Photo reduction of CO_2 to methanol via TiO_2 photocatalyst

Jeffrey C. S. Wu[†] and Hung-Ming Lin

Department of Chemical Engineering, National Taiwan University, Taipei, Taiwan 10617, R.O.C

ABSTRACT. Greenhouse gas such as CO_2 is the primary cause of global warming. Alternative energy source should be provided without producing more CO_2, such as solar energy. One of the best routes to remedy CO_2 is to transform it to hydrocarbons using photo reduction. In our study, CO_2 was photocatalytically reduced to produce methanol using a Hg lamp with wavelength 365 nm in a steady-state optical-fiber photo reactor. The optical-fiber photo reactor, comprised of near 120 Cu/TiO_2-coated fibers, was designed and assembled to transmit and spread light uniformly inside reactor. TiO_2 film was coated on optical fiber using dip-coating method. Titania and Cu-loaded solutions were prepared by a thermal hydrolysis method. The thickness of Cu/TiO_2 film was 53 nm and consisted of very fine spherical particle with diameter of near 14 nm. The XRD spectra indicated the anatase phase of all TiO_2 and Cu/TiO_2 films. The wavelength of absorption edge was on 367 nm, equivalent to near 3.3 eV. Most active Cu species on TiO_2 surface were Cu_2O clusters, and played an important role for the formation of methanol. The methanol yield increased with UV irradiative intensity. Photo activity increased with increasing Cu loadings. Maximum methanol rate was 0.45 μmole/g-cat•hr using 1.2 wt%-Cu/TiO_2 catalyst under 16 W/cm^2 irradiation, 1.3 bar pressure of CO_2, and 5000 seconds mean residence time. Higher than 1.2 wt% Cu loading gave less rate of methanol yield because of the masking effect of Cu_2O clusters on the surface of TiO_2.

1. INTRODUCTION

Greenhouse gases such as CO_2, CH_4 and CFCs are the primary causes of global warming. The atmospheric concentration of CO_2 has recently increased owing to human activity, further accelerating the greenhouse effect. In response, the Kyoto Protocol of the United Nations Framework Convention on Climate Change mandated a return of CO_2 emission levels to those of 1990. To solve the CO_2 problem permanently requires transforming CO_2 into another useful or non-toxic compounds. Upgrading CO_2 to reusable hydrocarbon resources would benefit humans and the environment.

The energy grade of CO_2 is low from a thermodynamic perspective, accounting for why any transformation to hydrocarbon requires energy infusion. The energy source should be provided without producing more CO_2, such as solar energy. Plants use solar energy to perform natural photosynthesis, but the energy transformation is low at the cost of supporting their lives. Even under the optimal artificial conditions, energy efficiency can only reach about 10% in macro alga under full sun light [1]. Solar energy is the Earth's ultimate power supply. All energy forms except geothermal or nuclear, such as fossil fuel, bio-material, hydropower and wind are various kinds of transformation from solar energy. Consequently, the photoreduction of CO_2 is particularly interesting, and achieving a high efficiency for this reaction is highly desired. The ultimate goal is to demonstrate that artificial photosynthesis may be implemented via the photoreduction of CO_2 to produce hydrocarbons, such as methanol or methane. That is, solar energy is transformed and stored as chemical energy. Moreover, methanol is the most promising photo-reduced product of carbon dioxide because it can be transformed into other useful chemicals using conventional chemical technologies, or easily transported and used as fuel-like renewable energy.

Many researchers have shown that CO_2 can be reduced in water vapor or solvent by photocatalysts such as TiO_2 and ZnS [2, 3]. Equation (1) describes the overall reaction.

$$CO_2 + 2H_2O \xrightarrow{h\nu} CH_3OH + \frac{3}{2}O_2 \tag{1}$$

The efficient photoreduction of CO_2 with H_2O is one of the most challenging tasks of environmental catalysts. As well known, titania is a photo-excited catalyst. The bandgap of anatase form TiO_2 is 3.2 eV, making it a perfect candidate for UV illumination.

Titania-supported copper plays a crucial role for promoting the reduction of CO_2 [4]. The yield of photo products can be changed substantially under different experimental conditions such as UV wavelength, UV intensity, additives of reaction media and reactor configuration. Other variables, such as CO_2 pressure, moisture and residence time are also important in photo reducing CO_2.

Practical applications of TiO_2 photocatalyst for the remediation of vapor-phase CO_2 streams often require immobilizing the photocatalyst in a packed-bed photo reactor. A variety of heterogeneous supports have been

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[†] E-mail: cswu@ntu.edu.tw

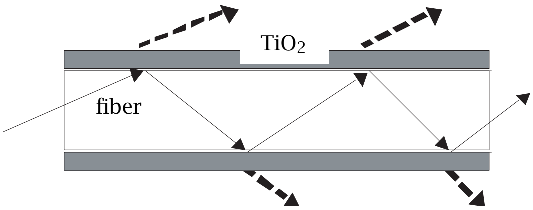


Figure 1. *The schematic of light transmission and spread of* TiO$_2$ *coated-optical fiber.*

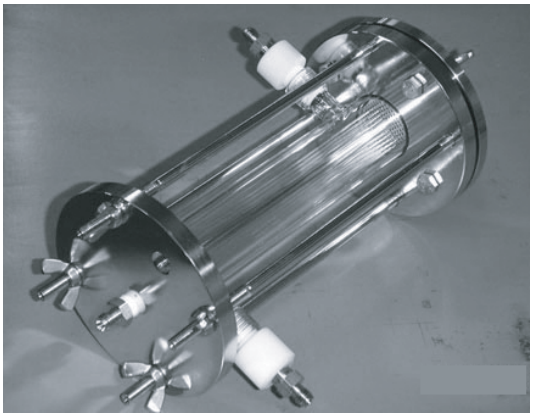


Figure 2. *Photo of optical-fiber photo reactor.*

explored including glass surface [5, 6], lamp casings [7], reactor walls [8], fiberglass cloth [9], quartz rods [10] and monoliths [11, 12]. The transmission and uniform distribution of light energy are important in designing a photo reactor which differs completely from the traditional reactor. A TiO$_2$-coated fiber-optical cable reactor has been demonstrated the inherent advantages over a packed-bed reactor in photo reactions [13, 14]. Figure 1 shows that light is transmitted into an optical fiber. The light is spitted to two beams when hitting the internal surface fiber due to the difference of refraction index between TiO$_2$ coating and quartz core. Part of light is reflected and transmitted along the fiber, while the rest penetrates and excites the titania layer at the interface. Thus the electron-hole (e^- and h^+) pairs are generates then conduct the following photo reactions. Therefore, optical fibers can be used to radiate the light uniformly inside a photo reactor. The preparation and characteristics of TiO$_2$ film on optical fibers are essential for the development of a photo reactor. The goal of this study is to develop a photo-reactor system to carry out the photo reduction of CO$_2$. In regard to the light source, it can be collected from the sun using focus reflection dish.

2. EXPERIMENTAL

The TiO$_2$ solutions for coating on optical fiber were prepared by thermal hydrolysis method. Titanium butoxide (97%, Aldrich, USA) and polyethylene glycol (PEG, molecular weight of 20000, Merck, Darmstadt, Germany) were added to 0.1 M nitric acid solution. The volume ratio of titanium butoxide to HNO$_3$ was 1 : 6, and the weight of PEG was 50% of that of TiO$_2$. The appropriate amount of copper precursor, CuCl$_2$, was added to obtain the desired Cu loading of TiO$_2$. The mixed solution was heated to 80°C for 8 hours. PEG was added to prevent cracking during the drying and calcination of the film. Furthermore, PEG increased the viscosity of the solution and dispersed TiO$_2$ particles uniformly in the solution. The appearance of pure TiO$_2$ solution was transparently milky.

Optical fiber was obtained from the E-Tone Technology Company of Taiwan. The polymeric shield on the optical fiber was burned off in a furnace at 400°C. The remaining quartz core had a diameter of 112 μm. Using the same procedure, TiO$_2$ coatings were applied to glass plates that were 5 cm long, 2 cm wide and 0.1 cm thick, for characterization. Both quartz fiber and the glass plate were cleaned by 5 M NaOH solution in an ultrasonic cleaner. They were then rinsed in deionized water and dried before applying dip-coating procedure. The bare fiber was immersed into the solution vertically, and then pulled up at various rates by a step motor. The rates of pulling-up ranged from 5 to 50 mm/min. The TiO$_2$ film was dried in air at 150°C by a rate of 1°C/min from the ambient temperature, and maintained at 150°C for 3 hours. Then it was calcined at 500°C for another 5 hours.

The TiO$_2$ phase of the film was determined using the X-ray diffractometer, MAC Science M03XHF, scanning from 20–80°. The UV-visible absorption was measured by transmission mode using a Varian Cary spectrophotometer 100, at wavelengths from 200–800 nm. The microstructure of the TiO$_2$ film on the optical fiber was inspected using scanning electro microscopy (SEM) LEO 1530 (Germany). X-ray photoelectron spectroscopy (XPS) was conducted for elemental analysis on a spectrometer of VG Microtech MT500.

An optical-fiber photo reactor (OFPR), comprised of TiO$_2$-coated fibers, was designed and assembled to transmit light form one end of the OFPR module to the fiber-supported TiO$_2$ film as shown in Figure 2. Near 120 fibers with 16 cm long were inserted into the OFPR, which had a diameter of 3.2 cm and was 16 cm long. The both sides of OFPR were sealed using O-rings and passed the leakage test. Figure 3 schematically illustrates the reactor system. The OFPR was illuminated from the quartz window of one side by a Hg lamp with a peak light intensity at 365 nm. The light intensity could adjust from 1 to 16 W/cm^2. The whole OFPR was wrapped up using aluminum foil to avoid the interference of indoor lamps during the reaction. Supercritical-fluid grade CO$_2$ was purchased from Air Products (USA) to avoid any hydrocarbon contamination. It was certified maximum hydrocarbons less than 20 ppb. CO$_2$ was

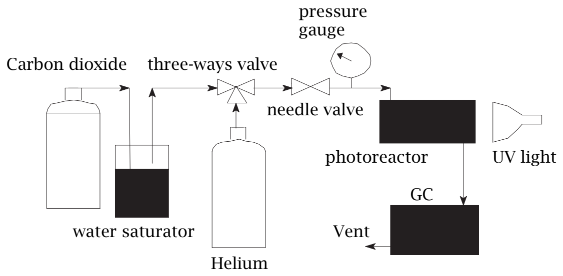


Figure 3. *Schematic of photo reaction system.*

bubbled through a water saturator to carry moisture. The partial pressure of moisture could be adjusted by the temperature of saturator. The reactor was tightly closed during the reaction and was purged one hour using helium before switching to CO_2. The flow rate of CO_2 was $\sim 3\,\mathrm{ml/min}$ and equivalent to residence time of 5000 seconds. Total pressure was in the range of $1.05 \sim 1.4$ bar. All reaction data was taken at steady state which attained in near one hour after turning on UV light.

Reaction products were analyzed via a sampling loop of 2.5 ml on-line by a GC/FID equipped with a 2 m long Porapak Q column. Analysis results indicated that methanol was the dominant hydrocarbon. Blank reactions were carried out to ensure that hydrocarbon production was solely from the photoreduction of CO_2. One blank was UV-illuminated without the catalyst, and another was in the dark with the catalyst and CO_2 under the same experimental conditions. No hydrocarbon was detected in the above blank tests.

3. RESULTS AND DISCUSSION

Figure 4 shows the SEM micrographs of bare optical fiber and cross-section TiO_2 film on top of the fiber. The bare fiber was smooth after removing polymeric shield as shown in Figure 4(a). The thickness of 1.2 wt% Cu/TiO_2 films was near 53 nm on the surface of optical fiber as shown in Figure 4(b). The film was transparent, colorless and uniformly flat without cracks. The XRD spectra in Figure 5 shows the diffraction pattern of various Cu/TiO_2 and pure TiO_2 films. Thermal treatment at 500°C for 5 hours resulted in well crystallized anatase-type TiO_2. No copper diffraction peak was observed in the XRD spectra indicating that copper was finely dispersed on TiO_2. The UV-visible absorption spectra of films are shown in Figure 6. The light absorbed by the TiO_2 films were all below 380 nm in the UV-Vis spectra indicating that the bandgap of the TiO_2 film near 3.3 eV. The UV-visible absorptions of Cu/TiO_2 catalysts were similar to that of pure titania.

Table 1 summaries the crystalline size and band gap of prepared Cu/TiO_2 films. The average crystalline sizes of all films ranged from 13.4 to 14.0 nm, which were calculated from the Scherrer's equation according to the peak broadening of XRD spectra. The crystalline sizes of Cu/TiO_2 were slightly smaller than that of TiO_2. In general, the crystalline size was primarily influenced by calcined temperature, and Cu loading had negligible effect. The band gaps were ranged from 3.31 to 3.37 eV estimated by extrapolating the absorption edge of UV-Vis spectrum to x-axis, that is, approximately 367 nm. Those are typical TiO_2 band gap indicating the Cu loadings did not affect the band structure of TiO_2.

Table 1. *Characteristics of* Cu/TiO_2 *catalysts.*

Cu loading (wt%)	Crystalline size[a] (nm)	Band gap[b] (eV)
0	14.0	3.34
0.52	13.4	3.31
1.20	13.4	3.37
2.06	13.4	3.35

a: Estimated by Scherrer's equation from XRD spectra.
b: Estimated from the UV-Vis spectra.

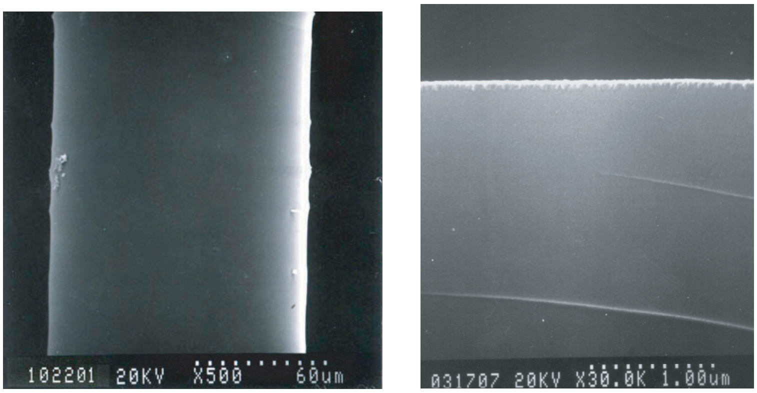
Table 2. *Molar ratios of* Cu/Ti *on* Cu/TiO_2 *and surface* OH *ratios.*

Catalyst	Cu/Ti		OH ratio[c]
wt%	Surface[a] (XPS)	Bulk[b] (calculated)	
0	0	0	0.169
0.52	0.012	0.008	0.178
1.20	0.029	0.015	0.205
2.06	0.077	0.028	0.243

a: estimated from the XPS peak intensity and sensitivity factor.
b: calculated from the precursors of $CuCl_2$ and titanium butoxide in preparation.
c: Surface OH to total O (1s) of catalyst.

Table 2 lists the molar ratios of element composition of Cu/TiO_2. The bulk composition was calculated from the amount of precursors in preparation procedure. The surface composition was estimated from the peak intensity of XPS, which usually only detected ~ 1 nm depth of a sample. The Cu/Ti ratios of surface were higher than those of bulk indicating that most Cu was dispersed on the surface of catalysts. The higher the Cu loading, the higher the surface Cu ratio was. In addition, the ratio of hydroxyl group (OH)/oxygen on catalyst surface increased with in increasing Cu loading.

Figure 7 shows the methanol yields versus light intensity under the partial pressures CO_2 and H_2O at 1.29 and 0.026 bar, respectively. The yield increased with light intensity in the range of 1 to $16\,\mathrm{W/cm^2}$. Pure TiO_2 gave very little methanol yield while Cu/TiO_2 significantly increased the yield. The maximum yield of methanol was $0.45\,\mu$mole/g-cat•hr using 1.2 wt% Cu/TiO_2 catalyst under light intensity of $16\,\mathrm{W/cm^2}$. Cu_2O served as active center for methanol synthesis in photocatalysis [15, 16]. Increasing Cu loading resulted in increasing photo activity as expected. Cu_2O also served as electron trap to reduce the recombination rate of electron-hole pairs during photo excitation of photocatalyst. Surface hydroxyl (OH) of TiO_2



(a) (b)

Figure 4. SEM *micrographs* (a) *Optical fiber and* (b) *Cross-section of* 1.2 wt% Cu/TiO_2 *film on optical fiber.*

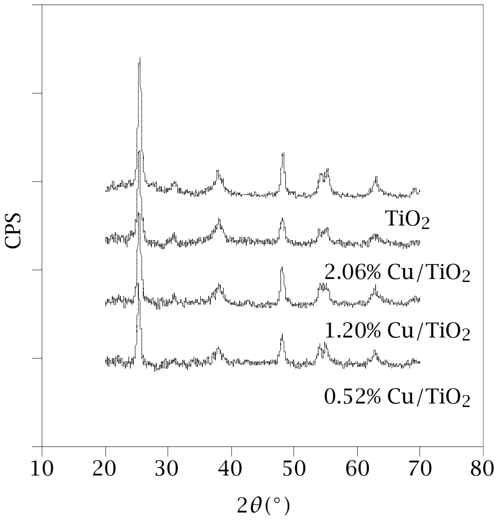


Figure 5. XRD *of* Cu/TiO_2 *catalysts.*

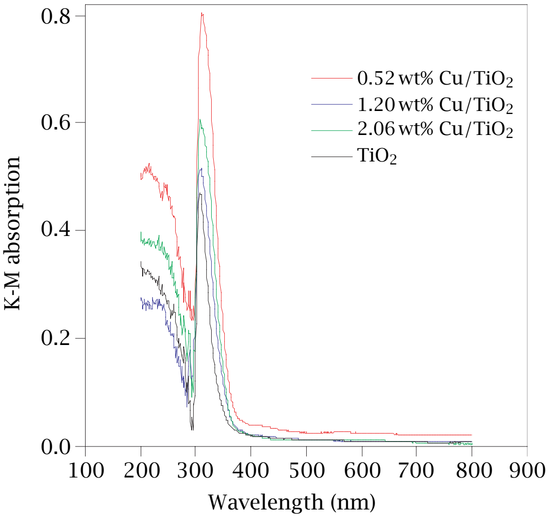


Figure 6. UV-Vis *spectra of Catalysts.*

can promote the adsorption of reactant, CO_2, so that photo reaction was enhanced [16]. The amount of surface hydroxyl on TiO_2 increased with increasing Cu loading (Table 2). Thus the overall photo activity of CO_2 reduction significantly increased. However, excess Cu_2O clusters on the surface also masked the surface of TiO_2 resulting in less light exposure of catalyst. Consequently the photo excitation of electron and hole pair was declined because less photo energy was absorbed. So there existed an optimum Cu loading on photo catalysts. An Cu loading of 1.2 wt% was found be have the highest yields of methanol under our experimental conditions.

The power of light intensity was calculated to be 0.5 in the methanol rate equation by linear regression. In general, photo activity is directly proportional to the light intensity. However, if light was over supplied than need like our experimental condition, the power of light intensity in the rate equation would shift from one to half.

4. CONCLUSION

The catalytic reduction of CO_2 has great advantage over green plants of not having to support a living system. One of goals of this research is to develop a highly photo-efficient reactor for converting solar energy to chemical energy, such as, methanol from CO_2 via photo energy. In this study, the thickness of the films was near 53 nm after calcination at 500°C, and the average size of the nanocrystals in the TiO_2 film was near 14 nm. The photo reduction of CO_2 with H_2O was successfully demonstrated in a photo reactor with Cu/TiO_2-coated optical fibers. So far maximum methanol yield was 0.46 μmole/g-cat-hr under UV irradiation. Optical fibers provide an uniform light distribution in a photo reactor that spreads light energy more efficiently than

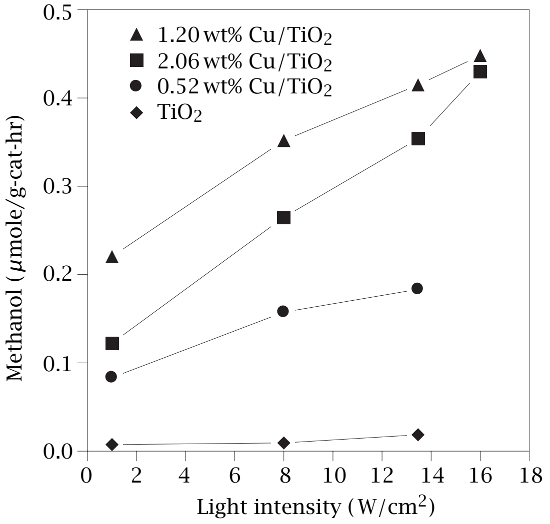


Figure 7. *The methanol yield in optical-fiber photo reactor, reaction temperature* 75°C, CO_2 *pressure* 1.29 *bar,* H_2O *pressure* 0.026 *bar.*

a traditional packed-bed reactor. In addition, a higher processing capacity is possible because the catalyst can disperse on a large external area of optical fibers in a given reactor volume. Furthermore, OFPR is a promising photo reactor that can be applied to any aqueous or gas-phase photo reaction.

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