catalysts

MDPI

Article

The Impact of Amount of Cu on CO_2 Reduction Performance of Cu/TiO_2 with NH_3 and H_2O

Akira Nishimura [1,*], Yoshito Sakakibara [1], Akira Koshio [2] and Eric Hu [3]

[1] Division of Mechanical Engineering, Graduate School of Engineering, Mie University, 1577 Kurimamachiya-cho, Tsu, Mie 514-8507, Japan; 419M117@m.mie-u.ac.jp
[2] Division of Chemistry for Materials, Graduate School of Engineering, Mie University, 1577 Kurimamachiya-cho, Tsu, Mie 514-8507, Japan; koshio@chem.mie-u.ac.jp
[3] School of Mechanical Engineering, The University of Adelaide, Adelaide 5005, Australia; eric.hu@adelaide.edu.au
* Correspondence: nisimura@mach.mie-u.ac.jp; Tel.: +81-59-231-9747

Abstract: This study has investigated the impact of molar ratio of CO_2 to reductants NH_3 and H_2O as well as that of Cu loading on CO_2 reduction characteristics over Cu/TiO_2. No study to optimize the reductants' combination and Cu loading weight in order to enhance CO_2 reduction performance of TiO_2 has been investigated yet. This study prepared Cu/TiO_2 film by loading Cu particles during the pulse arc plasma gun process after coating TiO_2 film by the sol-gel and dip-coating process. As to loading weight of Cu, it was regulated by change in the pulse number. This study characterized the prepared Cu/TiO_2 film by SEM and EPMA. Additionally, the performance of CO_2 reduction has been investigated under the illumination condition of Xe lamp with or without ultraviolet (UV) light. It is revealed that the molar ratio of $CO_2/NH_3/H_2O$ is optimized according to the pulse number. Since the amount of H^+ which is the same as that of electron is needed to produce CO decided following the theoretical CO_2 reduction reacting with H_2O or NH_3, larger H^+ is needed with the increase in the pulse number. It is revealed that Cu of 4.57 wt% for the pulse number of 200 is the optimum condition, whereas the molar quantity of CO per unit weight of Cu/TiO_2 with and without UV light illumination is 34.1 mol/g and 12.0 mol/g, respectively.

Keywords: Cu/TiO_2 film photocatalyst; CO_2 reduction characteristics with NH_3 and H_2O; Cu loading weight; optimum combination of reductants; visible light response

Citation: Nishimura, A.; Sakakibara, Y.; Koshio, A.; Hu, E. The Impact of Amount of Cu on CO_2 Reduction Performance of Cu/TiO_2 with NH_3 and H_2O. *Catalysts* **2021**, *11*, 610. https://doi.org/10.3390/catal11050610

Academic Editor: Fernando Fresno

Received: 26 April 2021
Accepted: 7 May 2021
Published: 10 May 2021

1. Introduction

Since the concentration of CO_2 in the atmosphere has increased notably since the Industrial Revolution, each country has declared its goal in order to reduce the amount of CO_2 emission. In Japan, the prime minister has declared to reduce the effective CO_2 emission to zero by 2050. However, the global average concentration of CO_2 in the atmosphere increased up to 410 ppmV in September 2020, which is an increase of 25 ppmV since 2009 [1]. Consequently, the break-through technology is required to reduce the amount of CO_2 in the world.

It is known that there are some approaches to reduce CO_2 emission, e.g., reduction of CO_2 emission, CO_2 capture and storage (CCS), and CO_2 capture and utilization (CCU). This study focuses on photocatalytic CO_2 reduction using photocatalyst. CO_2 could be converted into fuel species such as CO, CH_4, CH_3OH, etc., by photocatalyst [2–4]. TiO_2 is commonly used as the photocatalyst to reform CO_2 into fuel species, such as CO, CH_4, CH_3OH, and H_2, etc., with ultraviolet (UV) light [4–6], since it is useful, economical, and exhibits strong endurance for chemicals and corrosion [7]. However, pure TiO_2 can only work under UV light illumination which accounts for only 4% in sunlight [3]. Therefore, it is not effective to utilize sunlight, which is a renewable energy source. If the visible light, of which 44% of solar energy reaching the earth is [3], it could be utilized for photocatalytic reduction by TiO_2, and the CCU system utilizing renewable energy would be constructed.

Many approaches have attempted to enhance the CO_2 reduction performance of TiO_2 as a photocatalyst by expanding the wavelength of light absorbed by TiO_2. One of the popular methods is to dope precious metals, such as Pd [8], Pt [9], Ru, Pt-Ru alloy [10], and Au [11], for preparing the visible light-driven TiO_2. A hierarchical pore network and morphology to prepare the bio-templated TiO_2 catalyst [12], heteroleptic iridium complex supported on graphite carbon nitride [13], TiO_2 synthesis using superficial fluid technology [14], and N-doped reduced graphene oxide-promoted nano TiO_2 [15] were attempted to prepare the visible light driven TiO_2. Doped various metal ions have been applied, but among them, and this study considers that Cu is a promising dopant. Cu has an ability to absorb a wider wavelength, from 400 to 800 nm [16,17], which can cover most of visible light range. It was reported that Cu/TiO_2 had the superiority to pure TiO_2. Cu/Cu^+ fabricated Ti^{3+}/TiO_2 performed 8 mol/g of CH_4 production, which was 2.6 times as large as Ti^{3+}/TiO_2 [18]. Cu/TiO_2 prepared by a facile solvothermal method performed CO and CH_4 production up to 4.48 mol/g and 5.34 mol/g, which is 10 times larger compared to that of TiO_2 [19]. Cu/TiO_2 which was prepared by a sonothermal-hydrothermal route that performed 6.6 mol/g of CH_4 and 472.5 mol/g of CH_3OH in KOH/H_2O medium [20]. It was reported that the synthesized Cu_2O/TiO_2 showed the performance of 3.5 mol/g of CO production while that of TiO_2 was 0.1 mol/g [16]. These results [16,18–20] were achieved under the visible light illumination condition. The other well-known doped metals, e.g., Pd, Ag, and Au, are too precious to be applied in industrial usage. To spread a breakthrough technology to reduce the amount of CO_2 in the world, this study thinks that we had better select an economical and abundant material. Due to the reported performances, as well as low cost and large reserves, Cu is thought to be a preferable candidate compared to precious metals.

For the CO_2 reduction, a reductant is important as a partner for reaction. According to review papers [6,21], H_2O and H_2 are generally used as reductant. It is necessary to decide the optimum reductant which provides the proton (H^+) for the reduction reaction to enhance the CO_2 reduction performance. From the past studies [22–24], the reaction scheme of CO_2 reduction with H_2O can be shown as below:

<Photocatalytic reaction>

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

<Oxidization reaction>

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

<Reduction reaction>

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

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

As to the reaction scheme of CO_2 reduction reacting with H_2, it is known as below [25]:

<Photocatalytic reaction>

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

<Oxidization reaction>

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

<Reduction reaction>

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

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

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

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

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

Though the previous studies investigated CO_2 reduction reacting with H_2O or H_2 [6,21], the effect of NH_3 having $3H^+$, which is superior to H_2O and H_2, on photocatalytic CO_2 reduction characteristics is not examined yet other than the previous studies conducted by Nishimura et al. using Fe [26] or Cu [27]. The previous study [26] investigated only one combination ratio of CO_2, NH_3 and H_2O for Fe/TiO_2 photocatalyst. The other previous study reported the effect of ratio of CO_2, NH_3 and H_2O on CO_2 reduction characteristics over Cu/TiO_2 [27]. However, the effect of loading weight of Cu on the CO_2 reduction characteristics with NH_3 and H_2O was not reported though the amount of loaded metal is important to improve the CO_2 reduction performance using Cu/TiO_2 [28]. Therefore, it is necessary to optimize the loading weight of Cu with a different combination condition of NH_3 and H_2O in order to enhance the CO_2 reduction characteristics over Cu/TiO_2. As to the reaction scheme to reduce CO_2 with NH_3, it is as follows [25,29]:

<Photocatalytic reaction>

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

<Oxidization reaction>

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

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

<Reduction reaction>

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

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

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

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

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

The aims of this study are as follows:

(1) To reveal the impact of loading weight of Cu on CO_2 reduction characteristics using Cu/TiO_2.
(2) To reveal the effect of molar ratio of CO_2 to reductants NH_3 and H_2O on CO_2 reduction characteristics over Cu/TiO_2.

After these aims are completed, it is expected that a high-performance photocatalyst, which can absorb the wide-ranging wavelength of light effectively, as well as provide sufficient H^+ matched with the number of electrons as shown in the reaction scheme, is developed. The key point to complete the aims is to optimize the amount of Cu as well as the combination of CO_2, NH_3, and H_2O. This study focuses on the effective utilization of light energy with the aid of a doped metal and reductants combination. It matches with the scope of this journal which is the photocatalytic CO_2 reduction utilizing light energy effectively.

This study investigates the CO_2 reduction characteristics reacting with NH_3 and H_2O over Cu/TiO_2 photocatalyst film under the illumination condition of Xe lamp with or without UV light. The combination of $CO_2/NH_3/H_2O$ is changed for 1:1:1, 1:0.5:1, 1:1:0.5, 1:0.5:0.5, 3:2:3, 3:8:12, 3:12:18 to decide the optimum molar ratio for $CO_2/NH_3/H_2O$. The reaction scheme of CO_2 reduction reacting with H_2O or NH_3 reveals that the theoretical molar ratio of CO_2/H_2O to produce CO or CH_4 is 1:1 or 1:4, respectively, and that of CO_2/NH_3 to produce CO or CH_4 is 3:2 or 3:8, respectively. Consequently, this study assumes that the molar ratios to produce CO and CH_4 are $CO_2/NH_3/H_2O$ = 3:2:3 and 3:8:12, respectively, based on the theory. In addition, this study controlled the amount of Cu loaded on TiO_2 film during pulse arc plasma gun process. This study changed the pulse number by 100, 200 and 500 to control the loading weight of Cu.

2. Results and Discussion

2.1. The Characterization Evaluation of Cu/TiO_2 Film

Figure 1 represents SEM and EPMA (electron probe microanalyzer) images of Cu/TiO_2 film which is coated on netlike glass disc. The SEM and EPMA data of Cu/TiO_2 for the pulse number of 100, 200, 500 are shown. This study obtained the black and white SEM images at 1500 times magnification, which were available for EPMA analysis. As to the EPMA image, this study indicates the concentrations of each element in observation area by the diverse colors. When the amount of element is large, light colors, e.g., white, pink, and red are used. On the other hand, dark colors, e.g., black and blue, are used to display small amounts of elements. It is seen from Figure 1 that we can observe the TiO_2 film having a teeth-like shape coated on the netlike glass fiber irrespective of pulse number. It is believed that the temperature distribution of TiO_2 solution adhered on the netlike glass disc was not even during firing process since the thermal conductivity of Ti and SiO_2 at 600 K which are 19.4 W/(m·K) and 1.82 W/(m·K), respectively [30]. Since the thermal expansion and shrinkage around netlike glass fiber occurred, a thermal crack formed within the TiO_2 film. Accordingly, the TiO_2 film on the netlike glass fiber was teeth-like. As to Cu, we can observe that nanosized Cu particles are loaded on TiO_2 uniformly since nanosized Cu particles are emitted by the pulse arc plasma gun process. In addition, the amount of Cu particles increases with the increase in pulse number as expected. The observation area, i.e., the center part of netlike glass disc having a diameter of 300 μm, is analyzed by EPMA in order to measure the amount of loaded Cu within the TiO_2 film. The ratio of Cu to Ti is calculated by averaging the data detected in the observation area. The amount of element Cu within Cu/TiO_2 film for the pulse number of 100, 200 and 500 are counted by 1.62 wt%, 4.57 wt%, and 7.95 wt%, respectively, indicating that the weight of loaded Cu increases with the increase in the pulse number quantitatively. On the other hand, total weights of Cu/TiO_2 for the pulse number of 100, 200, and 500, which were measured by an electron balance, are 0.05 g, 0.06 g, and 0.08 g, respectively.

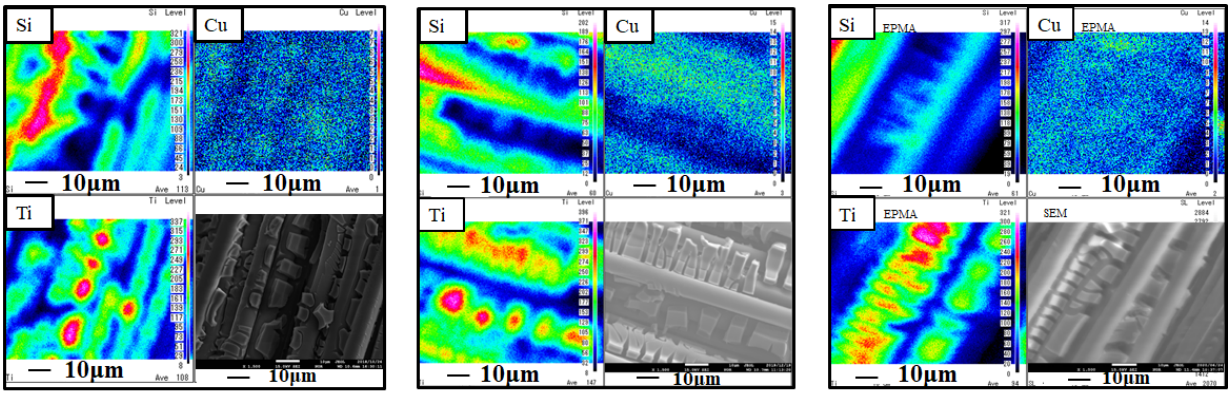


Figure 1. SEM and EPMA images of Cu/TiO_2 film which is coated on netlike glass disc. The left images show the data for the pulse number of 100, the center images show the data for the pulse number of 200, and the right images show the data for the pulse number of 500.

2.2. The CO_2 Reduction Characteristics over Cu/TiO_2 for a Pulse Number of 100

Figures 2 and 3 present the concentration change of formed CO with the time under the Xe lamp with or without UV light, respectively. In these figures, the produced CO is evaluated quantitatively by the molar quantity of CO per unit weight of photocatalyst having a unit of mol/g. The other fuels were not detected. As to a blank test, this study conducted the same experiment under no Xe lamp illumination condition as a reference case before the experiment. We detected no fuel during the blank test as we hoped. As to the stability, e.g., repeating use, this has not been tested in this study. As to the reproducibility of experiments, this study shows the data averaging three times

experiments. The experimental error through the experiments investigated in this study is distributed approximately from 0% to 20%.

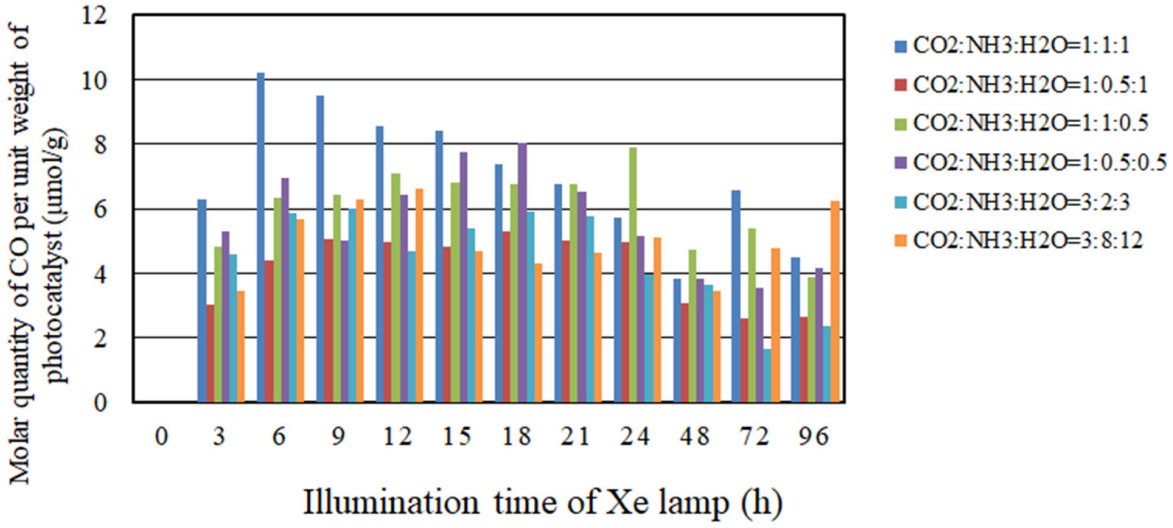


Figure 2. Comparison of molar quantity of CO per unit weight of photocatalyst under the illumination condition of Xe lamp with UV light. The pulse number is 100. The highest CO_2 reduction characteristic is obtained under the condition of the molar ratio of $CO_2/NH_3/H_2O$ = 1:1:1 where the molar quantity of CO per unit weight of photocatalyst is 10.2 mol/g.

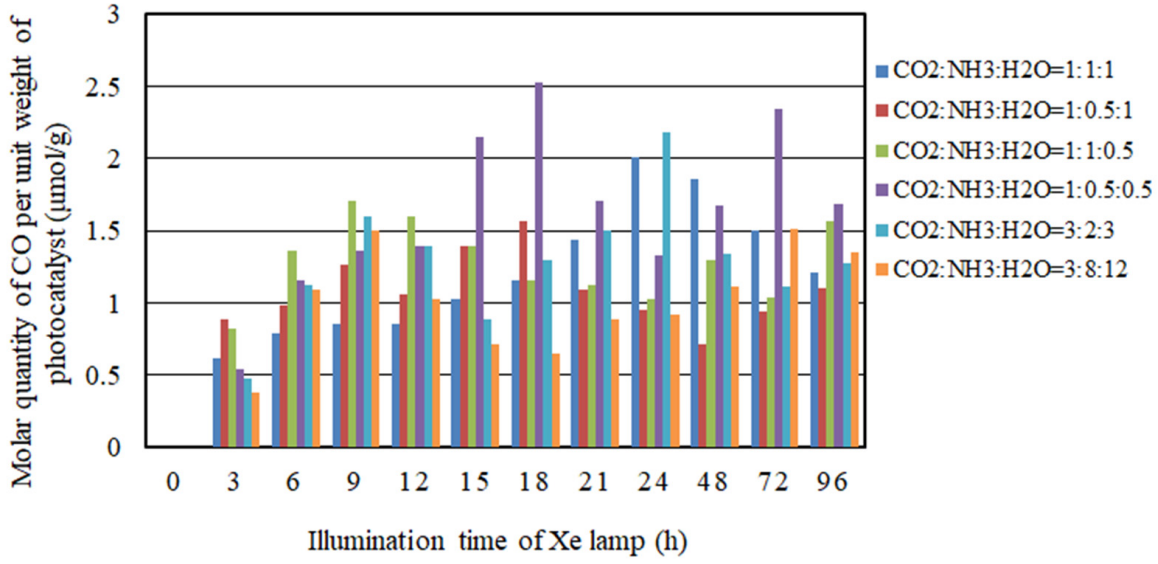


Figure 3. Comparison of molar quantity of CO per unit weight of photocatalyst under the illumination condition of Xe lamp without UV light. The pulse number is 100. The highest CO_2 reduction characteristic is obtained under the condition of the molar ratio of $CO_2/NH_3/H_2O$ = 1:0.5:0.5 where the molar quantity of CO per unit weight of photocatalyst is 2.52 mol/g.

It is revealed from Figure 2 that the CO_2 reduction performance for the molar ratio of $CO_2/NH_3/H_2O$ = 1:1:1 is the highest where the molar quantity of CO per unit weight of photocatalyst is 10.2 mol/g. According to the reaction scheme of CO_2 reduction reacting with H_2O or NH_3, the molar ratio of CO_2/H_2O to produce CO or CH_4 is 1:1 or 1:4, respectively, based on the theory. In addition, the theoretical molar of CO_2/NH_3 to produce CO or CH_4 is 3:2, 3:8, respectively. Consequently, this study assumes that the theoretical molar ratios of $CO_2/NH_3/H_2O$ are 3:2:3 and 3:8:12 to produce CO and CH_4, respectively. However, it is revealed that the molar ratio of $CO_2/NH_3/H_2O$ = 1:1:1 does not match with them. The ionized Cu which is doped on TiO_2 can provide free electrons to be used

during the reduction reaction [31]. Therefore, the reductants NH_3 and H_2O are adequate to produce CO in this study though they are smaller than the values according to the reaction scheme. It is also seen from Figures 2 and 3 that the produced CO decreases after attaining the maximum value. The decrease in the produced CO is thought to be caused due to the oxidization of CO with O_2 [32] which is by-product as explained by Equation (2) in the reaction scheme of CO_2 reduction reacting with H_2O. Therefore, this study does not establish that it is caused by the deactivation of photocatalyst.

As to the impact of NH_3 on CO_2 reduction characteristics using Cu/TiO_2, the authors' previous study [27] had revealed the following conclusions: The highest produced CO for the case of molar ratio of $CO_2/NH_3/H_2O$ = 1:0.5:0.5 exhibits approximately four times compared to that for the case of molar ratio of CO_2/H_2O = 1:0.5. In addition, the produced 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. It is known from the theoretical reaction scheme to reduce CO_2 with NH_3 that 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_2 = 1:0.5. When comparing the highest produced CO under the condition of $CO_2/NH_3/H_2O$ = 3:8:12 to that under the condition of CO_2/H_2O = 3:12, it is confirmed that the highest produced CO under the condition of molar ratio of $CO_2/NH_3/H_2O$ = 3:8:12 is approximately three times compared to that under the condition of molar ratio of CO_2/H_2O = 3:12. Therefore, it is clear that NH_3 has the potential to enhance CO_2 reduction characteristics of Cu/TiO_2 investigated in this study.

On the other hand, it can be seen from Figure 3 that the CO_2 reduction performance for the molar ratio of $CO_2/NH_3/H_2O$ = 1:0.5:0.5 is the highest where the molar quantity of CO per unit weight of the photocatalyst is 2.52 mol/g. Additionally, it is obvious that the amount of the total reductants is smaller than that in the case with UV light. When the Xe lamp is illuminated without UV light, the light intensity and wavelength range of light are smaller and narrower respectively, compared to the illumination condition with UV light as described before. It is known from the theoretical reaction scheme of CO_2 reduction reacting with H_2O or NH_3 that an electron is produced by the photochemical reaction which is influenced by the light illumination condition. In addition, H^+ whose amount is the same as that of electron is needed to produce CO. Since the produced electron might be smaller due to the smaller light input, it is believed that the amount of needed H^+ is smaller. Therefore, it is revealed that the highest CO_2 reduction characteristics is obtained under the condition of the molar ratio of $CO_2/NH_3/H_2O$ = 1:0.5:0.5, while total reductants are smaller compared to the case with UV light.

2.3. The CO_2 Reduction Characteristics over Cu/TiO_2 for a Pulse Number of 200

Figures 4 and 5 present the change of formed CO with the time under the illumination condition of Xe lamp with or without UV light, respectively. As to these figures, the produced CO is evaluated quantitatively by the molar quantity of CO per unit weight of photocatalyst having a unit of mol/g. The other fuels were not detected in this study. The data obtained under the condition of molar ratio of $CO_2/NH_3/H_2O$ = 3:12:18 are shown in Figure 4 to investigate the CO_2 reduction performance under the larger H^+ supply condition. As to a blank test, this study conducted the same experiment under the condition of no illumination of Xe lamp as a reference case before the experiment. We detected no fuel during the blank test, as we hoped.

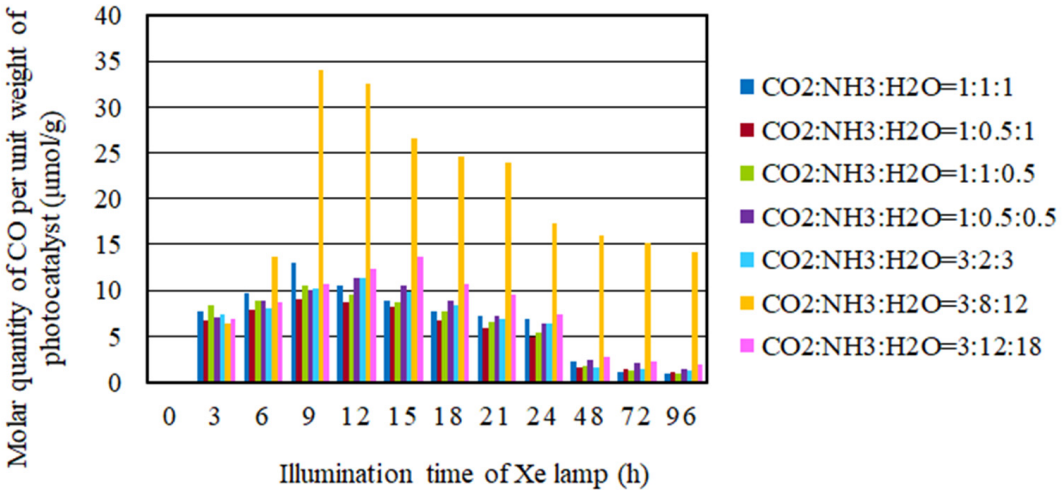


Figure 4. Comparison of molar quantity of CO per unit weight of photocatalyst under the illumination condition of Xe lamp with UV light. The pulse number is 200. The highest CO_2 reduction characteristic is obtained under the condition of the molar ratio of $CO_2/NH_3/H_2O$ = 3:8:12 where the molar quantity of CO per unit weight of photocatalyst is 34.1 mol/g.

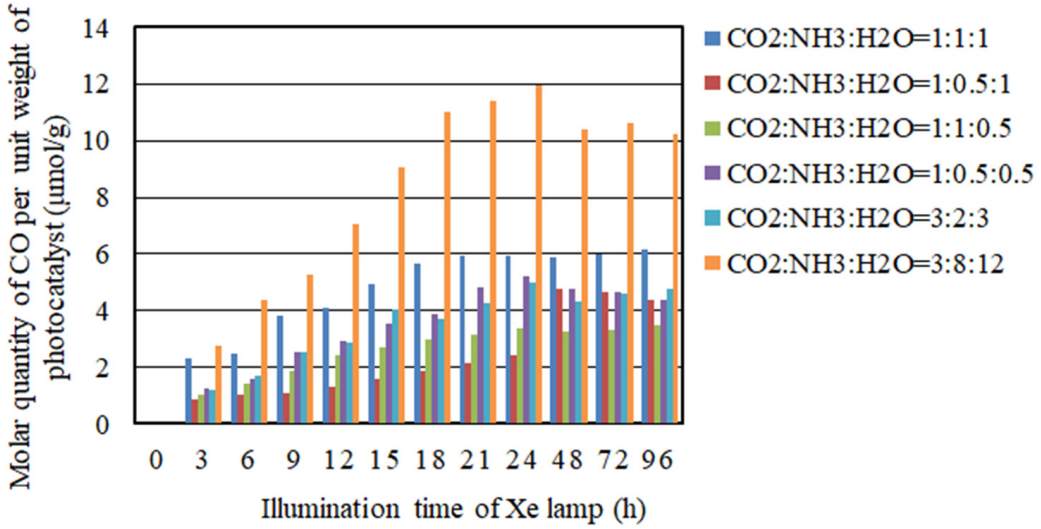


Figure 5. Comparison of molar quantity of CO per unit weight of photocatalyst under the illumination condition of Xe lamp without UV light. The pulse number is 200. The highest CO_2 reduction characteristic is obtained under the condition of the molar ratio of $CO_2/NH_3/H_2O$ = 3:8:12 where the molar quantity of CO per unit weight of photocatalyst is 12.0 mol/g.

It is revealed from Figures 4 and 5 that the CO_2 reduction characteristics under the condition of the molar ratio of $CO_2/NH_3/H_2O$ = 3:8:12 is the highest where the molar quantity of CO per unit weight of photocatalyst are 34.1 mol/g and 12.0 mol/g, respectively. The highest CO_2 reduction performance was obtained under the condition of the molar ratio of $CO_2/NH_3/H_2O$ = 3:8:12. According to the quantitative analysis by EPMA as shown above, the weight percentages of Cu within the Cu/TiO_2 film for the pulse number of 100 and 200 are 1.62 wt% and 4.57 wt%, respectively. When the amount of Cu increases, the total amount of free electron emitted from Cu during the photochemical reaction increases. Since the amount of H^+ which is the same as that of electron is needed to produce CO referring to the reaction scheme of CO_2 reduction reacting with H_2O or NH_3, larger H^+ is needed in the case of pulse number of 200. It is assumed that the theoretical molar ratios of $CO_2/NH_3/H_2O$ are 3:2:3 and 3:8:12 to produce CO and CH_4 respectively. However, it is revealed that the molar ratio of $CO_2/NH_3/H_2O$ = 3:8:12 is the most suitable for CO production in this study. The larger H^+ condition such as the molar ratio of

$CO_2/NH_3/H_2O$ = 3:12:18 was also examined to confirm whether larger H^+ is needed to produce more CO and CH_4 or not, resulting that the CO_2 reduction performance is lower compared to the molar ratio of $CO_2/NH_3/H_2O$ = 3:8:12. From these results, the optimum molar ratio of $CO_2/NH_3/H_2O$ is found to be 3:8:12.

2.4. The CO_2 Reduction Characteristics over Cu/TiO_2 for a Pulse Number of 500

Figures 6 and 7 present the change of formed CO with the time under the Xe lamp with or without UV light, respectively. In these figures, the produced CO is evaluated quantitatively by the molar quantity of CO per unit weight of photocatalyst having a unit of mol/g. The other fuels were not detected in this study. The data obtained under the condition of molar ratio of $CO_2/NH_3/H_2O$ = 3:12:18 are shown in Figure 6 to investigate the larger H^+ supply condition. As to a blank test, this study conducted the same experiment under the condition of no illumination of Xe lamp as a reference case before the experiment. We detected no fuel during the blank test, as we hoped.

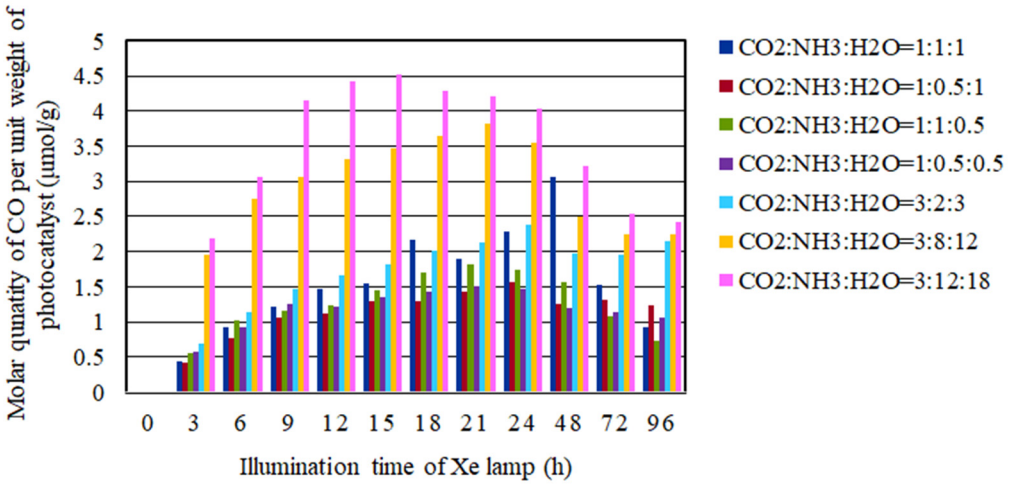


Figure 6. Comparison of molar quantity of CO per unit weight of photocatalyst under the illumination condition of Xe lamp with UV light. The pulse number is 500. The highest CO_2 reduction characteristic is obtained under the condition of the molar ratio of $CO_2/NH_3/H_2O$ = 3:12:18 where the molar quantity of CO per unit weight of photocatalyst is 4.4 mol/g.

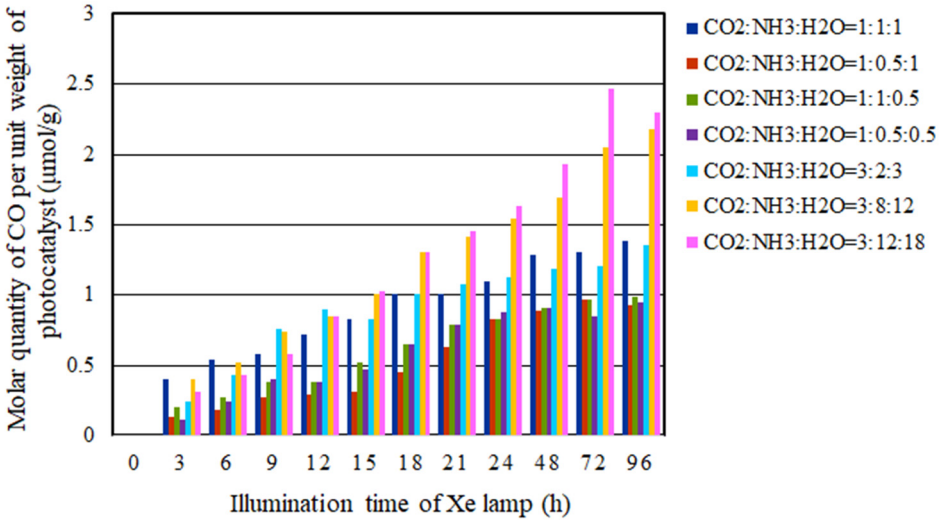


Figure 7. Comparison of molar quantity of CO per unit weight of photocatalyst under the illumination condition of Xe lamp without UV light. The pulse number is 500. The highest CO_2 reduction characteristic is obtained under the condition of the molar ratio of $CO_2/NH_3/H_2O$ = 3:12:18 where the molar quantity of CO per unit weight of photocatalyst is 2.5 mol/g.

It is revealed from Figures 6 and 7 that the CO_2 reduction characteristic under the condition of the molar ratio of $CO_2/NH_3/H_2O$ = 3:12:18 is the highest where the molar quantity of CO per unit weight of photocatalyst are 4.4 mol/g and 2.5 mol/g, respectively. It is revealed from Figures 6 and 7 that the highest CO_2 reduction characteristic is obtained under the condition of the molar ratio of $CO_2/NH_3/H_2O$ = 3:12:18. According to the quantitative analysis by EPMA, the weight percentages of element Cu in the Cu/TiO_2 film for the pulse number of 100, 200, and 500 are 1.62 wt%, 4.57 wt%, and 7.95 wt%, respectively. As mentioned above, the total amount of free electron emitted from Cu during the photochemical reaction increases when the amount of Cu increases. Since the amount of H^+, which is the same as that of electron is needed to produce CO referring to the theoretical reaction scheme of CO_2 reduction reacting with H_2O or NH_3, a larger amount of H^+ is needed in the case of a pulse number of 500 compared to the case of a pulse number of 200. Consequently, the optimum molar ratio of $CO_2/NH_3/H_2O$ is found to be 3:12:18. However, the molar quantity of CO per unit weight of photocatalyst is 4.4 mol/g under the condition of the molar ratio of $CO_2/NH_3/H_2O$ = 3:12:18, which is smaller than that under the condition of the molar ratio of $CO_2/NH_3/H_2O$ = 3:8:12 for a pulse number of 200. It might be thought that the CO_2 reduction characteristic is promoted with the increase in Cu loading weight. However, it is thought that too much Cu loading brings to cover the surface of the TiO_2 film [33,34]. As a result, CO_2 and reductants cannot reach the surface of TiO_2 film sufficiently. From these discussions, it is obvious that there is an optimum loading amount of Cu in order to promote CO_2 reduction characteristics with NH_3 and H_2O.

The considered conditions shown in the case of pulse number of 100, 200, and 500 are different in this study. The aim of this study is to clarify the optimum molar ratio of $CO_2/NH_3/H_2O$ for the improvement of CO_2 reduction performance of Cu/TiO_2. In the case of pulse number of 100, the optimum molar ratio of $CO_2/NH_3/H_2O$ is 1:1:1 with UV light while that is 1:0.5:0.5 without UV light. Therefore, it is not necessary to investigate the larger reductant ratio condition such as $CO_2/NH_3/H_2O$ = 3:12:18. On the other hand, in the case of pulse number of 200, the optimum molar ratio of $CO_2/NH_3/H_2O$ is 3:8:12 under the condition both with and without UV light. To optimize the molar ratio, the molar ratio of $CO_2/NH_3/H_2O$ = 3:12:18 which was larger reductant ratio condition was investigated under the condition of Xe lamp with UV light in this study. However, in the case of pulse number of 500, the optimum molar ratio of $CO_2/NH_3/H_2O$ is found to be 3:12:18 under the condition both with and without UV light, resulting that it was necessary to investigate the larger reductant ratio condition. This is the reason why the reported experimental conditions are different among the cases of pulse number of 100, 200, and 500 in this study.

The highest CO_2 reduction performance of Cu/TiO_2 is the molar quantity of CO per unit weight of photocatalyst of 34.1 mol/g which is obtained in the case of pulse number of 200. According to previous reports on the CO_2 reduction characteristic of the other metals doped TiO_2, Pt/TiO_2, and Ru/TiO_2 performed the molar quantity of CO per unit weight of photocatalyst of 12 mol/g and 13 mol/g, respectively, after the Xe lamp illumination time of 20 h in the case of CO_2/H_2O [10]. Pd/TiO_2 performed the molar quantity of CO per unit weight of photocatalyst of 10 mol/g after the Xe ark lamp illumination time of 3 h in the case of CO_2/H_2O [35]. On the other hand, Ag/TiO_2 with activated carbon performed the molar quantity of CO per unit weight of photocatalyst of 1.6 mol/g after a Xe lamp illumination time of 4 h in the case of CO_2/liquid H_2O [36]. According to the comparison of the CO_2 reduction performance of Cu/TiO_2 prepared in this study with that of other metal-doped TiO_2, the superiority of Cu/TiO_2 is confirmed.

2.5. The Quantum Efficiency Evaluation

Quantum efficiency is a well-known factor used to indicate the photocatalytic activity and efficiency [37]. The quantum efficiency is calculated by the following equations [6,38]:

$$\eta = (N_{output}/N_{input}) \times 100 \quad (20)$$

$$N_{input} = (I \times t \times \lambda \times A_{re})/(h \times c) \quad (21)$$

$$N_{output} = N_{CO} M_{CO} N_A \quad (22)$$

where η is the quantum efficiency (%), N_{input} is the photon number absorbed by photocatalyst (-), N_{output} is the photon number used in photocatalytic reaction (-), I is the light intensity of UV light (W/cm^2), t is the time illuminating UV light (t), λ is the wavelength limit of light that the photocatalyst can absorb for the photocatalytic reaction (m), A_{re} is the reaction surface area of photocatalyst assumed to be equal to the surface area of netlike glass disc (cm^2), h is Plank's constant (=6.626 $\times$ 10^{-34})(J·s), c is light speed (=2.998 $\times$ 10^8)(m/s), N_{CO} is the electron number required to form CO of a molecular (=2)(-), M_{CO} is the molar number of formed CO (mol), N_A is Avogadro's number. In this study, I agreed during all experiments where the illumination condition of Xe lamp with UV light and without UV light were 58.2 mW/cm^2 and 33.5 mW/cm^2, respectively. t under both UV light and without UV light were 345,600 s (=96 h).

Figures 8 and 9 show the quantum efficiencies among different molar ratios of $CO_2/NH_3/H_2O$ with and without UV light, respectively. In Figures 8 and 9, the results in the case of pulse number of 200 which provided the highest CO_2 reduction characteristic in this study are shown. It is revealed from Figures 8 and 9 that the highest quantum efficiency is obtained under the condition of the molar ratio of $CO_2/NH_3/H_2O$ = 3:8:12 irrespective of illumination condition of Xe lamp, which follows the results shown in Figures 4 and 5. It is obvious that the largest molar quantity of CO per unit weight of photocatalyst is 4.4 mol/g in this study. Compared to the previous studies on CO_2 reduction using Cu/TiO_2 with H_2O, as mentioned above [16,18–20], the amount of molar quantity of CO per unit weight of photocatalyst is approximately the same level.

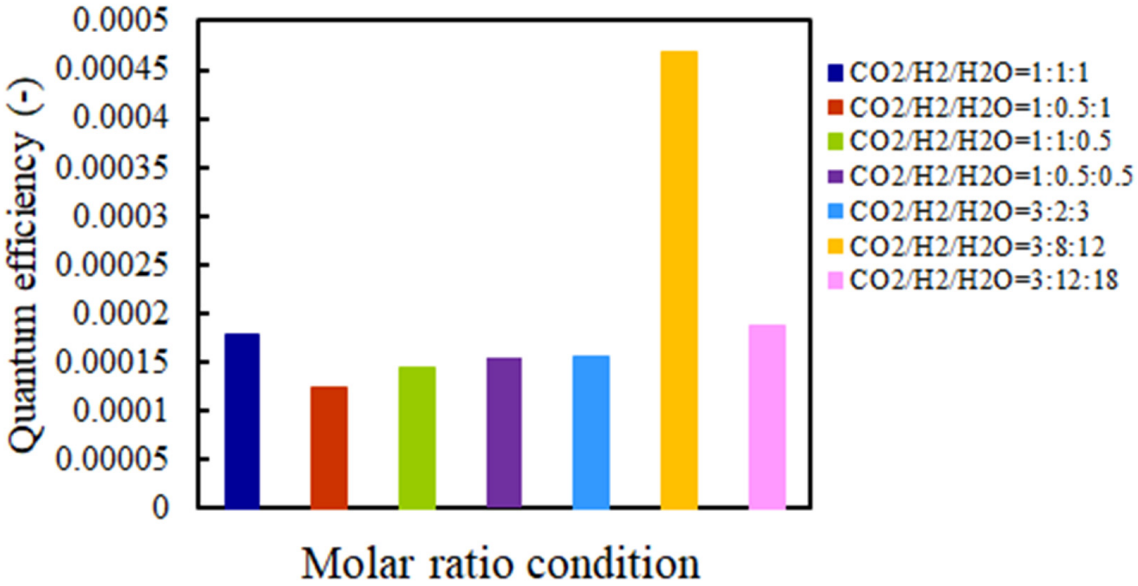


Figure 8. Comparison of quantum efficiency among different molar ratios with UV light. The pulse number is 200. The highest quantum efficiency is obtained under the condition of the molar ratio of $CO_2/NH_3/H_2O$ = 3:8:12.

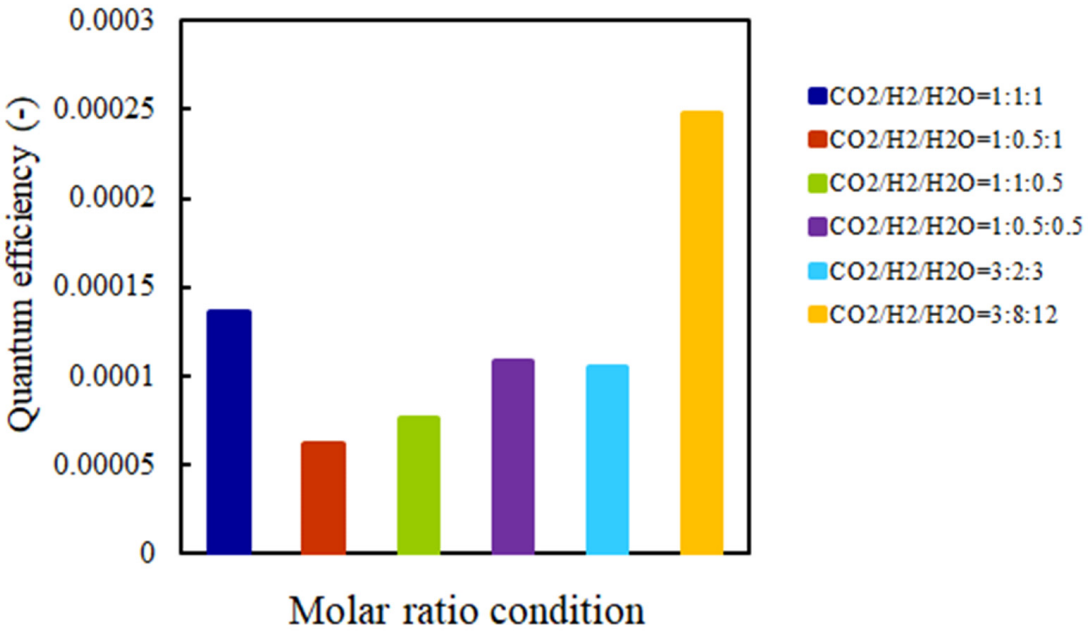


Figure 9. Comparison of quantum efficiency among different molar ratios without UV light. The pulse number is 200. The highest quantum efficiency is obtained under the condition of the molar ratio of $CO_2/NH_3/H_2O$ = 3:8:12.

The highest quantum efficiency is 4.69×10^{-4} when the Xe lamp with UV light is illuminated. On the other hand, it is 2.47×10^{-4} under the illumination condition of the Xe lamp without UV light in this study. According to the previous study [31], Cu/TiO_2 (2 wt% of Cu) performed the quantum efficiency of 1.56×10^{-2} in the case of CO_2/H_2O with UV light illumination. The other study reported that Cu/TiO_2 (1 wt% of Cu) showed the quantum efficiency of 1.41×10^{-2} in the case of CO_2/H_2O with UV light illumination [39]. The quantum efficiency obtained in this study is lower than that obtained in previous studies. The reason is thought to be that the total amount of electron needed in this study for photochemical reaction is too large due to the combination of two H^+ suppliers, i.e., NH_3 and H_2O. It is thought that (i) capturing the maximum visible light region, and (ii) draining the photogenerated charges on light irradiation towards Cu/TiO_2 surface [40] may be possible ways to improve the quantum efficiency.

This study has revealed the relationship between the optimum loading weight of Cu and the combination of reductants, such as NH_3 and H_2O, in order to improve the CO_2 reduction performance of TiO_2. As the next step, it can be considered to improve the CO_2 reduction performance of Cu/TiO_2 with NH_3 and H_2O further. The combination of different doped metals may be tried to promote the CO_2 reduction performance further in the near future. According to the previous studies [6,21], 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 were conducted to promote the CO_2 reduction performance of TiO_2 with H_2O. For the combination of $CO_2/NH_3/H_2O$, the electron number emitted from the dopant had better fit with H^+ number according to the theoretical reaction scheme. The electron number should match with H^+ number to produce fuel. Although this study selects Cu^+ ion in order to enhance the CO_2 reduction characteristic over TiO_2, the co-doping Cu with the other metal which has a larger positive ion would provide the positive impact to enhance the CO_2 reduction characteristic with reductants NH_3 and H_2O. Therefore, it is expected that the CO_2 reduction performance is promoted by the combination of different metal doping in the case of $CO_2/NH_3/H_2O$.

3. Experiments

3.1. The Preparation Proceure of Cu/TiO$_2$ Film

This study prepared TiO_2 film by sol-gel and dip-coating process [27]. $[(CH_3)_2CHO]_4Ti$ (Purity of 95 wt%, produced by Nacalai Tesque Co., Kyoto, Japan) of 0.3 mol, anhydrous

C_2H_5OH (purity of 99.5 wt%, produced by Nacalai Tesque Co., Kyoto, Japan) of 2.4 mol, distilled water of 0.3 mol, and HCl (purity of 35 wt%, produced by Nacalai Tesque Co., Kyoto, Japan) of 0.07 mol were mixed for preparing the TiO_2 sol solution. This study coats the TiO_2 film on a netlike glass fiber (SILIGLASS U, produced by Nihonmuki Co., Tokyo, Japan) by sol-gel and dip-coating processes. The glass fiber, having a diameter of about 10 m, weaved as a net, is collected to be the diameter of approximately 1 mm. The porous diameter of glass fiber and the specific surface area are about 1 nm and 400 m^2/g, respectively from the specifications of netlike glass fiber. The netlike glass fiber is composed of SiO_2 of 96 wt%. The opening space of the netlike glass fiber is approximately 2 mm × 2 mm. Since the netlike glass fiber has porous characteristics, the netlike glass fiber can capture the TiO_2 film easily during sol-gel and dip-coating processes. Additionally, we can expect that CO_2 is more easily absorbed by the prepared photocatalyst due to the porous characteristics of the netlike glass fiber. This study cut the netlike glass fiber to be disc form having diameter of 50 mm and thickness of 1 mm. This study immersed the netlike glass disc into TiO_2 sol solution controlling the speed at 1.5 mm/s and drew it up controlling the fixed speed at 0.22 mm/s. After that, this study dried it out and fired under a controlled firing temperature (*FT*) and firing duration time (*FD*) to fasten the TiO_2 film to the base material. This study set *FT* and *FD* at 623 K and 180 s, respectively.

After the coating of TiO_2, this study loads Cu on the TiO_2-coated netlike glass disc by the pulse arc plasma gun process [27] emitting Cu nano-particles uniformly via an applied high voltage. The pulse number can control the quantity of Cu loaded on TiO_2. This study set the pulse number at 100, 200, and 500. This study applied the pulse arc plasma gun device (ARL-300, produced by ULVAC, Inc., Chigasaki, Japan) which has a Cu electrode. The diameter of the Cu electrode for Cu loading was 10 mm. The Cu nano-particles were emitted from Cu electrode with applying the voltage of 200 V after the TiO_2 coated on netlike glass disc was set in the vacuumed vessel. The pulse arc plasma gun evaporates Cu electrode into fine particulate form over the TiO_2 in the concentric area whose diameter is 100 mm when the distance between Cu electrode and the TiO_2 is set to be 160 mm. Due to the distance between Cu electrode and TiO_2 film of 150 mm, this study can spread Cu particles over TiO_2 film uniformly.

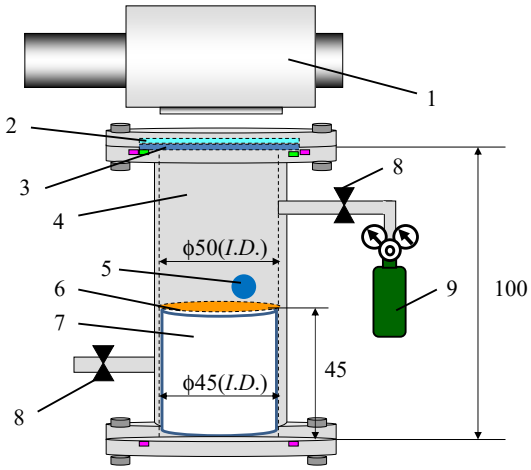
3.2. The Characterization Procedure of Cu/TiO_2 Film

This study evaluated the characteristics of external and crystal structure of Cu/TiO_2 film prepared above by SEM (JXA-8530F, produced by JEOL Ltd., Tokyo, Japan) and EPMA (JXA-8530F, produced by JEOL Ltd., Tokyo, Japan) [27]. These procedures use electron to analyze characterization, resulting that the sample should conduct electricity. Since the netlike glass disc used for base material to coat Cu/TiO_2 film cannot conduct electricity, the vaporized carbon was deposited by the carbon deposition device (JEE-420, produced by JEOL Ltd., Tokyo, Japan) on the surface of the Cu/TiO_2 film before analyzing its characterization. The thickness of the deposited carbon was approximately 2030 nm. The electrons are emitted from the electrode to the sample setting the acceleration voltage and current of 15 kV and 3.0×10^{-8} A respectively, in order to analyze the external structure of Cu/TiO_2 film using SEM. After the character X-ray is analyzed using EPMA at the same time, the amount of chemical element is clarified referring to the relation between character X-ray energy and atomic number. SEM and EPMA have the space resolution of 10 mm. The EPMA analysis can support to clarify the structure of prepared photocatalyst as well as to measure the quantity of loaded metal within TiO_2 film on the netlike glass disc as base material.

3.3. The Exprimental Procedure of CO_2 Reduciton

Figure 10 illustrates the experimental apparatus where the reactor consists of a stainless tube having a scale of 100 mm (*H.*) × 50 mm (*I.D.*), the Cu/TiO_2 film coated on netlike glass disc having a scale of 50 mm (*D.*) × 1 mm (*t.*) positioned on the Teflon cylinder having a scale of 50 mm (*H.*) × 50 mm (*D.*), a quartz glass disc having a scale

of 84 mm (*D*.) × 10 mm (*t*.), a sharp cut filter removing the wavelength of light which is below 400 nm (SCF-49.5C-42L, produced by SIGMA KOKI CO. LTD., Tokyo, Japan), a 150 W Xe lamp (L2175, produced by Hamamatsu Photonics K. K.), mass flow controller, and CO_2 gas cylinder (purity of 99.995 vol%) [27]. The reactor size for charging CO_2 is 1.25×10^{-4} m^3. The light of Xe lamp positioned on the stainless tube is illuminated toward Cu/TiO_2 film passing the sharp cut filter and the quartz glass disc located on the top of the stainless tube. The wavelength of light illuminated from Xe lamp is ranged from 185 nm to 2000 nm. The sharp cut filter can eliminate the UV from the Xe lamp, resulting in the wavelength of light illuminating the Cu/TiO_2 film ranged from 401 nm to 2000 nm. Figure 11 shows the light transmittance characteristics of the sharp cut filter to remove the wavelength of the light, indicating that it can guarantee the removal of the wavelength of light under 400 nm [27]. The mean light intensity of light illuminated from Xe lamp without the sharp cut filter is 58.2 mW/cm^2, while, with sharp cut filter, it is 33.5 mW/cm^2.



1. Xe lamp, 2. Sharp cut filter, 3. Quartz glass disc, 4. Stainless tube,
5. Gas sampling tap, 6. Photocatalyst, 7. Teflon cylinder, 8. Valve,
9. CO_2 gas cylinder (99.995 vol%)

Figure 10. Schematic diagram of CO_2 reduction experimental apparatus. The reactor consists of stainless tube, Cu/TiO_2 film positioned on Teflon cylinder, a quartz glass disc, a sharp cut filter, a 150 W Xe lamp, mass flow controller, CO_2 gas cylinder.

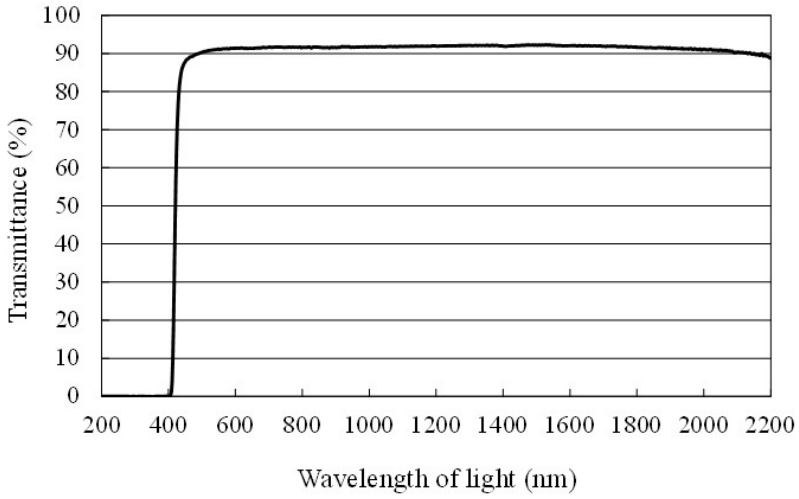


Figure 11. Light transmittance characteristics of sharp cut filter. The filter can cut off the wavelength of light which is below 400 nm.

After filling CO_2 gas whose purity of 99.995 vol% in the reactor vacuumed by a vacuum pump for 15 min, the valves installed at the inlet and the outlet of reactor were closed during CO_2 reduction experiment with NH_3 + H_2O. After that, this study confirmed the pressure of 0.1 MPa and gas temperature at 298 K in the reactor. Then, we injected the NH_3 aqueous solution (NH_3 purity of 50 vol%) into the reactor via the gas sampling tap, and turned on the Xe lamp at that time. The amount of injected NH_3 aqueous solution was changed depending on the considered molar ratio. Due to the heat of the infrared light components illuminated by the Xe lamp, the injected NH_3 aqueous solution was vaporized. The temperature in the reactor attained at 343 K within an hour, and it was maintained at 343 K during the CO_2 reduction experiment. The molar ratio of $CO_2/NH_3/H_2O$ was changed by 1:1:1, 1:0.5:1, 1:1:0.5, 1:0.5:0.5, 3:2:3, 3:8:12, 3:12:18. The reacted gas filled in the reactor was extracted by gas syringe via gas sampling tap and it was analyzed by an FID gas chromatograph (GC353B, produced by GL Science) and a methanizer (MT221, produced by GL Science). The FID gas chromatograph and methanizer have minimum resolutions of 1 ppmV.

4. Conclusions

From the investigation in this study, the following conclusions could be drawn:

(i) Cu particles whose size is nano-scale could be loaded on TiO_2 uniformly by the pulse arc plasma gun process. The weight percentages of element Cu within the Cu/TiO_2 film for pulse numbers of 100, 200, and 500 increase with the increase in the pulse number, which are 1.62 wt%, 4.57 wt%, and 7.95 wt%, respectively.

(ii) As to the pulse number of 100, the CO_2 reduction characteristic under the condition of the molar ratio of $CO_2/NH_3/H_2O$ = 1:1:1 is the highest where the molar quantity of CO produced for per unit weight of photocatalyst is 10.2 mol/g with UV light. However, the CO_2 reduction characteristic under the condition of the molar ratio of $CO_2/NH_3/H_2O$ = 1:0.5:0.5 is the highest where the molar quantity of CO produced for per unit weight of photocatalyst is 2.52 mol/g without UV light.

(iii) As to the pulse number of 200, the CO_2 reduction characteristics under the condition of the molar ratio of $CO_2/NH_3/H_2O$ = 3:8:12 is the highest under the illumination conditions both with and without UV light, where the molar quantity of CO produced per unit weight of photocatalyst are 34.1 mol/g and 12.0 mol/g, respectively.

(iv) In the case of pulse number of 500, the CO_2 reduction characteristic under the condition of the molar ratio of $CO_2/NH_3/H_2O$ = 3:12:18 under the illumination conditions both with and without UV light is the highest where the molar quantity of CO produced per unit weight of photocatalyst are 4.4 mol/g and 2.5 mol/g, respectively. It is revealed that the optimum loading weight of Cu is 4.57 wt% in order to promote CO_2 reduction characteristic with NH_3 and H_2O.

(v) This study clarifies that the highest quantum efficiencies with and without UV light illumination are 4.69×10^{-4} and 2.47×10^{-4}, respectively.

Author Contributions: Conceptualization: A.N.; methodology: A.K.; data curation: Y.S.; writing—original draft preparation: A.N.; writing—review and editing: E.H. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Data Availability Statement: The authors agree with the data availability presented in this study.

Acknowledgments: The authors acknowledge for the contribution by Shoji Nakamura who is the technician belonging to Mie University.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Global Monitoring Laboratory. Available online: https://www.esrl.noaa.gov/gmd/ccgg/trends/global.html (accessed on 9 December 2020).
2. Matavos-Aramyan, S.; Soukhakian, S.; Jazebizadeh, H.M.; Moussavi, M.; Hojjati, M.R. On Engineering Strategies for Photoselective CO_2 Reduction—A through Review. *Appl. Mater. Today* **2020**, *18*, 1–40.
3. Remiro-Buenamanana, S.; Garcia, H. Photoassisted CO_2 Conversion to Fuels. *Chem. Cat Chem. Minirev.* **2019**, *11*, 342–356.
4. Abdullah, H.; Khan, M.M.R.; Ong, H.R.; Yaakob, Z. Modified TiO_2 Photocatalyst for CO_2 Photocatalytic Reduction: An Overview. *J. CO_2 Util.* **2017**, *22*, 15–32. [CrossRef]
5. Sohn, Y.; Huang, W.; Tagipour, F. Recent progress and perspectives in the photocatalytic CO_2 reduction of Ti-oxide-based nanomaterials. *Appl. Surf. Sci.* **2017**, *396*, 1696–1711. [CrossRef]
6. Nahar, S.; Zain, M.F.M.; Kadhum, A.A.H.; Abu, H.H. Advances in Photocatalytic CO_2 Reduction with Water: A review. *Materials* **2017**, *10*, 629. [CrossRef] [PubMed]
7. Tahir, M.; Amin, N.S. Indium-doped TiO_2 Nanoparticles for Photocatalytic CO_2 Reduction with H_2O Vapors to CH_4. *Appl. Catal. B Envion.* **2015**, *162*, 98–109. [CrossRef]
8. Su, K.Y.; Chen, C.Y.; Wu, R.J. Preparation of Pd/TiO_2 Nanowires for the Photoreduction of CO_2 into Renewable Hydrocarbon Fuels. *J. Taiwan Inst. Chem. Eng.* **2019**, *96*, 409–418. [CrossRef]
9. Zhao, Y.; Wei, Y.; Wu, X.; Zheng, H.; Zhao, Z.; Liu, J.; Li, J. Graphene-wrapped Pt/TiO_2 Photocatalysts with Enhanced Photogenerated Charges Separation and Reactant Adsorption for High Selective Photoreduction of CO_2 to CH_4. *Appl. Catal. B Environ.* **2018**, *226*, 360–372. [CrossRef]
10. Wei, Y.; Wu, X.; Zhao, Y.; Wang, L.; Zhao, Z.; Huang, X.; Liu, J.; Li, J. Efficient Photocatalysts of TiO_2 Nanocrystals-supported PtRu Alloy Nanoparticles for CO_2 Reduction with H_2O: Synergetic Effect of Pt-Ru. *Appl. Catal. B Environ.* **2018**, *236*, 445–457. [CrossRef]
11. Zeng, S.; Vahidzadeh, E.; VanEssen, C.G.; Kar, P.; Kisslinger, R.; Goswami, A.; Zhang, Y.; Mahdi, N.; Riddell, S.; Kobryn, A.E.; et al. Optical Control of Selectivity of High Rate CO_2 Photoreduction via Interband- or Hot Electron Z-scheme Reaction Pathways in Au-TiO_2 Plasmonic Photonic Crystal Photocatalyst. *Appl. Catal. B Environ.* **2020**, *267*, 1–11. [CrossRef]
12. Hashermizadeh, I.; Golovko, V.B.; Choi, J.; Tsang, D.C.W.; Yip, A.C.K. Photocatalytic Reduction of CO_2 to Hydrocarbons Using Bio-templated Porous TiO_2 Architectures under UV and Visible Light. *Chem. Eng. J.* **2018**, *347*, 64–73. [CrossRef]
13. Kumar, A.; Kumar, P.; Borkar, R.; Bansiwal, A.; Labhsetwar, N.; Jain, S.L. Metal-organic Hybrid: Photoreduction of CO_2 Using Graphic Carbon Nitride Supported Heteroleptic Iridium Complex under Visible Light Irradiation. *Carbon* **2017**, *123*, 371–379. [CrossRef]
14. Camarillo, R.; Toston, S.; Martinez, F.; Jimenez, C.; Rincon, J. Preparation of TiO_2-based Catalyst with Supercritical Fluid Technology: Characterization and Photocatalytic Activity in CO_2 Reduction. *J. Chem. Tech. Biotech.* **2017**, *92*, 1710–1720. [CrossRef]
15. Lin, L.Y.; Nie, Y.; Kavadiya, S.; Soundappan, T.; Biswas, P. N-doped Reduced Graphene Oxide Promoted Nano TiO_2 as a Bifunctional Adsorbent/Photocatalyst for CO_2 Photoreduction: Effect of N Species. *Chem. Eng. J.* **2017**, *316*, 449–460. [CrossRef]
16. Aguirre, M.E.; Zhou, R.; Eugene, A.J.; Guzman, M.I.; Grela, M.A. Cu_2O/TiO_2 Heterostructure for CO_2 Reduction through a Direct Z-scheme: Protecting Cu_2O from Photocorrosion. *Appl. Catal. B Environ.* **2017**, *217*, 485–493. [CrossRef]
17. Kavil, Y.N.; Shaban, Y.A.; Farawati, R.K.A.; Orif, M.I.; Zobidi, M.; Khan, S.U.M. Photocatalytic Conversion of CO_2 into Methanol over Cu-C/TiO_2 Nanoparticles under UV Light and Natural Sunlight. *J. Photochem. Photobiol. A Chem.* **2017**, *347*, 244–253. [CrossRef]
18. Zhu, S.; Chen, X.; Li, Z.; Ye, X.; Liu, Y.; Chen, Y.; Yang, L.; Chen, M.; Zhang, D.; Li, G.; et al. Cooperation between Inside and Outside of TiO_2: Lattice Cu^+ Accelerates Carrier Migration to the Surface of Metal Copper for Photocatalytic CO_2 Reduction. *Appl. Catal. B Environ.* **2020**, *264*, 1–10. [CrossRef]
19. She, H.; Zhao, Z.; Bai, W.; Huang, J.; Wang, L.; Wang, Q. Enhanced Performance of Photocatalytic CO_2 Reduction with Synergistic Effect between Chitosan and Cu: TiO_2. *Mater. Res. Bull.* **2020**, *124*, 1–7. [CrossRef]
20. Olowoyo, J.O.; Kumar, M.; Dash, T.; Saran, S.; Bhandari, S.; Kumar, U. Self-organized Copper Impregnation and Doping in TiO_2 with Enhanced Photocatalytic Conversion of H_2O and CO_2 to Fuel. *Int. J. Hydrog. Energy* **2018**, *43*, 19468–19480. [CrossRef]
21. Tahir, M.; Amin, N.S. Advances in Visible Light Responsive Titanium Oxide Based Photocatalysts for CO_2 Conversion to Hydrocarbon Fuels. *Energy Convers. Manag.* **2013**, *76*, 194–214. [CrossRef]
22. Goren, Z.; Willner, I.; Nelson, A.J. Selective Photoreduction of CO_2/HCO_3^- to formate by aqueous suspensions and colloids of Pd-TiO_2. *J. Physic. Chem.* **1990**, *94*, 3784–3790. [CrossRef]
23. Tseng, I.H.; Chang, W.C.; Wu, J.C.S. Photoreduction of CO_2 Using Sol-gel Derived Titania and Titania-supported Copper Catalysts. *Appl. Catal. B* **2002**, *37*, 37–38. [CrossRef]
24. Izumi, Y. Recent Advances in the Photocatalytic Conversion of Carbon Dioxide to Fuels with Water and/or Hydrogen Using Solar Energy and Beyond. *Coord. Chem. Rev.* **2013**, *257*, 171–186. [CrossRef]
25. Lo, C.C.; Hung, C.H.; Yuan, C.S.; Wu, J.F. Photoreduction of Carbon Dioxide with H_2 and H_2O over TiO_2 and ZrO_2 in a Circulated Photocatalytic Reactor. *Sol. Energy Mater. Sci.* **2007**, *91*, 1765–1774. [CrossRef]
26. Nishimura, A.; Ishida, N.; Tatematsu, D.; Hirota, M.; Koshio, A.; Kokai, F.; Hu, E. Effect of Fe Loading Condition and Reductants on CO_2 Reduction Performance with Fe/TiO_2 Photocatalyst. *Int. J. Photoenergy* **2017**, *2017*, 1625274. [CrossRef]

27. Nishimura, A.; Sakakibara, Y.; Inoue, T.; Hirota, M.; Koshio, A.; Kokai, F.; Hu, E. 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*, 176–182.
28. Ambrozova, N.; Reli, M.; Sihor, M.; Kurstrowski, P.; Wu, J.C.S.; Koci, K. Copper and Platinum Doped Titania for Photocatalytic Reduction of Carbon Dioxide. *Appl. Surf. Sci.* **2018**, *430*, 475–487. [CrossRef]
29. Nemoto, J.; Goken, N.; Ueno, K. Photodecomposition of Ammonia to Dinitrogen and Dihydrogen on Platinized TiO_2 Nanoparticles in an Aqueous Solution. *J. Photochem. Photobiol. A Chem.* **2007**, *185*, 295–300. [CrossRef]
30. Japan Society of Mechanical Engineering. *Heat Transfer Hand Book*, 1st ed.; Maruzen: Tokyo, Japan, 1993; pp. 367–369.
31. Paulino, P.N.; Salim, V.M.M.; Resende, N.S. Zu-Cu Promoted TiO_2 Photocatalyst for CO_2 Reduction with H_2O under UV Light. *Appl. Catal. B Environ.* **2016**, *185*, 362–370.
32. Tahir, M.; Amin, N.A.S. Photo-induced CO_2 Reduction by Hydrogen for Selective CO Evolution in a Dynamic Monolith Photoreactor Loaded with Ag-Modified TiO_2 Nanocatalyst. *Int. J. Hydrog. Energy* **2017**, *42*, 15507–15522. [CrossRef]
33. Zhao, H.; Rao, G.; Wang, L.; Xu, J.; Liu, L.; Li, Y. Synthesis of Novel MgAl Layered Double Oxide Grafted TiO_2 Cuboids and their Photocatalytic Activity on CO_2 Reduction with Water Vapor. *Catal. Sci. Technol.* **2015**, *5*, 3288–3295. [CrossRef]
34. Zhang, R.; Huang, Z.; Li, C.; Zuo, Y.; Zhou, Y. Monolithic g-C_3N_4/Reduced Graphene Oxide Aerogel with in Situ Embedding of Pd Nanoparticles for Hydrogeneration of CO_2 to CH_4. *Appl. Suf. Sci.* **2019**, *475*, 953–960. [CrossRef]
35. Camarillo, R.; Toston, S.; Martinez, F.; Jimenez, C.; Rincon, J. Enhancing the Photocatalytic Reduction of CO_2 through Engineering of Catalysts with High Pressure Technology: Pd/TiO_2 Photocatalsyts. *J. Supercrit. Fluids* **2017**, *123*, 18–27. [CrossRef]
36. Jiang, Z.; Zhang, X.; Yuan, Z.; Chen, J.; Huang, B.; Dionysiou, D.D.; Yang, G. Enhanced Photocatalytic CO_2 Reduction via the Synergistic Effect between Ag and Activated Carbon in TiO_2/AC-Ag Ternary Composite. *Chem. Eng. J.* **2018**, *348*, 592–598. [CrossRef]
37. Hoque, M.A.; Guzman, M.J. Photocatalytic Activity: Experimental Features to Report in Heterogeneous Photocatalysis. *Materials* **2018**, *11*, 1990. [CrossRef]
38. Nishimura, A.; Inoue, T.; Sakakibara, Y.; Hirota, M.; Koshio, A.; Kokai, F.; Hu, E. Optimum Molar Ratio of H_2 and H_2O to Reduce CO_2 Using Pd/TiO_2. *Aims Mater. Sci.* **2019**, *6*, 464–483. [CrossRef]
39. Li, Y.; Wang, W.N.; Zhan, Z.; Woo, M.H.; Wu, C.Y.; Biswas, P. Photocatalytic Reduction of CO_2 with H_2O on Mesoporous Silica Supported Cu/TiO_2 Catalysts. *Appl. Catal. B Environ.* **2010**, *100*, 386–392. [CrossRef]
40. Razzaq, A.; Ali, S.; Asif, M. Layered Double Hydroxide (LDH) Based Photocatalysts: An Outstanding Strategy for Efficient Photocatalytic CO_2 Conversion. *Catalysts* **2020**, *10*, 1185. [CrossRef]