Conversion of CO₂ to Methanol via photo catalysis routes over nickel-loaded CdS under visible light irradiation

Nur Karimah binti Bakar¹, Bawadi bin Abdullah*¹,², Nonni Soraya Sambudi¹,³, Laksmi Dewi Kasmiarno⁴

¹Department of Chemical Engineering, Universiti Teknologi PETRONAS, Seri Iskandar 32610, Perak, Malaysia
²Center of Contaminant Control and Utilization (CenCoU), Institute of Contaminant Management for Oil and Gas, Universiti Teknologi PETRONAS, 32610 Seri Iskandar, Perak, Malaysia
³Advanced Integrated Membrane System (AIMS), Institute of Sustainable Building, Universiti Teknologi PETRONAS, Seri Iskandar 32610, Perak, Malaysia
⁴Department of Chemical Engineering, Universitas Pertamina, Simprug 12220, Jakarta Selatan, Indonesia

*Email: bawadi_abdullah@utp.edu.my

Abstract. The abundance of carbon dioxide gas in the atmosphere raises concerns as it affects the environmental sustainability, human’s wellbeing as well as the nature. The photocatalysis conversion of carbon dioxide produces valuable gas and limits environmental issue in the same time. Therefore, it attracts the attention to synthesize photocatalyst that is active under visible light irradiation since sunlight provides abundant photon energy mostly in visible light range. In this study, CdS as visible light-active photocatalyst is loaded with nickel to improve its performance to convert CO₂ to methanol under irradiation of 500 W of Xe lamp as visible light source. The spherical nanoparticles morphology can be observed for synthesized CdS and Ni/CdS by using field emission scanning electron microscopy (FE-SEM) analysis. The yield of methanol was examined by using high performance liquid chromatography (HPLC). The result shows that the yield can be improved from 11 µmol/g-catalyst to 2348 µmol/g-catalyst by loading of 3wt% of nickel in CdS. The further loading of nickel decreased the yield of methanol.

Keywords: nickel loaded CdS, CO₂, methanol, photocatalyst, visible light

1. Introduction
Carbon dioxide is the element that present naturally in the atmosphere and its existence in the carbon cycle is not something that raises concern specifically on the environment. However, with the execution of human activities especially industrial activities, abnormal alteration of the amount of the carbon dioxide in the atmosphere can be observed as carbon dioxide become the primary greenhouse gas, which exceeded 400 ppm in atmosphere in 2015 [1]. Its effect on global climate has been highlighted which drives the efforts to reduce its amount in atmosphere. The conversion of CO₂ to energy in the form of fuel has served as attractive solution in reducing the amount of CO₂ due to fuel’s high specific energy.

There are various methods that have been employed for reducing the concentration of CO₂ such as sorption of CO₂ to functionalized materials, increasing quantity of carbon sink (using marine organisms such as algae, phytoplankton, etc), and injecting CO₂ at the bottom of the sea [2]. The photocatalytic
conversion of CO$_2$ is an environmentally friendly approach for the utilization of CO$_2$ by using sunlight as sustainable source of energy [2]. TiO$_2$ has been widely used to convert CO$_2$ to mainly methane, methanol, and formic acid [2]. However, UV light needs to be employed for this process, which hindered the utilization of visible light which holds main percentage of light spectrum in sunlight. Therefore, Cds is proposed in this study to convert CO$_2$ to methanol due to its short band gap which causes it to be active under visible light irradiation. Additionally, Cds performed better in comparison to TiO$_2$ for the production of methanol and formaldehyde [2]. Previous research by Li et al, [3] performed the photoreduction of CO$_2$ to form methanol by using Bi$_2$S$_3$/CdS, where CdS alone could produce 160 µmol/g-catalyst of methanol, while addition of Bi$_2$S$_3$ could improve the production to 613 µmol/g-catalyst. Another attempt by incorporating Zn in CdS matrix could improve the production of methanol from 2.5 µmol/h.g-catalyst to 16 µmol/h.g-catalyst [4]. However, these results need further improvement to make this technology viable. Hence, this study aims to improve the production of methanol from carbon dioxide, by utilizing nickel as dopant in CdS matrix, which has not been utilized before for the photoreduction of CO$_2$ to methanol. Nickel loaded CdS has shown excellent performance for photocatalytic water splitting to produce hydrogen, where the hydrogen production was enhanced by doping CdS with nickel [5]. In this study, the incorporation of nickel in CdS could enhance the conversion of CO$_2$ to methanol up to 200 times.

2. Materials and Method

2.1. Materials
Cadmium nitrate tetrahydrate (Cd(NO$_3$)$_2$.4H$_2$O) was purchased from Acros Organics (India), sodium sulphide (Na$_2$S) was purchased from Sigma Aldrich (USA), Ni(NO$_3$)$_2$ was purchased from Merck (USA), ethanol was purchased from HmBG Chemicals (Malaysia), and sodium hydroxide (NaOH) was purchased from Fisher Scientific (UK). All chemicals were used as purchased without further purification.

2.2. Synthesis of photocatalyst
A solution of cadmium nitrate, Cd(NO$_3$)$_2$.4H$_2$O at concentration of 0.1 mol was heated at 60°C for 2 h. A solution containing 0.05 mol of Na$_2$S was then added into the cadmium nitrate solution, which was then allowed to react for 2 h at 200 rpm of stirring. The colloidal solution was obtained through centrifugation of solution at 4000 rpm stirring for 15 m, continued by washing with ethanol. The precipitate of CdS was then obtained by heating the colloid in the oven for 1 h at 60°C. In order to synthesize nickel loaded CdS, a specific amount of nickel nitrate, Ni(NO$_3$)$_2$ was added during the heating of cadmium nitrate. The nickel loading was varied at 3 different percentages of Ni/CdS: 3wt% Ni, 20wt% Ni, and 40wt% Ni.

2.3. Photocatalytic reduction of CO$_2$
Firstly, the CO$_2$ source was connected with the reactor using a tightly closed tube. Inside the reactor, suspension of CdS in 0.2 M NaOH solution was prepared. The solution was then purged with CO$_2$ for 30 min at ambient pressure. The photoreduction was then started by irradiating the reactor under 500 W Xe lamp. The liquid sample was withdrawn every 20 min to detect the methanol yield by using High Performance Liquid Chromatography (HPLC) technique. The step was repeated for Ni/CdS samples.

2.4. Characterization of photocatalyst
The surface morphologies CdS and Ni/CdS were examined using FE-SEM (Ultra 55 Carl Zeiss, Germany). Fourier-transform Infrared Spectroscopy (FT-IR) analysis (Perkin Elmar Spectrum One, USA) was conducted to investigate the functional groups on the photocatalyst samples and recorded at 4000 to 450 cm$^{-1}$ regions. The crystallinity and phase of samples were characterized using X-ray diffractometry (XRD) spectroscopy using X’Pert Powder & Empyrean PANalytical with Cu Kα irradiation ($\lambda=1.54$). The diffraction angles (20) were recorded from 20° to 75°, and included step size
of 1°/step, and exposure time of 1s/step. The methanol detection was performed using HPLC (Jeol JMS-T100LP) (Jeol, Japan) with absolute methanol used as standard.

3. Results and Discussion

3.1. Morphology, crystallization and functional groups
The morphologies of CdS and 20wt%-Ni/CdS show similar spherical shape as can be seen in Fig. 1. The ranges of particle size for CdS and 20wt%-Ni/CdS are from 15 nm to 26 nm, and 13 nm to 21 nm, respectively. Therefore, the loading of nickel in CdS matrix does not change the morphology and size of CdS. The XRD pattern (Fig. 2) show crystallinity of CdS which can been seen at diffraction angles of 27.06°, 44.34°, and 52.28° which are attributed to (111), (220), and (311), respectively [3, 6-8]. The 20wt%-Ni/CdS shows similar peaks as CdS. The shifting at diffraction angle of 27.06° is not observed as can be found for doped CdS [9]. However, Ni$^{2+}$ still can be loaded in CdS lattice due to its smaller ionic radii size in comparison to Cd$^{2+}$, where it can be incorporated at vacant sites of CdS lattice [7]. In order to reveal the loading of Ni in CdS matrix, FTIR analysis was performed.

Figure 1. SEM images of (a and b) CdS, (c and d) Ni/CdS (20wt% of Ni)
The FTIR spectra of CdS and 20wt%-Ni/CdS nanoparticles are shown in Fig. 3. At Fig. 3a, the peaks shown at 3435 cm\(^{-1}\) corresponds to the free O-H group and the peak at 1617 cm\(^{-1}\) is due to the presence of hydroxyl group of water [10]. The O-C=O asymmetric stretching vibration molecule corresponds to peak at 1384 cm\(^{-1}\) [10, 11]. The C-O stretching vibration of absorbed CO\(_2\) is observed at 1108 cm\(^{-1}\) [10, 11], while the stretching of Cd-S is shown at the band of 620 cm\(^{-1}\) [8]. The FTIR spectrum of the nickel doped CdS (20wt%) nanoparticles is shown in the Figure 3b. The peak at 3467 cm\(^{-1}\) shows the presence of O-H group which represents the stretching vibration of the absorbed water on the surface of nanoparticles [10]. The peak at 1620 cm\(^{-1}\) on the other hand is due to OH bending vibration of the water molecule [10]. The O-C=O asymmetric stretching vibrations molecule corresponds to peak at 1384 cm\(^{-1}\) [10, 11]. The C-O stretching vibration of absorbed CO\(_2\) gives its strong peak at 1109 cm\(^{-1}\) [10, 11]. The weak peak at 618 cm\(^{-1}\) may be due to the C-H stretching [10, 12]. The shifting of Cd-S stretching to 654 cm\(^{-1}\) can be observed for 20wt%-Ni/CdS, which can be caused by the doping of Ni\(^{2+}\) in CdS matrix [13]. While the assigned band observed at 535 cm\(^{-1}\) shows the presence of Ni–S stretching mode in the loaded nanoparticle [10].

3.2. CO\(_2\) conversion to methanol

From Fig. 4, it is observed that the concentration of methanol continues to rise up to approximately 11 µmol/g catalyst during the second hour before decreasing to below 1 µmol/g catalyst at the next hour by using CdS. It can be safely said that the CdS reached its optimum capacity of photocatalytic activity during the second hour as the yield of the methanol on the following 3 hours continues to drop. The photocatalytic reduction under 3 variations of Ni/CdS showed that the optimum nickel loading is at 3wt% compared to the other 20wt% and 40wt%. When compared with the unloaded CdS, 3wt%-Ni/CdS has exceeded the methanol yield by almost 200 times (2438 µmol/g catalyst) at 4 hours irradiation time. This can be due to the loaded photocatalyst capability of suppressing electron recombination, which allows the electron to be separated from the hole [14]. The loading of photocatalyst has also known to improve the excitation of electron to conduction band [14].

![Figure 2. XRD spectra of CdS and 20wt%-Ni/CdS](image)
The available electrons are then used for the reduction of carbon dioxide into methanol. However, in this case, a further increase from 3% of the nickel loading does not yield a higher amount of methanol. The highest methanol yields for 20wt%-Ni/CdS and 40wt%-Ni/CdS are found at 3 hours and 4 hours for 1974 µmol/g catalyst and 1984 µmol/g catalyst, respectively. This is due to a deterioration of photocatalytic performance, which is likely due to the increased scattering and absorbance of photons through excess nickel in the photocatalytic system. The excess amount of nickel is causing a shield to be formed which disables light from reaching the surface of CdS photocatalyst [15, 16].
Additionally, the excessive nickel amount leads to crystal defects that act as recombination centers of electrons, which hinder them to reduce CO$_2$ [15]. Previous studies also show that methanol is the major photocatalytic product of CO$_2$ by using CdS [2, 17]. In comparison with previous study by Kandy and Gaikar [17], Ni/CdS in this study shows better performance than CdS nanorods which can reach the production of methanol at 140 $\mu$mol/g. However, it has lower performance compared to CdS/g-C$_3$N$_4$ composite which could yield methanol at a rate of 1200 $\mu$mol/g/h [18].

4. Conclusion
The photoconversion of CO$_2$ to methanol was performed by using nickel loaded CdS under visible light irradiation. The presence of nickel can be detected by using FTIR analysis through the Ni-S stretching mode. The XRD analyses show crystallinity of CdS, with visible peaks at diffraction angles of (111), (220), and (311). The loading of nickel in CdS could improve the yield of methanol to more than 200 times at 2438 $\mu$mol/g-catalyst. In comparison with previous studies, Ni/CdS could improve the production of liquid fuel from CO$_2$ through photocatalytic process with satisfactory result. However, to optimize the yield of methanol, further studies need to be performed to observe the effect of Ni loading at low amount upon the methanol yield. Additionally, this study could serve as preliminary result on the loading of Ni in CdS matrix for photoreduction of CO$_2$ under visible light irradiation.

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6. References
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