Book Chapter

Impact of Pd Loading on CO₂ Reduction Performance over Pd/TiO₂ with H₂ and H₂O

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**Abstract**

This study investigated the impact of molar ratio of CO$_2$ to reductants H$_2$O and H$_2$, as well as Pd loading weight on CO$_2$ reduction performance with Pd/TiO$_2$ as the photocatalyst. The Pd/TiO$_2$ film photocatalyst is prepared by the sol-gel and dip-coating process to prepare TiO$_2$ film and the pulse arc plasma method is used to dope Pd on TiO$_2$ film. The prepared Pd/TiO$_2$ film was characterized by SEM, EPMA, STEM, EDS, and EELS. This study also investigated the performance of CO$_2$ reduction under the illumination condition of Xe lamp with or without ultraviolet (UV) light. As a result, it is revealed that when the molar ratio of CO$_2$/H$_2$/H$_2$O is set at 1:0.5:0.5, the best CO$_2$ reduction performance has been obtained under the illumination condition of Xe lamp with and without UV light. In addition, it is found that the optimum Pd loading weight is 3.90 wt%. The maximum molar quantities of CO and CH$_4$ produced per unit weight of photocatalyst are 30.3 μmol/g and 22.1 μmol/g, respectively, for the molar ratio of CO$_2$/H$_2$/H$_2$O = 1:0.5:0.5 under the condition of Xe lamp illumination with UV light. With UV light, C$_2$H$_4$ and C$_2$H$_6$, as well as CO and CH$_4$ are also produced by the Pd/TiO$_2$ film photocatalyst prepared in this study.

**Keywords**

Pd/TiO$_2$ Photocatalyst; CO$_2$ Reduction; Pd Loading Weight; Combination of Reductants
Introduction

The Paris Agreement adopted in 2015 set the goal that the increase in average temperature in the world from the industrial revolution by 2030 should be kept less than 2 K. However, the global mean concentration of CO$_2$ in the atmosphere has increased up to 410 ppmV in December 2019, which increased by 25 ppmV since 2009 [1]. Therefore, it is requested to develop a new CO$_2$ reduction/utilization technology in order to reduce the amount of CO$_2$ in the atmosphere.

Reducing or converting CO$_2$ into fuel by photocatalyst became a hot R&D area. TiO$_2$ is commonly used as a photocatalyst for CO$_2$ reduction since it is convenient, inexpensive, and has strong durability for chemicals and corrosion [2]. TiO$_2$ is a popular photocatalyst that can reduce CO$_2$ into CO, CH$_4$, CH$_3$OH, and H$_2$ etc. with ultraviolet (UV) light [3–5].

Since pure TiO$_2$ can only be activated under UV light illumination, it is not very effective under sunlight illumination as UV light accounts for only approximately 4% in the solar spectrum. In addition, the rate of electron/hole pair recombination is faster than the rate of chemical interaction between the absorbents during redox reactions when using pure TiO$_2$ [6].

Many attempts have been reported to improve the performance of the TiO$_2$ [3]. Doping precious metals such as Pt [7], Ag [8], Au [9], Cu [10,11], using composite materials formed by GaP and TiO$_2$ [12], combining CdS/TiO$_2$ in order to utilize two photocatalysts that have different band gaps [13], adding carbon-based AgBr nanocomposites into TiO$_2$ [14], sensitizing CuInS$_2$ and TiO$_2$ hybrid nanofibers [15], and preparing a procedure of TiO$_2$ using two alcohols (ethanol and isopropyl alcohol) and supercritical CO$_2$ [16] are some of the attempts to promote the performance of TiO$_2$. Though the CO$_2$ reduction performance was improved to a certain degree in these attempts, the concentrations of the products were still low, which were ranging from 1 to 150 μmol/g-cat [7–16].
Among various metals that have been used for doping, Pd is considered as a favorite candidate [17–19], since Pd can extend the absorption band to 400–800 nm [20,21], which covers the whole visible light range. Pd/TiO₂ performs a higher reduction performance compared to pure TiO₂, especially, to produce hydrocarbon [20–22]. In addition, it is known that the CO₂ reduction performance of Pd/TiO₂ is superior to that of TiO₂ from the viewpoint of producing CH₄ and H₂ [7,19]. This is due to the work function of Pd, which reflects the electron donating or accepting ability. In addition, it is thought that Pd loaded on TiO₂ functions to increase the efficiency of photogenerated electrons for the formation of reductive products.

According to the literature survey, H₂O or H₂ were normally used as the reductants for CO₂ reduction over Pd/TiO₂ [17–23]. In studies of CO₂ reduction with H₂O [17–22], the mixture ratio of CO₂ and H₂O was fixed. According to the report on CO₂ reduction with H₂ [23], the molar ratio of CO₂:H₂ was fixed at 1:4, but the impact of the ratio on CO₂ reduction performance of Pd/TiO₂ was not investigated. Though it is thought that the mixture ratio of CO₂ and reductants influences the CO₂ reduction performance of Pd/TiO₂, there was no other study investigating it nor the effect of using both H₂O and H₂ as reductants on CO₂ reduction over Pd/TiO₂ except the study conducted by the authors [24]. In addition, the metal loading weight with TiO₂ is important to improve the CO₂ reduction performance [25,26]. However, there was no study so far to qualify the improvement.

To promote the CO₂ reduction performance, the optimum reductant providing the proton (H⁺) should be clarified. According to the previous studies [27–30], the reaction mechanism to reduce CO₂ with H₂O can be summarized as shown below:

\[
\text{TiO}_2 + h\nu \rightarrow h^+ + e^- \quad (1)
\]
<Oxidization>

\[ 2H_2O + 4h^+ \rightarrow 4H^+ + O_2 \]  \hspace{1cm} (2)

<Reduction>

\[ CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O \]  \hspace{1cm} (3)

\[ CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O \]  \hspace{1cm} (4)

\[ 2CO_2 + 12H^+ + 12e^- \rightarrow C_2H_4 + 4H_2O \]  \hspace{1cm} (5)

\[ 2CO_2 + 14H^+ + 14e^- \rightarrow C_2H_6 + 4H_2O \]  \hspace{1cm} (6)

The reaction mechanism to reduce CO\(_2\) with H\(_2\) can be summarized as shown below [30,31].

<Photocatalytic reaction>

\[ TiO_2 + h\nu \rightarrow h^+ + e^- \]  \hspace{1cm} (7)

<Oxidization>

\[ H_2 \rightarrow 2H^+ + 2e^- \]  \hspace{1cm} (8)

<Reduction>

\[ CO_2 + e^- \rightarrow CO_2^- \]  \hspace{1cm} (9)

\[ CO_2^- + H^+ + e^- \rightarrow HCOO^- \]  \hspace{1cm} (10)

\[ HCOO^- + H^+ \rightarrow CO + H_2O \]  \hspace{1cm} (11)

\[ CO_2 + 8e^- + 8H^+ \rightarrow CH_4 + 2H_2O \]  \hspace{1cm} (12)

\[ 2CO_2 + 12e^- + 12H^+ \rightarrow C_2H_4 + 4H_2O \]  \hspace{1cm} (13)

\[ 2CO_2 + 14e^- + 14H^+ \rightarrow C_2H_6 + 4H_2O \]  \hspace{1cm} (14)

Though a few studies using pure TiO\(_2\) under CO\(_2\)/H\(_2\)/H\(_2\)O condition were reported [32–34], the effect of ratio of CO\(_2\), H\(_2\),
and H\textsubscript{2}O, as well as the effect of Pd loading on CO\textsubscript{2} reduction characteristics was not investigated previously.

The purpose of this study is to clarify the effect of molar ratio of CO\textsubscript{2} to reductants of H\textsubscript{2} and H\textsubscript{2}O on CO\textsubscript{2} reduction characteristics with Pd/TiO\textsubscript{2}. Additionally, the present study also aims to clarify the optimum combination of reductants, as well as Pd loading weight with TiO\textsubscript{2}.

The present study employed TiO\textsubscript{2} films coated on netlike glass fibers (SILIGLASS U, Nihonmuki Co., Tokyo, Japan) by the sol-gel and dip-coating process. The glass fiber whose diameter is about 10 μm is weaved as a net, resulting in the diameter of collected fiber of approximately 1 mm. As to the specification of each fiber, the porous diameter is approximately 1 nm and the specific surface area is approximately 400 m\textsuperscript{2}/g. The composition of netlike glass fiber is SiO\textsubscript{2} of 96 wt%. The aperture area is approximately 2 mm × 2 mm. Due to the porous structure of the netlike glass fiber, the TiO\textsubscript{2} film can be captured on netlike glass fiber easily in the step of preparation by sol-gel and dip-coating procedure. Additionally, it was believed that CO\textsubscript{2} would be more easily absorbed by the prepared photocatalyst since the porous fiber has a large surface area [35,36].

After the coating of TiO\textsubscript{2}, nanosized Pd particles were loaded on TiO\textsubscript{2} by the pulse arc plasma method applying high voltage. The pulse number can be controlled by the quantity of Pd loaded. The Pd loading weight on TiO\textsubscript{2} was measured by Electron Probe Micro Analyzer (EPMA).

In this paper, the characterization of Pd/TiO\textsubscript{2} was conducted by Scanning Electron Microscope (SEM), EPMA, Scanning Transmission Electron Microscope (STEM), Energy Dispersive X-ray Spectrometer (EDS), and Electron Energy Loss Spectrum (EELS) analysis before the CO\textsubscript{2} reduction experiment. The performances of CO\textsubscript{2} reduction with H\textsubscript{2} and H\textsubscript{2}O under the condition of illuminating Xe lamp including or excluding UV light were investigated in this paper. The combination of CO\textsubscript{2}/H\textsubscript{2}/H\textsubscript{2}O was changed for 1:0.5:0.5, 1:0.5:1, 1:1:0.5, 1:1:1,
and 1:2:2 based on molar ratio to clarify the optimum combination of $\text{CO}_2/\text{H}_2/\text{H}_2\text{O}$ for $\text{CO}_2$ reduction with Pd/TiO$_2$. If the amount of $\text{H}_2$ is larger than that of $\text{H}_2\text{O}$, it is thought that the effect of $\text{H}_2\text{O}$ on the photocatalytic reaction is higher. On the other hand, if the amount of $\text{H}_2\text{O}$ is larger than that of $\text{H}_2$, it is thought that the effect of $\text{H}_2\text{O}$ on the photocatalytic reaction is higher. This study investigated the effect of $\text{H}_2$ or $\text{H}_2\text{O}$ on the $\text{CO}_2$ reduction performance of Pd/TiO$_2$ under the condition of $\text{CO}_2/\text{H}_2/\text{H}_2\text{O}$ for the first time, so the originality of this study could be justified. In addition, the effect of Pd loading weight with TiO$_2$ on $\text{CO}_2$ reduction performance was also investigated in this study.

**Results and Discussion**

**Characterization Analysis of Pd/TiO$_2$ Film**

Figures 1 and 2 show SEM images of TiO$_2$ film and Pd/TiO$_2$ film coated on netlike glass disc, respectively. The SEM images were taken at 1500 times magnification. In these figures, the red circles indicate TiO$_2$ according to EPMA results. Figure 3 and Figure 4 show EPMA results of TiO$_2$ and Pd/TiO$_2$ film coated on netlike glass disc, respectively. The data with the weight percentage of Pd to Pd/TiO$_2$ film of 4.97 wt% are shown in Figure 4 as an example. In these figures, the different colors indicate the concentrations of each element in the observation area. For example, light colors such as white, pink, and red mean the quantity of element is small.

According to these figures, it is clear that TiO$_2$ film was coated on netlike glass fiber. In addition, it is observed that the crack is formed on the TiO$_2$ film. Since the thermal conductivity is different between Ti and SiO$_2$, which are 19.4 W/(m K) and 1.82 W/(m K), respectively at 600 K [37], the temperature distribution of TiO$_2$ solution adhered on the netlike glass disc was not uniform during the firing process, as a result, cracks were formed on the TiO$_2$ film by the thermal expansion and shrinkage around netlike glass fiber. As to the crystal structure of TiO$_2$, it is thought to be anatase since the firing temperature was set at 623 K in this study. A previous study [38] found the crystal structure of prepared TiO$_2$ was anatase if the firing temperature
was from 673 K to 873 K, while it would be rutile if the firing temperature was 973 K. The uniform loading of nanosized Pd particles on TiO$_2$ was observed according to Figure 3.

The observation area of diameter of 300 μm is analyzed by EPMA to evaluate the quantity of loaded Pd within TiO$_2$ film. Twenty observation points obtained from several samples were used to determine the weight percentages of Pd and Ti in this study. As a result, the weight percentages of Pd to Pd/TiO$_2$ film prepared by changing pulse number in this study are 0.49 wt%, 3.90 wt%, and 4.97 wt%, while the weight percentage of Ti are 99.51 wt%, 96.10 wt%, and 95.03 wt%, respectively.

**Figure 1:** SEM result of TiO$_2$ film coated on netlike glass disc.
Figure 2: SEM result of Pd/TiO$_2$ film coated on netlike glass disc.

Figure 3: EPMA result of TiO$_2$ film coated on netlike glass disc.
Figure 4: EPMA result of Pd/TiO$_2$ film coated on netlike glass disc.

Figure 5 shows STEM and EDS results of Pd/TiO$_2$ film coated on netlike glass disc. 250,000 times magnification STEM image was used for the EDS analysis. It is observed that Pd is coated on TiO$_2$ film according to STEM image, which is confirmed from EDS image. It is also observed that the layout of Pd and Ti are separated. The thickness of the Pd coated is approximately 60 nm. Nanosized Pd particles are loaded on TiO$_2$ dispersedly.
Figure 5: STEM and EDS analysis result of Pd/TiO$_2$ film coated on netlike glass disc.

Figure 6 shows EELS spectra of Pd in Pd/TiO$_2$ film which peaks at around 540 eV. Comparing the spectra peaks of Pd nanowire with that of Pd metal and PdO in [39], the EELS spectra of Pd metal matches that in Figure 6. Therefore, it is believed that the Pd in Pd/TiO$_2$ prepared in this study exists as Pd metal. Since the photoreduction performance of Pd/TiO$_2$ was higher than that of PdO/TiO$_2$ [40,41], the desirable Pd/TiO$_2$ without oxidization was proved to be prepared in this study.
Figure 6: EELS spectra of Pd in Pd/TiO$_2$.

Impact of Molar Ratio of CO$_2$, H$_2$, and H$_2$O, as well as Pd Loading Weight on CO$_2$ Reduction Performance

Figures 7, 8, 9, and 10 show the change in concentration of formed CO, CH$_4$, C$_2$H$_4$, and C$_2$H$_6$ with Pd/TiO$_2$ film coated on netlike glass disc with the time under the condition of Xe lamp illumination with UV light, respectively. In these figures, the impact of molar ratio of CO$_2$, H$_2$, and H$_2$O, as well as Pd loading weight are also presented. Before this experiment, a blank test without Xe lamp illumination had been carried out as a reference, resulting that no fuel was detected as expected. Table 1, 2, 3, and 4 list the maximum concentration of formed CO, CH$_4$, C$_2$H$_4$, and C$_2$H$_6$ under the condition shown in Figures 7, 8, 9, and 10, respectively.
Figure 7: Change in concentration of formed CO with the illumination time among different molar ratios of CO$_2$/H$_2$/H$_2$O and Pd loading weight with ultraviolet (UV) light illumination.

Figure 8: Change in concentration of formed CH$_4$ with the illumination time among different molar ratios of CO$_2$/H$_2$/H$_2$O and Pd loading weight with UV light illumination.
Figure 9: Change in concentration of formed C$_2$H$_4$ with the illumination time among different molar ratios of CO$_2$/H$_2$/H$_2$O and Pd loading weight with UV light illumination.

Figure 10: Change in concentration of formed C$_3$H$_6$ with the illumination time among different molar ratios of CO$_2$/H$_2$/H$_2$O and Pd loading weight with UV light illumination.
Table 1: Comparison of maximum concentration of formed CO with illumination time among different molar ratios of CO$_2$/H$_2$/H$_2$O and Pd loading weight with UV light illumination.

|        | 1:0.5:0.5 | 1:0.5:1 | 1:1:0.5 | 1:1:1 | 1:2:2 |
|--------|------------|---------|---------|-------|-------|
| 0.44 wt% | 91 ppmV    | 80 ppmV | 63 ppmV | 45 ppmV | 18 ppmV |
| 3.90 wt% | 313 ppmV   | 268 ppmV| 193 ppmV| 171 ppmV| 109 ppmV|
| 4.97 wt% | 107 ppmV   | 66 ppmV | 66 ppmV | 56 ppmV | 51 ppmV |

Table 2: Comparison of maximum concentration of formed CH$_4$ with illumination time among different molar ratios of CO$_2$/H$_2$/H$_2$O and Pd loading weight with UV light illumination.

|        | 1:0.5:0.5 | 1:0.5:1 | 1:1:0.5 | 1:1:1 | 1:2:2 |
|--------|------------|---------|---------|-------|-------|
| 0.44 wt% | 143 ppmV   | 72 ppmV | 123 ppmV| 31 ppmV| 0 ppmV |
| 3.90 wt% | 227 ppmV   | 166 ppmV| 121 ppmV| 134 ppmV| 85 ppmV|
| 4.97 wt% | 211 ppmV   | 113 ppmV| 113 ppmV| 108 ppmV| 48 ppmV |

Table 3: Comparison of maximum concentration of formed C$_2$H$_4$ with illumination time among different molar ratios of CO$_2$/H$_2$/H$_2$O and Pd loading weight with UV light illumination.

|        | 1:0.5:0.5 | 1:0.5:1 | 1:1:0.5 | 1:1:1 | 1:2:2 |
|--------|------------|---------|---------|-------|-------|
| 0.44 wt% | 0 ppmV     | 0 ppmV  | 0 ppmV  | 0 ppmV| 0 ppmV |
| 3.90 wt% | 28 ppmV    | 20 ppmV | 15 ppmV | 0 ppmV| 0 ppmV |
| 4.97 wt% | 0 ppmV     | 0 ppmV  | 0 ppmV  | 0 ppmV| 0 ppmV |

Table 4: Comparison of maximum concentration of formed C$_2$H$_6$ with illumination time among different molar ratios of CO$_2$/H$_2$/H$_2$O and Pd loading weight with UV light illumination.

|        | 1:0.5:0.5 | 1:0.5:1 | 1:1:0.5 | 1:1:1 | 1:2:2 |
|--------|------------|---------|---------|-------|-------|
| 0.44 wt% | 0 ppmV     | 0 ppmV  | 0 ppmV  | 0 ppmV| 0 ppmV |
| 3.90 wt% | 18 ppmV    | 9 ppmV  | 0 ppmV  | 0 ppmV| 0 ppmV |
| 4.97 wt% | 0 ppmV     | 0 ppmV  | 0 ppmV  | 0 ppmV| 0 ppmV |
According to Figure 7, 8, 9, and 10 and Tables 1, 2, 3, and 4, the CO₂ reduction performance to produce CO, CH₄, C₂H₄, and C₂H₆ is the highest at the molar ratio of CO₂/H₂/H₂O = 1:0.5:0.5. Since the reaction scheme of CO₂/H₂/H₂O has not been fully understood, Equations (1)–(15) are used to explain the results. Equations (1)–(15) show that the theoretical molar ratio of CO₂ with H₂O or H₂ to produce CO is 1:1. On the other hand, the theoretical molar ratio of CO₂ with H₂O or H₂ to produce CH₄ is 1:4. In addition, CH₄, C₂H₄, and C₂H₆ are produced in the series after CO is produced. For example, producing CH₄ needs four times H⁺ and electrons as many as producing CO needs. The other fuels such as C₂H₄ and C₂H₆ need more H⁺ and electrons compared to producing CH₄. Since Pd has a high reduction performance [21,22,40], it is thought that the optimum molar ratio of CO₂/total reductants to produce CH₄, C₂H₄, and C₂H₆ is smaller than the theoretical molar ratio required. Moreover, since the molar ratio of H₂ is the same as that of H₂O under the molar ratio of CO₂/H₂/H₂O = 1:0.5:0.5 condition, the effect of H₂ or H₂O is not higher than that of the other to obtain the optimum molar ratio of CO₂/H₂/H₂O over Pd/TiO₂ photocatalyst. However, according to Tables 1, 2, 3, and 4, the CO₂ reduction performance for the condition that the molar ratio of H₂O is larger than that of H₂ is better, resulting in that the effect of H₂O is bigger than that of H₂ to promote the CO₂ reduction performance over Pd/TiO₂ totally in this study.

In addition, it is known from Figures 7, 8, 9, and 10 and Tables 1, 2, 3, and 4 that the maximum concentration of produced fuel is obtained when Pd loading weight is 3.90 wt% irrespective of fuel type. One might think that the CO₂ reduction performance is promoted with increasing Pd loading weight. However, it is believed that too much Pd loading causes covering the surface of TiO₂ film [42,43], resulting in that CO₂ and reductants cannot attain the surface of TiO₂ film sufficiently. Consequently, it is clear that there is an optimum Pd loading weight to promote CO₂ reduction performance with H₂ and H₂O.

Tables 5, 6, 7, and 8 list the maximum molar quantities of CO, CH₄, C₂H₄, and C₂H₆ per unit weight of photocatalyst under the condition of Xe lamp illumination with UV light, respectively.
The quantities of Pd/TiO$_2$ coated on netlike glass disc for Pd loading weight of 0.44 wt%, 3.90 wt%, and 4.97 wt% are 0.05 g, 0.05 g, and 0.09 g, respectively. These quantities of Pd/TiO$_2$ coated on netlike glass disc were measured by an electric balance comparing the weights of several samples before and after preparing Pd/TiO$_2$ film on netlike glass fiber. The photocatalytic activity evaluation using molar quantities of product per weight of photocatalyst was adopted as in the recent photocatalyst studies [44–47].

According to Tables 5, 6, 7, and 8, the maximum molar quantities of CO, CH$_4$, C$_2$H$_4$, and C$_2$H$_6$ per unit weight of photocatalyst are obtained for the molar ratio of CO$_2$/H$_2$/H$_2$O = 1:0.5:0.5. In addition, it is known that the maximum molar quantity of fuel per unit weight of photocatalyst is obtained for Pd loading weight of 3.90 wt% irrespective of fuel type. It is thought that these results agree with the results shown in Figures 11, 12, 13, and 14.

Table 5: Comparison of the maximum molar quantity of CO per unit weight of photocatalyst with illumination time among different molar ratios of CO$_2$/H$_2$/H$_2$O and Pd loading weight with UV light illumination (unit: µmol/g).

|          | 1:0.5:0.5 | 1:0.5:1 | 1:1:0.5 | 1:1:1 | 1:2:2 |
|----------|-----------|---------|---------|-------|-------|
| 0.44 wt% | 9.27      | 8.18    | 9.06    | 4.63  | 1.81  |
| 3.90 wt% | 30.4      | 26.0    | 18.9    | 16.6  | 10.6  |
| 4.97 wt% | 5.97      | 3.66    | 3.52    | 3.10  | 2.84  |

Table 6: Comparison of the maximum molar quantity of CH$_4$ per unit weight of photocatalyst with illumination time among different molar ratios of CO$_2$/H$_2$/H$_2$O and Pd loading weight with UV light illumination (unit: µmol/g).

|          | 1:0.5:0.5 | 1:0.5:1 | 1:1:0.5 | 1:1:1 | 1:2:2 |
|----------|-----------|---------|---------|-------|-------|
| 0.44 wt% | 14.6      | 7.33    | 6.91    | 3.20  | 0     |
| 3.90 wt% | 22.1      | 16.1    | 11.8    | 13.1  | 8.25  |
| 4.97 wt% | 11.8      | 6.28    | 6.85    | 6.04  | 2.69  |
Table 7: Comparison of the maximum molar quantity of C$_2$H$_4$ per unit weight of photocatalyst with illumination time among different molar ratios of CO$_2$/H$_2$/H$_2$O and Pd loading weight with UV light illumination (unit: µmol/g).

|          | 1:0.5:0.5 | 1:0.5:1 | 1:1:0.5 | 1:1:1 | 1:2:2 |
|----------|-----------|---------|---------|-------|-------|
| 0.44 wt% | 0         | 0       | 0       | 0     | 0     |
| 3.90 wt% | 2.69      | 1.91    | 1.46    | 0     | 0     |
| 4.97 wt% | 0         | 0       | 0       | 0     | 0     |

Table 8: Comparison of the maximum molar quantity of C$_2$H$_6$ per unit weight of photocatalyst with illumination time among different molar ratios of CO$_2$/H$_2$/H$_2$O and Pd loading weight with UV light illumination (unit: µmol/g).

|          | 1:0.5:0.5 | 1:0.5:1 | 1:1:0.5 | 1:1:1 | 1:2:2 |
|----------|-----------|---------|---------|-------|-------|
| 0.44 wt% | 0         | 0       | 0       | 0     | 0     |
| 3.90 wt% | 1.75      | 0.91    | 0       | 0     | 0     |
| 4.97 wt% | 0         | 0       | 0       | 0     | 0     |

Figure 11 shows the change in concentration of formed CO with the Pd/TiO$_2$ film with the time under the condition of Xe lamp illumination without UV light. In this figure, the impact of molar ratio of CO$_2$, H$_2$, and H$_2$O, as well as Pd loading weight is also presented. Before this experiment, a blank test without Xe lamp illumination had been carried out as a reference, resulting in that no fuel was detected as expected. Table 9 lists the maximum concentration of formed CO under the condition shown in Figure 11.
According to Figure 11 and Table 9, the CO$_2$ reduction performance to produce CO is the highest at the molar ratio of CO$_2$/H$_2$/H$_2$O = 1:0.5:0.5 and the maximum concentration of produced fuel is obtained for Pd loading weight of 3.90 wt%. These results are the same as that in the case of illuminating Xe lamp with UV light. The reason why these results are obtained is thought to be the same as explained above in the case of illuminating Xe lamp with UV light. It is found from Figure 11 that the concentration of formed CO is smaller than that under the condition of Xe lamp with UV light. There were no other fuels such as CH$_4$, C$_2$H$_4$, and C$_2$H$_6$ detected under the condition of Xe lamp illumination without UV light. It is thought that the
responsiveness of visible light with Pd/TiO$_2$ prepared in this study was too low.

Table 10: Comparison of maximum molar quantity of CO per unit weight of photocatalyst with illumination time among different molar ratios of CO$_2$/H$_2$/H$_2$O and Pd loading weight without UV light illumination (unit: µmol/g).

|        | 1:0.5:0.5 | 1:0.5:1 | 1:1:0.5 | 1:1:1 | 1:2:2 |
|--------|-----------|---------|---------|-------|-------|
| 0.44 wt% | 3.97      | 3.58    | 3.34    | 3.37  | 2.63  |
| 3.90 wt% | 6.34      | 5.42    | 4.64    | 4.03  | 3.21  |
| 4.97 wt% | 2.77      | 2.11    | 2.56    | 2.06  | 1.63  |

Table 10 shows the maximum molar quantity of CO per unit weight of photocatalyst under the condition of Xe lamp illumination without UV light. The maximum molar quantity of CO per unit weight of photocatalyst is obtained for the molar ratio of CO$_2$/H$_2$/H$_2$O = 1:0.5:0.5 at Pd loading weight of 3.90 wt%. This result is the same as that in the case of illuminating Xe lamp with UV light.

In this study, the maximum molar quantity of CH$_4$ per unit weight of photocatalyst is 22.1 µmol/g for the molar ratio of CO$_2$/H$_2$/H$_2$O = 1:0.5:0.5 at Pd loading weight of 3.90 wt% under the condition of Xe lamp illumination with UV light. This maximum value is obtained after 6 h of illumination. According to the previous studies reported, the molar quantities of CH$_4$ per unit weight of photocatalyst in the case of CO$_2$/H$_2$O with Pd/TiO$_2$ were 25 µmol/g, 4.8 µmol/g, and 1.9 µmol/g [21,22,40]. These molar quantities of CH$_4$ per unit weight of photocatalyst were obtained after 8 [21], 6 [22], and 24 [40] h of illumination, respectively. Another study [23] reported that the molar quantity of CH$_4$ per unit weight of photocatalyst in the case of CO$_2$/H$_2$ with Pd/TiO$_2$ was 356 µmol/g which was obtained after 3 h of illumination.

In this study, the maximum molar quantity of CO per unit weight of photocatalyst is 30.3 µmol/g for the molar ratio of CO$_2$/H$_2$/H$_2$O = 1:0.5:0.5 at Pd loading weight of 3.90 wt% under
the condition of Xe lamp illumination with UV light. This maximum value is obtained after illumination time of Xe lamp of 6 h. The previous studies reported that the molar quantities of CO per unit weight of photocatalyst in the case of CO₂/H₂O with Pd/TiO₂ were 0.12 μmol/g and 0.13 μmol/g [22,39], while the study reported that the molar quantity of CO per unit weight of photocatalyst in the case of CO₂/H₂ with Pd/TiO₂ was 45 μmol/g [23]. These molar quantities of CO per unit weight of photocatalyst were obtained after illumination of 6 [22], 5 [39], and 3 [23] h, respectively.

Compared to the other studies, CO₂ reduction performance in terms of producing CH₄ or CO per unit weight of photocatalyst obtained in this study does not necessarily imply that the photocatalyst was prepared. Additionally, the best time to obtain the highest molar quantity of produced fuel per unit weight of photocatalyst is almost the same as the previous studies. However, in terms of producing the other fuels such as C₂H₄ and C₂H₆, which are difficult to produce through CO₂ reduction and were not reported in the other studies, are confirmed in this study. According to the previous study [21], Pd/TiO₂ could produce hydrocarbon such as C₂H₆ more effectively compared to the other photocatalysts. The CO₂ molecules activated at Pd sites react with H⁺ and the electrons to produce the intermediate Pd-C=O. Meanwhile, a small amount of CO is generated by C=O desorption, but Pd-C=O further interacts with the dissociated H to form a Pd-C species. Finally, the carbon species generated continue to react with the H species at Pd sites to produce CH₄.

During the CH₄ formation process, some intermediates (such as ·CH, ·CH₂, and ·CH₃) are produced, and C₂H₆ is obtained when two ·CH₃ species interact with each other. Since C₂H₄ and C₂H₆ have high heating values, producing these fuels have a profound significance in CO₂ utilization. Therefore, it can be said that this study has realized the photocatalyst having high CO₂ reduction performance.

Though it is thought that the doped Pd can provide the free electron not only to prevent the recombination of electron and hole produced but also to improve light absorption effect, it is necessary to improve the CO₂ reduction performance further.
This study suggests that different metals should be doped on TiO$_2$ to promote the CO$_2$ reduction further. 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 reported to promote the CO$_2$ reduction performance of TiO$_2$ with H$_2$O [4,48]. Then, the promotion of CO$_2$ reduction performance by different metal doping is expected when the combination of CO$_2$/H$_2$/H$_2$O is considered. For example, Fe which can absorb the shorter wavelength light than Pd can [48] should be co-used since the amount of light absorbed by the photocatalyst can be increased and an effective utilization of wide range light can be realized by the combination of Fe and Pd.

**Materials and Method**

**Preparation of Pd/TiO$_2$ Photocatalyst**

The TiO$_2$ film used in this study was prepared using the sol-gel and dip-coating procedure [24,49,50]. At first, [((CH$_3$)$_2$CHO)$_4$Ti (95 wt% purification, produced by Nacalai Tesque Co., Kyoto, Japan) of 0.3 mol, anhydrous C$_2$H$_5$OH (99.5 wt% purification, produced by Nacalai Tesque Co.) of 2.4 mol, distilled water of 0.3 mol, and HCl (35 wt% purification, produced by Nacalai Tesque Co.) of 0.07 mol were mixed to make the TiO$_2$ sol solution. As the basis to coat TiO$_2$ film, the sheet of netlike glass fiber was cut into a disc shape whose diameter and thickness were 50 mm and 1 mm, respectively. The disc shaped netlike glass fiber was then immersed into the TiO$_2$ sol solution at a speed of 1.5 mm/s and lifted at 0.22 mm/s. The disc was dried and heated at the controlling firing temperature ($FT$) and the firing duration time ($FD$) of 623 K and 180 s, respectively. After the TiO$_2$ film was coated on netlike glass disc, the pulse arc plasma method was selected to load Pd on the TiO$_2$ film. The pulse arc plasma gun device (ARL-300, produced by ULVAC, Inc., Suzuka, Japan) with Pd electrode having a diameter of 10 mm was used in this study. The quantity of loaded Pd was controlled by pulse number. In this study, the pulse number was varied from 100 to 500, and Pd loading weight with TiO$_2$ was measured by EPMA, for each pulse number. It is confirmed that the Pd/TiO$_2$ film prepared in this way could not be removed from the netlike glass fiber by rubbing. Figure 12 shows the photos of
netlike glass disc before and after coating of Pd/TiO₂. Since the sheet of netlike glass disc does not have a scouring structure inside it, the TiO₂ film is coated on the surface of netlike glass fiber and Pd can be deposited on TiO₂ film by pulse arc plasma method.

Figure 12: Photos of netlike glass disc before and after coating of Pd/TiO₂ (left: Before; right: After).

Characterization of Pd/TiO₂ Film

The structural and crystal characteristics of Pd/TiO₂ film prepared were evaluated by using SEM (JXA-8530F, produced by JEOL Ltd., Tokyo, Japan), EPMA (JXA-8530F, produced by JEOL Ltd., Tokyo, Japan), and EELS (JEM-ARM2007 Cold, produced by JEOL Ltd., Tokyo, Japan). In order to analyze the sample by these equipments, carbon was coated on Pd/TiO₂ whose thickness was approximately 15 nm by the dedicated device (JEC-1600, produced by JEOL Ltd.) before analysis. This carbon coating was conducted for analysis, while the CO₂ reduction experiment was carried out without carbon coating. The carbon coating was not conducted for the right photo in Figure 1.

The electron was emitted on the sample by the electron probe applying the acceleration voltage of 15 kV and the current at $3.0 \times 10^{-8}$ A to analyze the surface structure of the sample by SEM. Simultaneously, EPMA detects the characteristic X-ray. The space resolutions for SEM and EPMA were set at 10 μm. The state of prepared photocatalyst, as well as the quantity of
doped metal within TiO$_2$ film could be known by EPMA analysis.

The electron probe emits electrons to the sample at the acceleration voltage of 200 kV, when the inner structure of the sample is analyzed by STEM. The size, thickness, and structure of loaded Pd were evaluated. The X-ray characteristics of the sample is detected by EDS at the same time. Therefore, the concentration distribution of chemical elements toward thickness direction of the sample is known. In the present paper, the concentration distribution of Ti, Pd, and Si were analyzed.

EELS is used to detect elements, as well as to determine oxidation states of transition metals. The EELS characterization was determined by JEM-ARM200F equipped with GIF Quantum having 2048 ch. The dispersion of 0.5 eV/ch for the full width at half maximum of the zero loss peak was achieved in the study.

**CO$_2$ Reduction Experiment**

Figure 13 shows the experimental setup of the reactor composed of a stainless tube (height of 100 mm and inside diameter of 50 mm), Pd/TiO$_2$ film coated on netlike glass disc (diameter of 50 mm and thickness of 1 mm) located on the teflon cylinder (height of 50 mm and diameter of 50 mm), a quartz glass disc (diameter of 84 mm and thickness of 10 mm), an edge cut filter cutting off the light whose wavelength 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, gas cylinder of CO$_2$ and H$_2$.

The reactor volume available for CO$_2$ is 1.25×10$^{-4}$ m$^3$. The light of Xe lamp which is located outside the stainless tube illuminates Pd/TiO$_2$ film coated on the netlike glass disc through the edge cut filter and the quartz glass disc that are at the top of the stainless tube. The wavelength of light illuminating by Xe lamp is distributed from 185 nm to 2000 nm. Since an edge cut filter can remove UV components of the light from the Xe lamp, the wavelength from Xe lamp is distributed from 401 to 2000 nm.
with the filter. Figure 14 shows the spectra data on light intensity of Xe lamp without the edge filter according to the catalog of Xe lamp company. Figure 15 shows the performance of the edge cut filter to cut off the wavelength of light whose wavelength is below 400 nm. The average light intensities of Xe lamp without and with the edge cut filter are 65.0 W/cm$^2$ and 40.5 W/cm$^2$, respectively.

CO$_2$ gas and H$_2$ gas whose purity were 99.995 vol% and 99.99999 vol%, respectively were controlled by mass flow controller and mixed in the buffer chamber before the experiment. The mixing ratio of CO$_2$ and H$_2$ was checked and confirmed by TCD gas chromatograph (Micro GC CP4900, produced by GL Science, Tokyo, Japan) before being introduced into the reactor. The distilled water was then injected into the reactor via gas sampling tap and when Xe lamp was turned on. The water was injected and vaporized by the heat of Xe lamp completely. The molar ratio of CO$_2$/H$_2$/H$_2$O was set at 1:0.5:0.5, 1:0.5:1, 1:1:0.5, 1:1:1, 1:2:2. The temperature in reactor rose up to 343 K within 1 h and was kept at about 343 K during the entire experiment.

In the CO$_2$ reduction experiment with UV light, samples of the gas in the reactor were taken every 6 h, while in the CO$_2$ reduction experiment without UV light samples were taken every 24 h due to the difference of reaction speed of prepared photocatalyst under these two conditions. The gas samples were analyzed using FID gas chromatograph (GC353B, produced by GL Science) and methanizer (MT221, produced by GL Science). FID gas chromatograph and methanizer can be analyzed in the minimum range of 1 ppmV.
Figure 13: Experimental setup for CO\textsubscript{2} reduction [49,50].

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

Figure 14: Spectra data on light intensity of Xe lamp without edge filter.
Figure 15: Characterization of edge cut filter to cut off the wavelength of light under 400 nm [49,50].

Conclusions

The following conclusions could be drawn from this study:

- The nanosized Pd particles could be loaded on TiO₂ uniformly by the pulse arc plasma method. Pd in Pd/TiO₂ prepared by this method exists in the form of Pd metal.
- The highest CO₂ reduction performance to produce CO, CH₄, C₂H₄, and C₂H₆ was obtained at the molar ratio of CO₂/H₂/H₂O = 1:0.5:0.5 with Xe lamp illumination with or without UV light. It is revealed that the molar ratio of CO₂/total reductants = 1:1 is the optimum to produce fuels.
- The maximum molar quantity of fuel per unit weight of photocatalyst is obtained at Pd loading weight of 3.90 wt% irrespective of fuel type. In this study, the maximum molar quantities of CO and CH₄ per unit weight of photocatalyst were 30.3 μmol/g and 22.1 μmol/g, respectively, for the molar ratio of CO₂/H₂/H₂O = 1:0.5:0.5 at Pd loading weight of 3.90 wt% under the condition of Xe lamp illumination with UV light.
- The Pd/TiO₂ photocatalyst prepared in this study could produce C₂H₄ and C₂H₆, as well as CO and CH₄, therefore, it can be said that the photocatalyst prepared in this study has realized to have the higher CO₂ reduction performance.
References

1. Greenhouse Gases Observing Satellite GOAST “IBUSUKI:0.5:0.5”. Available online at: http://www.goast.nies.go.jp/en/
2. Tahir M, Amin NS. Indium-doped TiO$_2$ nanoparticles for photocatalytic CO$_2$ reduction with H$_2$O vapors to CH$_4$. Appl. Catal. B: Environ. 2015; 162: 98–109.
3. Abdullah H, Khan MR, Ong HR, Yaakob Z. Modified TiO$_2$ photocatalyst for CO$_2$ photocatalytic reduction: An overview. J. CO$_2$ Util. 2017; 22: 15–32.
4. Sohn Y, Huang W, Taghipour F. Recent progress and perspectives in the photocatalytic CO$_2$ reduction of Ti-oxide-based nanomaterials. Appl. Surf. Sci. 2017; 396: 1696–1711.
5. Nahar S, Zain MFM, Kadhum AAH, Abu Hasan H. Advances in Photocatalytic CO$_2$ Reduction with Water: A Review. Materials. 2017; 10: 629.
6. Ola O, Maroto-Valer M. Review of material design and reactor engineering on TiO$_2$ photocatalysis for CO$_2$ reduction. J. Photochem. Photobiol. C: Photochem. Rev. 2015; 24: 16–42.
7. Xie S, Wang Y, Zhang Q, Deng W, Wang Y. MgO- and Pt-Promoted TiO$_2$ as an Efficient Photocatalyst for the Preferential Reduction of Carbon Dioxide in the Presence of Water. ACS Catal. 2014; 4: 3644–3653.
8. Khalid N, Ahmed E, Niaz N, Nabi G, Ahmad M, et al. Highly visible light responsive metal loaded N/TiO$_2$ nanoparticles for photocatalytic conversion of CO$_2$ into methane. Ceram. Int. 2017; 43: 6771–6777.
9. Tan LL, Ong WJ, Chai SP, Mohamed AR. Noble metal modified reduced graphene oxide/TiO$_2$ ternary nanostructures for efficient visible-light-driven photoreduction of carbon dioxide into methane. Appl. Catal. B: Environ. 2015; 166: 251–259.
10. Camarillo R, Tostón S, Martínez F, Jiménez C, Rincón J. Improving the photo-reduction of CO$_2$ to fuels with catalysts synthesized under high pressure: Cu/TiO$_2$. J. Chem. Technol. Biotechnol. 2017; 93: 1237–1248.
11. Aguirre ME, Zhou R, Eugene AJ, Guzman MI, Grela MA. Cu$_2$O/TiO$_2$ heterostructures for CO$_2$ reduction through a
direct Z-scheme: Protecting Cu$_2$O from photocorrosion. Appl. Catal. B: Environ. 2017; 217: 485–493.
12. Marcì G, García-López EI, Palmisano L. Photocatalytic CO$_2$ reduction in gas–solid regime in the presence of H$_2$O by using GaP/TiO$_2$ composite as photocatalyst under simulated solar light. Catal. Commun. 2014; 53: 38–41.
13. Beigi AA, Fatemi S, Salehi Z. Synthesis of nanocomposite CdS/TiO$_2$ and investigation of its photocatalytic activity for CO$_2$ reduction to CO and CH$_4$ under visible light irradiation. J. CO$_2$ Util. 2014; 7: 23–29.
14. Fang Z, Li S, Gong Y, Liao W, Tian S, et al. Comparison of catalytic activity of carbon-based AgBr nanocomposites for conversion of CO$_2$ under visible light. J. Saudi Chem. Soc. 2014; 18: 299–307.
15. Xu F, Zhang J, Zhu B, Yu J, Xu J. CuInS$_2$ sensitized TiO$_2$ hybrid nanofibers for improved photocatalytic CO$_2$ reduction. Appl. Catal. B: Environ. 2018; 230: 194–202.
16. Camarillo R, Tostón S, Martínez F, Jiménez C, Rincón J. Preparation of TiO$_2$-based catalysts with supercritical fluid technology: characterization and photocatalytic activity in CO$_2$ reduction. J. Chem. Technol. Biotechnol. 2017; 92: 1710–1720.
17. Tostón S, Camarillo R, Martínez F, Jiménez C, Rincón J. Supercritical synthesis of platinum-modified titanium dioxide for solar fuel production from carbon dioxide. Chin. J. Catal. 2017; 38: 636–650.
18. Jiao J, Wei Y, Zhao Y, Zhao Z, Duan A, et al. AuPd/3DOM-TiO$_2$ catalysts for photocatalytic reduction of CO$_2$: High efficient separation of photogenerated charge carriers. Appl. Catal. B: Environ. 2017; 209: 228–239.
19. Camarillo R, Tostón S, Martínez F, Jiménez C, Rincón J. Enhancing the photocatalytic reduction of CO$_2$ through engineering of catalysts with high pressure technology: Pd/TiO$_2$ photocatalysts. J. Supercrit. Fluids. 2017; 123: 18–27.
20. Chen W, Wang Y, Shangguan W. Metal (oxide) modified (M = Pd, Ag, Au and Cu) H$_2$SrTa$_2$O$_7$ for photocatalytic CO$_2$ reduction with H$_2$O: The effect of cocatalysts on promoting activity toward CO and H$_2$ evolution. Int. J. Hydrog. Energy. 2019; 44: 4123–4132.
21. Yu Y, Lan Z, Guo L, Wang E, Yao J, et al. Synergistic effects of Zn and Pd species in TiO$_2$ towards efficient photo-reduction of CO$_2$ into CH$_4$. New J. Chem. 2018; 42: 483–488.
22. Singhal N, Kumar U. Noble metal modified TiO$_2$: selective photoreduction of CO$_2$ to hydrocarbons. Mol. Catal. 2017; 439: 91–99.
23. Li N, Liu M, Yang B, Shu W, Shen Q, et al. Enhanced photocatalytic performance toward CO$_2$ hydrogenation over nanosized TiO$_2$-loaded Pd under UV irradiation. J. Phys. Chem. 2017; 121: 2923–2932.
24. Nishimura A, Inoue T, Sakakibara Y, Hirot a M, Koshio A, et al. Optimum molar ratio of H$_2$ and H$_2$O to reduce CO$_2$ using Pd/TiO$_2$. AIMS Mater. Sci. 2019; 6: 464–483.
25. Tasbihi M, Schwarze M, Edelmannová M, Spoeri C, Strasser P, et al. Photocatalytic reduction of CO$_2$ to hydrocarbons by using photodeposited Pt nanoparticles on carbon-doped titania. Catal. Today. 2019; 328: 8–14.
26. Su KY, Chen CY, Wu RJ. 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.
27. Goren Z, Willner I, Nelson AJ, Frank AJ. Selective photoreduction of CO$_2$/HCO$_3^-$ to Formate by Aqueous Suspensions and Colloids of Pd-TiO$_2$. J. Phys. Chem. 1990; 94: 3784–3790.
28. Tseng IH, Chang WC, Wu JCS. Photoreduction of CO$_2$ using sol–gel derived titania and titania-supported copper catalysts. Appl. Catal. B: Environ. 2002; 37: 37–48.
29. Nishimura A, Sugiura N, Fujita M, Kato S, Kato S. Influence of Preparation Conditions of Coated TiO$_2$ Film on CO$_2$ Reforming Performance. Kagaku Kogaku Ronbunshu. 2007; 33: 146–153.
30. Izumi Y. Recent advances in the photocatalytic conversion of carbon dioxide to fuels with water and/or hydrogen using solar energy and beyond. Co-ord. Chem. Rev. 2013; 257: 171–186.
31. Lo CC, Hung CH, Yuan CS, Wu JF. Photoreduction of carbon dioxide with H$_2$ and H$_2$O over TiO$_2$ and ZrO$_2$ in a circulated photocatalytic reactor. Sol. Energy Mater. Sol. Cells. 2007; 91: 1765–1774.
32. Mahmodi G, Sharifnia S, Madani M, Vatanpour V. Photoreduction of carbon dioxide in the presence of H$_2$, H$_2$O and CH$_4$ over TiO$_2$ and ZnO photocatalysts. Sol. Energy. 2013; 97: 186–194.

33. Jensen J, Mikkelsen M, Krebs FC. Flexible substrates as basis for photocatalytic reduction of carbon dioxide. Sol. Energy Mater. Sol. Cells. 2011; 95: 2949–2958.

34. Wu HY, Bai H, Wu JCS. Photocatalytic reduction of CO$_2$ using Ti-MCM-41 Photocatalysis in Monoethanolamine Solution for Methane Production. Ind. Eng. Chem. Res. 2014; 53: 11221–11227.

35. Korzhak AV, Ermokhina NI, Stroyuk AL, Bukhtiyarov VK, Raevskaya AE, et al. Photocatalytic hydrogen evolution over mesoporous TiO$_2$/metal nanocomposites. J. Photochem. Photobio. A: Chem. 2008; 198: 126–134.

36. Nishimura A, Tatematsu D, Toyoda R, Hirota M, Koshio A, et al. Effect of overlapping layout of Fe/TiO$_2$ on CO$_2$ reduction with H$_2$ and H$_2$O. Mof Sol. Photoen. 2019; 3: 1–8.

37. Feng H, Xu H, Feng H, Gao Y, Jin X. The sol-gel synthesis and photocatalytic activity of Gd-SiO$_2$-TiO$_2$ photocatalyst. Chem. Phys. Lett. 2019; 733: 136676.

38. Wang D, Zhou W, McCaughy B, Hampsey J, Ji X, et al. Electrodeposition of Metallic Nanowire Thin Films Using Mesoporous Silica Templates. Adv. Mater. 2003; 15: 130–133.

39. Yui T, Kan A, Saitoh C, Koike K, Ibusuki T, et al. Photochemical Reduction of CO$_2$ Using TiO$_2$: Effects of Organic Adsorbates on TiO$_2$ and Deposition of Pd onto TiO$_2$. ACS Appl. Mater. Interfaces. 2011; 3: 2594–2600.

40. Kočí K, Matějová L, Reli M, Čapek L, Matějka V, et al. Sol–gel derived Pd supported TiO$_2$-ZrO$_2$ and TiO$_2$ photocatalysts, their examination in photocatalytic reduction of carbon dioxide. Catal. Today. 2014; 230: 20–26.

41. Nishimura A, Ishida N, Tatematsu D, Hirota M, Koshio A, et al. Effect of Fe Loading Condition and Reductants on CO$_2$ Reduction Performance with Fe/TiO$_2$ Photocatalyst. Int. J. Photoenergy. 2017; 2017: 1–11.

42. Zhao H, Rao G, Wang L, Xu J, Liu L, et al. Synthesis of novel MgAl layered double oxide grafted TiO$_2$ cuboids and
their photocatalytic activity on CO₂ reduction with water vapor. Catal. Sci. Technol. 2015; 5: 3288–3295.
43. Zhang R, Huang Z, Li C, Zuo Y, Zhou Y. Monolithic g-C₃N₄/reduced graphene oxide aerogel with in situ embedding of Pd nanoparticles for hydrogenation of CO₂ to CH₄. Appl. Surf. Sci. 2019; 475: 953–960.
44. Kulandaivalu T, Rashid SA, Sabli N, Tan TL. Visible light assisted photocatalytic reduction of CO₂ to ethane using CQDS/Cu₂O nanocomposite photocatalyst. Diam. Relat. Mater. 2019; 91: 64–73.
45. Zhu Z, Huang WR, Chen CY, Wu RJ. Preparation of Pd–Au/TiO₂–WO₃ to enhance photoreduction of CO₂ to CH₄ and CO. J. CO₂ Util. 2018; 28: 247–254.
46. Tasbihi M, Fresno F, Simon U, Villar-Garcia IJ, Pérez-Dieste V, et al. On the selectivity of CO₂ photoreduction towards CH₄ using Pt/TiO₂ catalysts supported on mesoporous silica. Appl. Catal. B: Environ. 2018; 239: 68–76.
47. Wei Y, Wu X, Zhao Y, Wang L, Zhao Z, et al. Efficient photocatalyst of TiO₂ nanocrystals-supported PtRu alloy nanoparticles for CO₂ reduction with H₂O: Synergetic effect of Pt-Ru. Appl. Catal. B-Env. 2018; 236: 445–457.
48. Tahir M, Amin NS. Advances in visible light responsive titanium oxide-based photocatalysts for CO₂ conversion to hydrocarbon fuels. Energy Convers. Manag. 2013; 76: 194–214.
49. Nishimura A, Toyoda R, Tatematsu D, Hirota M, Koshio A, et al. Effect of molar ratio of H₂ and H₂O on CO₂ reduction characteristics of overlapped Cu/TiO₂. Int. J. Eng. Sci. Invent. 2018; 7: 18–28.
50. Japan Society of Mechanical Engineering. JSME Heat Transfer Handbook, 1st edn. Tokyo: Maruzen. 1993; 366-369.