Synthesis of WO₃/g-C₃N₄ Nanocomposite for Photocatalytic CO₂ Reduction Under Visible Light

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Greenhouse gas CO₂ emitted through the burning of fossil fuels is a main cause of global warming. Among the different alternatives, photocatalytic conversion of CO₂ using solar energy in the presence of highly efficient photocatalyst is most attractive for the production of solar fuels. In this work, graphitic carbon nitride (g-C₃N₄) dispersed tungsten oxide (WO₃) to construct WO₃/g-C₃N₄ heterojunction was synthesized through hydrothermal approach. The performance of photocatalysts were tested for photocatalytic CO₂ reduction with CH₄ to CO via dry reforming of methane (DRM) under visible light irradiation in a fixed bed photoreactor. The performance of composite catalysts was further tested for photo-catalytic CO₂ reduction via H₂O as reductant and bireforming of methane (BRM) under visible light irradiations. The maximum CO production of 310 µmol g-cat⁻¹ h⁻¹ was observed over WO₃/g-C₃N₄ composite catalyst which is 2.95 and 8.85 folds higher than using pristine g-C₃N₄ and WO₃ photocatalysts. Using BRM process, production of CO was further increased due to the addition of water into CO₂-methane system. In general, significantly enhanced photocatalytic performance of composite catalyst was obviously due to Z-scheme heterojunction formation with efficient charge carrier separation and good band positions under visible light irradiation. The newly developed composite catalysts can effectively be used for recycling greenhouse gases to fuels using solar energy and would be beneficial for cleaner environment.

1. Introduction

Global warming effects due to CO₂ emitted during fossil fuels combustions and other human activities is a major challenge, the world is facing (Khan and Tahir, 2019). The phototechnology via photocatalytic CO₂ reduction through different reforming technologies has been investigated over the years by many researchers. Besides, methane (CH₄) is another greenhouse gas, emitted from agricultural, fossil fuels and biomass process. The utilizing both CH₄ and CO₂ for the production of synthesis gas (CO and H₂) and higher hydrocarbons is a new development in the reforming technologies. The most commonly employed approach for the utilization of both CO₂ and CH₄ includes CO₂ reforming with CH₄ called dry reforming of methane (DRM) (Moral et al., 2018), which has several benefits such as minimizing their level in the atmosphere, and producing equimolar syngas mixture (H₂/CO=1.0).

In thermal reforming, DRM operates under higher reaction temperature, which produces coke and provides instability to catalyst. Using phototechnology, higher activity and photostability can be obtained, in addition of low-cost process for chemicals and fuels production. During the last few years, there has been growing research on photocatalytic CO₂ reduction through DRM under UV and visible light irradiations. Different photocatalysts such as La-doped TiO₂ (Tahir et al., 2017), Pt-loaded TiO₂ (Han et al., 2015), and Au/Rh modified TNTs (László et al., 2016) have been investigated for photocatalytic DRM process under UV-light irradiations. Recently, graphitic carbon nitride (g-C₃N₄), a 2D layered semiconductor material, is under investigation due to several benefits such as cheaper, easy to prepare and high stability (thermal/chemical). In addition, g-C₃N₄ is active under visible light irradiations due to narrow band gap energy (Eₘ~ 2.70 eV) (Shi et al., 2020), compared to wide band gap energy semiconductors such as TiO₂ (Eₘ~ 3.20 eV). Recently, there has been growing interest on the use of g-C₃N₄ photocatalyst for photocatalytic CO₂ reduction through different CO₂
reduction process. In this perspective, the use of Cu/g-C\textsubscript{3}N\textsubscript{4} (Tahir et al., 2017) for DRM under visible light irradiation was investigated. In addition of metals lading, coupling g-C\textsubscript{3}N\textsubscript{4} with other semiconductors can be a promising approach to maximize charges separation with higher visible light absorption. Tungsten oxide (WO\textsubscript{3}) is a very promising cocatalyst due to its lower band gap energy and higher oxidation potentials (Bafaqeer et al., 2019). In this perspective WO\textsubscript{3}/g-C\textsubscript{3}N\textsubscript{4} for enhanced photo-catalytic H\textsubscript{2} production has been reported (Fu et al., 2019). The conversion of greenhouse gases over WO\textsubscript{3}/g-C\textsubscript{3}N\textsubscript{4} catalyst for the production of synthesis gas and valuable fuels would be beneficial for efficient photo-catalytic CO\textsubscript{2} reduction under visible light.

In this study, fabrication of WO\textsubscript{3}/g-C\textsubscript{3}N\textsubscript{4} heterojunction composite for photocatalytic CO\textsubscript{2} reduction via dry reforming of methane (DRM) and bireforming of methane (BRM) under visible light has been investigated. The photocatalysts were synthesized using hydrothermal approach. The photoactivity of WO\textsubscript{3}/g-C\textsubscript{3}N\textsubscript{4} was further examined in different reforming systems to understand the role of sacrificial reagents in CO\textsubscript{2} reduction process. The effect of irradiation time and reaction mechanism to understand the role of each component in the composite catalyst was further investigated.

2. Experimental

2.1 Materials synthesis and characterization

The bulk g-C\textsubscript{3}N\textsubscript{4} was prepared by heating melamine (Sigma Aldrich) at 550 \degree C for 2 h in a muffle furnace under air atmosphere. The product obtained was grinded to get bulk g-C\textsubscript{3}N\textsubscript{4}, which was further treated with acetic acid and dried overnight to get g-C\textsubscript{3}N\textsubscript{4} (Tahir et al., 2020). For the synthesis of WO\textsubscript{3}/g-C\textsubscript{3}N\textsubscript{4} composite, ultrasonic assisted physical mixing approach was employed. Typically, 1 g of g-C\textsubscript{3}N\textsubscript{4} was dispersed in a methanol and stirred for 6 12 h to get uniform dispersion. Afterwards, specific amount of WO\textsubscript{3} (50 wt\% g-C\textsubscript{3}N\textsubscript{4}) dispersed in a methanol was added to above solution under stirring for another 12 h. Finally, samples were dried at 100 \degree C overnight to get WO\textsubscript{3}/g-C\textsubscript{3}N\textsubscript{4} composite samples. All the samples were characterized using XRD, PL< SEM, TEM and UV visible techniques. X-ray diffraction (XRD, RIGAKU), operated with Cu-K\textalpha\ radiation at \lambda=0.154178 nm, 40 kV and 30 mA. The morphologies were obtained by FESEM, ZEISS Crossbeam 340 and TEM, HITACHI HT7700. The PL analysis was conducted using Lab RAM HR Evolution, HORIBA and UV-visible analysis was conducted using Cary 100 Agilent, Model G9821 A.

2.2 Photoactivity test

The photoactivity test was conducted in a stainless steel photoreactor with diameter 6 cm, lighting surface 28 cm\textsuperscript{2} and total volume 150 cm\textsuperscript{3}. The reactor was equipped was a glass window for passing the light irradiations. The experiments were conducted for photocatalytic CO\textsubscript{2} reduction using H\textsubscript{2}O, H\textsubscript{2}, and CH\textsubscript{4} reducing agents. A HID Xenon lamp with power 35 W with wavelength 420 nm and intensity 20 mW cm\textsuperscript{-2} was used as a source of visible light. The lamp was located at the top of glass reactor and equipped with cooling fans to remove heat. Specifically, 150 mg powder photocatalyst was evenly dispersed at the bottom of stainless-steel chamber. High purity gases (CO\textsubscript{2}, 99.99 \% and CH\textsubscript{4}, 99.99 \%), regulated by mass flow controllers (MFC), were passed through the reactor to remove the air and to saturate the catalyst surface. The CO\textsubscript{2}/CH\textsubscript{4} feed ratio of 1.0 was used in all the experiments. All the experiments were conducted under normal temperature and atmospheric pressure. The products were analysed using gas chromatograph (GC 6890 N). The Carboxen-1010 PLOT Capillary Column equipped with a thermal conductivity detector (TCD) and a flame ionized detector (FID) was used for the separation of CO, CH\textsubscript{4}, CO and H\textsubscript{2} products.

3. Results and discussion

3.1 Catalyst characterization

Figure 1a shows XRD analysis of g-C\textsubscript{3}N\textsubscript{4} and WO\textsubscript{3}/g-C\textsubscript{3}N\textsubscript{4} composites. Obviously, g-C\textsubscript{3}N\textsubscript{4} presents two peaks positioned at 2-theta of 13.10\degree and 27.44\degree, relating to polymeric structure graphitic carbon nitride. Similarly, WO\textsubscript{3} peaks in WO\textsubscript{3}/g-C\textsubscript{3}N\textsubscript{4} composite were appeared at 2-\theta of 23.01\degree, 23.52\degree, 24.25\degree, 26.49\degree, 28.58\degree, 28.83\degree, 33.17\degree, 33.47\degree, 34.07\degree, 35.52\degree, 41.39\degree, 41.83\degree, 47.15\degree, 48.21\degree, and 49.81\degree, confirming the presence of WO\textsubscript{3} in the composite sample (Card no 01-083-0950) (Tahir et al., 2020). More importantly, all the peaks relating to g-C\textsubscript{3}N\textsubscript{4} were appeared in the composite of WO\textsubscript{3}/g-C\textsubscript{3}N\textsubscript{4}, confirming, successful fabrication of composite through ultrasonic approach. Figure 1b presents photoluminescence (PL) plots of pristine g-C\textsubscript{3}N\textsubscript{4} and WO\textsubscript{3}/g-C\textsubscript{3}N\textsubscript{4} composite. Obviously, highest PL intensity was obtained in pristine g-C\textsubscript{3}N\textsubscript{4} due to fast charges recombination rate. However, a gradual declined in PL intensity was observed when g-C\textsubscript{3}N\textsubscript{4} was coupled with WO\textsubscript{3}. This declined in PL intensity was due to faster charge carrier separation with hindered recombination rate over the WO\textsubscript{3}/g-C\textsubscript{3}N\textsubscript{4} composite sample. This further confirms successful fabrication of WO\textsubscript{3}/g-C\textsubscript{3}N\textsubscript{4} heterojunction.
Figure 1: (a) X-ray diffraction patterns of g-C3N4 and WO3/g-C3N4 composite samples; (b) Photoluminescence analysis for g-C3N4 and WO3/g-C3N4 samples

Figure 2: FE-SEM analysis of (a) g-C3N4 and (b) WO3/g-C3N4 samples; (c) TEM analysis of WO3/g-C3N4 samples, (d) UV-visible analysis of g-C3N4, WO3 and WO3/g-C3N4 photocatalysts.

The morphology of g-C3N4 and WO3/g-C3N4 composite were further investigated using FESEM and TEM characterization techniques and results are demonstrated in Figure 2. Figure 2a show morphology of g-C3N4, in which, obvious two-dimensional folded sheets of graphitic carbon nitrides could be observed. FESEM image in Figure 2b shows morphology of WO3/g-C3N4 composite. It could be seen a good dispersion of WO3 with g-C3N4 nanosheets. A further interaction of WO3 with 2D g-C3N4 nanosheets could be observed in TEM image as demonstrated in Figure 2c. Obviously, WO3 microspheres were distributed over g-C3N4 nanosheets, producing a heterojunction between both the semiconductors.

The UV-visible analysis was further conducted to determine band gap energy and light absorption trends of g-C3N4 and WO3/g-C3N4 samples. Obviously, both g-C3N4 and WO3/g-C3N4 has response of light absorption under visible light. The light absorption wavelengths of 461.35, 443.58 and 432.96 nm were obtained for WO3.
g-C$_3$N$_4$ and WO$_3$/g-C$_3$N$_4$ samples. This confirms higher visible light absorption of the samples and would be beneficial for photocatalytic CO$_2$ reduction applications (Tahir et al., 2020). The band gap energies of 2.70, 2.81 and 2.88 eV were obtained for WO$_3$, g-C$_3$N$_4$ and WO$_3$/g-C$_3$N$_4$ samples.

### 3.2 Photocatalytic CO$_2$ reduction

The photoactivity test of g-C$_3$N$_4$, WO$_3$ and WO$_3$/g-C$_3$N$_4$ for photocatalytic CO$_2$ reduction with CH$_4$ in the presence of water through bi-reforming of methane (BRM) under visible light irradiations in a fixed bed photoreactor. The amount of photocatalyst loaded was 0.15 g, dispersed uniformly inside the reactor. The feed ratio of CO$_2$/CH$_4$ of 1.0 was employed for all the experiments. All the reactions were conducted at normal temperature and atmospheric pressure.

Figure 3a shows photocatalytic CO$_2$ reduction for the production CO evolution over g-C$_3$N$_4$, WO$_3$ and WO$_3$/g-C$_3$N$_4$ photocatalysts during photocatalytic CO$_2$ reduction with H$_2$O/CH$_4$ photocatalysts. Using pure WO$_3$, 35 µmol g-cat$^{-1}$h$^{-1}$ for CO was detected. Comparatively, 105 µmol g-cat$^{-1}$h$^{-1}$ of CO was obtained over g-C$_3$N$_4$ photocatalyst. Obviously, lower photoactivity was attained over WO$_3$ due to its reduction potential (+0.76 eV) (Ye and Web, 2019), which is more positive than is required for CO$_2$ reduction (-0.48 eV). Besides, g-C$_3$N$_4$ has 2D layered structure, and efficient charges separation efficiency for photocatalytic reaction in addition of higher reduction potential (CB -1.20 eV). When, WO$_3$/g-C$_3$N$_4$ were coupled highest photoactivity of 310 µmol g-cat$^{-1}$h$^{-1}$ of CO was attained. This significantly enhanced photoactivity of WO$_3$/g-C$_3$N$_4$ composite was evidently due to faster charges separation with good oxidation and reduction potentials for DRM reaction under visible light irradiations (Guo et al., 2020). This confirms significantly enhanced performance of WO$_3$/g-C$_3$N$_4$ composite and it can be further employed for investigating different reforming reactions.

**Figure 3:** (a) Photocatalytic CO$_2$ reduction by CH$_4$/H$_2$O to CO over different catalysts; (b) Photocatalytic DRM and BRM for CO$_2$ reduction over WO$_3$/g-C$_3$N$_4$; (c) Performance analysis of reforming systems for CO$_2$ reduction to CO; (d) proposed schematic mechanism of CO$_2$ reduction to CO over WO$_3$/g-C$_3$N$_4$ composite.
The performance of WO3/g-C3N4 composite catalyst was further tested in different reforming reactions such as DRM, BRM and RWGS reaction. The production of CO in Figure 3b shows 8.2 folds-higher production of CO using BRM process compared to DRM process under the same reaction conditions. The higher photocatalytic activity for CO evolution through BRM process was due to adding water (H2O) in CO2/CH4 feed system. The water provides higher number of protons (H+) with the involvement of lower light energy. This confirms BRM process is more efficient for maximizing the photoactivity of WO3/g-C3N4 composite due to the presence of both methane/waters reducing agents with CO2 during photocatalysis process.

The performance of WO3/g-C3N4 composite catalyst was further tested in different photocatalytic systems such as reduction of CO2 with H2O, photocatalytic reversed water gas shift reaction (RWGSR), DRM and BRM reactions as shown in Figure 3c. It could be seen that highest CO evolution rate was attained during CO2 reduction in the presence of hydrogen through RWGSR reaction. Using DRM process lowest CO production was obtained due to high stability of CO2 and CH4 molecules. Using water and CO2, higher amount of CO was evolved compared to DRM reaction, but lower than RWGSR and BRM reactions. All these findings confirm that not only photocatalyst, but reforming reactions are also important to maximize photocatalysis process. The selection of both photocatalyst and reducing agents are crucial for selective production of fuels during CO2 conversion under visible light irradiation.  Previously, photocatalytic CO2 reduction with H2O over Pd–Au/TiO2–WO3 for CO and CH4 production (Zhu et al., 2018), higher CO/CH4 production over WO3–TiO2/Cu2ZnSnS4 (Raza et al., 2020) and WO3/g-C3N4 with CO and CH4 production (Li et al., 2020) have been investigated. Comparatively, efficient photocatalytic CO2 reduction with CO and H2 production through DRM and BRM was observed over WO3/g-C3N4 composite through the involvement of Eq(1) and Eq(2).

\[ \text{CH}_4 + \text{CO}_2 \rightarrow 2\text{CO} + 2\text{H}_2 \quad \Delta H_{298K} = +247\text{kJ/mol} \]  
\[ 3\text{CH}_4 + \text{CO}_2 + 2\text{H}_2\text{O} \rightarrow 4\text{CO} + 8\text{H}_2 \quad \Delta H_{298K} = +220\text{kJ/mol} \]  

3.3 Reaction mechanism

The photocatalytic CO2 reduction using water/methane reducing agents over WO3/g-C3N4 composite under visible light involves oxidation and reduction reaction through the involvement of electrons and holes has been illustrated in Figure 3d. When visible light strike over the composite catalyst WO3 is activated first due to its lower bandgap energy (Eg~ 2.70 ) as illustarted in Eq(3), producing electrons and holes. As the CB of WO3 is more positive (CB~ 0.74) (Ye  and Wen., 2019) than g-C3N4 conduction band (CB~ -1.20). The photogenerated electrons have potential to transfer from CB of WO3 towards VB of g-C3N4, enabling their efficient separation (Eq4). The photogenerated electrons are consued during CO2 reduction process with CO production and holes were consumed for water and methane oxidation through the reactions in Eqs(5) to (7).

\[ \text{WO}_3 \xrightarrow{hv} \text{WO}_3(e^-) + \text{WO}_3(h^+) \]  
\[ g - \text{C}_3\text{N}_4 + \text{WO}_3(e^-) \rightarrow g - \text{C}_3\text{N}_4(e^-) + \text{WO}_3 \]  
\[ \text{CO}_2 + 2\text{H}^+ + 2e^- \rightarrow \text{CO} + 2\text{H}_2\text{O} \]  
\[ \text{H}_2\text{O} + 2\text{h}^+ \xrightarrow{hv} 2\text{H}^+ + 1/2\text{O}_2 \]  
\[ \text{CH}_4 + \text{h}^+ \xrightarrow{hv} \text{H}^+ + \bullet \text{CH}_3 \]  

According to experimental results, CO2 was efficiently converted to CO through different reforming reactions such as DRM, BRM and RWGSR reactions. The significantly enhanced phototacivity for CO2 reduction over WO3/g-C3N4 composite was due to Z-scheme heterojunction formation with efficient charges separation.

4. Conclusions

The WO3/g-C3N4 composite catalyst was successfully synthesized and tested for photocatalytic CO2 reduction under visible light irradiations. In Z-scheme WO3/g-C3N4 composite, efficient charge separation was observed enabling more production of CO during photocatalytic dry and bireforming reactions. The highest CO production of 310 µmol g-cat⁻¹h⁻¹ over WO3/g-C3N4 composite was achieved. The performance of different reforming reactions such as dry reforming of methane, bireforming of methane and reverse water gas shift
reactions were further investigated. Using BRM and RWGS reactions, highest amount of CO was evolved under the same reaction conditions. It could be concluded that WO_3/g-C_3N_4 heterojunction is a promising photocatalyst for photocatalytic CO_2 reduction under visible light irradiation and can be employed in other solar energy assisted applications due to efficient charges separation and higher visible light absorption.

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Reference

Bafaqeer A., Tahir M., Amin N.A.S., 2019, Well-designed ZnV_2O_6/g-C_3N_4 2D/2D nanosheets heterojunction with faster charges separation via pCN as mediator towards enhanced photocatalytic reduction of CO_2 to fuels, Applied Catalysis B: Environmental, 242, 312-326.


László B., Baán K., Varga E., Oszkó A., Erdőhelyi A., Kónya Z., Kiss J., 2016, Photo-induced reactions in the CO_2-methane system on titanate nanotubes modified with Au and Rh nanoparticles, Applied Catalysis B: Environmental, 199, 473-484.


Tahir B., Tahir M., Amin N.A.S., 2017, Photocatalytic Carbon Dioxide and Methane Reduction to Fuels over La-Promoted Titanium Dioxide Nanocatalyst, Chemical Engineering Transactions, 56, 1123-1128.


Tahir B., Tahir M., Nawawi M.G.M., 2020, Highly stable 3D/2D WO_3/g-C_3N_4 Z-scheme heterojunction for stimulating photocatalytic CO_2 reduction by H_2O/H_2 to CO and CH_4 under visible light, Journal of CO_2 Utilization, 41, 101270.
