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## **CARBON DIOXIDE PHOTOCONVERSION. THE EFFECT OF TITANIUM DIOXIDE IMMOBILIZATION CONDITIONS AND PHOTOCATALYST TYPE**

Anna CYBULA, Marek KLEIN, Anna ZIELIŃSKA-JUREK, Marcin JANCZAREK,  
Adriana ZALESKA

Department of Chemical Technology, Gdansk University of Technology, 80-233 Gdansk, Poland, e-mail:  
adriana.zaleska@pg.gda.pl

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**Abstract.** Carbon dioxide and water vapor were effectively photoconverted to methane using either pure or modified-TiO<sub>2</sub> and UV-Vis irradiation. The process of photoconversion in the gas phase was carried out in a tubular reactor equipped with a perforated TiO<sub>2</sub>-coated support. The effect of selected parameters of TiO<sub>2</sub> immobilization procedure, such as the time and temperature of drying step and the photocatalyst amount, on photocatalytic efficiency was investigated. The effect of TiO<sub>2</sub> loading with Ag/Au nanoparticles on CO<sub>2</sub> photoconversion efficiency was also studied. CH<sub>4</sub> was found to be the major photoreduction product. The highest methane production was observed after irradiation of CO<sub>2</sub>+H<sub>2</sub>O mixture over Au-TiO<sub>2</sub> photocatalyst. After one hour of UV-Vis irradiation 503 ppm of methane was formed.

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*keywords:* TiO<sub>2</sub>, photoreduction, CO<sub>2</sub> photoconversion, titanium dioxide

### **1. Introduction**

The reduction of carbon dioxide has recently been regarded as an important research area in chemical technology, not only for solving the problems resulting from environmental pollution, but also for finding ways to maintain carbon resources, which are being depleted by burning fossil fuels. Photocatalytic CO<sub>2</sub> conversion offers a promising way for clean, low cost and environmentally friendly production of fuels by solar energy. Photocatalytic reduction of CO<sub>2</sub> could be carried out in CO<sub>2</sub>-saturated aqueous solution containing suspended TiO<sub>2</sub> (Li et al., 2010; Dey et al., 2004) liquid CO<sub>2</sub> (Kaneco et al., 1997), high pressure CO<sub>2</sub> system with TiO<sub>2</sub> powders suspended in isopropyl alcohol (Kaneco et al., 1998) and in the gas phase - CO<sub>2</sub> with H<sub>2</sub>O vapor irradiated over TiO<sub>2</sub> (Tan et al., 2008; Xia et al., 2007; Nguyen et al., 2008; Tan et al., 2006). The UV-irradiated TiO<sub>2</sub> surface can generate electrons to reduce the CO<sub>2</sub> molecules present in aqueous and gaseous streams at ambient temperature and pressure conditions. Photogenerated electron-hole pairs migrate to the surface and in the presence of H<sub>2</sub>O molecules lead to the reduction of CO<sub>2</sub> in CH<sub>4</sub> and compounds

such as  $C_2H_2$ ,  $CH_3OH$ ,  $C_2H_5OH$  at the solid-gas interface (Usubharatana et al., 2006; Varghese et al., 2009).

Photocatalytic reactions could be carried out in the presence of pure and modified  $TiO_2$  (Fujishima et al., 2006; Chatterjee et al. 2005; Zaleska, 2008). Zhang et al. (2011) studied the effect of calcination temperature (375, 450, 550°C) and dopant concentration of iodine ( $I_2$ ) (5, 10, 15 wt.%) on the efficiency of photoconversion. A fixed amount of powder catalyst (200 mg) was dispersed on a glass-fiber filter and placed at the bottom of the cylindrical photoreactor. The photocatalytic activities of the I- $TiO_2$  powders were investigated by photocatalytic reduction of  $CO_2$  with  $H_2O$  under visible light ( $>400$  nm) and also under UV-visible illumination. CO was found to be the major photoreduction product. A high efficiency of  $CO_2$  reduction was observed for 10 wt.% I- $TiO_2$  photocatalysts (the highest CO yield equivalent to  $2.4 \mu mol \cdot g^{-1} \cdot h^{-1}$ ) under visible light. The highest activity in the presence of UV-Vis light showed 5 wt.% I- $TiO_2$ , calcined at 375°C (600 ppm after 90 minutes), and the increase in calcination temperature decreased the efficiency of the process of photoreduction. Too high iodine doping level may result in recombination centers and thus lower the photocatalytic activity (Zhang et al., 2011). Photocatalytic reduction of  $CO_2$  with  $H_2O$  in the gaseous phase was studied by Chen et al. (2009) using thin films P-25 (prepared by reactive magnetron sputtering) under UV irradiation (100 W). The main product of the reaction of methane was also detected in the form of trace amounts of other hydrocarbons such as methanol. The highest concentration of the products was observed for pure anatase, and the lowest for pure rutile. Chen et al. (2009) have shown that there is synergy between  $CO_2$  concentration and the temperature of the process. The highest methane yields were produced under the optimal combination of high  $CO_2$  concentration (approximate 45% volume) and elevated temperature (approximately 80°C). Under these conditions, after 4 h of irradiation 200 nmol of methane were received. It was also noted that conditions of  $TiO_2$  film synthesis at the surface of boro-silicate glass (e.g. deposition angle during current magnetron sputtering) affected the effectiveness of the process (Chen et al., 2009). The results obtained by Tan et al. (2006) confirmed that  $CO_2$  could be reformed in the presence of water vapor and  $TiO_2$ -P 25 pellets into  $CH_4$  under continuous UV irradiation at ambient conditions. Total  $CH_4$  yield was 200 ppm and lower than 100 ppm after 48 h of irradiation with UVC (253.7 nm) and UVA (365 nm), respectively (Tan et al., 2006). Li et al. (2010) studied a photoconversion process using Cu/ $TiO_2$ - $SiO_2$ . Glass wool was placed in the reactor as the support for the glass fiber filter loaded with a thick film of powder catalysts. The glass wool support was also moisturized with 3.0 g deionized water to maintain saturated water vapor in the reactor. Irradiation source was a Xenon lamp (irradiation intensity  $2.4 \text{ mW/cm}^2$ ). The measured production rate of the products increased with the irradiation time and reached a peak value at around 4 h. The methane production rate was  $13.2 \mu mol/(g \cdot h)$ . It was found that a photocatalyst after regeneration can be used again for photoconversion process but its activity is already significantly lower (Li et al., 2010).



Photocatalytic reduction of CO<sub>2</sub> with H<sub>2</sub>O in the gaseous phase was studied by Nguyen et al. (2008) using Cu-Fe/TiO<sub>2</sub> catalyst coated on optical fibers under UVA and UVC irradiation. Methane and ethylene were observed as the main products to evolve from this photoreactor. The presence of Fe as a co-dopant in Cu/TiO<sub>2</sub> photocatalyst was found to synergistically reduce CO<sub>2</sub> with H<sub>2</sub>O to ethylene at the quantum yield and total energy efficiency of 0.024% and 0.016%, respectively. This phenomenon could be explained by an efficient charge transfer mechanism between TiO<sub>2</sub> as a support and Cu as well as Fe as co-dopants. Methane was formed more favorably than ethylene on Cu/TiO<sub>2</sub>. Meanwhile, Fe as a co-dopant on Cu/TiO<sub>2</sub> photocatalyst was found to depress methane formation. The highest ethylene production rate was observed for TiO<sub>2</sub> doped with 0.25 wt.% of Cu and 0.25 wt.% of Fe and it was 0.53 μmol(g·h)<sup>-1</sup> (Nguyen et al., 2008). Thus, the efficiency of currently available TiO<sub>2</sub>-based photocatalysts is still not sufficient for practical use. Therefore, the development of new ones and optimization of existing photocatalysts exhibiting activity upon visible light with surface characteristics of improved performance and of high chemical and physical stability are crucial for broader scale utilization of photocatalytic systems in commercial applications. To avoid the above listed problems and to improve solar photocatalytic CO<sub>2</sub>-to-light hydrocarbons conversion two main approaches are proposed: (1) TiO<sub>2</sub> modification to increase the spectral sensitivity of TiO<sub>2</sub>-based photocatalysts to visible light and to compete with electron-hole recombination (by metal and non-metal co-doping), and (2) enhancement of interface surface area by photoreactor design.

Apart from photocatalyst properties, the activity is also affected by the method and parameters of a photocatalyst immobilization procedure. In our investigation, TiO<sub>2</sub>-based photocatalyst was deposited on the surface of a flat perforated steel tray, easily removable from the reactor. The photoreactor was equipped with a parabolic, aluminum mirror to concentrate light. Thus, the aim of this study was to investigate the effect of selected parameters of immobilization step, such as the time and temperature of drying and the photocatalyst amount, on photocatalytic efficiency.

## 2. Experimental

### 2.1. Materials

TiO<sub>2</sub> P-25 having mixed anatase and rutile structure 4:1 (particle size 40 nm, S<sub>BET</sub> = 50m<sup>2</sup>/g), was obtained from Evonik, Germany. Titanium isopropoxide (pure p.a.; TIP) was purchased from Aldrich and used as titanium source for the preparation of TiO<sub>2</sub> nanoparticles. Hydrogen tetrachloroaurate(III) tetrahydrate (99.9%) and silver nitrate were provided by POCh and used as starting materials for the preparation of gold/silver nanoparticles. Sodium borohydride and ascorbic acid (99%) were purchased from Aldrich and used as reducing agents. Cyclohexane was used as continuous oil phase, sodium bis-(2-ethylhexyl) sulfosuccinate (AOT) purchased from



Aldrich as surfactants, 2-propanol as a cosurfactant and aqueous solution as the dispersed phase.

## 2.2. Photocatalytic conversion of carbon dioxide

Compressed CO<sub>2</sub> from a cylinder was led to the photoreactor via a gas flow meter, a safety tank equipped with a manometer and an absorber with demineralized water. The reactor chamber was purged with CO<sub>2</sub> gas for 30 min with 80 dm<sup>3</sup>·h<sup>-1</sup> gas flow rate. The reaction system was maintained at 4903 Pa positive pressure. After 30 min purging, the reaction chamber was closed and irradiated using 1000 W Xenon lamp (Oriol), which emits both UV and visible light. The optical path included a 10 cm thick water filter to cut off IR. A schematic illustration of the batch reactor system for the CO<sub>2</sub> photoreduction test is shown in Fig. 1.

The photocatalytic reduction CO<sub>2</sub> was tested in a bench-scale photocatalytic reactor (V=314 cm<sup>3</sup>) with a perforated TiO<sub>2</sub>-cover tray. The reactor chamber was made of a cylindrical quartz tube (i.d. 50 mm, length 160 mm) and equipped with inlet and outlet valves, as shown in Fig. 2.

Perforated removable trays were placed in the quartz tube, which served as a reaction chamber and was positioned over aluminum parabolic mirror with 188.4 cm<sup>2</sup> collecting area. Thus, the in-going gas phase passed through the perforated barrier and was irradiated from the top by incident radiation, and from the bottom by reflected light.

The TiO<sub>2</sub> suspension was prepared by addition of an appropriate amount of water to 0.5 g of the photocatalyst. Both sides of the internal element of the photoreactor were coated with TiO<sub>2</sub>-based suspension by painting procedure. The obtained TiO<sub>2</sub>-coated support was dried from 5 to 35 hours at different temperatures (80, 120 or 160°C). A steel or plastic support was used to check the impact of such a support on the effectiveness of the process.

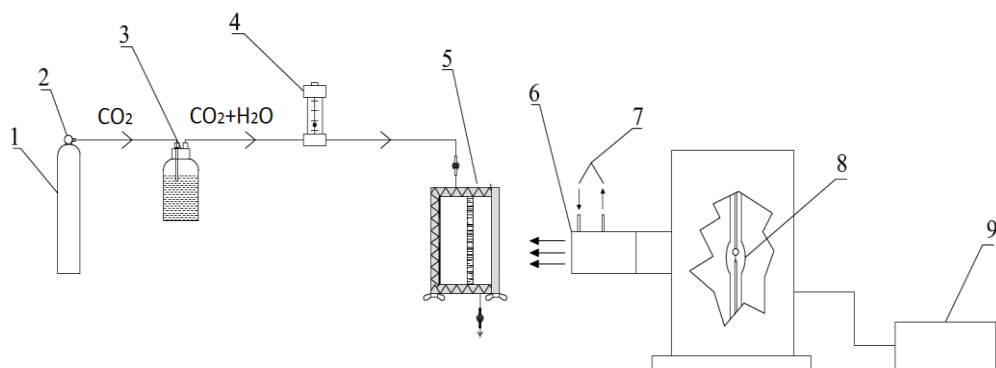


Fig. 1. Schematic illustration of the batch reactor system for the CO<sub>2</sub> photoreduction test:

- 1) cylinder of CO<sub>2</sub>; 2) gas cylinder valve; 3) water bubbler; 4) gas flow meter; 5) photoreactor equipped with a quartz window; 6) water filter; 7) inlet and outlet cooling water; 8) xenon lamp; 9) feeder



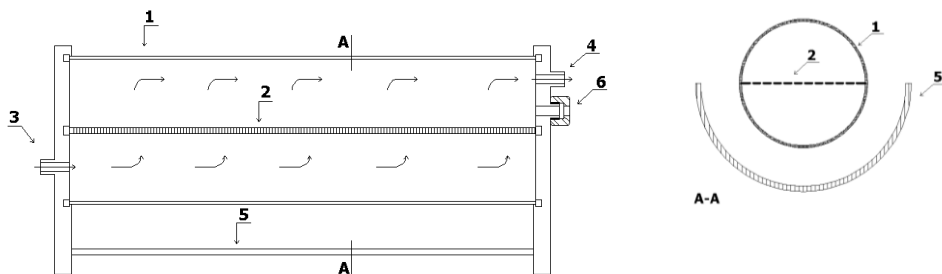


Fig. 2. Schematic diagram of the photoreactor: 1) quartz tube; 2) perforated  $\text{TiO}_2$ -covered tray; 3) gas inlet; 4) gas outlet; 5) parabolic mirror; 6) sampling port

### 2.3. Gas chromatographic analysis

A Perkin-Elmer model Clarus 500 gas chromatograph was used together with a porapak-Q 100-120 mesh column (2 m x 2.1 mm i.d.) equipped with a flame ionization detector. In each case a  $0.200 \text{ cm}^3$  of gaseous sample were injected in a splitless mode. The operating conditions were as follows: the initial GC column temperature  $105^\circ\text{C}$ . The injector temperature was  $150^\circ\text{C}$  and the detector temperature was  $220^\circ\text{C}$ . The carrier gas used was nitrogen. The flow was kept at a constant  $17 \text{ cm}^3/\text{min}$ . The gas phase from the reaction chamber was sampled by the gas-tight membrane. The gas samples were analyzed in a duplicate at given periods of time. The retention time for methane, ethene and ethane was respectively 0.74, 1.31 and 1.58 minutes.

### 3. Results and discussion

For studying the photocatalytic conversion of  $\text{CO}_2$  into light hydrocarbon with the  $\text{TiO}_2$ , it was necessary to investigate the influence of the selected parameters affecting the step of photocatalyst immobilization (e.g. the drying temperature and time, the type of support and  $\text{TiO}_2$  amount). The efficiency of  $\text{CO}_2$  photoconversion was estimated as methane concentration after 1 h irradiation of  $\text{CO}_2 + \text{H}_2\text{O}$  mixture over  $\text{TiO}_2$  supported on the surface of a flat perforated steel tray. The  $\text{TiO}_2$  P-25/UV-Vis system was chosen as a reference generating methane as the main product of  $\text{CO}_2$  photoconversion. Commercially available  $\text{TiO}_2$  P25 was chosen for this investigation as a standard used in heterogeneous photocatalysis. The effect of these parameters was achieved in separate experiments and is presented in Tables 1-3. Table 1 shows the efficiency of methane generation in the presence of P-25 dried in different temperatures after a coating process. It was found that the increase of drying temperature from  $80$  to  $120^\circ\text{C}$  resulted in the increase of methane concentration from 36 to 66 ppm, respectively. However, as the drying temperature increased up to  $160^\circ\text{C}$ ,  $\text{CH}_4$  concentration decreased, reaching the lowest value equal to 4.7 ppm (see Table 1).



The effect of the drying time of TiO<sub>2</sub> suspension deposited on the surface of a flat perforated steel tray on CO<sub>2</sub> photoconversion efficiency is presented in Table 2. The obtained data suggested, that the increase in drying time from 5 to 20 h resulted in the increase of methane concentration from 24 to 90 ppm. However, time elongation to 35 h caused only slight increase in methane concentration. After 60 min. irradiation of CO<sub>2</sub>+H<sub>2</sub>O mixture over TiO<sub>2</sub> dried in 35 h, methane concentration was 99 ppm. Thus, a 20-hour drying time was chosen for further investigations to save energy during the preparation procedure.

Table 1. The effect of drying temperature TiO<sub>2</sub> on CO<sub>2</sub> photoconversion efficiency (drying time: 20 h, photocatalyst: P-25, average photocatalyst amount: 0.37 g)

Drying temperature [°C]	Methane concentration after 1h exposure for UV-Vis irradiation [ppm]
80	36
120	66
160	4.7

Table 2. The effect of drying time TiO<sub>2</sub> on CO<sub>2</sub> photoconversion efficiency (drying temperature: 120°C, photocatalyst: P-25, average photocatalyst amount: 0.37 g)

Drying time [h]	Methane concentration after 1h exposure for UV-Vis irradiation [ppm]
5	24
20	90
35	99

The influence of TiO<sub>2</sub> amount applied to the surface during coating procedure on CO<sub>2</sub> photoconversion was also investigated and is presented in Table 3. The enhancement in the photocatalytic efficiency for higher amount of P-25 deposited on the porous steel tray was observed. It is expected that introducing a higher amount of TiO<sub>2</sub> can extend the surface area of the available photocatalyst and raise efficiency of CO<sub>2</sub> photoconversion. Methane concentration will amount to 39, 90 and 135 ppm for TiO<sub>2</sub> mass equal to 0.2541, 0.3642 and 0.4825 g, respectively. Further increase in TiO<sub>2</sub> amount resulted in mechanical instability of the obtained TiO<sub>2</sub> thin film. It was noticed that for a higher amount of the photocatalyst, TiO<sub>2</sub> layer suffered cracking and TiO<sub>2</sub> partly fell away during the photoconversion process.

Steel and plastic trays were tested as TiO<sub>2</sub> support materials. Both trays had the same size and perforation pattern. The same coating procedure resulted in a much lower amount deposited on the surface of the plastic tray due to weaker adhesive properties. The amount of the photocatalyst deposited on the surface of the steel and plastic plates was equal to 0.37 and 0.08 g of TiO<sub>2</sub>, respectively. Thus, the application



of a plastic support caused the decrease in methane concentration to 34 ppm after 1 h of irradiation (see Table 4).

Table 3. The effect of TiO<sub>2</sub> amount on CO<sub>2</sub> photoconversion efficiency (drying temperature 120°C, drying time 20 h, photocatalyst P-25)

Mass of the photocatalyst deposited on the surface of a perforated steel tray [g]	Methane concentration after 1h exposure for UV-Vis irradiation [ppm]
0.2541	39
0.3642	90
0.4825	135

Table 4. The effect of the type of support on CO<sub>2</sub> photoconversion efficiency (drying temperature 120 °C, drying time 20 h, photocatalyst P-25)

Type of support	Methane concentration after 1h exposure for UV-Vis irradiation [ppm]
steel	90
plastic	34

After selecting conditions of the photocatalyst immobilization step, TiO<sub>2</sub> modified with noble metals was used for CO<sub>2</sub> photoconversion. TiO<sub>2</sub> modified with monometallic nanoparticles (Ag or Au) and TiO<sub>2</sub> modified with bimetallic nanoparticles (Ag/Au) were prepared using a microemulsion system (water/AOT/cyclohexane) according to the procedure described by Zielinska-Jurek et al. (2011). The efficiency of methane generation, after a 1 h exposure of CO<sub>2</sub>+H<sub>2</sub>O mixture to UV-Vis irradiation over noble metal modified TiO<sub>2</sub>, are presented in Table 5.

Table 5. The efficiency of CO<sub>2</sub> photoconversion in the presence of TiO<sub>2</sub> modified with noble metal nanoparticles (immobilization conditions: drying temperature 120°C, drying time 20 h, a steel perforated tray)

Type of dopant	Metal precursor used during preparation	Amount of metal precursors used during preparation [mol. %]		TiO <sub>2</sub> source <sup>1</sup>	Methane concentration after 1h exposure to UV-Vis irradiation [ppm]	Mass of the photocatalyst [g]
		Au	Ag			
Ag	AgNO <sub>3</sub>	-	6.5	TIP	493	0.4002
Au	HAuCl <sub>4</sub>	1.5	-	TIP	503	0.4165
Ag/Au	AgNO <sub>3</sub> and HAuCl <sub>4</sub>	0.5	2.5	TIP	164	0.4636

<sup>1</sup>TIP – TiO<sub>2</sub> obtained by hydrolysis of titanium(IV) isopropoxide in the microemulsion system



Higher efficiency of CO<sub>2</sub> photoconversion was observed for TiO<sub>2</sub> modified with gold nanoparticles. 503 ppm of methane were obtained in the presence of the sample 1.5% Au/TiO<sub>2</sub> after one hour of exposure to UV-Vis irradiation. Photoconversion efficiency for the modified photocatalyst bimetal nanoparticles Ag-Au/TiO<sub>2</sub> after a 1 h exposure to UV-Vis irradiation was 164 ppm. The obtained results suggested that the deposition of gold or silver nanoparticles on the surface of TiO<sub>2</sub> resulted in the enhancement of CO<sub>2</sub> photoconversion efficiency. Noble metals deposited or doped with TiO<sub>2</sub> have high Schottky barriers among the metals and thus act as electron traps, facilitating electron-hole separation and promoting the interfacial electron transfer process (Li et al., 2010; Dey et al., 2004). Additionally, noble-metal nanoparticles have often been used to extend the absorption properties from the ultraviolet to visible region and to enhance the photocatalytic activity of titanium(IV) oxide (Kaneco et al., 1997; Tan et al., 2008; Xia et al., 2007; Nguyen et al., 2008). Silver and gold nanoparticles possess the ability to absorb visible light, due to localized surface plasmon resonance (LSPR).

#### 4. Conclusions

Selected parameters of TiO<sub>2</sub> immobilization on the surface of inert support in the CO<sub>2</sub> photoconversion were investigated. It was found that drying temperature and time, the type of support, as well as the amount of used TiO<sub>2</sub> significantly affected the efficiency of the CO<sub>2</sub> photoreduction process. The highest methane concentration was observed since TiO<sub>2</sub> was deposited on the surface of a perforated steel tray and dried at 120°C for 20 h. It has been found that with the increase of the mass of TiO<sub>2</sub> the efficiency of the process increases. Up to five-fold higher methane concentration was observed after 1 h irradiation in the presence of TiO<sub>2</sub> modified with noble metal nanoparticles than that of pure TiO<sub>2</sub>.

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#### References

- CHATTERJEE, D., DASGUPTA, S., 2005, Visible light induced photocatalytic degradation of organic pollutants, *J. Photochem. Photobiol. C* 6, 186–205.
- CHEN, L., GRAHAM, M., LI G., GENTER, D., DIMITRIJEVIC, N., GRAY, K., 2009, Photoreduction of CO<sub>2</sub> by TiO<sub>2</sub> nanocomposites synthesized through reactive direct current magnetron sputter deposition, *Thin Sol. Films* 517, 5641–5645.
- DEY, G.R., BELAPURKAR, A.D., KISHORE, K., 2004, Photo-catalytic reduction of carbon dioxide to methane using TiO<sub>2</sub> as suspension in water, *J. Photochem. Photobiol. A*, 163, 503–508.
- FUJISHIMA, A., ZHANG, X., 2006, Titanium dioxide photocatalysis: present situation and future approaches, *C.R. Chimie*, 9, 750–760.





- KANECO, S., KURIMOTO, H., OHTA, K., MIZUNO, T., SAJI, 1997, A., Photocatalytic reduction of CO<sub>2</sub> using TiO<sub>2</sub> powders in liquid CO<sub>2</sub> medium, *J. Photochem. Photobiolog. A* 109, 59–62.
- KANECO, S., SHIMIZU, Y., OHTA, K., MIZUNO, T., 1998, Photocatalytic reduction of high pressure carbon dioxide using TiO<sub>2</sub> powders with a positive hole scavenger, *J. Photochem. Photobiol. A*, 115, 223–226.
- LI, Y., WANG, W., ZHAN, Z., WOO, M., PRATIM, B., 2010, Photocatalytic reduction of CO<sub>2</sub> with H<sub>2</sub>O on mesoporous silica supported Cu/TiO<sub>2</sub> catalysts, *Appl. Catal. B*, 100, 386–392.
- NGUYEN, T.V., WU, J.C.S., CHIOU, C.H., 2008, Photoreduction of CO<sub>2</sub> over Ruthenium dye-sensitized TiO<sub>2</sub>-based catalysts under concentrated natural sunlight, *Catal. Commun.* 9, 2073–2076.
- NGUYEN, T.V., WU, J.C.S., 2008, Photoreduction of CO<sub>2</sub> in an optical-fiber photoreactor: Effects of metals addition and catalyst carrier, *Appl. Catal. A: Gen.* 335, 112–120.
- TAN, S.S., ZOU, L., HU, E., 2008, Kinetic modelling for photosynthesis of hydrogen and methane through catalytic reduction of carbon dioxide with water vapour, *Cat. Today* 138, 125–129.
- TAN, S.S., ZOU, L., HU, E., 2006, Photocatalytic reduction of carbon dioxide into gaseous hydrocarbon using TiO<sub>2</sub> pellets, *Cat. Today*, 115, 269–273.
- USUBHARATANA, P., MCMARTIN, D., VEAWAB, A., TONTIWACHWUTHIKUL, P., 2006, Photocatalytic Process for CO<sub>2</sub> Emission Reduction from Industrial Flue Gas Streams, *Ind. Eng. Chem. Res.* 45, 2558–2568.
- VARGHESE, O.K., PAULOSE, M. LATEMPA, T.J. GRIMES C.A., 2009, High-Rate Solar Photocatalytic Conversion of CO<sub>2</sub> and Water Vapor to Hydrocarbon Fuels, *Nano Letters* 9, 731–737.
- XIA, X.H., JIA, Z.J., YU, Y., LIANG, Y., WANG, Z., MA, L.L., 2007, Preparation of multi-walled carbon nanotube supported TiO<sub>2</sub> and its photocatalytic activity in the reduction of CO<sub>2</sub> with H<sub>2</sub>O, *Carbon* 45, 717–721.
- ZALESKA, A., 2008, Doped-TiO<sub>2</sub>: A Review, *Recent Pat. Eng.* 2, 157–164.
- ZHANG, Q., LI Y., ACKERMAN E., GAJDARDZISKA-JOSIFOVSKA M., LI H., 2011, Visible light responsive iodine-doped TiO<sub>2</sub> for photocatalytic reduction of CO<sub>2</sub> fuels, *Appl. Catal. A: Gen.* 400, 195–202.
- ZIELIŃSKA-JUREK A., KOWALSKA E., SOBCZAK J., LISOWSKI W., OHTANI B., ZALESKA, A., 2011, Preparation and characterization of monometallic (Au) and bimetallic (Ag/Au) modified-titania photocatalysts activated by visible light, *Appl. Catal. B* 101, 504–514.



