



Photoreduction of CO₂ over Ruthenium dye-sensitized TiO₂-based catalysts under concentrated natural sunlight

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ABSTRACT

Metal doped TiO₂ catalyst sensitized with Ru^{II}(2,2'-bipyridyl-4,4'-dicarboxylate)₂-(NCS)₂ (N3 dye) is employed to photoreduce CO₂ with H₂O under concentrated natural sunlight to fuels in an optical-fiber photoreactor. Production rate of methane of 0.617 μmol/g-cat h is measured on N3-dye-Cu(0.5 wt%)-Fe(0.5 wt%)/TiO₂ coated on optical fiber in April 12, 2007 in Taipei, Taiwan with the average concentrated solar light intensity of 20 mW/cm². Full absorption of visible light of N3-dye along with efficient charge transfer in N3 dye-TiO₂ system give rise to the superior photoreduction of the resulting dye adsorbed catalyst.

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1. Introduction

Photocatalyst has been much paid attention by scientists worldwide since the first photoelectrolysis of water to hydrogen was reported by Fujishima and Honda [1]. Its miracle roles are then investigated in many fields from renewable energy to environmental treatment [2]. One of interesting studies in the environmental treatment is photodegradation of various kinds of dyes discharged from textile industries [3–5]. In contrast to this process, combination of dye with photocatalyst and charge mediator was found to efficiently produce electricity in a dye-sensitized solar cell [6–8] rather than dye decomposition. Dye in such solar cell functions as an antenna to absorb visible light from the sun. Meanwhile, photocatalyst in this solar cell is assigned the role of charge basin from which free electrons produced by excited dye are utilized to produce electricity [9].

Solar energy nowadays is one of the essential sources to save human beings from the coming shortage of energy as well as the warming effect caused by using fossil fuels. Artificial CO₂ reduction by using sunlight that resembles natural photosynthesis is a direct method to both decrease greenhouse gas and supply sustainable energy to us. Although this concept seems to simply solve the serious issue of energy shortage, too low efficiency of the process re-

quires much more studies to bring it to practical applications [10,11].

Inspired by the photosynthesis of plants, Ozcan et al. has been studied the effect of dye adsorbed on photocatalyst on the photoreduction of CO₂ with H₂O to fuels under artificial light [12]. However, the employment of organic dye has limited the efficiency of the system [12]. Owing to the successful stories of dye-sensitized solar cell as previously mentioned, reduction of CO₂ over Ruthenium dye-sensitized TiO₂-based catalysts in an optical-fiber photoreactor is investigated in this current work. Photoactivity comparison of the catalyst under artificial light and concentrated natural sunlight are also studied and discussed.

2. Experimental

Commercial titanium dioxide powder (P25, Degussa) was used as a TiO₂ source. Cu(NO₃)₂ · 3H₂O and Fe(NO₃)₃ · 9H₂O (Aldrich) were employed as precursors of metal dopants on TiO₂ support. Ru^{II}(2,2'-bipyridyl-4,4'-dicarboxylate)₂-(NCS)₂ (also called N3 dye, Solaronix) was used as a dye sensitizer that was dissolved in ethanol (99.5%) to obtain a 3 mM dye solution. The polymer clad of optical fiber (ET tone Taiwan) was removed by calcination at 500 °C for 3 h. This step was followed by washing off the remained residue with 10 M NaOH aqueous solution and distilled water in ultrasonic bath, three times for each.

TiO₂ slurry with corresponding metal salts was prepared by adding aqueous polyethylene glycol solution with the metal salts to TiO₂ powder in a mortar under vigorous grinding with pestle

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[6]. The prepared uniform slurry was coated on optical fibers by dip coating method or on glass plates by a doctor blade technique. The detailed procedures are presented elsewhere [13]. Dye adsorbed catalyst was obtained by dipping the corresponding catalyst into the dye solution of 3 mM for 24 h. Thus dye adsorbed catalyst was then rinsed with ethanol (99.5%) to obtain a monolayer of dye on the catalyst surface. The resulting dye adsorbed catalyst was finally put in an oven at 80 °C for 30 min to remove the residue solvent on the surface of catalyst.

TiO₂ thin films were characterized with X-ray diffraction (XRD, Phillips, Cu K_α radiation) for crystallinity, scanning electron microscopy with energy dispersive X-ray spectrometer (SEM-EDX, Philips XL30, EDAX DX4) for the film thickness and surface morphology and nitrogen adsorption (Micromeritics ASAP 2000) for the BET specific surface area. The band-gap energies of TiO₂ films were determined by UV–vis diffuse reflectance spectroscopy (UV–vis DRS, Varian Cary 100). The baseline of UV–vis DRS was determined by using a standard BaSO₄ layer in contact with a bare glass plate.

Quantum yield (ϕ) of the reaction as well as the amount of catalyst coated on carriers including glass plate and optical fiber is determined by the methods that were discussed in details in our previous report [13].

Photocatalytic reaction was carried out in a continuous circular Pyrex glass reactor (216 cm³) with a quartz window for conduction of light irradiation. Catalyst coated optical fibers were fabricated in the reactor in a way such that the light source (high pressure Hg lamp, 150 W or concentrated natural sunlight) can enter along the fibers to conduct the photocatalytic reaction on its surface as illustrated in the report of Wu et al. [14]. The artificial light (320–500 nm) was supplied by Exfo Acticure 4000 with a highest intensity at 365 nm using an appropriate color filter. The light intensity was measured with a Lumen meter (Exfo). In order to determine the photoactivity of catalyst under real sun, concentrated natural sunlight was collected by using a solar concentrator (Himawari, Japan) as shown in Fig. 1. The reflection dish of the solar concentrator is able to track the sun trajectory during a day. So we can obtain the maximum sunlight intensity. The concentrated sunlight is transmitted via an optical cable and focused on the window of the photo reactor. The light intensity is then measured at the window of the reactor with unit of mW/cm². The reactor was covered with a heating tape connected to temperature controller with a thermocouple placed at the top of the catalyst bed to main-

tain the reaction at around 75 °C. The reactor was purged by CO₂ gas bubbling through distilled water for 1 h at 75 °C before and during the reaction. The space velocity of CO₂ gas and H₂O vapor was maintained at 0.72 h⁻¹ for every experiment. The outlet gases were analyzed at some periods of time by using GC equipped with FID and porapak Q column.

3. Results and discussion

The specific surface area of Cu(0.5 wt%)-Fe(0.5 wt%)/TiO₂ is 48.7 m²/g that is slightly decreased as compared to that of bare TiO₂-P25 (50 m²/g). Slight decrease in band-gap energy is also observed on Cu(0.5 wt%)-Fe(0.5 wt%)/TiO₂ as compared to bare TiO₂-P25 with the values of 3.11 and 2.90 eV, respectively. These results are resulted from the addition of Cu and Fe on TiO₂. Nevertheless, X-ray diffraction patterns of bare TiO₂ and metal doped TiO₂ catalysts in Fig. 2 presents similar crystallinity, which could be ascribed to the well dispersion of metals on TiO₂ surface.

UV–vis spectroscopies of different TiO₂-based thin films are shown in Fig. 3. Bare TiO₂ inherently presents UV light absorption. Meanwhile, owing to the small band-gap of Fe₂O₃ [15], Cu(0.5 wt%)-Fe(0.5 wt%)/TiO₂ is found to relatively absorb visible light. When Cu(0.5 wt%)-Fe(0.5 wt%)/TiO₂ is adsorbed with N3-dye, the resulting catalysts depicts strong absorption in the full range of visible light as shown in Fig. 3c. For the test of dye stability, N3-dye-Cu(0.5 wt%)-Fe(0.5 wt%)/TiO₂ after the photocatalytic reaction of 6 h is also measured in Fig. 3d. The UV–vis spectrum of dye adsorbed catalyst after the reaction is found to shift to the red region. It is well agreed that some dyes either in aqueous solution [16] or as a monolayer on Langmuir–Blodgett films [17,18] could be aggregated under too low pH value [16] or UV irradiation [17,18] to form dimer molecules. These dimer molecules that are also called J-aggregate dimers were found to shift the UV–vis spectra of their corresponding monomer molecules to the red region [16]. Accordingly, the red-shift observed in Fig. 3d could be ascribed to the above J-aggregate phenomenon. In other words, N3 dye that is adsorbed on TiO₂ catalyst is found to be stable under UV irradiation as well as CO₂ photoreduction. This result could be ascribed to the efficient charge transfer in N3-dye-TiO₂ system. Otherwise, N3 dye would be observed to be decomposed after the photoreaction.

The rate and quantum yield of methane and ethylene production over TiO₂-based catalysts under artificial light are shown in



Fig. 1. Photo of solar concentrator employed in this present study.

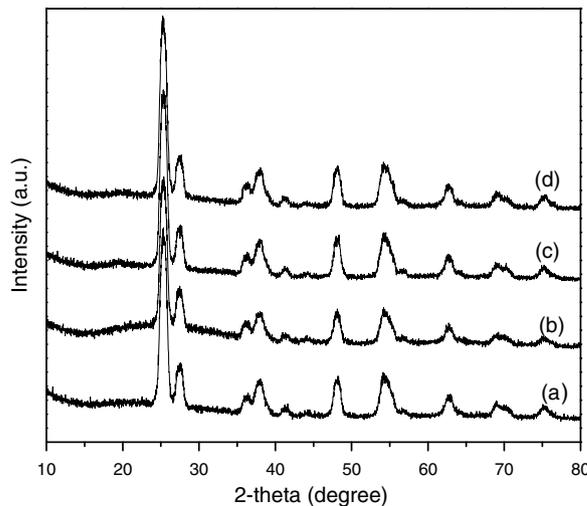


Fig. 2. X-ray diffraction patterns of different catalysts. (a) TiO₂-P25, (b) Cu(1 wt%)/TiO₂, (c) Fe(1 wt%)/TiO₂ and (d) Cu(1 wt%)-Fe(1 wt%)/TiO₂.

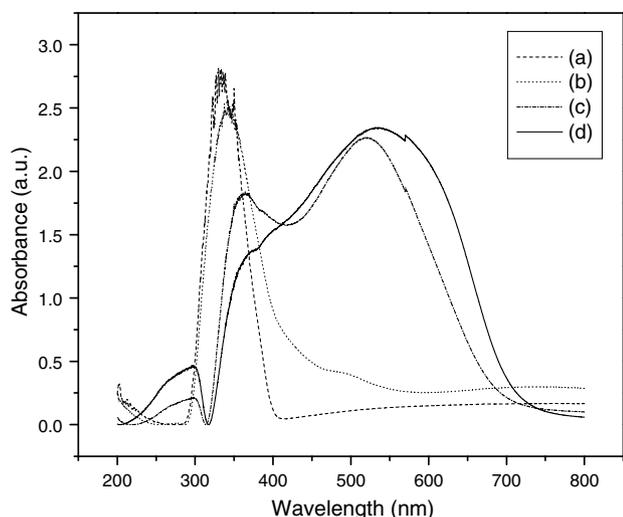


Fig. 3. UV-vis spectroscopy of different TiO₂-SiO₂ mixed oxide thin films. (a) TiO₂, (b) Cu(0.5 wt%)-Fe(0.5 wt%)/TiO₂, (c) N3-dye-Cu(0.5 wt%)-Fe(0.5 wt%)/TiO₂-as prepared and (d) N3-dye-Cu(0.5 wt%)-Fe(0.5 wt%)/TiO₂-after the reaction of 6 h.

Table 1

Production rate of methane and ethylene over TiO₂ based-catalysts under artificial light

Photocatalyst	Ethylene production rate (μmol/g-cat h) ^a	Methane production rate (μmol/g-cat h) ^a
Cu(0.5 wt%)-Fe(0.5 wt%)/TiO ₂ /glass plate	0.049	0.060
Cu(0.5 wt%)-Fe(0.5 wt%)/TiO ₂ /optical fiber	0.575	0.914
N3-dye-Cu(0.5 wt%)-Fe(0.5 wt%)/TiO ₂ /glass plate	0.033	0.148
N3-dye-Cu(0.5 wt%)-Fe(0.5 wt%)/TiO ₂ /optical fiber	0.562	0.847

^a Methane and ethylene production rate were determined on the basis of average production rate after the reaction time of 4 h. The artificial light was in the range of 320–500 nm with the intensity of 225 mW/cm².

Tables 1 and 2, respectively. It is found that production rate of methane and ethylene are similar over both Cu(0.5 wt%)-Fe(0.5 wt%)/TiO₂ and N3-dye-Cu(0.5 wt%)-Fe(0.5 wt%)/TiO₂ catalysts coated on optical fibers. Accordingly, quantum yields of methane and ethylene production over these catalysts are also observed comparable as shown in Table 2. The results in Table 1 imply that N3 dye is not effective for improvement of methane and ethylene production over the catalysts coated on glass fiber. Meanwhile, N3 dye is found to bring about the improvement of methane evolution on the catalyst coated on glass plate as shown in Table 1. This phenomenon could be explained by the direct contact between light and dye in catalyst coated on glass plate. Whereas, in the case of catalyst coated on optical fiber the light is scattered in TiO₂ matrix when it is reaching to the adsorbed dye. Although the glass plate is a promising carrier for dye adsorbed catalyst to increase methane production, its total fuel production rate is too low as compared to that of dye adsorbed catalyst coated on optical fiber as depicted in Table 1.

Accordingly, for the experiments using concentrated natural sunlight as the irradiation source, optical fiber is employed as a catalyst carrier. The data are shown in Table 3. Interestingly, N3 dye is observed to increase the photoactivity of Cu(0.5 wt%)-Fe(0.5 wt%)/TiO₂ catalyst up to over 100% under concentrated nat-

Table 2

Quantum yield (ϕ) and energy efficiency (η) of ethylene and methane production over different catalysts under artificial light

Photocatalyst	C ₂ H ₄ evolution		CH ₄ evolution		η_{total} (%)
	ϕ (%) ^a	η (%) ^a	ϕ (%) ^a	η (%) ^a	
Cu(0.5 wt%)-Fe(0.5 wt%)/TiO ₂ /optical fiber	0.0235	0.008	0.0245	0.008	0.016
N3-dye-Cu(0.5 wt%)-Fe(0.5 wt%)/TiO ₂ /optical fiber	0.0226	0.008	0.0228	0.007	0.015

^a One photon energy at 365 nm is 5.45×10^{-19} J. Photon energy absorbed by fibers is 17.4 mW (17.4×10^{-3} J s⁻¹). Total numbers of absorbed photon per second are 3.19×10^{16} .

Table 3

Production rate of methane over catalysts under concentrated natural sunlight^a

Photocatalyst	Methane production rate (μmol/g-cat h) ^b
Cu(0.5 wt%)-Fe(0.5 wt%)/TiO ₂ /optical fiber	0.281 ^c
N3-dye-Cu(0.5 wt%)-Fe(0.5 wt%)/TiO ₂ /optical fiber	0.617 ^d

^a Concentrated natural sunlight was obtained by using the solar concentrator as illustrated in the experimental section.

^b Methane production rate was determined on the basis of average production rate after the reaction time of 4 h.

^c Experiment for Cu(0.5 wt%)-Fe(0.5 wt%)/TiO₂ catalyst was carried out in May 4, 2007 in Taipei, Taiwan from 9.20 am to 2.50 pm under average concentrated solar light intensity of 60 mW/cm².

^d Experiment for Ru-dye-Cu(0.5 wt%)-Fe(0.5 wt%)/TiO₂ catalyst was carried out in April 12, 2007 in Taipei, Taiwan from 9.20 am to 2.50 pm under average concentrated solar light intensity of 20 mW/cm².

ural sunlight. The superior photo production of dye adsorbed catalyst could be ascribed to the strong absorption of N3 dye in visible range as presented in Fig. 3c. Although dye adsorbed catalyst is observed to produce both methane and ethylene under artificial light, it is only photoactive towards methane production under concentrated natural sunlight as shown in Table 3. This result could be resulted from the too low intensity of concentrated natural sunlight, which might not supply enough driving force to reduce CO₂ to ethylene.

It is also interestingly to compare the data in Tables 1 and 3. Under artificial light irradiation with the intensity of 225 mW/cm² (Table 1), the production rate of methane and ethylene over Cu(0.5 wt%)-Fe(0.5 wt%)/TiO₂ catalyst coated on optical fiber are 0.575 and 0.914 μmol/g-cat h, respectively, which is found in the same order of magnitude with those of N3-dye-Cu(0.5 wt%)-Fe(0.5 wt%)/TiO₂ counterpart. However, under the concentrated natural sunlight with the average intensity of ca. 60 mW/cm², Cu(0.5 wt%)-Fe(0.5 wt%)/TiO₂ catalyst coated on optical fiber only produces methane with very low production rate of 0.281 μmol/g-cat h. Meanwhile, N3-dye-Cu(0.5 wt%)-Fe(0.5 wt%)/TiO₂ catalyst coated on optical fiber still maintains almost the same order of magnitude for methane production under concentrated natural sunlight as compared to that under artificial light irradiation (Tables 1 and 3) despite the average intensity of concentrated natural sunlight of only ca. 20 mW/cm². These results once again could be ascribed to the strong visible light absorption of the N3-dye-Cu(0.5 wt%)-Fe(0.5 wt%)/TiO₂ catalyst as compared to that of Cu(0.5 wt%)-Fe(0.5 wt%)/TiO₂ counterpart. Note that the wavelength of our artificial light is 320–500 nm while the wavelength of the concentrated sunlight is extended to the range of 500–800 nm. The N3-dye-Cu(0.5 wt%)-Fe(0.5 wt%)/TiO₂ catalyst can fully absorb the light energy of 500–800 nm but Cu(0.5 wt%)-Fe(0.5 wt%)/TiO₂ catalyst cannot as shown in Fig. 3. Another

possible explanation of this phenomenon might result from the efficient charge transfer in the N3-dye-TiO₂ system, which is supported by the stable UV-vis spectrum of N3-dye adsorbed TiO₂ after 6 h-photoreaction in Fig. 3d.

4. Conclusions

N3 dye is found to substantially improve the photoactivity of Cu(0.5 wt%)-Fe(0.5 wt%)/TiO₂ catalyst towards methane production under concentrated natural sunlight. The superior photoactivity of the N3 dye adsorbed TiO₂ catalyst towards methane production under concentrated natural sunlight is ascribed to its full visible light absorption. Photoactivity of N3 dye adsorbed catalyst towards CO₂ reduction is stable up to 6 h under artificial light and concentrated natural sunlight irradiation, presenting the efficient charge transfer in N3-dye-TiO₂ system as well as the promising application of dye adsorbed catalyst in fuel production.

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