Article

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Heat Transfer Analysis on Promotion of CO_2 Reduction Performance of P_4O_{10}/TiO_2 Photocatalyst by Black Body Material

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Abstract: Since the photocatalytic reaction is a surface reaction, enhancing the gas movement around photocatalyst would promote photocatalytic CO_2 reduction performance. A new approach to enhance the gas movement around the photocatalyst by the natural thermosiphon movement of gasses around photocatalyst using black body material was proposed and confirmed experimentally, but the heat transfer mechanism on the phenomena was not clarified yet. The purpose of this study is to clarify the heat transfer mechanism of it. This study calculated the temperature of mixed gases of CO_2 and NH_3 around P_4O_{10}/TiO_2 photocatalyst by the heat transfer formula. It is revealed that there was no difference between the increase temperature (T_g) from the temperature at the beginning of the CO_2 reduction experiment (T_{ini}) and the temperature of mixed gases of CO_2 and NH_3 measured by thermocouple in the experiment (T_e) under the illumination condition with a visible light (VIS) + an infrared light (IR) and IR only. The heat transfer model proposed by this study has predicted T_g well under the illumination condition with VIS + IR and IR only well. On the other hand, it is revealed that the difference between T_g and T_e was as large as 10 ℃ under the illumination condition with an ultra violet light (UV) + VIS + IR.

Keywords: heat transfer analysis; P_4O_{10}/TiO_2 photocatalyst; CO_2 reduction with NH_3; black body material; infrared ray; mass transfer promotion

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1. Introduction

Photocatalyst is one of promising technology to utilize the solar light, i.e. renewable energy. The photocatalytic reduction process can convert CO_2 into fuel species such as CO, CH_4, CH_3OH, etc. [1–3]. TiO_2 is one of popular photocatalysts used for the CO_2 reduction. However, TiO_2 works only under UV light illumination, which is accounted for only 4 % in a sunlight [4]. On the other hand, a visible light (VIS) and an infrared light (IR) are accounted for 44 % and 52 % of solar energy reaching the earth, respectively [4]. If the photocatalyst absorbing VIS and IR could be developed, the performance of CO_2 reduction would be improved significantly.

According to the literature review [1,5], many attempts to extend the light absorption of photocatalyst from an ultra violet light (UV) to VIS or near IR were carried out. Metal doping is one of approaches normally used to extend the light absorption performance of photocatalyst from UV to VIS [1]. Cu, Fe, Ag, Au and In, etc. were investigated as a dopant. Ag-nano particles/TiO_2 nanowire exhibited the excellent performance, which has produced 983 mol/g of CO [6,7]. It was 109 times as large as pure TiO_2. As to the photocatalyst study to extend the absorption of light wavelength up to IR, there are some reports [8–11]. Under the illumination condition whose wavelength is ranged from 200 nm to 2400 nm, $W_{18}O_{49}$/g-C_3N_4 composite has exhibited the production of 45 mol/g of CO and 28 mol/g of CH_4 [8]. WS_2/Bi_2S_3 nanotube has exhibited the absorption of VIS and near IR light (wavelength: 420 nm – 1100 nm), producing 28 mol/g of CH_3OH and 25 mol/g of C_2H_5OH [9]. CuInZnS decorated g-C_3N_4 has extended the absorbed wavelength of light from 200 nm to 1000 nm,

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which has produced CO of 38 mol/g [10]. Hierarchical $ZnIn_2S_4$ nanorods prepared by solvothermal method has produced 54 mol/g of CO and 9 mol/g of CH_4 [11].

The authors' previous studies [12,13] have prepared P_4O_{10}/TiO_2 which could extend the absorbed wavelength of light up to IR. Under IR light illumination condition, the largest molar quantity of CO per unit weight of photocatalyst for P_4O_{10}/TiO_2 film in the case of CO_2/H_2O is 2.36 mol/g, while that in the case of CO_2/NH_3 is 33.4 mol/g [12,13].

Another way to promote CO_2 reduction performance was to enhance the gas movement around the photocatalyst, which was proposed by the authors [14,15]. According to the authors' calculation, the mass transfer time of 10^5 s to 10^{-1} s was slower than the photo reaction time of 10^{-9} s to 10^{-15} s [16]. Consequently, the mass transfer was an inhibition factor to promote the CO_2 reduction performance of photocatalyst. Another reason causing the low reforming rate of photocatalytic CO_2 reduction was the re-organization of the products. Since the reaction surface was covered by products, the movement of the reactants to the reaction surface was prevented and the reverse reaction, i.e. re-oxidization, which reproduces CO_2 from products such as CO and CH_4 is occurred. Consequently, it is desirable that CO and CH_4 are removed from the reaction surface as soon as they are produced. On the other hand, a new approach to enhance the gas movement around the photocatalyst was the natural thermosiphon movement of gasses around photocatalyst using black body material, which had been conducted by the authors [14,15]. The CO_2 reduction performance was improved by placing a black body material with the appropriate heat capacity due to the enhancement of the natural thermosiphon movement of gasses around TiO_2 photocatalyst [14]. The maximum concentration of formed CO with using black body materials was 2 to 5 times as large as the case without using black body material [14]. In addition, this effect was also confirmed for the case of P_4O_{10}/TiO_2 photocatalyst absorbing VIS and IR [15]. Under the illumination condition with IR only, the concentration of formed CO has increased by 4 ppmV – 13 ppmV due to black body material compared to no black body material case. The temperature in reactor has risen by 2.0 ℃ – 3.1 ℃ due to black body material compared to no black body material case. It is thought the mass transfer surrounding the photocatalyst is promoted by the natural thermosiphon movement of gases around the photocatalyst created by black body material [14,15]. However, the heat transfer mechanism on the phenomena is not clarified yet. To promote the CO_2 reduction performance of photocatalyst more, the heat transfer mechanism to obtain the temperature rise should be revealed.

Therefore, the purpose of this study is to clarify the heat transfer mechanism to heat up the temperature of gases around the photocatalyst after absorbing the heat by a black body material. This study calculates the temperature of gases around the photocatalyst by the heat transfer formulas and compares with the temperature of gases measured by thermocouple in the CO_2 reduction experiment in the authors' previous study [15].

2. Results and Discussion

2.1. Relationship between Temperature Rise of Mixed Gases of CO_2 and NH_3 in Reactor and the Maximum Concentration of Formed CO

Figures 1–3 show relationships between temperature rise of mixed gases of CO_2 and NH_3 in reactor and the maximum concentration of formed CO with and without black body material among different molar ratios of CO_2/NH_3 under the illumination conditions with UV + VIS + IR, VIS + IR and IR only, respectively [15]. In these figures, the temperature rise from the temperature at the start of CO_2 reduction experiment to the temperature when the concentration of formed CO attains the maximum value [15] is shown.

It can be seen from **Figure 1** that the temperature of mixed gases of CO_2 and NH_3 in reactor under the illumination condition with UV + VIS + IR rises by 3.8 ℃ – 6.2 ℃ due to black body materials, compared to that without black body material. According to this figure, the maximum concentration of formed CO increases by 21 ppmV – 71 ppmV due to black body materials, compared to that without black body material. It is seen from **Figure 2** that the temperature of mixed gases of CO_2 and NH_3 in reactor under the illumination condition with VIS + IR rises by 1.0 ℃ – 2.9 ℃ due to black body materials, compared to that without black body material. According to this figure, the maximum concentration of formed CO increases by 19 ppmV – 40 ppmV due to black body materials, compared to that without black body material. It is seen from **Figure 3** that the temperature of mixed gases of CO_2 and NH_3 in reactor under the illumination condition with IR only rises by 2.0 ℃ – 3.1 ℃ due to black body materials, compared to that without black body material. According to this figure, the maximum concentration of formed CO increases by 4 ppmV – 13 ppmV due to black body materials, compared to that without black body material. It is thought that the mass transfer surrounding the P_4O_{10}/TiO_2 photocatalyst is promoted by the natural thermosiphon movement of gases around the P_4O_{10}/TiO_2 photocatalyst created by black body materials irrespective of the illumination condition. This study would like to discuss and clarify the heat transfer mechanism to heat up the temperature of gases around P_4O_{10}/TiO_2 photocatalyst due to black body material in the following section.

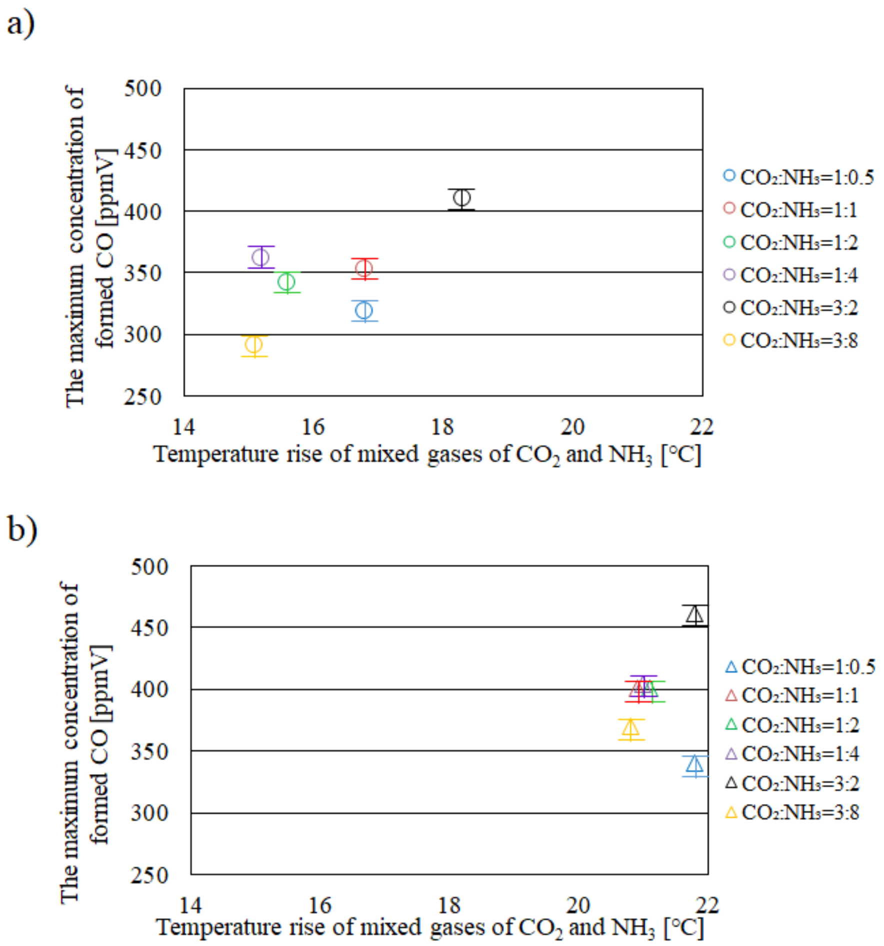

Figure 1. Relationships between temperature rise of mixed gases of CO_2 and NH_3 in reactor and the maximum concentration of formed CO among different molar ratios of CO_2/NH_3 under the illumination condition with UV + VIS + IR (a): without black body material, b): with black body materials) [15].

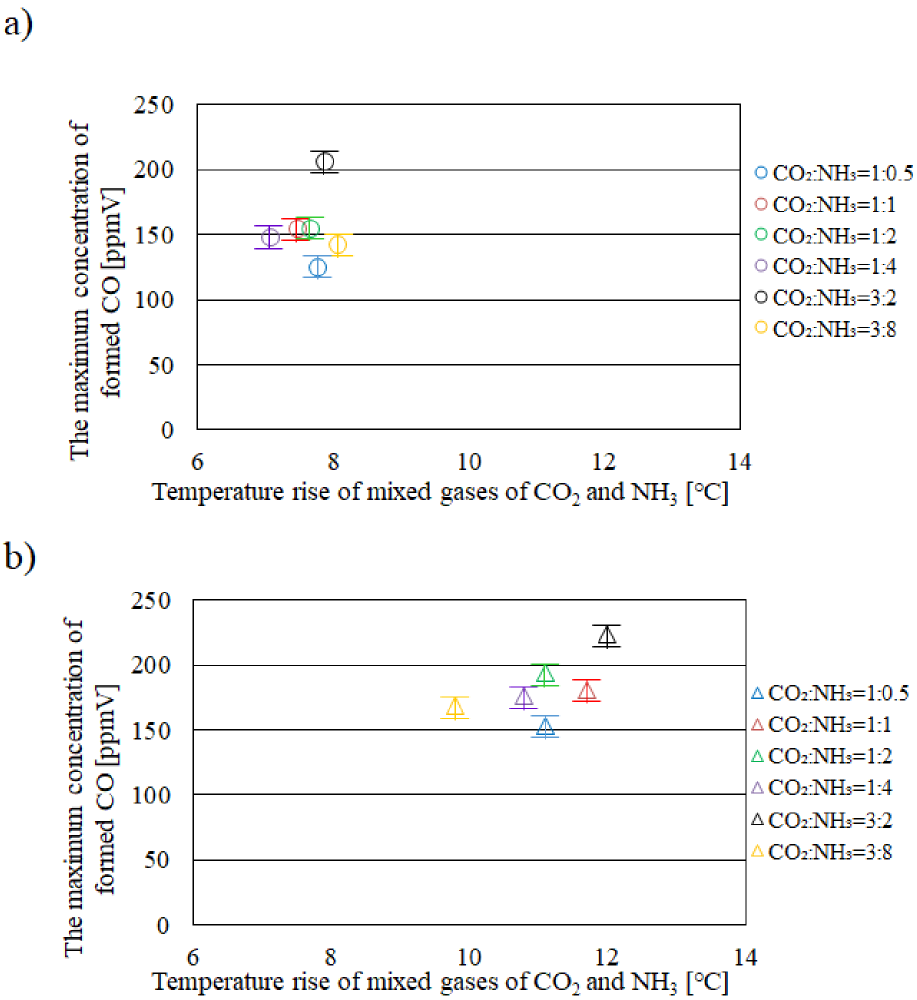

Figure 2. Relationships between temperature rise of mixed gases of CO_2 and NH_3 in reactor and the maximum concentration of formed CO among different molar ratios of CO_2/NH_3 under the illumination condition with VIS + IR (a): without black body material, b): with black body materials) [15].

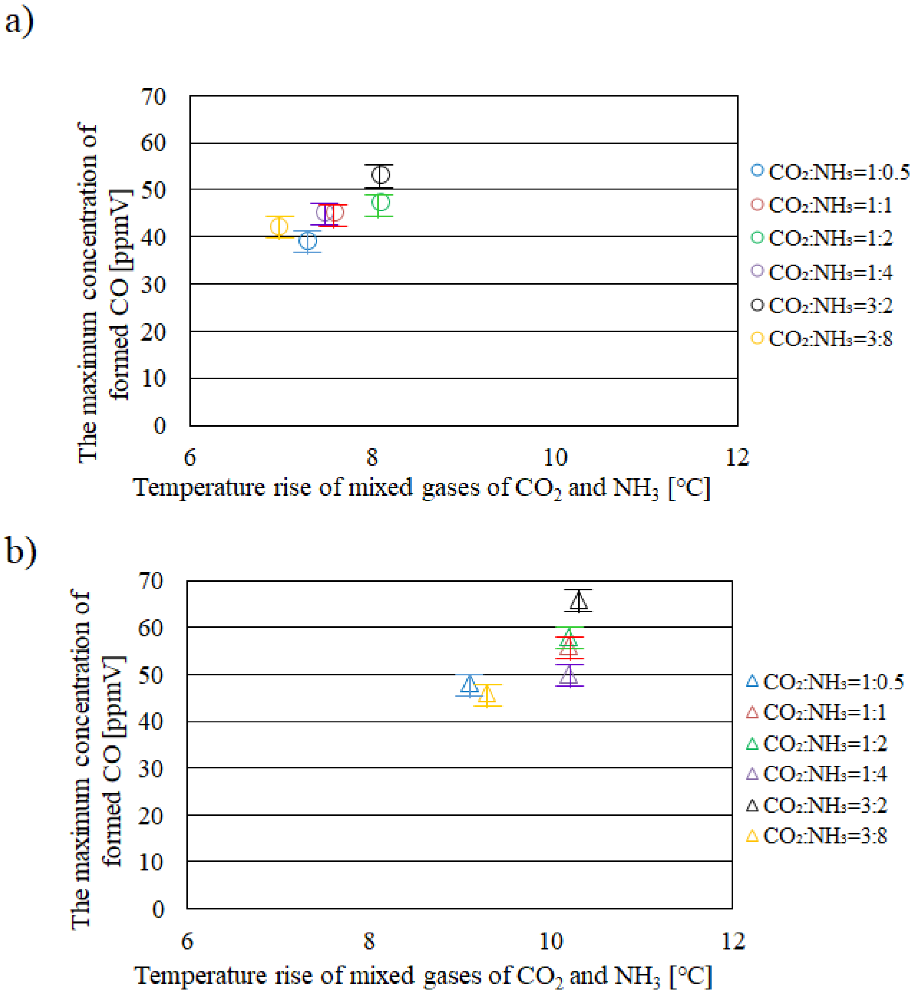

Figure 3. Relationships between temperature rise of mixed gases of CO_2 and NH_3 in reactor and the maximum concentration of formed CO among different molar ratios of CO_2/NH_3 under the illumination condition with IR only (a): without black body material, b): with black body materials) [15].

2.2. *Heat Transfer Mechanism to Heat up Temperature of Mixed Gases of CO_2 and NH_3 around P_4O_{10}/TiO_2 Photocatalyst due to Black Body Material*

This study calculated the increased temperature of mixed gases of CO_2 and NH_3 (T_g) from the initial temperature (T_{ini}) at the beginning of the CO_2 reduction experiment. **Table 1** lists the comparison of T_g with the temperature of mixed gases of CO_2 and NH_3 measured by thermocouple in the experiment (T_e) in the authors' previous study [15]. In this table, T_{in}, T_g, T_e and $T_g - T_e$ among different molar ratios under the illumination conditions with UV + VIS + IR, VIS + IR and IR only are shown. This table indicates the effect of temperature rise due to black body material.

Table 1. Comparison of T_{in} (initial temperature of CO_2 reduction experiment), T_g (increased temperature of mixed gases of CO_2 and NH_3), T_e (temperature of mixed gases of CO_2 and NH_3 measured by thermocouple in the experiment) and $T_g - T_e$ among different molar ratios under the illumination condition with UV + VIS + IR, VIS + IR and IR only.

UV + VIS + IR					
CO_2 [mol]	NH_3 [mol]	T_{in} [℃]	T_g [℃]	T_e [℃]	$T_g - T_e$ [℃]
1	0.5	24.7	36.7	46.5	9.8

1	1	24.0	36.5	44.9	8.4
1	2	24.1	36.8	45.2	8.4
1	4	24.2	36.9	45.2	8.3
3	2	24.1	36.4	45.9	9.5
3	8	24.4	37.1	45.2	8.1
VIS + IR					
CO_2 [mol]	NH_3 [mol]	T_{in} [℃]	T_g [℃]	T_e [℃]	$T_g - T_e$ [℃]
1	0.5	25.4	36.3	36.8	0.5
1	1	25.0	36.3	36.7	0.4
1	2	24.5	36.0	35.6	-0.4
1	4	24.6	36.1	35.4	-0.7
3	2	24.3	35.4	35.5	0.1
3	8	24.4	35.9	34.2	-1.7
IR only					
CO_2 [mol]	NH_3 [mol]	T_{in} [℃]	T_g [℃]	T_e [℃]	$T_g - T_e$ [℃]
1	0.5	25.3	34.2	34.8	0.6
1	1	24.6	33.8	34.8	1.0
1	2	24.6	33.9	34.9	1.0
1	4	24.4	33.7	35.6	1.9
3	2	24.7	33.7	35.0	1.3
3	8	25.0	34.3	34.3	0

It is seen from **Table 1** that $T_g - T_e$ is nearly 0 under the illumination conditions with VIS + IR and IR only. Therefore, the heat transfer model proposed by this study predicts T_g well under the illumination conditions with VIS + IR and IR only. On the other hand, it is found from **Table 1** that $T_g - T_e$ is larger under the illumination condition with UV + VIS + IR. This study assumes that the heat absorbed by black body material is converted from the illuminated light. In the heat transfer analysis, the heat absorbed by black body material is calculated by the light intensity measured using the light intensity meter. However, the heat converted from the light with each wave length is not calculated exactly. The emissive power of black body is a function of wavelength of light and is larger with the increase in the wavelength of light, especially within IR range [17]. Therefore, the heat absorbed by black body material under the illumination condition with UV + VIS + IR might be underestimated in this study. **Table 2** lists T_g and $T_g - T_e$ calculated by the heat absorbed by black body materials which are 1.6 times or 1.7 times as large as that applied for T_g shown in **Table 1** among different molar ratios under the illumination condition with UV + VIS + IR. According to **Table 2**, it is revealed that $T_g - T_e$ in case of the heat absorbed by black bod material, which is 1.6 times as large as that applied for T_g shown in **Table 1,** is ranged from 0.5 ℃ to 2.5 ℃. In addition, $T_g - T_e$ in case of the heat absorbed by black bod material, which is 1.7 times as large as that applied for T_g shown in **Table 1,** is ranged from -0.8 ℃ to 1.3 ℃. It is known from **Table 2** that $T_g - T_e$ becomes smaller compared with that shown in **Table 1**, indicating that the prediction accuracy of the heat model proposed by this study would be improved. Therefore, this study would like to investigate the measurement procedure of light intensity following the light illumination condition and the heat conversion process for each wave length of light in the near future.

Table 2. Comparison of T_g and $T_g - T_e$ which are calculated by the heat absorbed by black bod materials which are 1.6 times or 1.7 times as large as that applied for T_g shown in Table 1 among different molar ratios under the illumination condition with UV + VIS + IR.

1.6 Q			
CO_2 [mol]	NH_3 [mol]	T_g [℃]	$T_g - T_e$ [℃]
1	0.5	44.0	2.5
1	1	44.1	0.8

1	2	44.4	0.8
1	4	44.5	0.7
3	2	43.8	2.1
3	8	44.7	0.5
	1.7 Q		
CO_2 [mol]	NH_3 [mol]	T_g [℃]	$T_g - T_e$ [℃]
1	0.5	45.2	1.3
1	1	45.3	-0.4
1	2	45.7	-0.5
1	4	45.8	-0.6
3	2	450	0.9
3	8	46.0	-0.8

From the investigation of this study, it is confirmed that the mass transfer surrounding P_4O_{10}/TiO_2 photocatalyst is promoted by the natural thermosiphon movement of gases around P_4O_{10}/TiO_2 photocatalyst created by black body materials. The gases around P_4O_{10}/TiO_2 photocatalyst are heated and the temperature of gases of product from the photocatalytic CO_2 reduction increases, resulting that the gases would move upward. As a result, the fresh reacted gases of CO_2 and NH_3, which are blocked by the product from the photocatalytic CO_2 reduction, i.e. CO, can reach the surface of photocatalyst. Since the photocatalytic reaction is a surface reaction, we can claim that this approach to improve the mass transfer is effective.

3. Experiments

3.1. Preparation Procedure of P_4O_{10}/TiO_2 Film and Black Body Material

The P_4O_{10}/TiO_2 film adopted in this study was prepared by sol-gel and dip-coating process as explained in the reference [15]. The P_4O_{10}/TiO_2 film was coated on a netlike glass fiber (SILLIFGLASS U, manufacture: Nihonmuki Co., Tokyo, Japan) via sol-gel and dip-coating processes. The glass fiber having the diameter of about 10 m, which is weaved as a net, is assembled to be the diameter of about 1 mm. From the specification on netlike glass fiber, the porous diameter of glass fiber and the specific surface area are approximately 1 nm and 400 m^2/g, respectively. The netlike glass fiber is composed of SiO_2 of 96 wt%. The netlike glass fiber has the opening space of about 2 mm × 2 mm. Since the netlike glass fiber has a porous characteristic, the netlike glass fiber can trap the P_4O_{10}/TiO_2 film easily via sol-gel and dip-coating processes. The netlike glass fiber is cut to be the disc form with the diameter of 50 mm and the thickness of 1 mm. The weight ratio of P_4O_{10} to TiO_2 was 2.0 wt%, which was confirmed by EPMA (Electron Probe Microanalyzer) analysis quantitatively [15].

The black body material adopted by this study was prepared by spraying the black body spray (TA410KS, manufacture: ICHIKEN TASCO Corp., Osaka, Japan) on both surfaces of the Cu disc. The emissivity of black body spray was 0.94. This study adopted the Cu solid disc with the diameter of 50 mm and the thickness of 1.4 mm as a base material for spraying black body spray. The Cu solid disc had the diameter of 50 mm, which was equal to the inside diameter of the reactor. The emissivity of the polished Cu surface was 0.01 [18]. The used Cu solid disc had a purity of 99.90 % [19]. The specific heat, thermal conductivity, and thermal diffusivity of Cu at 30 °C were 0.386 kJ/(kg·K), 398 W/(m·K), and 117 mm^2/s, respectively [18]. Three Cu solid discs, which were sprayed by the black body spray, were installed in the reactor in this study, referring the authors' previous study [14]. According to the authors' previous study [14], the promotion of CO_2 reduction performance was not obtained by one Cu solid disc but three Cu solid discs. **Figure 4** displays the black body material prepared by this study and the Cu solid disc before spraying black body spray [14,15].

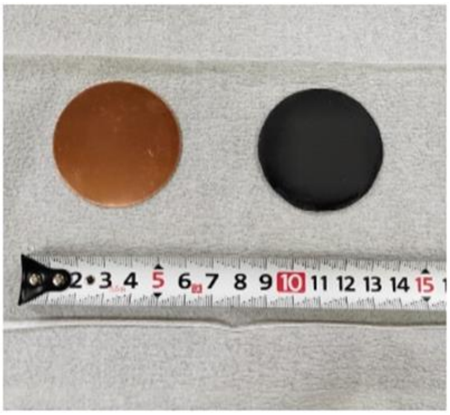

Figure 4. Photo of black body material adopted for the heat transfer analysis and Cu solid disc before splaying black body spray [14,15].

3.2. The Experimental Procedure of CO_2 Reduction and Temperature Measurement

Figure 5 illustrates the experimental apparatus [15] applied for heat transfer analysis in this study. The reactor consists of a stainless tube having the scale of 100 mm (*H.*) × 50 mm (*I.D.*), P_4O_{10}/TiO_2 film coated on the netlike glass disc having the scale of 50 mm (*H.*) × 50 mm (*D.*), a quartz glass disc having the 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, manufacture: SIGMA KOKI CO LTD., Tokyo, Japan) or 800 nm (ITF-50C-85IR, manufacture: SIGMA KOKI CO LTD., Tokyo, Japan), a 150 W Xe lamp (L2175, manufacture: Hamamatsu Photonics K. K.), mass flow controller and CO_2 gas cylinder (purity: 99.995 vol%) and NH_3 gas cylinder (purity: 99.99 vol%). The reactor size for charging the gases was 1.25×10^{-4} m^3. The three black body materials were located under the P_4O_{10}/TiO_2 film coated on a netlike glass disc. The light of the Xe lamp positioned on the stainless tube was illuminated toward P_4O_{10}/TiO_2 film. Since the netlike glass disc had the aperture area of the net, i.e. 4 mm^2 for each, the illuminated light can reach the black body material. The light of Xe lamp located on the stainless tube was illuminated toward 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 wavelength of light illuminated from Xe lamp was distributed from 185 nm to 2000 nm. The sharp cut filter can remove UV and VIS from the Xe lamp, resulting that the wavelength of light illuminating on P_4O_{10}/TiO_2 film was ranged from 401 nm to 2000 nm or 801 nm to 2000 nm [20]. The mean light intensity of light illuminated from Xe lamp from 185 nm to 2000 nm was 70.4 mW/cm^2, that from 401 nm to 2000 nm was 60.7 mW/cm^2, and that from 801 nm to 2000 nm was 46.6 mW/cm^2, which were measured by light intensity meter (Nova ii; manufacture: OPHIR Japan).

After filling the CO_2 gas with a purity of 99.995 vol% and NH_3 with a purity of 99.99 vol%, they were controlled by a mass controller and introduced into the reactor pre-vacuumed by a vacuum pump for 15 min. The valves installed at the inlet and the outlet of the reactor were closed during CO_2 reduction with NH_3. After that, this study confirmed the pressure of 0.1 MPa and the gas temperature at 298 K in the reactor. Due to the heat of IR light components illuminated by the Xe lamp, the temperature of the gas in the reactor rose. The temperature of the experimental room was controlled and set at 293 K by an air conditioner. The molar ratio of CO_2/NH_3 was changed by 1:0.5, 1:1, 1:2, 1:4, 3:2, and 3:8. The reacted gas filled in the reactor was extracted by gas syringe via a gas sampling tap and it was analyzed by an FID gas chromatograph (GC353B, manufacture: GL Science) and a methanizer (MT221, manufacture: GL Science). The FID gas chromatograph and methanizer have a minimum resolution of 1 ppmV. The temperature of the gas in the reactor was measured by a B-type thermocouple installed in the tap, which was located 1 mm above the P_4O_{10}/TiO_2 film coated on a netlike glass disc. The measurement error of the thermocouple is within 0.1 °C. The CO_2 reduction experiment was conducted up to 8 hours. Gas sampling and temperature measurements were carried out from the start of the experiment until 8 hours by 2 hours. In this study, the maximum concentration of CO which in only produced from CO_2 reduction and the maximum temperature rise obtained from the authors' previous study [15] are used.

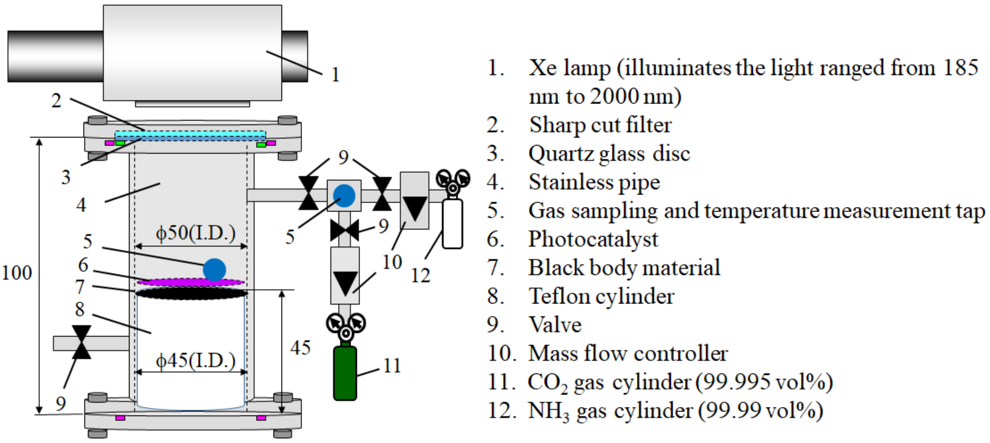

Figure 5. Schematic drawing of CO_2 reduction experimental set-up applied for heat. transfer analysis in this study [15].

4. Calculation Procedure for Heat Transfer Analysis

4.1. Heat Transfer Formulas

This study considers the heat transfer from P_4O_{10}/TiO_2 photocatalyst which is coated on netlike glass disc fitted on the black body materials to the gases over P_4O_{10}/TiO_2 photocatalyst. This study assumes that the illuminated light is converted into heat finally and absorbed by black body materials. Since the light intensity is different following the light illumination condition as described above, the converted heat which is absorbed by black body materials decreases in the order from UV +VIS + IR, VIS + IR to IR only. The temperature of mixed gases of CO_2 and NH_3, T_g, is calculated by the following formula:

$$Q = hA\left(T_g - T_{ini}\right) \tag{1}$$

where Q is a heat absorbed by black body materials [Q], h is a heat transfer coefficient [W/(m^2·K)], A is a heat transfer area (= surface area of Cu disc on one side) [m^2], T_{ini} is an initial temperature of CO_2 reduction experiment) [15] [K]. This study assumes that T_g is equal to the surface temperature of P_4O_{10}/TiO_2 photocatalsyt and black body material. In other words, this study assumes that the mixed gases of CO_2 and NH_3 are heated up by P_4O_{10}/TiO_2 photocatalsyt and black body material from T_{ini} to T_g. h is calculated by the following formula:

$$h = \frac{Nu \cdot \lambda}{d} \tag{2}$$

where Nu is Nusselt number [–], is a thermal conductivity of the mixed gasses of CO_2 and NH_3 [W/(m·K)] and d is the representative length for each local Nu [m]. Nu is obtained from the following formula which can be applied for a laminar free convection heat transfer over a vertical flat plate [21].

$$Nu_x = \frac{0.631 \mathrm{Pr}^{\frac{2}{5}}}{\left(\mathrm{Pr} + 0.9\sqrt{\mathrm{Pr}} + 0.4\right)^{\frac{1}{5}}} \left(\frac{g\beta q x^4}{\nu^2 \lambda}\right)^{\frac{1}{5}} \tag{3}$$

where Pr is Prandtl number [-], g is a gravitational acceleration (= 9.81) [m^2/s], is a volume expansion coefficient [1/K], q is a heat transfer rate (= Q/A), x is a position (= 5 mm interval up to Cu disc radius of 25 mm) [m], is a kinetic viscosity [m^2/s]. The physical properties are calculated at the mean temperature of a quartz glass installed under the Xe lamp, which is 343 K, and the maximum temperature of mixed gases of CO_2 and NH_3 measured by thermocouple in the CO_2 reduction experiment [15]. Under this condition, Pr for CO_2 and NH_3 are 0.766 and 0.95, respectively [21]. for CO_2 and NH_3 are 0.0097×10^{-6} m^2/s and 0.51525×10^{-6} m^2/s, respectively [22]. for CO_2 and NH_3 are 19.94×10^{-3} W/(m·K) and 42.95×10^{-3} W/(m·K), respectively [21]. for CO_2 and NH_3 are 3.722×10^{-6}

1/K and 3.790×10^{-6} 1/K, respectively. Each physical property under the different molar ratio conditions of CO_2/NH_3 is calculated based on the weight ratio of mixed gasses of CO_2 and NH_3. This study considers Q is converted from the illuminated light finally, which is calculated by the light intensity measured under each light illumination condition as described above, i.e. 1.08 W for UV + VIS + IR, 0.952 W for VIS + IR and 0.735 W for IR only. A is 1963×10^{-6} m^2. According to these equations as shown above, T_g for each molar ratio of CO_2/NH_3 under each light illumination condition is obtained. In addition, T_g is compared with the maximum temperature measured by thermocouple in the CO_2 reduction experiment in the authors' previous study [15].

5. Conclusions

This study has developed a simple convective heat transfer model to calculate the temperature of mixed gases of CO_2 and NH_3 around P_4O_{10}/TiO_2 photocatalyst and the black body material in the reactor, which was validated by experimental data in the authors' previous study [15]. As a result, the following conclusions are drawn:

(i) It is revealed that the heat transfer model proposed by this study can predict T_g well under the illumination condition with VIS + IR and IR only.

(ii) It is revealed that $T_g - T_e$ is larger, e.g. 10 °C under the illumination condition with UV + VIS + IR compared with that under the illumination conditions with VIS + IR and IR only.

(iii) $T_g - T_e$ under the illumination condition with UV + VIS + IR becomes smaller by increasing the heat absorbed by black bod materials by 1.6 times or 1.7 times as large as the case of calculation using the light intensity measured by the light intensity meter.

(iv) The mass transfer surrounding P_4O_{10}/TiO_2 photocatalyst is promoted by the natural thermosiphon movement of the gases around P_4O_{10}/TiO_2 photocatalyst created by black body material according to the heat transfer analysis conducted in this study.

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

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References

1. Jesic, D.; Jurkovic, L. D.; Pohar, A.; Suhadolnik, L.; Likozar, B. Engineering Photocatalytic and Photoelectrocatalytic CO_2 Reduction Reactions: Mechanisms, Intrinsic Kinetics, Mass Transfer Resistances, Reactors and Multi-scale Modeling Simulations. *Chemical Engineering Journal* **2021**, 407, DOI: 10.1016/j.cej.2020.126799.
2. Kaushik, R.; Singh P. K.; Halder, A. Modulation Strategies in Titania Photocatalyst for Energy Recovery and Environmental Remediation. *Catalysis Today* **2022**, 384-386, 45-69.
3. Wang, Z. W.; Shi, Y. Z.; Liu, C.; Kang, Y. Y.; Wu, L. Cu^+-Ti^{3+} Interface Interaction Mediated CO_2 Coordination model for Controlling the Selectivity of Photocatalytic Reduction CO_2. *Applied Catalysis B: Environmental* **2022**, 301, DOI:10.1016/j.apcatb.2021.120803.
4. Remiro-Buenamanana, S.; Garcia, H. Photoassisted CO_2 Conversion into Fuels. *Chem. Cat Chem. Minirev.* **2019**, 11, 342-356.
5. Cai, Y.; Luo, F.; Guo, Y.; Guo, F.; Shi, W.; Yang, S. Near-infrared Light Driven $ZnIn_2S_4$-based Photocatalysts for Environmental and Energy Applications: Progress and Perspectives. *molecules* **2023**, 28, DOI:10.3390/molecules28052142.
6. Tahir, M. Synergistic Effect in MMT-dispersed Au/TiO_2 Monolithic Nanocatalyst for Plasma-absorption and Metallic Interband Transitions Dynamic CO_2 Photoreduction to CO. *Appl. Catal. B Environ* **2017**, 219, 329-343.
7. Tahir, M.; Tahir, B.; Amin, N. A. S. Synergistic Effect in Plasmonic Au/Ag Alloy NPs Co-coated TiO_2 NWs toward Visible-light Enhanced CO_2 Photoreduction to Fuels. *Appl. Catal. B Enviorn* **2017**, 204, 548-560.
8. Hong, L. F.; Guo, R. T.; Yuan, Y.; Ji, X. Y.; Lin, Z. D.; Gu, J. W.; Pan, W. G. Urchinlike $W_{18}O_{49}/g$-C_3N_4 Z-Scheme Heterojunction for Highly Efficient Photocatalytic Reduction of CO_2 under Full Spectrum Light. *Energy Fuels* **2021**, 35, 11468-11478.

9. Dai, W.; Yu, J.; Luo, S.; Hu, X.; Yang, L.; Zhang, S.; Li, B.; Luo, X.; Zou, J. WS_2 Quantum Dots Seeding in Bi_2S_3 Nanotubes: A Novel Vis-NIR Light Sensitive Photocatalyst with Low-Resistance Junction Interface for CO_2 Reduction. *Chemical Engineering Journal* **2020**, 389, DOI:10.1016/j.cej.2019.123430.
10. Gan, J.; Wang, H.; Hu, H.; Su, M.; Chen, F.; Xu, H. Efficient Synthesis of Tunable Band-Gap CuInZnS Decorated g-C_3N_4 Hybrids for Enhanced CO_2 Photocatalytic Reduction and Near-Infrared- Triggered Photordegradation Performance. *Applied Surface Science* **2021**, 564, DOI:10.1016/j.apsusc.2021.150396.
11. Yu, M.; Lv, X.; Idris, A. M.; Li, S.; Lin, J.; Lin, H.; Wang, J.; Li, Z. Upconversion Nanoparticles Coupled with Hierarchical $ZnIn_2S_4$ Nanorods as a Near-Infrared Responsive Photocatalyst for Photocatalytic CO_2 Reduction. *Journal of Colloid and Interface Science* **2022**, 612, 782-791.
12. Nishimura, A.; Mae, H.; Kato, T.; Hu, E. Utilization from ultraviolet to infrared light for CO_2 reduction with P_4O_{10}/TiO_2 photocatalyst. *Physics & Astronomy International Journal* **2022**, 6, 145-154.
13. Nishimura, A.; Mae, H.; Hannyu R.; Hu, E. Impact of loading amount of P_4O_{10} on CO_2 reduction performance of P_4O_{10}/TiO_2 with H_2O extending absorption range from ultraviolet to infrared light. *Physics & Astronomy International Journal* **2022**, 6, 186-194.
14. Nishimura, A.; Kato, T.; Mae, H.; Hu, E. Impact of black body material enhanced gas movement on CO_2 photocatalytic reduction performance. *catalysts* **2022**, 12, DOI:10.3390/catal12050470.
15. Nishimura, A.; Hanyu, R.; Mae, H.; Hu, E. Impact of Black Body Material on CO_2 Reduction Performance of P_4O_{10}/TiO_2 with NH_3. *Journal of Physics and Chemistry Research* **2023**, 5, DOI:10.36266/JPCR/155.
16. Nishimura, A.; Komatsu, N.; Mitsui, G.; Hirota, M.; Hu, E. CO_2 Reforming into Fuel Using TiO_2 Photocatalyst and Gas Separation Membrane. *Catalysis Today* **2009**, 148, 341-349.
17. Holman, J. P. Heat Transfer, 8th ed.; *McGRAW-HILL, INC.*: New York, USA, 1997; p. 400.
18. Japan Society of Mechanical Engineering. *Heat Transfer Hand Book*, 1st ed.; Maruzen: Tokyo, Japan, 1993; pp. 238, 367-369.
19. Tahir, M.; Amin, N.S. Photocatalytic Reduction of Carbon Dioxide with Water Vapors over Montmorillonite Modified TiO_2 Nanocomposites. *Appl. Catal. B. Environ.* **2013**, 142-143, 512-522.
20. Nishimura, A.; Mitsui, G.; Nakamura, K.; Hirota, M.; Hu, E. CO_2 reforming characteristics under visible light response of Cr- or Ag-doped TiO_2 prepared by sol-gel and dip-coating process. *Int. J. Photoenergy.* **2012**, Article ID 184169, DOI:10.1155/2012/184169.
21. Aihara, T. *Heat Transfer Engineering*, 1st ed.; Syokabo: Tokyo, Japan, 1994, pp.107, 274.
22. Hasatani, M.; Kimura, J. Basis and Application for Combustion, 2nd ed.; Kyoritsu Shuppan: Tokyo, Japan, 1986, p.276.