Reactive Magnetron Sputter Deposition of Copper on TiO_2 Support for Photoreduction of CO_2 to CH_4

Reactive Magnetron Sputter Deposition of Copper on TiO_2 Support for Photoreduction of CO_2 to CH_4

Nantiya Jantarasorn[1], Okorn Mekasuwandumrong[2], Peter Kelly[3] and Piyasan Praserthdam[1]

[1]Center of Excellence on Catalysis and Catalytic Reaction, Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University, Bangkok, 10330, Thailand
[2]Department of Chemical Engineering, Faculty of Engineering and Industrial Technology, Silpakorn University, Nakorn Pathom 73000, Thailand
[3]Surface Engineering Group, School of Engineering, Manchester Metropolitan University, Manchester, M1 5GD, United Kingdom

Corresponding author: piyasan.p@chula.ac.th

Abstract. In this work, nanocrystalline Cu/TiO2 catalysts have been synthesized by using pulsed direct current (DC) reactive magnetron sputtering of Cu targets in an Ar atmosphere onto P25-TiO_2 support. The oscillating bowl was used to make the uniform coating on the substrate. The Cu doping content was varied by adjusting the coating time. The thus-obtained catalysts were characterized by using the X-ray diffraction (XRD), UV-Vis spectroscopy, scanning electron microscopy (SEM), and energy dispersive X-ray spectroscopy (EDX). The photocatalytic activities of all catalysts were studied via the photocatalytic reduction of CO_2 and H_2O to CH_4 under UV irradiation, and compared with the pure TiO_2 support and conventional-impregnation-made Cu/TiO_2. The results showed that the photocatalytic performance of sputtering-made Cu/TiO_2 catalyst was much better than the pure TiO_2 support. Therefore, reactive magnetron sputtering was a promising technique for deposition of metal onto the support and use as the catalytic process.

1. Introduction

Presently, the environmental problem from the emission of pollutant gases became much more serious. CO_2 (Carbon dioxide) is the main product from human activates such as combustion of industrial fuels and vehicle engine. The solution to the problems is reduction of releasing gas into the atmosphere or takes advantage from it. CO_2 can used for generate the important products by direct and indirect process. In direct process, it is widely used in cooler system, extinguisher, dry ice and so on. In indirect process, it is used for generate chemical commercial such as urea, polycarbonate, methanol, acetic acid, formaldehyde and so on [1-2].

Photocatalytic reduction of CO_2 is one of the interesting processes. This technology will convert photocatalytic CO_2 reduction with water as a reducing agent into hydrocarbon fuels and useful chemical compounds such as carbon Monoxide (CO), methane (CH_4), methanol (CH_3OH), formic Acid (HCOOH) and formaldehyde (HCHO) by irradiation with UV light at room temperature and atmospheric pressure [3-4]. Photo-chemical technique is more attractive because of its relatively low cost, environmental friendly, generate none pollution, no requirement of thermal energy. Moreover, it

is easy for control process because photochemical reaction need only light to activate substrate to generate products.

Many photocatalytic CO_2 reduction catalysts have been attentively studied such as TiO_2 , ZnO, ZrO_2 , CeO_2 , WO_3, SnO_2, GaP, SiC, $SrTiO_3$ [5]. Among various semiconductor materials, the most extensively used photocatalysts is TiO_2, because its high stability, high photosensitivity, non-toxic nature, wide availability and low cost [6]. However, TiO_2 has wider bandgap, high electron-hole recombination rate and weak CO_2 adsorption. Therefore, it has very low photocatalytic activity for CO_2 reduction in the water. So, it is interesting to modify the crystal structure, particle size, electronic structure, lifetime of charge carrier, electron-hole (e-h) recombination probability of TiO_2 for increase photocatalytic activity for CO_2 conversion [8]. There are several pathway for improve its quality such as doping with metals or non-metals. Some metal such as platinum (Pt), silver (Ag), copper (Cu), nickel (Ni) or metal oxide such as copper oxide (Cu_XO), nickel oxide (NiO) were deposited on semiconductor. For increased lifetime of the photogenerated electrons and hole via effective charge carrier separation and retardation of electron-hole recombination rate and increasing quantum yield [7-8]. In several studies, Cu nanoparticles deposited on the TiO_2 surface can reduced the band gap energy of TiO_2 and shifted the band edge from the UV region to the visible region (strongly absorb visible light) and facilitate the separation of photoexcited e^- h^+ pairs that showed effectiveness in CO_2 photoreduction [9-10].

Generally, deposition of metal on TiO_2 surface can be mostly done by conventional impregnation method, which required the solution of metal precursor, heat treatment and generate waste. Reactive magnetron sputtering offers the new direct metal deposition method on catalyst powder, which can be done in one-step and no waste generate in the process [11].

In this research, Cu/TiO_2 catalysts were prepared by using reactive magnetron sputtering to deposit the Cu on TiO_2 surface. The obtained catalysts were characterized by using the X-ray diffraction (XRD), UV-Vis spectroscopy, scanning electron microscopy (SEM), and energy dispersive X-ray spectroscopy (EDX). The photocatalytic activities of all catalysts were studied via the photocatalytic reduction of CO_2 and H_2O to CH_4 under UV irradiation and compare it with the catalyst prepared by conventional impregnation method.

2. Experiment

2.1. Materials

Commercial Degussa P25 nanocatalyst from AERO-XIDE1 was sourced as a TiO_2 powder. Copper(II) nitrate trihydrate ($Cu(NO_3)_2$ $3H_2O$,>98% purity from Aldrich), and Cu target (Copper Metal, 99.5% purity) were used as a chemicals in the surface modification process.Carbon dioxide (CO_2 ,≥99.999 %) was used as an oxidizing agent in photocatalytic reaction.

2.2. Surface modification of TiO_2

There are two preparation methods for Cu/TiO_2 catalysts including incipient wetness impregnation method and reactive magnetron sputtering method. In incipient wetness impregnation methods, 2 g of TiO_2 was doped with an aqueous solution of copper (II) nitrate trihydrate ($Cu(NO_3)_2$ $3H_2O$) via different the weight ratios of dopant/ TiO_2 at 1 (Im1) and 3 (Im2) wt%, respectively. The solution of the metal precursor was slowly dropped onto the TiO_2 support to obtain the desired ratio and dried in oven 110 ℃ overnight before calcined in a box furnace at 400 ℃, heating rate 10 ℃/min for 2 h with air flow.

In reactive magnetron sputtering method, 2 g of TiO_2 was loaded in sputtering chamber. Synthesis condition including power 200W, voltage 350V and frequency 200kHz were used. Reactive sputtering of Cu target was done in argon atmosphere onto P25-TiO_2 support. The oscillating bowl was used to make the uniform coating on the substrate. The sputtering time was varied at 2.5 (Sp1) and 7.5 (SP2) min respectively.

2.3. Photocatalytic reaction

The photocatalytic reduction of CO_2 with water were carried out in a photoreactor system. UV-light bulbs (Philips' Germi-cidal Ozone UV Quartz Glass UVC Bulb : 16 watt, 6 bulbs) were install around a cylindrical quartz reactor . A certain amount of each catalyst (0.5 g) dispersed into a stirred slurry reactor (SSR), which contained 150 mL of deionized water. After the reaction system was already, compressed CO_2 (≥99.999 %) was presented into the system from inlet tube in the cylindrical quartz reactor. By using a mass flow controller at a flow rate of 100 ml min^{-1} for 30 min. to purge air and saturate the solution. The reactor is closed during the reaction, and a magnetic stirrer agitated the catalyst-suspended solution throughout the experiment. The photocatalytic reaction was started by turned on the UV light, and irradiation was continued for 6 h.

The resultant gas samples were analyzed online by using, a GC-14B (Shimadzu) gas chromatograph equipped with a flame ionization detector (FID) and a Porapak-Q column for hydrocarbon analysis.

3. Results and discussion

3.1. Physiochemical properties of Cu/TiO_2 catalysts

Table 1. The physical properties of thus-obtained catalysts.

Sample	Wt% of Cu		Crystallite size (nm)			%Rutile
	ICP	EDX	Anatase	Rutile	CuO	
P25	-	-	20	23	-	21
Im1	0.68	3.42	18	22	-	20
Im2	2.47	5.67	17	21	-	18
Sp1	0.73	4.89	19	25	n.d.	22
Sp2	2.21	6.15	19	23	45.00	25

In this paper, nanocrystalline Cu/TiO_2 catalysts have successfully been prepared by using magnetron sputtering method. The physical properties of thus-obtained catalysts are summarized in table 1. The Cu doping content was measured by ICP and EDX techniques. Increasing of sputtering time from 2.5 to 7.5 min resulted in the increase of Cu doping content from 0.73 to 2.21 wt%. It can be seen that the Cu loading content increased linearly with increasing of the sputtering time, which suggested that the Cu sputtering from Cu target was directly deposited on the TiO_2 support. To compare the sputtering-made catalyst, two catalysts with similar Cu content loading were prepared by using conventional impregnation method.

Figure 1 shows the XRD pattern of P25-TiO_2 support and Cu/TiO_2 catalysts prepared by magnetron sputtering and conventional impregnation methods. All catalysts exhibited the main characteristic peak of anatase TiO_2 phase ($2\theta = 25.34°$) with small additional peak of rutile TiO_2 phase ($2\theta = 27.42°$) [12]. Small peak of CuO was also observed in sputtering-made samples, which due to the formation of larger CuO particles comparing with impregnation one. The crystallite size and phase contents of the all samples were calculated by their XRD patterns according to the methods of the Debye–Scherrer equation and Spurr (as summarized in table 1). It can be seen that the TiO_2 crystallite size and rutile phase content did not change much after addition of Cu by both sputtering and conventional impregnation methods.

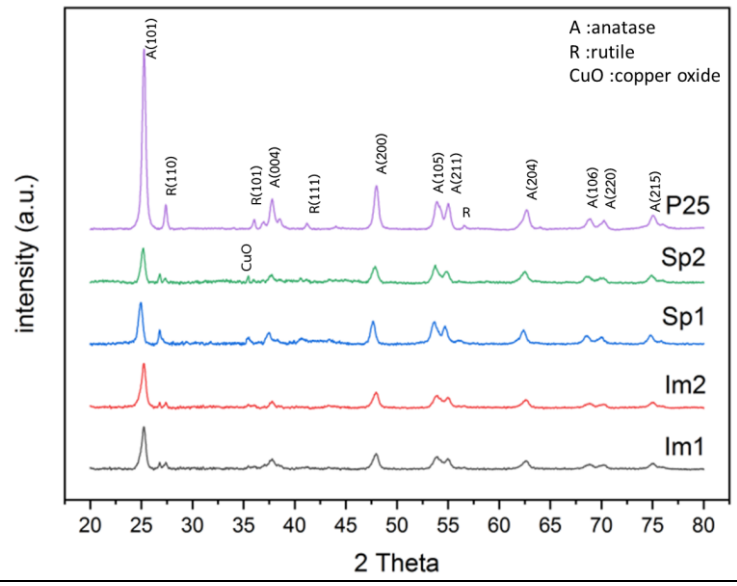

Figure 1. XRD pattern of P25-TiO_2 support and Cu/TiO_2 prepared by magnetron sputtering and conventional impregnation methods.

Figure 2 shows UV-Vis spectra of all catalysts. Addition with Cu with both methods resulted in an increase in the absorption of the TiO_2 photocatalyst in the visible region (400-700nm). Moreover, increasing of Cu doping content also improved the visible light adsorption [12-13]. The lowering of band gap by the doping may eventually leads to Fermi level reducing, improving the photosensitivity of the catalysts. The energy band gaps (E_{bg}) of all the catalyst samples were obtained from the extrapolation of Tauc plot to the abscissa of photon energy and results are presented in table 2. The band gap energy of P-25 (3.18 eV) decreased to 2.87 and 3.01 eV after doping with Cu by impregnation and sputtering methods, respectively.

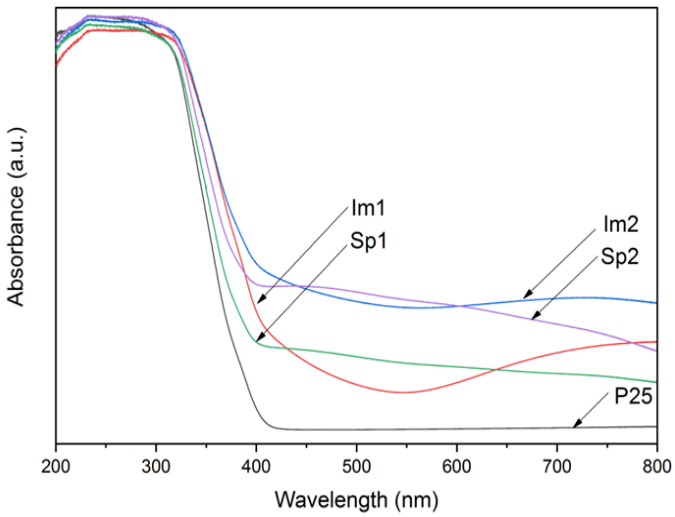

Figure 2. Presents the UV–Vis absorbance spectra of the P25-TiO_2 and Cu/TiO_2 prepared by using the magnetron sputtering and conventional impregnation methods.

SEM was employed to investigate the morphology of the as-synthesized Cu/TiO_2 catalysts as presented in figure 3. The micrographs clearly showed the agglomeration of nanosized spherical particles. There are not much difference between the Cu/TiO_2 catalysts prepared by both methods. To investigate the elemental composition of thus-obtained catalysts, EDX was employed as also

summarized in table 1. The similar trend with ICP was also observed but the Cu content determined by EDX was much higher than those determined by ICP methods. This probably due to the formation of CuO by both methods mainly occurred on the TiO_2 surface and not deposited deep through the TiO_2 pore.

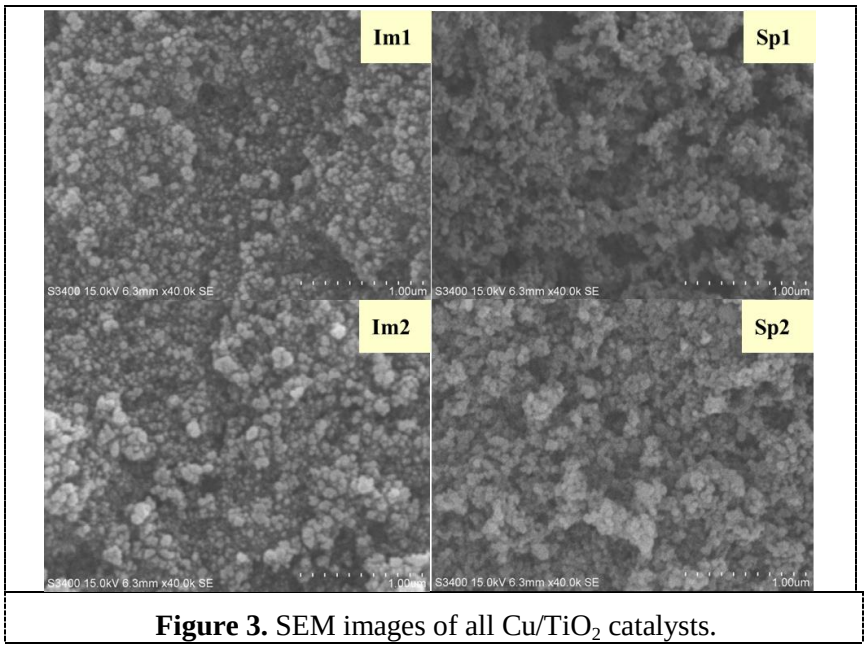

Figure 3. SEM images of all Cu/TiO_2 catalysts.

3.2. Photocatalytic activity

Table 2. The band gap energy of thus-obtained catalysts and CH_4 production rate.

Sample	Band gap energy (eV)	CH_4 production rate ($\mu mole.gcat^{-1}.h^{-1}$)
P25	3.18	0.27
Im1	2.81	0.74
Im2	2.87	0.88
Sp1	3.09	1.25
Sp2	3.01	1.86

The catalytic activity of Cu/TiO_2 catalysts prepared by magnetron sputtering and conventional impregnation methods were tested in photocatalytic reduction of CO_2 and H_2O to methane at atmospheric temperature and pressure for 6 hours. The CH_4 production rates are summarized in table 2. Lower CH_4 production rates of P25 were due to the fast recombination of photo-generated electron-hole pairs. Doping with Cu into TiO_2 resulted in the improvement of CH_4 production rate [13-14]. In photocatalytic process, electron (e^-) and hole (h^+) are generated during the photocatalytic process. Due to the short lifetime, they can recombine immediately or can participate in oxidation and reduction process. The holes can oxidize H_2O or H_2 while the photo-excited electrons can reduce CO_2 to form CO, CH_4 and CH_3OH. When doping with Cu metals on the TiO_2 surface, the Cu can trap the CB electrons, which prolong the electron-hole recombination process and improve the photocatalytic activity[13-14].

4. Conclusion

Reactive magnetron sputtering technique has successfully been used to deposit nanocrystalline CuO on the TiO_2 support. The Cu doping content increased linearly with prolong sputtering time. Doping with Cu did not changed the catalyst morphology and TiO_2 crystallite size, while, it increased the adsorption at visible light range[12-13]. The photocatalytic reduction performance of sputtering-made Cu/TiO_2 catalyst was much better than the pure TiO_2 support. Therefore, reactive magnetron sputtering was a promising technique for deposition of metal onto the support and use as the catalytic process.

5. References

[1] M. Takeuchi, Y. Sakamoto, and S. Niwa 2001 Study on CO2 global recycling system *Science of the total environment* vol. 277 no. 1-3 pp. 15-19
[2] I.-H. Tseng, W.-C. Chang, and J. C. Wu 2002 Photoreduction of CO2 using sol–gel derived titania and titania-supported copper catalysts *Applied Catalysis B: Environmental* vol. 37 no. 1 pp. 37-48
[3] M. Cokoja, C. Bruckmeier, B. Rieger, W. A. Herrmann, and F. E. Kuehn 2011 Transformation of carbon dioxide with homogeneous transition-metal catalysts: a molecular solution to a global challenge? *Angewandte Chemie International Edition* vol. 50 no. 37 pp. 8510-8537
[4] W. Qingli *et al.* 2015 Photoreduction of CO2 using black TiO2 films under solar light *Journal of CO*2 *Utilization* vol. 12 pp. 7-11
[5] K. Wenderich and G. Mul 2016 Methods, mechanism, and applications of photodeposition in photocatalysis: a review *Chemical reviews* vol. 116 no. 23 pp. 14587-14619
[6] H. Yamashita, A. Shiga, S.-i. Kawasaki, Y. Ichihashi, S. Ehara, and M. Anpo 1995 Photocatalytic synthesis of CH4 and CH3OH from CO2 and H2O on highly dispersed active titanium oxide catalysts *Energy conversion and management* vol. 36 no. 6-9 pp. 617-620
[7] S. Das and W. W. Daud 2014 A review on advances in photocatalysts towards CO2 conversion *Rsc Advances* vol. 4 no. 40 pp. 20856-20893
[8] Y. Ohama and D. Van Gemert 2011 *Application of titanium dioxide photocatalysis to construction materials: state-of-the-art report of the RILEM Technical Committee* 194-*TDP* Springer Science & Business Media
[9] H. Yan, T. Zhao, X. Li, and C. Hun 2015 Synthesis of Cu-doped nano-TiO2 by detonation method *Ceramics International* vol. 41 no. 10 pp. 14204-14211
[10] H. Li, C. Li, L. Han, C. Li, and S. Zhang 2016 Photocatalytic reduction of CO2 with H2O on CuO/TiO2 catalysts *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects* vol. 38 no. 3 pp. 420-426
[11] M. Ratova, R. Klaysri, P. Praserthdam, and P. J. Kelly 2018 Visible light active photocatalytic C-doped titanium dioxide films deposited via reactive pulsed DC magnetron co-sputtering: Properties and photocatalytic activity *Vacuum* vol. 149 pp. 214-224
[12] H. W. Nasution, E. Purnama, S. Kosela, and J. Gunlazuardi 2005 Photocatalytic reduction of CO2 on copper-doped Titania catalysts prepared by improved-impregnation method *Catalysis Communications* vol. 6 no. 5 pp. 313-319
[13] Y. Li, W.-N. Wang, Z. Zhan, M.-H. Woo, C.-Y. Wu, and P. Biswas 2010 Photocatalytic reduction of CO2 with H2O on mesoporous silica supported Cu/TiO2 catalysts *Applied Catalysis B: Environmental* vol. 100 no. 1-2 pp. 386-392
[14] B. Xin, P. Wang, D. Ding, J. Liu, Z. Ren, and H. Fu 2008 Effect of surface species on Cu-TiO2 photocatalytic activity *Applied Surface Science* vol. 254 no. 9 pp. 2569-2574

Acknowledgments

This research is supported by the Ratchadapisek Sompoch Endowment Fund (2016), Chulalongkorn University (CU-59-006-IC) and Newton Mobility Grants.