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Photo reduction of CO_2 to methanol using optical-fiber photoreactor

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Abstract

Greenhouse gases such as CO_2 are the primary cause of global warming. One of the best routes to remedy CO_2 is to transform it to hydrocarbons using photo reduction. CO_2 was photocatalytically reduced to produce methanol using a Hg lamp with wavelength 365 nm in a steady-state optical-fiber photoreactor. The optical-fiber photoreactor, comprised of nearly 120 Cu/TiO_2-coated fibers, was designed and assembled to transmit and spread light uniformly inside the reactor. TiO_2 film was coated on optical fiber using a dip-coating method. Cu-loaded titania solutions were prepared by a thermal hydrolysis method. The thickness of Cu/TiO_2 film was 53 nm. The coating film consisted of very fine spherical particles with diameters of near 14 nm. The XRD spectra indicated the anatase phase for all TiO_2 and Cu/TiO_2 films. The wavelength of absorption edge on Cu/TiO_2 was near 367 nm, equivalent to a bandgap of 3.3 eV. The most active Cu species on TiO_2 surface were Cu_2O clusters, and they played an important role for the formation of methanol. The methanol yield increased with UV irradiative intensity. Maximum methanol rate was 0.45 μmole/g cat h using 1.2 wt.%-Cu/TiO_2 catalyst at 1.29 bar of CO_2, 0.026 bar of H_2O, and 5000 s mean residence time under 16 W/cm^2 UV irradiation. Higher than 1.2 wt.% Cu loading gave a lower rate of methanol yield because of the masking effect of Cu_2O clusters on the TiO_2 surface. The Langmuir–Hinshelwood model was established by correlating experimental data to describe the kinetic behavior. An optimum pressure ratio of H_2O/CO_2 was found in the photo reduction of CO_2 for maximum methanol yield.

Keywords: Photocatalysis; Renewable energy; Optical-fiber photoreactor; CO_2 reduction; 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 steadily increased owing to human activity and this accelerates the greenhouse effect. Recently, the Kyoto Protocol of the United Nations Framework Convention on Climate Change mandated a return of CO_2 emission levels to those of 1990. On the other hand, upgrading CO_2 to reusable hydrocarbons is one the best routes to overcome the energy shortage. The energy grade of CO_2 is low from a thermodynamic perspective so that any transformation of CO_2 requires energy input. Solar energy should be one of the best candidates because it is abundant and can be supplied without producing CO_2. Consequently, the photo reduction of CO_2 is highly desired. In this way, solar energy is transformed and stored as chemical energy similar to photosynthesis.

CO_2 can be photocatalytically reduced in water vapor or solvent by photocatalysts such as TiO_2 [1]. To find a highly efficient photocatalyst for the reduction of CO_2 with H_2O is one of the most challenging tasks. Eq. (1) gives an example of overall photo reduction transforming CO_2 to methanol. Methanol is the most promising product from the reduction of CO_2, because it can be easily transported, stored and can be used as gasoline-additives for automobiles. Titania-supported copper plays a crucial role for promoting the reduction of CO_2 in methanol formation [2]. The yield of photo products can be changed substantially under different experimental conditions such as UV wavelength, light 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:

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

Practical applications of TiO_2 photocatalyst for the remediation of vapor-phase CO_2 streams often require immobilizing the photocatalyst in a packed-bed photoreactor.

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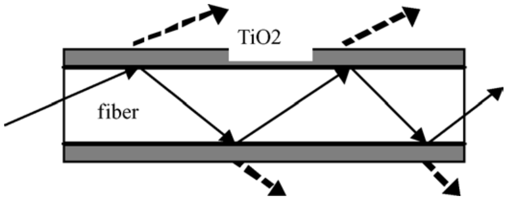


Fig. 1. The schematic of light transmission and spread of TiO_2 coated-optical fiber.

A variety of heterogeneous supports have been explored, including glass surface [3,4], quartz rods [5] and monoliths [6,7]. The transmission and uniform distribution of light energy are important in designing a photoreactor, which differs completely from a traditional reactor. TiO_2-coated fiber-optical cable reactors have demonstrated some inherent advantages over packed-bed reactors in photo reactions [8,9]. Fig. 1 shows that light is transmitted into an optical fiber. The light is split to two beams when hitting the internal surface fiber, due to the difference of refraction index between the TiO_2 coating and the quartz core. Part of the 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 generated; these then conduct the following photo reactions. Therefore, optical fibers can be used to radiate the light uniformly inside a photoreactor. The goal of this study is to develop a photo-reactor system in order to carry out the photo reduction of CO_2 in vapor phase. The preparation and characteristics of TiO_2 film on optical fibers are essential for the development of a photoreactor. In regard to the light source, artificial light can be used currently. However, light energy can be collected from the sun using a focus reflection dish in the future.

2. Experimental

The TiO_2 solutions were prepared using a thermal hydrolysis method for coating on optical fibers. Titanium butoxide (97%, Aldrich, USA) and polyethylene glycol (PEG, molecular weight of 20 000, Merck, Darmstadt, Germany) were added to a 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 TiO_2. An 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 h. 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 fibers were 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 fiber had a diameter of 112 μm. Each quartz fiber was cleaned by a 5 M NaOH solution in an ultrasonic cleaner, then rinsed in de-ionized water and dried before applying dip-coating procedure. The bare fiber was immersed into the solution vertically, 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 h. Then it was calcined at 500 °C for another 5 h. The same procedure of TiO_2 coatings was also applied to glass plates that were 5 cm long, 2 cm wide and 0.1 cm thick, for characterization.

Fig. 2. Photo of optical-fiber photoreactor.

The TiO_2 phase of the film was determined using the X-ray diffractometer, MAC Science M03XHF, scanning from 20° to 80°. The UV–vis absorption was measured by transmission mode using a Varian Cary spectrophotometer 100, at wavelengths from 200 to 800 nm. The microstructure of the TiO_2 film on the optical fiber was inspected using a scanning electro microscope (SEM) LEO 1530 (Germany). X-ray photoelectron spectroscopy (XPS) was conducted for elemental analysis on a spectrometer of VG Microtech MT500.

An optical-fiber photoreactor (OFPR) was designed and assembled to transmit light from one side of the OFPR module to the fiber-supported TiO_2 film, as shown in Fig. 2. About 120 fibers 16 cm long were inserted into the OFPR, which had a diameter of 3.2 cm and was 16 cm long. The circular side-plates of OFPR were sealed using O-rings and the system passed the leakage test. Fig. 3 schematically illustrates the reactor system. The OFPR was irradiated through the quartz window of one side using a Hg lamp with a peak light intensity at 365 nm. The light intensity entering the quartz window could be adjusted from 1 to 16 W/cm^2. The whole OFPR was

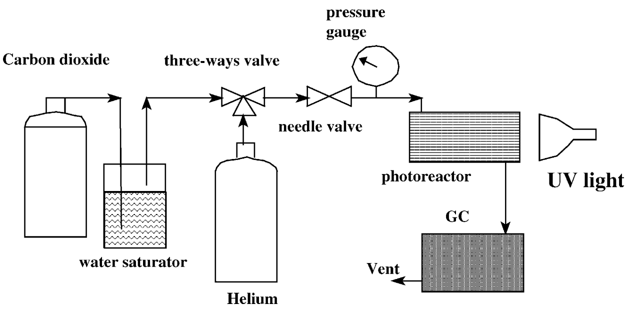


Fig. 3. Schematic of photo reaction system.

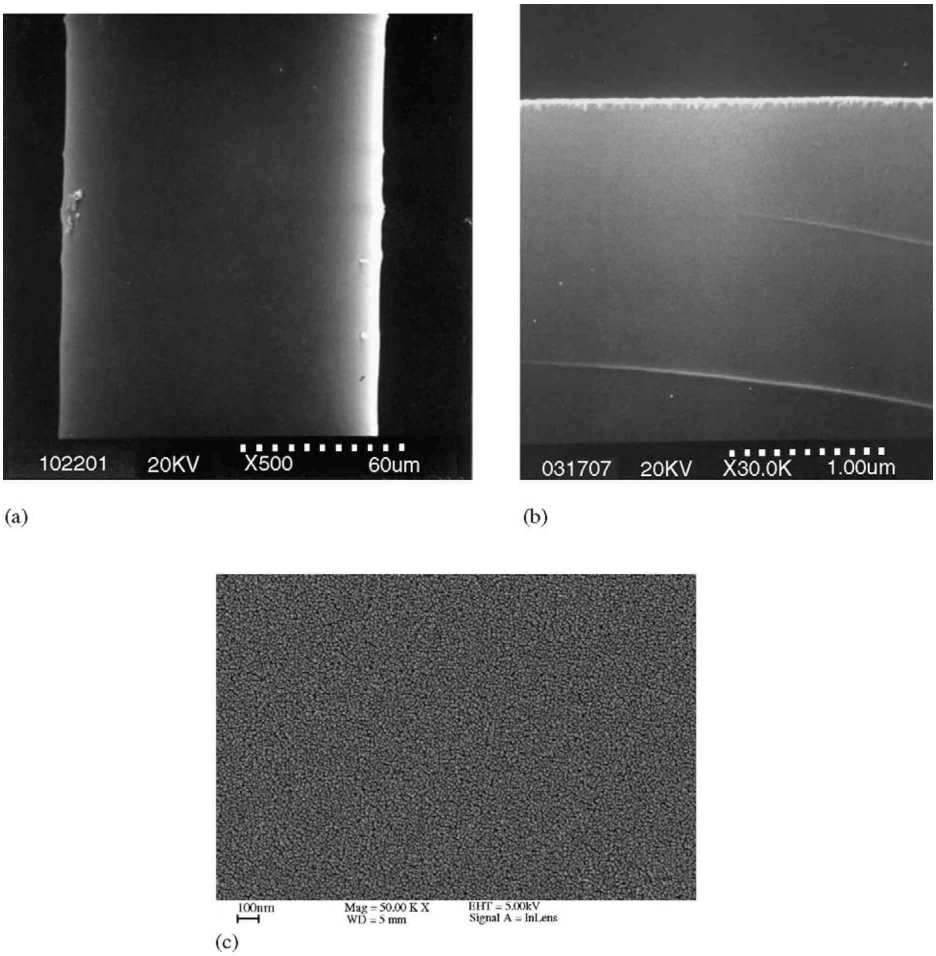
wrapped using aluminum foil to avoid the interference of indoor lamps during the reaction. Supercritical-fluid grade CO_2 was purchased from Air Products (USA) to avoid any hydrocarbon contamination. It was certified that the maximum amount of hydrocarbons was less than 20 ppb. CO_2 was bubbled through a water saturator to carry moisture. The reactor was tightly closed and maintained at 75 °C by heating tape during the reaction. The reactor was purged for one hour using helium before switching to CO_2. The flow rate of CO_2 was ~3 ml/min and this was equivalent to a residence time of 5000 s based on the reactor volume. The pressure of CO_2 was in the range of 1.05–1.4 bar, and the water pressure could be adjusted by the temperature of saturator. All reaction data was taken at steady state which could be attained in about 1 h after turning on the UV light.

Reaction products were analyzed via a sampling loop of 2.5 ml on-line by a GC equipped with FID using 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 photo reduction of CO_2. One blank was UV-irradiated without the catalyst, and another was in the dark with the catalyst under the same experimental conditions. No hydrocarbon was detected in the above blank tests.

3. Results and discussion

3.1. Characteristics of catalysts

Fig. 4 shows the SEM micrographs of bare optical fiber, cross-section of Cu/TiO_2 film and top view of TiO_2 film on top of the fibers. The bare fiber was smooth after removing polymeric shield, as shown in Fig. 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 Fig. 4(b). Fig. 4(c) shows that the TiO_2 film consisted of very fine spherical particles with diameters of ~14 nm. The film was transparent, colorless and uniformly flat without cracks. The films of TiO_2 and other Cu-loaded-TiO_2 on fibers were also had the same thickness. The XRD spectra in Fig. 5 shows the diffraction pattern of various Cu/TiO_2 and pure TiO_2 films. Thermal treatment at 500 °C for 5 h 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–vis absorption spectra of films are shown in Fig. 6. The absorption spectra below 300 nm decreased abruptly due to the background subtracting of the underlayer glass plate. The TiO_2 films absorbed light below a wavelength of 380 nm in the UV–vis spectra, indicating its bandgap near 3.3 eV. The UV–vis absorptions of Cu/TiO_2



(a) (b) (c)

Fig. 4. SEM micrographs: (a) an optical fiber, (b) the cross-section of 1.2 wt.% Cu/TiO_2 film on an optical fiber, and (c) the top view of TiO_2 film on an optical fiber.

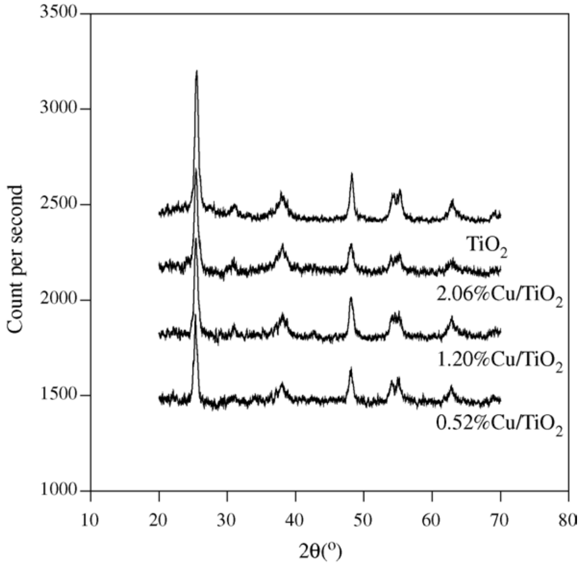


Fig. 5. XRD of TiO_2 and Cu/TiO_2 catalysts.

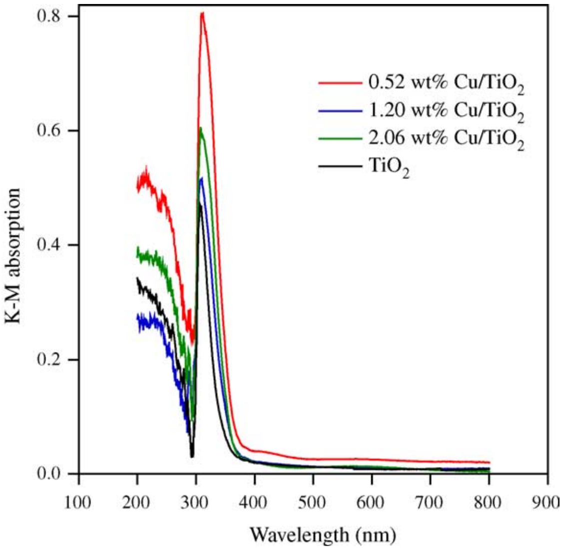


Fig. 6. UV–vis spectra of TiO_2 and Cu/TiO_2 catalysts.

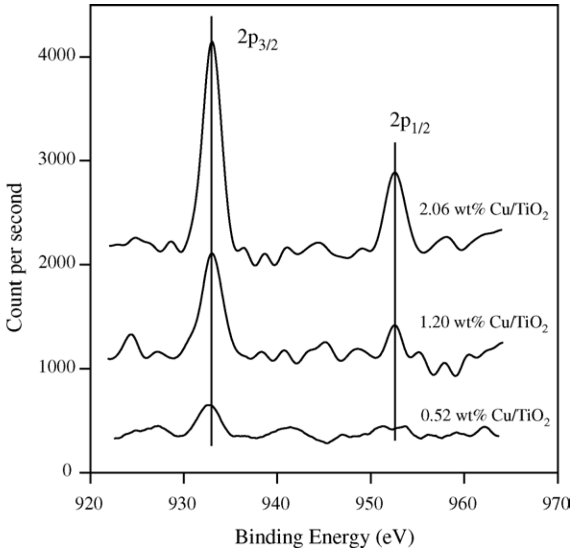


Fig. 7. XPS of Cu 2p on Cu/TiO_2 catalysts.

catalysts were similar to those of pure titania. Fig. 7 shows the results of Cu (2p) XPS spectra on Cu/TiO_2 with three different Cu loadings. According to the positions of binding energies (2p3/2, 932.8 eV; 2p1/2, 952.8 eV) and the shape of the peaks, the copper on the surface of TiO_2 might exist in multiple-oxidation states, but Cu(I) would be the primary species [10].

Table 1 summaries the crystalline sizes and band gaps of prepared Cu/TiO_2 films. The average crystalline sizes of all films ranged from 13.4 to 14.0 nm; these values were calculated from the Scherrer equation according to the peak broadening of XRD spectra. The crystalline sizes of Cu/TiO_2 were only 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 bandgaps ranged from 3.31 to 3.37 eV, as estimated by extrapolating the absorption edge of VU–vis spectrum to the abscissa of zero absorption, approximately at 367 nm. These values are typical TiO_2 bandgaps indicating that the Cu loadings did not affect the band structure of TiO_2.

Table 2 lists the molar ratios of elemental compositions of different copper-loaded-TiO_2 catalysts. The bulk composition was calculated from the amount of precursors in the preparation procedure. The surface composition was estimated from the peak intensity of XPS, which usually 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 was, the higher the surface Cu ratio was. The XPS spectrum of O (1s) was de-convolved and the individual peak intensity was used to estimate the ratio of hydroxyl group (OH, 532.7 eV) and total oxygen on catalyst

Table 1
Characteristics of Cu/TiO_2 catalysts

Cu loading (wt.%)	Crystalline size[a] (nm)	Bandgap[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 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 (wt.)	Cu/Ti		OH ratio[a]
	Surface[b] (XPS)	Bulk[c] (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] Surface OH to total O (1s) by XPS peak intensity.
[b] Estimated from the XPS peak intensity.
[c] Calculated from the precursors of $CuCl_2$ and titanium butoxide in preparation.

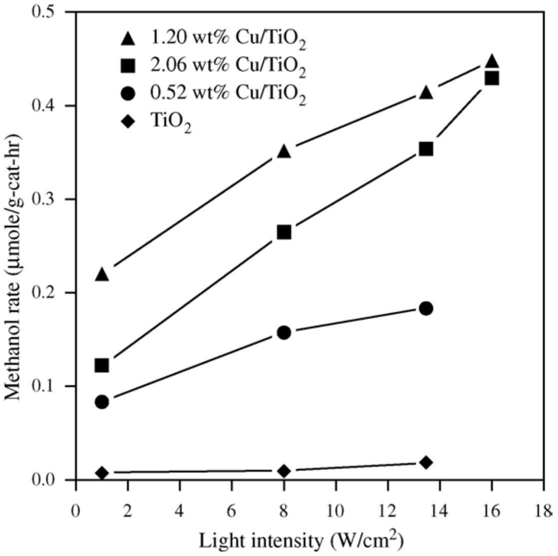


Fig. 8. The methanol yield in optical-fiber photoreactor, reaction temperature: 75 °C; CO_2 pressure: 1.29 bar; H_2O pressure: 0.026 bar.

surface. The results are also listed in Table 2. The OH/total oxygen ratio of Cu/TiO_2 was higher than that of pure TiO_2, and the ratio increased with increasing Cu loadings.

3.2. *Photo reduction of CO_2*

Fig. 8 shows the methanol yields versus light intensity under the partial pressures of CO_2 and H_2O at 1.29 and 0.026 bar, respectively, at 75 °C. The yield increased with light intensity in the range of 1–16 W/cm^2. Pure TiO_2 gave very little methanol yield, while Cu/TiO_2 significantly improved the yield. The maximum yield of methanol was 0.45 μmole/g cat h using 1.2 wt.% Cu/TiO_2 catalyst under a light intensity of 16 W/cm^2. Since the primary status of copper was Cu(I) (as shown in Fig. 7), Cu_2O was suggested to be the active center for methanol formation in CO_2 photo reduction [10,11]. Increasing Cu loading resulted in increasing photo activity, as expected. Cu_2O could also serve as an electron trap to reduce the recombination rate of electron-hole pairs during photo excitation of photocatalyst. Surface hydroxyls (OH) of TiO_2 could also promote the adsorption of the reactant, CO_2, so that the photo reaction was enhanced [11]. 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 would be an optimum Cu loading on Cu/TiO_2 catalysts for maximum methanol yield. An Cu loading of 1.2 wt.% was found to give the highest yields of methanol under our experimental conditions.

The influences of CO_2 and water pressure were also investigated. Fig. 9 shows the methanol yields versus different CO_2 pressures under fixed light intensity, 13.5 W/cm^2 and water pressure, 0.026 bar, at 75 °C. The methanol yields increased with CO_2 pressure, reaching a maximum of 0.415 μmole/g cat h at 1.29 bar, then decreased with further increasing of CO_2 pressure on 1.20 wt.% Cu/TiO_2. The other two catalysts showed similar trends with lower methanol yields. Fig. 10 shows the methanol yields versus various pressure ratios of H_2O/CO_2 under fixed light intensity, 13.5 W/cm^2. The methanol yields also increased with H_2O/CO_2 ratios, then decreased with higher ratios. Such phenomena implied a competitive adsorption of reactants, i.e., CO_2 and H_2O, on the active sites during photo reduction. Thus there existed optimum pressures of CO_2 and H_2O in the photo reduction.

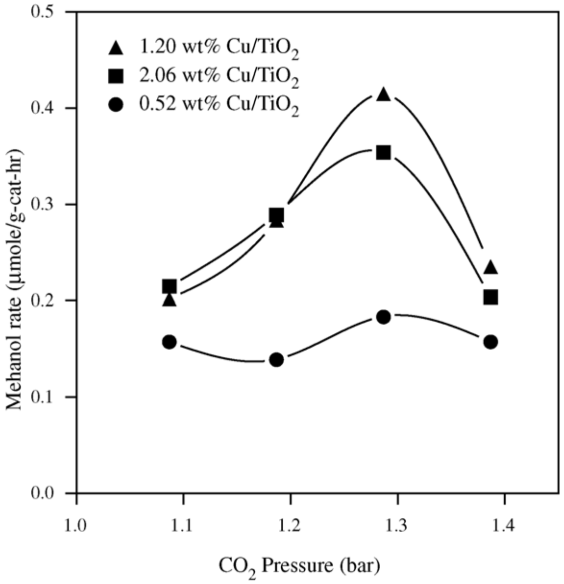


Fig. 9. The methanol yield in optical-fiber photoreactor, reaction temperature: 75 °C; light intensity: 13.5 W/cm^2; H_2O pressure 0.026 bar.

As shown in Eq. (2), a Langmuir–Hinshelwood (L–H) model was employed to correlate the experimental data of CO_2, water, light intensity and methanol yield. Both reactants, CO_2

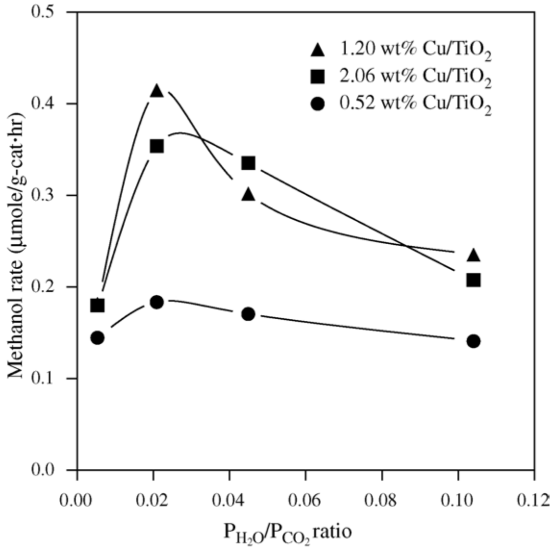


Fig. 10. The methanol yield in optical-fiber photoreactor, reaction temperature: 75 °C; light intensity 13.5 W/cm^2.

Table 3
Adsorption equilibrium and rate constants[a] of Langmuir–Hinshelwood model

Parameters	Value	Error with 95% confidence
k (μmole/g cat bar^3 h)	2481	±1149
a	0.20	±0.16
K_1 (bar^{-1})	51.7	±11.2
K_2 (bar^{-1})	0.01	±0.22

[a] Estimated by correlation of experimental data on 1.20 wt.% Cu/TiO_2 catalyst.

and H_2O, were assumed to be adsorbed on the same active sites of the catalyst surface. The reaction was considered to be irreversible because the partial pressures of products, methanol and oxygen, were very low. Multiple-variable non-linear regression was applied the data of 1.20 wt.% Cu/TiO_2. The best fitted rate constant, k, and adsorption equilibrium constants, K_1 and K_2, are listed in Table 3. The value of water adsorption equilibrium constant, K_1, was 51.7 bar^{-1}, that was nearly three orders of magnitude higher than that of CO_2, K_2, 0.01 bar^{-1}. The value of K_2 was near zero, indicating that the adsorption of CO_2 was very weak, while water was strongly adsorbed on the catalyst surface:

$$\text{Rate} = \frac{kP_{H_2O}^2 P_{CO_2} I^a}{(1 + K_1 P_{H_2O} + K_2 P_{CO_2})^3} \tag{2}$$

where k is the methanol rate constant (μmole/g cat bar^3 h), I the light intensity (W/cm^2), a the power of light intensity, K_1 the adsorption equilibrium constant of H_2O (bar^{-1}), K_2 the adsorption equilibrium constant of CO_2 (bar^{-1}).

It is well known that the surface of TiO_2 becomes superhydrophilic when irradiated by UV light. Therefore, water molecules would cover most of the surface of TiO_2 catalyst during photo reduction. Our CO_2 photo reduction was carried out at very low water pressure ranging from 0.0072 to 0.12 bar. At high H_2O/CO_2 ratio, CO_2 would need to compete with H_2O on the active sites in order to react with adsorbed H_2O. Thus reducing H_2O pressure (or raising CO_2 pressure) increases the reaction rate. However, when H_2O pressure is much lower than that of CO_2, e.g. $H_2O/CO_2 < 0.02$, less water coverage could decrease the reaction rate. Therefore there exists an optimum CO_2 pressure at a given H_2O pressure, or an optimum H_2O/CO_2 ratio as shown in Figs. 9 and 10, respectively.

Apparent elementary steps of the CO_2 photo reduction are derived in Eqs. (3)–(8) according to the results of L–H model (Eq. (2)). The rate-limiting step was assigned to be the formation of methanol (Eq. (5)). The detailed mechanism of the methanol formation could not be revealed from our present study. The adsorption of CO_2 and H_2O and the desorption of methanol and oxygen were not bottle necks of the photo reduction of CO_2 under our experimental conditions:

$$H_2O + S \xleftrightarrow{K_1} H_2O{-}S \tag{3}$$

$$CO_2 + S \xleftrightarrow{K_2} CO_2{-}S \tag{4}$$

$$2H_2O{-}S + CO_2{-}S \xrightarrow{k_3} CH_3OH{-}S + O_2{-}S + O{-}S, \quad \text{rate-limiting} \tag{5}$$

$$CH_3OH{-}S \xleftrightarrow{K_4} CH_3OH + S \tag{6}$$

$$2O{-}S \xleftrightarrow{K_5} O_2 + S \tag{7}$$

$$O_2{-}S \xleftrightarrow{K_6} O_2 + S \tag{8}$$

As the effect of light intensity, the power of light intensity was estimated to be ~0.2 in the methanol rate equation (Eq. (2)) within 1–16 W/cm^2 UV irradiation. In general, photo activity would be directly proportional to the light intensity. However, if more light flux was supplied than the demand of photo reaction, the power of light intensity in the rate equation would gradually shift from one to less than 0.5 [12]. The light flux of our experiment was probably over-supplied. In such a case, the light flux should be decreased in order to increase quantum efficiency. On the other hand, larger reactor volume or higher CO_2 flow rate can be used under the same light flux.

4. Conclusion

The catalytic reduction of CO_2 has great advantages over green plants of not having to support a living system. This research has demonstrated 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 photoreactor with Cu/TiO_2-coated optical fibers. So far, the maximum methanol yield was 0.46 μmole/g cat h under 365 nm UV irradiation. Compared with a traditional packed-bed reactor, an optical-fiber provides a medium to transmit light throughout the reactor. Thus light energy can be spread more efficiently. 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 photoreactor that can be used in gas or aqueous phases in other photo reactions in the future.

Acknowledgements

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