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CO₂ Reduction Characteristics of Cu/TiO₂ with Various Reductants

Akira Nishimura

Abstract

Cu-doped TiO₂ (Cu/TiO₂) film photocatalyst was prepared by combination of sol-gel and dip-coating process and pulse arc plasma method. The effect of Cu/TiO₂ photocatalyst on CO₂ reduction performance with reductants of H₂O and H₂ or NH₃ was investigated. In addition, the overlapping two Cu/TiO₂ coated on netlike glass discs were also investigated. The CO₂ reduction performance of Cu/TiO₂ film was tested under illumination of Xe lamp with or without ultraviolet (UV) light, respectively. As to the condition of CO₂/H₂/H₂O, the best CO₂ reduction performance has been achieved under the condition of CO₂/H₂/H₂O = 1:0.5:0.5 with UV light illumination as well as without UV light illumination. The theoretical molar ratio of CO₂/H₂O or CO₂/H₂ to produce CO is 1:1. Since the molar ratio of CO₂/H₂/H₂O = 1:0.5:0.5 can be regarded as the molar ratio of CO₂/total reductants = 1:1, it is believed that the results of this study follow the reaction scheme of CO₂/H₂O and CO₂/H₂. On the other hand, as to the condition of CO₂/NH₃/H₂O, the best CO₂ reduction performance has been achieved under the condition of CO₂/H₂/H₂O = 1:1:1 with UV light illumination as well as without UV light illumination.

Keywords: CO₂ reduction, Cu/TiO₂ photocatalyst, reductants combination, visible light, overlapping effect

1. Introduction

Paris Agreement adopted in 2015 sets the goal that the increase in average temperature in the world from the industrial revolution by 2030 should be kept less than 2 K. However, due to the increase in the averaged concentrations of CO₂ in the atmosphere to 410 ppmV in December 2019 [1], CO₂ reduction or utilization technologies to recycle CO₂ are urgently required.

There are six vital CO₂ conversions: chemical conversions, electrochemical reductions, biological conversions, reforming, inorganic conversions, and photochemical reductions [2, 3]. Recently, artificial photosynthesis or the photochemical reduction of CO₂ to fuel has become an attractive route due to its economically and environmentally friendly behavior [2].

The application of CO₂ as a raw material can produce chemicals and energy to diminish the CO₂ accumulation in the atmosphere [2]. If we consider energy producing possibilities, one possibility is the photochemical conversion of CO₂ into value-added chemicals which could be used as fuel [4].

The most widely used photocatalyst for the photocatalytic reactions is TiO₂ due to its availability, chemical stability, low cost, and resistance to corrosion [5]. It is

well known that CO₂ can be reduced into fuels, e.g., CO, CH₄, CH₃OH, H₂, etc. by using TiO₂ as the photocatalyst under ultraviolet (UV) light illumination [6–9]. However, pure TiO₂ has the limitation. It is only active when irradiated by UV light, which is not effective under sunlight. Since the solar spectrum only consists of about 4% of UV light, sunlight is not able to activate the TiO₂ effectively for photocatalytic reaction. In addition, TiO₂ has a high electron/hole pair recombination rate compared to the rate of chemical interaction with the absorbed species for redox reactions [10].

Recently, studies on CO₂ photochemical reduction by TiO₂ have been carried out from the viewpoint of performance promotion by extending absorption wavelength toward visible region. It was reported that a transition metal doping is useful technique for extending the absorbance of TiO₂ into the visible region [11–15]. Noble metal doping such as Pt, Pd, Au and Ag [11], Au, Pd-three dimensionally ordered macroporous TiO₂ [12], composition materials formed by GaP and TiO₂ [13], nanocomposite CdS/TiO₂ combining two different band gap photocatalysts [14], and carbon-based AgBr nanocomposited TiO₂ [15], had been attempted to overcome the shortcomings of the pure TiO₂. They could improve the CO₂ reduction performance; however, the concentrations in the products achieved in all the attempts so far were still low, ranging from 1 to 150 μmol/g-cat [11–16].

Though various metals have been used for doping [11–16], Cu is considered as a favorite candidate. Cu can extend the absorption band to 600–800 nm [17, 18], which covers the whole visible light range. Cu-decorated TiO₂ nanorod thin film performed 10 times yield as large as TiO₂ for C₂H₅OH production [19]. Cu-loaded N/TiO₂ also showed the good performance which yielded eight times as large as TiO₂ for CH₄ production [20]. Noble metals such as Pt and Au are too expensive to be used in industrial scale. Therefore, Cu is the best candidate because of its high efficiency and low cost compared to noble metals. Due to its availability as well as above described characteristics, Cu is selected as the dopant in this study.

Since a reductant is necessary for CO₂ reduction to produce fuel; H₂O and H₂ are usually used as reductants according to the review papers [7, 9]. To promote the CO₂ reduction performance of photocatalyst, it is important to select the optimum reductant which provides the proton (H⁺) for the reaction scheme of CO₂ reduction with H₂O is as follows [21–23]:

<Photocatalytic reaction>

<Oxidization>

<Reduction>

The reaction scheme of CO₂ reduction with H₂ is as follows [24]:

<Photocatalytic reaction>

<Oxidization>

<Reduction>

The reaction scheme to reduce CO₂ with NH₃ can be summarized as shown below [24, 25]:

<Photocatalytic reaction>

<Oxidization>

<Reduction>

There are some reports on CO₂ reduction with either H₂O or H₂ [7, 9]. However, the effect of using H₂O and H₂ or NH₃ together as reductants is not investigated well. Though a few studies using pure TiO₂ under CO₂/H₂/H₂O condition were reported [24, 26], the effect of ratio of CO₂, H₂ and H₂O or NH₃ as well as the effect of Cu doping with TiO₂ on CO₂ reduction performance of photocatalyst were not investigated previously.

Consequently, the purpose of this chapter is to clarify the effect of molar ratio of CO₂ to H₂O and H₂ or NH₃ on the performance of CO₂ reduction with Cu/TiO₂. The CO₂ reduction performance with H₂O and H₂ or NH₃ using Cu/TiO₂ coated on netlike glass fiber as photocatalyst under the condition of illuminating Xe lamp with or without UV light was investigated. Cu is loaded on TiO₂-coated netlike glass fiber by pulse arc plasma method which can emit nanosized Cu particles by applying high electron potential difference. The amount of loaded Cu can be controlled by the pulse number. Cu/TiO₂ prepared was characterized by Scanning Electron Microscope (SEM) and Electron Probe Micro Analyzer (EPMA), Transmission Electron Microscope (TEM), Energy Dispersive X-ray Spectrometry (EDX), and Electron Energy Loss Spectrum (EELS) analysis. The CO₂ reduction performance with H₂O and H₂ or NH₃ under the condition of illuminating Xe lamp with or without UV

light was investigated. The molar ratio of $\text{CO}_2/\text{H}_2/\text{H}_2\text{O}$ was changed for 1:1:1, 1:0.5:1, 1:1:0.5, 1:0.5:0.5 to clarify the optimum combination of $\text{CO}_2/\text{H}_2/\text{H}_2\text{O}$ for CO_2 reduction with Cu/TiO_2 . According to the reaction scheme to reduce CO_2 with H_2O or NH_3 as shown above, the theoretical molar ratio of $\text{CO}_2/\text{H}_2\text{O}$ to produce CO or CH_4 is 1:1 or 1:4, respectively, while that of CO_2/NH_3 to produce CO or CH_4 is 3:2, 3:8, respectively. Therefore, this study assumes that the molar ratio of $\text{CO}_2/\text{NH}_3/\text{H}_2\text{O} = 3:2:3$ and $3:8:12$ are theoretical molar ratio to produce CO and CH_4 , respectively. Moreover, the effect of overlapping two layers of Cu/TiO_2 -coated netlike glass fiber on CO_2 reduction performance with H_2 and H_2O was investigated.

2. Experiment

2.1 Preparation of Cu/TiO_2 film

The combination of sol-gel and dip-coating process was used for preparing TiO_2 film. TiO_2 sol solution was made by mixing $[(\text{CH}_3)_2\text{CHO}]_4\text{Ti}$ (purity of 95 wt%, Nacalai Tesque Co.) of 0.3 mol, anhydrous $\text{C}_2\text{H}_5\text{OH}$ (purity of 99.5 wt%, Nacalai Tesque Co.) of 2.4 mol, distilled water of 0.3 mol, and HCl (purity of 35 wt%, Nacalai Tesque Co.) of 0.1 mol. Netlike glass fiber was cut like a disc, and its diameter and thickness were 50 mm and 1 mm, respectively. The netlike glass fiber disc was dipped into TiO_2 sol solution at the speed of 1.5 mm/s and pulled up at the fixed speed of 0.2 mm/s. Then, it was dried out and fired under the controlled firing temperature (FT) and firing duration time (FD), resulting that TiO_2 film was fastened on the netlike glass fiber. FT and FD were set at 623 K and 180 s, respectively. Cu was loaded on TiO_2 film by pulse arc plasma method. The pulse arc plasma gun device (ULVAC, Inc., ARL-300) having Cu electrode whose diameter was 10 mm was applied for Cu loading. After the netlike glass fiber coated with TiO_2 was set in chamber of the pulse arc plasma gun device which was vacuumed, the nanosized Cu particles were emitted from Cu electrode with applying the electrical potential difference of 200 V. The pulse arc plasma gun can evaporate Cu particle over the target in the circle area whose diameter is 100 mm when the distance between Cu electrode and the target is 160 mm. Since the difference between Cu electrode and TiO_2 film was 150 nm in the present study, Cu particle can be evaporated over TiO_2 film uniformly. The amount of loaded Cu was controlled by the pulse number. In the present study, the pulse number was set at 100. Since the netlike glass fiber is transparent, the light can pass through the netlike glass fiber. The present study has also investigated if two layers of two Cu/TiO_2 coated on netlike glass fiber put on the top of the other (with certain distance, i.e., overlapping), what impact/improvement would be on the CO_2 reduction performance. The overlapping two layers of Cu/TiO_2 coated on netlike glass fiber is expected to utilize the light effectively as well as to increase the amount of photocatalyst used for CO_2 reduction.

2.2 Characterization of Cu/TiO_2 film

The structure and crystallization characteristics of Cu/TiO_2 film were evaluated by SEM (JXS-8530F, JEOL Ltd.), EPMA (JXA-8530F, JEOL Ltd.), TEM (JEM-2100/HK, JEOL Ltd.), EDX (JEM-2100F/HK, JEOL Ltd.), and EELS (JEM-ARM2007 Cold, JEOL Ltd.). Since these measurement instruments use electron for analysis, the sample should be an electron conductor. Since netlike glass disc was not an electron for analysis, the carbon vapor deposition was conducted by the dedicated device (JEE-420, JEOL Ltd.) for Cu/TiO_2 coated on netlike glass disc before analysis. The thickness of carbon deposited on sample was approximately 20–30 nm.

The electron probe emits the electrons to the sample under the acceleration voltage of 15 kV and the current of 3.0×10^{-8} A, when the surface structure of sample is analyzed by SEM. The characteristic X-ray is detected by EPMA at the same time, resulting that the concentration of channel element is analyzed according to the relationship between the characteristic X-ray energy and the atomic number. The spatial resolutions of SEM and EPMA are 10 μ m. The EPMA analysis helps not only to understand the coating state of prepared photocatalyst but also to measure the amount of doped metal within TiO₂ film on the base material.

The electron probe emits the electron to the sample under the acceleration voltage of 200 kV, when the inner structure of sample is analyzed by TEM. The size, thickness, and structure of loaded Cu were evaluated. The characteristic X-ray is detected by EDX at the same time, resulting that the concentration distribution of chemical element toward thickness direction of the sample is analyzed. In the present study, the concentration distribution of Ti and Cu were analyzed.

EELS can be applied not only for element detection but also determination of oxidization states of some transition metals. The EELS characterization was performed by JEM-ARM200F equipped with GIF Quantum having 2048 ch. The dispersion of 0.5 eV/ch can be achieved for the full width at half maximum of the zero loss peak.

2.3 CO₂ reduction experiment

Figure 1 [27, 28] shows the experimental set-up of the reactor composing of stainless tube (100 mm (H.) $\times$ 50 mm (I.D.)), Cu/TiO₂ film coated on netlike glass disc (50 mm (D.) $\times$ 1 mm (t.)) located on the Teflon cylinder (50 mm (H.) $\times$ 50 mm (D.)), a quartz glass disc (84 mm (D.) $\times$ 10 mm (t.)), a sharp cut filter cutting off the light whose wavelength is below 400 nm (SCF-49.5C-42 L, SIGMA KOKI CO. LTD.), a 150 W Xe lamp (L2175, Hamamatsu Photonics K. K.), mass flow controller, and CO₂ gas cylinder. The volume of reactor to charge CO₂ is 1.3×10^{-4} m³. The light of Xe lamp which is located inside the stainless tube illuminates Cu/TiO₂ film coated on the netlike glass disc through the sharp cut filter and the quartz glass disc that are at the top of the stainless tube. The wavelength of light from Xe lamp is ranged from 185 to 2000 nm. Since the sharp cut filter can remove UV components of the light from the Xe lamp, the wavelength of light from Xe lamp is ranged from 401 to 2000 nm with the filter. **Figure 2** [29] shows the performance of the sharp cut filter to cut off the wavelength is below 400 nm. The

Figure 1.
Schematic drawing of CO₂ reduction experimental set-up (left: CO₂/H₂/H₂O system; right: CO₂/NH₃/H₂O system).

Figure 2.
Light transmittance data of sharp cut filter.

average light intensity of Xe lamp without and with the sharp cut filter is 58.2 and 33.8 mW/cm², respectively.

In the CO₂ reduction experiment with H₂ and H₂O, CO₂ gas with the purity of 99.9 vol% which were controlled by mass flow controller was mixed in the buffer chamber and introduced into the reactor which was pre-vacuumed by a vacuum pump. The mixing ratio of CO₂ and H₂ was confirmed by TCD gas chromatograph (Micro GC CP4900, GL Science) before introducing into the reactor. After confirming the mixing ratio of CO₂ and H₂, the distilled water was injected into the reactor through a gas sampling tap by syringe and Xe lamp illumination was turned on the same time. The amount of injected water was measured and controlled by the syringe. The injected water vaporized completely in the reactor. The molar ratio of CO₂/H₂/H₂O was set at 1:1:1, 1:0.5:1, 1:1:0.5, 1:0.5:0.5. Due to the heat of Xe lamp, the temperature in reactor was attained at 343 K within an hour and kept an approximately 343 K during the experiment.

In the CO₂ reduction experiment with NH₃ and H₂O, after purging the reactor with CO₂ gas of 99.9 vol% purity introduced in the reactor, which was pre-vacuumed by a vacuum pump, for 15 minutes, the valves located at the inlet and the outlet of reactor were closed. After confirming the pressure and gas temperature in the reactor at 0.1 MPa and 298 K, respectively, the NH₃ aqueous solution (NH₃; 50 vol%), which was changed according to the planed molar ratio, was injected into the reactor through gas sampling tap, and Xe lamp illumination was turned on the same time. The NH₃ aqueous solution injected was vaporized completely in the reactor. Due to the heat of Xe lamp, the temperature in the reactor was attained at 343 K within an hour and kept at approximately 343 K during the experiment. The molar ratio of CO₂/NH₃/H₂O was set at 1:1:1, 1:0.5:1, 1:1:0.5, 1:0.5:0.5, 3:2:3, 3:8:12, respectively. The gas in the reactor was sampled every 24 hours during the experiment. The gas samples were analyzed by FID gas chromatograph (GC353B, GL Science). Minimum resolution of FID gas chromatograph and methanizer is 1 ppmV.

3. Results and discussion

3.1 Characterization analysis of Cu/TiO₂ film

Figure 3 shows SEM image of Cu/TiO₂ film coated on netlike glass disc [28]. The SEM image was taken at 1500 times magnification. **Figure 4** shows EPMA image of

Cu/TiO₂ film coated on netlike glass disc [28]. EPMA analysis was carried out for SEM images taken by 1500 times magnification. In EPMA image, the concentration of each element in observation area is indicated by the different colors. Light colors, for example, white, pink, and red indicate that the amount of element is large, while dark colors like black and blue indicate that the amount of element is small.

From these figures, it can be observed that TiO₂ film was coated on netlike glass fiber. During firing process, the temperature profile of TiO₂ solution adhered on the netlike glass disc was not even due to the different thermal conductivities of Ti and SiO₂. Their thermal conductivities of Ti and SiO₂ at 600 K are 19.4 and 1.8 W/(m·K) [30], respectively. Due to thermal expansion and shrinkage around netlike glass fiber, it can be considered that thermal crack is formed on the TiO₂ film.

In addition, it is observed from **Figure 4** that nanosized Cu particles are loaded on TiO₂ uniformly, resulted from that the pulse arc plasma method can emit nanosized Cu particles.

To evaluate the amount of loaded Cu within TiO₂ film quantitatively, the observation area, which is the center of netlike glass disc, of diameter of 300 μm is analyzed by EPMA. The ratio of Cu to Ti is counted by averaging the data obtained in this area. As a result, the weight percentages of elements of Cu and Ti in the Cu/TiO₂ film are 0.6 and 99.4 wt%, respectively.

Figure 3.
SEM image of Cu/TiO₂ film coated on netlike glass disc.

Figure 4.
EPMA image of Cu/TiO₂ film coated on netlike glass disc.

Figures 5 and 6 show TEM and EDX images of Cu/TiO₂ film, respectively [27]. ESX analysis was carried out using TEM image taken by 150,000 times magnification. According to **Figure 6**, it is observed that Cu particles are distributed in TiO₂ film. Though many Cu particles are loaded on the upside of TiO₂ film, it is not confirmed that the Cu layer is formed.

Figure 7 shows EELS spectra of Cu in Cu/TiO₂ film [27]. From this figure, the peaks at around 932 and 952 eV can be observed. Compared to the report investigating peaks of Cu, Cu₂O, and CuO [31], the EELS spectra of Cu₂O matches with **Figure 7**. Therefore, Cu in Cu/TiO₂ prepared in this study exists as Cu⁺ ion in Cu₂O. It was reported that the heterojunctions between CuO and TiO₂ contributed to the promotion of the photoactivity [32]. In addition, it was reported that Cu⁺ was more active than Cu²⁺ [33]. Therefore, it is expected that Cu⁺ would play a role to enhance the CO₂ reduction performance in this study. **Figure 8** shows EELS spectra of TiO₂ referred from EELS data base [34]. Comparing **Figure 8** with **Figure 7**, EELS spectra of TiO₂ is very different from EELS spectra of Cu in Cu/TiO₂.

3.2 Effect of molar ratio of CO₂, H₂, and H₂O on CO₂ reduction characteristics

Figures 9 and 10 show the concentration changes of CO and CH₄ produced in the reactor along the time under the illumination of Xe lamp with UV light,

Figure 5.
TEM image of Cu/TiO₂ film.

Figure 6.
EDX images of Cu/TiO₂ film.

Figure 7.
EELS spectra of Cu in Cu/TiO₂.

Figure 8.
EELS spectra of TiO₂ referred from EELS data base [34].

Figure 9.
Change of concentration of CO with time for several molar ratios of CO₂/H₂/H₂O under illumination condition with UV light.

respectively. **Figures 11 and 12** show the molar quantities of CO and CH₄ per weight of photocatalyst in the reactor along the time under the illumination of Xe lamp with UV light, respectively. The amount of Cu/TiO₂ is 0.2 g. In this experiment, a blank test, that was running the same experiment without illumination of Xe lamp,

had been carried out to set up a reference case. No fuel was produced in the blank test as expected.

According to **Figures 9–12**, the CO₂ reduction performance is the highest for the molar ratio of CO₂/H₂/H₂O = 1:0.5:0.5. Since the reaction scheme of CO₂/H₂/H₂O is not fully understood, this study refers to the reaction scheme of CO₂/H₂O and CO₂/H₂ as shown by Eqs. (1)–(12). It is known from the reaction scheme that the theoretical molar ratio of CO₂/H₂O and CO₂/H₂ to produce CO is 1:1. On the other hand, the theoretical molar ratio of CO₂/H₂O and CO₂/H₂ to produce CH₄ is 1:4. Since the molar ratio of CO₂/H₂/H₂O = 1:0.5:0.5 can be regarded as the molar ratio of CO₂/total reductants = 1:1, it is believed that the results of this study follow the reaction scheme presented in Eqs. (1)–(12). Comparing the CO production with the CH₄ production, CO is produced first. According to Eq. (5), it is believed that some CO might be converted into CH₄. Therefore, the start of CH₄ production is slower than that of CO production. Producing CH₄ needs four times H⁺ and electrons as many as producing CO needs. Therefore, it is revealed that the optimum molar ratio

Figure 10.

Change of concentration of CH₄ with time for several molar ratios of CO₂/H₂/H₂O under illumination condition with UV light.

Figure 11.

Change of molar quantity of CO per unit weight of photocatalyst with time for several molar ratios of CO₂/H₂/H₂O under illumination condition with UV light.

Figure 12.
Change of molar quantity of CH₄ per unit weight of photocatalyst with time for several molar ratios of CO₂/H₂/H₂O under illumination condition with UV light.

Figure 13.
Change of concentration of CO with time for several molar ratios of CO₂/H₂/H₂O under illumination condition without UV light.

of CO₂/H₂/H₂O is decided by the CO production scheme. Though CO decreases after reaching the peak, CH₄ increases gradually.

According to Hinojosa-Reyes et al. [35], TiO₂ and Cu₂O formation leads to the photocatalytic activity since Cu₂O is a semiconductor with small band gap energy. In addition, Cu performs to avoid the electron and hole recombination and promotes the charge transfer. In this study, it seems that the effect of Cu and Cu₂O on photoactivity is performed.

Figures 13 and 14 show the concentration changes of CO produced and the molar quantity of CO per weight of photocatalyst in the reactor under the illumination of Xe lamp without UV light, respectively. In this experiment, CO is the only fuel produced from the reactions.

According to **Figures 13 and 14**, the CO₂ reduction performance is also the highest for the molar ratio of CO₂/H₂/H₂O = 1:0.5:0.5 in this case. It is considered that the same reaction mechanism as mentioned above is conducted. The CO₂ reduction performance of Cu/TiO₂ under the illumination condition without UV

Figure 14.

Change of molar quantity of CO per unit weight of photocatalyst with time for several molar ratios of $\text{CO}_2/\text{H}_2/\text{H}_2\text{O}$ under illumination condition without UV light.

Figure 15.

Change of concentration of CO for Cu/TiO_2 overlapped with time for several molar ratios of $\text{CO}_2/\text{H}_2/\text{H}_2\text{O}$ under illumination condition with UV light.

light is lower than that under the illumination condition with UV light. Therefore, it can be claimed that Cu/TiO_2 obtains the main photoenergy from UV light.

3.3 Effect of overlapping of Cu/TiO_2 film with H_2 and H_2O on CO_2 reduction characteristics

Figures 15 and 16 show the concentration change of CO and CH_4 produced in the reactor under the illumination of Xe lamp with UV light, with two Cu/TiO_2 films coated on netlike glass discs overlapped, respectively. The photocatalyst is coated on both upper and lower surfaces of the top disc and only the upper surface of the bottom disc.

Figures 17 and 18 show the molar quantities of CO and CH_4 per weight of photocatalyst in the reactor along the time under the Xe lamp with UV light, respectively. The total amount of Cu/TiO_2 on two discs is 0.4 g.

Figure 16.
Change of concentration of CH₄ for Cu/TiO₂ overlapped with time for several molar ratios of CO₂/H₂/H₂O under illumination condition with UV light.

Figure 17.
Change of molar quantity of CO per unit weight of photocatalyst for Cu/TiO₂ overlapped with time for several molar ratios of CO₂/H₂/H₂O under illumination condition with UV light.

Figure 18.
Change of molar quantity of CH₄ per unit weight of photocatalyst for Cu/TiO₂ overlapped with time for several molar ratios of CO₂/H₂/H₂O under illumination condition with UV light.

According to **Figures 15–18**, the CO₂ reduction performance is the highest for the molar ratio of CO₂/H₂/H₂O = 1:0.5:0.5, the same as that in the case of single Cu/TiO₂ disc. In addition, the order of CO₂ reduction performance of Cu/TiO₂ overlapped is the same as that of single Cu/TiO₂. However, comparing **Figures 15 and 16** with **Figures 9 and 10**, the concentrations of CO and CH₄ for two Cu/TiO₂ discs overlapped are higher than those for single Cu/TiO₂ disc under every molar ratio of CO₂/H₂/H₂O. The highest concentration of CO for Cu/TiO₂ overlapped is 7273 ppmV, which is 1.4 times as large as that for single Cu/TiO₂. On the other hand, the highest concentration of CH₄ for Cu/TiO₂ overlapped is 516 ppmV, which is 1.7 times as large as that for single Cu/TiO₂. In the case of two discs overlapped, the following things are believed: (i) the amount of photocatalyst used for photocatalysis reaction is increased, (ii) the electron transfer between two Cu/TiO₂ films promotes the activity of photocatalysis reaction, and (iii) the lower positioned Cu/TiO₂ disc utilizes the light passing through the top disc.

However, comparing **Figures 17 and 18** with **Figures 11 and 12**, the molar quantities of CO and CH₄ per weight of photocatalyst in two discs case are lower than those for single Cu/TiO₂ disc case under every molar ratio of CO₂/H₂/H₂O. The highest molar quantity of CO per weight of photocatalyst in two discs overlapped case is 82 µmol/g, which is 54% of that in single disc case. Similarly, the highest molar quantity of CH₄ per weight of photocatalyst in two discs overlapped case is 5.8 µmol/g, which is 65% of that in single disc case. The reasons of this result are considered to be: (i) some parts of the Cu/TiO₂ film on the lower positioned disc cannot receive the light, (ii) if the produced fuel remains in the space between two discs, the reactants of CO₂, H₂, and H₂O would be blocked to reach the surface of photocatalyst, resulting that the photochemical reaction could not be carried out well even though the light is illuminated for photocatalyst.

Figures 19 and 20 show the concentration changes of CO produced and the molar quantity of CO per weight of photocatalyst in the reactor with two overlapped Cu/TiO₂ film coated on netlike glass disc under the illumination of Xe lamp without UV light, respectively. In this experiment, CO is the only produced from the reactions.

According to **Figures 19 and 20**, the CO₂ reduction performance in two discs case is the highest for the molar ratio of CO₂/H₂/H₂O = 1:0.5:0.5 which is the same as

Figure 19.

Change of concentration of CO for Cu/TiO₂ overlapped with time for several molar ratios of CO₂/H₂/H₂O under illumination condition without UV light.

Figure 20. Change of molar quantity of CO per unit weight of photocatalyst for Cu/TiO₂ overlapped with time for several molar ratios of CO₂/H₂/H₂O under illumination condition without UV light.

that in the single disc case. The order of CO₂ reduction performance in two discs is the same as that in the single disc case. However, comparing **Figure 19** with **Figure 13**, the concentrations in two discs case are higher than those in single case under every molar ratio of CO₂/H₂/H₂O. The highest concentration of CO in two discs case is 271 ppmV, which is 2.8 times as large as that in single disc case. The same reasons explained in the case of illumination with UV light can be thought to cause the results.

In addition, comparing **Figure 20** with **Figure 14**, the molar quantity of CO per weight of photocatalyst in two Cu/TiO₂ discs overlapped case is singly higher than that in the single disc case under every molar ratio of CO₂/H₂/H₂O. The highest molar quantity of CO per weight of photocatalyst is 3.1 μmol/g in two disc cases, which is 1.1 times as large as that in the single disc case. Though the effect of overlapping layout is not obtained under the illumination condition with UV light, the effect of overlapping layout is confirmed under the illumination condition without UV light. Since the photochemical reaction rate and the amount of produced fuel are small under the no-UV illumination condition compared to that with UV light, it would be beneficial to the mass transfer between produced fuels and reactants of CO₂, H₂, and H₂O on the surface of photocatalyst in no-UV cases [36]. As a result, the mass transfer and photochemical reaction are carried out effectively in no-UV cases. Therefore, the effect of overlapping layout is obtained in no-UV cases. According to the previous reports [37, 38], the mass transfer is an inhibition factor to promote the CO₂ reduction performance of photocatalyst, and it is necessary to control the mass transfer rate to meet the photochemical reaction rate. **Figure 21** illustrates the comparison of mass and electron transfer within overlapped two photocatalysts in UV and no-UV illumination cases [27].

3.4 Effect of molar ratio of CO₂, NH₃ and H₂O on CO₂ reduction characteristics

Figures 22 and 23 show the concentration changes of formed CO and CH₄, along the time under the Xe lamp with UV light, respectively. The amount of Cu/TiO₂ on the netlike glass disc is 0.1 g. Before the experiments, a blank test, which was running the same experiment without illumination of Xe lamp, had been carried out to set up a reference case. No fuel was produced in the blank test as expected.

Figure 21. Comparison of mass and electron transfer within overlapped two photocatalysts between the illumination condition with UV light and without UV light.

Figure 22. Comparison of concentration of formed CO among several molar ratios of $CO_2/NH_3/H_2O$ under the illumination condition with UV light.

According to **Figures 22 and 23**, the CO_2 reduction performance is the highest for the molar ratio of $CO_2/NH_3/H_2O = 1:1:1$.

According to the reaction scheme to reduce CO_2 with H_2O or NH_3 as shown by Eqs. (1)–(5), (13)–(20), the theoretical molar ratio of CO_2/H_2O to produce CO or CH_4 is 1:1 or 1:4, respectively, while that of CO_2/NH_3 to produce CO or CH_4 is 3:2,

Figure 23.
 Comparison of concentration of formed CH₄ among several molar ratios of CO₂/NH₃/H₂O under the illumination condition with UV light.

3:8, respectively. Therefore, this study assumes that the molar ratio of CO₂/NH₃/H₂O = 3:2:3 and 3:8:12 is theoretical molar ratio to produce CO and CH₄, respectively. However, the molar ratio of CO₂/NH₃/H₂O = 1:1:1 is not matched with these theoretical molar ratios to produce CO and CH₄. Since the ionized Cu doped with TiO₂ provides free electron for the reduction reaction process [39], the reductants of NH₃ and H₂O which are less than the values indicated in the theoretical scheme are enough for producing CO and CH₄ in this study. The highest molar quantities of CO and CH₄ per weight of photocatalyst in the reactor, which are obtained for the molar ratio of CO₂/NH₃/H₂O = 1:1:1, are 10.2 and 1.8 μmol/g, respectively.

In addition, it is confirmed from **Figure 22** that the concentration of formed CO is increased from the start of illumination of Xe lamp and decreased after attaining the peak concentration. However, the concentration of formed CO increases again after 48 hours. It is believed that the decrease in the concentration of formed CO is resulted from the oxidization reaction between CO and O₂ which is by-product as shown in Eq. (3) [40]. Since the produced CO might be remained near the photocatalyst due to high absorption performance of netlike glass fiber, this oxidization reaction is thought to be occurred. The increase in the concentration of formed CO after 48 hours might be due to the difference in reaction rates between CO₂/H₂O and CO₂/NH₃ condition. It is also revealed that the maximum concentration of formed CO is higher when the molar of NH₃ is higher than that of H₂O. Since the number of H⁺ which can be provided is 3 and 2 for NH₃ and H₂O, respectively, it is considered that NH₃ is effective for promoting the reduction performance of Cu/TiO₂. Furthermore, it is found from **Figures 22** and **23** that the concentration of formed CH₄ starts to increase after the decreasing of CO concentration. According to the reaction schemes, the more H⁺ and electron are needed to produce CH₄, resulting that the production of CH₄ starts later.

Figure 24 shows the concentration changes of formed CO along the time under the Xe lamp without UV light. In this experiment, CO is the only fuel produced from the reactions, that is, no CH₄ was detected. Before the experiments, a blank test, which was running the same experiment without illumination of Xe lamp, had been carried out to set up a reference case. No CO or CH₄ was produced in the blank test as expected. According to **Figure 24**, the CO₂ reduction performance is the best

Figure 24.

Comparison of concentration of formed CO among several molar ratios of $\text{CO}_2/\text{NH}_3/\text{H}_2\text{O}$ under the illumination condition without UV light.

for the molar ratio of $\text{CO}_2/\text{NH}_3/\text{H}_2\text{O} = 1:1:1$. In addition, it is confirmed from **Figure 24** that the concentration of formed CO is increased from the start of illumination of Xe lamp and decreased after reaching the maximum concentration. However, the concentration of formed CO is increased gradually again after a while. It can be considered that the same reaction mechanism under the illumination condition with UV light as mentioned above occurred.

3.5 Proposal to improve the CO_2 reduction performance with H_2O and H_2 or NH_3

Under the condition of $\text{CO}_2/\text{H}_2/\text{H}_2\text{O}$, the highest molar quantity of CO per weight of photocatalyst is $153 \mu\text{mol/g}$ in a single disc case with UV light illumination. The CO production performance achieved in this study is approximately 500 times as large as that reported in [24, 26] which is owing to Cu doping. The CH_4 production performance achieved in this study is almost the same as that reported in [24]. Since the doped Cu provides the free electron preventing recombination of electron and hole produced as well as the improvement of the light absorption effect, the big improvement of CO_2 reduction performance is obtained in this study.

One way to further promote the CO_2 reduction performance may be that different metals should be doped on the higher and the lower positioned photocatalysts discs. The co-doped such as PbS-Cu/TiO_2 , Cu-Fe/TiO_2 , Cu-Ce/TiO_2 , Cu-Mn/TiO_2 , and Cu-CdS/TiO_2 would promote the CO_2 reduction performance of TiO_2 under the $\text{CO}_2/\text{H}_2\text{O}$ condition [7, 9]. When the combination of $\text{CO}_2/\text{H}_2/\text{H}_2\text{O}$ is considered, the ion number of dopant is important to match the number of electron emitted from the dopant with H^+ as shown by the reaction schemes of $\text{CO}_2/\text{H}_2\text{O}$ and CO_2/H_2 . The same number of electron and H^+ are necessary for fuel production. Though Cu^+ ion is applied to promote the CO_2 reduction performance with TiO_2 in this study, it is expected that the co-doping of Cu and the other metal having larger positive ion might have positive effect for CO_2 reduction with H_2 and H_2O . In addition, the dopant like Fe, which can absorb the shorter wavelength light than Cu [17, 41, 42], should be used at the higher positioned layer. The wavelength of light becomes long

after penetrating the higher positioned photocatalyst [36]. Therefore, it may be an effective way for utilization of wide wavelength range light that the higher positioned Fe/TiO₂ which absorbs the shorter wavelength light and the lower positioned Cu/TiO₂ which absorbs the longer wavelength light are overlapped. This idea is similar to the concept of hybridizing two photocatalysts having different band gaps [13, 42, 43].

On the other hand, under the condition of CO₂/NH₃/H₂O, the highest molar quantities of CO and CH₄ per weight of photocatalyst in the reactor, which are obtained for the molar ratio of CO₂/NH₃/H₂O = 1:1:1, are 10.2 and 1.8 μmol/g, respectively. Compared to the previous research on CO₂ reduction with H₂ and H₂O over pure TiO₂, the CO₂ reduction performance of photocatalyst prepared in this study is approximately 35 times as large as that reported in Refs. [24, 39], which is owing to not only Cu doping but also the combination of NH₃ and H₂O. The CO production performance over the Cu/TiO₂ prepared in this study is approximately 3 times as large as that reported in the reference [44]. However, the CH₄ production performance of Cu/TiO₂ prepared in this study is one twentieth as large as that of Cu/TiO₂ reported in the other reference [45]. Therefore, it is necessary to promote the conversion from NH₃ into H₂ in order to improve the reduction performance according to the reaction scheme to reduce CO₂ with NH₃. One way to promote the conversion from NH₃ into H₂ is thought to be using Pt as a dopant. It was reported that Pt/TiO₂ was effective to dissolve NH₃ aqueous solution into N₂ and H₂ [25].

4. Conclusions

The conclusions on this chapter are as follows:

- i. Cu in Cu/TiO₂ prepared by this study exists in the form of Cu⁺ ion in Cu₂O.
- ii. Under the condition of CO₂/H₂/H₂O, the highest concentrations of CO and CH₄ produced as well as the highest molar quantities of CO and CH₄ per weight of photocatalyst for Cu/TiO₂ are obtained for CO₂/H₂/H₂O ratio of 1:0.5:0.5. Since the molar ratio of CO₂/H₂/H₂O = 1:0.5:0.5 can be regarded as the molar ratio of CO₂/total reductants = 1:1, it is believed that the results of this study follow the reaction scheme of CO₂/H₂O and CO₂/H₂.
- iii. Under the condition of CO₂/H₂/H₂O, the highest concentration of CO in two discs case is 1.4 times as large as that in the single disc case, while the highest concentration of CH₄ is 1.7 times with UV light illumination. Under the illumination condition without UV light, the highest concentration of CO with two Cu/TiO₂ disc is 2.8 times as large as that with single Cu/TiO₂ disc.
- iv. Under the condition of CO₂/H₂/H₂O, the highest molar quantity of CO per weight of photocatalyst with two Cu/TiO₂ discs overlapped is 54% of that with single Cu/TiO₂ disc with UV light illumination. The highest molar quantity of CH₄ per weight of photocatalyst with two Cu/TiO₂ discs overlapped is 65% of that with single Cu/TiO₂ disc.
- v. Under the condition of CO₂/H₂/H₂O, the molar quantity of CO per weight of photocatalyst with two Cu/TiO₂ discs overlapped is slightly (1.1 times) higher than that with single Cu/TiO₂ disc without UV light illumination.

- vi. Under the condition of $\text{CO}_2/\text{NH}_3/\text{H}_2\text{O}$, the molar ratio of $\text{CO}_2/\text{NH}_3/\text{H}_2\text{O}$ is 1:1:1 under the illumination condition with UV as well as without UV. The highest molar quantities of CO and CH_4 per weight of photocatalyst obtained in this study are 10.2 and 1.8 $\mu\text{mol/g}$, respectively.

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Author details

Akira Nishimura
Mie University, Tsu, Japan

*Address all correspondence to: nisimura@mach.mie-u.ac.jp

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