PREPARATION AND CHARACTERIZATION OF PHOTOCATALYST FOR THE CONVERSION OF CO_2 TO METHANOL

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PREPARATION AND CHARACTERIZATION OF PHOTOCATALYST FOR THE CONVERSION OF CO_2 TO METHANOL

NUR SABRINA BINTI RAHMAT

Thesis submitted in partial fulfilment of the requirements
for the award of the degree of
Bachelor of Chemical Engineering (Pure)

Faculty of Chemical & Natural Resources Engineering
UNIVERSITI MALAYSIA PAHANG

JANUARY 2015

SUPERVISOR'S DECLARATION

We hereby declare that we have checked this thesis and in our opinion, this thesis is adequate in terms of scope and quality for the award of the degree of Bachelor of Chemical Engineering (Pure).

Signature	:
Name of main supervisor	: P. M. DR. MD MAKSUDUR RAHMAN KHAN
Position	: ASSOCIATE PROFESSOR
Date	: JANUARY 2015

STUDENT'S DECLARATION

I hereby declare that the work in this thesis is my own except for quotations and summaries which have been duly acknowledged. The thesis has not been accepted for any degree and is not concurrently submitted for award of other degree.

Signature :
Name : NUR SABRINA BINTI RAHMAT
ID Number : KA11050
Date : JANUARY 2015

Dedication

To my beloved parents, family and friends.
Thank you for always being there for me.

ACKNOWLEDGEMENT

Special thanks to Universiti Malaysia Pahang (UMP), that will soon become my alma mater, particularly Faculty of Chemical Engineering and Natural Resources that had given me the chance to complete my undergraduate research project for my bachelor degree. I am very pleased to recognize my supportive supervisor, P. M. Dr. Md Maksudur Rahman Khan who has contributed so much in helping me to complete my undergraduate research project. My gratification for his contribution can never be enough and this undergraduate research project would have not been completed successfully if it was not for his help and presence. Thank you.

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Finally, I would like to dedicate special thanks to my peer especially Vignes Rasiah and others for always being there for me and also to those who indirectly give moral support to me during the whole two semesters carrying out this undergraduate research project. May Allah SWT bless all of you. Thank you.

ABSTRACT

Due to the reliance of the world on fossil fuel as major source of energy, the 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 address the CO_2 emission and energy crisis. The methanol produces from the photocataytic conversion can be used as source of fuel. CdS is a classical photocatalyst shows high activity under ultraviolet (UV) light irradiation. UV light covers only 4% of the solar light spectrum, hence visible light active photocatalyst for CO2 conversion is important. In the present work, Bi_2S_3/CdS was synthesized as an effective visible light responsive photocatalyst for CO_2 reduction. The Bi_2S_3/CdS photocatalyst was prepared by the hydrothermal reaction between the precursors. The prepared powder was calcined at 250 ℃ in the muffle furnace. The catalyst was characterized by X-ray diffraction (XRD) and Fourier Transform Infrared spectroscopy (FTIR). The product has been analysed by using gas chromatograph flame ionization detector (GC-FID). The photocatalytic activity in methanol production as a function of time has been investigated. The maximum yield of methanol was obtained after 6 hours of reaction. The effect of CdS concentration in Bi_2S_3/CdS photocatalyst was investigated and the yields of methanol were increased with increasing of CdS concentration. The maximum yield of methanol was obtained with Bi_2S_3/CdS with 45 % of CdS. The present works shown the potentially of Bi_2S_3/CdS for CO_2 reduction under visible light.

ABSTRAK

Kebergantungan dunia kepada bahan api fosil sebagai sumber utama tenaga telah menyebabkan pelepasan karbon dioksida kepada alam sekitar tidak dapat dielakkan dan berlakunya pemanasan global. Cara yang cemerlang untuk menangani krisis pelepasan karbon dioksida dan tenaga adalah dengan fotopemangkin pengurangan karbon dioksida Untuk mejana methanol metana dan lain-lain. Metanol yang dihasilkan dari penukaran photocataytic boleh digunakan sebagai sumber bahan api. CdS adalah fotomangkin klasik yang menunjukkan aktiviti yang tinggi di bawah sinaran ultraviolet (UV). Cahaya UV hanya meliputi 4% daripada spektrum cahaya matahari, justeu cahaya fotomangkin aktif untuk penukaran karbon dioksida adalah penting. Dalam kajian ini, Bi_2S_3/CdS telah disintesis sebagai fotomangkin responsif cahaya yang boleh dilihat berkesan untuk pengurangan karbon dioksida. Bi_2S_3/CdS fotomangkin telah disediakan oleh reaksi hidroterma antara prekursor. Serbuk telah dibakar pada 250 ℃ dalam meredam relau. Pemangkin yang dicirikan oleh pembelauan sinar-X (XRD) dan Fourier Transform spektroskopi inframerah (FTIR). Produk reaksi ini telah dianalisis dengan menggunakan alat kromatografi gas pengesan pengionan nyala (GC-FID). Aktiviti fotopemangkinan dalam pengeluaran metanol sebagai fungsi masa telah disiasat. Hasil maksimum metanol telah diperolehi selepas 6 jam tindak balas. Kesan kepekatan CdS dalam Bi_2S_3/CdS fotomangkin telah disiasat dan hasil metanol telah meningkat dengan peningkatan kepekatan CdS. Hasil maksimum metanol telah diperolehi dengan Bi_2S_3/CdS dengan 45% daripada CdS. Kerja-kerja ini ditunjukkan yang berpotensi daripada Bi_2S_3/CdS untuk pengurangan karbon dioksida di bawah cahaya yang boleh dilihat.

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1 INTRODUCTION

1.1 Motivation and statement of problem

Sustainable development depends directly on the availability of sufficient energy resources, consumption over restoration ratios and effects of energy on the environment (Ghoniem AF., 2011). Consequently, rapid industrialization and modernization has amplified energy demands while fossil fuels have remained as the main source of energy, exacerbating critical social issues like security of energy supply and climate change (Gill SS et al., 2010).

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 a 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 (C. Song, 2006). 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 (S.C. Roy et al., 2010). By using this way, carbon dioxide emissions can be reduced and energy crisis can be solved.

The most popular photocatalytic material with excellent stability, innocuity and low price (H.-C. Yang et al., 2009), three-dimensional, larger surface and regular structure (G.K. Mor et al., 2006) is titanium dioxide (TiO_2). Differ from the massive or grainy semiconductor materials, TiO_2 structures show typically a super hydrophilic behaviour (J.M. Macak et al., 2007) and quickly transfer electron (K. Zhu et al., 2007). However, TiO_2 have a 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) (M. Hoffmann et al., 1995). It is well known that the band gaps of CdS and Bi_2S_3 are narrower and the potentials of conduction bands are more negative compare to other photocatalysts (Vogel R et al., 1994).

The ideal photocatalyst having 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.

1.2 Objectives

The following are the objectives of this research:

- To prepare, modify and characterize Bi_2S_3/CdS photocatalysts.
- To use the obtained Bi_2S_3/CdS as a photocatalyst for the photocatalytic reduction of carbon dioxide to methanol with water under visible light radiation

1.3 Scope of this research

The following are the scope of this research:

- The CdS was modified by Bi_2S_3 and the obtained Bi_2S_3/CdS were used as a photocatalyst for the photocatalytic reduction of carbon dioxide to methanol with water under visible light radiation.
- The Bi_2S_3, CdS and Bi_2S_3/CdS photocatalysts were characterized by X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR).
- The photocatalytic activities of the Bi_2S_3, CdS and Bi_2S_3/CdS photocatalysts for reducing carbon dioxide, CO_2 to methanol, CH_3OH under visible light irradiation were investigated by Fourier transform infrared spectroscopy (FTIR) and gas chromatography/flame ionization detection (GC/FID).

2 LITERATURE REVIEW

2.1 Overview

This paper presents about the CdS and Bi_2S_3 which are synthesize into a new type of heterostructure photocatalyst which lower the photocatalytic efficiency of TiO_2 under visible light irradiation by decomposing the water, H_2O to produce methanol as the a reusable hydrocarbon.

2.2 Fundamentals in photocatalysis

Photocatalysis is a process in which light radiation shaving energy equal to or greater than the band gap energy (E_{bg}) of a semiconductor strikes on its surface and generates electron (e−) hole and (h+) pairs. The photogenerated electrons and holes participate in various oxidation and reduction processes to produce final products. However, if the charges fail to find any trapped species on the surface or their energy band gap is too small, they recombine immediately releasing unproductive energy as heat (Kavita K, et al., 2004). In particular, the activity of heterogeneous photocatalysis depends on :

(a) composition of reaction medium
(b) adsorption of reactants on semiconductor surface
(c) type of semiconductor and its crystallographic or morphological characteristics
(d) ability of semiconductor to absorb UV (ultraviolet) or visible light (Hd Lasa et al, 2005)

During photoreduction process, several processes related to catalyst, interface and donor-acceptor are involved as explained in Figure 2.1. In catalyst related process, there is production of electrons and holes by absorbing photons. The lifetime of the charges is few nanoseconds only, therefore several recombine immediately and others participate in carrying various chemical reactions. Interface related process consists of transfer of electrons and adsorption on catalyst surface and mass transfer. In donor–acceptor related process, electrons and holes which escape from the excitation regions are trapped by adsorbed species, which become active and participate in various reduction and oxidation process.

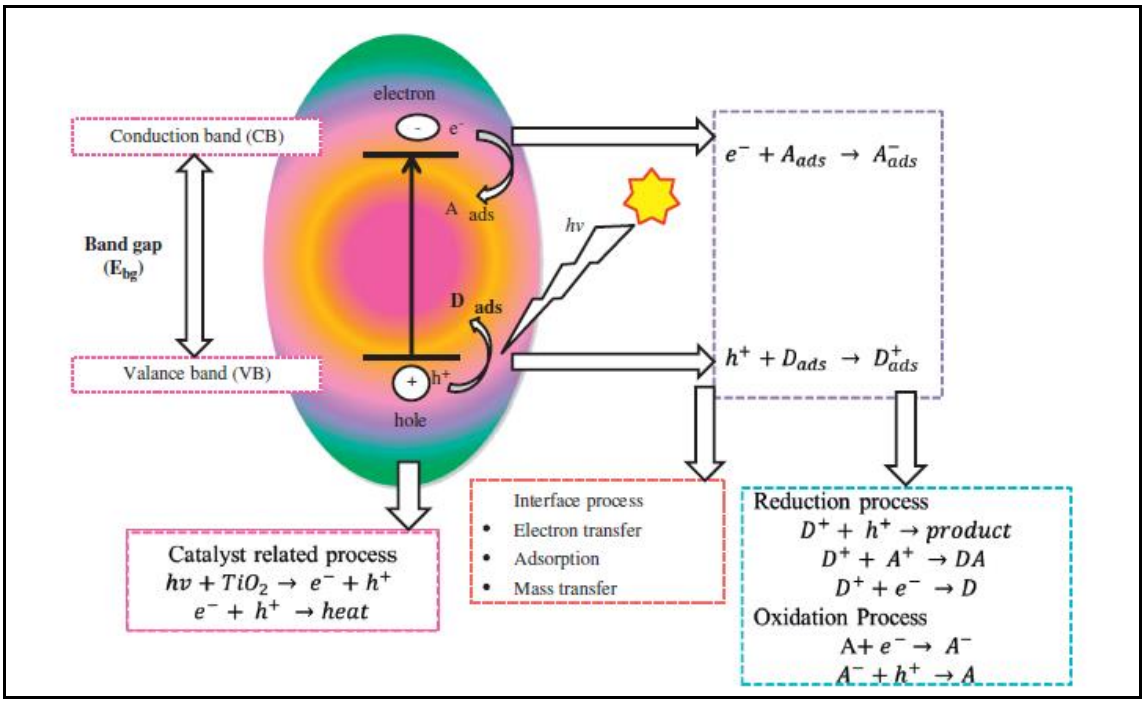


Figure 2-1 Schematic representation of band gap formation and photocatalytic processes (Muhammad Tahir et al., 2013)

Detailed explanation of photoreduction surface phenomenon for heterogeneous photocatalysis is presented in Figure 2.2. The heterogeneous photocatalysis mechanism is very complex and many possibilities or reaction paths are possible. This depends on the life of charge particles if their energy band gap is lower and recombines immediately.

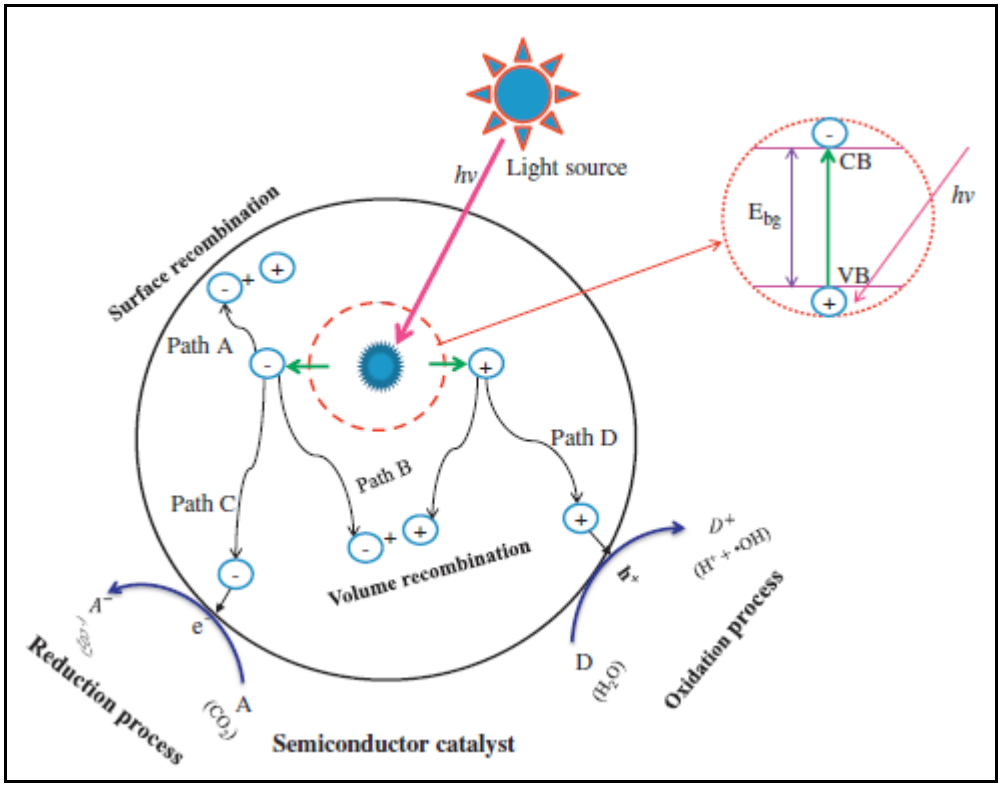


Figure 2-2 Mechanism and pathways for photocatalytic oxidation and reduction processes on the surface of heterogeneous photocatalyst. (Muhammad Tahir et al., 2013)

However, if the charge particles have enough band gap energies to separate, then the following possibilities or paths are possible (Arakawa H et al., 2001) :

a) The photoinduced charges move towards the surface of semiconductor and transfer electrons or holes to adsorbed species. The electron transfer process is more effective if pre-adsorbed species already exist at the surface. At the surface, semiconductor can donate electron to reduce acceptors (Path C), in turn a hole can transfer to the surface where an electron from donor species can combine with the surface hole, oxidizing donor species (Path D).

b) During charges transfer process, there is possibility of electron–hole recombination. Recombination of separated electron and holes can possible in the volume or at the surface of semiconductor with the release of unproductive heat.

c) Surface recombination (Path A) occurred when electrons and holes recombine on the semiconductor surface. On the other hand, if charges have the opportunity to recombine inside the semiconductor volume, then this process is called volume recombination (Path B).

2.3 Decomposition of water, H_2O

The photocatalytic reduction of CO_2 with H_2O to reusable hydrocarbon resources such as methanol is found to be a prospective way to reduce carbon dioxide emissions and resolve the energy crisis. The catalyst is use to split the H_2O. When H_2O decompose and split into O_2 and H_2, the stoichiometric ratio of its products is 2:1 :

$$2\ H_2O \overset{\text{photon energy} > 1.23eV}{\rightleftharpoons} 2\ H_2 + \ O_2$$

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 (J. Head, J. Turner, 2001). 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. These values are true only for a completely reversible reaction at standard temperature and pressure (1 bar and 25 °C).

The potential must be less than 3.0V to make efficient use of the energy present across the full spectrum of sunlight. Water splitting can transfer charges, but not be able to avoid corrosion for long term stability. Defects within crystalline photocatalysts can act as recombination sites, ultimately lowering efficiency.

Materials used in photocatalytic water splitting fulfill the band requirements outlined previously and typically have dopants and/or co-catalysts added to optimize their performance.

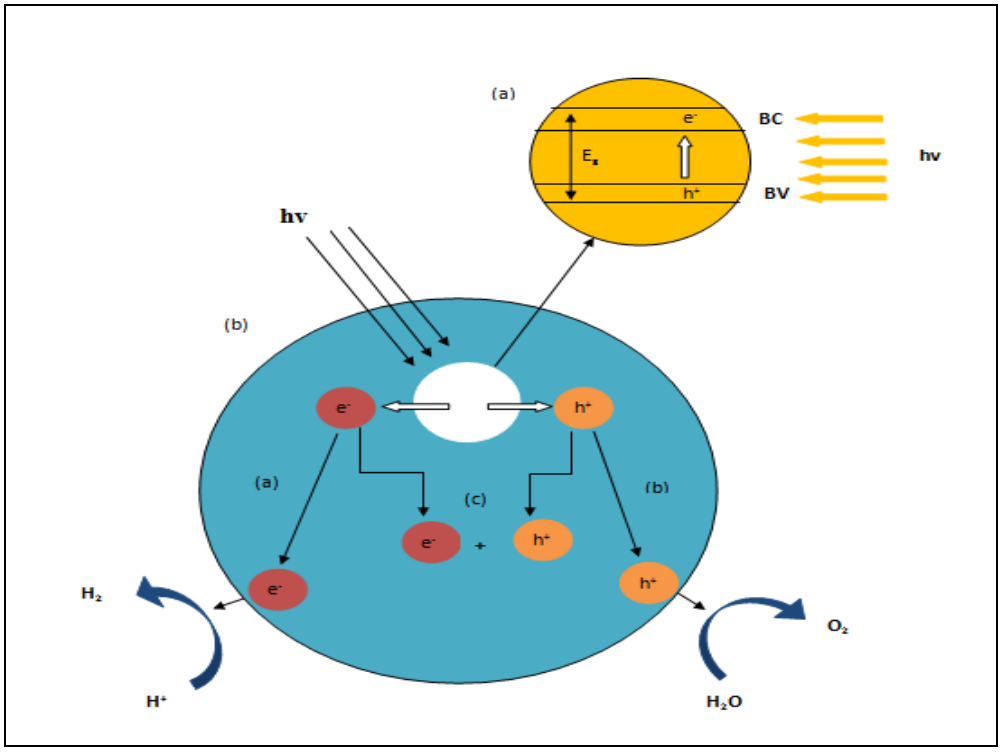


Figure 2-3 Illustration of the decomposition and splitting of water, H_20

2.4 Selection of Bi_2S_3/CdS as the catalyst

The effectiveness of semiconductors to transfer photo-induced electron toward adsorbed species depends on the semiconductor conductance band and redox potential of adsorbates. The band gap of semiconductor indicates its ability to absorb photons. Usually large band gap materials are most suitable for CO_2 reduction applications as they can provide enough redox potentials to execute chemical reaction. However, large band gaps require higher input energy (Linsebigler A L et al, 1995).

The limitation of photocatalytic activity for semiconductors can also be overcome by surface modification. Semiconductor surface modification has three advantages :

(a) inhibiting recombination by increasing charge separation which ultimately increases efficiency

(b) enhancing wavelength response

(c) increasing selectivity or yield of desired product

The design of molecular size catalysts within zeolite and other porous materials having micro pores is of special interest due to distinct physical and chemical properties (Mori K et al., 2012). Micro structured materials have many advantages including higher internal surface area, ion exchange capacities and porous structure allowing the molecules to diffuse in to pores cavities and remain intact during cluster growth (Anpo M, 1995). Different types of sensitizers such as coupling semiconductors, carbon nanotubes, and some novel sensitizers could also be used to improve photocatalytic activity and selectivity under solar spectrum.

It is well known that the band gaps of CdS and Bi_2S_3 are narrower and the potentials of conduction bands are more negative compare to other photocatalysts. The CdS and Bi_2S_3 have higher quantum efficiency, which decrease the combining ratio of electrons and holes. It can also absorb more than 5% sunlight in the ultraviolet since it is a narrow band gap semiconductor.

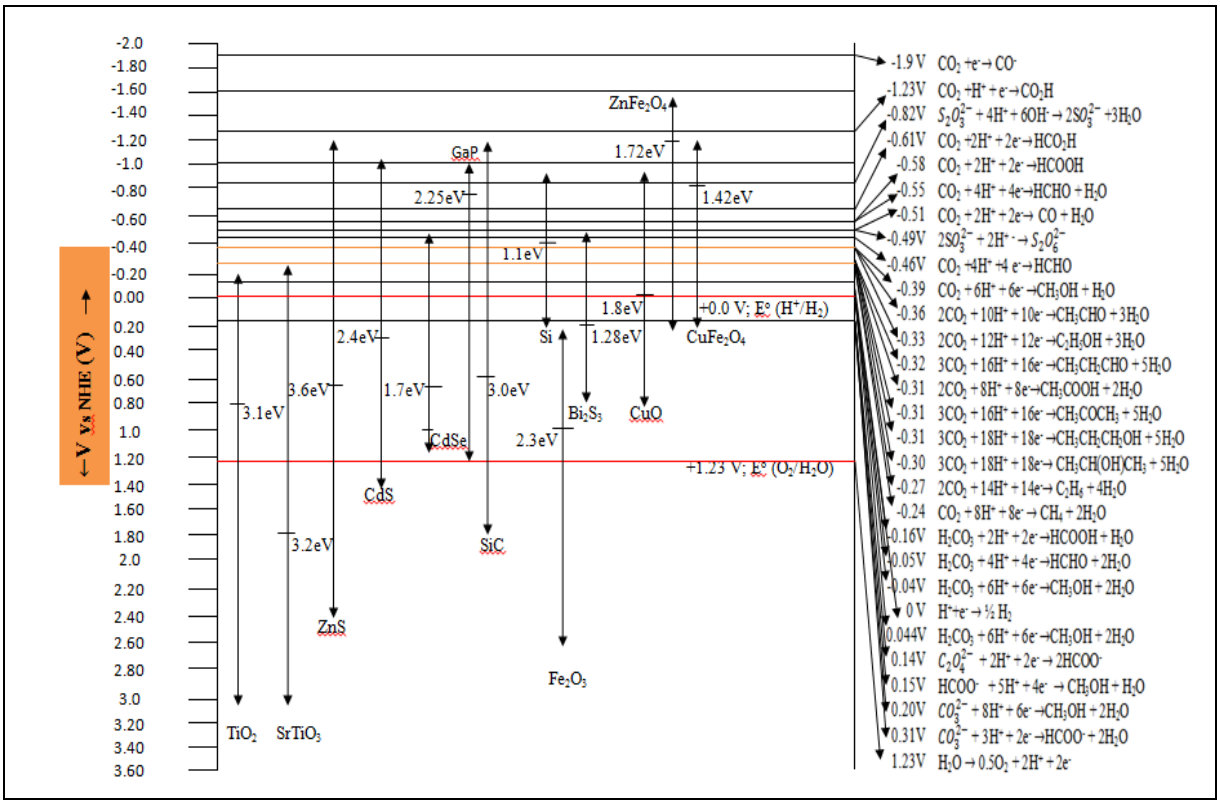


Figure 2-4 Illustration of the bandgap of semiconductors in photocatalytic

In 1979, Inoue et al. first reported that CO_2 bubbled in water was reduced to HCHO, HCOOH and CH_3OH over various semiconductor photocatalysts, such as CdS, TiO_2, ZnO, GaP and SiC under photoirradiation of their aqueous suspension. Aliwi and Al-Jubori carried out the photoreduction of CO_2 in the presence of H_2S over typical sulfides such as bismuth sulfide (Bi_2S_3) and cadmium sulfide (CdS). HCHO and HCOOH were produced in this reaction.

The photocatalytic reduction of CO_2 over hexagonal CdS nanocrystallites prepared in N, N-dimethylformamide (DMF) was investigated by Fujiwara and his co-workers and they found that sulfur vacancies on the surface of nanocrystallites can be formed by the adsorption of excess Cd^{2+} to the surface, which resulted in a remarkable increase of photocatalytic activity. Eggins and his co-workers performedthe photocatalytic reduction of CO2 to dimeric andtetrameric products, namely oxalate, glyoxylate, glycolate andtartrate using aqueous CdS or ZnS colloids containing tetramethylammonium chloride.

2.5 Summary

This paper presents about the CdS and Bi_2S_3 can be utilized as sensitizers and applied to synthesize a new type of heterostructure photocatalyst which can solve the instability of sulphides and lower the photocatalytic efficiency of TiO_2 under visible light irradiation. A better photoabsorption performance can be determined from the yield of methanol with the photocatalytic activity of Bi_2S_3/CdS.

3 MATERIALS AND METHODS

3.1 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.

3.2 Preparation of photocatalysts

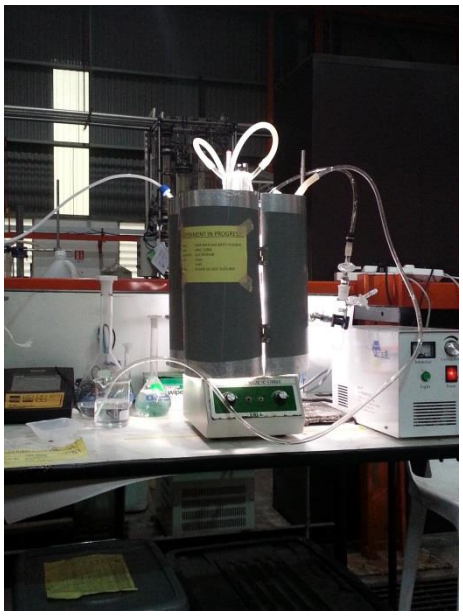
The Bi_2S_3/CdS catalyst was prepared by following direct hydrothermal method. $Cd(NO_3)_2.4H_2O$, $Bi(NO_3)_3.5H_2O$ and thio-urea of different compositions such as 6.02, 3.05 and 2.26 g, respectively were considered for the preparation followed by hydrolysis with 600 mL of deionized water in an autoclave 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% Bi_2S_3/CdS, 30% Bi_2S_3/CdS and 45% Bi_2S_3/CdS were prepared with the same method.

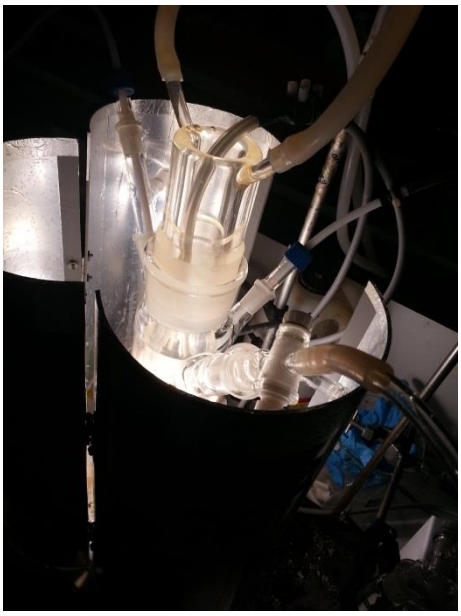
3.3 Characterization

The X-ray diffraction (XRD) patterns were obtained at room temperature using MSAL-XD2 diffractometer with Cu K_α radiation (operated at 36 kV and 30 mA, λ = 0.15406 nm). The Fourier transform infrared spectroscopy (FTIR) patterns were also obtained for both sample and products.

3.4 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 20.701, 1.225 and 3.789 g were dissolved in 300 mL of ultrafiltered 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. The concentrations of methanol in the samples were analysed using a gas chromatograph flame ionization detector (GC-FID).





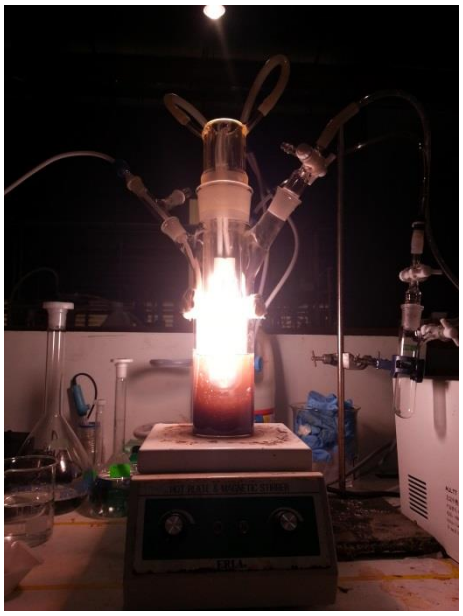


Figure 3-1 Illustration on how the experiment were done

4 RESULTS AND DISCUSSION

4.1 The presence of methanol

1. In a test tube, 1 ml of acetone + 3 drops of Jones oxidation reagent were added.
2. In a test tube, 1 ml of acetone + 200 μL of pure methanol + 3 drops of Jones oxidation reagent were added.
3. In a test tube, 1 ml of acetone + 200 μL of sample + 3 drops of Jones oxidation reagent were added.
4. For the calibration procedure and UV method, 250 μL solution and 2.5 ml of distilled water, each from the test tubes were put in cuvettes and the UV was run.

Figure 4-1 The sample from the experiment

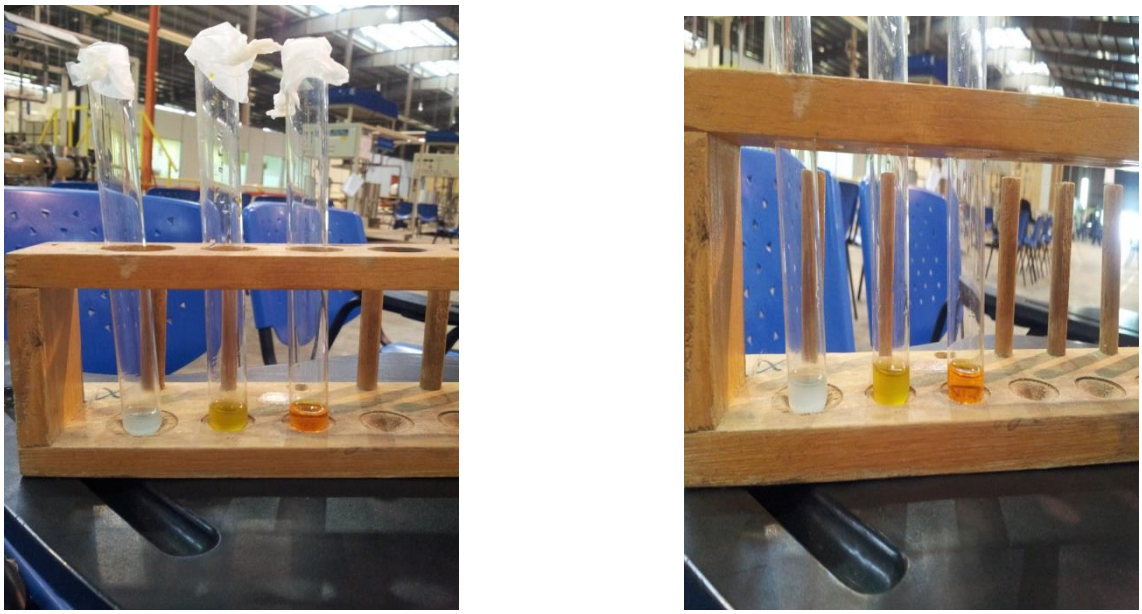


Figure 4-2 The pure methanol, the sample and the Jones oxidation reagent

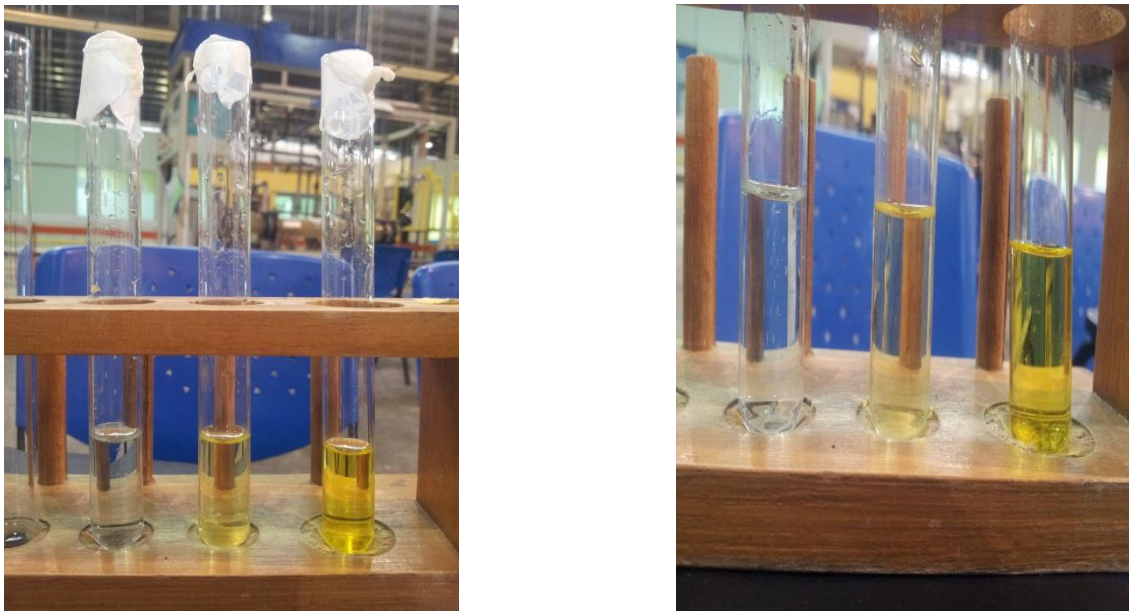
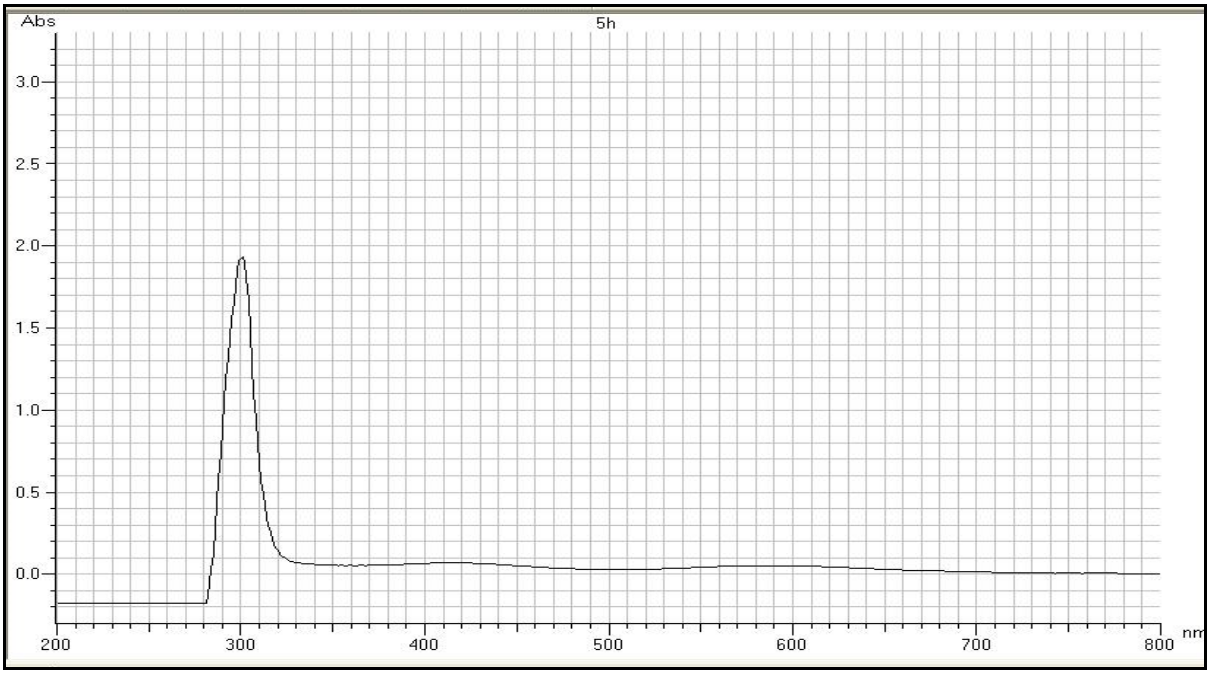


Figure 4-3 The pure methanol, the sample and the Jones oxidation reagent after diluted with water to run in UV-Vis spectrometer

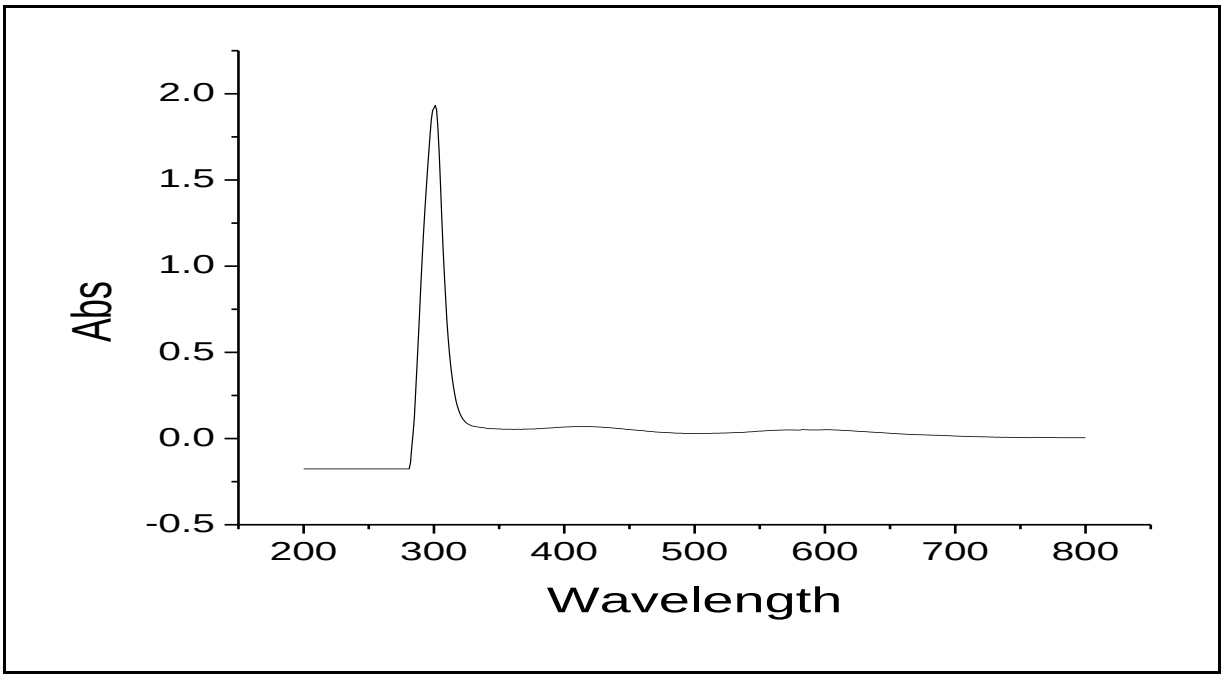
4.2 UV-Vis spectroscopy analysis

The UV-Vis spectra in the range of 200-800 nm was measured with a Daojin UV-2550PC diffuse reflectance spectroscope.

The results are as below :

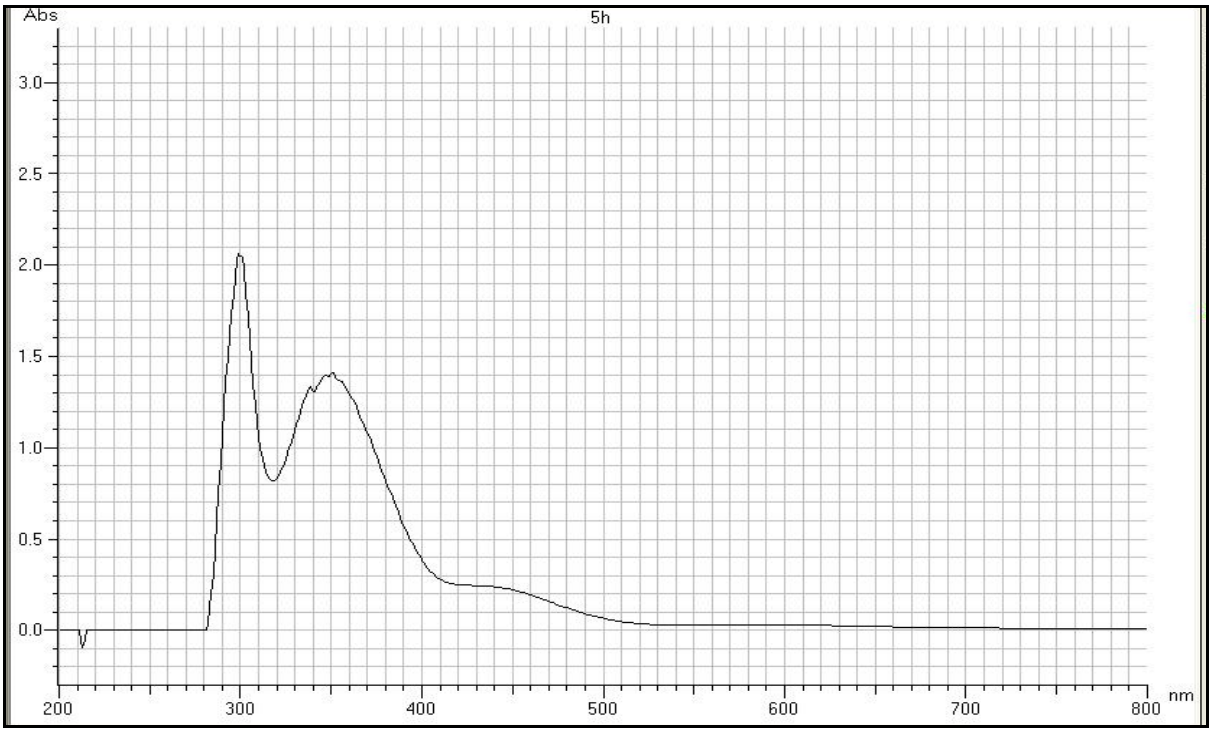


(a)

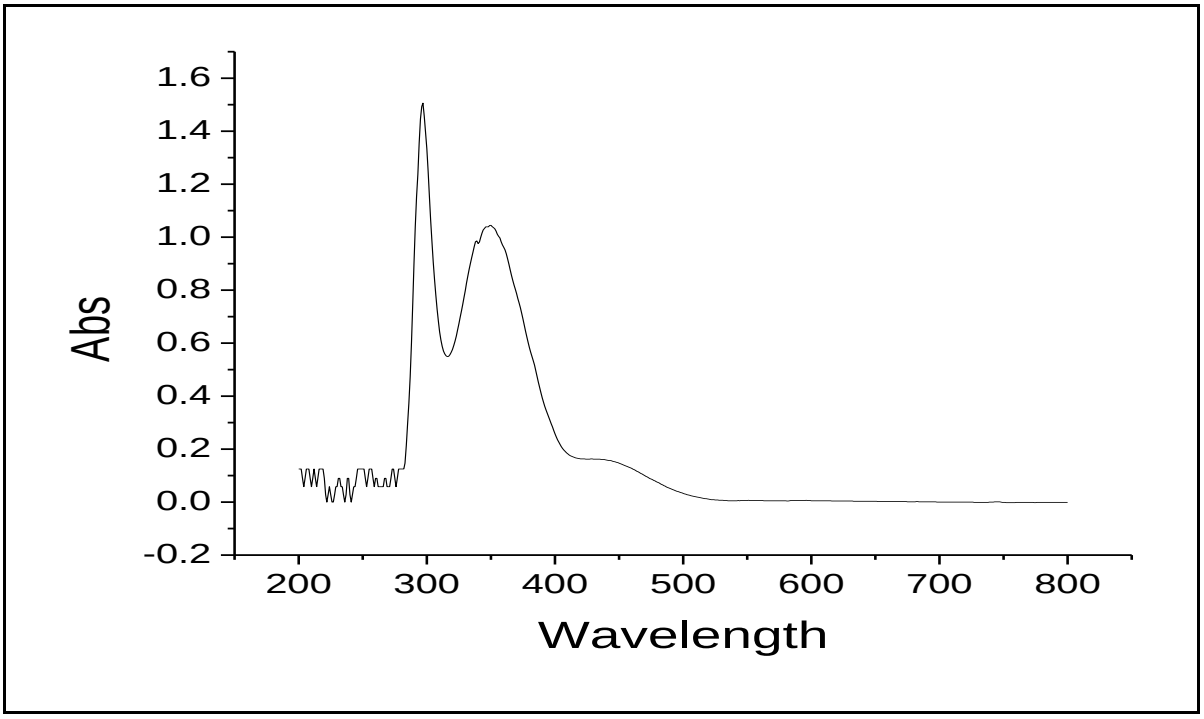


(b)

Figure 4-4 (a) & (b) Pure methanol detection by UV-Vis



(a)



(b)

Figure 4-5 (a) & (b) Methanol detection in a sample by UV-Vis

4.3 X-ray Diffraction (XRD) analysis

The XRD pattern of pure CdS is shown in the Figure 4.6 (2θ=3-80◦), was used as a reference for the structural analysis of as-prepared Bi_2S_3/CdS photocatalysts. XRD patterns of various as-prepared photocatalysts are shown in Figure 2(1-d) 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%). 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) (Figure 4.6).

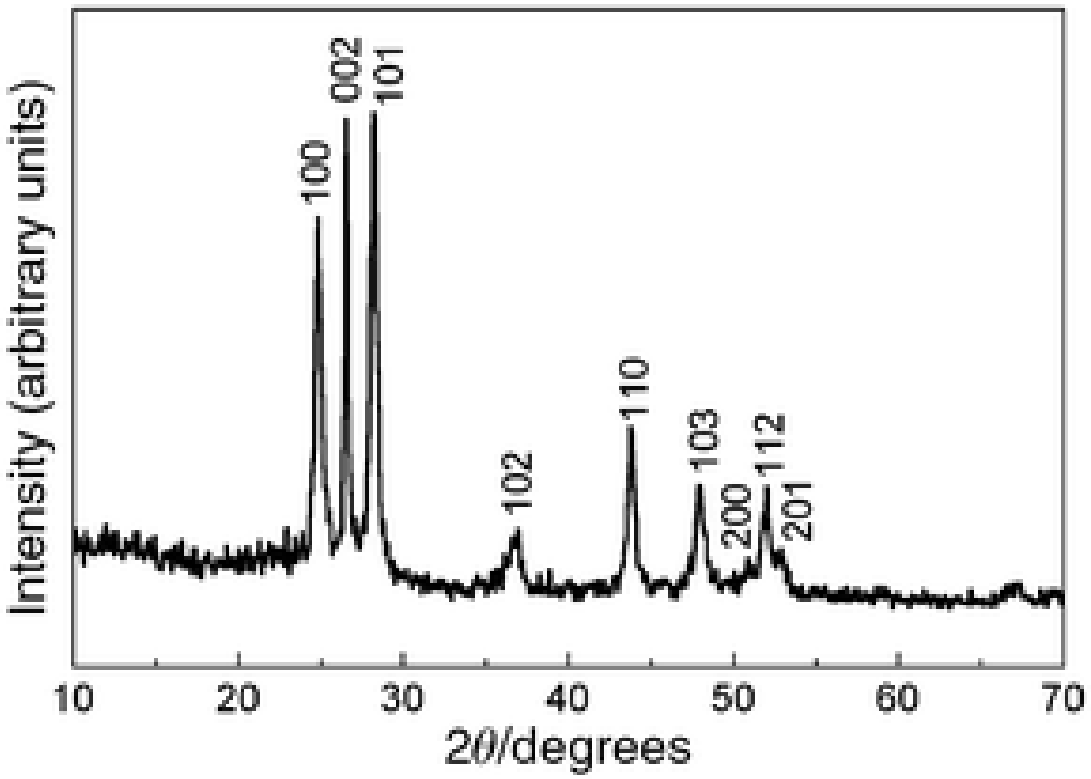


Figure 4-6 XRD pattern of CdS shown as a reference

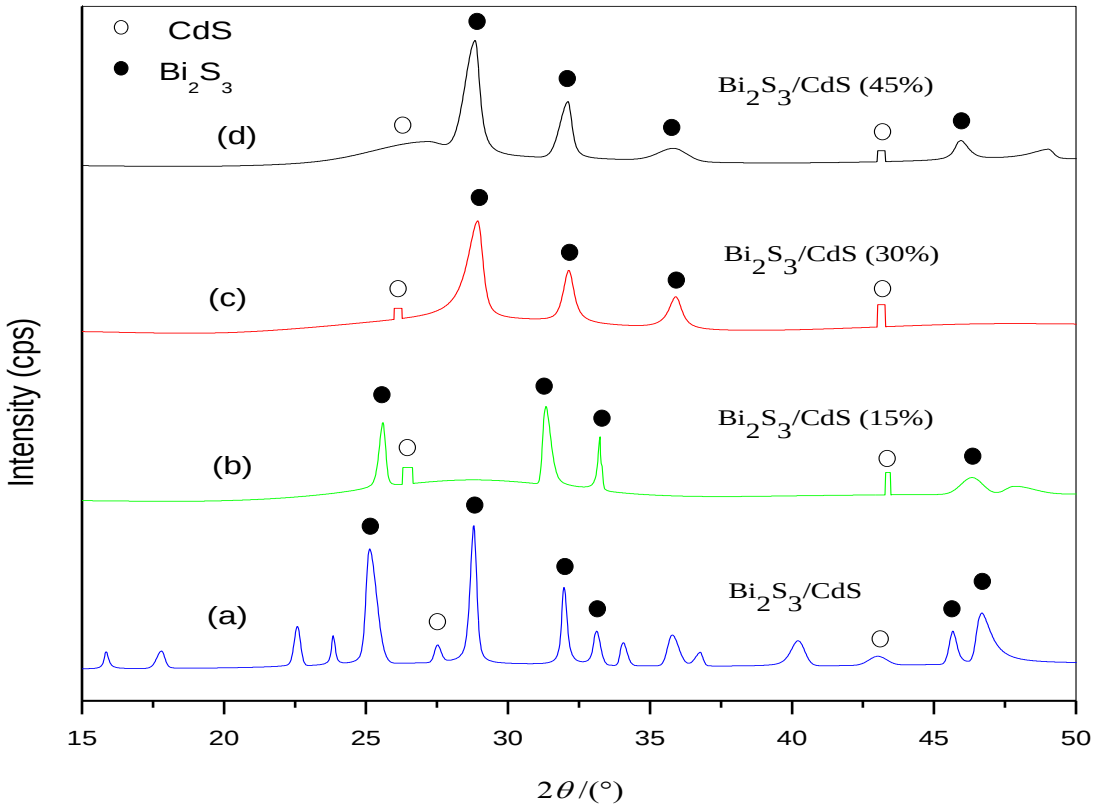


Figure 4-7 XRD patterns of various photocatalysts (a) Bi_2S_3/CdS (b) Bi_2S_3/CdS (15%) (c) Bi_2S_3/CdS (30%) (d) Bi_2S_3/CdS (45%)

It can be seen from the XRD spectrum of the Bi_2S_3 in Figure 4.7 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 Bi_2S_3 structure is orthorhombic.

Moreover, the peaks of all the Bi_2S_3/CdS photocatalysts in Figure 4.7 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 with each other and make a hetero junction to show catalytic activities.

4.4 Fourier Transform Infrared Spectroscopy (FTIR) analysis

FTIR was carried out to identify the component and chemical compositions which exist in the Bi_2S_3/CdS photocatalysts and the product which is methanol from the photocatalytic reaction testing. From Figure 4.8, it can be seen that from FTIR spectra of adsorbed Bi_2S_3/CdS are from 500 – 2000 cm^{-1} while photocatalysts of Bi_2S_3/CdS (15%), Bi_2S_3/CdS (30%) and Bi_2S_3/CdS (45%) are adsorbed from 500 – 700 cm^{-1}.

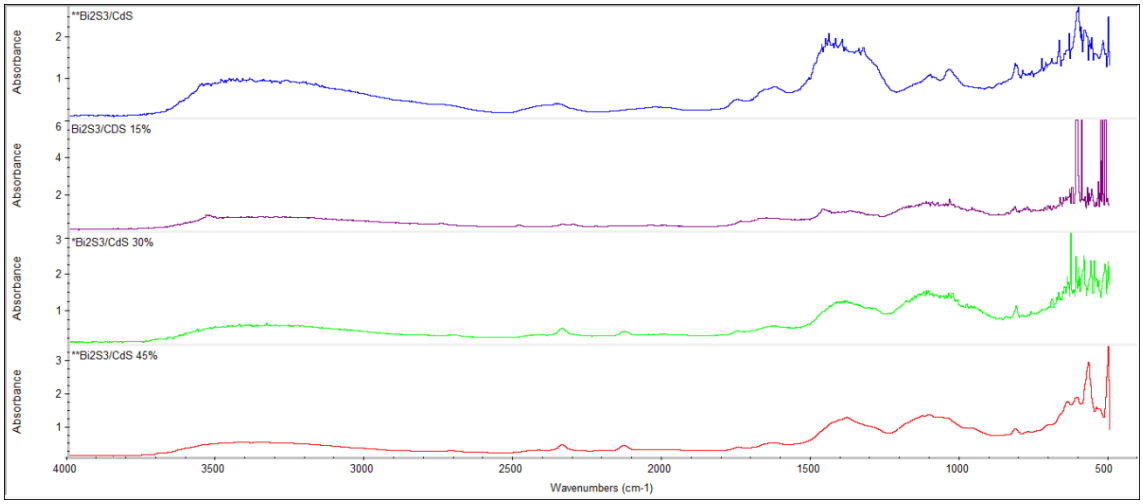


Figure 4-8 FTIR patterns of various photocatalysts

From Figure 4.9, it can be seen that from FTIR spectra of adsorbed methanol at room temperature of 298 K, formation of several absorption bands in the wavenumber region at 3000 - 3600 cm^{-1} and above 1400 cm^{-1}. The intensity of absorption bands decreased after evacuation. Positions of these bands are very close to those of gaseous methanol. They can be attributed to undissociated methanol, which is weakly bound via H-bond on a cation-anion couple with basic character.

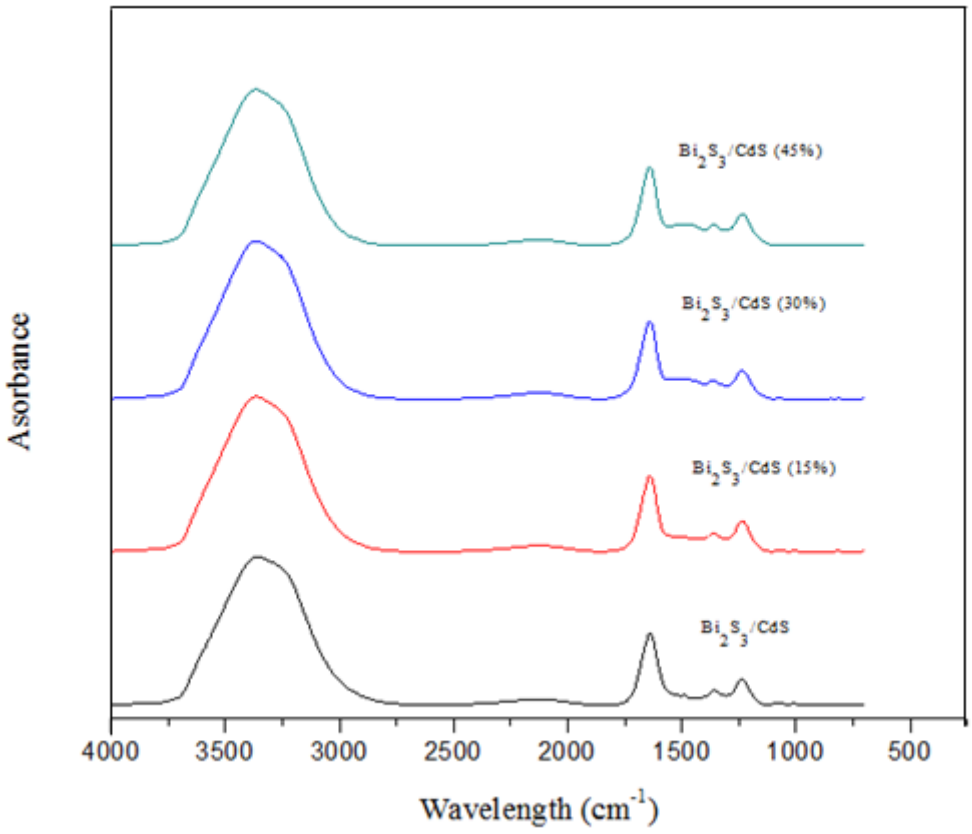


Figure 4-9 FTIR patterns from the photocatalytic reaction testing

4.5 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 Figure 4.10. From the figure, 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 20.04 μmole/g when the weight proportions of Bi_2S_3 to CdS were 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%.

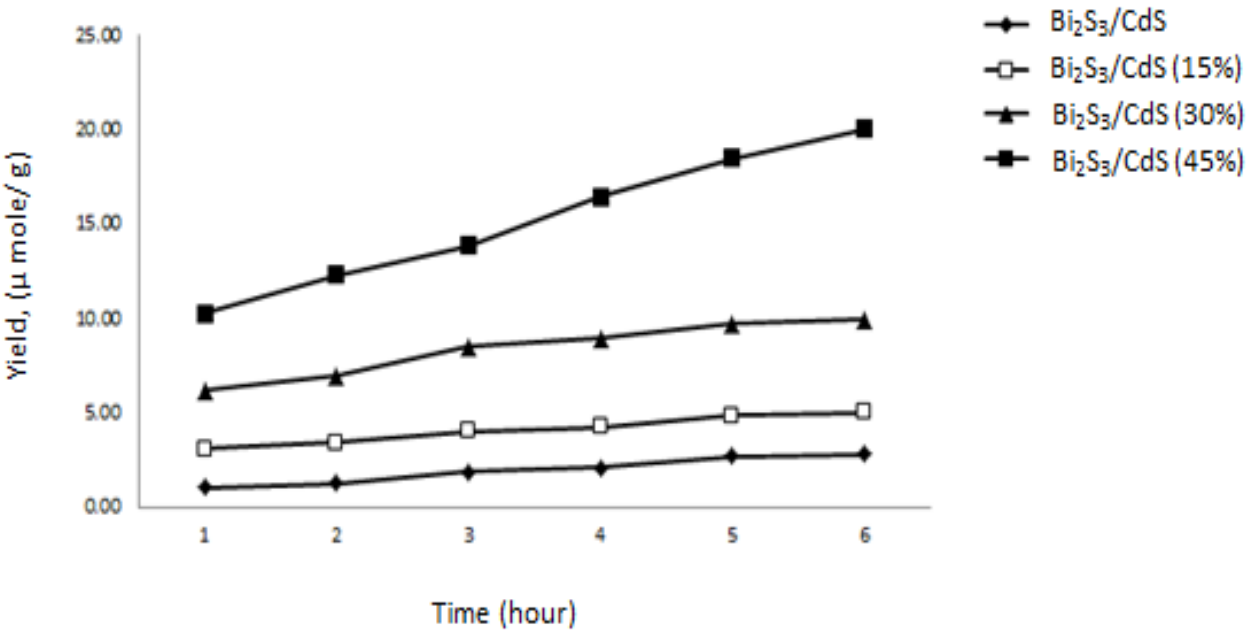


Figure 4-10 The yields of CH_3OH in the photocatalytic reduction of CO_2 with H_2O over various photocatalysts under visible light irradiation

The mechanism of photocatalytic reduction of CO_2 with H_2O to CH_3OH is shown in Figure 4.11. It can be seen from Figure 4 that both Bi_2S_3 and CdS can be used as photocatalyst 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 yield for. The detailed band structures are also pictured in Figure 4.11.

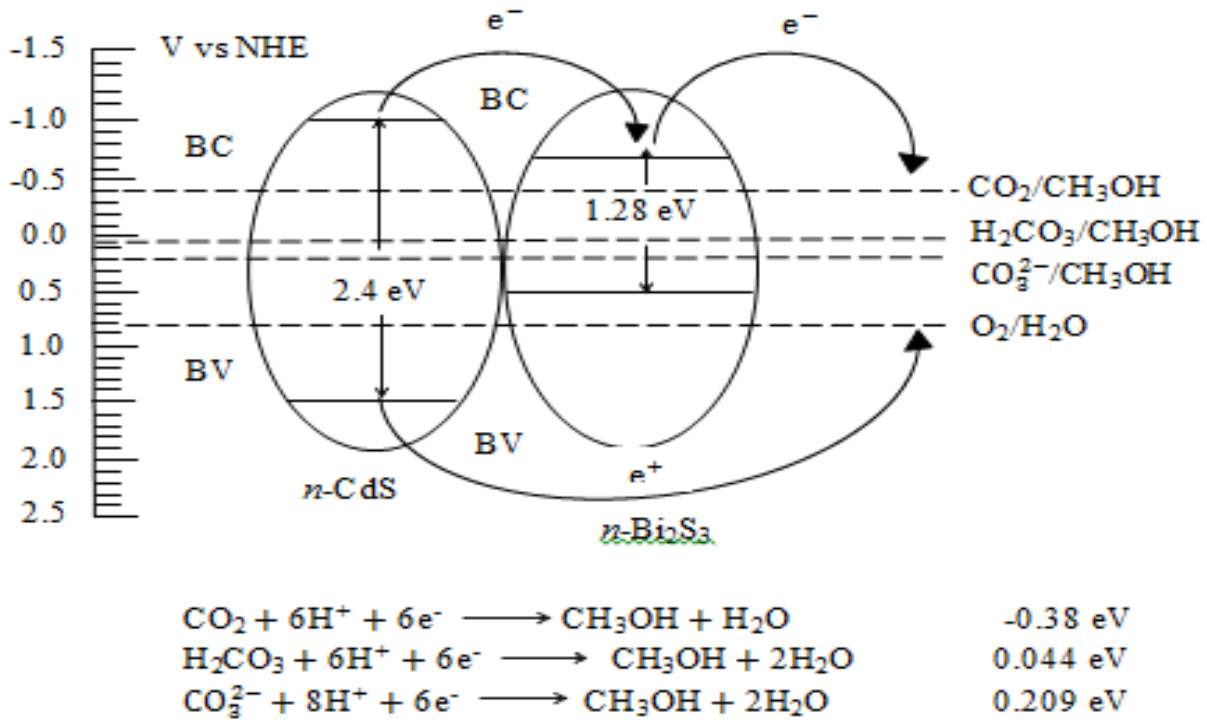


Figure 4-11 The mechanism of photocatalytic reduction for production of CH_3OH

5 CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

The Bi_2S_3/CdS photocatalyst were prepared by direct hydrothermal reactions between their corresponding salt and thio-urea. The Bi_2S_3/CdS photocatalyst was characterized by XRD. 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 5.04, 9.92 and 20.04 μmole/g, respectively.

5.2 Recommendations

Some recommendations to upgrade the effectiveness of this research had been identified through the whole experimental process of preparation and characterization of photocatalyst for the conversion of CO_2 to methanol which are:

i) Wear personal protective equipment (PPE) such as gloves and goggle during the preparation of the catalyst since the chemicals used in the experiment are hazardous to health ad irritant to eyes and skin.

ii) The temperature of the hydrothermal autoclave should be constant so that the catalyst produced is at the same temperature range.

iii) Use a ceramic mortar and pestle sets to reduce catalyst to very fine powders so that it can be produced larger amounts of methanol during photocatalytic activity.

iv) Continue to bubble to CO_2 so that the photocatalytic activity is continued to produce methanol.

v) Monitor the temperature during the photocatalytic activity. The temperature range should be 30-35℃ so that there is less loss of methanol to the air.

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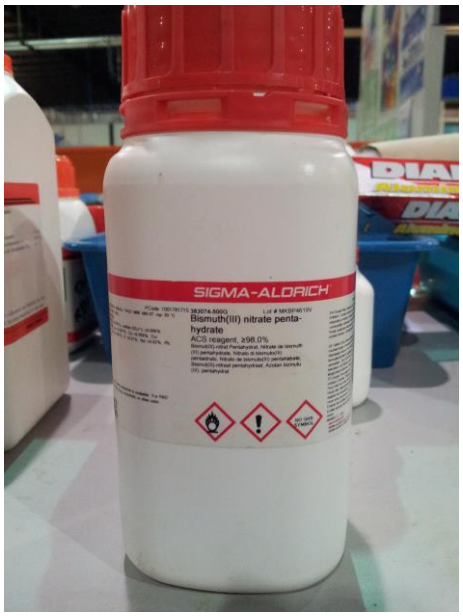
APPENDIXES

APPENDIX A.1

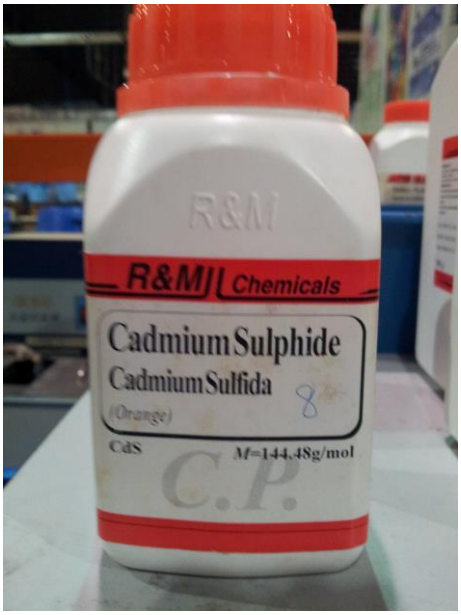
A.1.1 Chemicals



Bismuth (III) nitrate pentahydrate

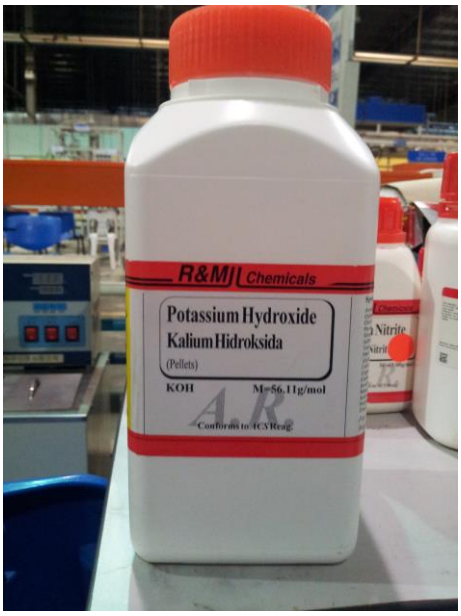
Cadmium nitrate tetrahydrate

Thio-urea

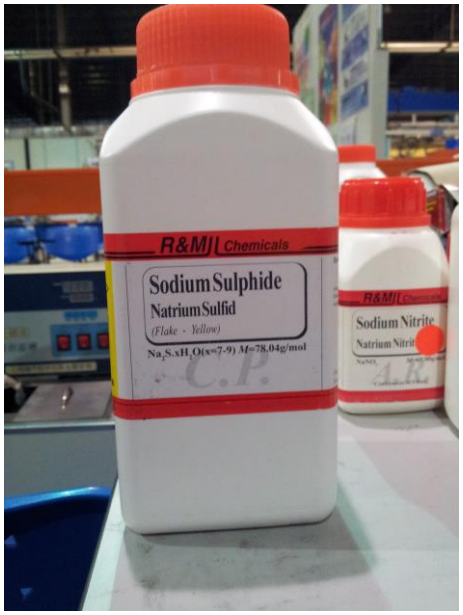


Cadmium sulphide

Sodium nitrite



Potassium hydroxide

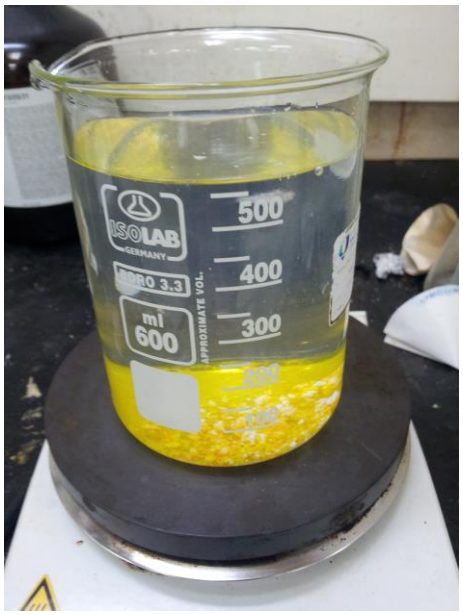


Sodium sulphide

A.1.2 Experiments

The pictures shown below are how the experiments were done.

A.1.2.1 Preparation of photocatalyst

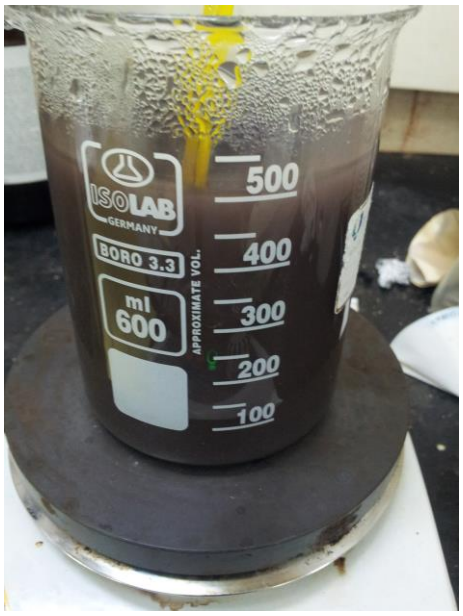


Before the experiment start

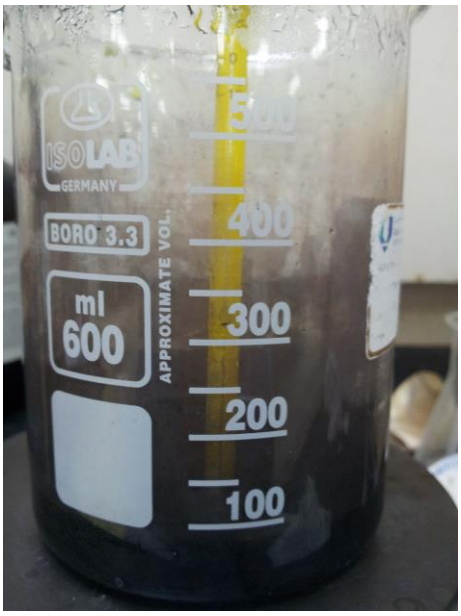
At the beginning of the experiment

Time = 1 hour

Time = 2 hours



Time = 3 hours

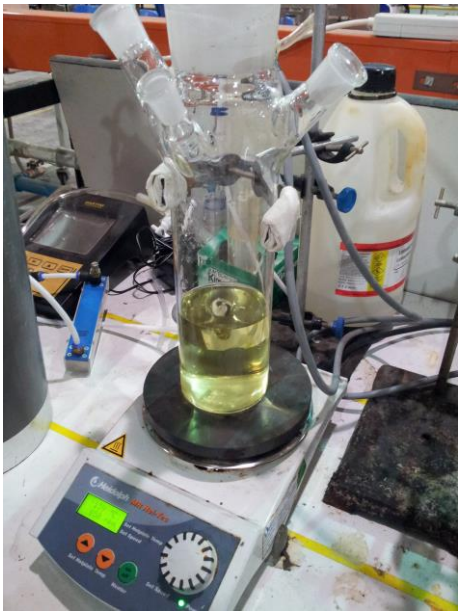


Time = 6 hours

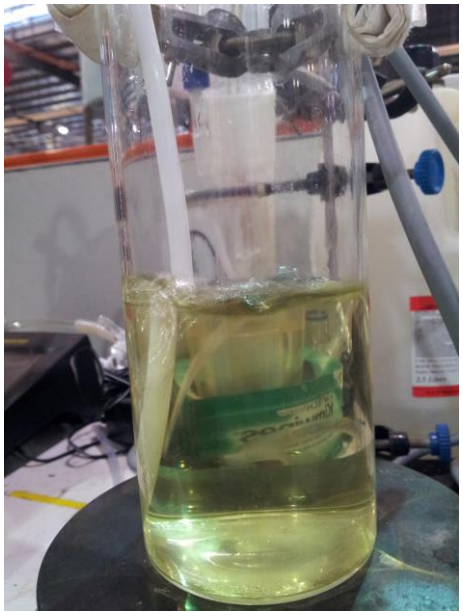
The catalyst after being dried in the oven for overnight

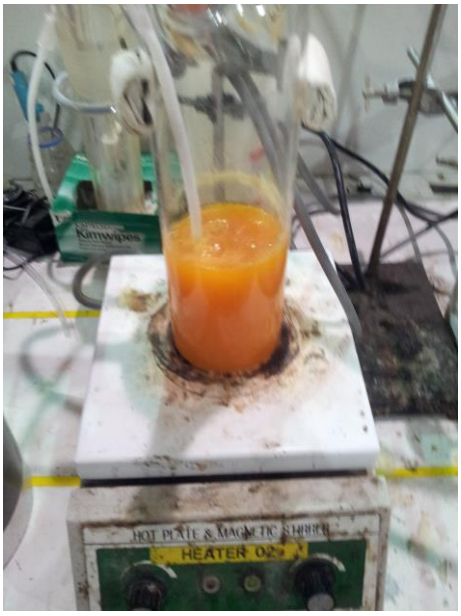
A.1.2.2 Photocatalytic reaction testing

The solution used in the reaction



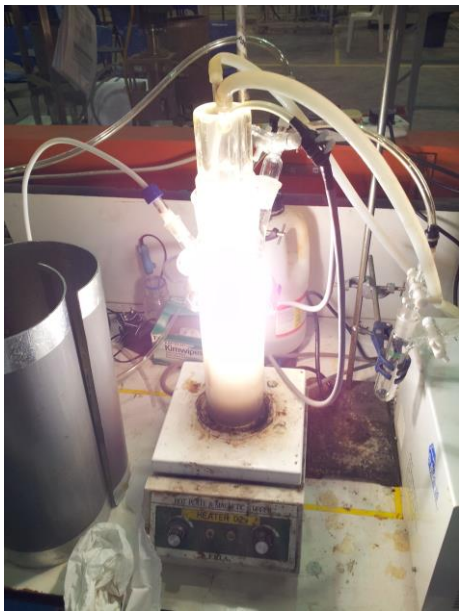
The set up of the reaction

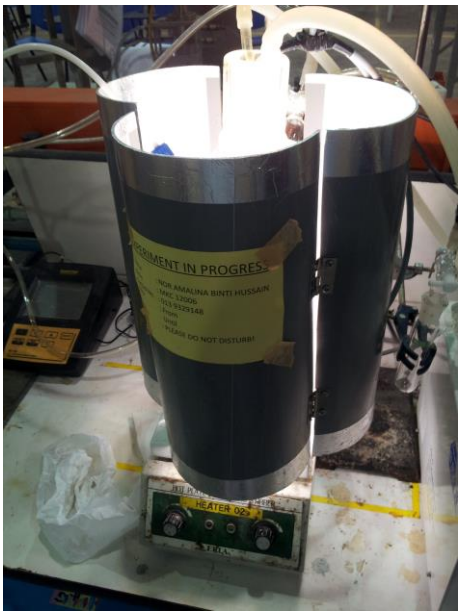




CO_2 was bubbled through the solution in the reactor before irradiation for 30 minutes

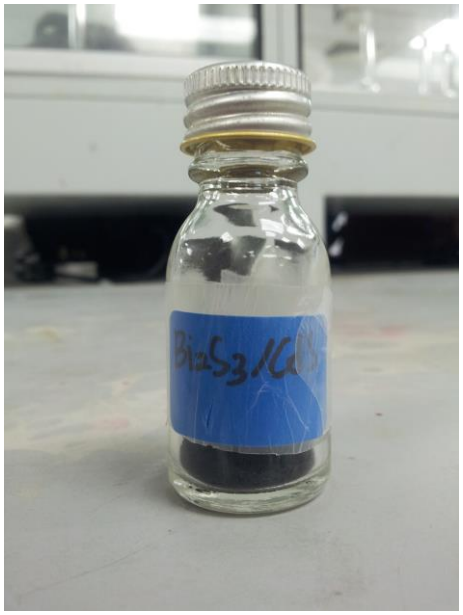
0.2 g of catalyst powder was added into the solution



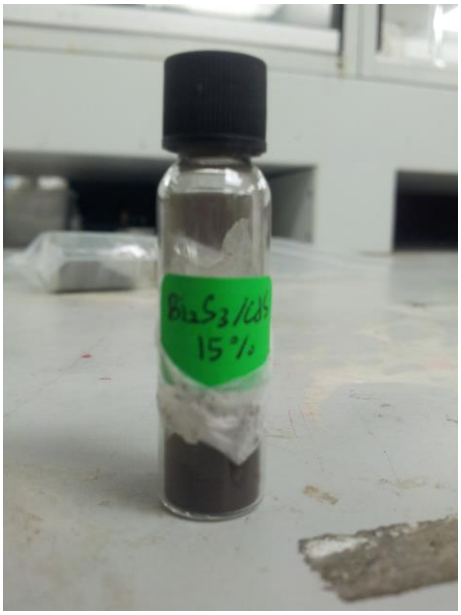


The irradiation lamp was turned on to start the photoreaction

A.1.3 Catalysts produced



Bi_2S_3/CdS catalyst

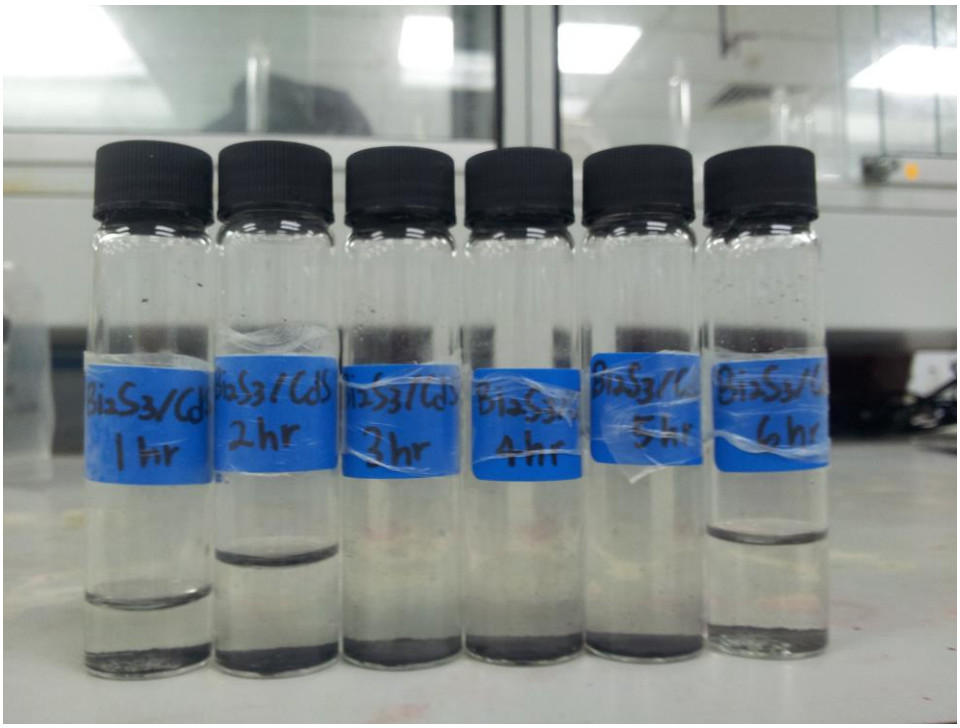


Bi_2S_3/CdS (15%) catalyst

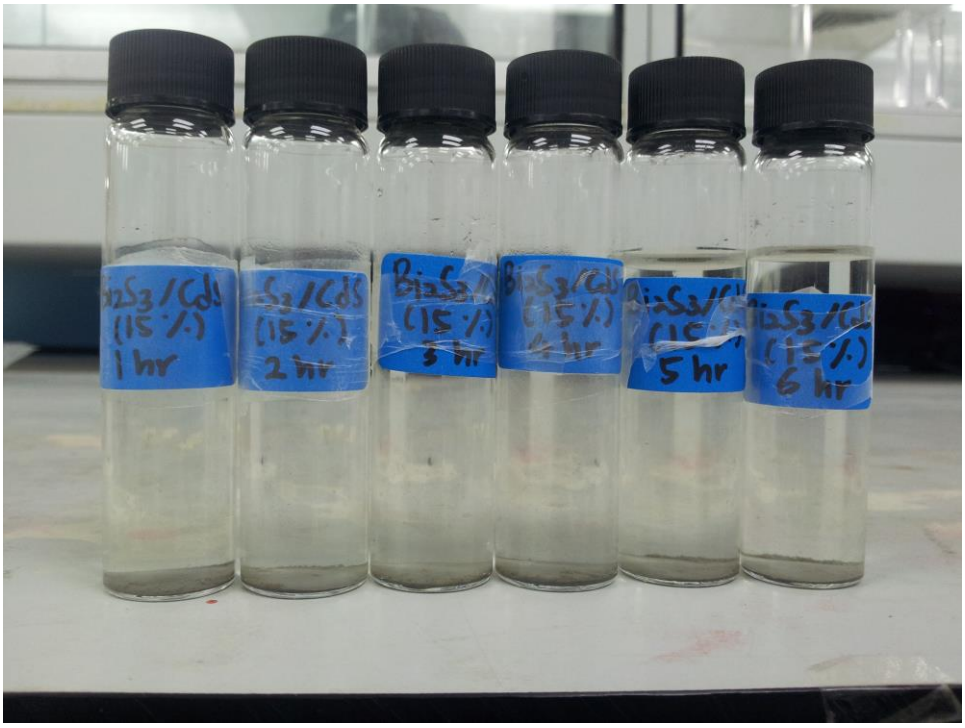
Bi_2S_3/CdS (30%) catalyst

Bi_2S_3/CdS (45%) catalyst

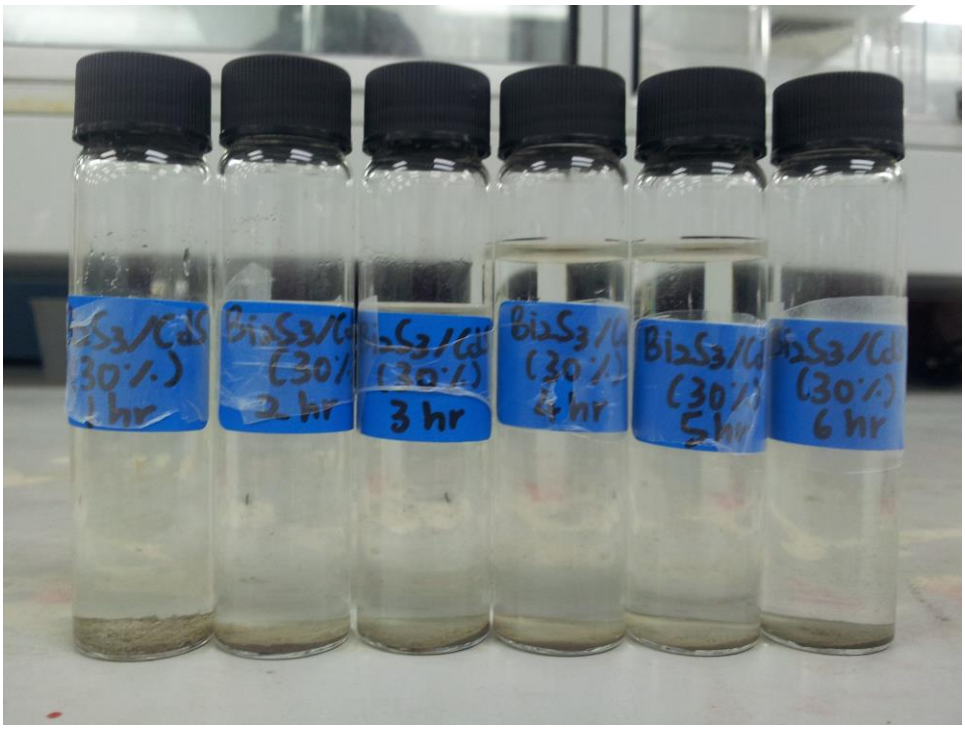
A.1.4 Products produced



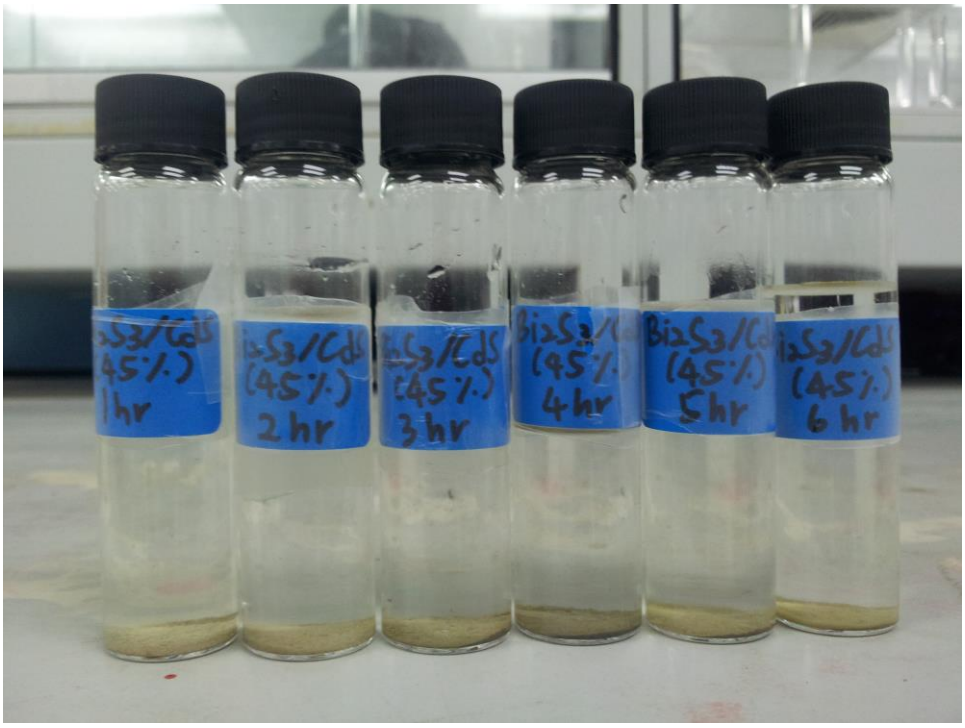
Using Bi_2S_3/CdS catalyst (1-6 hours)



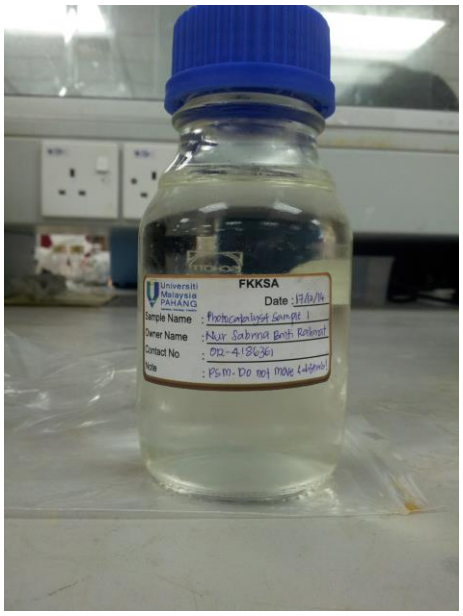
Using Bi_2S_3/CdS (15%) catalyst (1-6 hours)



Using Bi_2S_3/CdS (30%) catalyst (1-6 hours)

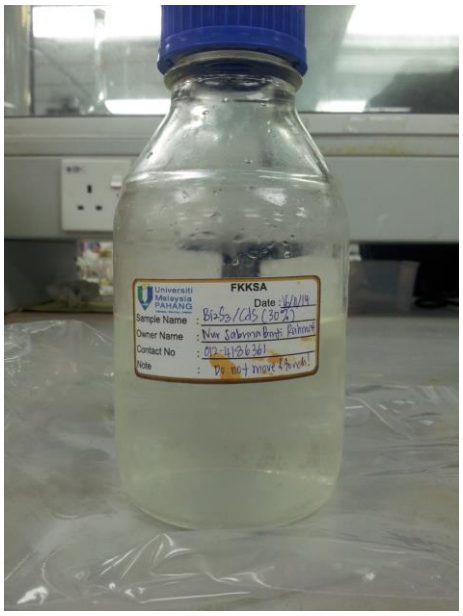


Using Bi_2S_3/CdS (45%) catalyst (1-6 hours)

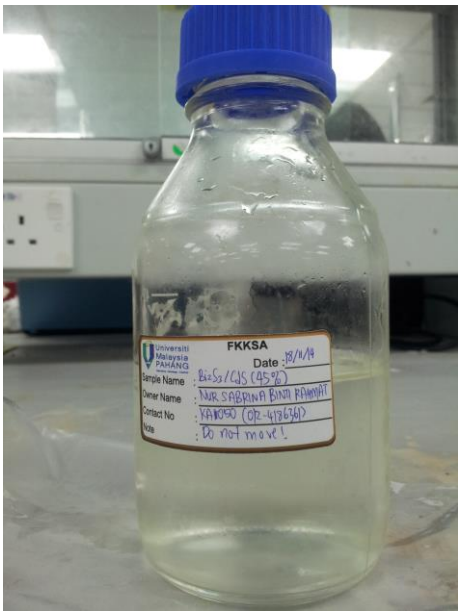


Using Bi_2S_3/CdS catalyst

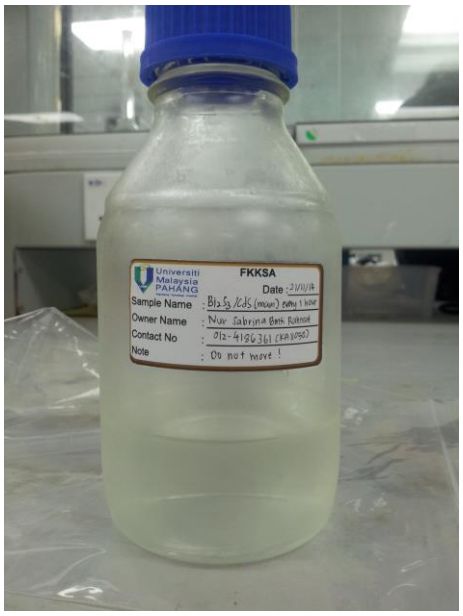
Using Bi_2S_3/CdS (15%) catalyst



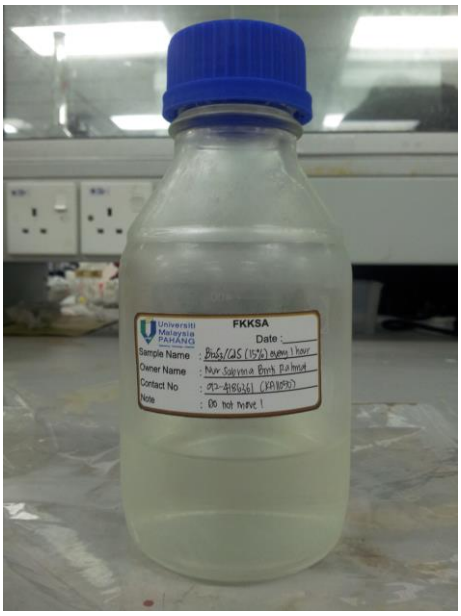
Using Bi_2S_3/CdS (30%) catalyst



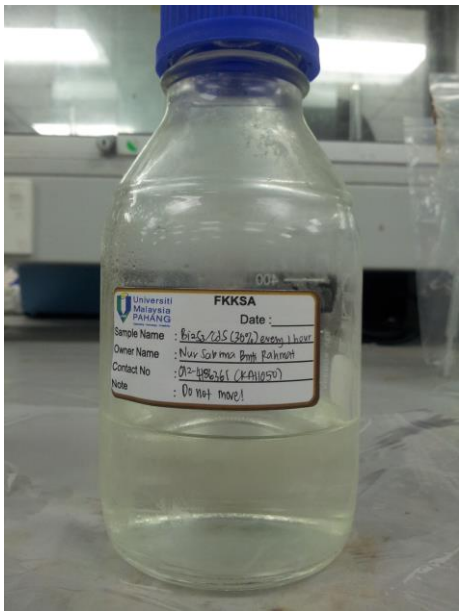
Using Bi_2S_3/CdS (45%) catalyst



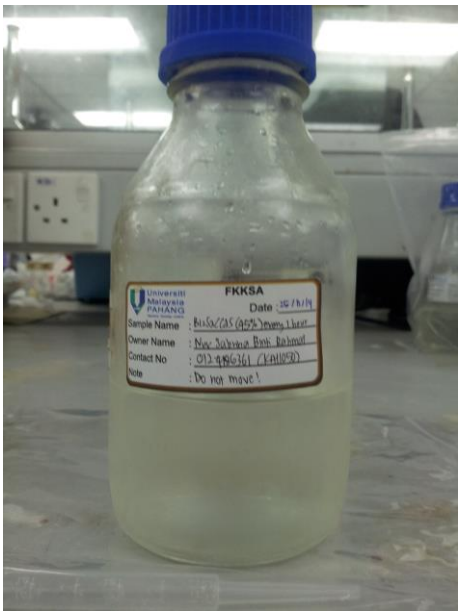
Using Bi_2S_3/CdS catalyst (1-6 hours)



Using Bi_2S_3/CdS (15)% catalyst (1-6 hours)

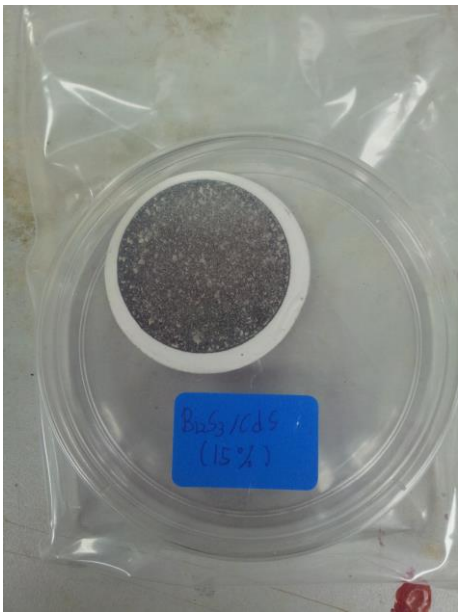


Using Bi_2S_3/CdS (30)% catalyst (1-6 hours)



Using Bi_2S_3/CdS (30)% catalyst (1-6 hours)

The precipitate of Bi_2S_3/CdS catalyst filtered after photocatalytic reaction



The precipitate of Bi_2S_3/CdS (15%) catalyst filtered after photocatalytic reaction

The precipitate of Bi_2S_3/CdS (30%) catalyst filtered after photocatalytic reaction

The precipitate of Bi_2S_3/CdS (45%) catalyst filtered after photocatalytic reaction

The precipitate of Bi_2S_3/CdS catalyst (1-6 hours) filtered after photocatalytic reaction

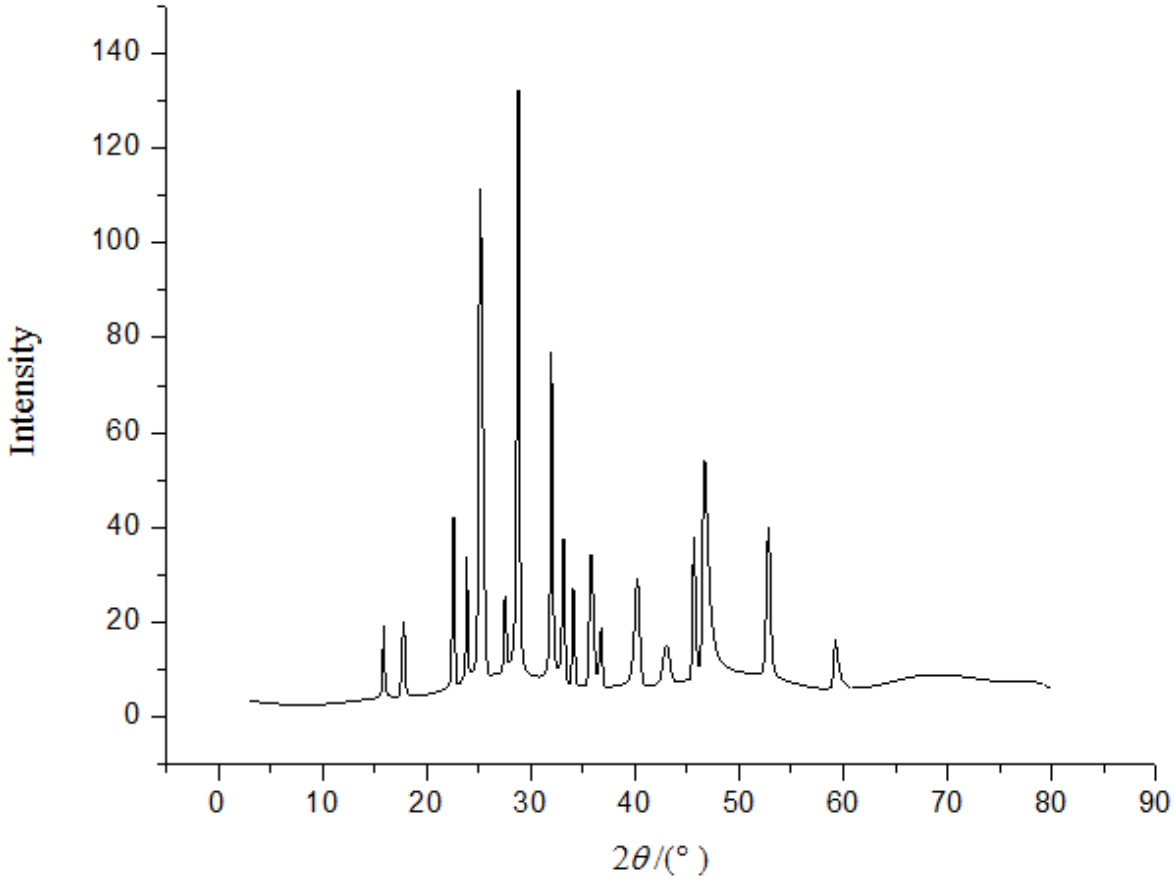
The precipitate of Bi_2S_3/CdS (15%) catalyst (1-6 hours) filtered after photocatalytic reaction

The precipitate of Bi_2S_3/CdS (30%) catalyst (1-6 hours) filtered after photocatalytic reaction

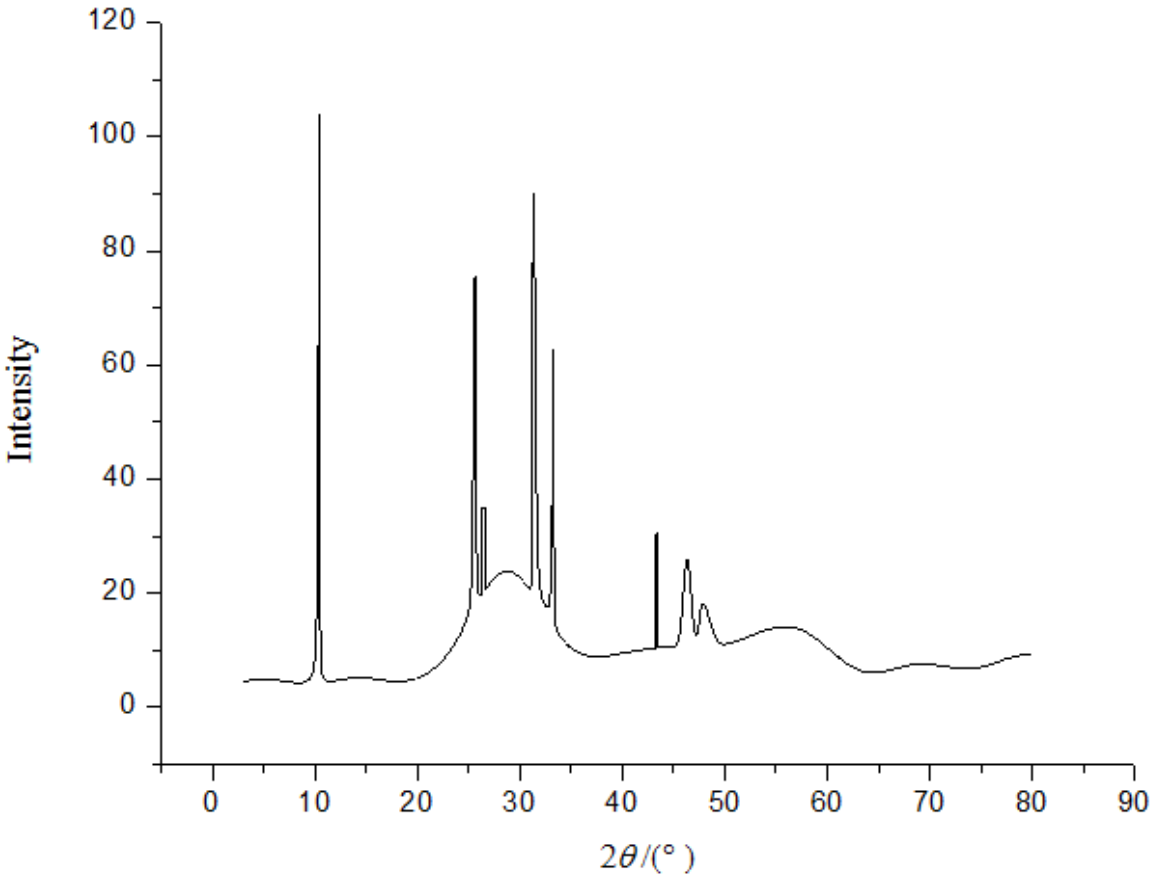
The precipitate of Bi_2S_3/CdS (45%) catalyst (1-6 hours) filtered after photocatalytic reaction

A.1.5 XRD Analysis

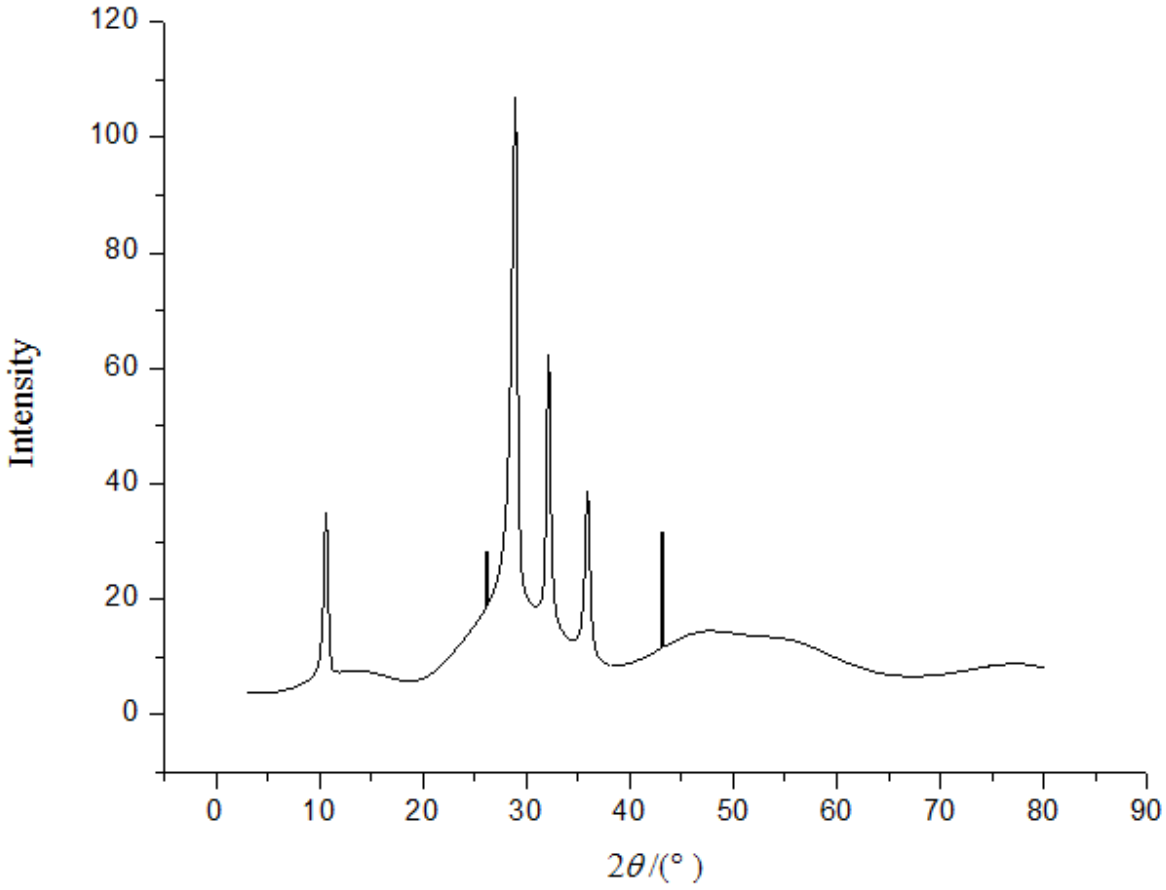
A.1.5.1 Bi_2S_3/CdS catalyst



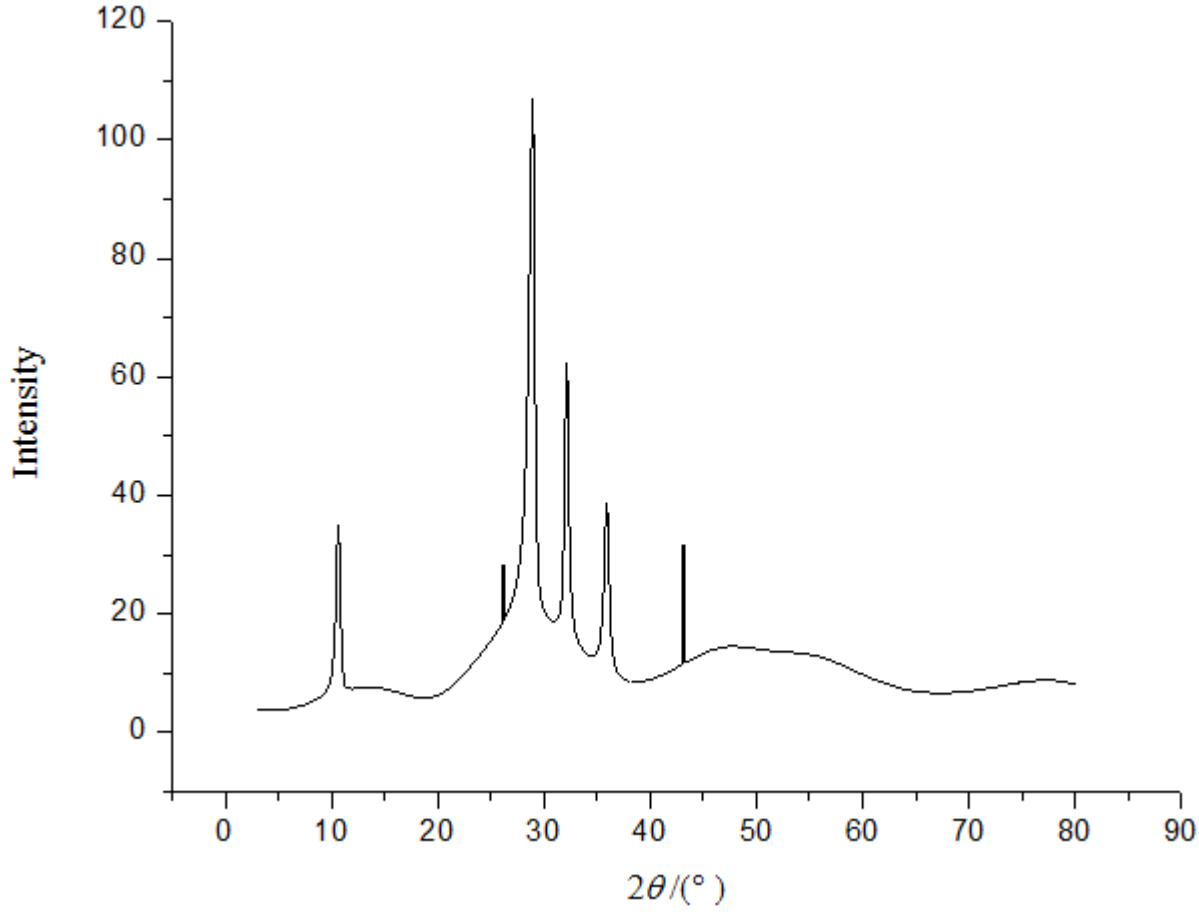
A.1.5.2 Bi_2S_3/CdS (15%) catalyst



A.1.5.3 Bi_2S_3/CdS (30%) catalyst

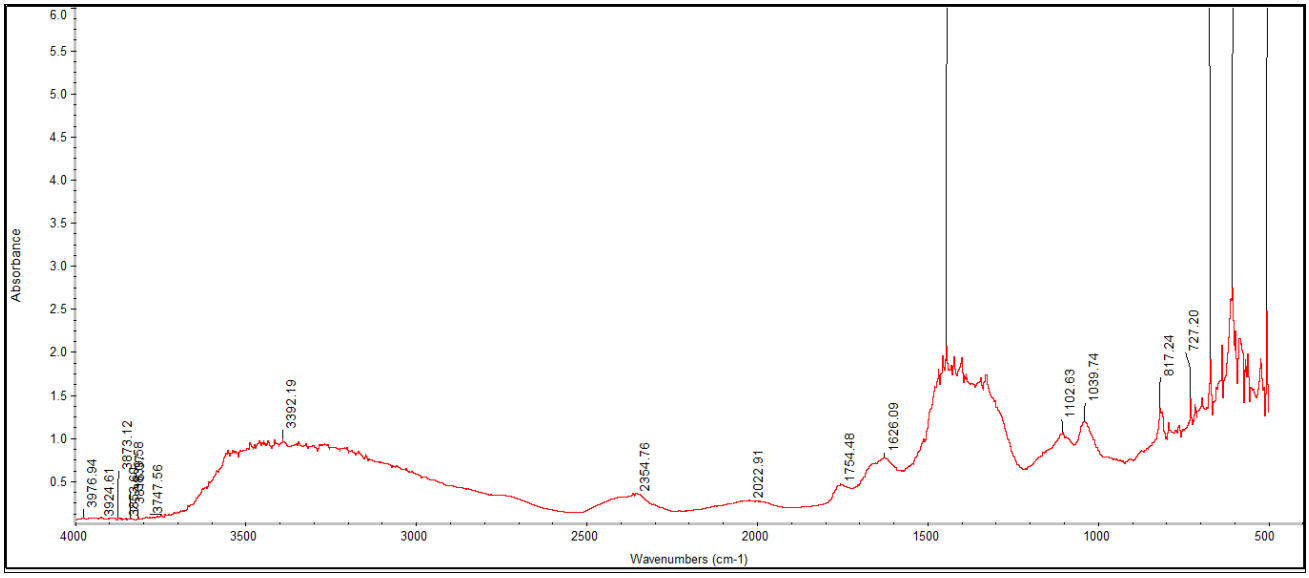


A.1.5.4 Bi_2S_3/CdS (45%) catalyst

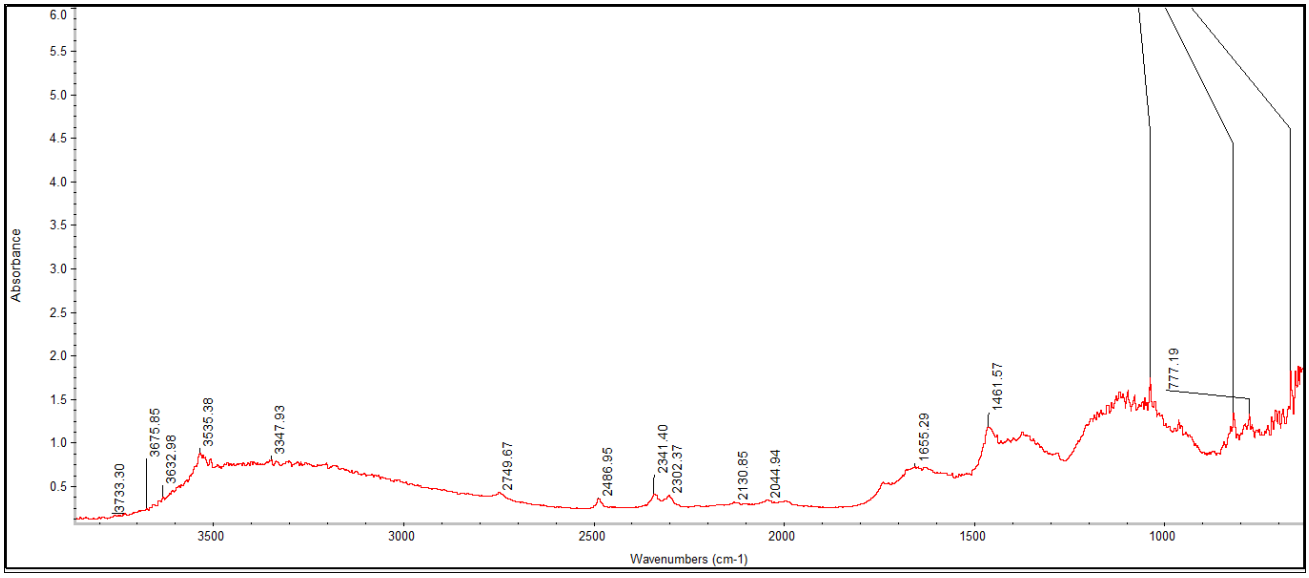


A.1.6 FTIR Analysis (Solid)

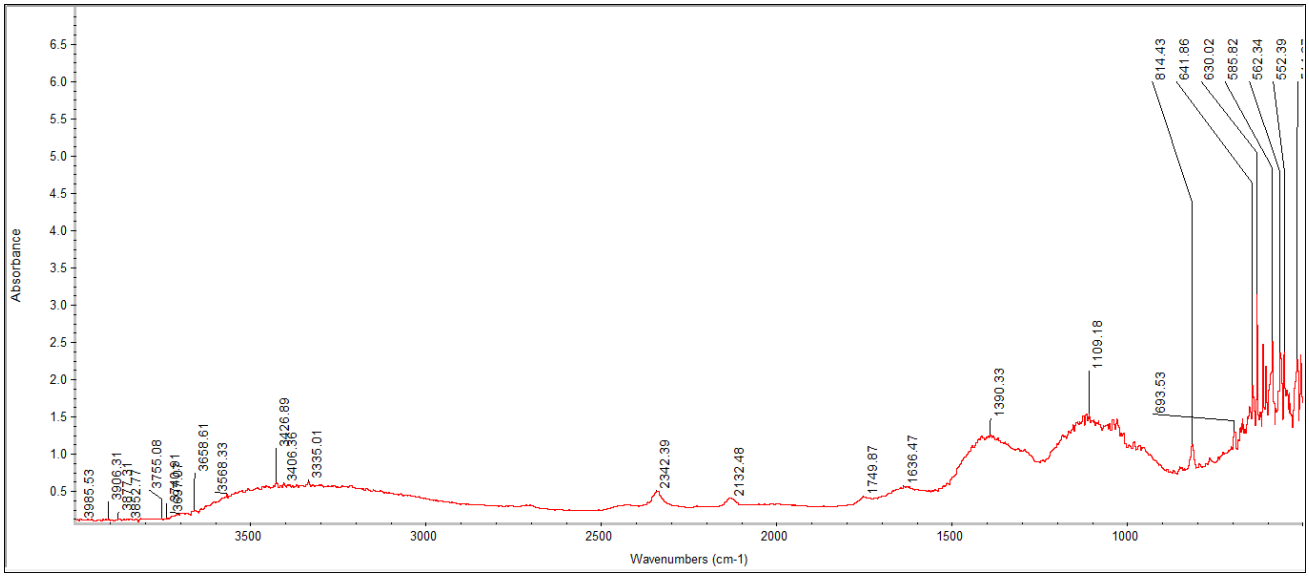
A.1.6.1 Bi_2S_3/CdS catalyst



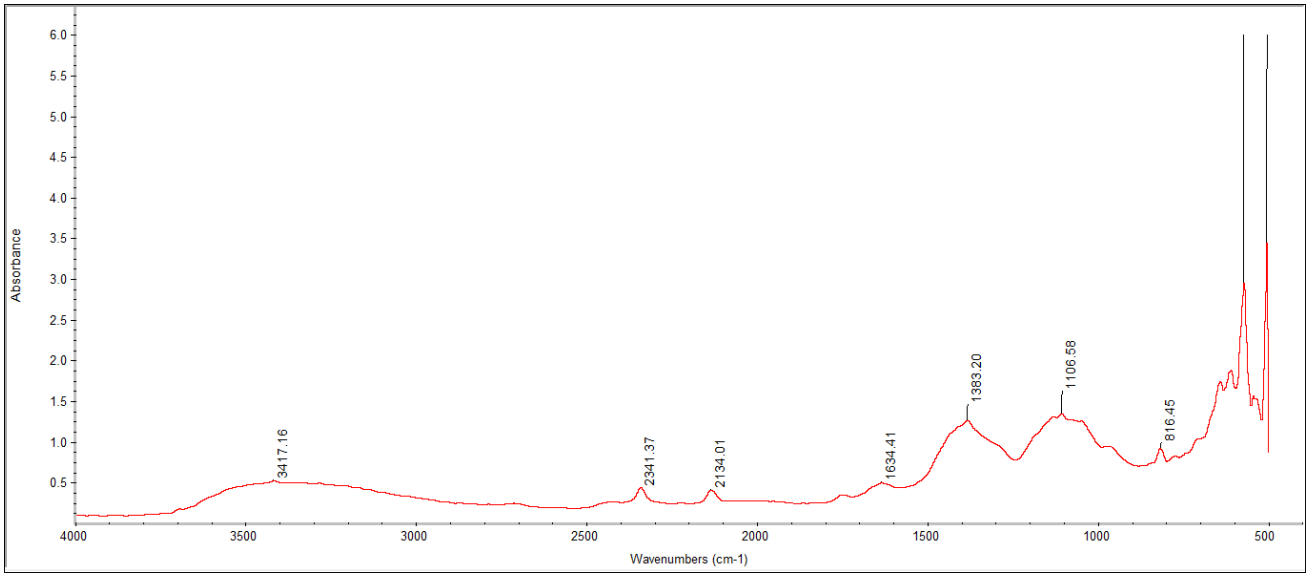
A.1.6.2 Bi_2S_3/CdS (15%) catalyst



A.1.6.3 Bi_2S_3/CdS (30%) catalyst

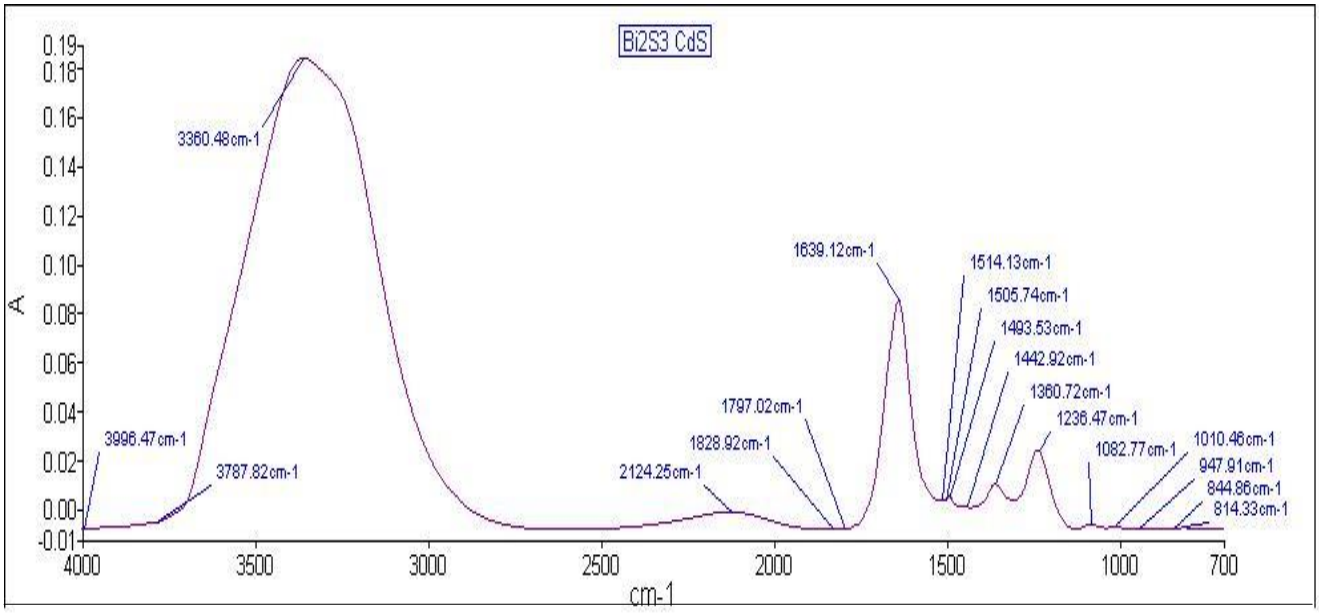


A.1.6.4 Bi_2S_3/CdS (45%) catalyst

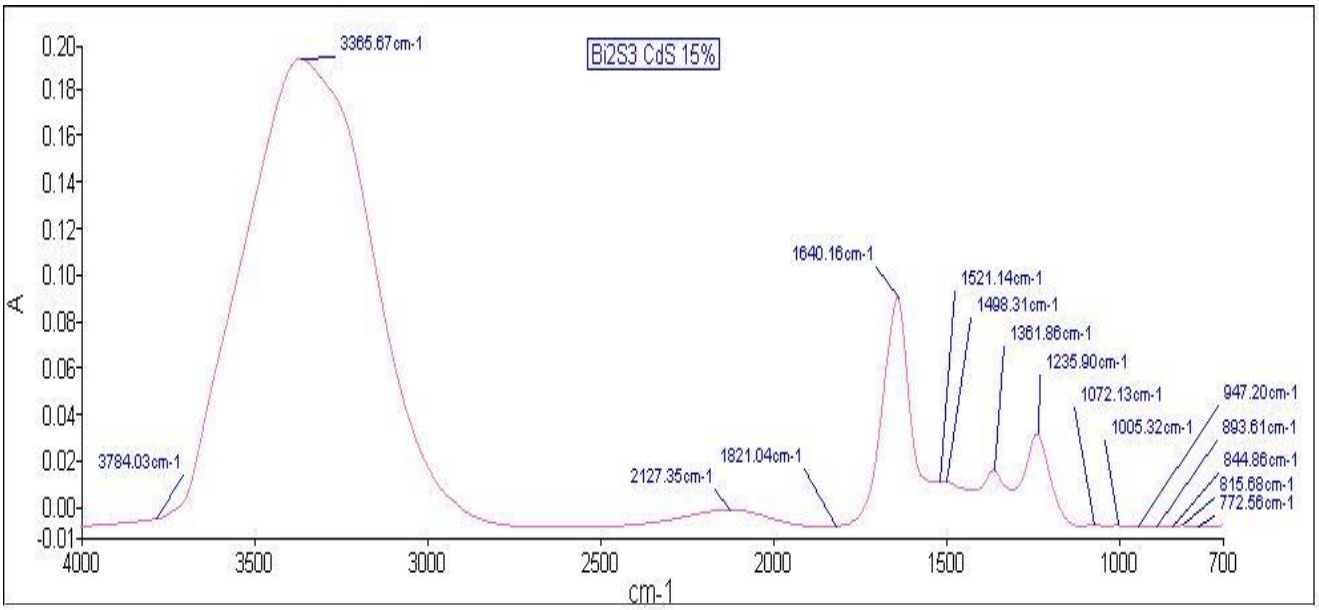


A.1.7 FTIR Analysis (Liquid)

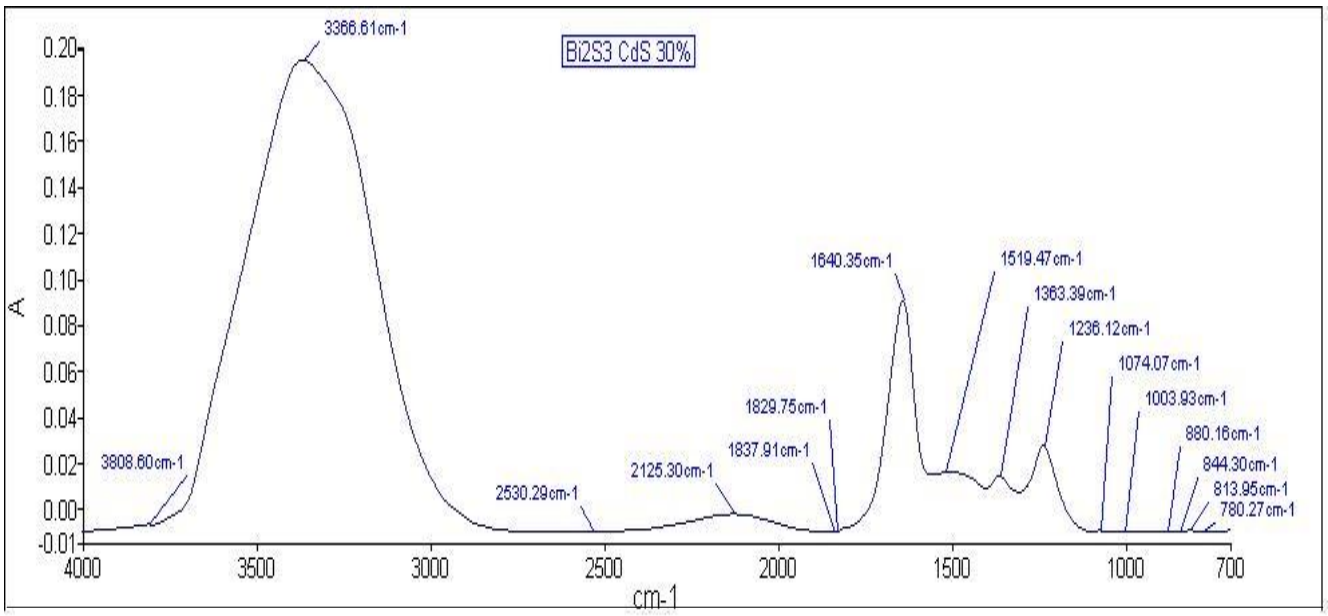
A.1.7.1 Bi_2S_3/CdS catalyst



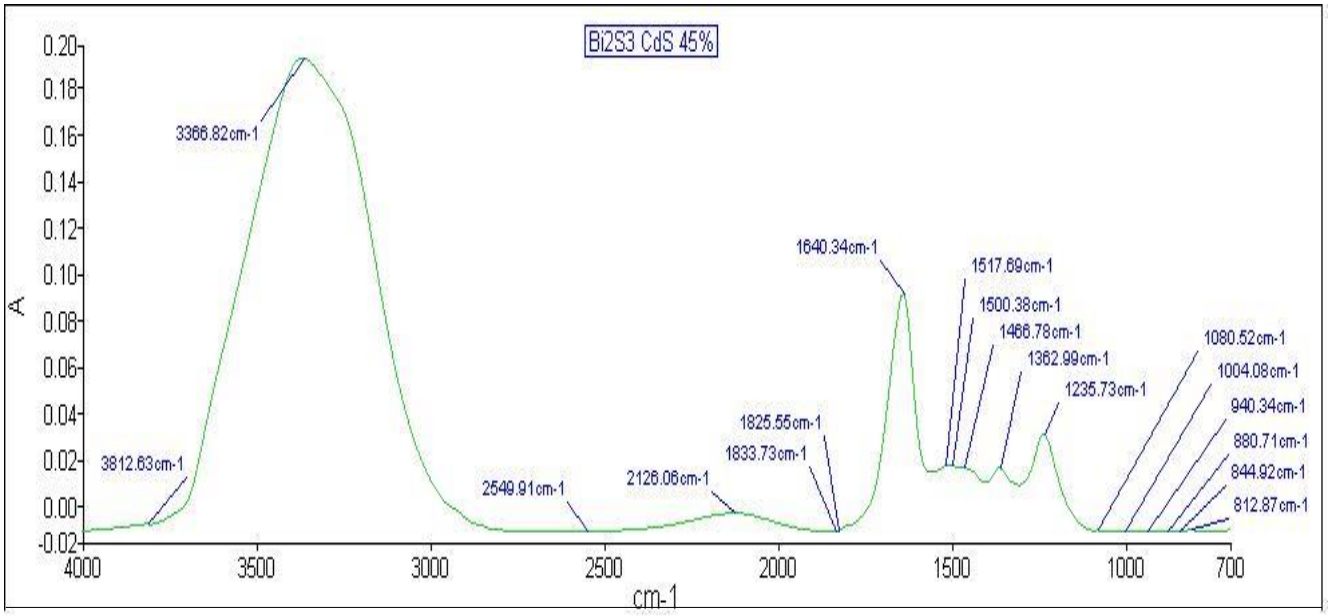
A.1.7.2 Bi_2S_3/CdS (15%) catalyst



A.1.7.3 Bi_2S_3/CdS (30%) catalyst



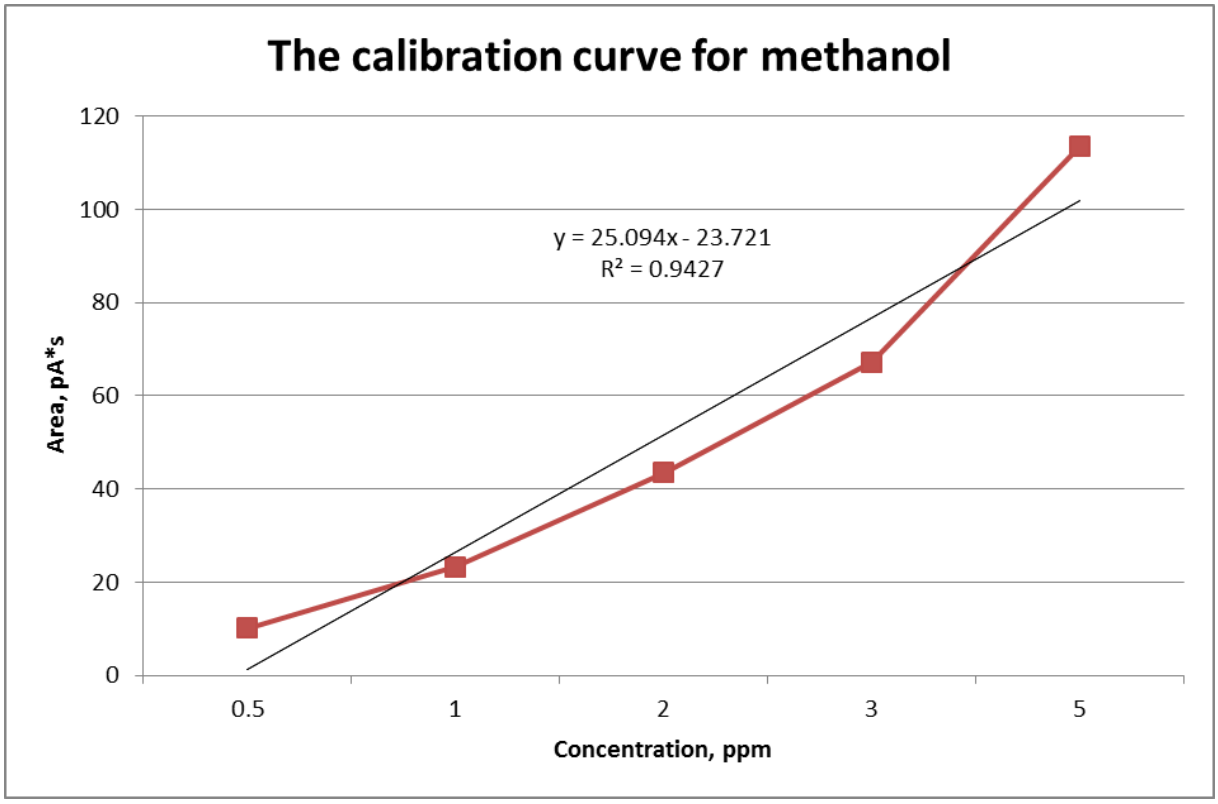
A.1.7.4 Bi_2S_3/CdS (45%) catalyst



A.1.8 GC-FID

A.1.8.1 Calibration curve

Ppm	Area
0.50	10.1125
1.00	23.3710
2.00	43.44089
3.00	67.22414
5.00	113.65617



A.1.8.2 Calculations in GC-FID

For the calculations, the formulas below are used :

$$\frac{Area\ of\ sample}{10.11247} \times 0.5\ ppm = a\ ppm \quad (1)$$

$$\frac{a\ ppm \times 10^{-3}}{32.04} = b\ \mu mole \quad (2)$$

$$b\ \mu mole \times 3.33 = c\ \ \mu mole/g \quad (3)$$

Bi_2S_3/CdS catalyst

Time (hour)	Area (pA*s)	ppm	µ mole	µ mole/ g (catalyst)	µ mole/ g (catalyst)
1	0.2	0.009889	3.08639×10^{-7}	1.02777×10^{-6}	1.03
2	0.25	0.012361	3.85798×10^{-7}	1.28471×10^{-6}	1.28
3	0.37	0.018294	5.70981×10^{-7}	1.90137×10^{-6}	1.90
4	0.41	0.020272	6.32709×10^{-7}	2.10692×10^{-6}	2.11
5	0.53	0.026205	8.17892×10^{-7}	2.72358×10^{-6}	2.72
6	0.55	0.027194	8.48756×10^{-7}	2.82636×10^{-6}	2.83

Bi_2S_3/CdS (15%) catalyst

Time (hour)	Area (pA*s)	ppm	µ mole	µ mole/ g (catalyst)	µ mole/ g (catalyst)
1	0.6	0.029666	9.25916×10^{-7}	3.0833×10^{-6}	3.08
2	0.67	0.033127	1.03394×10^{-6}	3.44302×10^{-6}	3.44
3	0.78	0.038566	1.20369×10^{-6}	4.00829×10^{-6}	4.01
4	0.83	0.041038	1.28085×10^{-6}	4.26523×10^{-6}	4.27
5	0.95	0.046972	1.46603×10^{-6}	4.88189×10^{-6}	4.88
6	0.98	0.048455	1.51233×10^{-6}	5.03606×10^{-6}	5.04

Bi_2S_3/CdS (30%) catalyst

Time (hour)	Area (pA*s)	ppm	μ mole	μ mole/ g (catalyst)	μ mole/ g (catalyst)
1	1.2	0.059333	1.85183×10^{-6}	6.1666×10^{-6}	6.17
2	1.35	0.066749	2.08331×10^{-6}	6.93742×10^{-6}	6.94
3	1.65	0.081582	2.54627×10^{-6}	8.47907×10^{-6}	8.48
4	1.74	0.086032	2.68516×10^{-6}	8.94157×10^{-6}	8.94
5	1.89	0.093449	2.91663×10^{-6}	9.71239×10^{-6}	9.71
6	1.93	0.095427	2.97836×10^{-6}	9.91795×10^{-6}	9.92

Bi_2S_3/CdS (45%) catalyst

Time (hour)	Area (pA*s)	ppm	μ mole	μ mole/ g (catalyst)	μ mole/ g (catalyst)
1	2	0.098888	3.08639×10^{-6}	1.02777×10^{-5}	10.28
2	2.4	0.118665	3.70366×10^{-6}	1.23332×10^{-5}	12.33
3	2.7	0.133499	4.16662×10^{-6}	1.38748×10^{-5}	13.87
4	3.2	0.15822	4.93822×10^{-6}	1.64443×10^{-5}	16.44
5	3.6	0.177998	5.55549×10^{-6}	1.84998×10^{-5}	18.50
6	3.9	0.192831	6.01845×10^{-6}	2.00414×10^{-5}	20.04