

Photocatalytic CO₂-Hydrogen Conversion via RWGSR over Ni/TiO₂ Nanocatalyst Dispersed in Layered MMT Nanoclay

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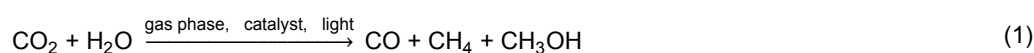
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The production of cleaner fuels from renewable and safer energy resources are highly demanding to mitigate energy crises and global warming. In this study, the use of cleaner photo-technology for selective and enhanced CO₂ reduction to fuels over nickel (Ni) modified titanium dioxide (TiO₂) dispersed in structured montmorillonite (MMT) nanoclay for photocatalytic CO₂-hydrogen conversion via reverse water gas shift (RWGS) reaction has been investigated. The catalyst samples, prepared by a single step sol-gel method, were characterised by XRD, FTIR, FESEM and UV-visible spectroscopy. XRD results revealed reduced in TiO₂ crystallite size with Ni and MMT loading and produced anatase phase of TiO₂. MMT is found efficient for the enhanced dispersion of TiO₂ while Ni-promoted efficient charges separation with hindered recombination rate over the structured MMT/TiO₂ nanocomposite. The photoactivity of Ni/TiO₂-MMT composite for CO₂ reduction was conducted in a continuous flow photoreactor using hydrogen as the reducing agent. The main products detected were CO and CH₄ with appreciable amounts of C₂H₄, C₂H₆ and C₃H₆ hydrocarbons. The maximum yield of CO produced as the main product over 3 wt% Ni-10 wt% MMT/TiO₂ catalyst was 9,429 μmole/g-cat, 209-fold higher than the amount of CO detected over the pure TiO₂. Evidently, Ni-promoted TiO₂ photocatalytic activity, while MMT is favourable for improved dispersion of Ni/TiO₂ catalyst. The dynamic and selective CO evolution was evidently due to efficient light distribution, enlarged active surface area and efficient charges separation with their hindered recombination rate by Ni and MMT. The stability of Ni/TiO₂ dispersed over MMT sustained over the irradiation time. With the use of green nanocomposite catalyst, CO₂ can be efficiently converted to cleaner fuels with all sustainable systems.

1. Introduction

Global warming caused by the drastic release of carbon dioxide (CO₂) induced by combustion of fossil fuels has drawn considerable attention to the need to address environmental challenges related to climate change (Ye et al., 2015). Among the other alternative methods for CO₂ mitigations, photocatalytic water splitting (Reverberi et al., 2016) and CO₂ reduction to fuels using light irradiation provides pathways toward economical and cleaner process (Low et al., 2017). Pioneered work on photocatalytic CO₂ reduction was conducted for the first time in 1979 and the products detected were CH₃OH, HCOOH, HCHO, CH₃COOH and CH₄ over semiconductors TiO₂, ZnO, WO₃, CdS and SiC (Inoue et al., 1979). During the past three decades, excessive efforts have been established to maximise activity, and selectivity of many semiconductors using different reducing agent, photo-catalysts and photo-reactors.

In the field of photocatalytic CO₂ reduction, the most of work has been related to using water as a reducing agent. Thermodynamically, H₂O is hardly reducible and CO₂ reduction with H₂O yielded lower amounts of products while selectivity is dependent on photo-catalysts and reaction system as discussed in Eq(1) and Eq(2) (Tahir et al., 2017a).





Recently, hydrogen (H_2) is reported as an efficient reductant to maximise CO_2 reduction efficiency and products selectivity through reverse water gas shift (RWGS) reaction and CO_2 -methanation reaction as explained in Eq(3) and Eq(4). Photocatalytic CO_2 reduction to CO by H_2 over Ag/ TiO_2 NWs (Tahir et al., 2017d), has been reported with improved yield rate and selectivity. Photocatalytic RWGS CO_2 reduction could be a potentially workable to produce cleaner fuels with higher yield and selectivity.



Titanium dioxide (TiO_2) as a semiconductor has attracted many researchers due to its numerous rewards such as relatively low price, non-toxic, excessive available, resistant to chemicals, and relatively high oxidative potentials (Kim et al., 2017). Conversely, photocatalytic efficiency of the pure TiO_2 is low due fast photo-generated charges recombination rate.

Surface modification of TiO_2 structure with electron acceptors using metals such as Au, Ag, Cu, Pt, Ce and La is a proven strategy to improve efficiency (Ali et al., 2017). Among the metals, Ni is attracting much attention due to appropriate fermi levels to transfer electrons from TiO_2 to metal co-catalyst, low cost and abundantly available. Ni/ TiO_2 activity can further be enhanced by their dispersion into the green clay structures. Using nanoclay as a support in which Ni/ TiO_2 can be distributed on the surface of a suitable matrix, an efficient hetero-junction is produced. The other numerous benefits of natural clay materials are low cost, green materials and have high CO_2 adsorption capacity.

The most widely used clay mineral is montmorillonite (MMT) which is a multilayered nanoclay consists of octahedral sheet sandwiched between two silica tetrahedral sheets (Mulewa et al., 2017). This distinctive structure of MMT makes it suitable for high dispersion, enhanced sorption capacity and excellent charge trapping ability. Previously, the use of TiO_2 /MMT in photocatalytic CO_2 reduction applications has been successfully investigated (Tahir et al., 2017c). It is obvious from the literature that MMT is the most widely studied clay for the growth of TiO_2 nanoparticles. In this context, further research involving photocatalytic RWGS reaction over MMT supported Ni/ TiO_2 nanocatalyst for gas phase systems in a continuous monolith photoreactor to produce renewable fuels is warranted.

In this work, the use of Ni and MMT-clay to modify TiO_2 structure for photocatalytic CO_2 reduction via RWGS reaction in a continuous flow photoreactor has been investigated. The catalysts were synthesized by a modified sol-gel method and were characterized by XRD, FE-SEM, FTIR and UV-Vis spectroscopy. The role of Ni and MMT on the yield rate and products selectivity are critically discussed. In addition, the photocatalytic reaction mechanism for CO_2 reduction to CO via RWGS reaction was considered based on the experimental results.

2. Experimental

2.1 Catalyst preparation

The Ni/ TiO_2 dispersed over MMT nanoclay was synthesized through a direct and single step sol-gel method using Tetra-isopropyl orthotitanate (98 %, Merck) and MMT (1.4P, Aldrich). Typically, 10 mL titanium solution (Tetra-isopropyl orthotitanate (98 %, Merck) dispersed in 30 mL isopropanol) was taken into flask for the hydrolysis process. Next, the solution was hydrolysed by adding 7 mL acetic acid (1 M) diluted in 10 mL isopropanol under vigorous stirring. The mixture was stirred for another 24 h to get clear titanium sol. The solutions of nickel nitrate and montmorillonite (MMT (1.4P, Aldrich) dispersed in isopropanol) were added into titanium sol. The process of stirring was continued for another 6 h until the thick sol was obtained. The sol obtained was transferred into a glass container for the monolith coating. The cordierite ceramic monoliths with square channels were dipped into the sol. Any excess soil was blown off using hot compressed air. The coating procedure was repeated to ensure constant loading. The coated monoliths were dried at 80 °C for 12 h before calcined at 500 °C for 5 h. Catalyst loading was calculated by subtracting the coated monolith weight from the initial bare monolith weight.

2.2 Characterization

The crystalline phase was investigated using powder X-ray diffraction (XRD; Bruker D8 advance diffractometer, 40 kV and 40 mA) with Cu- $\text{K}\alpha$ radiation ($\lambda = 1.54 \text{ \AA}$). The infrared spectra were measured at room temperature in the range of 4,000 to 400 cm^{-1} with Spectrum 2000 Explorer Fourier Transformed

Infrared (FT-IR) Spectrometer. The scanning electron microscopy (SEM) was carried out with JEOL JSM6390 LV SEM instrument. UV-Vis diffuse reflectance absorbance spectra were determined using UV-vis spectrophotometer (Agilent, Cary 100) equipped with an integrated sphere. Fourier transform infrared (FTIR) spectroscopy was performed using Thermo Nicolet Avatar 360 FTIR spectrometer.

2.3 Photoactivity test

The reactor consists of stainless steel cylindrical vessel equipped with glass window of thickness 8 mm for passing out light irradiation. The catalyst coated monoliths with loading amount ~ 0.50 g was introduced inside the cylindrical stainless-steel chamber. The light source was a 200 W Hg lamp.

Prior to feeding, the reactor chamber was purged using purified helium (He) flow, then a mixture of gases (CO_2 , H_2 and He) was constantly streamed through the reactor for 1 h to saturate the catalyst. The temperature inside the reactor was maintained at 100°C using temperature controller. The gas mixture feed flow rate of 20 mL/min and CO_2/H_2 feed ratio of 1.0 was used in all the experiments. The products were analysed using an on-line gas chromatograph (GC-Agilent Technologies 6890 N, USA) equipped with thermal conductivity detector (TCD) and flame ionized detector (FID).

3. Results and discussion

3.1 Catalyst characterization

Figure 1a shows XRD patterns of TiO_2 , MMT and Ni/MMT-loaded TiO_2 nanocomposite samples. XRD patterns of TiO_2 nanoparticles (NPs) revealed pure anatase and crystalline phase structure. Similarly, XRD pattern of MMT reflects broad basal of (0 0 1) located at $2\theta = 3.70^\circ$, due to plate-shaped particles and stacking disorder of MMT layers. The XRD patterns of TiO_2 dispersed in MMT persisted its original reflection with no additional peaked appeared. However, all the TiO_2 peaks in MMT/ TiO_2 sample become broader and weaker, and prominent MMT peak (0 0 1) disappeared. This has confirmed that MMT layered structure has disordered with uniform dispersion of TiO_2 NPs. With Ni loading to MMT/ TiO_2 , XRD patterns of TiO_2 NPs and MMT/ TiO_2 composites persisted, while peaks of nickel in oxide or metal state were not detected due to its lower contents or its uniform dispersion in composite samples.

Figure 1b shows Infrared spectra of TiO_2 , MMT and Ni-MMT/ TiO_2 samples. The stretching bend at $1,616\text{ cm}^{-1}$ in the spectrum of pure TiO_2 , shows chemisorbed H_2O is negligible. The MMT spectrum presents broadband at around $3,633\text{ cm}^{-1}$ attributed to Al_2OH group of octahedral layer, while the bands at around $1,616\text{ cm}^{-1}$ can be allocated to -OH and stretching and bending vibration of water molecules. The peak at $1,049\text{ cm}^{-1}$ corresponds to a symmetric vibration of SiO_2 tetrahedra while several peaks between $1,000$ and 500 cm^{-1} can be attributed to Al-IV tetrahedra. The peaks between $1,000$ and 500 cm^{-1} were assigned to bending vibration of Si-O. On the other hand, MMT/ TiO_2 and Ni-MMT/ TiO_2 samples show similar patterns as like TiO_2 . The stretching band at about $1,049\text{ cm}^{-1}$ and very weak stretching at 450 to 550 cm^{-1} were observed due to the asymmetric stretching vibration of SiO_2 tetrahedra.

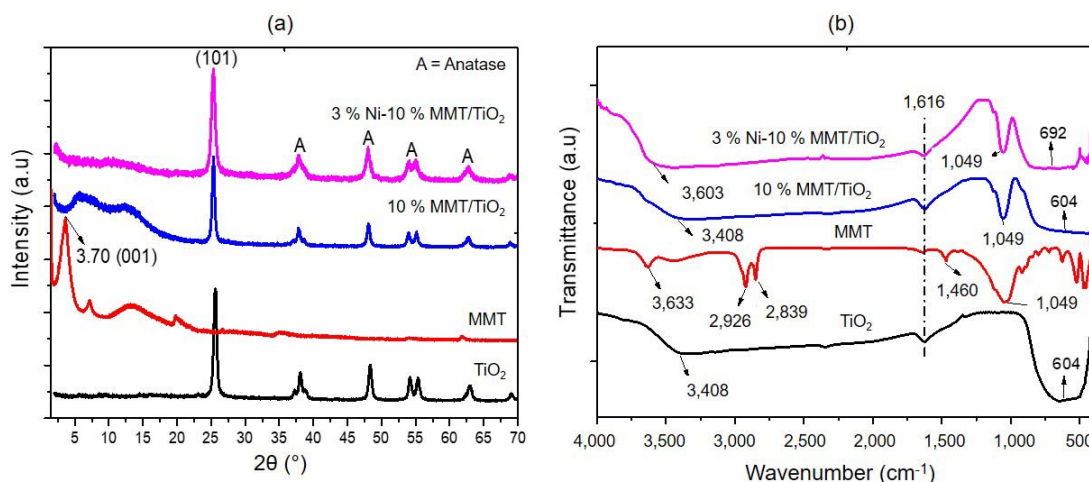


Figure 1: (a) XRD analysis and (b) FTIR analysis of TiO_2 , MMT and Ni/MMT loaded TiO_2 samples

The structure and morphology of TiO_2 , Ni/MMT-loaded TiO_2 samples is presented in Figure 2. SEM in Figure 2a shows MMT sheets stacked together. The uniform, spherical in shape and mesoporous TiO_2 nano-particles

are obvious in Figure 2b. Figure 2c illustrates SEM images of MMT/TiO₂ composite structure. Evidently, MMT layers are completely destroyed and TiO₂ NPs are well distributed with MMT, confirming efficient intercalation process, thus producing delaminated MMT/TiO₂ nanocomposite.

The addition of Ni into MMT/TiO₂ composite samples shows similar morphology as like MMT/TiO₂ but with more obvious TiO₂ NPs. This revealed successful development of Ni/TiO₂ NPs dispersed in MMT to produce Ni-MMT/TiO₂ composite sample.

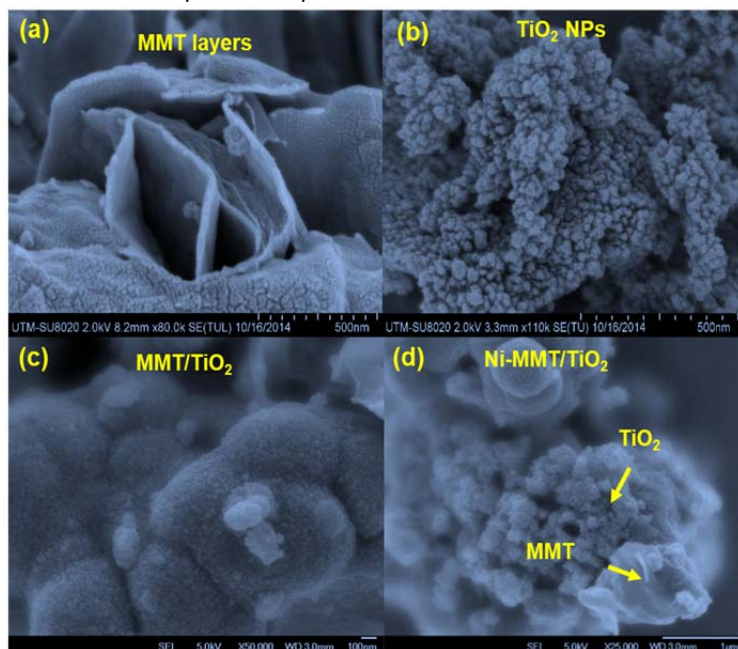


Figure 2: FESEM analysis of MMT and Ni/MMT-loaded TiO₂ nanoparticles. SEM images of (a) MMT layers, (b) TiO₂ NPs, (c) MMT-loaded TiO₂ NPs, and (d) Ni/MMT-loaded TiO₂ NPs

The UV–Vis diffuse reflectance absorbance spectra of the TiO₂, MMT/TiO₂ and Ni-MMT/TiO₂ samples are presented in Figure 3. Adding MMT into TiO₂, there was no significant effect on the absorption spectra, however, it was gradually shifted towards visible region with Ni-loading. The band gap of the samples was calculated according to plot of $(\alpha h\nu)^2$ vs photon energy (eV). The band gap energy of 3.11 and 3.10 eV obtained for TiO₂ and MMT/TiO₂ samples. However, the TiO₂ band gap energy was further reduced to 3.05 eV in Ni-loading MMT/TiO₂ samples. It is obvious that there is a gradual decrease in the band gap energy in Ni-loading TiO₂ samples compared to pure TiO₂ NPs.

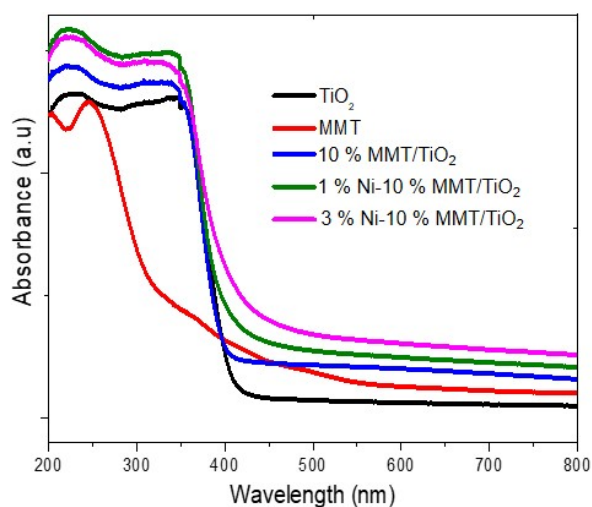


Figure 3: Diffuse reflectance absorbance spectra of TiO₂ NPs, MMT and Ni/MMT-loaded TiO₂ samples

3.2 Photocatalytic CO₂ reduction with H₂

Firstly, control experiments for photocatalytic CO₂ reduction with H₂ were conducted in the presence of photocatalysts. Using all types of catalysts, carbon-containing compounds were not detected in the reaction system without reactants or light irradiations. Any carbon-containing compounds produced were derived from CO₂ photo-reduction only.

The effect of MMT-loading onto the catalytic activity of TiO₂ for photocatalytic CO₂ reduction to CO and CH₄ in the presence of H₂ as reducing agent at temperature 100 °C, irradiation time 2 h and CO₂/H₂ feed ratio 1.0 is presented in Figure 4a. Using all types of catalyst samples, CO was detected as the main product which was apparently due to RWGS reaction of CO₂ reduction with H₂. The pure TiO₂ has low photoactivity which gradually increased in MMT supported TiO₂ samples. Similarly, MMT/TiO₂ composite also promoted the production of CH₄. This was evidently due to efficient charge transfer, higher surface area and efficient CO₂ adsorption in MMT/TiO₂ samples. The optimal 10 wt% MMT/ TiO₂ sample was the most active over which the highest amount of CO and CH₄ were produced. Figure 4b shows the effect of irradiation time and Ni-loading on continuous production of CO during RWGS reaction of CO₂ with H₂ at CO₂/H₂ feed ratio 1.0, 100 °C and feed flow rate 20 mL/min. Initially, production of CO was much significant and then gradually reached to steady state in Ni-loaded MMT/TiO₂ samples. This significantly higher yield of CO in Ni-MMT/TiO₂ composite catalyst was due to efficient RWGS reaction in Eq(3), hindered charges recombination rate by Ni and efficient light distribution inside monolith photoreactor.

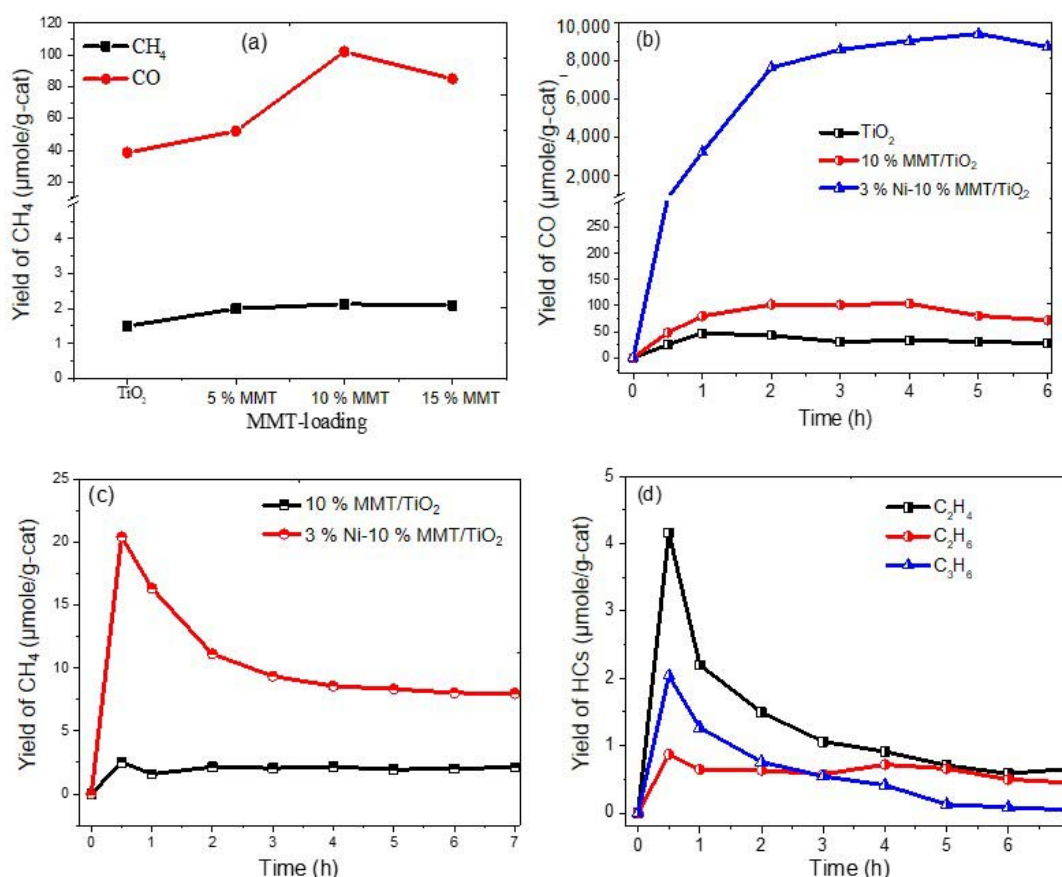


Figure 4: (a) Effect of MMT-loading on TiO₂ for CO and CH₄ production, (b) Effect of Ni-loading on the activity of MMT/TiO₂ samples for selective CO production, (c) CH₄ production over Ni-MMT/TiO₂ samples, (d) Production of C₂-C₃ hydrocarbons over Ni-MMT/TiO₂ composite catalyst

The highest reaction rate of CO over 3 wt% Ni-10 wt% MMT/TiO₂ was 2,268 μmole g-cat⁻¹ h⁻¹, while it was only 26 and 8.5 μmole g-cat⁻¹ h⁻¹ over 10 % MMT/TiO₂ and TiO₂ NPs, respectively. These results show that CO₂ can efficiently and continuously be converted to cleaner fuels using Ni/TiO₂ dispersed in MMT nanoclay.





Figure 4c depicts the production of CH₄, in which CH₄ was produced in appreciable amount with Ni-MMT/TiO₂ catalyst. Similarly, production of higher hydrocarbons over Ni-MMT/TiO₂ is presented in Figure 4d. Among the hydrocarbons, C₂H₄ is detected in more quantity than C₂H₆ and C₃H₆ while their productions were decreased over the irradiation time. The decreased in hydrocarbons production was perhaps due to their oxidation as explained in Eq(5) and Eq(6). The CO₂ can efficiently be converted to CO and hydrocarbons using Ni as active metal and MMT as green clay materials in a continuous flow photoreactor system. The performance of Ni-MMT/TiO₂ catalyst was further compared with the reported values in literature. The amount of CO of 5.19 μmole g-cat⁻¹ h⁻¹ over g-C₃N₄/Bi₂WO₆ (Li et al., 2015), CO of 289.30 over 3 % Fe-10 % MMT/TiO₂ (Tahir et al., 2017b), a CO production of 1.91 μmole g-cat⁻¹ h⁻¹ was obtained over V-W-loaded TiO₂ in monolith photoreactor (Xiong et al., 2017) and Ag/TiO₂ NWs with CO production of 983 μmole g-cat⁻¹ h⁻¹ (Tahir et al., 2017b). The significantly enhanced performance of Ni-MMT/TiO₂ composite catalysts due to synergistic effect of Ni and MMT in a monolith photoreactor, resulting in enhanced activity and selectivity.

4. Conclusions

Photocatalytic CO₂ reduction to CO via RWGS reaction over Ni/TiO₂ nanocatalyst dispersed in MMT layered nanoclay has been successfully investigated. The yield rate of CO₂ reduction was increased significantly by introducing Ni in MMT/TiO₂ composite sample. Nickel is found to be very efficient for preventing charges recombination rate while MMT promoted Ni/TiO₂ dispersion with enhanced CO₂ adsorption. Monolithic support promoted efficient light distribution resulting in selective production of fuels. The finding of this study can be explored further for the production of other chemicals and fuels under solar energy irradiation.

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References

- Ali K.A., Abdullah A.Z., Mohamed A.R., 2017, Visible light responsive TiO₂ nanoparticles modified using Ce and La for photocatalytic reduction of CO₂: Effect of Ce dopant content, *Applied Catalysis A, General*, 537, 111-120.
- Inoue T., Akira F., Satoshi K., Kenichi H., 1979. Photoelectrocatalytic reduction of carbon dioxide in aqueous suspensions of semiconductor powders, *Nature*, 277, 637-638.
- Kim H.R., Razaq A., Grimes C.A., 2017, Heterojunction p-n-d Cu₂O/S-TiO₂/CuO: Synthesis and application to photocatalytic conversion of CO₂ to methane, *Journal of CO₂ Utilization*, 20, 91-96.
- Li M., Zhang L., Fan X., Zhou Y., Wu M., Shi J., 2015, Highly selective CO₂ photoreduction to CO over g-C₃N₄/Bi₂WO₆ composites under visible light, *Journal of Materials Chemistry A*, 3, 5189-5196.
- Low J., Cheng B., Yu J., 2017, Surface modification and enhanced photocatalytic CO₂ reduction performance of TiO₂: a review, *Applied Surface Science*, 392, 658-686.
- Mulewa W., Tahir M., Amin N.A.S., 2017, MMT-supported Ni/TiO₂ nanocomposite for low temperature ethanol steam reforming toward hydrogen production, *Chemical Engineering Journal*, 326, 956-969.
- Reverberi A.P., Klemeš J.J., Varbanov P.S., Fabiano B., 2016, A review on hydrogen production from hydrogen sulphide by chemical and photochemical methods, *Journal of Cleaner Production*, 136, 72-80.
- Tahir B., Tahir M., Amin N.A.S., 2017a, Photocatalytic Carbon Dioxide Reduction to Fuels Over Cu-Loaded g-C₃N₄ Nanocatalyst under Visible Light, *Chemical Engineering Transactions*, 56, 403-408.
- Tahir B., Tahir M., Amin N.A.S., 2017b, Photocatalytic CO₂ Reduction to CO over Fe-loaded TiO₂/Nanoclay Photocatalyst, *Chemical Engineering Transactions*, 56, 1111-1116.
- Tahir M., Tahir B., Amin N.A.S., 2017c, Photocatalytic Reverse Water Gas Shift CO₂ Reduction to CO over Montmorillonite Supported TiO₂ Nanocomposite, *Chemical Engineering Transactions*, 56, 319-324.
- Tahir M., Tahir B., Amin N.A.S., Zakaria Z.Y., 2017d, Photo-induced reduction of CO₂ to CO with hydrogen over plasmonic Ag-NPs/TiO₂ NWs core/shell hetero-junction under UV and visible light, *Journal of CO₂ Utilization*, 18, 250-260.
- Xiong Z., Lei Z., Ma S., Chen X., Gong B., Zhao Y., Zhang J., Zheng C., Wu J.C.S., 2017, Photocatalytic CO₂ reduction over V and W codoped TiO₂ catalyst in an internal-illuminated honeycomb photoreactor under simulated sunlight irradiation, *Applied Catalysis B, Environmental*, 219, 412-424.
- Ye S., Wang R., Wu M.-Z., Yuan Y.-P., 2015, A review on g-C₃N₄ for photocatalytic water splitting and CO₂ reduction, *Applied Surface Science*, 358, 15-27.