CHEMICAL ENGINEERING TRANSACTIONS
VOL. 72, 2019
A publication of AIDIC
The Italian Association of Chemical Engineering
Online at www.aidic.it/cet
Guest Editors: Jeng Shiun Lim, Azizul Azri Mustaffa, Nur Nabila Abdul Hamid, Jiří Jaromír Klemeš

ISBN 978-88-95608-69-3; **ISSN** 2283-9216
DOI: 10.3303/CET1972058

Fabrication of SWCNTs Modified TiO_2 Nanocomposite towards Enhanced Photocatalytic Carbon Dioxide Reduction to Fuels under Visible Light

Beenish Tahir, Muhammad Tahir*, Noraishah Saidina Amin, Hajar Alias

Chemical Reaction Engineering Group (CREG), School of Chemical and Energy Engineering, Faculty of Engineering, Universiti Teknologi Malaysia (UTM), 81310 UTM Johor Bahru, Johor, Malaysia.
mtahir@cheme.utm.my

In this study, fabrication of single wall carbon nanotubes modified titanium dioxide (SWCNTs/TiO_2) composite catalyst for selective and enhanced photocatalytic CO_2 reduction to fuels has been investigated. The samples were synthesized by a modified one-pot sol-gel method and were characterized by X-ray diffraction (XRD), Scanning Electrons Microscopy (SEM) and Photoluminescence (PL) Spectroscopy. The pure anatase phase with reduced crystal size and hindered charges recombination was obtained by modifying TiO_2 with SWCNTs. The performance of newly developed nano-catalyst was investigated for photo-induced CO_2-hydrogen reduction under visible light irradiations. The products detected were CO, CH_4 and CH_3OH with appreciable amounts of C_2-C_3 hydrocarbons. The yield of CO as the main product over 5 wt% SWCNTs/TiO_2 was 1,220 µmole g-cat.$^{-1}$ h^{-1}, a 5.35 times more than the pure TiO_2 NPs. Similarly, yield of methanol of 23.4 µmole g-cat.$^{-1}$ h^{-1} was detected, 6.5 folds the amount produced over the pure TiO_2 NPs. The SWCNTs found to be efficient to enhance TiO_2 activity due to its ability to capture visible light irradiations with proficient charges separations over the TiO_2 surface. The higher interaction between SWCNTs/TiO_2, efficient adsorption-desorption and hindered charges recombination rate promoted the photoactivity and products selectivity. The reaction mechanism to understand the role of SWCNTs in TiO_2 for CO_2-hydrogen conversion is also deliberated.

1. Introduction

Global warming effects due to excessive release of CO_2 and energy crises are the major challenges facing by the mankind (Nasir et al., 2018). The level of CO_2 in the atmosphere has been increasing every year because of combustion of fossil fuels, burning of forest and deforestation by human activities (Low et al., 2018). Among the different alternatives, utilization of CO_2 through chemical process is a promising approach for the production of chemicals and fuels. However, higher stability of CO_2 molecule demands input energy which leads to uneconomical process (Yang et al., 2016). One promising pathways to both problems is photocatalytic CO_2 reduction under visible light irradiations. Thus, photocatalytic CO_2 conversion by the use of light irradiation is an attractive pathway which has potential to convert solar energy and CO_2 to high energy content compounds such as CH_4, CH_3OH and hydrocarbons (Xiong et al., 2018).
In the field of photocatalytic CO_2 reduction applications, in most of research work, water has been used as the reducing agent, yet H_2O is hardly reducible (Shao et al., 2018). Therefore, CO_2 conversion by H_2O is not significant and selectivity is not appreciable due to wide range of products distributions (Olivo et al., 2015). Among the different reductants, hydrogen (H_2) has been reported as an efficient reductant for photocatalytic CO_2 conversion via photocatalytic reverse water gas shift (PRWGS) reaction (Tahir et al., 2015). During the last years, titanium dioxide (TiO_2) has been employed as a semiconductor material due to its benefits of low cost and appropriate band structure, yet has lower photoactivity. (Paulino et al., 2016). The lower performance of TiO_2 is because of fast charges recombination rate while active only under UV-light irradiations (Tahir, 2018). TiO_2 photoactivity can be improved by loading with metals and modifying with low cost and renewable materials and using H_2 as reductant (Tahir et al., 2015).

Paper Received: 12 July 2018; Revised: 16 September 2018; Accepted: 27 October 2018

Please cite this article as: Tahir B., Tahir M., Amin N.S., Alias H., 2019, Fabrication of swcnts modifiedtio 2 nanocomposite towards enhanced photocatalytic carbon dioxide reduction to fuels under visible light, Chemical Engineering Transactions, 72, 343-348
DOI:10.3303/CET1972058

Recently, carbon based materials, in particular, carbon nanotubes (CNTs) such as electron (e^-) transportation and trapping and provision of bridge for the flow of photo-excited electrons that helps to hinder the recombination of charge carriers. More importantly, carbon nanotubes exhibit novel electrical, thermal and optical properties with high surface area that makes them conductive under visible spectrum (Umer et al., 2019). Carbon nanotubes have high surface area, reduce the rapid recombination of electron/hole pairs and assists in harvesting the solar light, thus have capacity to enhance the photocatalytic activity under visible light (Yousefzadeh et al., 2013). Researchers have confirmed that the electron transportation properties of CNTs provide a comfortable pathway to direct the flow of photo-generated electron/hole pairs, which increases the life-span of charge carriers; generated by photo-catalyst upon solar light irradiations. Among the CNTs, single wall carbon nanotubes (SWCNTs) has much attractions due to their characteristics to capture and transport electrons efficiently in the SWCNTs/TiO_2 composite samples (Li et al., 2016). The use of SWCNTs/TiO_2 composite for photocatalytic CO_2 reduction by H_2 would be an attractive pathway for sustainable fuels production. However, there is no report available on the use of SWCNTs/TiO_2 composite catalyst in RWGS reaction for selective CO and hydrocarbons production.

In this study, fabrication of SWCNT modified TiO_2 structure for photocatalytic CO_2 reduction by H_2 reducing agent via photocatalytic reverse water gas shift (RWGS) reaction under visible light irradiation has been investigated. The nanocatalysts were synthesized using single step sol-gel approach and were characterized with XRD, FESEM and PL characterization techniques. The performance of photo-catalysts was tested in a fixed bed photoreactor under visible light irradiations. The main products detected were CO, methanol and C_1-C_3 hydrocarbons. The reaction mechanism was proposed based on the experimental results.

2. Experimental

2.1 Catalyst preparation

For the synthesis of SWCNTs/TiO_2 composites, one-pot single step sol-gel method was used. Typically, 30 mL isopropanol was placed in a flask and 10 mL titanium solution was dispersed under magnetic stirring. The hydrolysis process was conducted by adding dropwise solution of 0.1 M acetic acid. This process of hydrolysis was continued by 24 h before modifying with SWCNTs. For purification SWCNTs were dispersed in 6 M HNO_3 and H_2SO_4 mixture, ultra-sonicated for 60 min, and then washed with deionized water until the pH value reached to 7.0 before dried in the oven for 12 h. Subsequently, functionalized CNTs dispersed in isopropanol were added into titanium sol. Finally, samples were dried at 100 °C overnight and calcined at 500 °C for 5 h under N_2 flow. Powder X-ray diffraction (XRD; Bruker D8 advance diffract meter, 40 kV and 40 mA) with Cu- Kα radiation (λ= 1.54 A°) was used to determine crystalline phase. The morphology was investigated using scanning electron microscopy (SEM) carried out with JEOL JSM6390 LV SEM. Photo-luminance (PL) spectra of the samples were carried out by using Raman Spectrometer (Lab RAM HR Evolution, HORIBA) with 325 nm emitting laser, which act as an excitation source.

2.2 Photoactivity test

The reactor consists of a stainless-steel cylindrical vessel with a length 5.5 cm and a total volume 150 cm^3. The lamp used was a 300 W Xe lamp for visible light source located at the top of the reactor glass window. The 0.5 g catalyst was uniformly distributed at the bottom of reactor for photo-activity test. 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. Before turning on the lamp, pressure inside the reactor was increased to 0.2 bars above the atmospheric by closing the outlet valve and finally inlet valve was closed for batch mode experiments. The temperature inside the reactor of 100 °C was maintained using temperature controller. Similarly, CO_2/H_2 feed ratio of 1.0 was used in all the experiments using mass flow controllers (MFC). On-line gas chromatograph (GC-Agilent Technologies 6890 N, USA) was used for products analysis.

3. Results and discussion

3.1 Catalyst characterization

Figure 1a presents XRD spectra of pure TiO_2 and SWCNTs/TiO_2 samples, which confirms a pure crystalline and anatase phase. The XRD pattern of SWCNTs presents reflection of (0 0 2) and (1 0 1) at 2θ = 25.93° and 42.74°, evidently due to graphitic structure of CNTs. However, all these peaks dispersed in CNTs/TiO_2 composite samples but TiO_2 persisted its original reflection. Besides, TiO_2 peaks in CNTs-loaded TiO_2 samples become broader and weaker, which revealed controlled crystal growth of TiO_2 NPs with the mesoporous structure.

For understanding the trapping and transfer property of electron-hole pairs in modified photo-catalysts, photoluminescence (PL) analysis can be employed. Figure 1b presents TiO_2 and 5 wt% SWCNTs loaded TiO_2 samples peaks, excited at wavelength 325 nm. It is evidenced that PL spectra intensity depends on the photo-generated charges recombination. Obviously, higher PL intensity was obtained in the pure TiO_2 which is in accordance of higher charges recombination rate. However, a significant decreased in PL intensity was observed with SWCNTs loaded TiO_2 sample. This low PL intensity indicates a decrease in charges recombination rate due to trapping of electrons by SWCNTs. Thus, addition of SWCNTs into TiO_2 provides faster charges separation which will enable higher photocatalytic CO_2 reduction efficiency.
The structure and morphology of TiO_2 and SWCNTs/TiO_2 samples is presented in Figure 2. The uniform size with spherical structure of TiO_2 nano-particles can be seen in Figure 2a. Figure 2b presents SEM analysis of SWCNTs/TiO_2 sample. Evidently, there was good interaction between TiO_2 NPs and carbon nanotubes, confirming efficient charges separation process, thus producing SWCNTs/TiO_2 nanocomposite using sol-gel method.

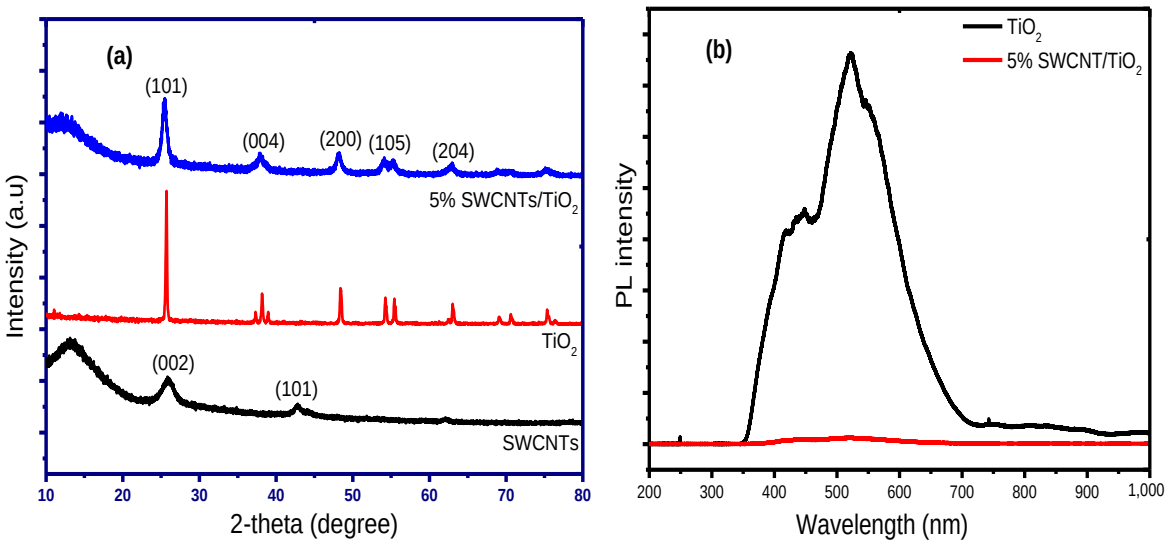

Figure 1: (a) X-ray diffraction patterns of TiO_2, SWCNTs and SWCNTs/TiO_2 catalysts; (b) Photoluminscience analysis of TiO_2 and 5 wt% SWCNTs modified TiO_2 samples.

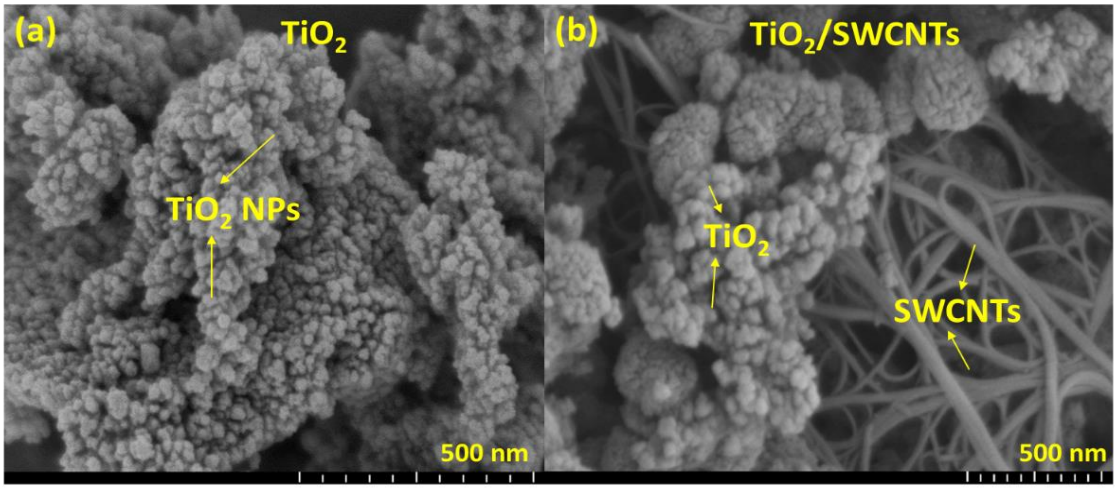

Figure 2: SEM images of TiO_2 and TiO_2/SWCNTs samples: (a) SEM image of TiO_2 nanoparticles, (b) SEM image of TiO_2/SWCNTs sample.

3.2 Photocatalytic CO_2 reduction with H_2

Firstly, quality control experiments were conducted in the presence of photocatalyst and light irradiations but in the absent of reactants. Using all types of systems, in the products gas mixture, carbon containing compounds were not detected without reactants or light irradiations. Therefore, all the products would be originated during CO_2 reduction process under light irradiations.

The performance of SWCNTs loaded TiO_2 for photocatalytic CO_2 reduction with H_2 with the production of CH_4, CH_3OH, CO and hydrocarbons under visible light irradiations is presented in Figure 3. Figure 3a presents the production of CH_4, CH_3OH and CO over TiO_2 and SWCNTs-loaded TiO_2 samples. Obviously, production of CO was detected as the main products while its yield over SWCNTs/TiO_2 was significantly higher than using pure TiO_2. Production of methanol was greatly improved while methane was reduced using SWCNTs loaded TiO_2 samples. This confirmed that photocatalytic CO_2 reduction by H_2 via RWGS reaction is a favourable process which has improved the productivity for selective products. However, significantly improved efficiency was due to larger surface area, efficient trapping and transport of electrons by SWCNTs and visible light absorption. Figure 3b demonstrates the production of hydrocarbons over TiO_2 and SWCNTs-loaded TiO_2 samples. Among the hydrocarbon, C_2H_4 was produced in appreciable amounts with lower amounts of C_2H_6 and C_3H_8. Evidently, production of hydrocarbons was significantly higher in the presence of SWCNTs/TiO2 samples compared to pure TiO_2 NPs.

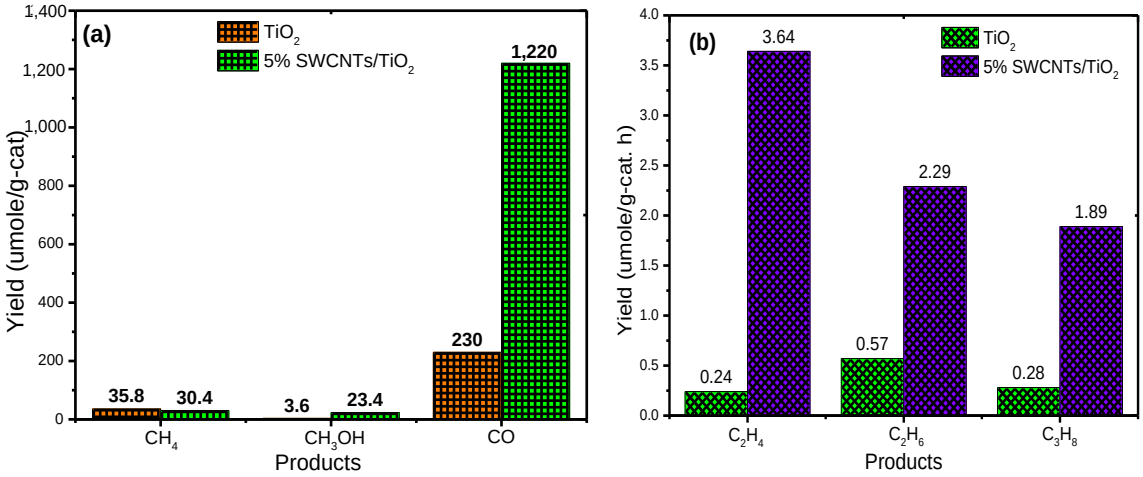

Figure 3: Performance analysis of TiO2 and SWCNTs/TiO2 activity for CO2 reduction with H2 to CO, CH3OH and hydrocarbons at 100 °C, time 2 h and CO2/H2 feed ratio 1.0; (a) Production of CO, CH4 and CH3OH; (b) Production of hydrocarbons.

The yield rates and selectivity of different products over TiO_2 and SWCNTs/TiO_2 with their selectivity are presented in Table 1. The yield of CO over 5 wt% SWCNTs/TiO_2 was 1,220 µmole g-cat.$^{-1}$ h^{-1}, a 5.35 times the pure TiO_2 NPs. Similarly, yield of methanol of 23.4 µmole g-cat.$^{-1}$ h^{-1} was detected, 6.5 folds the amount produced over pure TiO_2 NPs. Similar trends in enhanced SWCNTs/TiO_2 photo-activity was observed in hydrocarbons production. The enhanced in photoactivity was due to more production of electrons with their hindered charges recombination rate by SWCNTs. The selectivity for CO production over TiO_2 increased from 85.03 to 95.19 % in 5 wt% SWCNTs loaded TiO_2 samples. These results show that CO_2 can efficiently be converted to CO using SWCNTs loaded TiO_2 catalyst via RWSG reaction. Similar observations have been reported over Cu-modified g-C_3N_4 for photocatalytic CO_2-CO conversion applications (Shi et al., 2018). The enhanced photocatalytic hydrogen production over $MoSe_2$-modified WO_3 loaded with CNTs have been reported previously in the literature (Tahir et al., 2018).

Table 1: Summary of yield rates and selectivity of products over TiO_2 and SWCNTs/TiO_2 samples

Samples	Yield rate (µmole g-cat^{-1} h^{-1})						Selectivity (%)		
	CO	CH_4	CH_3OH	C_2H_4	C_2H_6	C_3H_8	CO	CH_4	CH_3OH
TiO_2	230	35.8	3.6	0.24	0.57	0.28	85.03	13.24	1.33
5% SWCNTs/TiO_2	1,220	30.4	23.4	3.64	2.29	1.89	95.19	2.37	0.28

3.3 Reaction mechanism

During the photocatalytic reverse water gas shift reaction, CO_2 is reacted with H_2 for the production of CO, CH_3OH and hydrocarbons as the potential products over SWCNTs/TiO_2 samples. Therefore, possible reaction mechanism is illustrated in Eqs (1)-(6).

$$TiO_2 \longrightarrow e^- + h^+ \quad (1)$$

$$SWCNT + e^- \longrightarrow SWCNT - e^- \quad (2)$$

$$CO_2 + H_2 \longrightarrow CO + H_2O \text{ (RWGSR)} \quad (3)$$

$$CO_2 + 3H_2 \longrightarrow CH_3OH + H_2O \quad (4)$$

$$CO_2 + 2H_2 \longrightarrow CH_4 + O_2 \quad (5)$$

$$2CO_2 + 3H_2 \longrightarrow C_2H_6 + 2O_2 \quad (6)$$

First, electron-hole pairs were produced over the TiO_2 surface under visible light irradiation as explained in Eq (1). The photo-generated electrons were trapped by SWCNTs in the composite of SWCNTs/TiO_2, resulting in their efficient separation as explained in Eq(2). The electrons were transferred toward CO_2 for its reduction while holes were consumed for hydrogen oxidation. The oxidation and reduction process promoted CO_2 reduction by H_2 via RWGS reaction (Eq (3)). As there was efficient production of electrons due to SWCNTs, H^+ radicals and active electrons effectively reduced CO_2 to CH_3OH, CH_4 and C_2H_6 as explained in Eqs (4) - (6). Accordingly, CO was the main product with selectivity above 95%, confirming favorable RWGS reaction for CO_2 reduction to CO over SWCNTs/TiO_2 nanocomposites under visible light irradiations.

The proposed schematics of photocatalytic CO_2 reduction by H_2 over SWCNTs/TiO_2 catalyst under visible light irradiations is depicted in Figure 4. It is obvious that light irradiations strike over the catalyst, activated it with the production of electrons and holes (e^-/h^+) pairs. These photo-generated charges react with CO_2 and H_2 for the production of CO. The production of CO as the main products would be explained on the base of TiO_2 conductance band and CO_2/CO reduction potential. As the TiO_2 CB (-0.50 V) is higher than CO_2/CO reduction potential (-0.48 V), the production of CO would be possible (Shakeri et al., 2015). Significantly enhanced photo-catalytic activity of CO_2 conversion to CO was due to visible light responsive, faster charges separation and appropriate band structure for the production of chemicals and fuels. On the other hand, production of CH_3OH and hydrocarbons would be due to more production of electrons and their efficient utilization in CO_2 reduction process due to SWCNTs/TiO_2 composite sample. Therefore, SWCNTs is promising for electron trapping and transporting materials and could be used in solar energy applications for selective fuels production.

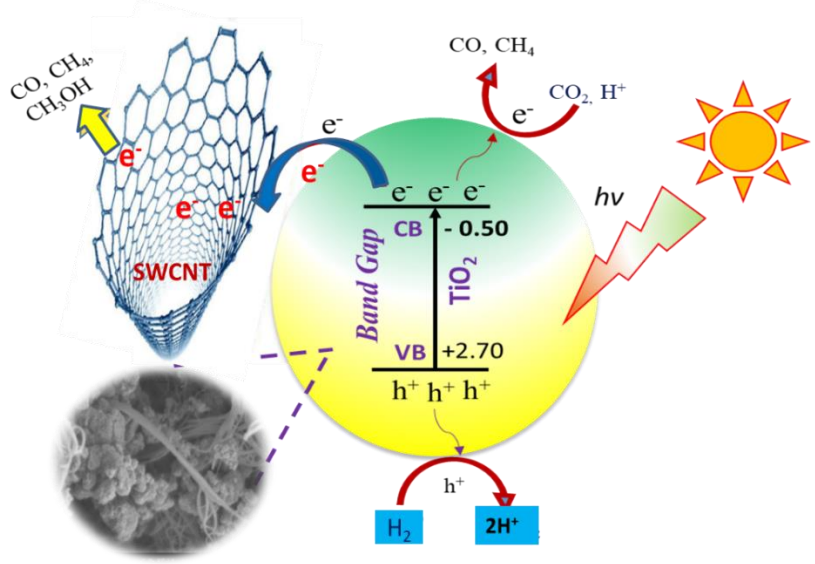

Figure 4: Schematic presentation of photocatalytic RWGS reaction over SWCNTs/TiO_2 photocatalyst.

4. Conclusions

In this study, successful fabrication of SWCNTs loaded TiO_2 nanocomposites for photocatalytic CO_2 reduction by H_2 under visible light irradiation has been reported. The newly developed composite catalysts found efficiency for photocatalytic CO_2 reduction to CO, CH_4, CH_3OH and hydrocarbon fuels. The yield and selectivity was promisingly improved over the TiO_2 due to efficient charges separation by SWCNTs. The highest yield rate of CO as the key product observed over SWCNT/TiO_2 was 1,220 μmole-g-cat $^{-1}h^{-1}$ at selectivity 95%, much higher when compared with pure TiO_2 photo-catalyst. Similarly, an appreciable amount of CH_3OH and hydrocarbons were obtained in SWCNTs loaded TiO_2 samples. This significant improvement in TiO_2 photoactivity with SWCNTs loaded TiO_2 was evidently due to visible light responsive and faster charges separation. Therefore, composite catalyst synthesized in this study reveals efficient photocatalytic behavior for solar energy assisted fuels production.

Acknowledgements

The authors would like to extend their deepest appreciation to Ministry of Education (MOE) Malaysia and Universiti Teknologi Malaysia (UTM), Malaysia for the financial support of this research under FRGS (Fundamental Research Grant Scheme, Vot 4F876) and Research University Grant (Vot 17H06).

Reference

Li L., Chao W., Mengling Ni., Chii S., 2016, Enhanced photocatalytic activity of TiO_2/single-walled carbon nanotube (SWCNT) composites under UV-A irradiation, Separation and Purification Technology, 169, 273-278.

Low J., Qiu S., Xu D., Jiang C., Cheng B., 2018, Direct evidence and enhancement of surface plasmon resonance effect on Ag-loaded TiO_2 nanotube arrays for photocatalytic CO_2 reduction, Applied Surface Science, 434, 423-432.

Nasir S., Tahir M.,, Khairiraihanna J., Thanabalan M.,Murid H., 2018, A critical review on TiO_2 based photocatalytic CO_2 reduction system: Strategies to improve efficiency, Journal of CO_2 Utilization 26, 98-122.

Olivo A., Trevisan V., Ghedini E., Pinna F., Bianchi C.L., Naldoni A., Cruciani G., Signoretto M., 2015, CO_2 photoreduction with water: Catalyst and process investigation, Journal of CO_2 Utilization, 12, 86-94.

Paulino P.N., Salim V.M.M., Resende N.S., 2016, Zn-Cu promoted TiO_2 photocatalyst for CO_2 reduction with H_2O under UV light, Applied Catalysis B: Environmental, 185 ,362-370.

Shakeri J., Farrokhpour H., Hadadzadeh H., Joshaghani M., 2015, Photoreduction of CO_2 to CO by a mononuclear Re(i) complex and DFT evaluation of the photocatalytic mechanism, RSC Adv., 5 (51), 41125-41134.

Shao K., Wang Y., Iqbal M., Lin L., Wang K., Zhang X., He M., He T., 2018, Modification of Ag nanoparticles on the surface of $SrTiO_3$ particles and resultant influence on photoreduction of CO_2, Applied Surface Science, 434, 717-724.

Shi G., Yang L., Liu Z., Chen X., Zhou J., Yu Y., 2018, Photocatalytic reduction of CO_2 to CO over copper decorated g-C_3N_4 nanosheets with enhanced yield and selectivity, Applied Surface Science, 427, 1165-1173.

Tahir B., Tahir M., Amin N.S., 2015, Photoreactor Carbon Dioxide Reduction with Hydrogen in a Continuous Catalytic Monolith Photoreactor, Chemical Engineering Transactions, 45, 259-264.

Tahir M., 2018, Photocatalytic carbon dioxide reduction to fuels in continuous flow monolith photoreactor using montmorillonite dispersed Fe/TiO_2 nanocatalyst, Journal of Cleaner Production, 170, 242-250.

Tahir M., Tahir B., 2016, Dynamic photocatalytic reduction of CO_2 to CO in a honeycomb monolith reactor loaded with Cu and N doped TiO_2 nanocatalysts, Applied Surface Science, 377, 244-252.

Tahir M.B., Nabi G., Iqbal T., Sagir M., Rafique M., 2018, Role of $MoSe_2$ on nanostructures WO_3-CNT performance for photocatalytic hydrogen evolution, Ceramics International, 44 (6), 6686-6690.

Umer M., Tahir M., Azam, M.U., Jaffar M.., 2019, Metals free MWCNTs@TiO_2@MMT heterojunction composite with MMT as a mediator for fast charges separation towards visible light driven photocatalytic hydrogen evolution, Applied Surface Science 463,747-757.

Xiong Z., Kuang C.-C., Lin K.-Y., Lei Z., Chen X., Gong B., Yang J., Zhao Y., Zhang J., Xia B., Wu J.C.S., 2018, Enhanced CO_2 photocatalytic reduction through simultaneously accelerated H_2 evolution and CO_2 hydrogenation in a twin photoreactor, Journal of CO_2 Utilization, 24, 500-508.

Yang M.-Q., Xu Y.-J., 2016, Photocatalytic conversion of CO_2 over graphene-based composites: current status and future perspective, Nanoscale Horizon, 1 (3), 185-200.

Yousefzadeh S., Reyhani A., Naseri N., Moshfegh A.Z., 2013, MWCNT/WO_3 nanocomposite photoanode for visible light induced water splitting, Journal of Solid State Chemistry, 204, 341-347.