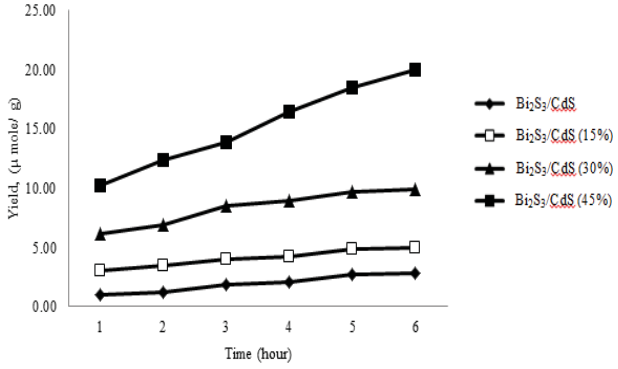

Fig. 4 The yields of CH_3OH in the photocatalytic reduction of CO_2 with H_2O over various photocatalysts under visible light irradiation

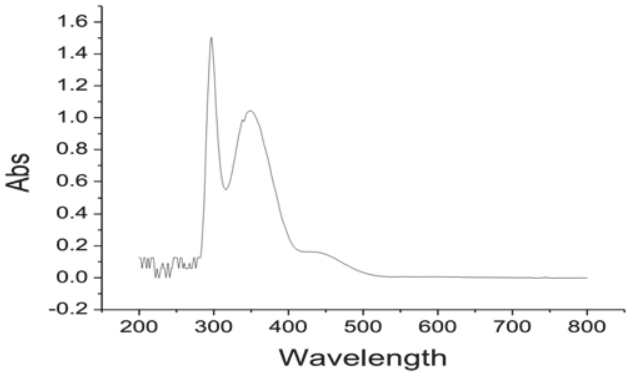

Fig. 5 Methanol detection in a sample by UV spectrophotometer

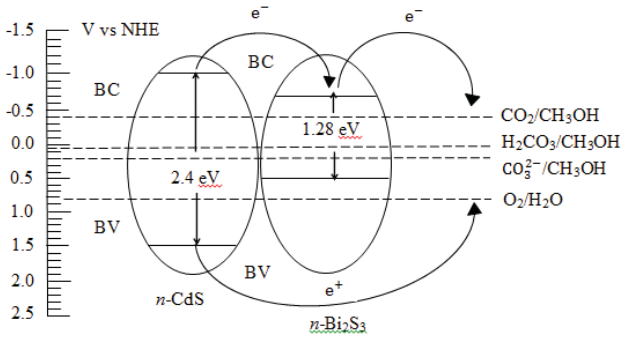

Fig. 6 The mechanism of photocatalytic reduction for production of CH_3OH

This is because the potentials of conduction bands of Bi_2S_3 and CdS are more negative than all those of methanol yield for. Fig. 6 that both $Bi_2S_3$and CdS can be used as the photocatalysts for reducing $CO_2$to CH_3OH under visible light. This is because the potentials of conduction bands of Bi_2S_3 and CdS are more negative than all those of methanol yielded for CO_2 (g), H_2CO_3, CO_3^{2-} etc. in water [14].

IV. Conclusion

The Bi_2S_3/CdS photocatalyst were prepared by direct hydrothermal reactions between their corresponding salt and thiourea. The Bi_2S_3/CdS photocatalyst were characterized by XRD and FTIR. The modification of CdS with Bi_2S_3 can enhance its photocatalytic activity and visible light response. The highest yields of methanol over Bi_2S_3/CdS photocatalyst with 15%, 30% and 45% weight proportions under visible light irradiation were 5, 9.92 and 20 μmole/g, respectively.

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