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Effect of overlapping layout of Fe/TiO_2 on CO_2 reduction with H_2 and H_2O

Abstract

Fe-doped TiO_2 (Fe/TiO_2) film photocatalyst was prepared by sol-gel dip-coating, and pulse arc plasma process. The netlike glass fiber was used as a base material for the photocatalyst since it had a porous structure. The CO_2 reduction performance with H_2 and H_2O into CO over the Fe/TiO_2 photocatalyst was investigated. In addition, this study investigated overlapping two Fe/TiO_2 coated on netlike glass fiber in order to utilize the light more effectively as well as increase the amount of photocatalyst for CO_2 reduction. The characterization of prepared Fe/TiO_2 film coated on netlike glass fiber was analyzed by SEM, EPMA, TEM, EDX and EELS. Furthermore, the CO_2 reduction performance of the Fe/TiO_2 film was tested under a Xe lamp with or without ultraviolet (UV) light, respectively. The results show that the CO_2 reduction performance peaks under the condition of $CO_2/H_2/H_2O$=1:1:0.5 in both cases with UV light and without UV light illumination. The highest concentration of CO with the Fe/TiO_2 overlapped photocatalyst is 1.2 times of that with the single Fe/TiO_2 photocatalyst. On the other hand, results also show the highest molar quantity of CO per weight of photocatalyst for Fe/TiO_2 overlapped is almost half of single Fe/TiO_2.

Keywords: photocatalyst, Fe-doped TiO_2, CO_2 reduction, reductants, overlapping effect

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Introduction

Due to mass consumption of fossil fuels, global warming and fossil fuels depletion have become serious global environmental problems in the world. After the industrial revolution, the averaged concentration of CO_2 in the world has been increased from 278ppmV to 403ppmV by 2016.[1] Therefore, it is necessary to develop a new CO_2 reduction or utilization technology in order to recycle CO_2. There are six vital CO_2 conversions mechanisms: chemical conversions, electrochemical reductions, biological conversions, reforming, inorganic conversions, and photochemical reductions.[2, 3] Recently, artificial photosynthesis or the photochemical reduction of CO_2 to fuel (e.g. CO) has become an attractive route due to its economically and environmentally friendly behavior.[2] TiO_2 is the principle catalyst used for almost all types of photocatalysis reaction. It is well reported that CO_2 can be reduced into fuels e.g. CO, CH_4, CH_3OH, and H_2 etc. with TiO_2 as the photocatalyst under ultraviolet (UV) light illumination.[2,4–7] However, the CO_2 reduction performance of TiO_2 is still low since TiO_2 has a large bandgap energy (~3.2 eV) and a rapid electron hole recombination rate.[5] Recently, studies on CO_2 photochemical reduction by TiO_2 have been carried out from the viewpoint of performance promotion by extending absorption range towards visible region.[8–15] N-doped reduced graphene oxide promotion,[8] modified using Ce and La for TiO_2 nanoparticles[9], heterostructured g-C_3N_4/Ag-TiO_2,[10] noble metal doping such as Pt, Pd, Rh, Au, and Ag,[11] nanocomposite CdS/TiO_2 combining two different band gap photocatalysts,[12] N_2 modified TiO_2,[13] light harvesting complex of green plants assisted Rh-doped TiO_2,[14] and dye sensitized TiO_2,[15] have been attempted to overcome the shortcoming of the pure TiO_2. They did improve the CO_2 reduction performance, however, the amount of the products achieved in all the attempts were still unsatisfactory, ranging from 1µmol/g-cat to 350 µmol/g-cat.[8–15] Therefore, a breakthrough in increasing the concentration level of products is necessary to advance the CO_2 reduction technology in order to make the technology practically useful.

It was reported that doping transition metal was a useful technique for extending the absorbance of TiO_2 into the visible region.[16] For doping, various metal ions have been used, but among them, Fe^{3+} is considered as a strong candidate as it has a similar radius to Ti^{4+} (Fe^{3+} = 78.5pm, Ti^{4+} = 74.5pm)[17] and can easily fit into the crystal lattice of TiO_2.[16,18,19] Moreover, the redox potential (energy differential) of Fe^{2+}/Fe^{3+} is close to that of Ti^{3+}/Ti^{4+}, resulting in shifting its optical absorption into the visible region.[16,18,19] The performance of Fe-doped TiO_2 (Fe/TiO_2) was reported for degradation of oxalic acid,[20] rhodamine-B[21] and methyl orange,[22] resulting that the performance is superior to pure TiO_2. Extending the absorbance of TiO_2 into the visible region such as 600nm was also reported.[18–20] However, the application of Fe/TiO_2 for CO_2 reduction is not investigated well compared to phtocatalytic degradation. Due to easy availability as well as above described characteristics, Fe is selected as the dopant in the present study.

Since a reductant is necessary for CO_2 reduction to produce fuel, H_2O and H_2 are usually used as reductant according to the review papers.[5,7] To promote the CO_2 reduction performance, it is important to select the optimum reductant which provides the proton (H^+) for the reduction reaction. The reaction scheme of CO_2 reduction with H_2O is as follows:[23–25]

<Photocatalytic reaction>

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

<Oxidization>

$$H_2O + h^+ \rightarrow \cdot OH + H^+ \quad (2)$$

$$\cdot OH + H_2O + h^+ \rightarrow O_2 + 3H^+ \quad (3)$$

<Reduction>

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

The reaction scheme of CO_2 reduction with H_2 is as follows:[26]

<Photocatalytic reaction>

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

<Oxidization>

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

<Reduction>

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

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

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

Though there are some reports on CO_2 reduction with H_2O or H_2,[5,7] the effect of combination of H_2O and H_2 is not investigated well. Though a few studies using pure TiO_2 under $CO_2/H_2/H_2O$ condition were reported,[26–28] the combined effect of ratio of CO_2, H_2 and H_2O and metal doping on CO_2 reduction performance were not investigated. Though Nishimura et al.[29] reported the combined effect of ratio of CO_2, H_2 and H_2O over Fe/TiO_2 under the illumination condition with UV light, they did not investigate that under the illumination condition without UV light. To clarify the effect of doping Fe, it is important to examine the CO_2 reduction performance under the illumination condition without UV light. In addition, the previous study[29] did not investigate to promote the CO_2 reduction performance for different ratios of CO_2, H_2 and H_2O, e.g., by changing the amount of phototcatalyst or overlapping two photocatalysts. Therefore, the aim of the present study is to clarify the optimum ratio of $CO_2/H_2/H_2O$ for promoting the CO_2 reduction performance with Fe/TiO_2 photocatalyst.

In this study, TiO_2 film is coated by sol-gel and dip-coating process on netlike glass fiber (SILIGLASS U, Nihonmuki Co.). The netlike glass fiber is a net composed of glass fiber whose diameter is about 10 µm. The fine glass fibers are knitted, resulting that the diameter of aggregate fiber is about 1mm. According to manufacturer's specifications of netlike glass fiber, the porous diameter of glass fiber is about 1nm and the specific surface area is about 400m^2/g. The netlike glass fiber consists of SiO_2 whose purity is over 96 wt%. The aperture of net is about 2mm×2mm. Since the netlike glass fiber has a porous characteristic, it is believed that TiO_2 film is captured by netlike glass fiber easily during sol-gel and dip-coating process. In addition, it can be expected a CO_2 absorption performance of prepared photocatalyst is promoted due to the porous structure of netlike glass fiber.

Then, Fe is loaded on the TiO_2 coated netlike glass fiber by pulse arc plasma method which can emit nanosized Fe particles uniformly by applying high electrical potential difference. The amount of loaded Fe can be controlled by pulse number. In this study, the pulse number is set at 100.

Since the netlike glass fiber has aperture of net, the light can pass through the netlike glass fiber. The present study has investigated overlapping two Fe/TiO_2 coated on netlike glass fiber in order to utilize the light more effectively as well as increase the amount of photocatalyst for CO_2 reduction. Though the effect of overlapping two Fe/TiO_2 coated on netlike glass fiber on CO_2 reduction performance with H_2O was reported by Nishimura et al.,[30] it was not investigated for $CO_2/H_2/H_2O$. In addition, Nishimura et al.[30] prepared Fe/TiO_2 by sol-gel dip-coating process only. Since it is difficult to dope a metal on TiO_2 uniformly by sol-gel dip-coating process,[30] this study selects the pulse arc plasma process to dope Fe. It is believed that electron transfer between overlapping two Fe/TiO_2 coated on netlike glass fiber is carried out.[30] Therefore, it is expected that the CO_2 reduction performance is promoted under many H^+ production condition such as $CO_2/H_2/H_2O$ due to matching the electron according to Eqs. (1)-(9).

In this study, Fe/TiO_2 prepared was characterized by Scanning Electron Microscope (SEM) and Electron Probe Micro Analyzer (EPMA), Transmission Electron Microscope (TEM), Energy Dispersive X-ray Spectrometry (EDX) and Electron Energy Loss Spectrum (EELS) analysis. The CO_2 reduction performance with H_2 and H_2O using Fe/TiO_2 coated on netlike glass fiber as photocatalyst under the condition of illuminating Xe lamp with or without UV light were investigated. The molar ratio of $CO_2/H_2/H_2O$ was set at 1:0.5:0.5, 1:1:0.5, 1:0.5:1, and 1:1:1 to determine the optimum ratio of $CO_2/H_2/H_2O$. In addition, the effect of overlapping two Fe/TiO_2 coated netlike glass fiber on CO_2 reduction performance was investigated.

Experiments

Preparation of Fe/TiO$_2$ film

Sol-gel and dip-coating process was used for preparing TiO_2 film. TiO_2 sol solution was made by mixing $[(CH_3)_2CHO]_4Ti$ (purity of 95 wt%, Nacalai Tesque Co.) of 0.3mol, anhydrous C_2H_5OH (purity of 99.5 wt%, Nacalai Tesque Co.) of 2.4 mol, distilled water of 0.3 mol, and HCl (purity of 35 wt%, Nacalai Tesque Co.) of 0.07 mol. Netlike glass fiber was cut to disc, and its diameter and thickness were 50mm and 1mm, respectively. The netlike glass disc was dipped into TiO_2 sol solution at the speed of 1.5mm/s and pulled up at the fixed speed of 0.22 mm/s. Then, it was dried out and fired under the controlled firing temperature (*FT*) and firing duration time (*FD*), resulting that TiO_2 film was fastened on the base material. *FT* and *FD* were set at 623K and 180s, respectively. Fe was then loaded on TiO_2 film by pulse arc plasma method. The pulse arc plasma gun device (ULVAC, Inc., ARL-300) having Fe electrode whose diameter was 10mm was applied for Fe loading. After the netlike glass fiber coated with TiO_2 was set in the chamber of the pulse arc plasma gun device, where was vacuumed, the nanosized Fe particles were emitted from Fe electrode with applying the electrical potential difference of 200V. The pulse arc plasma gun can evaporate Fe particle over the target in the circle area whose diameter is 100 mm when the distance between Fe electrode and the target is 160mm. Since the distance between Fe electrode and TiO_2 film was 150 mm, Fe particle can be evaporated over TiO_2 film uniformly. The amount of loaded Fe was controlled by pulse number. In this study, the pulse number was set at 100. To promote the CO_2 reduction performance, overlapping layout of two photoatalysts were investigated. The photocatalyst coated on both upper and lower surfaces of netlike glass disc was overlapped over the other photocatalyst coated on upper surface of netlike glass disc.

Characterization of Fe/TiO$_2$ film

The structure and crystallization characteristics of Fe/TiO_2 film were evaluated by SEM (JXA-8530F, JEOL Ltd.), EPMA (JXA-8530F, JEOL Ltd.), TEM (JEM-2100F/HK, JEOL Ltd.), EDX (JEM-2100F/HK, JEOL Ltd.) and EELS (JEM-ARM2007 Cold, JEOL Ltd.). Since these measuring instruments use electron for analysis, the sample should be an electron conductor. Since netlike glass disc is not an electron conductor, the carbon vapor deposition was conducted by the dedicated device (JEE-420, JEOL Ltd.) for Fe/TiO_2 coated on netlike glass disc before analysis. The thickness of carbon deposited on samples was approximately 20-30nm.

The electron probe emits the electrons to the sample under the acceleration voltage of 15 kV and the current of 3.0×10^{-8} A, when the surface structure of sample is analyzed by SEM. The characteristic X-ray is detected by EPMA at the same time, resulting that the concentration of chemical element is analyzed according to the relationship between the characteristic X-ray energy and the atomic number. The spatial resolution of SEM and EPMA is 10μm. The EPMA analysis helps not only to understand the coating state of prepared photocatalyst but also to measure the amount of doped metal within TiO_2 film on the base material.

The electron probe emits the electron to the sample under the acceleration voltage of 200 kV, when the inner structure of sample is analyzed by TEM. The size, thickness and structure of loaded Fe were evaluated. The characteristic X-ray is detected by EDX at the same time, resulting that the concentration distribution of chemical element toward thickness direction of the sample can be analyzed. In this study, the concentration distributions of Ti and Fe were analyzed.

EELS can be applied not only for detecting elements but also for determination of oxidation states of some transition metals. The EELS characterization was performed by JEM-ARM200F equipped with GIF Quantum having 2048ch. The dispersion of 0.5eV/ch can be achieved of the full width at half maximum of the zero loss peak.

CO_2 reduction experiment

Figure 1 shows the experimental set-up of the reactor consisting of stainless pipe (100mm(*H.*)×50mm(*I.D.*)), a netlike glass disc coated with Fe/TiO_2 film (50mm(*D.*)×1mm(*t.*)) which is located on the teflon cylinder (50mm (*H.*)×50mm (*D.*)), a quart glass disc (84mm(*D.*)×10mm(*t.*)), a sharp cut filter which cuts off the light of wavelength below 400nm (SCF–49.5C-42L, SIGMA KOKI CO. LTD.), a 150 W Xe lamp (L2175, Hamamatsu Photonics K. K.), mass flow controller, CO_2 gas cylinder and H_2 gas cylinder.

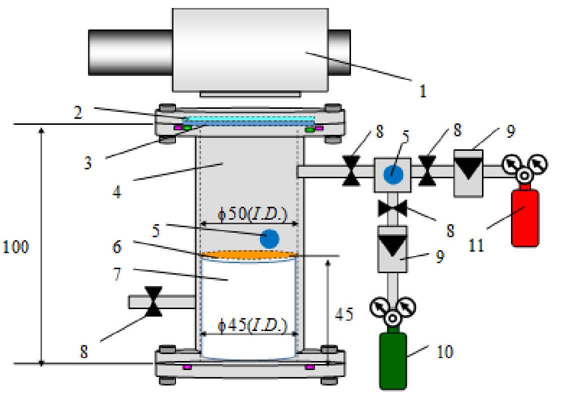

Figure 1 Schematic drawing of CO_2 reduction experimental set-up.

The reactor has volume of $1.25\times 10^{-4}m^3$, which is available for CO_2. The light of Xe lamp, through the sharp cut filter and the quartz glass disc that are at the top of the stainless pipe, illuminates the netlike glass disc coated with Fe/TiO_2 film, which is located inside the stainless pipe. The wavelength of light from Xe lamp is ranged from 185 nm to 2000nm. The Xe lamp can be fitted with a sharp cut filter to remove UV components of the light. With the filter, the wavelength of light from Xe lamp is ranged from 401nm to 2000nm. Figure 2 shows the light transmittance data of the sharp cut filter to prove the removal of the light whose wavelength is below 400nm. The average light intensity of Xe lamp on the photocatalyst without and with setting the sharp cut filter is 75.3 mW/cm^2 and 68.2 mW/cm^2, respectively.

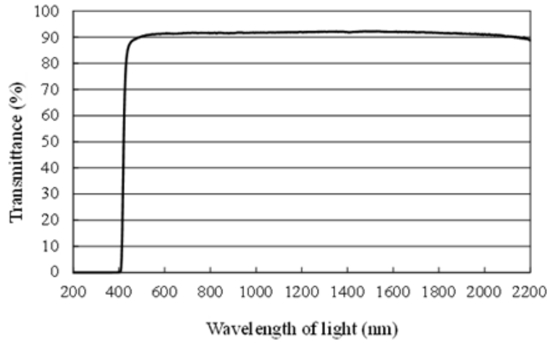

Figure 2 Light transmittance data of sharp cut filter.

In the CO_2 reduction experiment with H_2 and H_2O, CO_2 gas of 99.995 vol% purity and H_2 gas of 99.99999 vol% purity were mixed in the buffer chamber, and introduced in the reactor which was pre-vacuumed by a vacuum pump. The mixing ratio of CO_2 and H_2 was controlled by a mass flow controller and confirmed by a TCD gas chromatogragh (Micro GC CP4900, GL Science) before introducing into the reactor. After confirming the mixing ratio of CO_2 and H_2, the distilled water was injected into the reactor through gas sampling tap and Xe lamp illumination was turned on at the same time. The molar ratio of $CO_2/H_2/H_2O$ was set at 1:0.5:0.5, 1:1:0.5, 1:0.5:1, and 1:1:1, respectively. The injected water vaporized completely in the reactor. Due to the heat of Xe lamp, the temperature in reactor was attained at 343K within an hour and kept at approximately 343K during the experiment.

The gas in the reactor was sampled every 24 hours during the experiment. The gas samples were analyzed by FID gas chromatograph (GC353B, GL Science) and methanizer (MT221, GD Science). Minimum resolution of FID gas chromatograph and methanizer is 1ppmV.

Results and discussion

Characterization of Fe/TiO_2 film

Figures 3 & 4 show EPMA images of TiO_2 and Fe/TiO_2 film, respectively. EPMA analysis was carried out for 1500 times magnification SEM images. In EPMA image, the concentrations of each element in observation area are indicated by the different colors. Light colors, for example, white, pink, and red indicate that the amount of element is large, while dark colors like black and blue indicate that the amount of element is small.

From these figures, it can be observed that TiO_2 film with teeth like shape was coated on netlike glass fiber. It is also seen that TiO_2 film builds a bridge among several glass fibers like reported also in.[30] During firing process, the temperature profile of TiO_2 solution adhered on the netlike glass disc was not even due to the different thermal conductivities of Ti and SiO_2. Their thermal conductivities of Ti and SiO_2 at 600 K are 19.4 W/(mK) and 1.82 W/(mK), respectively.[31] Due to the thermal expansion and shrinkage around netlike glass fiber, thermal crack formed on TiO_2 film. Therefore, TiO_2 film on netlike glass fiber was teeth like. As to Fe, it is observed from Figure 3 that nanosized Fe particles loaded on TiO_2 uniformly, resulting from that the pulse arc plasma method can emit nanosized Fe particles.

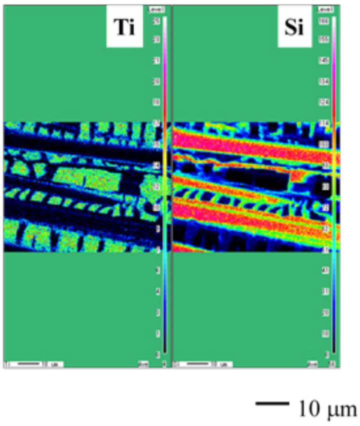

Figure 3 EPMA image of TiO$_2$ film.

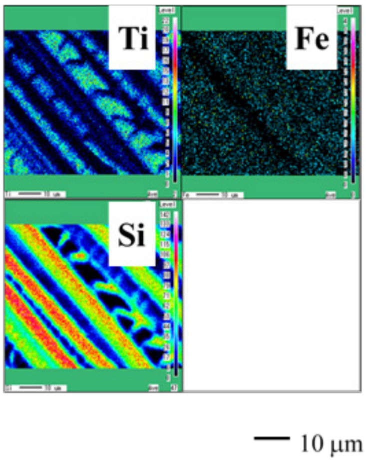

Figure 4 EPMA image of Fe/TiO$_2$ film.

To evaluate the amount of loaded Fe within TiO$_2$ film quantitatively, the observation area, which is the center of netlike glass disc, of diameter of 300 µm is analyzed by EPMA. The ratio of Fe to Ti in this observation area is counted by averaging the data obtained in this area. As a result, the weight percentages of elements Fe and Ti in the Fe/TiO$_2$ film are 1.84 wt% and 98.16 wt%, respectively.

Figure 5 shows EDX images of Fe/TiO$_2$. EDX analysis was carried out using 160000 times magnification TEM images. In these figures, the yellow circle indicates the existence of Fe. From this figure, it is observed that Fe particle is loaded on TiO$_2$ film, and no Fe layer has formed. The average size of Fe particle for Fe/TiO$_2$ loaded is approximately 28 nm where the longest length of Fe particle was used as a representative length.

Figure 6 shows EELS spectra of Fe in Fe/TiO$_2$ film. From this figure, the peaks at around 708eV and 720eV can be observed. Compared to EELS data base,[32] the EELS spectra of Fe$_2$O$_3$ (Hematite) matches with Figure 6. Therefore, Fe in Fe/TiO$_2$ prepared presents as Fe^{3+} ion in Fe$_2$O$_3$. Since the doped Fe emits the electron during the photochemical reaction and the electron plays a part in the fuel production from CO$_2$ under CO$_2$/H$_2$O condition[23–25] and CO$_2$/H$_2$ condition,[26] the ion number of Fe is important. For Fe/TiO$_2$ photocatalyst, the incorporated Fe^{3+} ions can substitute the octahedrally coordinated Ti^{4+} ions in TiO$_2$ lattice, which extends the photo-response of TiO$_2$ to the visible light region and promotes the formation of electron-hole pair significantly.[33] Since the Fe^{3+} ion acts as an electron-trapped agent, Fe/TiO$_2$ exhibits a low recombination rate of electron-hole pairs and high separation efficiency.[33]

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

Figures 7 and 8 show the concentration changes of CO produced and the molar quantity of CO per weight of photocatalyst in the reactor along the time under the Xe lamp with UV light on, respectively. The amount of Fe/TiO$_2$ on the netlike glass disc is 0.10g. In this experiment, CO is the only fuel produced from the reactions. Before the experiments, a blank test, that was running the same experiment without illumination of Xe lamp, had been carried out to set up a reference case. No fuel was produced in the blank test as expected.

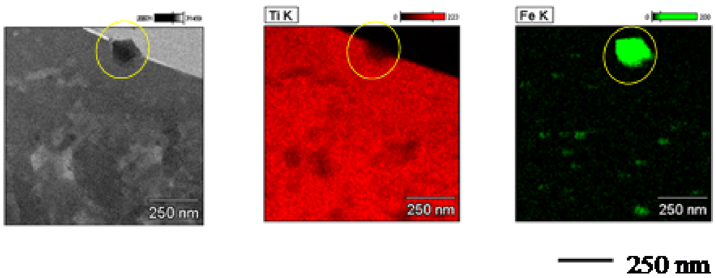

Figure 5 TEM image of Fe/TiO$_2$ film.

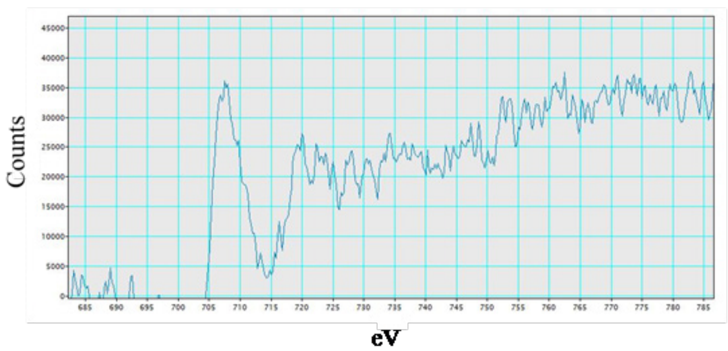

Figure 6 EELS spectra of Fe in Fe/TiO$_2$.

Citation: Nishimura A, Tatematsu D, Toyoda R, et al. Effect of overlapping layout of Fe/TiO$_2$ on CO$_2$ reduction with H$_2$ and H$_2$O. *MOJ Solar Photoen Sys.* 2019;3(1):1–8. DOI: 10.15406/mojsp.2019.03.00028

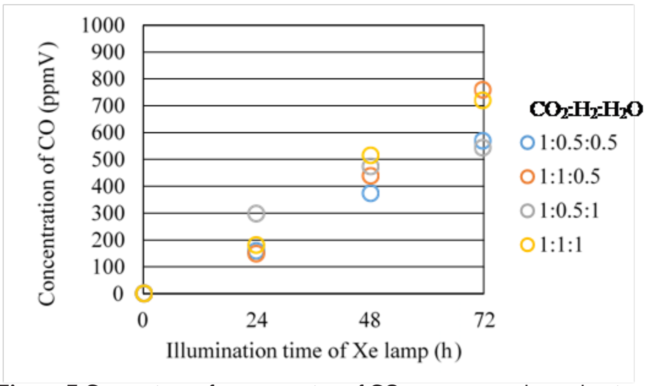

Figure 7 Comparison of concentration of CO among several moral ratios of CO$_2$/H$_2$/H$_2$O under the illumination condition with UV light.

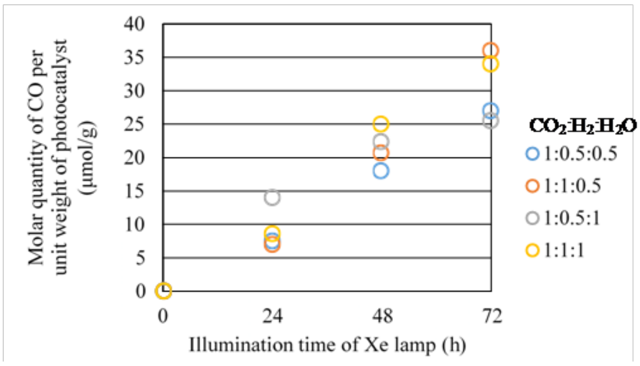

Figure 8 Comparison of molar quantity of CO per unit weight of photocatalyst among several moral ratios of CO$_2$/H$_2$/H$_2$O under the illumination condition with UV light.

According to Figures 7 & 8, the CO$_2$ reduction performance is the highest for the moral ratio of CO$_2$/H$_2$/H$_2$O=1:1:0.5. Since the reaction scheme of CO$_2$/H$_2$/H$_2$O is not clarified, this study refers to the reaction scheme of CO$_2$/H$_2$O and CO$_2$/H$_2$ as shown by Eqs. (1) – (9). It is known from Eqs. (1) – (9) that 2 H$^+$ and 2 electrons are necessary for producing CO in the case of CO$_2$/H$_2$O as well as that of CO$_2$/H$_2$. In other words, the same number of H$^+$ and electron is needed. According to Figure 6, Fe in Fe/TiO$_2$ prepared is in the form of Fe^{3+} ion in Fe$_2$O$_3$. Therefore, it is believed that 3 electrons are emitted per Fe, resulting that the electron rich state is formed. According to Eqs. (2), (3) and (6), H$^+$ is produced by the oxidization of reductant. Comparing H$_2$O with H$_2$, H$_2$O is a weaker reductant,[34] resulting that larger amount of H$_2$ is necessary to match the electron rich state. On the other hand, the lowest CO$_2$ reduction performance is obtained for the moral ratio of CO$_2$/H$_2$/H$_2$O = 1:0.5:1 according to Figures 7 and 8. This result also shows that larger moral ratio of H$_2$ compared to H$_2$O is necessary for the better CO$_2$ reduction performance of Fe/TiO$_2$.

Figures 9 & 10 show the concentration changes of CO produced and the molar quantity of CO per weight of photocatalyst in the reactor along the time under the Xe lamp without UV light on, respectively. In this experiment, CO is the only fuel produced from the reactions.

According to Figures 9 & 10, the CO$_2$ reduction performance is the best for the moral ratio of CO$_2$/H$_2$/H$_2$O=1:1:0.5 in the case of illumination condition with UV light. It is considered that the same reaction mechanism as mentioned above is occurred. The order of CO$_2$ reduction performance of Fe/TiO$_2$ without UV light is the same as that with UV light. It is revealed that the wave length of light doesn't influence on the CO$_2$ reduction characteristics of Fe/TiO$_2$ with H$_2$ and H$_2$O.

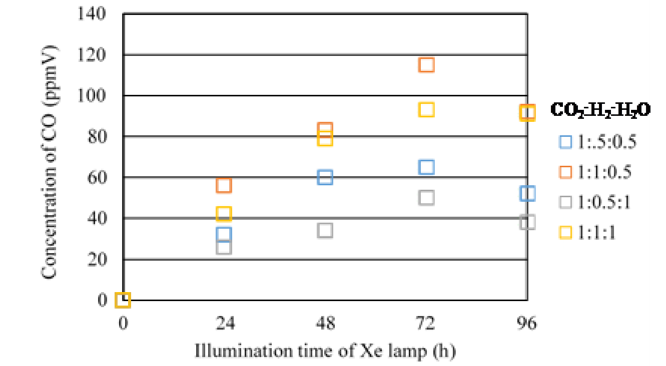

Figure 9 Comparison of concentration of CO among several moral ratios of CO$_2$/H$_2$/H$_2$O under the illumination condition without UV light.

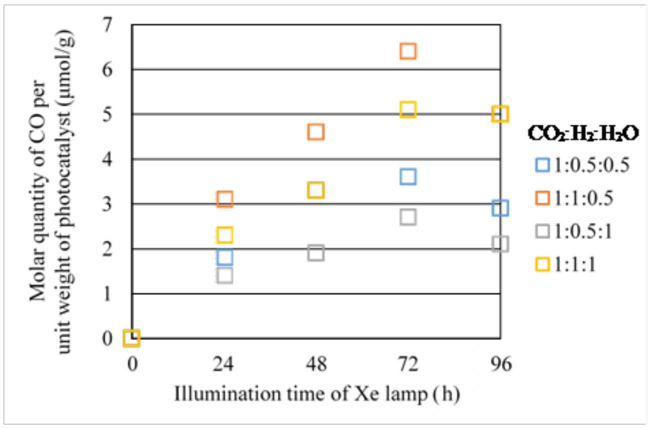

Figure 10 Comparison of molar quantity of CO per unit weight of photocatalyst among several moral ratios of CO$_2$/H$_2$/H$_2$O under the illumination condition without UV light.

Effect of overlapping on CO$_2$ reduction characteristics of Fe/TiO$_2$

Figures 11 & 12 show the concentration changes of CO produced and the molar quantity of CO per weight of photocatalyst in the reactor along the time under the Xe lamp with UV light on, for Fe/TiO$_2$ film coated on netlike glass disc overlapped, respectively. The total amount of Fe/TiO$_2$ overlapped is 0.25g.

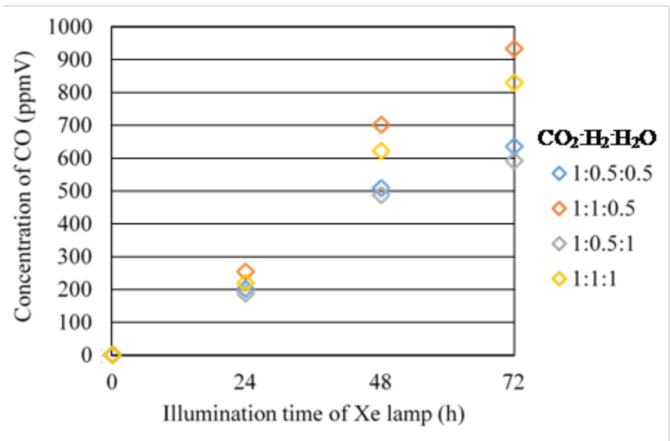

Figure 11 Comparison of concentration of CO for Fe/TiO$_2$ overlapped among several moral ratios of CO$_2$/H$_2$/H$_2$O under the illumination condition with UV light.

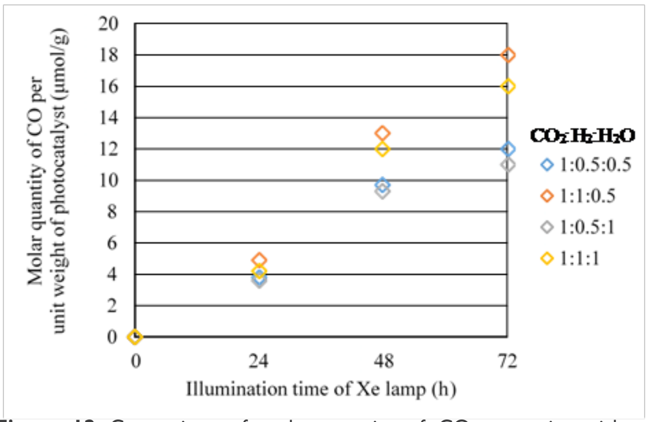

Figure 12 Comparison of molar quantity of CO per unit weight of photocatalyst for Fe/TiO$_2$ overlapped among several moral ratios of CO$_2$/H$_2$/H$_2$O under the illumination condition with UV light.

According to Figures 11 and 12, the moral ratio of CO$_2$/H$_2$/H$_2$O = 1:1:0.5 generates the best CO$_2$ reduction performance among various ratios, which is the like the case of the single Fe/TiO$_2$. In addition, the order of CO$_2$ reduction performance of Fe/TiO$_2$ overlapped is the same as that of single Fe/TiO$_2$. However, comparing Figure 11 with Figure 7, the concentration of CO for Fe/TiO$_2$ overlapped is higher than that for single Fe/TiO$_2$ under every molar ratio of CO$_2$/H$_2$/H$_2$O. The highest concentration of CO for Fe/TiO$_2$ overlapped is 993ppmV which is 1.2 times as large as that of single Fe/TiO$_2$. When overlapped, the following things may occur:

1. The total amount of photocatalyst used for photocatalysis reaction is increased.
2. The electron transfer between two Fe/TiO$_2$ films promotes the activity of photocatalysis reaction.
3. The lower positioned Fe/TiO$_2$ film utilizes the light passing through the higher positioned Fe/TiO$_2$ film.

However, comparing Figure 12 with Figure 8, the molar quantity of CO per weight of photocatalyst for Fe/TiO$_2$ overlapped is lower than that for single Fe/TiO$_2$ under every molar ratio of CO$_2$/H$_2$/H$_2$O. The highest molar quantity of CO per weight of photocatalyst is 18µmol/g which is half of single Fe/TiO$_2$. The reasons of this result are considered as follows:

1. Some area of lower positioned Fe/TiO$_2$ film can't receive the adequate light.
2. If the produced fuel CO remains in the space between two discs, the reactant of CO$_2$, H$_2$ and H$_2$O may be blocked to certain degree to reach the surface of photocatalyst, resulting that the photochemical reaction could not be carried out well even though the light is illuminated for photocatalyst. The mass and electron transfer mechanism for Fe/TiO$_2$ overlapped is illustrated in Figure 13.

From these results, the effective light utilization and mass transfer promotion are necessary for improvement of CO$_2$ reduction performance of Fe/TiO$_2$ overlapped.

Figures 14 &15 show the concentration changes of CO produced and the molar quantity of CO per weight of photocatalyst in the reactor along the time under the Xe lamp without UV light on, for Fe/TiO$_2$ film coated on netlike glass disc overlapped, respectively.

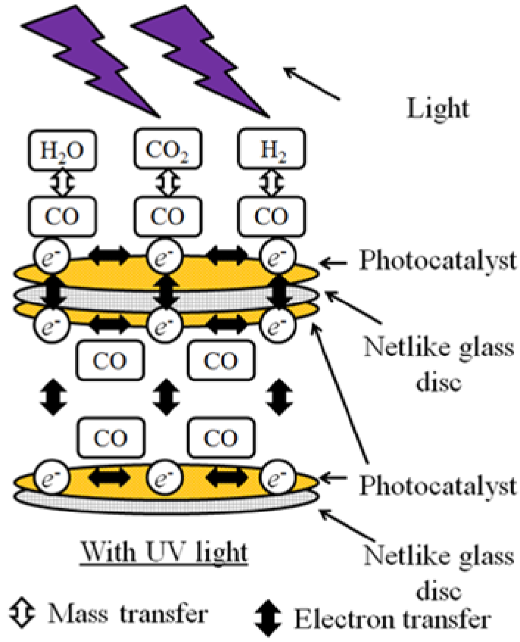

Figure 13 Mass and electron transfer mechanism for Fe/TiO$_2$ overlapped.

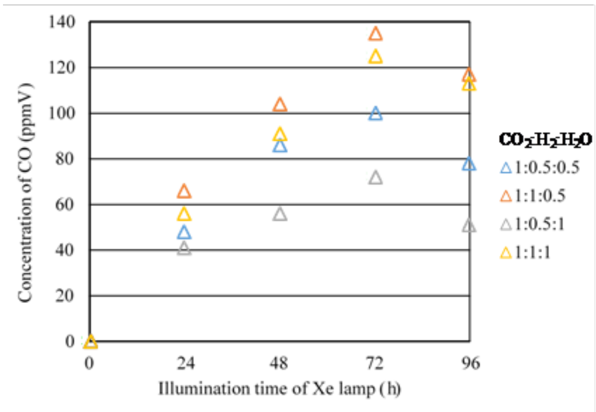

Figure 14 Comparison of concentration of CO for Fe/TiO$_2$ overlapped among several moral ratios of CO$_2$/H$_2$/H$_2$O under the illumination condition without UV light.

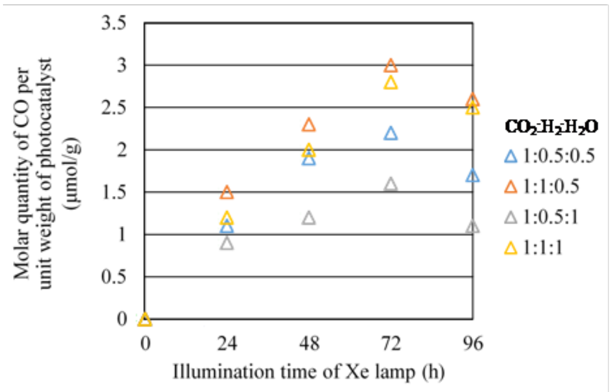

Figure 15 Comparison of molar quantity of CO per unit weight of photocatalyst for Fe/TiO$_2$ overlapped among several moral ratios of CO$_2$/H$_2$/H$_2$O under the illumination condition without UV light.

According to Figures 14 & 15, the moral ratio of $CO_2/H_2/H_2O$=1:1:0.5 again generates the best CO_2 reduction performance. The order of CO_2 reduction performance of Fe/TiO_2 overlapped is the same as that of single Fe/TiO_2. However, comparing Figure 14 with Figure 9, the maximum concentration of CO for Fe/TiO_2 overlapped is higher than that for single Fe/TiO_2 under every molar ratio of $CO_2/H_2/H_2O$. The highest concentration of CO for Fe/TiO_2 overlapped is 135ppmV which is about 1.2times as large as that for single Fe/TiO_2. The same reasons can explain this result as the illumination condition with UV light.

However, comparing Figure 15 with Figure 10, the molar quantity of CO per weight of photocatalyst for Fe/TiO_2 overlapped is lower than that for single Fe/TiO_2 under every molar ratio of $CO_2/H_2/H_2O$. The highest molar quantity of CO per weight of photocatalyst for overlapped case is only 3.0μmol/g which is almost half of single Fe/TiO_2.

In this study, the highest molar quantity of CO per weight of photocatalyst is 36μmol/g for single Fe/TiO_2 under the illumination condition with UV light. Compared to the previous research on CO_2 reduction with H_2 and H_2O over pure TiO_2, the CO production performance of photocatalysts prepared in this study is approximately 120 times as large as that reported in references,[26,28] which is owing to Fe doping. The CO production performance of Fe/TiO_2 prepared in this study is approximately 36 times as large as that of ZrO_2 reported in the reference.[26] This is due to that the doped Fe provides the free electron preventing recombination of electron and hole produced as well as improving the light absorption effect. Another way to further promote the CO_2 reduction performance may be using the netlike porous metal which has an appropriate area of aperture as a base material instead of netlike glass fiber. Since the netlike porous metal has good electrical conductivity, light permeability, and gas diffusivity, it can be expected that the CO_2 reduction performance can be further promoted. In addition, the other dopant like Cu, which can absorb the longer wavelength light than Fe,[19] should be used at lower positioned layers since the wavelength of penetrating light becomes long through higher positioned photocatalyst.[30] This proposal is similar to the concept of the hybrid photocatalyst using two photocatalysts having different band gaps.[35–37]

Conclusion

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

(1) TiO_2 could be coated on netlike glass fiber where it appears teeth like shape. Fe fine particles could be loaded on TiO_2 uniformly.

(2) Fe in Fe/TiO_2 prepared in this study is in the form of Fe^{3+} ion in Fe_2O_3.

(3) Under the illumination condition with UV as well as without UV, the concentration of produced CO and the molar quantity of CO per weight of photocatalyst for Fe/TiO_2 are the highest with the ratio of $CO_2/H_2/H_2O$ = 1:1:0.5. Since Fe in Fe/TiO_2 emits three electrons, the larger H_2 which is stronger reductant compared to H_2O is necessary to match the electron rich state.

(4) Under the illumination condition with UV as well as without UV, the concentration of produced CO for Fe/TiO_2 overlapped is higher than that for single Fe/TiO_2. The highest concentration of CO for Fe/TiO_2 overlapped is 1.2 times as large as that for single Fe/TiO_2.

(5) However, the molar quantity of CO per weight of photocatalyst for Fe/TiO_2 in overlapped case is lower than that for single Fe/TiO_2 case. The highest molar quantity of CO per weight of photocatalyst for Fe/TiO_2 overlapped is just half of single Fe/TiO_2.

(6) The CO_2 reduction performance of prepared Fe/TiO_2 is superior to the previous studies with TiO_2 under $CO_2/H_2/H_2O$ condition.

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Conflicts of interest

The authors declare that there is no conflicts of interest.

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