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Utilization from ultraviolet to infrared light for CO_2 reduction with P_4O_{10}/TiO_2 photocatalyst

Abstract

This study aims to extend the light spectrum which could be absorbed by TiO_2 to infrared ray light (IR) by loading P_4O_{10} in order to promote the CO_2 reduction performance of TiO_2 photocatalyst. Three ranges of light with P_4O_{10}/TiO_2 film are studied, which are ultra violet light (UV) + visible light (VIS) + IR, VIS + IR, and IR only. This study also investigates the impact of molar ratio of CO_2/H_2O or CO_2/NH_3 on the CO_2 reduction characteristics of P_4O_{10}/TiO_2 film. The largest CO_2 reduction performance in case of CO_2/H_2O and CO_2/NH_3 is obtained at CO_2:H_2O = 1:1 and CO_2:NH_3 = 3:2 respectively, irrespective of light illumination condition. With IR light illumination only, the largest molar quantity of CO per unit weight of photocatalyst for P_4P_{10}/TiO_2 film in case of CO_2/H_2O and CO_2/NH_3 is 2.36 µmol/g and 33.4 µmol/g, respectively.

Keywords: P_4O_{10}/TiO_2 photocatalyst, CO_2 reduction, Visible light, Infrared ray light, Reductant combination

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Introduction

The global average concentration of CO_2 in the atmospheric air has been increasing up to 416 ppmV in July 2022, indicating that it is an increase of 76 ppmV compared to 1980.[1] It is necessary to develop CO_2 reduction technologies to prevent the continues rise of global temperature.

Many researches have investigated that CO_2 can be converted/reduced into fuel species such as CO, CH_4, CH_3OH, and so on, by photocatalyst.[2-5] TiO_2 is one of popular photocatalysts applied for CO_2 reduction.[2-5] Pure TiO_2 can work under ultra violet light (UV) illumination condition only. UV light accounts for 4 % only in sunlight.[6] If we could use the visible light (VIS) and infrared ray light (IR) which accounts for 44 % and 52 % of solar energy reaching the earth[6] for photocatalytic CO_2 reduction, it would promote the photocatalytic CO_2 reduction performance significantly. Additionally, it can be claimed that the whole solar energy can be utilized for the photocatalytic CO_2 reduction.

As to the photocatalytic studies on extending the absorption of light wavelength from UV to VIS, many approaches have been tried.[7-16] One of the popular attempts is a metal doping. Cu is usually adopted as a metal dopant. Cu/TiO_2 has performed absorption of light whose wavelength is from 400 nm to 800 nm and produced CO of 0.5 µmol/g and H_2 of 4 µmol/g.[7] Cu_2O/TiO_2 has produced CO of 80 µmol/g under the Xe lamp illumination condition whose wavelength of light is 320 – 780 nm.[8] Cu ultrathin TiO_2 absorbing the light whose wavelength is from 400 nm to 800 nm has produced CO of 7 µmol/g.[9] Cu_2O/TiO_2 heterostructures absorbing the light whose wavelength is from 300 nm to 650 nm has produced CO of 2 µmol/g.[10] Pd is also adopted as a metal dopant. Pd/TiO_2 nanowire has performed the absorption of light whose wavelength is 350 nm – 700 nm, which has produced CH_4 yield of 26.7 µmol/g and CO yield of 50.4 µmol/g.[11] Pd/TiO_2 (3 wt% of Pd) extending the absorption limit up to 700 nm has produced CH_4 of 4.2 µmol/g and CO of 2.1 µmol/g.[12] Zn and Pd co-modified TiO_2 has exhibited CH_4 yield of 53.5 µmol/g under the illumination condition of 500 W Xe arc lamp whose wavelength of light is from 290 nm to 800 nm.[13] Pt is another candidate as a metal dopant. Graphene-wrapped Pt/TiO_2 has shown the light absorption from 300 nm to 750 nm, resulting in CO production of 320 µmol/g and CH_4 production of 45 µmol/g.[14] Pt/TiO_2 synthesized by thermal hydrolysis of two different precursors has exhibited the light absorption from 200 nm to 700 nm and produced CH_4 of 0.73 µmol/g and CO of 0.17 µmol/g.[15] Nanocrystal-supported $PtRu/TiO_2$ has performed the light absorption from 300 nm to 750 nm and CH_4 of 300 µmol/g.[16]

As to the photocatalytic studies on extending the absorbed wavelength up to IR, there are some reports.[17-20] $W_{18}O_{49}/g\text{-}C_3N_4$ composite has displayed the CO production of 45 µmol/g and CH_4 production of 28 µmol/g under the illumination condition whose wavelength is from 200 nm to 2400 nm.[17] WS_2/Bi_2S_3 nanotube has exhibited the absorption of VIS and near IR light (wavelength: 420 nm – 1100 nm), which has produced CH_3OH of 28 µmol/g and C_2H_5OH of 25 µmol/g.[18] CuInZnS decorated $g\text{-}C_3N_4$ has exhibited the absorption performance of light whose wavelength is from 200 nm to 1000 nm, performing the CO production of 38 µmol/g.[19] Hierarchical $ZnIn_2S_4$ nanorods has prepared by solvothermal method, which has produced CO of 54 µmol/g and CH_4 of 9 µmol/g.[20]

Though several studies on extending the absorbed light of wavelength up to IR have been reported, there is no report investigating the extension of light absorption performance of TiO_2 up to IR. Therefore, this study attempts to extend the light absorption performance of TiO_2 up to IR. According to the reference,[21] the composite photocatalyst of black phosphorus (P) and $g\text{-}C_3N_4$ has performed the H_2 production from H_2O under VIS and near IR light illumination condition. P has a layer structure absorbing the light whose wave length is from UV to IR. Therefore, this study investigates the preparation procedure of P/TiO_2 and its CO_2 reduction performance under IR light illumination condition. The purpose of this study is to investigate the CO_2 reduction performance of P/TiO_2 changing the wavelength of illuminated light by UV + VIS + IR, VIS + IR, and IR only. This study also investigates the impact of molar ratio of CO_2/H_2O or CO_2/NH_3 on the CO_2 reduction characteristics of P/TiO_2. For the photocatalytic CO_2 reduction reaction, a reductant is important since it is a partner for CO_2. It is found from review papers[22,23] that H_2O and H_2 are usually adopted as a reductant. It is necessary to clarify the optimum reductant providing the proton (H^+) for the reduction reaction in order to enhance the CO_2 reduction performance. According to the past studies,[24-26] we can show the reaction scheme of CO_2 reduction with H_2O as below:

<Photocatalytic reaction process>

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

<Oxidization reaction process>

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

<Reduction reaction process>

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

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

Regarding the reaction scheme of CO_2 reduction reacting with H_2, we can show it as follows:[27]

<Photocatalytic reaction process>

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

<Oxidization reaction process>

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

<Reduction reaction process>

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

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

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

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

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

Though the previous studies investigated CO_2 reduction reacting with H_2O or H_2,[22,23] the effect of NH_3 including $3H^+$, which outmatches H_2O and H_2, on photocatalytic CO_2 reduction performance is not investigated yet except for the previous studies carried out by the authors using Fe,[28] Cu[29,30] or Pd.[31] They have been investigated the combination of CO_2, H_2O and NH_3.[28-31] However, regarding the reaction scheme to reduce CO_2 with NH_3, we can show it as follows:[27,32]

<Photocatalytic reaction process>

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

<Oxidization reaction process>

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

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

<Reduction reaction process>

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

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

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

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

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

We investigate the CO_2 reduction characteristics of P/TiO_2 changing the wavelength of illuminated light by UV + VIS + IR, VIS + IR and IR only. In addition, this study also clarifies the optimum molar ratio of CO_2/H_2O or CO_2/NH_3 for the CO_2 reduction characteristics of P/TiO_2 changing the wavelength of illuminated light by UV + VIS + IR, VIS + IR, and IR only.

Experiments

The Preparation procedure of TiO_2 film

We prepared the TiO_2 film by sol-gel and dip-coating process.[29-31] $[(CH_3)_2CHO]_4Ti$ (purity: 95 wt%, producer: Nacalai Tesque Co., Kyoto, Japan) of 0.3 mol, anhydrous C_2H_5OH (purity: 99.5 wt%, producer: Nacalai Tesque Co., Kyoto, Japan) of 2.4 mol, distilled water of 0.3 mol, and HCl (purity: 35 wt%, producer: Nacalai Tesque Co., Kyoto, Japan) of 0.07 mol were mixed to prepare the TiO_2 sol solution. We coat the TiO_2 film on a netlike glass fiber (SILLIGLASS U, producer: Nihonmuki Co., Tokyo, Japan) via sol-gel and dip-coating process. The glass fiber with a diameter of about 10 μm, which is weaved as a net, is assembled to be the diameter of about 1 mm. According to the specification on netlike glass fiber, the porous diameter of glass fiber and the specific surface area is approximately 1 nm and 400 m^2/g, respectively. The netlike glass fiber consists of SiO_2 of 96 wt%. The netlike glass fiber has the opening space of about 2 mm×2 mm. The netlike glass fiber has porous characteristics, resulting that the netlike glass fiber can trap the TiO_2 film easily via sol-gel and dip-coating processes. In addition, it can be expected that CO_2 and reductant such as H_2O and NH_3 are more easily absorbed by the prepared photocatalyst since the netlike glass fiber has the porous characteristics. The netlike glass fiber is cut to be disc form with the diameter of 50 mm and thickness of 1 mm. We immersed the netlike glass disc into TiO_2 sol solution by controlling the speed at 1.5 mm/s and drew it up by controlling the fixed speed of 0.22 mm/s. We dried it out and fired it by controlling a firing temperature (*FT*) and a firing duration time (*FD*), resulting that the TiO_2 film is fastened on the base material. We set *FT* and *FD* at 623 K and 180 s, respectively.

The Preparation procedure of P_4O_{10}/TiO_2 film

In this study, P_4O_{10} is made from the red P by a mechanical synthesis.[33] The red P (average diameter: 75 μm, producer: Nacalai Tesque Co., Kyoto, Japan) was filled in a ball mill crusher (AV-1, producer: Asahi Rika Factory, Chiba, Japan) with Al_2O_3 ball whose diameter was 3/8 inch (HD-10, producer: NIKKATO CORPORATION, Osaka, Japan). The weight ratio of Al_2O_3 balls to red P particles in the ball mill crusher was set at 20.[33] Rotation with the speed of 600 rpm was kept for 12 hours, after that the P_4O_{10} was prepared.

The prepared P_4O_{10} particles were put into TiO_2 sol solution and mixed with TiO_2 sol solution by a magnetic stirrer for 60 min. After that, the netlike glass disc was immersed into this mixed solution. The following process was same as explained above. The weight ratio of P_4O_{10} to TiO_2 were set at 10 wt%. Figure 1 shows the photo of prepared P_4O_{10}/TiO_2 film coated on netlike glass disc.

The characterization procedure of P_4O_{10}/TiO_2 film

The characteristics of external and crystal structure of P loaded TiO_2 film were evaluated by SEM (JXA-8530F, producer: JEOL Lt., Tokyo, Japan) and EPMA (JXA-8530F, producer: JEOL Ltd., Tokyo, Japan).[29-31] In these procedures, we use electron to characterize a sample. Therefore, the sample should conduct electricity. The netlike glass disc which was used for base material to coat TiO_2 film cannot conduct electricity, resulting that we deposited the vaporized Pt by the means of the Pt coating device (JEC-1600, producer: JEOL Ltd., Tokyo, Japan) on the surface of the TiO_2 film before the characterization. The deposited Pt has the thickness of 15 nm. The electrode emits the electrons to the sample by setting the acceleration voltage and current at 15 kV and 3.0×10^{-8} A, respectively, to analyze the external structure of TiO_2 film by means of SEM. We analyze the

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character X-ray by means of EPMA at the same time, resulting that the amount of chemical element is estimated based on the relationship between character X-ray energy and atomic number. The space resolution of SEM and EPMA is 10 mm. We can clarify the structure of prepared TiO_2 photocatalyst by the EPMA analysis.

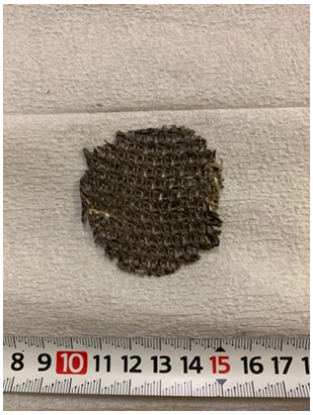

Figure 1 Photo of prepared P_4O_{10}/TiO_2.

In addition, this study also evaluated the chemical composition state of P_4O_{10}/TiO_2 film by XPS (PHI Quantera SXM™, producer: ULVAC. PHI. Inc., Chigasaki, Japan). This procedure uses X-ray to analyze the characterization. The X-ray is emitted from the probe whose diameter is 100 μm to the sample by setting the acceleration voltage of 15 kV. In this study, XPS analysis is conducted to identify the type of P loaded on TiO_2 film.

CO_2 reduction with H_2O

Figure 2 exhibits the experimental apparatus. The reactor consists of a stainless tube with a scale of 100 mm (*H.*)×50 mm (*I.D.*), TiO_2 film or P_4O_{10}/TiO_2 which is coated on netlike glass disc with a scale of 50 mm (*D.*)×1 mm (*t.*) positioned on the Teflon cylinder with a scale of 50 mm (*H.*)×50 mm (*D.*), a quartz glass disc having a scale of 84 mm (*D.*)×10 mm (*t.*), a sharp cur filter removing the wavelength of light which is below 400 nm (SCF-49.5C-42L, producer: SIGMA KOKI CO LTD., Tokyo, Japan) or 800 nm (ITF-50C-85IR, producer: SIGMA KOKI CO. LTD., Tokyo, Japan), a 150 W Xe lamp (L2175, producer: Hamamatsu Photonics K. K.), mass flow controller and CO_2 gas cylinder (purity: 99.995 vol%) in case of CO_2 reduction experiment with H_2O.[29] The reactor size for charging CO_2 is 1.25×10^{-4} m^3. The light of Xe lamp located on the stainless tube is illuminated toward TiO_2 film or P_4O_{10}/TiO_2 film passing the sharp cut filter and the quartz glass disc positioned on the top of stainless tube. The wavelength of light illuminated from Xe lamp is distributed from 185 nm to 2000 nm. The sharp cut filter can remove the UV from the Xe lamp, providing the wavelength of light illuminating TiO_2 film or P_4O_{10}/TiO_2 film ranged from 401 nm to 2000 nm or 801 nm to 2000 nm.[34] Figure 3 shows the light transmittance data of sharp cut filter cutting the wavelength below 400 nm to clarify the light illumination conditions as an example. The mean light intensity of light illuminated from Xe lamp from 185 nm to 2000 nm is 72.0 mW/cm^2, that from 401 nm to 2000 nm is 60.0 mW/cm^2, and that from 801 nm to 2000 nm is 51.0 mW/cm^2. After filling CO_2 gas with the purity of 99.995 vol% in the reactor pre-vacuumed by means of a vacuum pump for 15 min, we closed the valves which were installed at the inlet and the outlet of reactor during CO_2 reduction experiment with H_2O. We confirmed the pressure and gas temperature at 0.1 MPa and 298 K, respectively in the reactor. After that, the distilled H_2O was injected into the reactor via the gas sampling tap, resulting that the Xe lamp was turned on the same time. We changed the amount of injected H_2O according to the considering molar ratio. The injected H_2O solution was vaporized by the heat of IR light components illuminated by the Xe lamp. We confirmed that the temperature in the reactor attained at 343 K within an hour, and we kept at approximately 343 K during the CO_2 reduction experiment. We changed the molar ratio of CO_2/H_2O by 1:0.5, 1:1, 1:2 and 1:4. We extracted the reacted gas filled in the reactor by means of gas syringe via gas sampling tap and we analyzed using an FID gas chromatograph (GC353G, producer: GL Science) and a methanizer (MT221, producer: GL Science). The minimum resolution of FID gas chromatograph and methanizer is 1 ppmV. The CO_2 reduction experiment was conducted up to 8 hours. Gas sampling was carried out from the start of experiment till 8 hours by 2 hours.

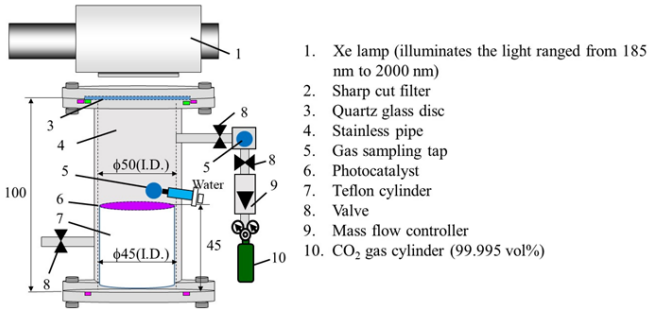

Figure 2 Schematic diagram of experimental apparatus of CO_2 reduction with H_2O. The reactor consists of stainless pipe, TiO_2 film or P_4O_{10}/TiO_2 film photocatalyst located on Teflon cylinder, a quartz glass disc, sharp cut filter, a 150 W Xe lamp, mass flow controller, CO_2 gas cylinder.

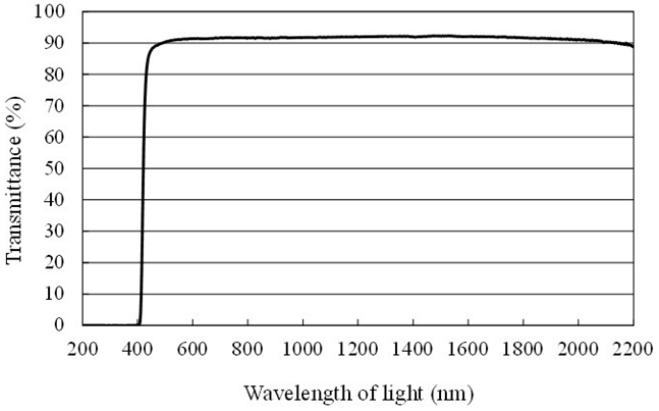

Figure 3 Light transmittance data of sharp cut filter cutting the wavelength below 400 nm.

CO_2 reduction with NH_3

Figure 4 exhibits the experimental apparatus. The reactor consists of a stainless tube with a scale of 100 mm (*H.*)×50 mm (*I.D.*), TiO_2 film or P_4O_{10}/TiO_2 film coated on netlike glass disc with a scale of 50 mm (*D.*)×1 mm (*t.*) positioned on the Teflon cylinder with a scale of 50 mm (*H.*)×50 mm (*D.*), a quartz glass disc with a scale of 84 mm (*D.*)×10 mm (*t.*), a sharp cut filter removing the wavelength of light which is below 400 nm (SCF-49.5C-42L, producer: SIGMA KOKI CO.LTD., Tokyo, Japan) or 800 nm (ITF-50C-85IR, producer: SIGMA KOKI CO. LTD., Tokyo, Japan), a 150 W Xe lamp (L2175, producer: Hamamatsu Photonics K. K.), mass flow controller, CO_2 gas cylinder (purity: 99.995 vol%) and NH_3 gas cylinder (purity: 99.99 vol%). The reactor size to charge CO_2 is 1.25×10^{-4} m^3. We illuminate the light of Xe lamp located on the stainless tube toward TiO_2 film or P_4O_{10}/TiO_2 film passing the sharp cut filter and the quartz glass disc positioned on the top of the stainless tube. The wave length of light illuminated from Xe lamp is distributed from 185 nm to 2000 nm. We can eliminate the UV from the Xe lamp by the sharp cut filter,

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resulting that the wavelength of light illuminating TiO_2 film or P_4O_{10}/TiO_2 film is distributed from 401 nm to 2000 nm or 801 nm to 2000 nm. The mean light intensity of light illuminated from Xe lamp from 185 nm to 2000 nm is 73.0 mW/cm^2, that from 401 nm to 2000 nm is 52.8 mW/cm^2, and that from 801 nm to 2000 nm is 44.0 mW/cm^2. After filling CO_2 gas with the purity of 99.995 vol%, the reactor was pre-vacuumed by means of a vacuum pump for 15 min, we closed the valves installed at the inlet and the outlet of reactor during CO_2 reduction with NH_3. We confirmed the pressure and temperature at 0.1 MPa and 298 K in the reactor. The temperature of gas in reactor rose due to the heat of IR light components illuminated by the Xe lamp. The temperature of experimental room was controlled and set at 293 K by air conditioner. This study changed the molar ratio of CO_2/NH_3 by 1:0.5, 1:1, 1:2, 1:4, 3:2 and 3:8. We extracted the reacted gas filled in the reactor by means of gas syringe via gas sampling tap and analyzed by means of a FID gas chromatograph (GC353B, producer: GL Science) and a methanizer (MT221, producer: GL Science). The minimum resolution of FID gas chromatograph and methanizer is 1 ppmV. The CO_2 reduction experiment was conducted up to 8 hours. Gas sampling was carried out from the start of experiment till 8 hours by 2 hours.

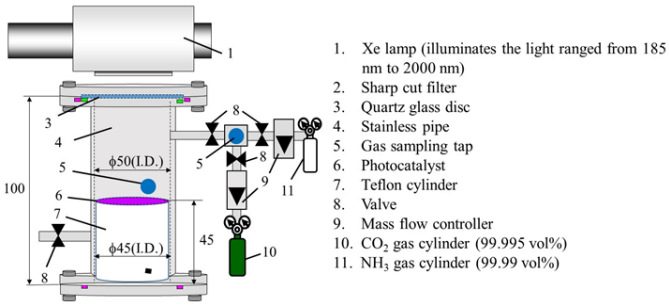

Figure 4 Schematic diagram of experimental apparatus of CO_2 reduction with NH_3. The reactor consists of stainless pipe, TiO_2 film or P_4O_{10}/TiO_2 film photocatalyst located on Teflon cylinder, a quartz glass disc, sharp cut filter, a 150 W Xe lamp, mass flow controller, CO_2 and NH_3 gas cylinder.

Results and discussion

The analysis of characterization of TiO_2 film

Figure 5 shows XPS (X-ray Photoelectron Spectroscopy) data of P in prepared P/TiO_2 film coated on netlike glass disc. In this study, Ar ion laser sputtering was conducted to analyze the characterization toward the thickness direction. Ar sputtering was controlled by the function of XPS and its etching rate of 1.5 nm/min can be converted into the etching rate in case of SiO_2. In this figure, the etching number is also shown. When the etching number increases, we can know the characteristics at more inside position of P/TiO_2 film. It is seen from Figure 5 that the $2P_{p3/2}$ spectrum shows the peaks with binding energies (BE) of 134 eV which indicates P_4O_{10}.[35] Therefore, it is confirmed that the P in the film exists in the form of P_4O_{10}.

Figure 6 shows SEM (Scanning Electron Microscope) and EPMA (Electron Probe Microanalyzer) images of TiO_2 film coated on netlike glass disc. We obtained the black and white SEM image whose magnification was 1500 times. It was also used for EPMA analysis. Regarding the EPMA images, we show the concentration distribution of each chemical element in observation area exhibited by the diverse colors. If the amount of chemical element is small, dark colors such as black and blue are adopted.

It is seen from Figure 6 that it can be seen TiO_2 film with a teeth-like shape is coated on the netlike glass fiber. We can think that the temperature distribution of TiO_2 solution which was adhered on the netlike glass disc was not even during firing process, resulting from that the thermal conductivity of Ti and SiO_2 at 600 K are 19.4 W/(m□K) and 1.82 W/(m□K), respectively.[36] Since the thermal expansion and shrinkage around the net like glass fiber might be occurred, it is thought a thermal crack formed within TiO_2 film.[30] Consequently, we can obtain TiO_2 film on the netlike glass fiber with teeth-like.

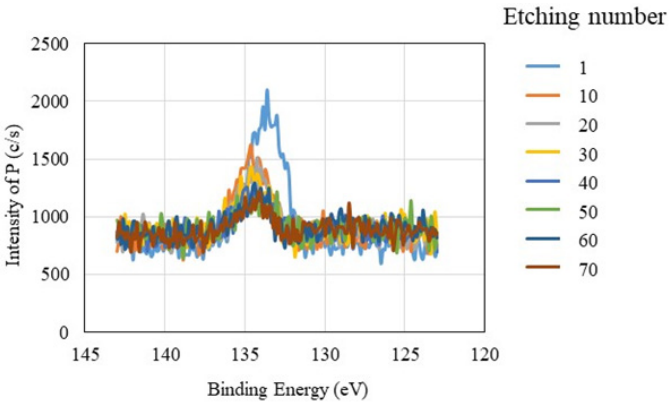

Figure 5 XPS analysis result on P in prepared P/TiO_2 film which is coated on netlike glass disc.

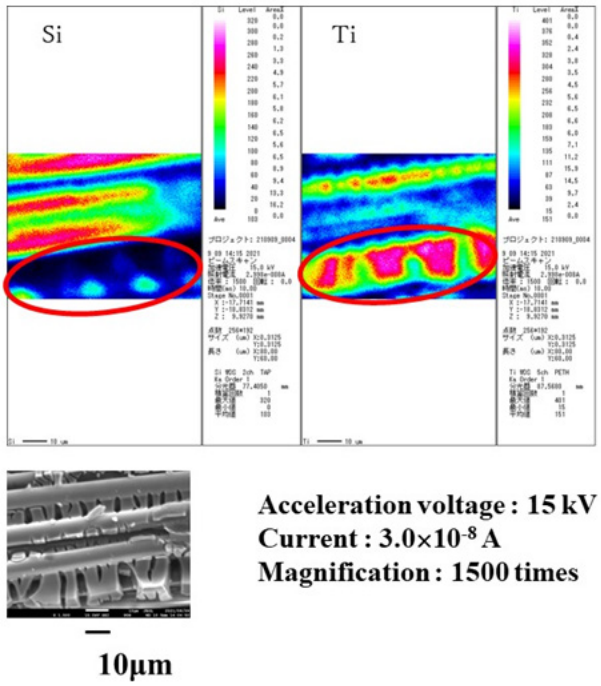

Figure 6 SEM and EPMA images of TiO_2 film coated on netlike glass disc.

Figure 7 shows SEM and EPMA images of P_4O_{10}/TiO_2 coated on netlike glass disc. It is seen from Figure 7 that the black and white SEM image whose magnification is 1500 times is applied for EPMA analysis. From Figure 7, it is found that TiO_2 film with a teeth-like shape coated on the netlike glass fiber, indicating the same tendency as Figure 6. In addition, P_4O_{10} is not detected in the area where many Ti are detected according to EPMA images. According to the etching number as shown in Figure 5, P_4O_{10} is loaded in the deep layer in TiO_2 film. In addition, it is thought that the concentrated TiO_2 sol solution which is adhered on net like glass fiber occurs the thermal expansion and shrinkage around the net like glass fiber due to large temperature difference between TiO_2 and SiO_2 composing of net like glass disc, resulting that a thermal crack formed within TiO_2 film as discussed

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above. Therefore, it is observed that P_4O_{10} is not detected in the area where many Ti are detected.

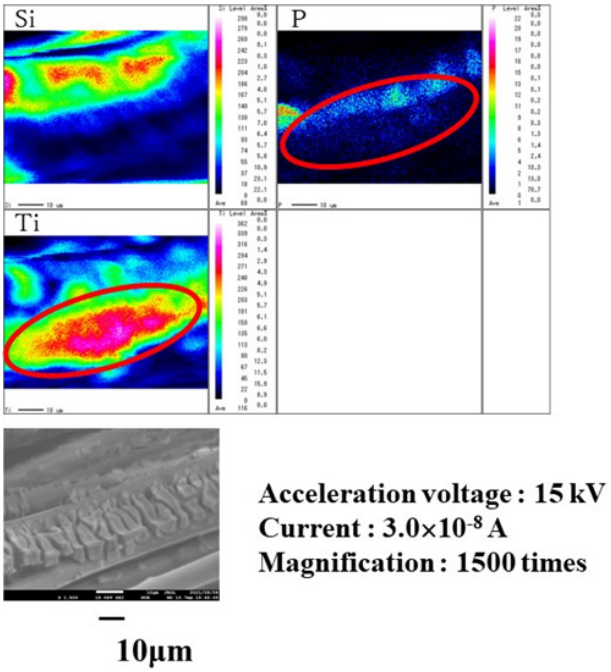

Figure 7 SEM and EPMA images of P_4O_{10}/TiO_2 film coated on netlike glass disc.

In addition, we analyze the center part of netlike glass disc with a diameter of 300 μm, which is the observation area, by EPMA to count the amount of loaded P_4O_{10} within the TiO_2 film. We estimate the ratio of P_4O_{10} to Ti by averaging the data detected in the observation area. The ratio of amount of P_4O_{10} to the total amount of P_4O_{10}/TiO_2 film counted is 13.45 wt%, which is approximately same as the preparation condition as described later. Therefore, the sol-gel and dip-coating process proposed by this study is effective to prepare P/TiO_2 film. On the other hand, we have measured the total weight of TiO_2 film and P_4O_{10}/TiO_2 film by an electron balance, which is 0.014 g and 0.018 g, respectively.

The CO_2 reduction characteristics of TiO_2 film with H_2O and NH_3 under the illumination condition with UV + VIS + IR

Figures 8 and 9 exhibit the concentration change of CO formed with time for TiO_2 in case of CO_2/H_2O or CO_2/NH_3 under the illumination condition with UV + VIS + IR. In Figures 8 and 9, this study evaluates the produced CO by the molar quantity of CO per unit weight of photocatalyst (μmol/g) quantitatively. The other fuels were not detected. Regarding a blank test, we carried out the same experiment under no Xe lamp illumination condition as a reference test before the experiment. As a result, no fuel was detected during the blank test as we expected. In addition, this study conducted that the CO_2 reduction experiment with H_2O or NH_3 without photocatalyst under the illumination condition with UV + VIS + IR. As a result, no fuel has been detected. Regarding the reproducibility of experiments, we show the average data of three experiments. After three time experiments, the change of surface structure can not be confirmed by the naked eye. Moreover, we have tried to touch the surface of photocatalyst, resulting that the degradation of surface has not been observed.

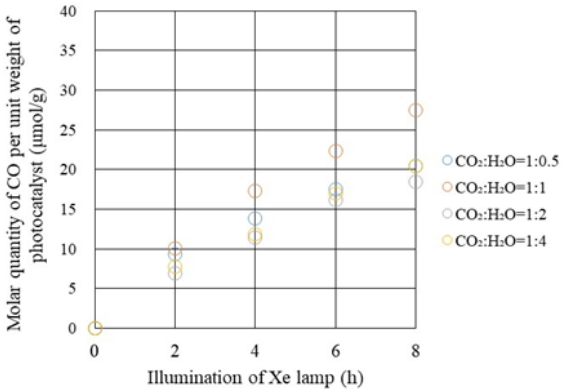

Figure 8 Comparison of molar quantity of CO per unit weight photocatalyst of TiO_2 film among different molar ratios in case of CO_2/H_2O under the illumination condition with UV + VIS + IR.

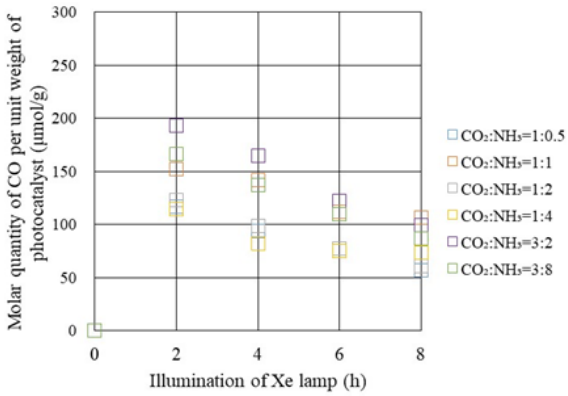

Figure 9 Comparison of molar quantity of CO per unit weight photocatalyst of TiO_2 film among different molar ratios in case of CO_2/NH_3 under the illumination condition with UV + VIS + IR.

Figure 8 also displays the molar quantity of CO per unit weight of photocatalyst increases with time. The formation rate of CO (μmol/g) is calculated by every 2 hours during the experiment time of 8 hours, resulting that it decreases after the illumination time of 2 hours irrespective of molar ratio of CO_2/H_2O. For example, in case of CO_2: H_2O = 1: 1, the 2 hours formation rate of CO is 0.09, 0.07, 0.05 and 0.02 μmol/h from the start to the end of CO_2 reduction experiment. Therefore, it can be expected the molar quantity of CO per unit weight of photocatalyst would be saturated if the illumination time extends over 8 hours. On the other hand, it is seen from Figure 9 that the molar quantity of CO per unit weight of photocatalyst shows the peak at the illumination time of 2 hours and decreases with time gradually. According to the reaction scheme of CO_2/NH_3 as shown by Eqs. (12) – (19), compared to CO_2/H_2O, the reaction process is complex and more electron are needed for the reaction with H^+ since NH_3 has $3H^+$. Since the CO_2 reduction performance of TiO_2 is low, it is thought that CO production would stop after the reaction surface covered by products.[37] If the reaction surface is covered by products, the reductant, i.e. CO_2 and NH_3 can not reach the reaction surface, resulting that CO production would stop.

It can be seen from Figure 8 that the molar quantity of CO per unit weight of photocatalyst is the largest in case of CO_2: H_2O = 1:1, providing the largest molar quantity of CO per unit weight of photocatalyst is 27.5 μmol/g. Additionally, it is found from Figure 9 that the molar quantity of CO per unit weight of photocatalyst is

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the largest in case of CO_2: NH_3 = 3:2, providing the largest molar quantity of CO per unit weight of photocatalyst is 193.0 μmol/g. The theoretical molar ratio to produce CO in case of CO_2/H_2O and CO_2/NH_3 is CO_2: H_2O = 1:1 and CO_2: NH_3=3:2, respectively, according to the reaction scheme of CO_2/H_2O and CO_2/NH_3 shown by Eqs. (1) – (19).

The CO_2 reduction characteristics of P_4O_{10}/TiO_2 film with H_2O and NH_3 under the illumination condition with UV + VIS + IR

Figures 10 and 11 present the concentration change of formed CO with time in case of CO_2/H_2O or CO_2/NH_3 under the illumination condition with UV + VIS + IR. The other fuels were not detected. Regarding the blank test, we carried out the same experiment under no Xe lamp illumination condition as a reference test before the experiment. As a result, no fuel was detected during the blank test as we expected. In addition, this study conducted that the CO_2 reduction experiment with H_2O or NH_3 without photocatalyst under the illumination condition with UV + VIS + IR. As a result, no fuel has been detected. As to the reproducibility of experiments, Figures 10 and 11 show the average data of three experiments. After three time experiments, the change of surface structure can not be confirmed by the naked eye. Moreover, we have tried to touch the surface of photocatalyst, resulting that the degradation of surface has not been observed.

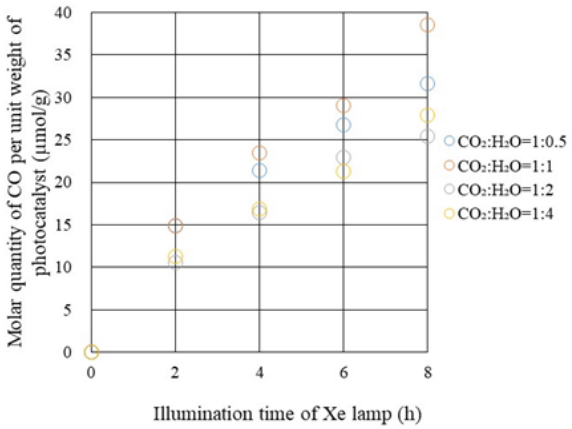

Figure 10 Comparison of molar quantity of CO per unit weight photocatalyst of P_4O_{10}/TiO_2 film among different molar ratios in case of CO_2/H_2O under the illumination condition with UV + VIS + IR.

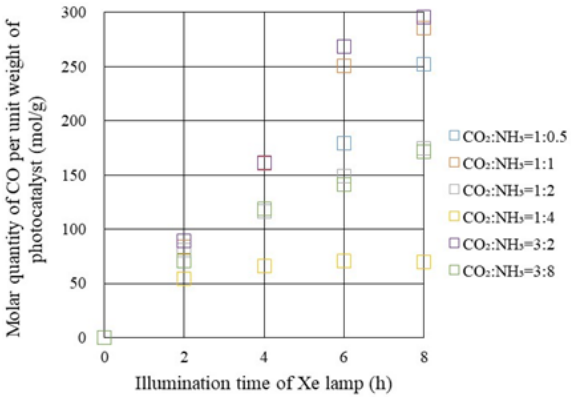

Figure 11 Comparison of molar quantity of CO per unit weight photocatalyst of P_4O_{10}/TiO_2 film among different molar ratios in case of CO_2/NH_3 under the illumination condition with UV + VIS + IR.

According to Figure 10, the molar quantity of CO per unit weight of photocatalyst increases with time. The formation rate of CO (μmol/g) is calculated by every 2 hours during the experiment time of 8 hours, which was found starting to decrease after 2 hours irrespective of molar ratio of CO_2/H_2O. For example, in case of CO_2: H_2O = 1:1, the 2 hours formation rate of CO is 0.1, 0.06, 0.04, 0.06 μmol/h from the start to the end of CO_2 reduction experiment. Therefore, it was thought that the molar quantity of CO per unit weight of photocatalyst would be saturated if the illumination time extends over 8 hours. On the other hand, according to Figure 11, the molar quantity of CO per unit weight of photocatalyst increases with time. However, the formation rate of CO (μmol/h) is calculated by every 2 hours during the experiment time of 8 hours, resulting that it indicates the saturation of formation rate of CO with time irrespective of molar ratio of CO_2/NH_3. For example, in case of CO_2: NH_3 = 3:2, the 2 hours formation rate of CO is 0.6, 0.5, 0.7, 0.2 μmol/h from the start to the end of CO_2 reduction experiment. Therefore, it was thought that the molar quantity of CO per unit weight of photocatalyst would be saturated if the illumination time extends over 8 hours. The reason why the difference of CO production characteristics between TiO_2 film and P_4O_{10}/TiO_2 film in case of CO_2/NH_3 occurred is due to the promotion of CO_2 reduction performance of TiO_2 by loading P_4O_{10}. As discussed later, the light absorption performance is improved, resulting that CO_2 reduction performance of P_4O_{10}/TiO_2 film is promoted. Therefore, the CO production keeps up to 8 hours as shown in Figure 11. Comparing the CO_2 reduction performance shown in Figures 10 and 11 with that in Figures 8 and 9, it is revealed that the CO_2 reduction performance of P_4O_{10}/TiO_2 film is superior to that of TiO_2 film, resulting that the light absorption range might be up to IR.

According to Figure 10, the molar quantity of CO per unit weight of photocatalyst is the largest in case of CO_2: H_2O = 1:1, providing the largest molar quantity of CO per unit weight of photocatalyst is 38.6 μmol/g. In addition, according to Figure 11, the molar quantity of CO per unit weight of photocatalyst is the largest in case of CO_2: NH_3 = 3:2, providing the largest molar quantity of CO per unit weight of photocatalyst is 295.4 μmol/g. The theoretical molar ratio to produce CO in case of CO_2/H_2O and CO_2/NH_3 is CO_2: H_2O = 1:1 and CO_2: NH_3 = 3:2, respectively, according to the reaction scheme of CO_2/H_2O and CO_2/NH_3 shown by Eqs. (1) – (19). Therefore, it can be said that the theoretical result is obtained for P_4O_{10}/TiO_2 film in this study. Additionally, compared the molar quantity of CO per unit weight of photocatalyst for P_4O_{10}/TiO_2 film to that for TiO_2 film, the molar quantity of CO per unit weight of photocatalyst for P_4O_{10}/TiO_2 film is larger than that for TiO_2 film. As to the case of CO_2: H_2O = 1:1, the molar quantity of CO per unit weight of photocatalyst for TiO_2 film increases by 11.1 ppmV by loading P_4O_{10}. As to the case of CO_2: NH_3 = 3:2, the molar quantity of CO per unit weight of photocatalyst for TiO_2 film increases by 102.4 ppmV by loading P_4O_{10}. Consequently, the promotion of CO_2 reduction performance of TiO_2 film is obtained by loading P_4O_{10}.

The CO_2 reduction characteristics of P_4O_{10}/TiO_2 film with H_2O and NH_3 under the illumination condition with VIS + IR

Figures 12 and 13 present the concentration change of formed CO with time for P_4O_{10}/TiO_2 film in case of CO_2/H_2O and CO_2/NH_3 under the illumination condition with VIS + IR. In Figures 12 and 13, we evaluate the produced CO by the molar quantity of CO per unit weight of photocatalyst with the unit of μmol/g quantitatively. We have not detected the other fuels. Regarding a blank test, we carried out the same experiment under no Xe lamp illumination condition as a reference test before the experiment. As a result, no fuel was

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detected during the blank test as we expected. In addition, this study conducted that the CO_2 reduction experiment with H_2O or NH_3 without photocatalyst under the illumination condition with VIS + IR. As a result, no fuel has been detected. Regarding the reproducibility of experiments, we show the average data of three experiments. After three time experiments, the change of surface structure can not be confirmed by the naked eye. Moreover, we have tried to touch the surface of photocatalsyt, resulting that the degradation of surface has not been observed. In addition, no fuel was detected from the CO_2 reduction experiment using TiO_2 film in case of CO_2/H_2O and CO_2/NH_3 under the illumination condition with VIS + IR. Therefore, it is confirmed from Figures 12 and 13 that the CO_2 reduction performance of P_4O_{10}/TiO_2 film is superior to that of TiO_2 film.

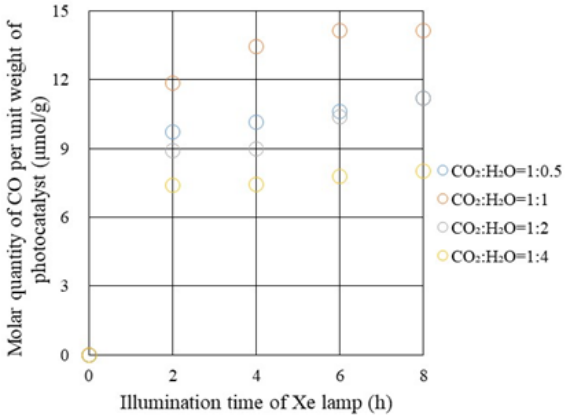

Figure 12 Comparison of molar quantity of CO per unit weight photocatalyst of P_4O_{10}/TiO_2 film among different molar ratios in case of CO_2/H_2O under the illumination condition with VIS + IR.

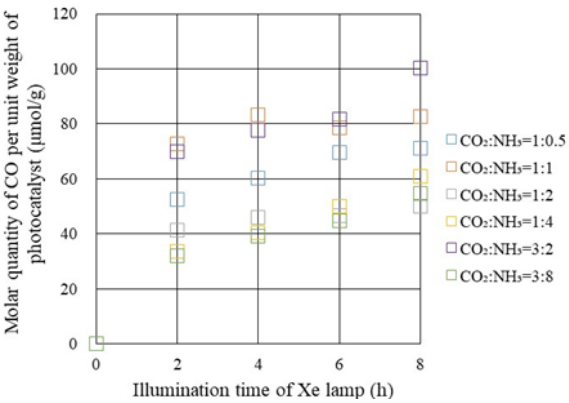

Figure 13 Comparison of molar quantity of CO per unit weight photocatalyst of P_4O_{10}/TiO_2 film among different molar ratios in case of CO_2/NH_3 under the illumination condition with VIS + IR.

According to Figure 12, the molar quantity of CO per unit weight of photocatalyst increases with time gradually. The formation rate of CO (μmol/h) is calculated by every 2 hours during the experiment time of 8 hours, indicating that the rate would be stable at 8 hours irrespective of molar ratio of CO_2/H_2O. For example, in case of CO_2: H_2O = 1:1, the 2 hours formation rate of CO is 0.06, 0.0003, 0.009, 0.006 μmol/h from the start to the end of the experiment. It can be expected that the molar quantity of CO per unit weight of photocatalyst would be saturated if the illumination time extends over 8 hours. On the other hand, according to Figure 13, the molar quantity of CO per unit weight of photocatalyst increases with time gradually. The formation rate of CO (□mol/h) is calculated by every 2 hours during the experiment time of 8 hours, resulting that it indicates the saturation of formation rate of CO with time irrespective of molar ratio of CO_2/NH_3. For example, in case of CO_2: NH_3 = 3:2, the 2 hours formation rate of CO is 0.5, 0.05, 0.03, 0.1 μmol/h from the start to the end of CO_2 reduction experiment. It can be expected that the molar quantity of CO per unit weight of photocatalyst would be saturated if the illumination time extends over 8 hours. Compared the molar quantity of CO per unit weight of photocatalyst for P_4O_{10}/TiO_2 film under the illumination condition with VIS + IR to that under the illumination condition with UV + VIS + IR, the molar quantity of CO per unit weight of photocatalyst for P_4O_{10}/TiO_2 film under the illumination condition with VIS + IR is smaller than that under the condition with UV + VIS + IR. The total amount of light absorption under the illumination condition with VIS + IR is smaller than that under the condition with UV + VIS + IR, resulting that the molar quantity of CO per unit weight of photocatalyst for P_4O_{10}/TiO_2 film under the illumination condition with VIS + IR is smaller than that under the condition with UV + VIS + IR. However, we can confirm that the light absorption performance of TiO_2 film extends to VIS by loading P_4O_{10}. It is also observed from Figures 12 and 13 that the molar quantity of CO per unit weight of photocatalyst is saturated up to the illumination time of 8 hours. It can be claimed that this tendency is obtained due to the lower CO_2 reduction performance under the illumination condition with VIS + IR compared to that under the illumination condition with UV + VIS + IR.

According to Figure 12, the molar quantity of CO per unit weight of photocatalyst is the largest in case of CO_2: H_2O = 1:1, providing the largest molar quantity of CO per unit weight of photocatalyst is 14.2 μmol/g. In addition, according to Figure 13, the molar quantity of CO per unit weight of photocatalyst is the largest in case of CO_2: NH_3 = 3:2, providing the largest molar quantity of CO per unit weight of photocatalyst is 100.4 μmol/g. The theoretical molar ratio to produce CO in case of CO_2/H_2O and CO_2/NH_3 is CO_2: H_2O = 1:1 and CO_2: NH_3 = 3:2, respectively, according to the reaction scheme of CO_2/H_2O and CO_2/NH_3 shown by Eqs. (1) – (19). Therefore, it can be said that the theoretical result is obtained for P_4O_{10}/TiO_2 film under the illumination condition with VIS + IR, which is same as that under the condition with UV + VIS + IR.

The CO_2 reduction characteristics of P_4O_{10}/TiO_2 film with H_2O and NH_3 under the illumination condition with IR

Figures 14 and 15 present the concentration change of formed CO with time for P_4O_{10}/TiO_2 film in case of CO_2/H_2O or CO_2/NH_3 under the illumination condition with IR. The other fuels were not detected. Regarding a blank test, we carried out the same experiment under no Xe lamp illumination condition as a reference test before the experiment. As a result, no fuel was detected during the blank test as we expected. In addition, this study conducted that the CO_2 reduction experiment with H_2O or NH_3 without photocatalyst under the illumination condition with IR. As a result, no fuel has been detected. Regarding the reproducibility of experiments, we show the average data of three experiments. After three time experiments, the change of surface structure can not be confirmed by the naked eye. Moreover, we have tried to touch the surface of photocatalyst, resulting that the degradation of surface has not been observed. In addition, no fuel was detected from the CO_2 reduction experiment using TiO_2 film in case of CO_2/H_2O and CO_2/NH_3 under the illumination condition with IR. Therefore, it is confirmed from Figures 14 and 15 that the CO_2 reduction performance of P_4O_{10}/TiO_2 film is superior to that of TiO_2 film.

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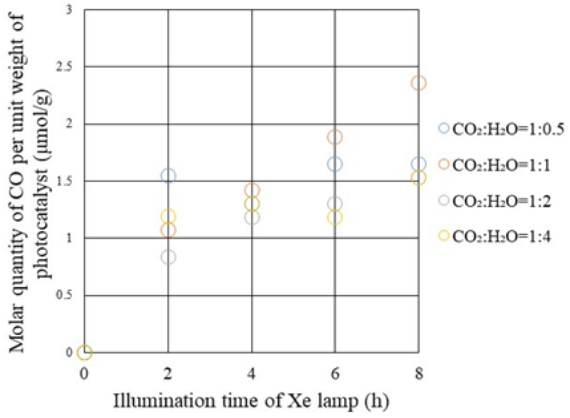

Figure 14 Comparison of molar quantity of CO per unit weight photocatalyst of P_4O_{10}/TiO_2 film among different molar ratios in case of CO_2/H_2O under the illumination condition with IR.

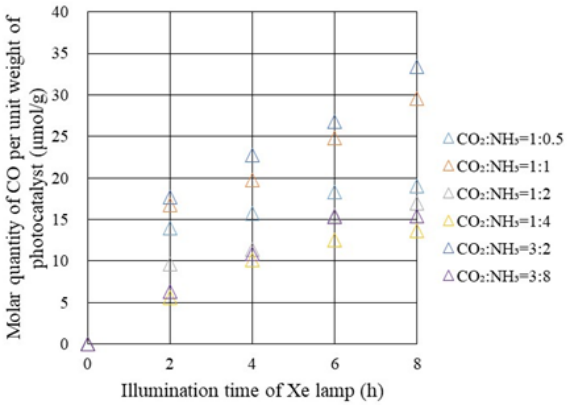

Figure 15 Comparison of molar quantity of CO per unit weight photocatalyst of P_4O_{10}/TiO_2 film among different molar ratios in case of CO_2/NH_3 under the illumination condition with IR.

According to Figure 14, the molar quantity of CO per unit weight of photocatalyst increases with time gradually. The formation rate of CO (μmol/h) is calculated by every 2 hours during the experiment time of 8 hours, resulting that it indicates the saturation of formation rate of CO with time irrespective of molar ratio of CO_2/H_2O. For example, in case of CO_2: H_2O = 1:1, the 2 hours formation rate of CO is 0.006, 0.002, 0.0008, 0.002 μmol/h from the start to the end of CO_2 reduction experiment. It can be expected that the molar quantity of CO per unit weight of photocatalyst would be saturated if the illumination time extends over 8 hours. On the other hand, according to Figure 15, the molar quantity of CO per unit weight of photocatalyst increases with time gradually. The formation rate of CO (μmol/h) is calculated by every 2 hours during the experiment time of 8 hours, resulting that it indicates the saturation of formation rate of CO with time irrespective of molar ratio of CO_2/NH_3. For example, in case of CO_2:NH_3 = 3:2, the 2 hours formation rate of CO is 0.1, 0.03, 0.03, 0.05 μmol/h from the start to the end of CO_2 reduction experiment. It can be expected that the molar quantity of CO per unit weight of photocatalyst would be saturated if the illumination time extends. Consequently, the same tendency is obtained for P_4O_{10}/TiO_2 film in case of CO_2/H_2O and CO_2/NH_3 under the illumination condition with IR. Compared the molar quantity of CO per unit weight of photocatalyst for P_4O_{10}/TiO_2 film under the illumination condition with IR to that under the illumination condition with UV + VIS + IR as well as that under the illumination condition with VIS + IR, the molar quantity of CO per unit weight of photocatalyst for P_4O_{10}/TiO_2 film under the illumination condition with IR is smaller compared to that under the illumination condition with UV + VIS + IR as well as that under the illumination condition with VIS + IR. Since the total amount of light absorption under the illumination condition with IR is smaller compared to that under the illumination condition with UV + VIS + IR as well as that under the illumination condition with VIS + IR, it is thought that the molar quantity of CO per unit weight of photocatalyst for P_4O_{10}/TiO_2 film under the illumination condition with IR is smaller compared to that under the illumination condition with UV + VIS + IR as well as that under the illumination condition with VIS + IR. However, it is revealed that the light absorption performance of TiO_2 film extends to IR by loading P_4O_{10}.

It is found from Figure 14 that the molar quantity of CO per unit weight of photocatalyst is the largest in case of CO_2: H_2O = 1:1, providing the largest molar quantity of CO per unit weight of photocatalyst is 2.36 μmol/g. Additionally, it is found from Figure 15 that the molar quantity of CO per unit weight of photocatalyst is the largest in case of CO_2: NH_3 = 3:2, providing the largest molar quantity of CO per unit weight of photocatalyst is 33.4 μmol/g. The theoretical molar ratio to produce CO in case of CO_2/H_2O and CO_2/NH_3 is CO_2: H_2O = 1:1 and CO_2 : NH_3 = 3:2, respectively, according to the reaction scheme of CO_2/H_2O and CO_2/NH_3 shown by Eqs. (1) – (19). Therefore, it can be said that the theoretical result is obtained for P_4O_{10}/TiO_2 film under the illumination condition with IR, which is same as that under the illumination condition with UV + VIS + IR and VIS + IR.

From the investigation by this study, it is revealed that P_4O_{10}/TiO_2 film can reduce CO_2 into CO with H_2O as well as NH_3 under the illumination condition with IR. This is a new finding on the photocatalytic CO_2 reduction of TiO_2. However, the CO_2 reduction performance with P_4O_{10}/TiO_2 film is still low. Therefore, it is necessary to improve the CO_2 reduction performance more. For example, it is thought that optimization of the amount of loaded P_4O_{10} is one approach. In addition, the preparation procedure of P for loading TiO_2 should be examined. The other type of P might have a potential to absorb IR light more. They are the next works.

Conclusion

This study has investigated the CO_2 reduction performance with P_4O_{10}/TiO_2 film in various wavelength range of illuminating light, i.e. in UV + VIS + IR or VIS + IR or IR ranges. In addition, this study also clarifies the optimum molar ratio of CO_2/H_2O and CO_2/NH_3 for the CO_2 reduction performance with P_4O_{10}/TiO_2 film in the wavelength ranges studied. The following conclusions are drawn from the study:

(1) In the light range of UV + VIS + IR, the molar quantity of CO per unit weight of photocatalyst of TiO_2 film is promoted by loading P_4O_{10} in case of CO_2/H_2O as well as CO_2/NH_3. As to the case of CO_2: H_2O = 1:1, the molar quantity of CO per unit weight of photocatalyst for TiO_2 film increases by 11.1 ppmV by loading P_4O_{10}. As to the case of CO_2: NH_3 = 3:2, the molar quantity of CO per unit weight of photocatalyst for TiO_2 film increases by 102.4 ppmV by loading P_4O_{10}.

(2) It has been revealed that the light absorption performance of TiO_2 film extends to VIS and IR ranges by loading P_4O_{10}.

(3) In case of CO_2/H_2O, the molar quantity of CO per unit weight of photocatalyst for TiO_2 film and P_4O_{10}/TiO_2 film is the largest in case of CO_2: H_2O = 1:1 under the condition with UV + VIS + IR, VIS + IR, and IR, which is the same as the theoretical molar ratio to produce CO according to the reaction scheme of CO_2/H_2O.

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(4) In case of CO_2/NH_3, the molar quantity of CO per unit weight of photocatalyst for TiO_2 film and P_4O_{10}/TiO_2 film is the largest in case of CO_2: NH_3 = 3:2 under the condition with UV + VIS + IR, VIS + IR, and IR, which is the same as the theoretical molar ratio to produce CO according to the reaction scheme of CO_2/NH_3.

(5) With IR light only, the largest molar quantity of CO per unit weight of photocatalyst for P_4O_{10}/TiO_2 film in case of CO_2/H_2O is 2.36 μmol/g, while that in case of CO_2/NH_3 is 33.4 μmol/g.

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Conflict of interest

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

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