

Article

The Impact of Amount of Cu on CO₂ Reduction Performance of Cu/TiO₂ with NH₃ and H₂O

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Abstract: This study has investigated the impact of molar ratio of CO₂ to reductants NH₃ and H₂O as well as that of Cu loading on CO₂ reduction characteristics over Cu/TiO₂. No study to optimize the reductants' combination and Cu loading weight in order to enhance CO₂ reduction performance of TiO₂ has been investigated yet. This study prepared Cu/TiO₂ film by loading Cu particles during the pulse arc plasma gun process after coating TiO₂ 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/TiO₂ film by SEM and EPMA. Additionally, the performance of CO₂ 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 CO₂/NH₃/H₂O 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 CO₂ reduction reacting with H₂O or NH₃, 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/TiO₂ with and without UV light illumination is 34.1 mol/g and 12.0 mol/g, respectively.

Keywords: Cu/TiO₂ film photocatalyst; CO₂ reduction characteristics with NH₃ and H₂O; Cu loading weight; optimum combination of reductants; visible light response

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1. Introduction

Since the concentration of CO₂ in the atmosphere has increased notably since the Industrial Revolution, each country has declared its goal in order to reduce the amount of CO₂ emission. In Japan, the prime minister has declared to reduce the effective CO₂ emission to zero by 2050. However, the global average concentration of CO₂ 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 CO₂ in the world.

It is known that there are some approaches to reduce CO₂ emission, e.g., reduction of CO₂ emission, CO₂ capture and storage (CCS), and CO₂ capture and utilization (CCU). This study focuses on photocatalytic CO₂ reduction using photocatalyst. CO₂ could be converted into fuel species such as CO, CH₄, CH₃OH, etc., by photocatalyst [2–4]. TiO₂ is commonly used as the photocatalyst to reform CO₂ into fuel species, such as CO, CH₄, CH₃OH, and H₂, etc., with ultraviolet (UV) light [4–6], since it is useful, economical, and exhibits strong endurance for chemicals and corrosion [7]. However, pure TiO₂ 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 TiO₂, and the CCU system utilizing renewable energy would be constructed.

Many approaches have attempted to enhance the CO₂ reduction performance of TiO₂ as a photocatalyst by expanding the wavelength of light absorbed by TiO₂. 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 TiO₂. A hierarchical pore network and morphology to prepare the bio-templated TiO₂ catalyst [12], heteroleptic iridium complex supported on graphite carbon nitride [13], TiO₂ synthesis using superficial fluid technology [14], and N-doped reduced graphene oxide-promoted nano TiO₂ [15] were attempted to prepare the visible light driven TiO₂. 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/TiO₂ had the superiority to pure TiO₂. Cu/Cu⁺ fabricated Ti³⁺/TiO₂ performed 8 mol/g of CH₄ production, which was 2.6 times as large as Ti³⁺/TiO₂ [18]. Cu/TiO₂ prepared by a facile solvothermal method performed CO and CH₄ production up to 4.48 mol/g and 5.34 mol/g, which is 10 times larger compared to that of TiO₂ [19]. Cu/TiO₂ which was prepared by a sonothermal-hydrothermal route that performed 6.6 mol/g of CH₄ and 472.5 mol/g of CH₃OH in KOH/H₂O medium [20]. It was reported that the synthesized Cu₂O/TiO₂ showed the performance of 3.5 mol/g of CO production while that of TiO₂ 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 CO₂ 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 CO₂ reduction, a reductant is important as a partner for reaction. According to review papers [6,21], H₂O and H₂ 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 CO₂ reduction performance. From the past studies [22–24], the reaction scheme of CO₂ reduction with H₂O can be shown as below:

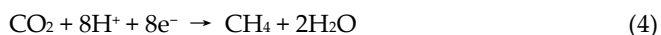
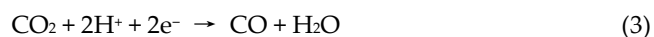
<Photocatalytic reaction>



<Oxidization reaction>



<Reduction reaction>



As to the reaction scheme of CO₂ reduction reacting with H₂, it is known as below [25]:

<Photocatalytic reaction>



<Oxidization reaction>



<Reduction reaction>





Though the previous studies investigated CO₂ reduction reacting with H₂O or H₂ [6,21], the effect of NH₃ having 3H⁺, which is superior to H₂O and H₂, on photocatalytic CO₂ 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 CO₂, NH₃ and H₂O for Fe/TiO₂ photocatalyst. The other previous study reported the effect of ratio of CO₂, NH₃ and H₂O on CO₂ reduction characteristics over Cu/TiO₂ [27]. However, the effect of loading weight of Cu on the CO₂ reduction characteristics with NH₃ and H₂O was not reported though the amount of loaded metal is important to improve the CO₂ reduction performance using Cu/TiO₂ [28]. Therefore, it is necessary to optimize the loading weight of Cu with a different combination condition of NH₃ and H₂O in order to enhance the CO₂ reduction characteristics over Cu/TiO₂. As to the reaction scheme to reduce CO₂ with NH₃, it is as follows [25,29]:

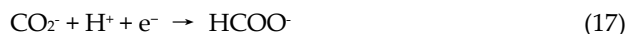
<Photocatalytic reaction>



<Oxidization reaction>



<Reduction reaction>



The aims of this study are as follows:

- (1) To reveal the impact of loading weight of Cu on CO₂ reduction characteristics using Cu/TiO₂.
- (2) To reveal the effect of molar ratio of CO₂ to reductants NH₃ and H₂O on CO₂ reduction characteristics over Cu/TiO₂.

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 CO₂, NH₃, and H₂O. 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 CO₂ reduction utilizing light energy effectively.

This study investigates the CO₂ reduction characteristics reacting with NH₃ and H₂O over Cu/TiO₂ photocatalyst film under the illumination condition of Xe lamp with or without UV light. The combination of CO₂/NH₃/H₂O 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 CO₂/NH₃/H₂O. The reaction scheme of CO₂ reduction reacting with H₂O or NH₃ reveals that the theoretical molar ratio of CO₂/H₂O to produce CO or CH₄ is 1:1 or 1:4, respectively, and that of CO₂/NH₃ to produce CO or CH₄ is 3:2 or 3:8, respectively. Consequently, this study

assumes that the molar ratios to produce CO and CH₄ are CO₂/NH₃/H₂O = 3:2:3 and 3:8:12, respectively, based on the theory. In addition, this study controlled the amount of Cu loaded on TiO₂ 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/TiO₂ Film

Figure 1 represents SEM and EPMA (electron probe microanalyzer) images of Cu/TiO₂ film which is coated on netlike glass disc. The SEM and EPMA data of Cu/TiO₂ 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 TiO₂ film having a teeth-like shape coated on the netlike glass fiber irrespective of pulse number. It is believed that the temperature distribution of TiO₂ solution adhered on the netlike glass disc was not even during firing process since the thermal conductivity of Ti and SiO₂ 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 TiO₂ film. Accordingly, the TiO₂ film on the netlike glass fiber was teeth-like. As to Cu, we can observe that nanosized Cu particles are loaded on TiO₂ 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 TiO₂ 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/TiO₂ 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/TiO₂ 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.

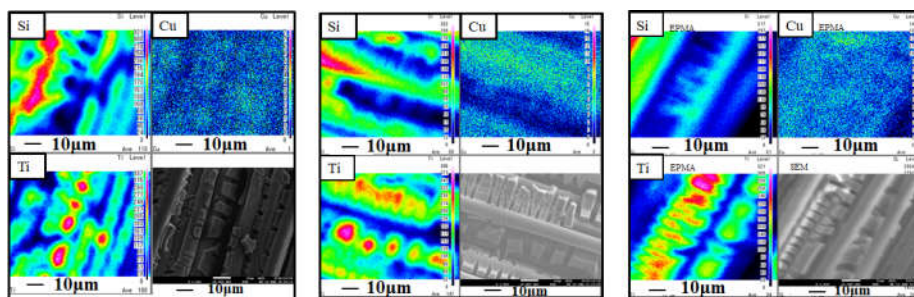


Figure 1. SEM and EPMA images of Cu/TiO₂ film which is coated on netlike glass disc. The left images show the data for the pulse number of 100, the center images show the data for the pulse number of 200, and the right images show the data for the pulse number of 500.

2.2. The CO₂ Reduction Characteristics Over Cu/TiO₂ 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%.

It is revealed from Figure 2 that the CO₂ reduction performance for the molar ratio of CO₂/NH₃/H₂O = 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 CO₂ reduction reacting with H₂O or NH₃, the molar ratio of CO₂/H₂O to produce CO or CH₄ is 1:1 or 1:4, respectively, based on the theory. In addition, the theoretical molar of CO₂/NH₃ to produce CO or CH₄ is 3:2, 3:8, respectively. Consequently, this study assumes that the theoretical molar ratios of CO₂/NH₃/H₂O are 3:2:3 and 3:8:12 to produce CO and CH₄, respectively. However, it is revealed that the molar ratio of CO₂/NH₃/H₂O = 1:1:1 does not match with them. The ionized Cu which is doped on TiO₂ can provide free electrons to be used during the reduction reaction [31]. Therefore, the reductants NH₃ and H₂O 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 O₂ [32] which is by-product as explained by Equation (2) in the reaction scheme of CO₂ reduction reacting with H₂O. Therefore, this study does not establish that it is caused by the deactivation of photocatalyst.

As to the impact of NH₃ on CO₂ reduction characteristics using Cu/TiO₂, the authors' previous study [27] had revealed the following conclusions: The highest produced CO for the case of molar ratio of CO₂/NH₃/H₂O = 1:0.5:0.5 exhibits approximately four times compared to that for the case of molar ratio of CO₂/H₂O = 1:0.5. In addition, the produced CO keeps some value approximately without rapid decrease before 24 h for CO₂/NH₃/H₂O conditions compared to the molar ratio of CO₂/H₂O = 1:0.5. It is known from the theoretical reaction scheme to reduce CO₂ with NH₃ that the more reaction step is needed to produce CO since NH₃ should be converted into H₂. Therefore, it is believed that the time to produce CO is longer compared to the molar ratio of CO₂/H₂ = 1:0.5. When comparing the highest produced CO under the condition of CO₂/NH₃/H₂O = 3:8:12 to that under the condition of CO₂/H₂O = 3:12, it is confirmed that the highest produced CO under the condition of molar ratio of CO₂/NH₃/H₂O = 3:8:12 is approximately three times compared to that under the condition of molar ratio of CO₂/H₂O = 3:12. Therefore, it is clear that NH₃ has the potential to enhance CO₂ reduction characteristics of Cu/TiO₂ investigated in this study.

On the other hand, it can be seen from Figure 3 that the CO₂ reduction performance for the molar ratio of CO₂/NH₃/H₂O = 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 CO₂ reduction reacting with H₂O or NH₃ 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 CO₂ reduction characteristics is obtained under the condition of the molar ratio of CO₂/NH₃/H₂O = 1:0.5:0.5, while total reductants are smaller compared to the case with UV light.

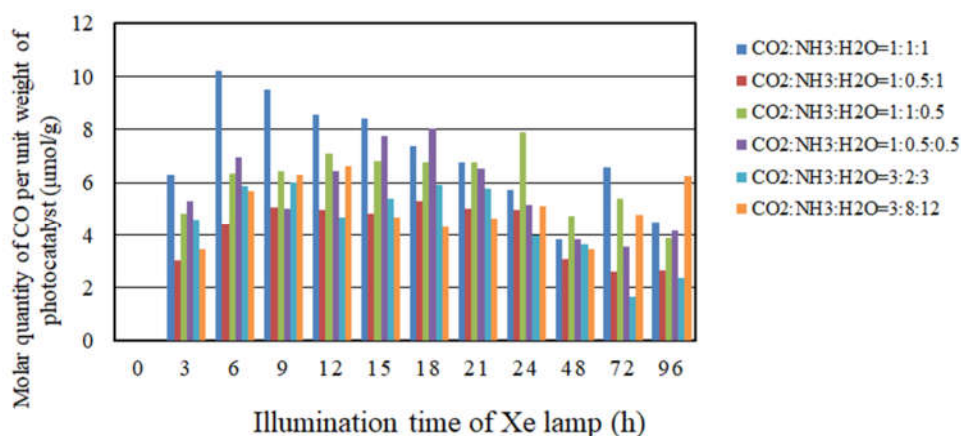


Figure 2. Comparison of molar quantity of CO per unit weight of photocatalyst under the illumination condition of Xe lamp with UV light. The pulse number is 100. The highest CO₂ reduction characteristic is obtained under the condition of the molar ratio of CO₂/NH₃/H₂O = 1:1:1 where the molar quantity of CO per unit weight of photocatalyst is 10.2 mol/g.

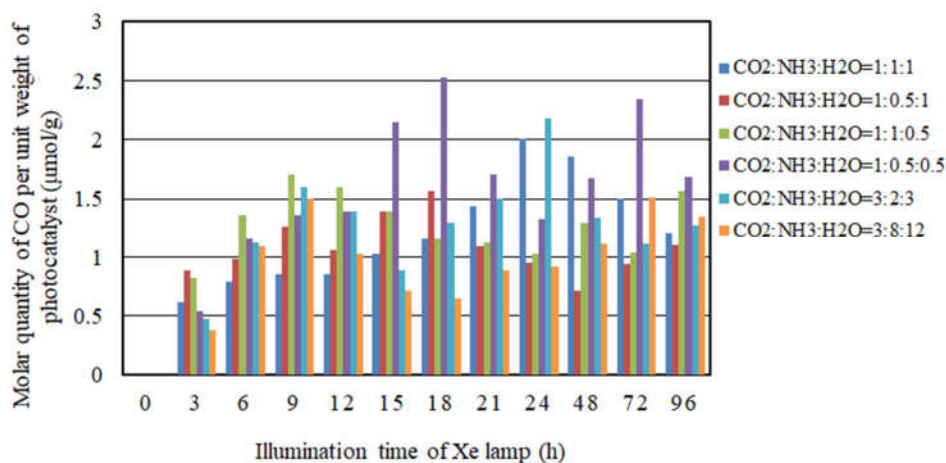


Figure 3. Comparison of molar quantity of CO per unit weight of photocatalyst under the illumination condition of Xe lamp without UV light. The pulse number is 100. The highest CO₂ reduction characteristic is obtained under the condition of the molar ratio of CO₂/NH₃/H₂O = 1:0.5:0.5 where the molar quantity of CO per unit weight of photocatalyst is 2.52 mol/g.

2.3. The CO₂ Reduction Characteristics Over Cu/TiO₂ 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 CO₂/NH₃/H₂O = 3:12:18 are shown in Figure 4 to investigate the CO₂ 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.

It is revealed from Figures 4 and 5 that the CO₂ reduction characteristics under the condition of the molar ratio of CO₂/NH₃/H₂O = 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 CO₂ reduction performance was obtained under the condition of the molar ratio of CO₂/NH₃/H₂O = 3:8:12. According to the quantitative analysis by EPMA as shown above, the weight percentages of Cu within the Cu/TiO₂ 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.

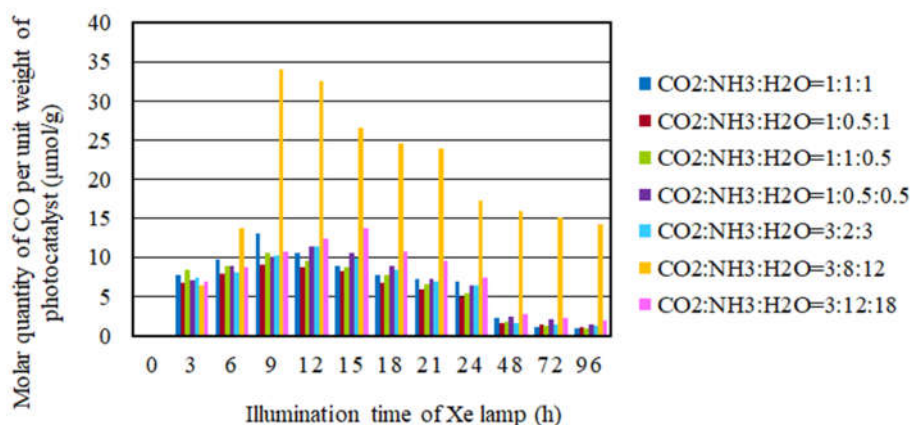


Figure 4. Comparison of molar quantity of CO per unit weight of photocatalyst under the illumination condition of Xe lamp with UV light. The pulse number is 200. The highest CO_2 reduction characteristic is obtained under the condition of the molar ratio of $CO_2/NH_3/H_2O = 3:8:12$ where the molar quantity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

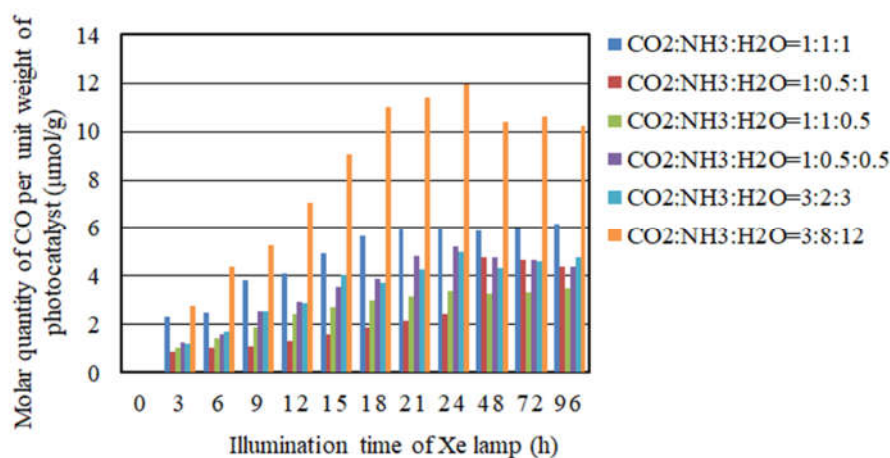


Figure 5. Comparison of molar quantity of CO per unit weight of photocatalyst under the illumination condition of Xe lamp without UV light. The pulse number is 200. The highest CO_2 reduction characteristic is obtained under the condition of the molar ratio of $CO_2/NH_3/H_2O = 3:8:12$ where the molar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

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 $\text{CO}_2/\text{NH}_3/\text{H}_2\text{O} = 3:12:18$ 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.

It is revealed from Figures 6 and 7 that the CO_2 reduction characteristic under the condition of the molar ratio of $\text{CO}_2/\text{NH}_3/\text{H}_2\text{O} = 3:12:18$ 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 $\text{CO}_2/\text{NH}_3/\text{H}_2\text{O} = 3:12:18$. According to the quantitative analysis by EPMA, the weight percentages of element Cu in the Cu/TiO₂ 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 $\text{CO}_2/\text{NH}_3/\text{H}_2\text{O}$ 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 $\text{CO}_2/\text{NH}_3/\text{H}_2\text{O} = 3:12:18$, which is smaller than that under the condition of the molar ratio of $\text{CO}_2/\text{NH}_3/\text{H}_2\text{O} = 3:8:12$ 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 TiO₂ film [33,34]. As a result, CO_2 and reductants cannot reach the surface of TiO₂ 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 $\text{CO}_2/\text{NH}_3/\text{H}_2\text{O}$ for the improvement of CO_2 reduction performance of Cu/TiO₂. In the case of pulse number of 100, the optimum molar ratio of $\text{CO}_2/\text{NH}_3/\text{H}_2\text{O}$ 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 $\text{CO}_2/\text{NH}_3/\text{H}_2\text{O} = 3:12:18$. On the other hand, in the case of pulse number of 200, the optimum molar ratio of $\text{CO}_2/\text{NH}_3/\text{H}_2\text{O}$ is 3:8:12 under the condition both with and without UV light. To optimize the molar ratio, the molar ratio of $\text{CO}_2/\text{NH}_3/\text{H}_2\text{O} = 3:12:18$ 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 $\text{CO}_2/\text{NH}_3/\text{H}_2\text{O}$ 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/TiO₂ 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 TiO₂, Pt/TiO₂, and Ru/TiO₂ 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 $\text{CO}_2/\text{H}_2\text{O}$ [10]. Pd/TiO₂ performed the molar quantity of CO per unit weight of photocatalyst of 10 mol/g after the Xe lamp illumination time of 3 h in the case of $\text{CO}_2/\text{H}_2\text{O}$ [35]. On the other hand, Ag/TiO₂ 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 $\text{CO}_2/\text{liquid H}_2\text{O}$ [36]. According to the comparison of the CO_2 reduction performance of Cu/TiO₂ prepared in this study with that of other metal-doped TiO₂, the superiority of Cu/TiO₂ is confirmed.

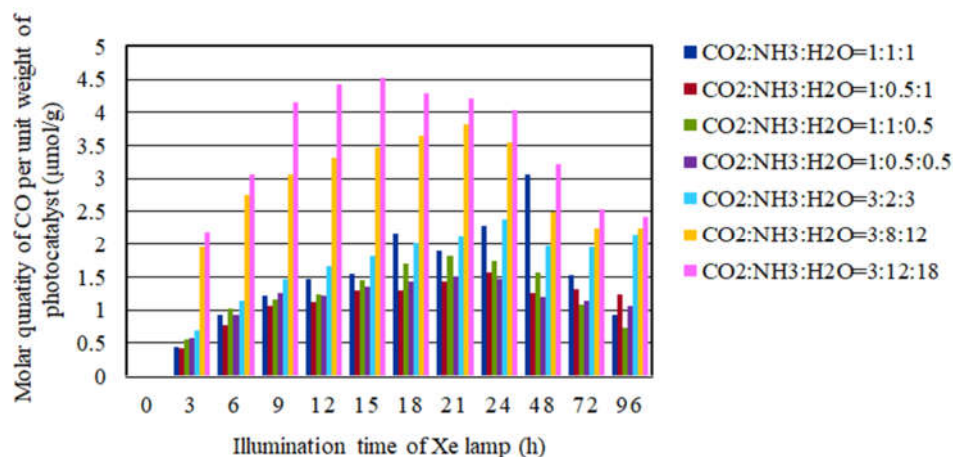


Figure 6. Comparison of molar quantity of CO per unit weight of photocatalyst under the illumination condition of Xe lamp with UV light. The pulse number is 500. The highest CO₂ reduction characteristic is obtained under the condition of the molar ratio of CO₂/NH₃/H₂O = 3:12:18 where the molar quantity of CO per unit weight of photocatalyst is 4.4 mol/g.

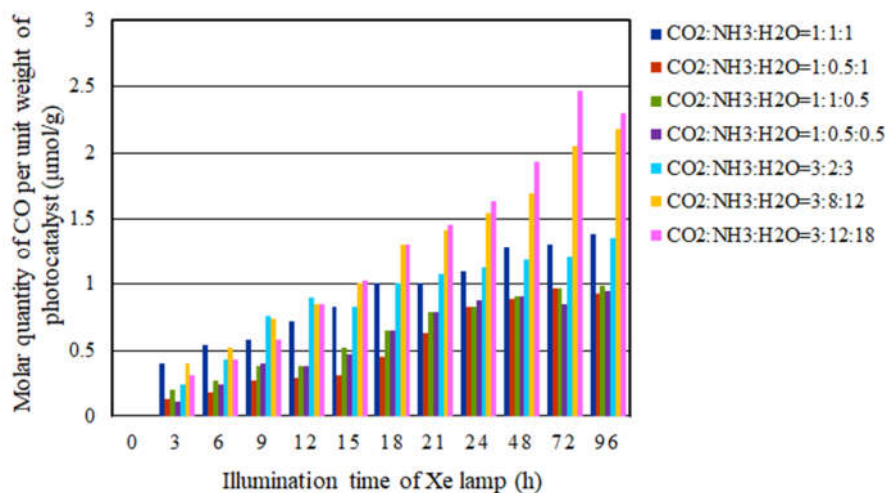


Figure 7. Comparison of molar quantity of CO per unit weight of photocatalyst under the illumination condition of Xe lamp without UV light. The pulse number is 500. The highest CO₂ reduction characteristic is obtained under the condition of the molar ratio of CO₂/NH₃/H₂O = 3:12:18 where the molar quantity of CO per unit weight of photocatalyst is 2.5 mol/g.

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]:

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

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

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

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/cm²), 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 (cm²), h is Planck'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/cm² and 33.5 mW/cm², 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 CO₂/NH₃/H₂O 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 CO₂ 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 CO₂/NH₃/H₂O = 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 CO₂ reduction using Cu/TiO₂ with H₂O, as mentioned above [16,18–20], the amount of molar quantity of CO per unit weight of photocatalyst is approximately the same level.

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/TiO₂ (2 wt% of Cu) performed the quantum efficiency of 1.56×10^{-2} in the case of CO₂/H₂O with UV light illumination. The other study reported that Cu/TiO₂ (1 wt% of Cu) showed the quantum efficiency of 1.41×10^{-2} in the case of CO₂/H₂O 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., NH₃ and H₂O. It is thought that (i) capturing the maximum visible light region, and (ii) draining the photogenerated charges on light irradiation towards Cu/TiO₂ surface [40] may be possible ways to improve the quantum efficiency.

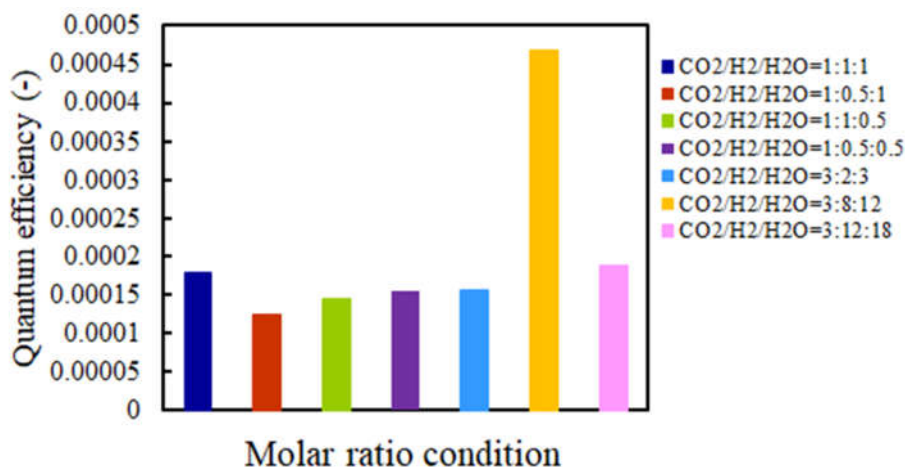


Figure 8. Comparison of quantum efficiency among different molar ratios with UV light. The pulse number is 200. The highest quantum efficiency is obtained under the condition of the molar ratio of CO₂/NH₃/H₂O = 3:8:12.

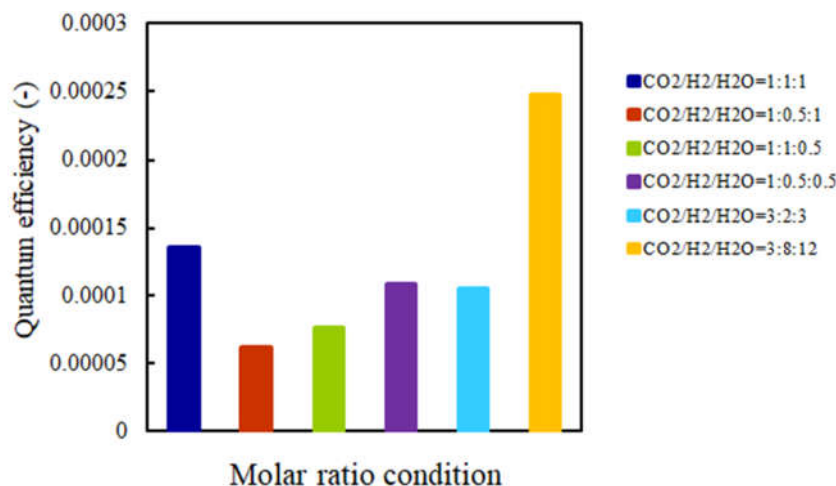


Figure 9. Comparison of quantum efficiency among different molar ratios without UV light. The pulse number is 200. The highest quantum efficiency is obtained under the condition of the molar ratio of CO₂/NH₃/H₂O = 3:8:12.

This study has revealed the relationship between the optimum loading weight of Cu and the combination of reductants, such as NH₃ and H₂O, in order to improve the CO₂ reduction performance of TiO₂. As the next step, it can be considered to improve the CO₂ reduction performance of Cu/TiO₂ with NH₃ and H₂O further. The combination of different doped metals may be tried to promote the CO₂ reduction performance further in the near future. According to the previous studies [6,21], the co-doped TiO₂ such as PbS-Cu/TiO₂, Cu-Fe/TiO₂, Cu-Ce/TiO₂, Cu-Mn/TiO₂, and Cu-CdS/TiO₂ were conducted to promote the CO₂ reduction performance of TiO₂ with H₂O. For the combination of CO₂/NH₃/H₂O, 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 CO₂ reduction characteristic over TiO₂, the co-doping Cu with the other metal which has a larger positive ion would provide the positive impact to enhance the CO₂ reduction characteristic with reductants NH₃ and H₂O. Therefore, it is expected that the CO₂ reduction performance is promoted by the combination of different metal doping in the case of CO₂/NH₃/H₂O.

3. Experiments

3.1. The Preparation Procedure of Cu/TiO₂ Film

This study prepared TiO₂ film by sol-gel and dip-coating process [27]. [(CH₃)₂CHO]₄Ti (Purity of 95 wt%, produced by Nacalai Tesque Co., Kyoto, Japan) of 0.3 mol, anhydrous C₂H₅OH (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 TiO₂ sol solution. This study coats the TiO₂ 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 μm, 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 μm and 400 m²/g, respectively from the specifications of netlike glass fiber. The netlike glass fiber is composed of SiO₂ 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 TiO₂ film easily during sol-gel and dip-coating processes. Additionally, we can expect that CO₂ 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 TiO₂ 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 TiO₂ film to the base material. This study set *FT* and *FD* at 623 K and 180 s, respectively.

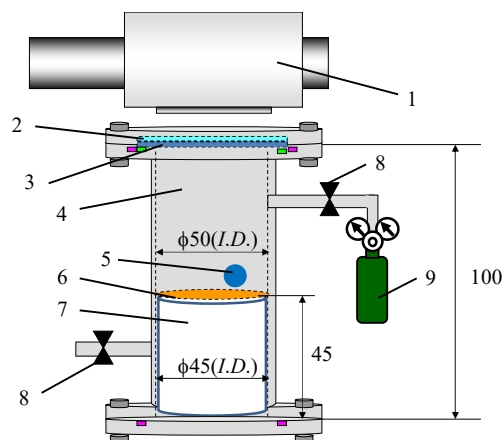
After the coating of TiO₂, this study loads Cu on the TiO₂-coated netlike glass disc by the pulse arc plasma gun process [27] emitting Cu nano-particles uniformly via an applied high voltage. The pulse number can control the quantity of Cu loaded on TiO₂. This study set the pulse number at 100, 200, 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 TiO₂ 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 TiO₂ in the concentric area whose diameter is 100 mm when the distance between Cu electrode and the TiO₂ is set to be 160 mm. Due to the distance between Cu electrode and TiO₂ film of 150 mm, this study can spread Cu particles over TiO₂ film uniformly.

3.2. The Characterization Procedure of Cu/TiO₂ Film

This study evaluated the characteristics of external and crystal structure of Cu/TiO₂ 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/TiO₂ 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/TiO₂ 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/TiO₂ 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 TiO₂ film on the netlike glass disc as base material.

3.3. The Experimental Procedure of CO₂ Reduciton

Figure 10 illustrates the experimental apparatus where the reactor consists of a stainless tube having a scale of 100 mm (*H.*) \times 50 mm (*I.D.*), the Cu/TiO₂ film coated on netlike glass disc having a scale of 50 mm (*D.*) \times 1 mm (*t.*) positioned on the Teflon cylinder having a scale of 50 mm (*H.*) \times 50 mm (*D.*), a quartz glass disc having a scale of 84 mm (*D.*) \times 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 CO₂ gas cylinder (purity of 99.995 vol%) [27]. The reactor size for charging CO₂ is 1.25×10^{-4} m³. The light of Xe lamp positioned on the stainless tube is illuminated toward Cu/TiO₂ 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/TiO₂ 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/cm², while, with sharp cut filter, it is 33.5 mW/cm².



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. CO₂ gas cylinder (99.995 vol%)

Figure 10. Schematic diagram of CO₂ reduction experimental apparatus. The reactor consists of stainless tube, Cu/TiO₂ film positioned on Teflon cylinder, a quartz glass disc, a sharp cut filter, a 150 W Xe lamp, mass flow controller, CO₂ gas cylinder.

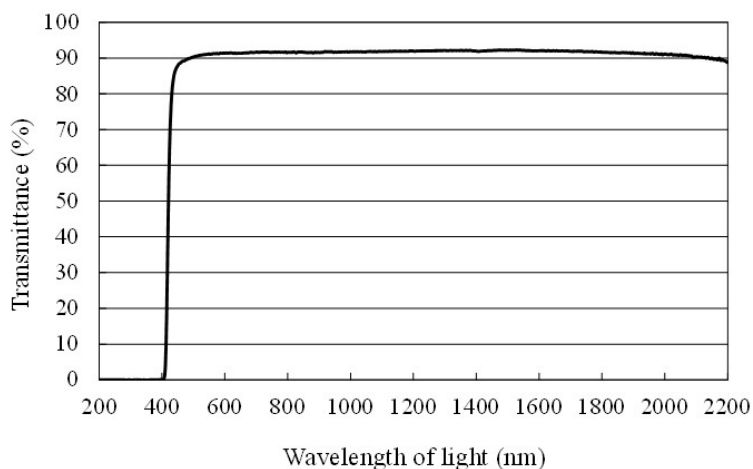


Figure 11. Light transmittance characteristics of sharp cut filter. The filter can cut off the wavelength of light which is below 400 nm.

After filling CO₂ 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 CO₂ reduction experiment with NH₃ + H₂O. After that, this study confirmed the pressure of 0.1 MPa and gas temperature at 298 K in the reactor. Then, we injected the NH₃ aqueous solution (NH₃ 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 NH₃ 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 NH₃ 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 CO₂ reduction experiment. The molar ratio of CO₂/NH₃/H₂O 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 TiO₂ uniformly by the pulse arc plasma gun process. The weight percentages of element Cu within the Cu/TiO₂ 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 CO₂ reduction characteristic under the condition of the molar ratio of CO₂/NH₃/H₂O = 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 CO₂ reduction characteristic under the condition of the molar ratio of CO₂/NH₃/H₂O = 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 CO₂ reduction characteristics under the condition of the molar ratio of CO₂/NH₃/H₂O = 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 CO₂ reduction characteristic under the condition of the molar ratio of CO₂/NH₃/H₂O = 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 CO₂ reduction characteristic with NH₃ and H₂O.
- (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.

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