



CeO₂-TiO₂ FOR PHOTOREDUCTION OF CO₂ TO METHANOL UNDER VISIBLE LIGHT: EFFECT OF CERIA LOADING

(CeO₂-TiO₂ untuk Penurunan CO₂ kepada Metanol di bawah Radiasi Cahaya Nampak: Kesan Pemuatan Ceria)

Hamidah Abdullah^{1,2}, Nur Aminatulmimi Ismail^{1*}, Zahira Yaakob², Maksudur R. Khan¹,
Syarifah Abd Rahim¹

¹Faculty of Chemical and Natural Resources Engineering,
Universiti Malaysia Pahang, 26300, Kuantan, Pahang, Malaysia

²Department of Chemical and Process Engineering, Faculty of Engineering and Built Environment,
Universiti Kebangsaan Malaysia, 43600 UKM Bangi, Selangor, Malaysia

*Corresponding author: aminatulmimi@ump.edu.my

Received: 21 October 2015; Accepted: 14 June 2016

Abstract

A visible light-driven photocatalyst, CeO₂-TiO₂ catalyst with different ceria loading was synthesized by impregnation method between TiO₂ powder and cerium oxide nanoparticles slurry. The prepared catalyst samples were characterized by X-ray diffraction (XRD), surface area analysis, UV-vis absorption spectroscopy and photoluminescence spectroscopy (PL). The band gap of CeO₂-TiO₂ catalyst was found to be 2.15 – 2.4 eV. The band gap reduction clearly indicated the successful loading of CeO₂ on TiO₂. The photocatalytic activity was determined by measuring the photoreduction of CO₂ to methanol in aqueous solution under visible light. The effect of cerium loading in the range of 1 to 5 wt% on the photocatalytic activity was studied and 2 wt% CeO₂-TiO₂ was found to exhibit the maximum photoactivity of 18.6 µmol/g.catalyst after 6 hours irradiation. Results showed that the prepared photocatalyst is visible light active and may be used as effective catalyst in photoreduction of CO₂ to methanol.

Keywords: metal oxide, photocatalyst, band gap, nanoparticles

Abstrak

Fotomangkin yang boleh diaplikasi di bawah radiasi cahaya nampak iaitu mangkin CeO₂-TiO₂ yang berbeza muatan ceria telah disintesis dengan kaedah impregnasi serbuk titanium dioksida dengan mendakan partikel nano cerium dioksida. Ciri mangkin yang dihasilkan dikaji dengan menggunakan pembelauan sinar-X (XRD), analisis luas permukaan, UV-Vis spektrofotometer dan spektroskopi fotoluminesen (PL). Jurang tenaga mangkin CeO₂-TiO₂ adalah di antara 2.15 eV hingga 2.4 eV. Pengurangan jurang tenaga jelas menunjukkan pemuatan CeO₂ ke atas TiO₂ telah berjaya. Aktiviti fotopemangkinan ditentukan melalui tindak balas penurunan gas karbon dioksida (CO₂) di dalam larutan akueus kepada metanol dan dijalankan di bawah radiasi cahaya nampak. Kesan pemuatan 1 hingga 5 peratus berat cerium ke atas TiO₂ terhadap aktiviti fotopemangkinan telah dikaji dan CeO₂-TiO₂ dengan 2 peratus berat cerium didapati menunjukkan fotosensitiviti maksimum iaitu penghasilan 18.6 µmol/g.mangkin selepas 6 jam radiasi. Hasil kajian menunjukkan bahawa fotomangkin yang dihasilkan adalah aktif di bawah cahaya nampak dan dijangka efektif untuk penurunan CO₂ kepada metanol.

Kata kunci: logam oksida, fotomangkin, jurang tenaga, partikel nano

Introduction

The photocatalytic reduction of carbon dioxide (CO₂) to fuel has been reported as an alternative way to tackle the global warming and shortage of fuels problem. Among the semiconductor photocatalysts that have been studied, titania dioxide (TiO₂) has been considered the most promising photocatalyst due to its non-toxic, low cost, and photostable [1]. One of the drawbacks of the existing semiconductor typically TiO₂ is that it has a wide band gap. This limits its catalytic activity under the visible light. In such cases, the photogenerated electron hole pair's recombination is fast, resulting less electron hole pairs availability that that can be utilized for CO₂ reduction. Several strategies have been reported by modifying the structure of TiO₂ to enhance its photoactivity under visible light and lower the recombination rate of photogenerated electron hole pairs. Among modifications made was doping rare earth element with the TiO₂. This study has demonstrated that the modified TiO₂ catalysts enhance the photocatalytic ability as to compare to TiO₂. Some examples are clearly shown in the researches of others; degradation of organic compounds such as Eu-TiO₂ for Rhodamine B (RB) degradation [2], La-TiO₂, Pr-TiO₂, Nd-TiO₂ for reduction of hexavalent chromium and degradation of methylene blue [3] and La-TiO₂ and Ce-TiO₂ for degradation of methylene blue [4].

Ceria was chosen by many researchers among the rare earth elements because it is one of the four most abundant rare earth elements. It appearances that composites of ceria-titania have shown remarkable photocatalytic activity under visible light irradiation for water splitting and degradation of organic compounds due to its capability in adsorbing visible light and inhibit the photogenerated electron hole pairs recombination [5]. To the best of our knowledge, there are a few reports on ceria-titania for CO₂ photoreduction. Recently, Xiong et al. and Matejova et al. studied the CeO₂-TiO₂ catalyst activity for photocatalytic conversion of CO₂ to liquid products (methanol and formaldehyde) and to gaseous products (CH₄ and CO), respectively [6,7]. However, the study was limited under UV light irradiation study only. Our previous study reported that CeO₂-TiO₂ showed a higher methanol yield than TiO₂ catalyst for CO₂ photocatalytic reduction under visible light irradiation [8]. This paper represents the extension of previous study by study the effect of ceria amount loading on characterization and CO₂ photocatalytic reduction to methanol under visible light irradiation.

Materials and Methods

Catalyst preparation

The CeO₂-TiO₂ powder was prepared based on our previous work [8]. In brief, firstly, CeO₂ nanoparticle slurry was prepared by dissolved required amount of (Ce (NO₃)₃.6H₂O) in 20% ethanol solution at 50 °C and subsequently, 3M (NH₄OH) was added under stirring. The process was completed when the reaction slurry color turned from colorless to light yellow. Then, 5 g of TiO₂ powder was added to the CeO₂ slurry and stirred for 5 hours. The slurry was filtered, dried at 100 °C overnight and calcined at 500 °C for 4 hours. The catalyst was prepared in 1 wt%, 2 wt% and 5 wt% of ceria loading.

Catalyst characterization

The crystalline structure and phase purity of the catalysts were determined by X-ray diffraction (XRD) analysis using Bruker D8 Focus Advance powder diffractometer with a Cu K α radiation of wavelength 0.15406 nm, scanned from 10 to 80° with 0.025° step size. The surface area and pore parameters of the samples was determined by nitrogen adsorption-desorption analysis at 77 K using a Micrometrics ASAP 2010, using the Brunauer- Emmet- Teller and Barrett- Joyner- Halenda (BET/ BJH) method over the pressure range $P/P_0 = 0.02 - 1.0$. The diffuse reflectance spectra of the catalyst samples over a range of 200 – 800 nm were recorded by a UV-vis-NIR spectrophotometer. The photoluminescence spectra were measured by Edinburgh FS920 photoluminescence spectroscopy, using Xenon Lamp (450W) as the excitation source and 300 nm as the excitation wavelength over a range of 330 to 600 nm.

Photocatalytic activity

The photoreduction of CO₂ was performed according to the procedure reported in our previous study [8]. In brief, 0.3 g catalyst powder was dispersed in the CO₂ aqueous solution. The CO₂ aqueous solution was prepared by bubbling 0.4 L.min⁻¹ of CO₂ for 30 minutes into 300 ml of 0.1 M NaOH solution in the reactor consists of 500 ml Pyrex glass reactor equipped with a quartz trap with 220 mm length which is irradiated using artificial visible light produced by a 500 W Xenon lamp (Jiquang, Shanghai) with a wavelength range of 300 to 800 nm. Then, the reaction was started by switching on the light. 5 ml of the suspension were withdrawn from the reactor at every 1 hour interval of reaction for 6 hours of irradiation period, while the gas products were collected using gas bags. The liquid and gas products were analyzed using Agilent Gas Chromatography (GC) with a flame ionization detector (FID) and thermal conductivity detector (TCD), respectively. Analytical results indicated that the methanol is the main product in liquid sample and no products were detected in the gaseous samples.

Results and Discussion

XRD analysis

The crystal phase identification and crystallite size estimation were usually checked by XRD. Figure 1 shows the XRD patterns of the as-synthesized CeO₂-TiO₂ with different cerium loading. It can be seen that the peaks at 20

values of 25.17° , 37.60° , 47.76° , 54.01° and 62.60° which are indexed to the (101), (004), (200), (105) and (204) planes of the anatase phase of TiO_2 (JCPDS: 21-1272) appeared for all samples. It is noteworthy that no cerium oxide peaks could be observed in the XRD spectra for samples with 1 wt% ceria loading. This might be due to all the ceria ions were incorporated into the structures of titania or the size of the particles which are too small that cannot be detected by XRD. On the other hand, the small peak of cerium oxide was seen to appear in the spectra for 2 wt% loading and the peaks were clearly seen for 5 wt% loading. The crystallite sizes of anatase of samples were calculated using Scherrer's equation according to (101) peak. The values are 9.9 nm, 9.8 nm and 9.2 nm for CeO_2 - TiO_2 samples of 1 wt%, 2 wt% and 5 wt% ceria loading on TiO_2 , respectively. The crystalline size of the anatase phase formed decreased with the content of Ce oxide doped, which indicates that the Ce species inhibit the growth of anatase TiO_2 crystallite and it agrees well with the literature report [9].

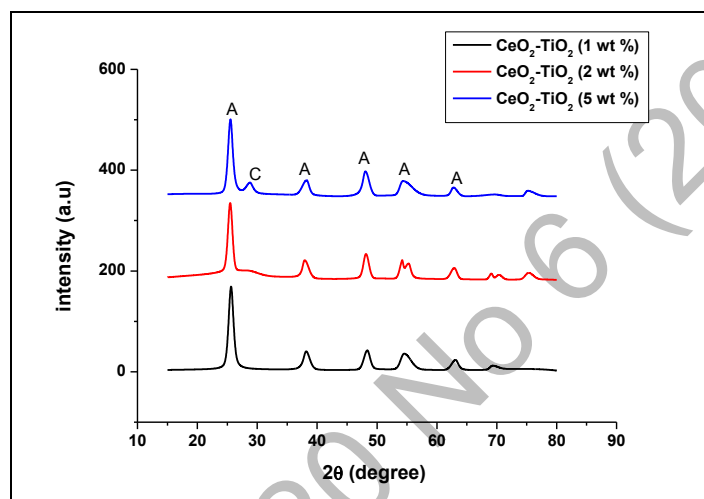


Figure 1. X-ray diffraction patterns of all photocatalysts (*A=anatase phase, C=Cerianite phase)

BET/BJH Analysis

Figure 2 shows the pore size distribution curves of all photocatalysts. The pore diameter was ranged from 8 – 15 nm indicating that the pores are mainly mesoporous in nature. The textural properties of the catalysts are summarized in Table 1, which shows that the surface area and pore volume changes was insignificantly with ceria loading of 1 wt% and 2 wt% but drastically decreases with 5 wt%. It was previously reported that the specific surface area and the pore volume of catalyst prepared by the impregnation method decrease with increasing metal loading [10].

Table 1. BET/BJH analysis of all photocatalyst

Sample	Surface area (m^2/g)	Pore volume (cm^3/g)	Mean pore size (nm)
CeO_2 - TiO_2 (1 wt%)	105.4	0.37	12
CeO_2 - TiO_2 (2 wt%)	104.9	0.40	15
CeO_2 - TiO_2 (5 wt%)	63.9	0.16	8

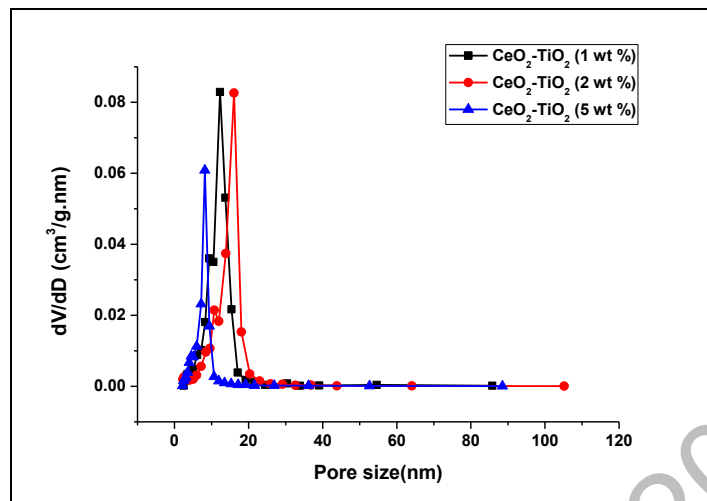


Figure 2. Pore size distribution of all photocatalysts

UV-Vis-NIR analysis

UV-Vis-NIR spectra of $\text{CeO}_2\text{-TiO}_2$ with different ceria loading are presented in Figure 3(a) to explore the influence of the ceria addition amount on the optical property of TiO_2 . From the Figure 3(a), a slight shift to the visible light region occurred as the amount of ceria was increased corresponds to a band gap of 2.4, 2.2 eV, and 2.15 eV for 1 wt%, 2 wt% and 5 wt% ceria loading on TiO_2 , respectively as shown in Figure 3(b). This indicates that the $\text{CeO}_2\text{-TiO}_2$ absorbs well in the visible light region due to presence of ceria. This is due to the charge transfer from impurity level to the conduction band. The impurity is caused by some of $\text{Ce}^{3+}/\text{Ce}^{4+}$ sites have been replaced by Ti^{4+} ions [11]. The absorption increases with the increasing of ceria content since the color of $\text{CeO}_2\text{-TiO}_2$ changes from pale yellow to yellow from the observation in the catalyst preparation.

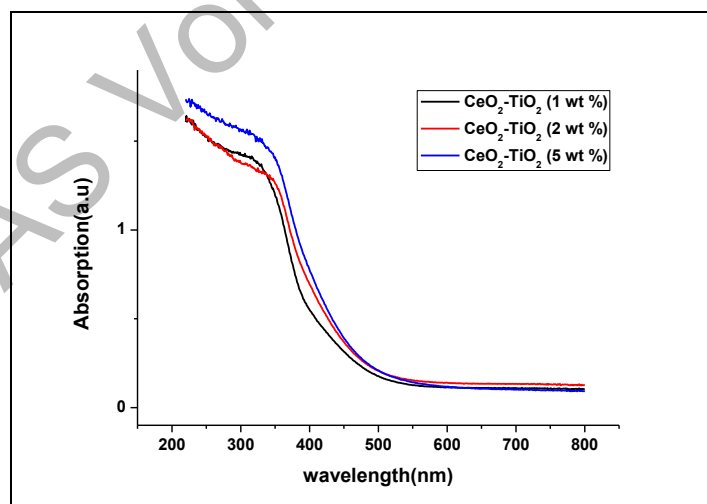


Figure 3(a). UV-vis NIR spectra of all photocatalysts

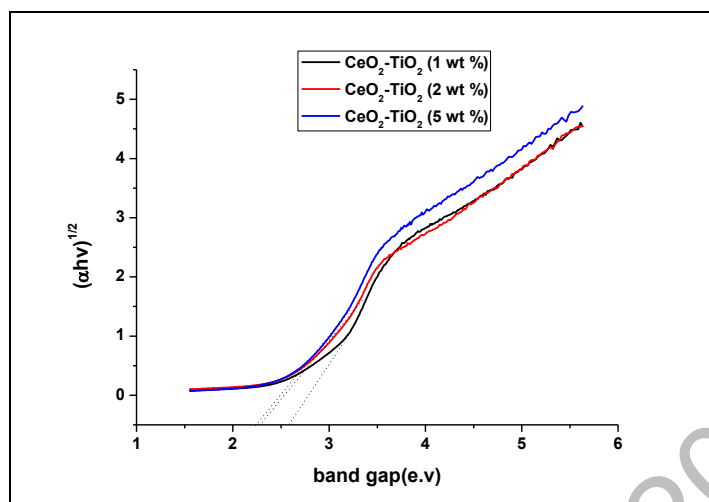


Figure 3(b). The optical absorption edges of all photocatalysts

Photoluminescence analysis

The photoluminescence spectra are useful to understand the surface process in which photogenerated electron-holes take part in photocatalysis. The existence of photoluminescence can be attributed to the recombination of excited electron-hole pairs. In Figure 4, there are two obvious PL peaks at 420 nm which attributed to the band-edge free exciton luminescence while the peak at 470 nm indicates the bound exciton luminescence [12]. The peaks positions for all samples are basically the same. However, the intensity of PL spectra is different. It shows that the intensity is decrease, indicating the lower rate of recombination of electron-hole pairs with increasing ceria loading. This is due to the possibility of Ce^{3+} ions existence in $\text{CeO}_2\text{-TiO}_2$ that could interact with holes and inhibit the recombination of photogenerated electron-holes [6].

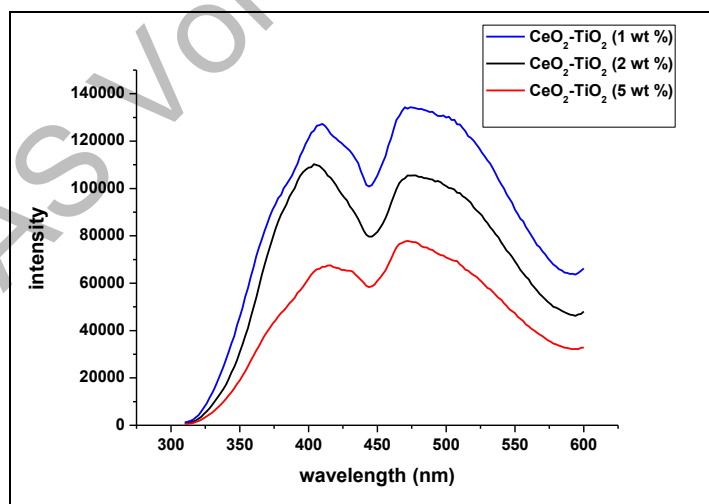


Figure 4. Photoluminescence Spectra of all photocatalysts

Photocatalytic activity

Methanol was determined in liquid phase while there were no products in gas phase. Other products such as formic acid and formaldehyde could also be formed [13], but they were undetectable. The methanol is possibly produced by the reduction of CO₂ and carbonate (CO₂ dissolve in water and form carbonate in water) as in Equation (1)-(3).



Figure 5 shows the yield of methanol formation by CO₂ photocatalytic reduction as functions of the irradiation time for CeO₂-TiO₂ with 1 wt%, 2 wt% and 5 wt% ceria loading. It can be seen that the yield of methanol increased with the irradiation time for all photocatalysts. The methanol yield increased with increasing ceria loading from 1 wt% to 2 wt%. This may be due to the extend response range into visible light region with increase the ceria loading, thus more photo energy could be absorbed by catalyst thus generate more electron-hole pairs. Moreover, the decreasing of electron hole recombination rate with increasing ceria loading also contributes in enhancing the methanol yield.

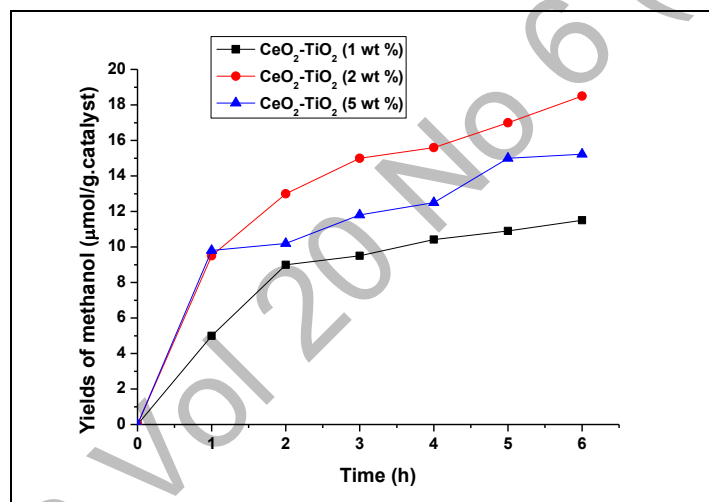


Figure 5. Yields of methanol as functions of irradiation time over all photocatalysts.

However, the methanol yield decreased after loading with 5 wt% ceria although the band gap and electron hole recombination rate decrease indicating that there is an optimum amount cerium loading for CeO₂-TiO₂. Moreover, the decreasing of specific surface area of 5 wt% CeO₂-TiO₂ catalyst also the factor that causes the decreasing in methanol yield since less reactant could be adsorbed onto the catalyst surface. The mechanism explanation of the decreasing of methanol yield could be described as follows: TiO₂ can adsorb carbonate species efficiently [14]. Then, CeO₂ which dispersed on the TiO₂ surface can absorb visible light and transfer the excited electrons to TiO₂ so that the carbonate species on the TiO₂ surface can be reduced to methanol. The coverage of TiO₂ surface by CeO₂ is optimum at 2 wt%, thus enough uncovered surface of TiO₂ for carbonate species adsorption. However, more CeO₂ has covered the surface of TiO₂ when the ceria loading increases to 5 wt%, resulted less surface of TiO₂ is in contact with carbonate species. Therefore, the photocatalytic activity decreases due to lowering of the available surface area even though the absorption of light by CeO₂ increases.

Conclusion

The series of CeO₂-TiO₂ nano photocatalysts with different ceria loading were synthesized and characterized. The characterization results show that crystallite size, the surface area, the band gap and the electron hole recombination rate decreased as the ceria loading increased. The best ceria loading percentage to obtain optimum methanol yield in CO₂ photocatalytic reduction under visible light irradiation is 2 wt%.

Acknowledgement

The authors would like to extend their deepest appreciate on to the Ministry of Education (MOE), Universiti Kebangsaan Malaysia and Universiti Malaysia Pahang for financial support of this research under RAGS (RDU131418) and FRGS (RDU120112).

References

1. Corma, A., and Garcia, H. (2013). Photocatalytic reduction of CO₂ for fuel production: Possibilities and challenges. *Journal of Catalysis*, 308: 168 – 175.
2. Zhang, Y., Zhang, H., Xu, Y., and Wang, Y. (2003). Europium doped nanocrystalline titanium dioxide: preparation, phase transformation and photocatalytic properties. *Journal of Materials Chemistry*, 13: 2261.
3. Parida, K. M. and Sahu, N. (2008). Visible light induced photocatalytic activity of rare earth titania nano-composites. *Journal of Molecular Catalysis A: Chemistry*: 287: 151 – 158.
4. Shi, H., Zhang, T., An, T., Li, B. and Wang, X. (2012). Enhancement of photocatalytic activity of nano-scale TiO₂ particles co-doped by rare earth elements and heteropolyacids. *Journal of Colloid Interface Science*, 380: 121 – 127.
5. Aman, N., Satapathy P. K., Mishra, T., Mahato, M., and Das, N. N. (2012). Synthesis and photocatalytic activity of mesoporous cerium doped TiO₂ as visible light sensitive photocatalyst. *Materials Research Bulletin*, 47: 179 – 183.
6. Matejova, L., Koci, K., Reli, M., Capek, L., Hospodkova, A., Peikertova, P., Matej, Z., Obalova, L., Wach, A., Kustrowski, P. and Kotarba, A. (2014). Preparation, characterization and photocatalytic properties of cerium doped TiO₂: On the effect of Ce loading on the photocatalytic reduction of carbon dioxide. *Applied Catalysis B: Environmental*, 152: 172 – 183.
7. Xiong, Z., Zhao, Y., Zhang, J. and Zheng, C. (2014). Efficient photocatalytic reduction of CO₂ into liquid products over cerium doped titania nanoparticles synthesized by a sol-gel auto-ignited method. *Fuel Processing Technology*, 135: 6 – 13.
8. Abdullah, H., Khan, M. R., Pudukudy, M., Yaakob, Z. and Ismail, N. M. (2015). CeO₂-TiO₂ as a visible light active catalyst for the photoreduction of CO₂ to methanol. *Journal of Rare Earths*, 33: 1155 – 1161.
9. Liu, Z., Guo, B., Hong, L. and Jiang, H. (2005). Preparation and characterization of cerium oxide doped TiO₂ nanoparticles. *Journal of Physics and Chemistry of Solids*, 66: 161 – 167.
10. Ioanna, G., Christina, F., Christos, K. and Soghomon, B. (2006). Molecular structure and catalytic activity of V₂O₅/TiO₂ catalysts for the SCR of NO by NH₃: In situ Raman spectra in the presence of O₂, NH₃, NO, H₂, H₂O, and SO₂. *Journal of Catalysis*. 239: 1 – 12.
11. Xu, A. W., Gao, Y. and Liu, H. Q. (2002). The preparation, characterization, and their photocatalytic activities of rare-earth-doped TiO₂ nanoparticles. *Journal of Catalysis*, 207: 151 – 157.
12. Wu, J., Liu, Q., Gao, P. and Zhu, Z. (2011). Influence of praseodymium and nitrogen co-doping on the photocatalytic activity of TiO₂. *Materials Research Bulletin*, 46: 1997 – 2003.
13. Tahir, M. and Amin, N. S. (2013). Advances in visible light responsive titanium oxide-based photocatalysts for CO₂ conversion to hydrocarbon fuels. *Energy Conversion Management*, 76: 194 – 214.
14. Inoue, T., Fujishima, A., Konishi, S. and Honda, K. (1979). Photoelectrocatalytic reduction of carbon dioxide in aqueous suspensions of semiconductor powders. *Nature*, 277: 637 – 638.