Physics & Astronomy International Journal

Research Article

Open Access

Impact of molar ratio of NH_3 and H_2O on CO_2 reduction performance over Cu/TiO_2 photocatalyst

Abstract

Cu-doped TiO_2 (Cu/TiO_2) film photocatalyst was prepared by sol-gel dip-coating, and pulse arc plasma process. The netlike glass fiber was used as a base material for the photocatalyst since it had a porous structure. The CO_2 reduction performance with NH_3 and H_2O into CO and CH_4 over the Cu/TiO_2 photocatalyst was investigated experimentally under the illumination condition with UV as well as without UV. In addition, the characterization of prepared Cu/TiO_2 film coated on netlike glass fiber was analyzed by SEM and EPMA. As a result, the CO_2 reduction performance peaks under the condition of $CO_2/NH_3/H_2O$=1:1:1 in both cases with UV light and without UV light illumination. The highest molar quantity of CO and CH_4 per weight of photocatalyst in the reactor is 10.2µmol/g and 1.76 µmol/g, respectively. Comparing the CO_2 reduction characteristics for $CO_2/NH_3/H_2O$ with that for CO_2/H_2O, it is concluded that the proper combination of NH_3 and H_2O would be effective for promoting the CO_2 reduction performance over Cu/TiO_2, for the improving of the reduction performance of Cu/TiO_2 being necessary to promote the conversion from NH_3 into H_2.

Keywords: photocatalyst, Cu/TiO_2, CO_2 reduction, optimum combination of NH_3 and H_2O

Volume 3 Issue 5 - 2019

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Received: September 06, 2019 | **Published:** September 12, 2019

Introduction

Due to the increase in the averaged concentration of CO_2 in the atmosphere to 408.3 ppmV in April 2019,[1] CO_2 reduction or utilization technologies to recycle CO_2 are urgently required. This study focuses on CO_2 reduction and conversion into fuel through photocatalytic process. TiO_2 is the principle catalyst used for almost all types of photocatalytic reaction. It is well reported that CO_2 can be reduced into fuels e.g. CO, CH_4, CH_3OH, and H_2 etc. with TiO_2 as the photocatalyst under ultraviolet (UV) light illumination.[2,4–7] However, the CO_2 reduction performance with TiO_2 is still low since TiO_2 has a large bandgap energy (~3.2 eV) and a rapid recombination rate of electron and hole.[5] Recently, studies on CO_2 photochemical reduction by TiO_2 have been carried out to promote the performance by extending absorption range towards visible region.[8–15] For example, the previous studies investigated doping previous metal such as Pt[8] Ag,[9] Au,[10] Cu[11,12] composite material formed by GaP and TiO_2,[13] complex assembly CdS/TiO_2 to utilize two photocatalysts that have different band gaps,[14] and carbon-based AgBr nanocomposites TiO_2[15] to promote the performance of TiO_2. Though the CO_2 reduction performance was improved by these attempts, the concentrations of the products were still low, which was ranging from 1µmol/g-cat to 150µmol/g-cat.[8–15] Therefore, a breakthrough in increasing the concentration level of products is necessary to advance the CO_2 reduction technology in order to make the technology practically useful.

It was reported that doping transition metal was a useful technique for extending the absorbance of TiO_2 into the visible region.[16] For doping, various metal ions have been used, but among them, 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 TiO_2 nanorod thin film performed ten times yields as large as TiO_2 for C_2H_5OH production.[19] Cu loaded Ni/TiO_2 also showed the good performance which yielded eight times as large as TiO_2 for CH_4 production.[20] Even under UV light illumination condition, Cu-decorated TiO_2 nanorod film yielded ten times as large as TiO_2 for CH_4 production.[21] Noble metal 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 CO_2 reduction to produce fuel, H_2O and H_2 are usually used as reductant according to the review papers.[5,7] To promote the CO_2 reduction performance, it is important to select the optimum reductant which provides the proton (H^+) for the reduction reaction. According to the previous studies,[22–25] the reaction scheme to reduce CO_2 with H_2O can be summarized as shown below:

<Photocatalytic reaction>

$$TiO_2 + h\nu \rightarrow h^+ + e^- \quad (1)$$

<Oxidization>

$$2H_2O + 4h^+ \rightarrow 4H^+ + O_2 \quad (2)$$

<Reduction>

$$CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O \quad (3)$$

$$CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O \quad (4)$$

The reaction scheme to reduce CO_2 with H_2 can be summarized as shown below:[26]

<Photocatalytic reaction>

$$TiO_2 + h\nu \rightarrow h^+ + e^- \quad (5)$$

<Oxidization>

$$H_2 \rightarrow 2H^+ + 2e^- \quad (6)$$

<Reduction>

$$CO_2 + e^- \rightarrow \cdot CO_2^- \quad (7)$$

$$\cdot CO_2^- + H^+ + e^- \rightarrow HCOO^- \quad (8)$$

$$HCOO^- + H^+ \rightarrow CO + H_2O \quad (9)$$

$$H^+ + e^- \cdot \rightarrow H \quad (10)$$

$$CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O \quad (11)$$

Though there are some reports on CO_2 reduction with H_2O or H_2,[5,7] the effect of NH_3 having $3H^+$ which is superior to H_2O and H_2 on CO_2 reduction performance of photocatalyst is not investigated yet without the previous study conducted by Nishimura et al.[30] using Fe/TiO_2.[27] Since the previous study[27] investigated only one combination ratio of CO_2, NH_3 and H_2O, the effect of ratio of CO_2, NH_3 and H_2O on CO_2 reduction performance of metal doped TiO_2 is not clarified yet. It is important to investigate the combination ratio of CO_2, NH_3 and H_2O in order to promote the CO_2 reduction performance of Cu/TiO_2 photocatalyst. The reaction scheme to reduce CO_2 with NH_3 can be summarized as shown below:[26,28]

<Photocatalytic reaction>

$$TiO_2 + h\nu \rightarrow h^+ + e^- \quad (12)$$

<Oxidization>

$$2NH_3 \rightarrow N_2 + 3H_2 \quad (13)$$

$$H_2 \rightarrow 2H^+ + 2e^- \quad (14)$$

<Reduction>

$$H^+ + e^- \rightarrow \cdot H \quad (15)$$

$$CO_2 + e^- \rightarrow \cdot CO_2 \quad (16)$$

$$\cdot CO_2^- + H^+ + e^- \rightarrow HCOO^- \quad (17)$$

$$HCOO^- + H^+ \rightarrow CO + H_2O \quad (18)$$

$$CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O \quad (19)$$

Consequently, the purpose of this study is to clarify the effect of molar ratio of CO_2 to NH_3 and H_2O on the performance of CO_2 reduction with Cu/TiO_2. The CO_2 reduction performance with NH_3 and H_2O using Cu/TiO_2 coated on netlike glass fiber as photocatalyst under the condition of illuminating Xe lamp with or without UV light was investigated. The combination of CO_2/NH_3/H_2O was changed for 1:1:1, 1:0.5:1, 1:1:0.5, 1:0.5:0.5, 3:2:3, 3:8:12 to determine the optimum ratio of CO_2/NH_3/H_2O. According to the reaction scheme to reduce CO_2 with H_2O or NH_3 as shown above, the theoretical moral 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, 3:8, respectively. Therefore, this study assumes that the moral ratio of CO_2/NH_3/H_2O=3:2:3 and 3:8:12 is theoretical moral ratio to produce CO and CH_4, respectively. In addition, the combination of CO_2/H_2O was also changed for 1:1, 1:0.5, 3:12 to clarify the effect of NH_3 on the CO_2 reduction characteristics of Cu/TiO_2.

Experiments

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 $[(CH_3)_2CHO]_4Ti$ (purity of 95 wt%, Nacalai Tesque Co.) of 0.3 mol, anhydrous C_2H_5OH (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. In this study, TiO_2 film is coated by sol-gel and dip-coating process on netlike glass fiber (SILIGLASS U, Nihonmuki Co.). The glass fiber whose diameter is about 10 μm weaved as a net, resulting in the diameter of collected fiber of approximately 1 mm. According to the specifications of netlike glass fiber, the porous diameter of glass fiber is approximately 1 nm and the specific surface area is approximately 400 m^2/g. The composition of netlike glass fiber is SiO_2 of 96 wt%. The aperture area is approximately 2 mm×2 mm. Due to the porous characteristic of the netlike glass fiber, TiO_2 film can be captured on netlike glass fiber easily during sol-gel and dip-coating process. In addition, it can be expected that CO_2 would be more easily absorbed by the prepared photocatalyst since the fiber has the porous characteristics. Netlike glass fiber was cut to disc, and its diameter and thickness were 50 mm and 1 mm, respectively. The netlike glass 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.

After the coating of TiO_2, Cu is loaded on the TiO_2 coated netlike glass fiber by pulse arc plasma gun method which can emit nanosized Cu particles uniformly by applying high electrical potential difference. The pulse number can control the quality of Cu loaded on TiO_2. In this study, the pulse number is set at 100. Cu was loaded on TiO_2 film by pulse arc plasma gun 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 distance between Cu electrode and TiO_2 film was 150 mm, Cu particle can be evaporated over TiO_2 film uniformly. The amount of loaded Cu was controlled by pulse number.

Characterization of Cu/TiO_2 film

The structure and crystallization characteristics of Cu/TiO_2 film were evaluated by SEM (JXA-8530F, JEOL Ltd.) and EPMA (JXA-8530F, 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 μm. 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.

CO_2 reduction experiment

Figure 1 shows the experimental set-up of the reactor composing of stainless tube (100 mm (*H.*)×50 mm (*I.D.*)), Cu/TiO_2 film coated on netlike glass disc (50 mm (*D.*)×1 mm (*t.*)) 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 cutting off the light whose wavelength is below 400 nm (SCF–49.5C-42L, SIGMA KOKI CO. LTD.), a 150 W Xe lamp (L2175, Hamamatsu Photonics K. K.), mass flow controller and CO_2 gas cylinder. The volume of reactor to charge CO_2 is 1.25×10^{-4} m^3. The light of Xe lamp which is located inside the stainless tube illuminates Cu/TiO_2 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 nm to 2000 nm. Since the sharp cut filter can remove UV components of the light form the Xe lamp, the wavelength of light from Xe lamp is ranged from 401 nm to 2000 nm with the filter. Figure 2 shows the performance of the sharp cut filter to cut off the wavelength of the light, which can prove to remove the light whose wavelength is below 400 nm. The average light intensity of Xe lamp without and with the sharp cut filter are 58.2 mW/cm^2 and 33.8 mW/cm^2, respectively.

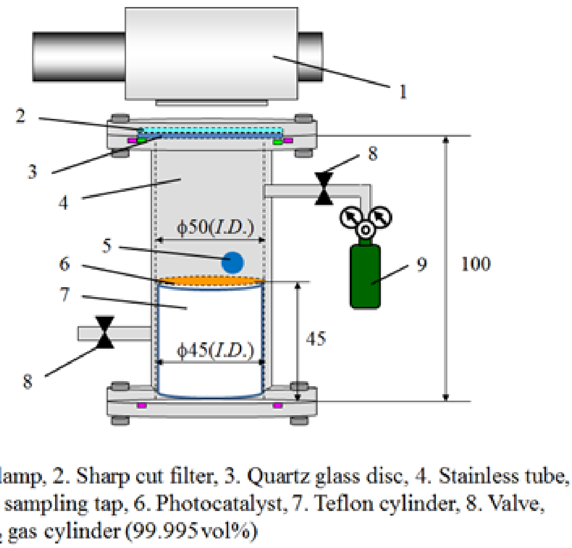

Figure 1 Schematic drawing of CO_2 reduction experimental set-up.

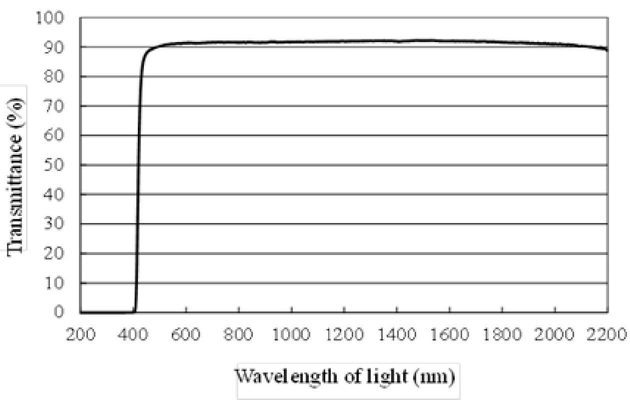

Figure 2 Light transmittance data of sharp cut filter.

In the CO_2 reduction experiment with H_2O or NH_3 + H_2O, after purging the reactor with CO_2 gas of 99.995 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 distilled water or NH_3 aqueous solution (NH_3; 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 distilled water or NH_3 aqueous solution injected 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 $CO_2/NH_{3/}H_2O$ 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) and methanizer (MT221, GD Science). Minimum resolution of FID gas chromatograph and methanizer is 1 ppmV.

Results and discussion

Characterization of Cu/TiO_2 film

Figure 3 shows SEM image of Cu/TiO_2 film coated on netlike glass disc. The SEM image was taken at 1500 times magnification. Figure 4 shows EPMA images of Cu/TiO_2 film coated on netlike glass disc. EPMA analysis was carried out for SEM images taken by 1500 times magnification. 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 with teeth like shape 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.[29] Due to the thermal expansion and shrinkage around netlike glass fiber, thermal crack formed on TiO_2 film. Therefore, TiO_2 film on netlike glass fiber was teeth like. As to Cu, it is observed from Figure 4 that nanosized Cu particles loaded on TiO_2 uniformly, resulting 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 µm is analyzed by EPMA. The ratio of Cu to Ti in this observation area 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 2.14 wt% and 97.86 wt%, respectively. This ratio is approximately same as the previous study prepared Cu/TiO_2 by pulse arc plasma gun method.[30]

Effect of molar ratio of CO_2 to NH_3 and H_2O on CO_2 reduction performance

Figures 5 and Figures 6 show the concentration changes of formed CO and CH_4 along the time under the Xe lamp with UV light, respectively. The amount of Cu/TiO_2 on the netlike glass disc is 0.05 g. Before the experiments, 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 5 and 6, 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, 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, 3:8, respectively. Therefore, this study assumes that the molar ratio of $CO_2/NH_3/H_2O$=3:2:3 and 3:8:12 is theoretical molar ratio to produce CO and CH_4, respectively. However, the molar ratio of $CO_2/NH_3/H_2O$=1:1:1 is not matched with these theoretical molar ratios to produce CO and CH_4. Since the ionized Cu doped with TiO_2 provides free electron for the reduction reaction process,[31] the reductants of NH_3 and H_2O which are less than the values indicated in the theoretical reaction scheme are enough for producing CO and CH_4 in this study. The highest molar quantity of CO and CH_4 per weight of photocatalyst in the reactor, which is obtained for the molar ratio of $CO_2/NH_3/H_2O$=1:1:1, is 10.2 µmol/g and 1.76 µmol/g, respectively.

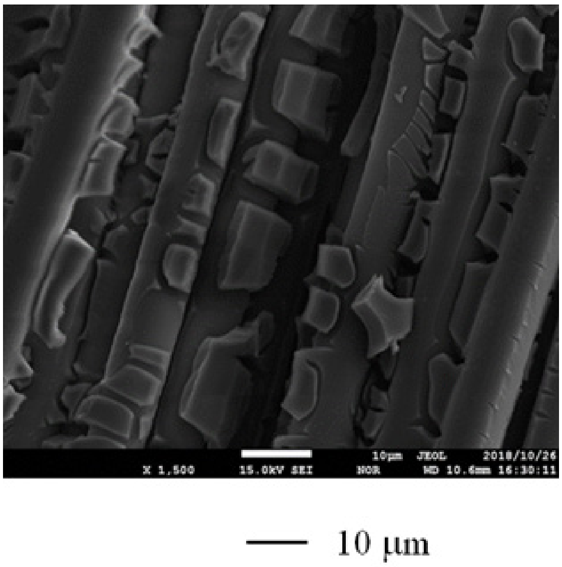

Figure 3 SEM image of Cu/TiO_2 film coated on netlike glass disc.

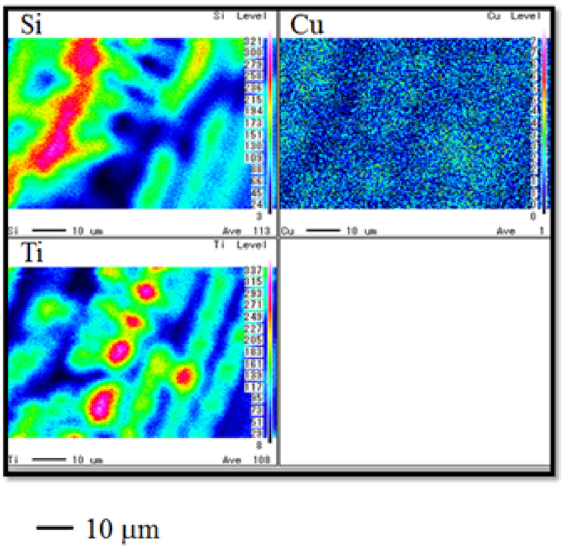

Figure 4 EPMA image of Cu/TiO_2 film coated on netlike glass disc.

In addition, it is confirmed from Figure 5 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 O_2 which is by-product as shown in Eq. (2).[32] 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 of reaction rates between CO_2/H_2O and CO_2/NH_3 condition. It is also revealed that the maximum concentration of formed CO is higher when the molar of NH_3 is higher than that of H_2O. Since the number of H^+ which can be provided is 3 and 2 for NH_3 and H_2O, respectively, it is considered that NH_3 is effective for promoting the reduction performance of Cu/TiO_2. Furthermore, it is found from Figure 5 and Figure 6 that the concentration of formed CH_4 starts to increase after the decreasing of CO concentration. According to the reaction schemes, the more H^+ and electron are needed to produce CH_4, resulting that the production of CH_4 starts later.

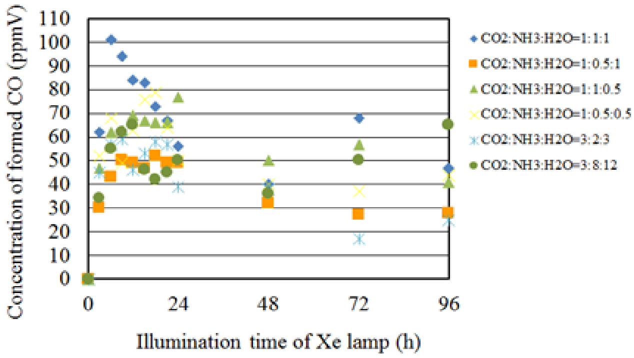

Figure 5 Comparison of concentration of formed CO among several molar ratios of $CO_2/NH_3/H_2O$ under the illumination condition with UV light.

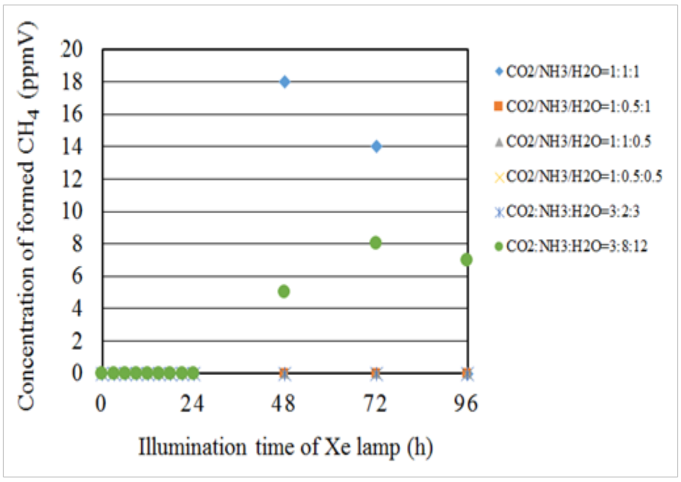

Figure 6 Comparison of concentration of formed CH_4 among several molar ratios of $CO_2/NH_3/H_2O$ under the illumination condition with UV light.

Figure 7 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, i.e. no CH_4 was detected. Before the experiments, 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 CO or CH_4 was produced in the blank test as expected. According to Figure 7, the CO_2 reduction performance

Citation: Nishimura A, Sakakibara Y, Inoe T, et al. Impact of molar ratio of NH_3 and H_2O on CO_2 reduction performance over Cu/TiO_2 photocatalyst. *Phys Astron Int J.* 2019;3(5):176‒182. DOI: 10.15406/paij.2019.03.00179

is the best for the molar ratio of $CO_2/NH_3/H_2O$=1:1:1 in the case of illumination condition without UV light. In addition, it is confirmed from Figure 7 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.

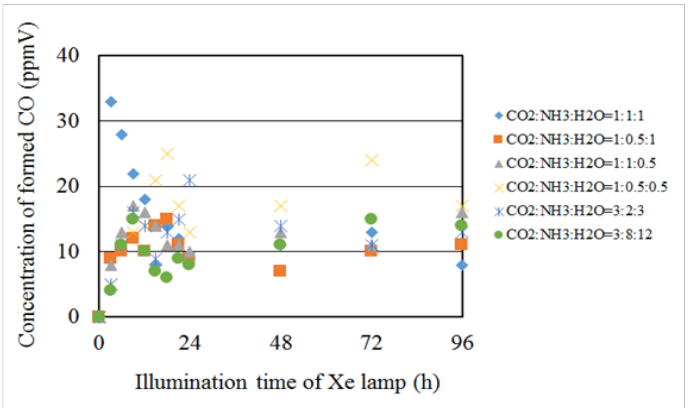

Figure 7 Comparison of concentration of formed CO among several molar ratios of $CO_2/NH_3/H_2O$ under the illumination condition without UV light.

Effect of NH_3 on CO_2 reduction performance over Cu/TiO_2

Figure 8 shows the concentration changes of formed CO along the time under the Xe lamp with UV light for the molar ratio of CO_2/H_2O=1:1 and that with various $CO_2/NH_3/H_2O$ ratios. Before the experiments, 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. It is seen from Figure 8 that the concentration of formed CO for the molar ratio of CO_2/H_2O=1:1 shows the peak soon after the start of illumination of Xe lamp and decreases gradually. It is thought that the decrease in the concentration of formed CO is caused by the oxidization reaction with CO and O_2.[32] In addition, it is found that the concentration of formed CO for every $CO_2/NH_3/H_2O$ condition is larger than that for the molar ratio of CO_2/H_2O=1:1. Therefore, it can conclude that the combination of NH_3 and H_2O is effective for the promotion of the CO_2 reduction performance over Cu/TiO_2.

Figure 9 shows the concentration changes of formed CO along the time under the Xe lamp with UV light for the molar ratio of CO_2/H_2O=1:0.5 and that with various $CO_2/NH_3/H_2O$ ratios. It is seen from Figure 9 that the concentration of formed CO for the molar ratio of CO_2/H_2O=1:0.5 shows the peak soon after the start of illumination of Xe lamp and decreases gradually, which indicates the same tendency as the molar ratio of CO_2/H_2O=1:1. It is also seen that the concentration of formed CO for every $CO_2/NH_3/H_2O$ condition is larger than that for the molar ratio of CO_2/H_2O=1:0.5. In addition, the concentration of formed CO keeps some value approximately without rapid decrease before 24 h for $CO_2/NH_3/H_2O$ conditions compared to the molar ratio of CO_2/H_2O=1:0.5. According to the reaction scheme to reduce CO_2 with NH_3 as shown before, the more reaction step is needed to produce CO since NH_3 should be converted into H_2. Therefore, it is believed that the time to produce CO is longer compared to the molar ratio of CO_2/H_2O=1:0.5.

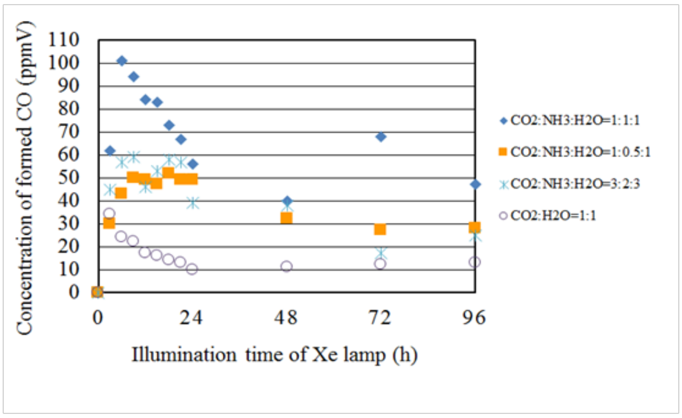

Figure 8 Comparison of concentration of formed CO between the molar ratio of CO_2/H_2O=1:1 and several molar ratios of $CO_2/NH_3/H_2O$ whose molar ratio of CO_2/H_2O is 1:1 under the illumination condition with UV light.

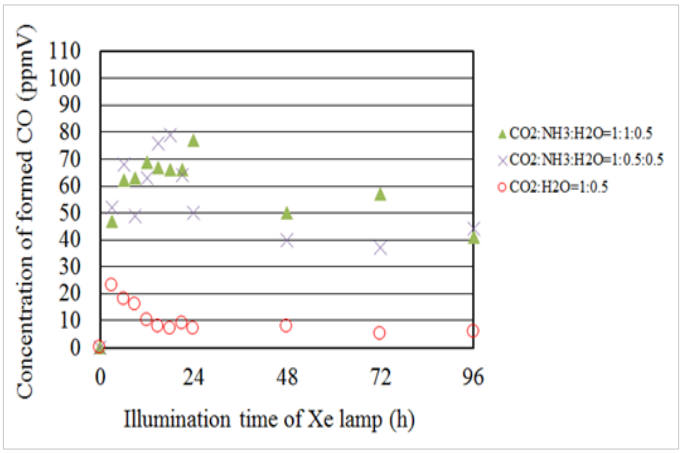

Figure 9 Comparison of concentration of formed CO between the molar ratio of CO_2/H_2O=1:0.5 and several molar ratios of $CO_2/NH_3/H_2O$ whose molar ratio of CO_2/H_2O is 1:0.5 under the illumination condition with UV light.

Figure 10 shows the concentration changes of formed CO along the time under the Xe lamp with UV light for the molar ratio of CO_2/H_2O=3:12 and that with various $CO_2/NH_3/H_2O$ ratios. It is seen from Figure 10 that the concentration of formed CO for the molar ratio of CO_2/H_2O=3:12 shows the peak soon after the start of illumination of Xe lamp and decreases gradually. In addition, the concentration of formed CO restarts to increase and gradually decrease again. This trend is different from the other CO_2/H_2O conditions. The ratio of H_2O is larger in this experiment compared to others, which indicates larger reductants provided for reduction reaction. Therefore, it is believed to keep CO production even though the oxidization reaction with CO and O_2 starts. Furthermore, it is also seen that the concentration of formed CO for the $CO_2/NH_3/H_2O$ condition is larger than that for the molar ratio of CO_2/H_2O=3:12. Consequently, it is revealed that the combination of NH_3 and H_2O is effective for promotion of the CO_2 reduction performance of Cu/TiO_2 for all conditions investigated in this study.

In this study, the highest molar quantity of CO and CH_4 per weight of photocatalyst in the reactor, which is obtained for the molar ratio of $CO_2/NH_3/H_2O$=1:1:1, is 10.2 µmol/g and 1.76 µmol/g, respectively. Compared to the previous research on CO_2 reduction with H_2 and H_2O

over pure TiO_2, the CO production performance of photocatalysts prepared in this study is approximately 35 times as large as that reported in references,[26,33] which is owing to not only Cu doping but also the combination of NH_3 and H_2O. The CO production performance over the Cu/TiO_2 prepared in this study is approximately 3 times as large as that reported in the reference.[12] However, the CH_4 production performance of Cu/TiO_2 prepared in this study is one twentieth as large as that of Cu/TiO_2 reported in the other reference.[34] Therefore, it is necessary to promote the conversion from NH_3 into H_2 in order to improve the reduction performance according to the reaction scheme to reduce CO_2 with NH_3. One way to promote the conversion from NH_3 into H_2 is thought to be using Pt as a dopant. It was reported that Pt/TiO_2 was effective to dissolve NH_3 aqueous solution into N_2 and H_2.[28] Another way to further promote the CO_2 reduction performance may be double overlapping arrangement of Cu/TiO_2 coated on netlike glass disc since the electron transfer between two overlapped photocatalyst was promoted by overlapping.[35] It can be suggested that different metals such as Cu and Pt should be doped on the higher and the lower positioned photocatalysts discs since 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 promoted the CO_2 reduction performance of TiO_2 under the CO_2/H_2O condition.[5,7]

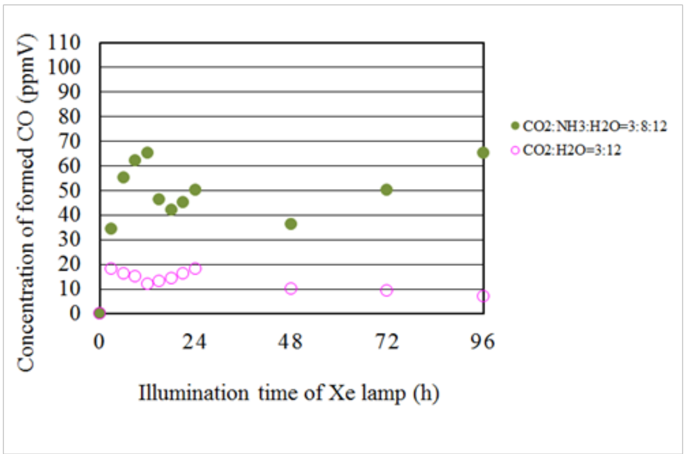

Figure 10 Comparison of concentration of formed CO between the molar ratio of CO_2/H_2O=3:12 and several molar ratios of $CO_2/NH_3/H_2O$ whose molar ratio of CO_2/H_2O is 3:12 under the illumination condition with UV light.

Conclusion

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

I. TiO_2 could be coated on netlike glass fiber where it appears teeth like shape. Cu fine particles could be loaded on TiO_2 uniformly

II. The CO_2 reduction performance is optimal when the molar ratio of $CO_2/NH_3/H_2O$ is 1:1:1 under the illumination condition with UV as well as without UV. The highest molar quantity of CO and CH_4 per weight of photocatalyst obtained in this study is 10.2 µmol/g and 1.76 µmol/g, respectively

III. It is found that the combination of NH_3 and H_2O is effective for promotion of the CO_2 reduction performance of Cu/TiO_2 since the concentration of formed CO with NH_3/H_2O is larger than that with H_2O only.

IV. It is necessary to promote the conversion from NH_3 into H_2 in order to improve the reduction performance of Cu/TiO_2 further.

Funding details

JSPS KAKENHI.

Acknowledgements

The authors would like to gratefully thank from JSPS KAKENHI Grant Number 16K06970 for the financial support of this work.

Conflicts of interests

The authors declare that there is no conflict of interest regarding the publication of this paper.

References

1. Greenhouse Gases Observing Satellite *GOSAT "IBUSUKI"*. 2019.
2. Das S, Daud WMAW. Photocatalytic CO_2 transformation into fuel: a review on advances in photocatalyst and photoreactor. *Renewable and Sustainable Energy Reviews*. 2014;39:765–805.
3. Sakakura T, Choi JC, Yasuda H. Transformation of carbon dioxide. *Chemical Reviews*. 2007;107(6):2365–2387.
4. Abdullah H, Khan MMR, Ong HR, et al. Modified TiO_2 photocatalyst for CO_2 photocatalytic reduction: an overview. *Journal of CO_2 Utilization*. 2017;22:15–32.
5. Sohn Y, Huang W, Taghipour F. Recent progress and perspectives in the photocatalytic CO_2 reduction of Ti-oxide-based nanomaterials. *Applied Surface Science*. 2017;396:1696–1711.
6. Neatu S, Macia-agullo JA, Garcia H. Solar light photocatalytic CO_2 reduction: general considerations and selected bench-mark photocatalysts. *International Journal of Molecular Science*. 2014;15:5246–5262.
7. Tahir M, Amin NS. Advances in visible light responsive titanium oxide-based photocatalysts for CO_2 conversion to hydrocarbon fuels. *Energy Conversion and Management*. 2013;76:194–214.
8. Xie S, Wang Y, Zhang Q, et al. MgO- and Pt-promoted TiO_2 as on efficient photocatalysts for the preferential reduction of carbon dioxide in the presence of water. *ACS Catalyst*. 2014;4:3644–3653.
9. Khalid NR, Ahmed E, Niaz NA, et al. Highly visible light responsive metal loaded N/TiO_2 nanoparticles for photocatalytic conversion of CO_2 into methane. *Ceramics International*. 2017;43(9):6771–6777.
10. Tan LL, Ong WJ, Chai SP, et al. Noble metal modified reduced graphene oxide/TiO_2 ternary nanostructures for efficient visible-light-driven photoreduction of carbon dioxide into methane. *Applied Catalysis B: Environmental*. 2015;166–167:251–259.
11. Camarillo R, Toston S, Martinez F, et al. Improving the photo-reduction of CO_2 to fuels with catalysts synthesized under high pressure: Cu/TiO_2. *Journal of Chemical Technology Biotechnology*. 2018;93:1237–1248.
12. Aguirre ME, Zhou R, Engene AJ, et al. Cu_2O/TiO_2 heterostructures for CO_2 reduction through a direct Z-scheme: protecting Cu_2O from photocorrosion. *Applied Catalysis B: Environmental*. 2017;217:485–493.
13. Marci G, Garcia-Lopez EI, Palmisano L. Photocatalytic CO_2 reduction in gas-solid regime in the presence of H_2O by using GaP/TiO_2 composite as photocatalyst under simulated solar light. *Catalysis Communications*. 2014:53:38–41.
14. Beigi AA, Fatemi S, Salehi Z. Synthesis of nanocomposite CdS/TiO_2 and investigation of its photocatalytic activity of CO_2 reduction to CO and CH4 under visible light irradiation. *Journal of CO_2 Utilization*. 2014;(7):23–29.

Citation: Nishimura A, Sakakibara Y, Inoe T, et al. Impact of molar ratio of NH_3 and H_2O on CO_2 reduction performance over Cu/TiO_2 photocatalyst. *Phys Astron Int J*. 2019;3(5):176–182. DOI: 10.15406/paij.2019.03.00179

15. Fang Z, Li S, Gong Y, et al. Comparison of catalytic activity of carbon-based AgBr nanocomposites for conversion of CO_2 under visible light. *Journal of Saudi Chemical Society*. 2014;18(4):299–307.

16. Wang JA, Ballesteros RL, Lopez T, et al. Quantitative determination of titanium lattice defects and solid-state reaction mechanism in iron-doped TiO_2 photocatalysts. *Journal of Physical Chemistry B*. 2001;105(40):9692–9698.

17. Nagaveni K, Hegde MS, Madras G. Structure and photocatalytic activity of Ti1-xMx$O_{2\pm d}$ (M=W, V, Ce, Zr, Fe, and Cu) synthesized by solution combustion method. *Journal of Physical Chemistry B*. 2004;108(52):20204–20212.

18. Yoong LS, Chong FK, Dutta BK. Development of copper-doped TiO_2 photocatalyst for hydrogen production under visible light. *Energy*. 2009;34(10):1652–1661.

19. Cheng M, Yang S, Chen R, et al. Copper-decorated TiO_2 nanorod thin films in optofluidic planner reactors for efficient photocatalytic reduction of CO_2. *International Journal of Hydrogen Energy*. 2017;42(15):9722-9732.

20. Khalid NR, Ahmed E, Niaz NA, et al. Highly visible light responsive metal loaded N/TiO_2 nanoparticles for photocatlytic conversion of CO_2 into methane. *Ceramics International*. 2017;43(9):6771–6777.

21. Tan JZY, Fernandez Y, Liu D, et al. Photoreduction of CO_2 using copper-decorated TiO_2 nanorod films with localized surface plasmon behavior. *Chemical Physics Letters*. 2012;531(6):149–154.

22. Goren Z, Willner I, Nelson AJ. Selective photoreduction of CO_2/HCO_3- to formate by aqueous suspensions and colloids of Pd-TiO2. *Journal of Physical Chemistry*. 1990;94:3784–3790.

23. Tseng IH, Chang WC, Wu JCS. Photoreduction of CO_2 using sol-gel derived titania and titania-supported copper catalysts. *Applied Catalysis B*. 2002;37:37–38.

24. Nishimura A, Sugiura N, Fujita M, et al. Influence of preparation conditions of coated TiO_2 film on CO_2 reforming performance. *Kagaku Kogaku Ronbunshu*. 2007;33:146–153.

25. Izumi Y. Recent advances in the photocatalytic conversion of carbon dioxide to fuels with water and/or hydrogen using solar energy and beyond. *Coordin Chem Rev*. 2013;257(1):171–186.

26. Lo CC, Hung CH, Yuan CS, et al. Photoreduction of carbon dioxide with H_2 and H_2O over TiO_2 and ZrO_2 in a circulated photocatalytic reactor. *Solar Energy Materials & Solar Cells*. 2007;91:1765–1774.

27. Nishimura A, Ishida N, Tatematsu D, et al. Effect of Fe loading condition and reductants on CO_2 reduction performance with Fe/TiO_2 photocatalyst. *International Journal of Photoenergy*. 2017;2017:11.

28. Nemoto J, Goken N, Ueno H. Photodecomposition of ammonia to dinitrogen and dihydrogen on platinized TiO_2 nanoparticules in an aqueous solution. *Journal of Photochemistry and Photobiology A: Chemistry*. 2007;185:295–300.

29. Japan Society of Mechanical Engineering. *Heat Transfer Hand Book*. 1st edn. Tokyo: Maruzen. 1993.

30. Nishimura A, Toyoda R, Tatematsu D, et al. Optimum reductants ratio for CO_2 reduction by overlapped Cu/TiO_2. *AIMS Materials Science*. 2019;6(2):214–233.

31. Paulino PN, Salim VMM, Resende NS. Zn-Cu Promoted TiO_2 Photocatalyst for CO_2 reduction with H2O under UV Light. *Applied Catalysis B: Environmental*. 2016;185:362–370.

32. Tahir M, Amin NAS. Photo-induced CO_2 reduction by hydrogen for selective CO evolution in a dynamic monolith photoreactor loaded with Ag-modified TiO2 nanocatalyst. *International Journal of Hydrogen Energy*. 2017;42(23):15507–15522.

33. Jensen J, Mikkelsen M, Krebs FC. Flexible substrates as basis for photocatalytic reduction of carbon dioxide. *Solar Energy Materials & Solar Cells*. 2011;95(11):2949–2958.

34. Ambrozova N, Reli M, Sihor M, et al. Copper and platinum doped titania for photocatalytic reduction of carbon dioxide. *Applied Surface Science*. 2018;430:475–487.

35. Nishimura A, Toyoda R, Tatematsu D, et al. Optimum reductants ratio for CO_2 reduction by overlapped Cu/TiO_2. *AIMS Materials Science*. 2019;6(2):214–233.

Citation: Nishimura A, Sakakibara Y, Inoe T, et al. Impact of molar ratio of NH_3 and H_2O on CO_2 reduction performance over Cu/TiO_2 photocatalyst. *Phys Astron Int J*. 2019;3(5):176–182. DOI: 10.15406/paij.2019.03.00179