Photocatalytic Carbon Dioxide Reduction to Fuels Over Cu-Loaded g-C₃N₄ Nanocatalyst under Visible Light

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Photocatalytic carbon dioxide (CO₂) conversion to chemicals and fuels has gained significant consideration in industrial and scientific research. In this study, photocatalytic CO₂ reduction to fuels over Cu-loaded graphitic carbon nitride (g-C₃N₄) under visible light irradiation has been investigated. The photocatalysts, synthesized by pyrolysis and impregnation method, were characterized by X-ray diffraction (XRD) Fourier transform infrared (FTIR) and Scanning electron microscopy (SEM). Interestingly, CO₂ was efficiently converted to CH₄ and CH₃OH with smaller amounts of C₂H₆ and C₂H₄ hydrocarbons. The yield of CH₄ evolution as the main product over 3 wt. % Cu/g-C₃N₄ was 217.8 µmole/g.cat under visible light irradiation, significantly higher than the amount of CH₄ produced over the pure g-C₃N₄ catalyst (119 µmole/g.cat). The enhancement was attributed to charge transfer property and suppressed recombination rate by Cu-metal. The Cu-metal loaded into g-C₃N₄ enhanced CO₂ reduction efficiency for CH₄ production while the pure g-C₃N₄ was promising for both CH₄ and CH₃OH production. The single step conversion of CO₂ to CH₄ and CH₃OH with appreciable amount of hydrocarbons under solar energy registered good photo-activity and selectivity of Cu/g-C₃N₄ catalyst. A photocatalytic reaction mechanism was proposed to corroborate with the experimental results over the Cu-loaded g-C₃N₄ photocatalyst.

1. Introduction

Increasing levels of carbon dioxide (CO₂) emissions in the atmosphere from fossil fuel combustion are widely recognized as one of the primary cause of greenhouse effect. Among the carbon capture and sequestration, development of an artificial photosynthesis system using solar energy is a promising strategy for the photocatalytic conversion of CO₂ to solar fuels (Tahir et al. 2015b). Among the solar fuels, the production of CO (Tahir et al. 2016a), CH₄ (Zhu et al. 2016) and CH₃OH (Gusain et al. 2016) via a single step CO₂ conversion, has sparked a new sustainable development in the field (He et al. 2016). Among the semiconductor materials, TiO₂ is the most widely studied photocatalyst due to its numerous advantages such as low cost and excellent chemical and thermal stability (Tahir et al. 2016b). However, TiO₂ is only active under UV-light irradiations and have poor photocatalytic activity due to the fast recombination of photo-generated charges (Tahir et al. 2015a). Considering the large portion of solar spectrum available, the demand for visible light responsive and low-cost photocatalysts has been regarded as an attractive area of research.

Recently, the use of graphitic carbon nitride (g-C₃N₄) as a photocatalyst has been promising alternatives due to advantages such as visible light responsive, low-cost synthesis and high chemical/thermal stability (Ma et al. 2016). In the recent years, there have been number of studies focused on photocatalytic CO₂ reduction by g-C₃N₄ based photocatalyst. However, the efficiency and selectivity of CO₂ conversion over pure g-C₃N₄ photocatalyst is still quite limited. The photocatalytic activity of g-C₃N₄ could be enhanced by loading with metals or combining with other semiconductor materials.

In this perspective, Pt-g-loaded CsN₄/kNbO₃ photocatalyst has been recently investigated for enhanced CO₂ photoreduction under visible light irradiations (Shi et al. 2015). The amine-functionalized g-C₃N₄ has been reported to improve CO₂ adsorption capacity with enhanced activity for CO₂ photoreduction into CH₄ and CH₃OH (Huang et al. 2015). Similarly, selective photocatalytic CO₂ reduction to CH₃OH has been reported using ZnO/g-C₃N₄ photocatalyst under visible light irradiations. The g-C₃N₄-N/TiO₂ photocatalyst has been investigated for...
the selective CO\textsubscript{2} photoreduction to CO (Zhou et al. 2014). Pt-loaded g-C\textsubscript{3}N\textsubscript{4} with improved day-light induced photocatalytic CO\textsubscript{2} reduction to CH\textsubscript{4} was explored. Significantly improved g-C\textsubscript{3}N\textsubscript{4} photoactivity was found with Pt-loading, perhaps, due to hindered charges recombination rate (Ong et al. 2015). On the other hand, copper based semiconductors are gaining large interest and are considered as efficient for selective CO\textsubscript{2} photoreduction over Cu-promoted g-C\textsubscript{3}N\textsubscript{4} catalyst would be appreciable to stimulate photocatalytic CO\textsubscript{2} reduction to selective fuels under visible light irradiations. In this study, highly active and visible light responsive Cu-promoted g-C\textsubscript{3}N\textsubscript{4} Nanosheets were successfully synthesized by thermal treatment of melamine. The photoactivity of different Cu-loaded g-C\textsubscript{3}N\textsubscript{4} catalysts were examined for selective CO\textsubscript{2} photoreduction to fuels. In addition, the photocatalytic reaction mechanism for CO\textsubscript{2} reduction were analysed based on the experimental results.

2. Experimental

2.1 Catalyst preparation and characterization

The g-C\textsubscript{3}N\textsubscript{4} was synthesized by the thermal treatment of Melamine (Sigma Aldrich AR ≥ 99%). In a typical process, 5 g of Melamine was put in a crucible with a cover then calcined in a Muffle Furnace and heated to 550 °C for 2 h. The sample was then washed with 0.1 mol/L nitric acid (Sigma Aldrich AR) and distilled water to remove any residual alkaline species (e.g. ammonia) adsorbed on the sample surface. After this, it was dried at 80 °C for 12 h in an oven. The Cu-loaded g-C\textsubscript{3}N\textsubscript{4} samples were prepared by a wet-impregnation and sonication method. 0.5 g of g-C\textsubscript{3}N\textsubscript{4} was dispersed in 20 mL water and specific amount of Cu(NO\textsubscript{3})\textsubscript{2}3H\textsubscript{2}O was added to it. The mixture was stirred for 4 h and then sonicated to get Cu-promoted g-C\textsubscript{3}N\textsubscript{4} Nanosheets. The sample was oven dried at 80 °C for 12 h then calcined at 450 °C for 1 h. The crystalline structure of the catalysts were ascertained by X-ray diffraction (XRD) recorded on a powder diffractometer (Bruker Advance D8, 40 kV, 40 mA) using a Cu Ka radiation source in the range of 2θ = 5-80 ° with a step size of 0.05 ° and counting time of 5 s. The Fourier transform infrared (FTIR) spectrum of the sample was recorded on a Thermo Nicolet Avatar 360 FTIR spectrometer. The surface morphology was examined using field emission scanning electron microscopy (FESEM JEOL model JSM-6700F, Japan).

2.2 Photoactivity testing

The reactor consists of stainless steel cylindrical vessel with a length of 5.5 cm and total volume of 150 cm\textsuperscript{3}. 10 mg powder photocatalyst was evenly placed inside the cylindrical stainless steel chamber, equipped with a quartz window for passing light irradiations. The source of light irradiation was a simulated sunlight having the same spectra with real sunlight. Compressed CO\textsubscript{2} (99.999 %) regulated by a mass flow controller (MFC) was bubbled through water saturator to carry moisture maintained at temperature of 30 °C. The reactor was purged and saturated for half an hour using a mixture of CO\textsubscript{2} and water prior to the start of the experiment. The temperature inside the reactor was controlled using temperature controller. The products were analyzed using an on-line gas chromatograph (GC-Agilent Technologies 6890 N, USA) equipped with thermal conductivity detector (TCD) and flame ionized detector (FID). Furthermore, FID detector was connected with a HP-PLOT Q capillary column and TCD detector was connected to UCW982, DC-200, Porapak Q and Mol Sieve 5A columns.

3. Results and discussion

3.1 Characterization analysis of catalysts

Figure 1 (a) presents the spectra of g-C\textsubscript{3}N\textsubscript{4} and Cu/g-C\textsubscript{3}N\textsubscript{4} samples and can be identified the presence of two peaks. The peak at 27.3 ° located at plane (002) presents interlayer stacked conjugated aromatic system, while the peak at ~ 13 ° with plane (100) reveals the intra-planar structural packing of the aromatic system. The signals corresponding to Cu in metal or oxides states were not detected in all the XRD patterns. This was possibly due to the lower amounts, which were below the detection limit of XRD or the Cu-species were highly dispersed over the g-C\textsubscript{3}N\textsubscript{4} structure. Figure 1 (b) shows Infrared spectra of g-C\textsubscript{3}N\textsubscript{4} and Cu-loaded g-C\textsubscript{3}N\textsubscript{4} samples. All the spectra bands are attributed to the samples containing g-C\textsubscript{3}N\textsubscript{4}. An absorption band at 805 cm\textsuperscript{-1} is associated with the bending nodes of the parent structure of g-C\textsubscript{3}N\textsubscript{4} in both the samples. The N-H stretch of the heterocyclic amines present in the g-C\textsubscript{3}N\textsubscript{4} structure are identified by the bands at 1248-1571. The band located at 1, 640 cm\textsuperscript{-1} is attributed to the stretching vibration band of the C-N of amines in g-C\textsubscript{3}N\textsubscript{4} (He et al., 2015).
Figure 1: (a) XRD analysis of Cu/g-C$_3$N$_4$ samples; (b) FTIR spectra of the corresponding samples.

Figure 2 exhibits the morphology of pure and modified g-C$_3$N$_4$ samples. From Figure 2 (a), it can be seen that g-C$_3$N$_4$ has obvious lamellar and irregular folding structures like wrinkled sheets, in which layers are stacked together. Meanwhile, 3 % Cu/g-C$_3$N$_4$ in Figure 2 (b) depicts porous g-C$_3$N$_4$ layers of sheet-like structure. The slight disparity between the two samples is possibly due to effective stirring and sonication during metal impregnation of Cu/g-C$_3$N$_4$ sample.

Figure 2: SEM images of Cu/g-C$_3$N$_4$ samples; (a) SEM image of g-C$_3$N$_4$, (b) SEM image of Cu/g-C$_3$N$_4$.

### 3.2 Photocatalytic CO$_2$ reduction with H$_2$O

Initially, blank experiments were conducted to confirm products formed were due to photoreduction of CO$_2$ only. Experiments were conducted in a gas phase system at 100 °C and irradiation time 2 h. In all types of catalysts, carbon containing compounds were not detected in the reaction system without reactants or light irradiations. Thus, any carbon containing compounds produced were derived from CO$_2$ photo-reduction with CH$_4$ and CH$_3$OH were found to be major CO$_2$ photo-reduction product in all the experiments. The effects of Cu loading on the activity of g-C$_3$N$_4$ for CO$_2$ reduction to CH$_4$ and CH$_3$OH under visible light irradiations are presented in Figure 3. With pure g-C$_3$N$_4$, the yield of CH$_4$ is lower but gradually increases with Cu loading until it attained an optimum yield at 3 wt. % Cu. With increasing Cu loading the yield decreases. This can be attributed to higher rates of charge recombination centres, resulting in reduced photoactivity (Liu et al. 2015). The effectiveness of Cu-loading was much appreciable for CH$_4$ production than the CH$_3$OH. On the other hand, yield of CH$_3$OH production gradually reduced with Cu-loading. The result indicates that the loading of the
pure catalyst (g-C$_3$N$_4$) with Cu metal become more efficient for CH$_4$ production, evidently due to reducing the band gap with hindered recombination rate of electron and hole pairs and ultimately increased in the product yield. However, pure g-C$_3$N$_4$ was more efficient for both CH$_4$ and CH$_3$OH production due to reason as discussed in reaction mechanism.

The effects of Cu onto g-C$_3$N$_4$ performance for CO$_2$ photo-reduction to hydrocarbons (C$_2$H$_4$ and C$_2$H$_6$) is presented in Figure 3 (b). Evidently, hydrocarbons were detected over all type of photocatalysts. However, Cu-loaded g-C$_3$N$_4$ have much appreciable effect of hydrocarbons production due to the more trapping and transport of electrons over Cu/g-C$_3$N$_4$ structure. Among the hydrocarbons, the yield of C$_2$H$_6$ was much higher in comparative to C$_2$H$_4$ and similar observation could be seen in all type of samples. This development has confirmed Cu-loaded g-C$_3$N$_4$ Nanosheets as a favourable visible light responsive photocatalyst for CH$_4$, CH$_3$OH and hydrocarbon production under solar energy.

![Figure 3: Effect of Cu loading onto the photoactivity of g-C$_3$N$_4$ Nanosheets for CO$_2$ reduction with H$_2$O to CH$_4$ and CH$_3$OH at 100 °C and irradiation time 2 h.](image)

![Figure 4: Photoreduction of CO$_2$ to hydrocarbons using H$_2$O reductant over Cu-loaded g-C$_3$N$_4$ samples under visible light irradiation and irradiation time 2 h.](image)
### 3.3 Reaction mechanism

The multi-step reaction pathway of the process splits into three parts: the formation of the CO$_2$ radical, water splitting and formation of CH$_4$, CH$_3$OH and hydrocarbons. The feasible reaction pathway for this process is given by reactions in Eqs (1) – (8).

\[
\begin{align*}
g\cdot C_3N_4 & \rightarrow e^- + h^+ \quad \text{visible light} \\
Cu^{2+} + 2e^- & \rightarrow Cu^{2+} / 2e^- \\
CO_2 + e^- & \rightarrow CO_2^- \\
H_2O + h^+ & \rightarrow OH^- + H^+ \\
CO_2 + 6H^+ + 6e^- & \rightarrow CH_3OH + H_2O \\
CO_2 + 8H^+ + 8e^- & \rightarrow CH_4 + 2H_2O \\
2CO_2 + 12H^+ + 12e^- & \rightarrow 2H_2 + 4H_2O \\
2CO_2 + 14H^+ + 14e^- & \rightarrow 2H_2 + 4H_2O
\end{align*}
\]

In the case of visible light irradiations, the photo-generated electrons and holes are produced over g-C$_3$N$_4$ photocatalyst. Eq (1) and (2) reveals photo-excited electron-hole pair production and their trapping by Cu-metal, resulting in prolonged lifetime of charges to precede oxidation and reduction process. The holes are used for oxidation of H$_2$O while electrons are consumed by CO$_2$ for its reduction as explained in Eq (3) and (4). Reactions in Eqs (5) to (8) divulged production of CH$_4$, CH$_3$OH and hydrocarbons through utilization of H$^+$ ions and electrons in multi-step process.

The photocatalytic activity is related to the band structure and the mechanism for the production of these products over Cu/g-C$_3$N$_4$ photocatalyst is explained in Figure 5. Under the light irradiations, VB electrons of g-C$_3$N$_4$ can transfer to Cu-metal which cause electron-hole pair separation. This is due to the possibility of electron trapping by the copper ions as a result of the difference in reduction potential of Cu$^{2+}$ which is more positive than the conduction band edge of g-C$_3$N$_4$ (-1.23 V vs. NHE). Since the reduction potential of CO$_2$/CH$_3$OH (-0.38 V) and CO$_2$/CH$_4$ (-0.24 V) are less than the conductance band of g-C$_3$N$_4$ (-1.23 V), thus production of these products are feasible. As discussed previously, g-C$_3$N$_4$ was favourable for CH$_3$OH production but copper has proven to be the preferred metal in the photoreduction of CO$_2$ to CH$_4$ as it demonstrates some level of selectivity for CH$_4$ production. Therefore, both reductant and metals are relatively important in photocatalytic CO$_2$ reduction applications for selective fuels.

![Figure 5: Schematic presentation of photocatalytic CO$_2$ reduction with H$_2$O to CH$_4$ and CH$_3$OH over Cu-loaded g-C$_3$N$_4$ photocatalyst under solar energy irradiations.](image-url)
4. Conclusions

Cu-loaded g-C$_3$N$_4$ nanosheets were developed for gas phase photocatalytic CO$_2$ reduction by H$_2$O under visible light irradiation. The yield rate of CO$_2$ reduction increased significantly by introducing Cu into g-C$_3$N$_4$ catalyst. The yield rate of CH$_4$ as the key product over Cu/g-C$_3$N$_4$ was 217.8 µmole-g-cat.$^{-1}$, 1.83 fold higher when compared with pure g-C$_3$N$_4$ photocatalyst. Besides, significant amount of CH$_3$OH with appreciable amounts of C$_2$ hydrocarbons were also detected in the product mixture. The experimental results conferred that g-C$_3$N$_4$ is an efficient material functional under solar energy while Cu-promoted enhanced the photocatalytic CO$_2$ reduction to solar fuels.

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