Effect Of Molar Ratio Of H_2 And H_2O On CO_2 Reduction Characteristics Of Overlapped Cu/Tio$_2$

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Abstract : *Cu-doped TiO_2 (Cu/TiO_2) film photocatalyst was prepared by sol-gel and dip-coating process, and pulse arc plasma method.The effect of Cu/TiO_2 photocatalyst on CO_2 reduction performance with reductants H_2O and H_2 was investigated. In addition, this study investigated overlapping two Cu/TiO_2 coated on netlike glass fiber discs in order to utilize the light effectively as well as increase the amount of photocatalyst used for CO_2 reduction. The characterization of prepared Cu/TiO_2 film coated on netlike glass fiber was analyzed by SEM, EPMA, TEM, EDX and EELS. Furthermore, the CO_2 reduction performance of Cu/TiO_2 film was tested under Xe lamp with or without ultraviolet (UV) light, respectively. As a result, the best CO_2 reduction performance has been achieved under the condition of $CO_2/H_2/H_2O = 1:0.5:0.5$ with UV light illumination as well as without UV light illumination.Under the illumination condition with UV light, the highest concentration of CO for Cu/TiO_2 overlapped is 1.4 times as large as that for single Cu/TiO_2, while the highest concentration of CH_4 for Cu/TiO_2 overlapped is 1.7 times as that for single Cu/TiO_2.Under the illumination condition without UV light, the highest molar quantity of CO per weight of photocatalyst for Cu/TiO_2 overlapped is 1.1 times as that for single Cu/TiO_2.*
Keywords –Cu/TiO_2 photocatalyst, CO_2 reduction, Overlapping effect, Reductant, Visible light response

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Date of Submission: 21-07-2018   Date of acceptance: 6-08-2018

I. INTRODUCTION

Due to mass consumption of fossil fuels, global warming and fossil fuels depletion have become serious global environmental problems in the world. After the industrial revolution, the averaged concentration of CO_2 in the world has been increased from 278 ppmV to 403 ppmV by 2016 [1]. Therefore, it is necessary to develop a new CO_2 reduction or utilization technology in order to recycle CO_2.

The application of CO_2 as a raw material in the production of chemicals and energy compromises a way to diminish the CO_2 accumulation in the atmosphere [2]. Among energy producing possibilities, one is the photochemical conversion of CO_2 into value-added chemicals which could be used as fuel [3].

The most widely used photocatalyst for the photocatalytic reactions is TiO_2 due to its availability, chemical stability, low cost and resistance to corrosion [4]. It is well known that CO_2 can be reduced into fuels e.g. CO, CH_4, CH_3OH, and H_2 etc. by using TiO_2 as the photocatalyst under ultraviolet (UV) light illumination [5-8]. However,using pure TiO_2 comes with its own limitations. It is only active when irradiated by UV light, which makes it not as effective under sunlight, since the solar spectrum only consists of about 4 % of UV light, sunlight is not able to active the TiO_2 effectively for photocatalystic reaction. Adding to that, TiO_2 has a high electron/hole pair recombination rate compared to the rate of chemical interaction with the adsorbed species for redox reactions [9].
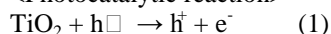
Recently, studies on CO_2 photochemical reduction by TiO_2 have been carried out from the viewpoint of performance promotion by extending absorption wavelength towards visible region. It was reported that doping transition metal was a useful technique for extending the absorbance of TiO_2 into the visible region [10-14].Noble metal doping such as Pt, Pd, Au and Ag [11], Au, Pd-three dimensionally ordered macroporous TiO_2 [12], composition material formed by GaP and TiO_2 [13], nanocomposite CdS/TiO_2 combining two different band gap photocatalysts [14],carbon-based AgBr nanocomposites TiO_2 [15],have been attempted to overcome the shortcomings of the pure TiO_2. They did improve the CO_2 reduction performance, however, the concentrations in the products achieved in all the attempts so far were still low, ranging from1 □ mol/g‐cat to 150 □ mol/g‐cat [11-15].

Though various metals have been used for doping, Cu is considered as a favorite candidate. Cu can extend the absorption band to 600-800 nm [16, 17], which covers the whole visible light range. Cu-decorated
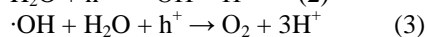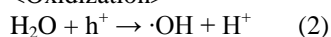
TiO$_2$ nanorod thin film performed ten times yield as large as TiO$_2$ in C$_2$H$_5$OH production [18]. Cu loaded N/TiO$_2$ also showed the good performance which yielded eight times as large as TiO$_2$ in CH$_4$ production [19]. Even under UV light illumination condition, Cu-decorated TiO$_2$ nanorod film yielded ten times as large as TiO$_2$ in CH$_4$ production [20]. Noble metals such as Pt and Au are too expensive to be used in industrial scale. Therefore, Cu is the best option 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 CO$_2$ reduction to produce fuel, H$_2$O and H$_2$ are usually used as reductant according to the review papers [6, 8]. To promote the CO$_2$ reduction performance of photocatalyst, it is important to select the optimum reductant which provides the proton (H$^+$) for the reduction reaction. The reaction scheme of CO$_2$ reduction with H$_2$O is as follows [21-23]:
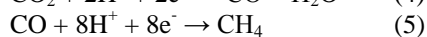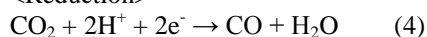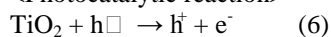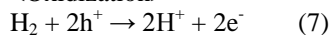
<Photocatalytic reaction>
$$TiO_2 + h\square \rightarrow h^+ + e^- \qquad (1)$$
<Oxidization>
$$H_2O + h^+ \rightarrow \cdot OH + H^+ \qquad (2)$$
$$\cdot OH + H_2O + h^+ \rightarrow O_2 + 3H^+ \qquad (3)$$
<Reduction>
$$CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O \qquad (4)$$
$$CO + 8H^+ + 8e^- \rightarrow CH_4 \qquad (5)$$

The reaction scheme of CO$_2$ reduction with H$_2$ is as follows [24]:

<Photocatalytic reaction>
$$TiO_2 + h\square \rightarrow h^+ + e^- \qquad (6)$$
<Oxidization>
$$H_2 + 2h^+ \rightarrow 2H^+ + 2e^- \qquad (7)$$
<Reduction>
$$CO_2 + e^- \rightarrow \cdot CO_2^- \qquad (8)$$
$$\cdot CO_2^- + H^+ + e^- \rightarrow HCOO^- \qquad (9)$$
$$HCOO^- + H^+ \rightarrow CO + H_2O \qquad (10)$$
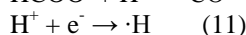$$H^+ + e^- \rightarrow \cdot H \qquad (11)$$
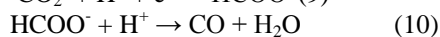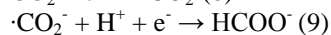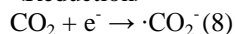$$CO_2 + 8e^- + 8 \cdot H \rightarrow CH_4 + 2H_2O \qquad (12)$$
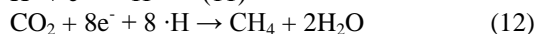
There are some reports on CO$_2$ reduction with either H$_2$O or H$_2$ [6, 8]. However, the effect of using H$_2$O and H$_2$ together as the reductant is not investigated well. Though a few studies using pure TiO$_2$ under CO$_2$/H$_2$/H$_2$O condition were reported [24-26], the effect of ratio of CO$_2$, H$_2$ and H$_2$O as well as the effect of Cu doping with TiO$_2$ on CO$_2$ reduction performance of photocatalyst were not investigated previously.

In this paper, TiO$_2$ film is coated by sol-gel and dip-coating process on netlike glass fiber (SILIGLASS U, Nihonmuki Co.). The netlike glass fiber is a net composed of glass fiber whose diameter is about 10 $\square$ m. The fine glass fibers are knitted, resulting that the diameter of aggregate fiber is about 1 mm. According to manufacture specifications of netlike glass fiber, the porous diameter of glass fiber is about 1 nm and the specific surface area is about 400 m^2/g. The netlike glass fiber consists of SiO$_2$ whose purity is over 96 wt%. The aperture of net is about 2 mm $\times$2 mm. Since the netlike glass fiber has a porous characteristic, it is believed that TiO$_2$ film is captured by netlike glass fiber easily during sol-gel and dip-coating process. In addition, it can be expected a CO$_2$ absorption performance of prepared photocatalyst is promoted due to the porous structure of netlike glass fiber.

Then, Cu is loaded on the TiO$_2$ coated netlike glass fiber by pulse arc plasma method which can emit nanosized Cu particles by applying high electrical potential difference. The amount of loaded Cu can be controlled by pulse number.In present study, the pulse number is 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 one on top of the other (with certain distance, i.e. overlapping), what impact/improvement would be on the CO$_2$ reduction performance. The overlapping is expected to utilize the light effectively as well as to increase the amount of photocatalyst used for CO$_2$ reduction.

In the present paper, Cu/TiO$_2$ was prepared and 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 CO$_2$ reduction performance with H$_2$ and H$_2$O under the condition of illuminating Xe lamp with or without UV light were investigated. The molar ratio of CO$_2$/H$_2$/H$_2$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 CO$_2$/H$_2$/H$_2$O for CO$_2$ reduction with Cu/TiO$_2$. In addition, the effect of overlapping two layers of Cu/TiO$_2$ coated netlike glass fiber on CO$_2$ reduction performance was investigated.

II. EXPERIMENT

1. Preparation of Cu/TiO$_2$ film

Sol-gel and dip-coating process was used for preparing TiO$_2$ film. TiO$_2$ sol solution was made by mixing [(CH$_3$)$_2$CHO]$_4$Ti (purity of 95 wt%, Nacalai Tesque Co.) of 0.3 mol, anhydrous C$_2$H$_5$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 0.07 mol. Netlike glass fiber was cut to 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 0.22 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 base material. 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 the chamber of the pulse arc plasma gun device, where 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 mm in the present study, Cu particle can be evaporated over TiO$_2$ film uniformly. The amount of loaded Cu was controlled by pulse number. In the present paper, the pulse number was set at 100.

2. Characterization of Cu/TiO$_2$ film

The structure and crystallization characteristics of Cu/TiO$_2$ film were evaluated by SEM (JXA-8530F, JEOL Ltd.), EPMA (JXA-8530F, JEOL Ltd.), TEM (JEM-2100F/HK, JEOL Ltd.), EDX (JEM-2100F/HK, JEOL Ltd.) and EELS (JEM-ARM2007 Cold, JEOL Ltd.).Since these measuring instruments use electron for analysis, the sample should be an electron conductor.Since netlike glass disc is not an electron conductor, 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 samples 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 chemical element is analyzed according to the relationship between the characteristic X-ray energy and the atomic number. The spatial resolution of SEM and EPMA is 10 □ 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 TiO$_2$ 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 paper, the concentration distribution of Ti and Cu were analyzed.

EELS can be applied not only for detecting elements but also for determination of oxidation 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 of the full width at half maximum of the zero loss peak.

3. CO$_2$ reduction experiment

Fig. 1 shows that experimental set-up of the reactor consisting of stainless pipe (100 mm (H.) ×50 mm (I.D.)), a netlike glass disc coated with Cu/TiO$_2$ film (50 mm (D.) × 1 mm (t.)) which is located on the teflon cylinder (50 mm (H.) ×50 mm (D.)), a quartz glass disc (84 mm (D.) ×10 mm (t.)),a sharp cut filter which cuts off the light of wavelength below 400 nm (SCF – 49.5C-42L, SIGMA KOKI CO. LTD.), a 150 W Xe lamp (L2175, Hamamatsu Photonics K. K.), mass flow controller, CO$_2$ gas cylinder and H$_2$ gas cylinder.

1. Xe lamp, 2. Sharp cut filter, 3. Quartz glass disc, 4. Stainless pipe,
5. Gas sampling tap, 6. Photocatalyst, 7. Teflon cylinder, 8. Valve,
9. Mass flow controller, 10. CO_2 gas cylinder (99.995 vol%),
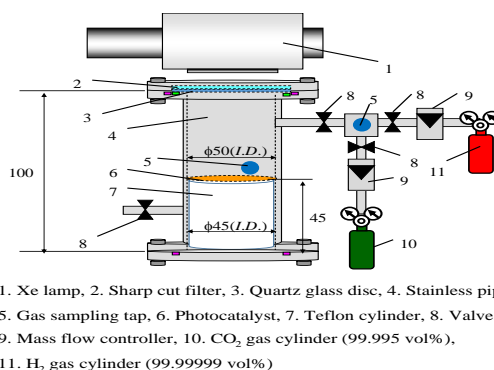11. H_2 gas cylinder (99.99999 vol%)

Fig.1 Schematic drawing of CO_2 reduction experimental set-up

The reactor volume available for CO_2 is 1.25×10^{-4} m^3. The light of Xe lamp, through the sharp cut filter and the quartz glass disc that are at the top of the stainless pipe, illuminates the netlike glass disc coated with Cu/TiO$_2$ film, which is located inside the stainless pipe. The wavelength of light from Xe lamp is ranged from 185 nm to 2000 nm. The Xe lamp can be fitted with a sharp cut filter to remove UV components of the light. With the filter, the wavelength from Xe lamp is ranged from 401 nm to 2000 nm.**Fig.2** showsthe light transmittance data of the sharp cut filter to prove the removal of the light whose wavelength is below 400 nm.The average light intensity of Xe lamp on the photocatalyst without and with setting the sharp cut filter is79.3 mW/cm^2 and 67.4 mW/cm^2, respectively.
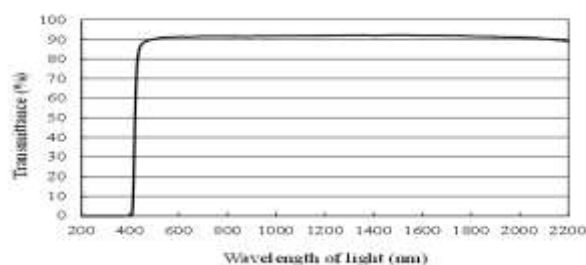

Fig.2 Light transmittance data of sharp cut filter

In the CO_2 reduction experiment, CO_2 gas with the purity of 99.995 vol% and H_2 gas with the purity of 99.99999 vol% which were controlled by mass flow controller were mixed in the buffer chamber, and introduced into the reactor which was pre-vacuumed by a vacuum pump. The mixing ratio of CO_2 and H_2 was confirmed by TCD gas chromatogragh (Micro GC CP4900, GL Science) before introducing into the reactor. After confirming the mixing ratio of CO_2 and H_2, the distilled water was injected into the reactor through gas sampling tap and Xe lamp illumination was turned on at the same time. The injected water vaporized completely in the reactor. The molar ratio of CO_2/H_2/$H_2O$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 at approximately 343 K during the experiment.

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) and methanizer (MT221, GD Science). Minimum resolution of FID gas chromatograph and methanizer is 1 ppmV.

III.   RESULTS AND DISCUSSION
1.   Characterization of Cu/TiO$_2$ film
Fig. 3 shows SEM image of Cu/TiO$_2$ film coated on netlike glass disc. The SEM image was taken at 1500 times magnification.**Fig. 4** shows EPMA images of Cu/TiO$_2$ film coated on netlike glass disc. EPMA analysis was carried out for 1500 times magnification SEM image.In EPMA image, the concentrations of each element in observation area are 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 TiO$_2$ film was coated on netlike glass fiber.During firing process, the temperature profile of TiO$_2$ solution adhered on the netlike glass disc was not even due to the different thermal conductivities of Ti and SiO$_2$. Their thermal conductivities of Ti and SiO$_2$ at 600 K are 19.4

W/(m・K) and 1.82 W/(m・K), respectively [27]. Due to the thermal expansion and shrinkage around netlike glass fiber, it can be considered that thermal crack formed on the TiO_2 film.

In addition, it is observed from Fig. 4 that nanosized Cu particles are loaded on TiO_2 uniformly, resulted from that the pulse arc plasma method can emit nanosized Cu particles.

To evaluate the amount of loaded Cu within TiO_2 film quantitatively, the observation area, which is the center of netlike glass disc, of diameter of 300 □ m 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 Cu and Ti in the Cu/TiO_2 film are 0.56 wt% and 99.44 wt%, respectively.
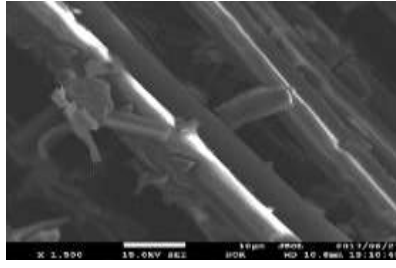

10 μm

Fig. 3 SEM image of CuTiO$_2$ film coated on netlike glass disc
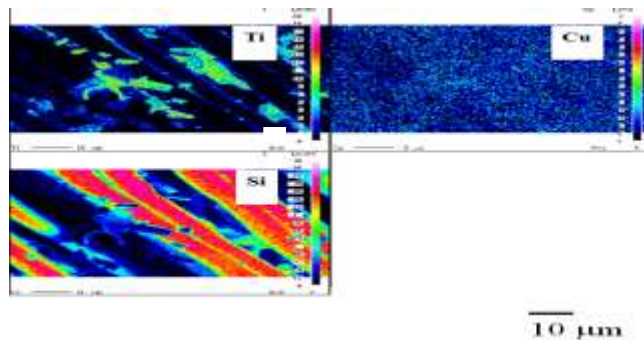
10 μm

Fig. 4 EPMA image of Cu/TiO$_2$ film coated on netlike glass disc

Figs 5 and 6 show TEM and EDX images of Cu/TiO_2 film, respectively.EDX analysis was carried out using 150000 times magnification TEM image. According to Fig. 6, it is observed that Cu particle are distributed in FiO_2 film.Though many Cu particles are loaded on the upside of TiO_2 film, it is not confirmed that the Cu layer is formed.
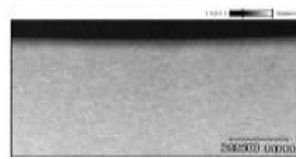
250 nm

Fig. 5 TEM image of Cu/TiO$_2$ film

250 nm

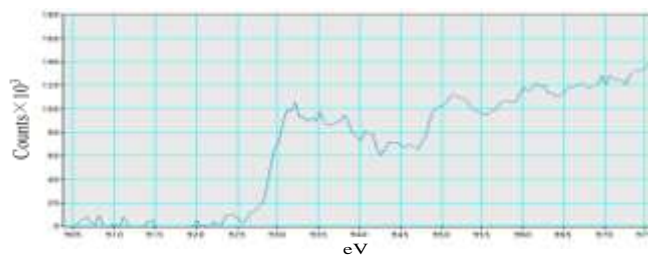**Fig. 6 EDX images of Cu/TiO$_2$ film**

Fig. 7 EELS spectra of Cu in Cu/TiO$_2$

Fig. 7 shows EELS spectra of Cu in Cu/TiO$_2$ film. From this figure, the peaks at around 932 eV and 952 eV can be observed. Compared to the report investigating the spectra peaks of Cu, Cu$_2$O and CuO [28], the EELS spectra of Cu$_2$Omatches with Fig. 7. Therefore, Cu in Cu/TiO$_2$ prepared in this study exists as Cu$^+$ ionin Cu$_2$O. It was reported that the heterojunctions between CuO and TiO$_2$ contributed to the promotion of the photoactivity [29]. In addition, it was reported that Cu$^+$ was more active than Cu^{2+} [30]. Therefore, it is expected that Cu$^+$ would play a role to enhance the CO$_2$ reduction performance in this study.

2. Effect of molar ratio of CO$_2$, H$_2$ and H$_2$O on CO$_2$ reduction characteristics of Cu/TiO$_2$

Figs. 8 and 9 show the concentration changes of CO and CH$_4$ produced in the reactor along the time under the Xe lamp with UV light on, respectively.**Figs. 10 and 11** 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 on, respectively. The amount of Cu/TiO$_2$ is 0.16 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.
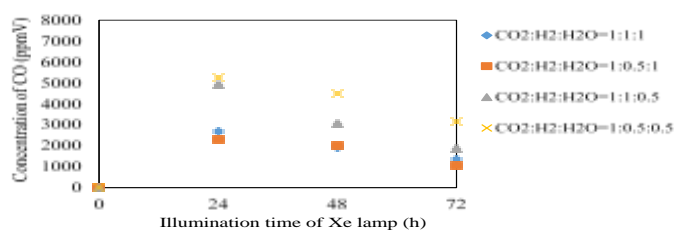

Fig. 8 Comparison of concentration of CO among several moral ratios of CO$_2$/H$_2$/H$_2$O under illumination condition with UV light
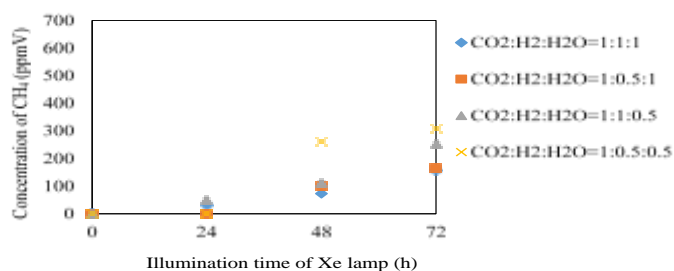

Fig. 9Comparison of concentration of CH$_4$ among several moral ratios of CO$_2$/H$_2$/H$_2$O under illumination condition with UV light
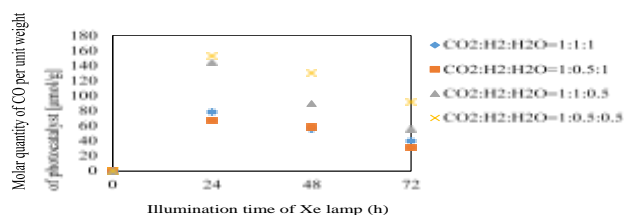

Fig. 10 Comparison of molar quantity of CO per unit weight of photocatalyst among several moral ratios of CO$_2$/H$_2$/H$_2$O under the illumination condition with UV light
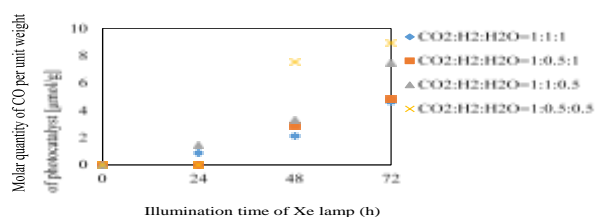
Fig. 11 Comparison of molar quantity of CH$_4$ per unit weight of photocatalyst among several moral ratios of CO$_2$/H$_2$/H$_2$O under the illumination condition with UV light

According to Figs. 8, 9, 10 and 11, the CO$_2$ reduction performance is the highest for the moral ratio of CO$_2$/H$_2$/H$_2$O = 1:0.5:0.5. Since the reaction scheme of CO$_2$/H$_2$/H$_2$O is not fully understood, this study refers to the reaction scheme of CO$_2$/H$_2$O and CO$_2$/H$_2$ as shown by (1) – (12).It is known from the reaction scheme that the theoretical moral ratio of CO$_2$/H$_2$O and CO$_2$/H$_2$ to produce CO is 1:1. On the other hand, the theoretical moral ratio of CO$_2$/H$_2$O and CO$_2$/H$_2$ to produce CH$_4$ is 1:4. Since the moral ratio of CO$_2$/H$_2$/H$_2$O = 1:0.5:0.5 can be regarded as the moral ratio of CO$_2$/total reductants = 1:1, it is believed that the results of this study follows reaction scheme presented in (1) - (12).Comparing the CO production with the CH$_4$ production, CO is produced first. According to (5), it is believed that some CO might be converted into CH$_4$. Therefore, the start of CH$_4$ production is slower than that of CO production. Producing CH$_4$ needs four times H$^+$ and electrons as many as producing CO needs. Therefore, it is revealed that the optimum moral ratio of CO$_2$/H$_2$/H$_2$O is decided by the CO production scheme. Though CO decreases after reaching the peak, CH$_4$ increases gradually.

Figs. 12 and 13 show the concentration changes of CO produced and the molar quantity of CO per weight of photocatalyst in the reactor under the Xe lamp without UV light on, respectively. In this experiment, CO is the only fuel produced from the reactions.
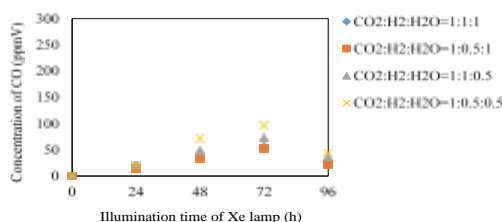

Fig. 12 Comparison of concentration of CO among several moral ratios of CO$_2$/H$_2$/H$_2$O under illumination conditions without UV light
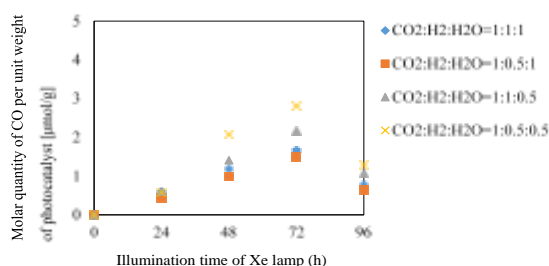

Fig. 13 Comparison of molar quantity of CO per unit weight of photocatalyst among several moral ratios of CO$_2$/H$_2$/H$_2$O under the illumination condition without UV light

According to Figs. 12 and 13,the CO$_2$ reduction performance is also the highest for the moral ratio of CO$_2$/H$_2$/H$_2$O = 1:0.5:0.5 in this case. It is considered that the same reaction mechanism as mentioned above is conducted. The CO$_2$ reduction performance of Cu/TiO$_2$ under the illumination condition without UV 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.   Effect of overlapping on CO$_2$ reduction characteristics of Cu/TiO$_2$
Figs. 14 and 15 show the concentration changes of CO and CH$_4$ produced in the reactor under the Xe lamp with UV light on, with two Cu/TiO$_2$ film coated on netlike glass discs overlapped, respectively.The photocatalyst is coated on both upper and lower surfaces of the top disc and only on the upper surface of the bottom disc.
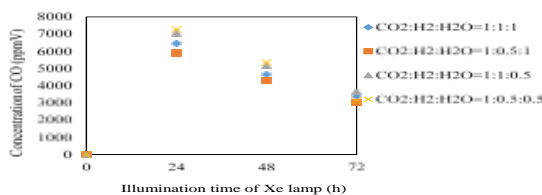
Fig. 14 Comparison of concentration of CO for Cu/TiO₂ overlapped among several moral ratios of CO₂/H₂/H₂O under the illumination condition with UV light

Fig. 15 Comparison of concentration of CH₄ for Cu/TiO₂ overlapped among several moral ratios of CO₂/H₂/H₂O under the illumination condition with UV light

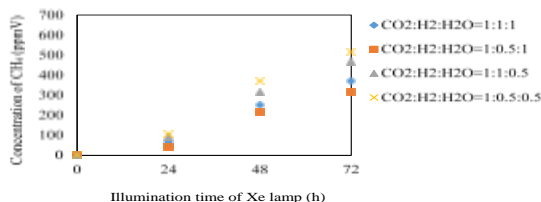**Figs. 16 and 17** show the molar quantities of CO and CH₄ per weight of photocatalyst in the reactor along the time under the Xe lamp with UV light on, respectively. The total amount of Cu/TiO₂ on two discs is 0.42 g.
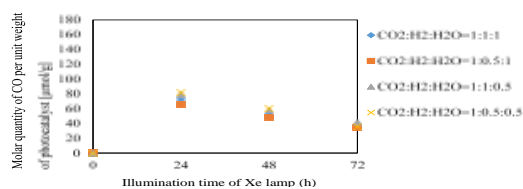

Fig. 16 Comparison of molar quantity of CO per unit weight of photocatalyst for Cu/TiO₂ overlapped among several moral ratios of CO₂/H₂/H₂O under the illumination condition with UV light

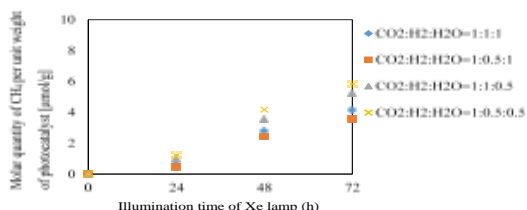**Fig. 17 Comparison of molar quantity of CH₄ per unit weight of photocatalyst for Cu/TiO₂ overlapped among several moral ratios of CO₂/H₂/H₂O under the illumination condition with UV light**

According to Figs. 14, 15, 16 and 17, the CO_2 reduction performance is the highest for the moral ratio of $CO_2/H_2/H_2O$ = 1:0.5:0.5, the same as that in the case of single Cu/TiO₂ disc.In addition, the order of CO_2 reduction performance of Cu/TiO₂ overlapped is thesame as that of single Cu/TiO₂. However, comparing Figs. 14 and 15 with Figs. 8 and 9, 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 $CO_2/H_2/H_2O$. 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. (iii) The lower positioned Cu/TiO₂ disc utilizes the light passing through the top disc.

However, comparing Figs. 16 and 17 with Figs. 10 and 11, 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 $CO_2/H_2/H_2O$. The highest molar quantity of CO per weight of photocatalyst in two discs overlapped case is 82 μ mol/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 μ mol/g, which is 65 % of that in single disc case.The reasons of this result are considered to be: (i) Some part of the Cu/TiO₂ film on the lower positioned disc can't receive the light. (ii) If the produced fuel remains in the space between two discs, the reactant of CO_2, H_2 and

H_2O 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.

Figs. 18 and 19 show the concentration changes of CO produced and the molar quantity of CO per weight of photocatalyst in the reactor with two overlapped Cu/TiO_2 film coated on netlike glass disc under the Xe lamp without UV light on, respectively. In this experiment, CO is the only fuel produced from the reactions.
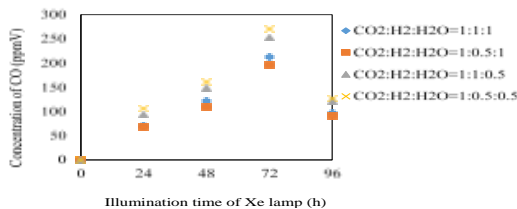

Fig. 18 Comparison of concentration of CO for Cu/TiO_2 overlapped among several moral ratios of $CO_2/H_2/H_2O$ under the illumination condition without UV light
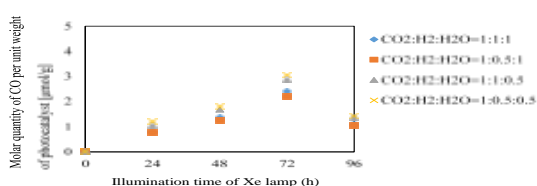

Fig. 19 Comparison of molar quantity of CO per unit weight of photocatalyst for Cu/TiO_2 overlapped among several moral ratios of $CO_2/H_2/H_2O$ under the illumination condition without UV light

According to Figs. 18 and 19, the CO_2 reduction performance in two discs case is the highest when the moral ratio of $CO_2/H_2/H_2O$ = 1:0.5:0.5 which is the same as that in the single disc case. The order of CO_2 reduction performance in two discs case is the same as that in the single disc case. However, comparing Fig. 18 with Fig. 12, the concentrations in two discs case are higher than those in single case under every molar ratio of $CO_2/H_2/H_2O$. 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 are thought to cause the results.

In addition, comparing Fig. 19 with Fig. 13, the molar quantity of CO per weight of photocatalyst in two Cu/TiO_2 discs overlapped case is slightly higher than that in the single disc case under every molar ratio of $CO_2/H_2/H_2O$. The highest molar quantity of CO per weight of photocatalyst is 3.1 $\square$ mol/g in two discs case, 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 fuel and reactant of CO_2, H_2 and H_2O on the surface of photocatalyst in no-UV cases [31]. 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 [32, 33], the mass transfer is an inhibition factor to promote the CO_2 reduction performance of photocatalyst and it is necessary to control the mass transfer rate to meet the photochemical reaction rate. **Fig. 20** illustrates the comparison of mass and electron transfer within overlapped two photocatalysts in UV and no-UV illumination cases.
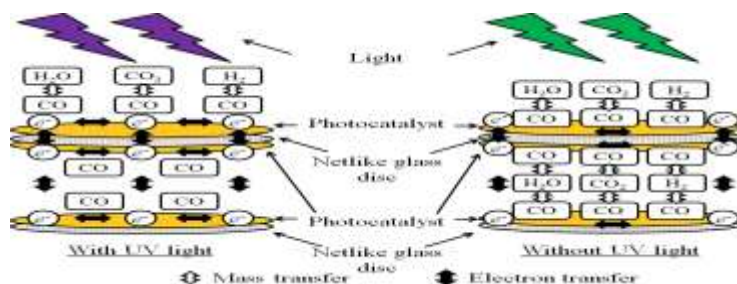

Fig. 20 Comparison of mass and electron transfer within overlapped two photocatalysts between the illumination condition with UV light and without UV light

In this study, the highest molar quantity of CO per weight of photocatalyst is 153 $\square$ mol/g in a single disc case under the illumination condition with UV light. The CO production performance achieved in this study isapproximately 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 isalmost 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 improving 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 TiO_2 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 CO_2/H_2O condition [6, 8]. When the combination of $CO_2/H_2/H_2O$ 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 scheme of CO_2/H_2O 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 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 [16, 34, 35], should be used at the higher positioned layer. The wavelength of light becomes long after penetrating the higher positioned photocatalyst [31]. Therefore, the overlapping of the higher positioned Fe/TiO_2 which absorbs the shorter wavelength light and the lower positioned Cu/TiO_2 which absorbs the longer wavelength light may be an effective way for utilization of wide range light.This idea is similar to the concept of hybridizing two photocatalysts having different band gaps [13, 36, 37].

IV.   CONCLUSION

Based on the investigation in this study, the following conclusions can be drawn.

(i)   The nanosized Cu particles could be loaded on TiO_2 uniformly through the sol-gel and dip-coating process, and pulse arc plasma method. Cu in Cu/TiO_2 prepared by this study exists in the form of Cu^+ ionin Cu_2O.

(ii)   Under the illumination condition with UV light as well as without UV light, the concentrations of CO and CH_4 produced as well as the molar quantities of CO and CH_4 per weight of photocatalyst for Cu/TiO_2 are the highest under the $CO_2/H_2/H_2O$ ratio of 1:0.5:0.5. It is believed that the optimum moral ratio of $CO_2/H_2/H_2O$ is determined by the CO production scheme of CO_2/H_2O and CO_2/H_2.

(iii)   Under the illumination condition with UV light as well as without UV light, the concentrations of CO and CH_4 produced in two overlapped Cu/TiO_2 discs case is higher than that in the single Cu/TiO_2 disc case. Under the illumination condition with UV light, 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 CH_4 is 1.7 times. Under the illumination condition without UV light, the highest concentration of CO with two Cu/TiO_2 discs is 2.8 times as large as that with single Cu/TiO_2 disc.

(iv)   Under the illumination condition with UV light, the molar quantities of CO and CH_4 per weight of photocatalyst with two Cu/TiO_2 discs overlapped are lower than those with single Cu/TiO_2 disc. The highest molar quantity of CO per weight of photocatalyst with two Cu/TiO_2 discs overlapped is 54 % of that with single Cu/TiO_2 disc. The highest molar quantity of CH_4 per weight of photocatalyst with two Cu/TiO_2 discs overlapped is 65 % of that with single Cu/TiO_2 disc.

(v)   Under the illumination condition without UV light, the molar quantity of CO per weight of photocatalyst with two Cu/TiO_2 discs overlapped is slightly (1.1 times) higher than that with single Cu/TiO_2 disc.

Acknowledgements

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