

## Research Article

# CO<sub>2</sub> Reforming Performance and Visible Light Responsibility of Cr-Doped TiO<sub>2</sub> Prepared by Sol-Gel and Dip-Coating Method

Akira Nishimura,<sup>1</sup> Go Mitsui,<sup>1</sup> Masafumi Hirota,<sup>1</sup> and Eric Hu<sup>2</sup>

<sup>1</sup>Division of Mechanical Engineering, Graduate School of Engineering, Mie University, 1577 Kurimamachiya-Cho, Tsu 514-8507, Japan

<sup>2</sup>School of Mechanical Engineering, The University of Adelaide, SA 5005, Australia

Correspondence should be addressed to Akira Nishimura, nisimura@mach.mie-u.ac.jp

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A Cr-doped TiO<sub>2</sub> film was prepared by sol-gel and dip-coating method and used as the photocatalyst for CO<sub>2</sub> reforming under the visible light. The ratio of amount of Cr added to amount of Ti in TiO<sub>2</sub> sol solution ( $R$ ) varied from 0 to 100 wt%. The total layer number of Cr-doped TiO<sub>2</sub> film ( $N$ ) coated was up to 7. The CO<sub>2</sub> reforming performance with the Cr-doped TiO<sub>2</sub> film was evaluated by illuminating under a Xe lamp with or without ultraviolet (UV) light. The concentration of CO which was a product from CO<sub>2</sub> reforming was maximized for  $R = 70$  wt% when  $N$  equals to 1. The visible light responsibility was also maximized for  $R = 70$  wt%. The amount of Cr within TiO<sub>2</sub> film coated on copper disc was increased with the increase in  $R$  up to 70 wt% and started to decrease when  $R$  is over 70 wt%. The CO<sub>2</sub> reforming performance of TiO<sub>2</sub> film with one layer Cr-doped was found better than that of TiO<sub>2</sub> film with multi Cr-doped layers under illuminating of UV light. Under the visible light, the performance was maximized at  $R = 70$  wt% and  $N = 7$  with one layer Cr-doped.

## 1. Introduction

Due to mass consumption of fossil fuels, global warming and fossil fuels depletion have become a serious global environmental problem in the world. After the industrial revolution, the averaged concentration of CO<sub>2</sub> in the world has been increased from 280 ppmV to 385 ppmV by 2008. Therefore, it is necessary to develop a new energy production technology with less or no CO<sub>2</sub> emission.

It is reported that CO<sub>2</sub> can be reformed into fuels, for example, CO, CH<sub>4</sub>, CH<sub>3</sub>OH, and H<sub>2</sub>, by TiO<sub>2</sub> photocatalyst under ultraviolet (UV) light illumination [1–6]. If this technique could be applied practically, a carbon circulation system would be able to be established with the use of solar energy.

Many works on this technology have been carried out, but mainly for the experimental systems that TiO<sub>2</sub> particle loaded with Cu, Pd, Pt reacts with CO<sub>2</sub> dissolved in solution [2–4, 7–11]. Recently, nanoscale TiO<sub>2</sub> [12, 13], porous shape TiO<sub>2</sub> [14], and TiO<sub>2</sub> film combined with metal [15] are developed for this process. However, the

fuel concentration in the products is still low ranging from 10 ppmV to 1000 ppmV [2–8, 10–13]. Therefore, a further way is necessary to investigate the ways to promote the CO<sub>2</sub> reforming performance of TiO<sub>2</sub> further.

In the applications such as water-splitting and purification of pollutant, the photoresponse extension of TiO<sub>2</sub> to the visible spectrum has been investigated well [16–20]. TiO<sub>2</sub> by itself can only work under UV light due to its wide bandgap of 3.0–3.2 eV, which means only about 4% of the incoming solar energy on the surface can be utilized [21]. On the other hand, the visible light accounts for 43% of whole solar energy [22]. Therefore, if the photoresponse of TiO<sub>2</sub> could be extended to the visible spectrum, the CO<sub>2</sub> reforming performance of TiO<sub>2</sub> technology would be improved significantly.

Doping with foreign ions is one of the most promising strategies for sensitizing TiO<sub>2</sub> to visible light and also for forming charge traps to keep electron-hole pairs separate [23]. The most popular dopants for modification of the optical and photo-electrochemical properties of TiO<sub>2</sub> are transition metals such as Cr, Fe, Ni, V, Mn, and Cu [19].

Choi et al. [24] carried out a systematic investigation of the photocatalytic activity of  $\text{TiO}_2$  doped with 21 different metal ions. It was found that doping with metal ions might extend the photoresponse of  $\text{TiO}_2$  into the visible spectrum by introducing additional energy levels in the band gap of  $\text{TiO}_2$ . In addition, an optimum concentration of dopant metal ions exists under specific conditions. If the concentration of dopant exceeds the optimum one, the photocatalytic activity declines because of charge recombination [19]. Many previous reports on metal-doped  $\text{TiO}_2$  used for photocatalytic degradation reaction of chemicals under visible light showed the activity enhancement only for a specific amount of doping ions, otherwise detrimental effects occur [25].

Many different techniques have previously been reported for metal doping of  $\text{TiO}_2$  such as wet impregnation [26], hydrothermal deposition [27], RF magnetron sputtering deposition [16, 17, 28, 29], flame reactor method [30], solid-state reactions [31], ion implantation [32], and pulsed laser deposition [33]. Recently, the sol-gel method is adopted for metal doping of  $\text{TiO}_2$  well [18–20, 25, 34–37] since this method can incorporate dopants into  $\text{TiO}_2$  lattice, resulting in preparation of the materials with other optical and also catalytic properties [38]. In addition, the integration of dopants into the sol during the gelation process facilitates direct interaction with  $\text{TiO}_2$  by sol-gel method [37].

Although many studies to extend the photoresponse extension of  $\text{TiO}_2$  to the visible spectrum were reported as described above, there are only a few reports on promoting the  $\text{CO}_2$  reforming performance using  $\text{TiO}_2$  [39]. In our former papers [40–43], we reported the investigation on the effect of  $\text{TiO}_2$  thin film preparation conditions for sol-gel and dip-coating method by the  $\text{CO}_2$  reforming experiment though it was carried out under the condition of illuminating UV light only.

Therefore, sol-gel and dip-coating method is adopted for photoresponse extension of  $\text{TiO}_2$  to the visible spectrum in this study. Since it was reported that the transition metals such as V, Cr, Mn, Fe, and Ni were effective for the photoresponse extension of  $\text{TiO}_2$  to the visible spectrum [28], Cr was selected at first as the dopant to check the feasibility of promoting  $\text{CO}_2$  reforming performance of  $\text{TiO}_2$  in this study.

In this paper, to promote the  $\text{CO}_2$  reforming performance of  $\text{TiO}_2$ , the preparation method for Cr-doped  $\text{TiO}_2$  was developed. Besides the characterization analyzed by Scanning Electron Microscope (SEM), Electron Probe Micro Analyzer (EPMA), and X-ray photoelectron spectroscopy (XPS), the influence of the ratio of the amount of Cr added to the amount of Ti in  $\text{TiO}_2$  sol solution ( $R$ ) and the total coating number of Cr-doped  $\text{TiO}_2$  film ( $N$ ) on  $\text{CO}_2$  reforming performance under Xe lamp illumination with or without UV light was investigated in this study.

## 2. Experiment

**2.1. Preparation Method of Cr-Doped  $\text{TiO}_2$  Film.** Sol-gel and dip-coating method was used for preparing Cr-doped  $\text{TiO}_2$  film in this study.  $\text{TiO}_2$  sol solution was made by

mixing  $[(\text{CH}_3)_2\text{CHO}]_4\text{Ti}$  (purity of 95 wt%, Nacalai Tesque Co.) of 0.1 mol, anhydrous  $\text{C}_2\text{H}_5\text{OH}$  (purity of 99.5 wt%, Nacalai Tesque Co.) of 0.8 mol, distilled water of 0.1 mol, and HCl (purity of 35 wt%, Nacalai Tesque Co.) of 0.008 mol. Cr powders (08819-15, Nacalai Tesque Co., particle size below  $74\ \mu\text{m}$ ), were added into  $\text{TiO}_2$  sol solution. Copper disc whose diameter and thickness were 50 mm and 1 mm, respectively, was dipped into Cr/ $\text{TiO}_2$  sol solution and pulled up at the fixed speed ( $RS$ ) 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 Cr-doped  $\text{TiO}_2$  film was fastened on the surface of copper disc.  $FT$  and  $FD$  were set at 623 K and 180 s, respectively. In this study,  $N$  varied from 1 to 7.

**2.2. Characterization of Cr-Doped  $\text{TiO}_2$  Film.** The surface structure and crystallization characteristics of Cr-doped  $\text{TiO}_2$  film were evaluated by SEM (JXA8900R, JEOL Ltd.) and EPMA (JXA8900R, JEOL Ltd.). The EPMA analysis helps us not only to understand the coating state of Cr and  $\text{TiO}_2$  on copper disc but also to measure the amount of doped Cr within  $\text{TiO}_2$  film on copper disc. Element distribution through thickness direction of Cr-doped  $\text{TiO}_2$  film was analyzed by XPS (PHI Quantera SXM, ULVAC-PHI, INC.) using a radiation source of Al radiation with the pass energy of 224.00 eV, the radiation current of 1.0 W, and the acceleration voltage of 15 kV.

**2.3. Apparatus and Procedure of  $\text{CO}_2$  Reforming Experiment.** Figure 1 illustrates that the experimental system set-up of  $\text{CO}_2$  reformer consists of a stainless pipe (100 mm ( $H.$ )  $\times$  50 mm ( $I.D.$ )), a copper disc (50 mm ( $D.$ )  $\times$  1 mm ( $t.$ )) coated with Cr-doped  $\text{TiO}_2$  film which is located on the teflon cylinder (50 mm ( $H.$ )  $\times$  50 mm ( $D.$ )), a quartz glass disc (84 mm ( $D.$ )  $\times$  10 mm ( $t.$ )), a colored glass filter which cuts off the light of wavelength below 380 nm, SCF-50S-38L, SIGMA KOKI CO., LTD.), Xe lamp (L2175, Hamamatsu Photonics K. K.), and  $\text{CO}_2$  gas cylinder. The reformer volume for  $\text{CO}_2$  charge is  $1.25 \times 10^{-4}\ \text{m}^3$ . Xe lamp is located over the stainless pipe. The light of Xe lamp illuminates the copper disc coated with Cr-doped  $\text{TiO}_2$  film, which is inserted into the stainless pipe, through the colored glass filter and the quartz glass disc fixed to the top of the stainless pipe. The wavelength of Xe lamp is ranged from 185 nm to 2000 nm. The Xe lamp can be fitted with a colored glass filter to remove UV components of the light. With the filter, the wavelength of light from Xe lamp is from 381 nm to 2000 nm. Figure 2 shows the light transmittance data of the colored glass filter to prove the removal of the light whose wavelength is below 380 nm. The average light intensity of Xe lamp on the copper disc without and with setting the colored glass filter is 57.53  $\text{mW}/\text{cm}^2$  and 43.67  $\text{mW}/\text{cm}^2$ , respectively.

In the  $\text{CO}_2$  reforming experiment,  $\text{CO}_2$  with purity of 99.995 vol% was flowed through the  $\text{CO}_2$  reformer as a purged gas for 15 minutes first. After that, the valves located at the inlet and the outlet of  $\text{CO}_2$  reformer were closed. After confirming the gas pressure and gas temperature in the  $\text{CO}_2$  reformer at 0.1 MPa and 298 K, respectively, the

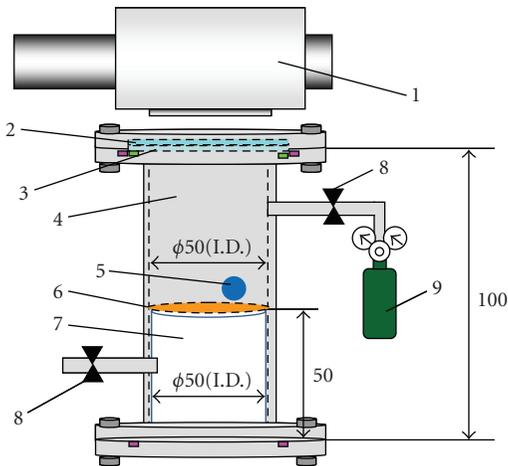


FIGURE 1: Schematic drawing of CO<sub>2</sub> reforming experimental system: 1: Xe lamp; 2: colored glass filter; 3: quartz glass disc; 4: stainless pipe; 5: gas sampling tap; 6: copper disc; 7: teflon cylinder; 8: valve; 9: CO<sub>2</sub> gas cylinder.

distilled water of 100  $\mu\text{L}$  was injected into the CO<sub>2</sub> reformer and Xe lamp illumination was turned on at the same time. The water was vaporized after injection. Despite of the heat of UV lamp, the temperature in CO<sub>2</sub> reformer was kept at about 343 K during the experiment. The amount of the injected water and the CO<sub>2</sub> in the CO<sub>2</sub> reformer are 5.56 mmol and 5.76 mmol, respectively. The gas in CO<sub>2</sub> reformer was sampled every 24 hours during the CO<sub>2</sub> reforming experiment. The gas samples were analyzed by FID gas chromatograph (GC353B, GL Science) and methanizer (MT221, GL Science). Minimum resolution of FID gas chromatograph and methanizer is 1 ppmV.

### 3. Results and Discussion

**3.1. Analysis of Cr-Doped TiO<sub>2</sub> Film by SEM and EPMA.** Figures 3 and 4 show SEM image and EPMA image of Cr-doped TiO<sub>2</sub> film prepared under the condition of  $R = 1$  wt%. This SEM image was taken at 1500 times magnification under the condition of acceleration voltage of 15 kV and current of  $3.0 \times 10^{-8}$  A. The red lined quadrangle area in Figure 3 was used for EPMA analysis shown in Figure 4. In Figure 4, the concentrations of Ti, Cr, and Cu in observation area are indicated by the difference of color. Light colors, for example, white, pink, and red indicate that the amount of element is large, while dark colors like black, blue, and green indicate that the amount of element is small.

The green circle in Figure 3 indicates the existence of Cr particle as shown in Figure 4. In addition, the yellow circles in Figure 3 indicate that the amount of Ti is large as shown in Figure 4. Moreover, the red circles illustrated in Figure 3 indicate that the amount of Cu is also large as pointed out by the white circles in Figure 4. These results represent the following:

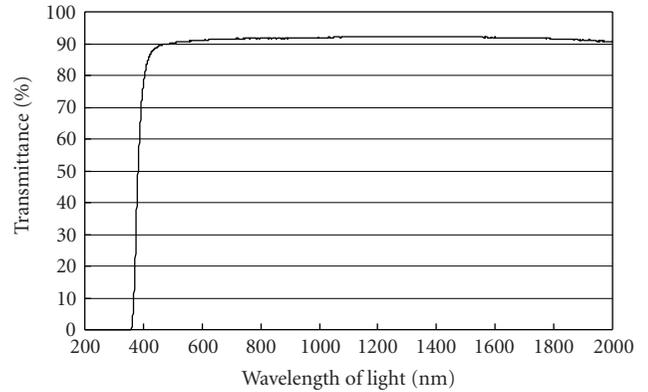
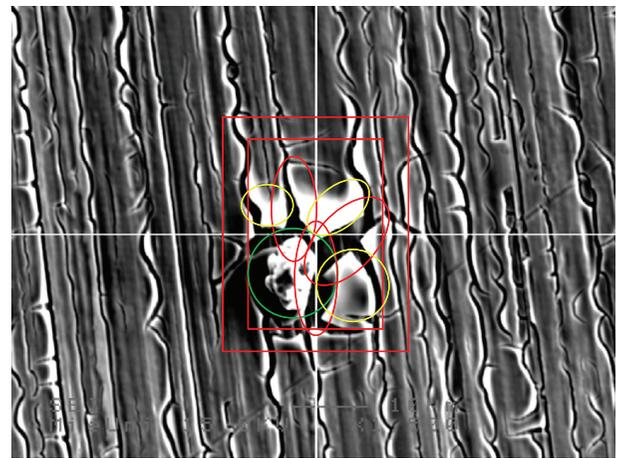


FIGURE 2: Light transmittance data of the colored glass filter.



— 10  $\mu\text{m}$   
 $\times 1500$

FIGURE 3: SEM image of Cr-doped TiO<sub>2</sub> film prepared under the condition of  $R = 1$  wt%.

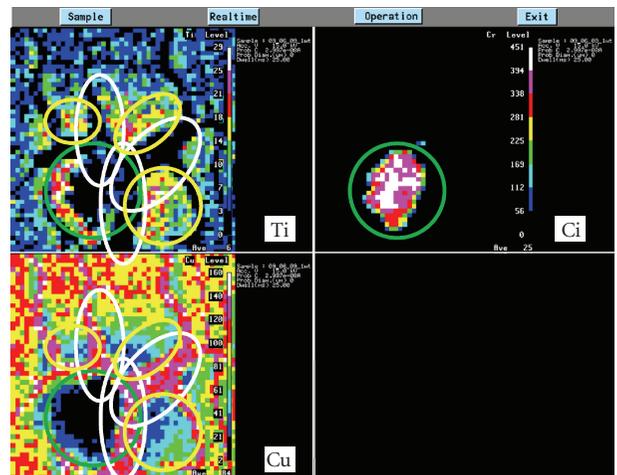


FIGURE 4: EPMA image of Cr-doped TiO<sub>2</sub> film prepared under the condition of  $R = 1$  wt%.

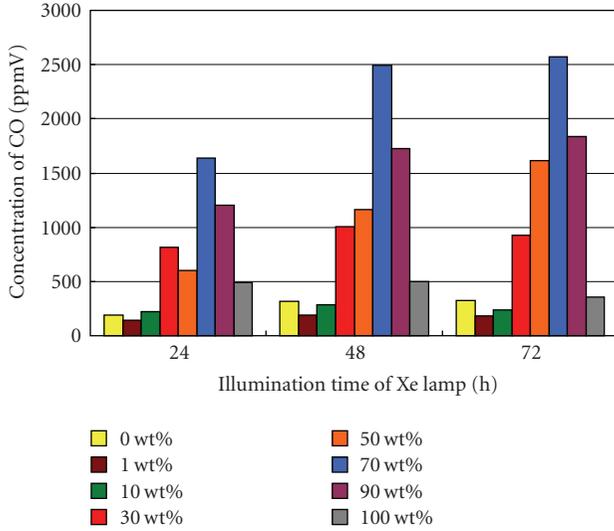


FIGURE 5: Comparison of produced concentration of CO among different  $R$  under the illumination condition with UV light.

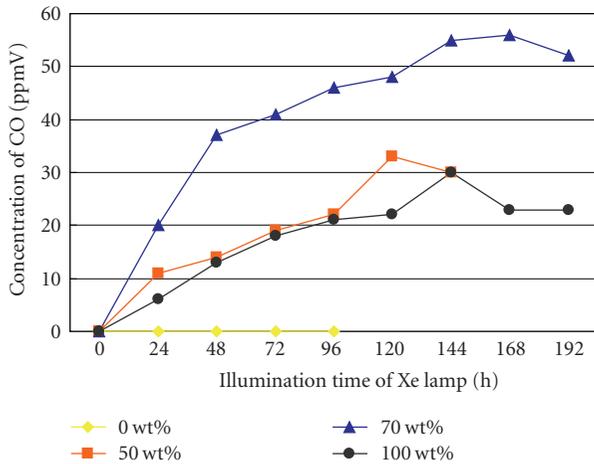


FIGURE 6: Comparison of produced concentration of CO among different  $R$  under the illumination condition without UV light.

- (i) Before firing, Cr/TiO<sub>2</sub> sol solution is adhered on the copper disc uniformly;
- (ii) During firing process, the temperature profile of Cr/TiO<sub>2</sub> sol solution adhered on the copper disc is not even due to the difference of thermal conductivity of Ti and Cr. The thermal conductivity of Ti and Cr at 600 K is 19.4 W/(m·K) and 80.5 W/(m·K), respectively [44]. Therefore, the thermal expansion around Cr particle and the thermal shrinkage around the other area of TiO<sub>2</sub> sol occur.
- (iii) Because of the thermal stress caused by the uneven distribution of temperature, the cluck around Cr and the shrinkage of TiO<sub>2</sub> film around the cluck occur after finishing firing process. Therefore, a large amount of Cu, which is an element of basis copper

disc of TiO<sub>2</sub> film, around Cr and a large amount of Ti around Cr are observed in Figure 4.

To evaluate the amount of doped Cr within TiO<sub>2</sub> film quantitatively, the observation area, which is the center of copper disc, of diameter of 300 μm is analyzed by EPMA. The ratio of Cr to Ti in this observation area is counted by averaging the data obtained in this observation area.

Table 1 indicates the relationship between each element ratio and different  $R$  values which is varied from 1 wt% to 100 wt% when the  $N$  was set at 1. According to this table, the ratio of Cr is increased with the increase in  $R$  up to 70 wt% since the amount of Cr powders added into TiO<sub>2</sub> sol solution is increased. However, the ratio of Cr starts to decrease if the  $R$  was over 70 wt%. The reason might be that when the amount of Cr powders in TiO<sub>2</sub> sol solution was too much, the shrinkage of TiO<sub>2</sub> film occurred. Therefore, the fixing strength of TiO<sub>2</sub> film to copper disc was weakened, resulting in the ratio of Cr being decreased for  $R$  over 70 wt%. The ratio of Cr to Ti shown in Table 1, which is a measured value, is different from the calculated  $R$  from the Cr powders added into TiO<sub>2</sub> sol solution because of the agglomeration of Cr powders in TiO<sub>2</sub> sol solution. Although Cr powders in TiO<sub>2</sub> sol solution were mixed by magnetic stirrer well and the powders were stored under no moisture condition before the experiment, it was still difficult to prevent it from the agglomeration for such a fine particle completely.

**3.2. The Optimum Doping Ratio of Cr.** Figure 5 shows the concentration change of CO from CO<sub>2</sub> reforming with illumination time of Xe lamp with UV light for several Cr-doped TiO<sub>2</sub> films prepared under the different  $R$  conditions. In this experiment, CO is the only fuel produced from CO<sub>2</sub> reforming. Since the concentration of CO started to decrease after illumination of 72 hours for every  $R$ , Figure 5 only shows the concentration up to 72 hours to compare the CO<sub>2</sub> reforming performance among different  $R$  conditions. Before this CO<sub>2</sub> reforming experiment without illumination of Xe lamp, has been carried out to set up a reference case. No fuel was produced in the blank test as expected. From Figure 5, it can be seen that the concentration of CO is increased with the increase in  $R$  up to 70 wt%. According to Table 1, the ratio of Cr is increased with the increase in  $R$  up to 70 wt%, then it starts to decrease. Therefore, it can be said that the result of CO<sub>2</sub> reforming experiment matches with the result of EPMA analysis.

To verify the photoresponse extension of TiO<sub>2</sub> to the visible spectrum by Cr doping, Figure 6 shows the concentration change of CO with illumination time of Xe lamp without UV light for several Cr-doped TiO<sub>2</sub> films prepared under different  $R$  conditions. In this figure, the data for  $R = 0$  wt%, 50 wt%, 70 wt%, and 100 wt% are shown. It is seen that the concentration of CO for  $R = 0$  wt% keeps 0 ppmV. Therefore, it means that the prepared TiO<sub>2</sub> film without Cr doping does not have the photoresponsibility of visible spectrum. On the other hand, TiO<sub>2</sub> film with Cr doping shows the photoresponse of visible spectrum since the CO is detected. In particular, Figure 6 indicates that the concentration of CO

TABLE 1: Relationship between each element and different  $R$ .

$R$ (wt%)	1	10	20	30	40	50	60	70	80	90	100
Element											
Cr (wt%)	5.5	7.1	8.2	11.3	13.2	15.3	18.9	22.4	17.0	18.0	18.6
Ti (wt%)	94.5	92.9	91.8	88.7	86.8	84.7	81.1	77.6	83.0	82.0	81.4
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

for  $R = 70$  wt% is the highest among the  $R$  conditions tested. Consequently, the optimum  $R$  is thought at 70 wt% under this experimental condition.

Figure 6 shows the concentration change with illumination time of Xe lamp without UV light more than 72 hours, since it was thought that the time to attain the peak concentration might be longer than that under Xe lamp with UV light [43, 45].

The result that  $R = 70$  wt% is the best in the experiment without UV light illumination agrees with the results shown in Table 1 and Figure 5. However, the peak concentration level of CO under the illumination without UV light is lower than that under the illumination with UV light.

The following points can be used to explain these results.

- (i) The CO<sub>2</sub> reforming performance is improved by Cr doping since the photoresponsibility of visible spectrum is realized. The light energy which can be used for CO<sub>2</sub> reforming is increased.
- (ii) On the other hand, the CO<sub>2</sub> reforming performance can also be declined by Cr doping since the recombination of hole and electron occurs. Though it is thought that sol-gel and dip-coating method can incorporate dopants into the TiO<sub>2</sub> lattice without lattice defect [38], the lattice defect which causes the recombination of hole and electron might have occurred in this study.
- (iii) The CO<sub>2</sub> reforming performance would be improved by Cr doping if the recombination of hole and electron could be prevented. According to the previous reports [2–4, 9–11], a metal loading is usually adopted to prevent the recombination of electron and hole under the condition of illumination of UV light.

The data shown in Table 1, Figures 5 and 6 are analyzed based on above three points, as follows.

- (1) From Figure 5, the concentration of CO for  $R = 1$  wt% and 10 wt % is lower than that for  $R = 0$  wt%. It is thought that the above described (ii) should have occurred in this experiment. Therefore, the amount of the Cr doping in a right range is necessary in order to improve the CO<sub>2</sub> reforming performance of TiO<sub>2</sub>.
- (2) As shown in Figure 5, the concentration of CO for  $R$  over 30 wt% is bigger than that for  $R = 0$  wt%. If the above described points (i) to (iii) were all in effect equally, the concentration of CO should not increase. Therefore, it is thought that the point (i) or (iii) should be dominant until  $R$  is up to 70 wt% as shown in Table 1.

- (3) It can be seen from Figure 5, the concentration of CO for  $R$  over 90 wt% is low, while the ratio of Cr for  $R$  over 90 wt% is not so small as shown in Table 1. If the concentration of CO would follow the amount of doped Cr, the concentration of CO for  $R = 100$  wt% should be higher than that for  $R < 50$  wt%. The reason is thought to be that when  $R$  is too high, Cr powders with TiO<sub>2</sub> sol might be removed away from copper disc surface that is, not in contact with the disc during dip-coating process. Although the amount of Cr powders in TiO<sub>2</sub> sol solution is increased under high  $R$  condition, the Cr in contact with copper disc might be decreased because the amount of Cr powders being removed from copper disc might increase more. Therefore, as a result, the CO<sub>2</sub> reforming performance for  $R$  over 90 wt% is declined.
- (4) Comparing Figure 5 with Figure 6, the concentration of CO under the illumination without UV light is lower than that under the illumination with UV light. Under the illumination condition of Xe lamp with UV light, it is thought that Cr doping promotes the CO<sub>2</sub> reforming performance due to prevention of recombination of electron and hole as well as photoresponsibility of visible spectrum. According to the previous reports [2–4, 9–11] as referred above, the prevention of recombination of electron and hole by metal loading effect can be obtained even though UV light is illuminated only. This electron plays the role of preventing the recombination of electron and hole produced by photocatalytic reaction. In addition, the introduction of additional energy levels in the band gap of TiO<sub>2</sub> by Cr doping extends the photoresponsibility of TiO<sub>2</sub> into the visible spectrum. Since the concentration of CO under the illumination without UV light is lower than that under the illumination with UV light, it can be concluded that the effect of preventing the recombination of electron and hole which is obtained by UV light is stronger than the increased effect of photoresponsibility of visible spectrum.

Since the product of CO<sub>2</sub> reforming is only CO in this experiment, it is thought that the reduction effect of TiO<sub>2</sub> is not so significant according to the reaction scheme [1, 2, 4, 8, 10, 42, 43] as shown in Figure 7. From Figure 7, more electron and proton are necessary to produce hydrocarbons like CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub>, and C<sub>2</sub>H<sub>6</sub>. When the reduction effect of TiO<sub>2</sub> is promoted, the concentration of CO which is a preproduct to the hydrocarbons is also increased. According

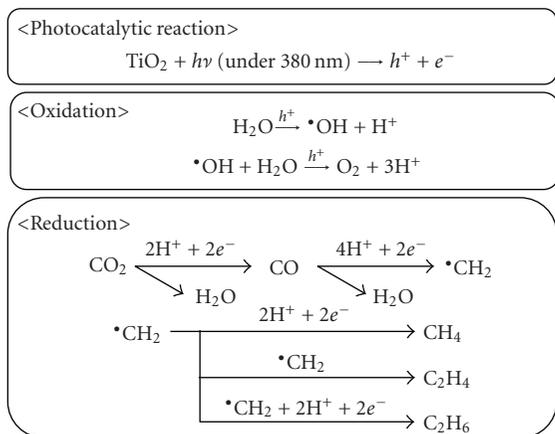


FIGURE 7: Reaction scheme of CO<sub>2</sub> reforming into fuel by TiO<sub>2</sub> photocatalyst ( $\cdot\text{OH}$ : hydroxy radical,  $\cdot\text{CH}_2$ : carben radical).

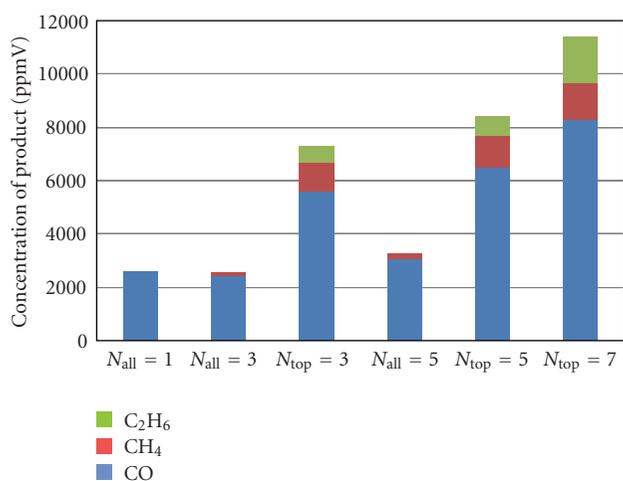


FIGURE 8: Comparison of product by CO<sub>2</sub> reforming after illumination of Xe lamp with UV light of 72 hours for several Cr-doped TiO<sub>2</sub> film prepared under conditions of different  $N$ .

to the previous studies [40–43], the increase in  $N$  is effective to promote the reduction performance of TiO<sub>2</sub> photocatalyst due to increase in the amount of TiO<sub>2</sub>. Under larger  $N$  condition, many electrons are produced by photocatalytic reaction due to the promotion of reduction performance of TiO<sub>2</sub>. So Cr is converted into ion-like Cr<sup>3+</sup> and electron in the CO<sub>2</sub> reforming process as many electrons produced by photocatalytic reaction support to convert Cr into ion and electron, resulting in extension of the photoresponse of TiO<sub>2</sub> into the visible spectrum. The effect of  $N$  of Cr-doped TiO<sub>2</sub> film on CO<sub>2</sub> reforming performance and photoresponsibility of visible spectrum is investigated further below.

**3.3. Effect of Coating Number of Cr-Doped TiO<sub>2</sub> Film on CO<sub>2</sub> Reforming Performance.** Figure 8 shows the comparison of concentration of product by CO<sub>2</sub> reforming after illumination of Xe lamp with UV light of 72 hours for several Cr-doped TiO<sub>2</sub> films prepared under conditions of different  $N$ .

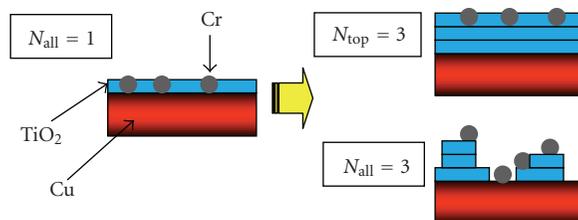


FIGURE 9: Difference of coating structure of Cr-doped TiO<sub>2</sub> film between  $N_{\text{all}}$  and  $N_{\text{top}}$ .

In this figure, the following two coating conditions were investigated: one is that Cr is doped in every layer ( $N_{\text{all}}$ ); the other is that Cr is doped only in the top layer ( $N_{\text{top}}$ ). In this experiment,  $R$  is fixed at 70 wt% in doping.

Figure 8 indicates that the total concentration of products is increased with the increase in  $N$ , because the amount of Cr-doped TiO<sub>2</sub> film coated on copper disc becomes larger with the increase in  $N$ . However, the degree of the increase in  $N$  for  $N_{\text{top}}$  cases is higher than that for  $N_{\text{all}}$  cases. In addition, it is seen that CH<sub>4</sub> and C<sub>2</sub>H<sub>6</sub> as well as CO are produced more for  $N_{\text{top}}$  compared with  $N_{\text{all}}$ . As described above, the cluck around Cr and the shrinkage of TiO<sub>2</sub> film around the cluck occur after finishing firing process. Each layer that is the base for next layer coating is weaker in  $N_{\text{all}}$  cases, resulting that the uniform coating for each layer is difficult to achieve. However, it is thought that the coating layers before the last coating are kept uniform in  $N_{\text{top}}$  cases. The reason why the concentration of CH<sub>4</sub> and C<sub>2</sub>H<sub>6</sub> is increased with the increase in  $N$  in  $N_{\text{top}}$  cases is thought to be the increase in the amount of TiO<sub>2</sub>. The difference of coating structure of Cr-doped TiO<sub>2</sub> films between  $N_{\text{all}}$  and  $N_{\text{top}}$  is illustrated in Figure 9.

Under experimental conditions of this study, the Cr-doped TiO<sub>2</sub> film for  $N_{\text{top}} = 7$  is the best for CO<sub>2</sub> reforming. After illumination of Xe lamp with UV light of 72 hours, the concentration of CO, CH<sub>4</sub>, and C<sub>2</sub>H<sub>6</sub> can reach 8306 ppmV (= 92.5 mmol/g-catalyst), 1367 ppmV (= 15.2 mmol/g-catalyst), and 1712 ppmV (= 19.1 mmol/g-catalyst), respectively. The method to calculate the amount of substance of product per weight of catalyst is as follows: the thickness of Cr-doped TiO<sub>2</sub> film should be measured first and then with the known surface area of copper disc of  $1.96 \times 10^{-3} \text{ m}^2$  and the density of TiO<sub>2</sub> of 3900 kg/m<sup>3</sup> [46], the mass of TiO<sub>2</sub> can be calculated. XPS analysis was used to measure the thickness of Cr-doped TiO<sub>2</sub> film. Figure 10 shows the Cu element profile through thickness direction of the Cr-doped TiO<sub>2</sub> film in the case of  $N_{\text{top}} = 7$  by the XPS analysis. XPS spectra of Cu 3p are detected. In this XPS analysis, the sputtering rate is about 0.8 nm/min. It is seen that the intensity of Cu is increased dramatically from about 600 nm in this case. It alludes to that the basis copper disc is at the depth of 600 nm, that is, the thickness of the TiO<sub>2</sub> film is 600 nm. In this calculation, the weight of Cr has been ignored since Cr was doped in top layer only.

To verify the effect of photoresponse extension of TiO<sub>2</sub> to the visible spectrum for  $N_{\text{top}} = 7$ , Figure 11 shows the

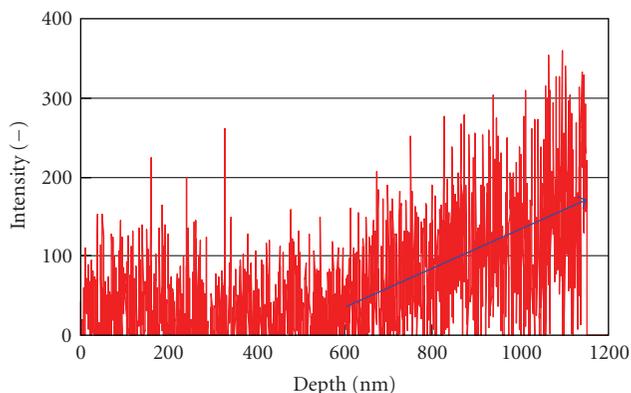


FIGURE 10: Cu element profile through thickness direction of the Cr-doped TiO<sub>2</sub> film under the condition of  $N_{\text{top}} = 7$  by XPS analysis.

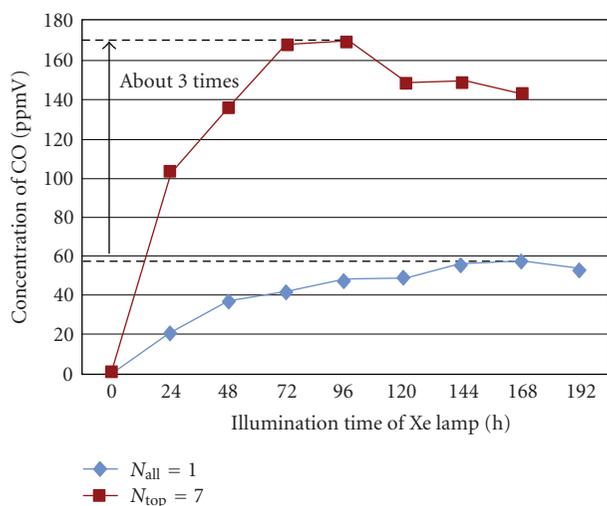


FIGURE 11: Comparison of concentration change of CO by CO<sub>2</sub> reforming with illumination time of Xe lamp without UV light of 72 hours for  $N_{\text{all}} = 1$  and  $N_{\text{top}} = 7$ .

concentration change of product by CO<sub>2</sub> reforming with illumination time of Xe lamp without UV light. The data for  $N_{\text{all}} = 1$  under  $R = 70$  wt% is also shown in this figure for comparison. Although CH<sub>4</sub> is produced from the experiment for  $N_{\text{top}} = 7$ , the concentration is below 10 ppmV. Therefore, Figure 11 shows the concentration of CO only. It shows that the peak value of concentration of CO for  $N_{\text{top}} = 7$  is about 3 times as large as that of  $N_{\text{all}} = 1$ . This proves that in the case of  $N_{\text{top}} = 7$ , the photoresponsibility of visible spectrum is also promoted by the increase in the amount of TiO<sub>2</sub> and the converted Cr ion-like Cr<sup>3+</sup> brought by encouragement of reduction performance of photocatalyst. Since the concentration of product under the illumination without UV light is lower than the concentration of product under the illumination with UV light, the effect of preventing the recombination of electron and hole is bigger than the realization of photoresponsibility of visible spectrum in the case of  $N_{\text{top}} = 7$ . However, the concentration of product for  $R = 0$  wt% is at such a low level as shown in Figures 5 and 6.

So, it can be concluded that CO<sub>2</sub> reforming performance of TiO<sub>2</sub> is promoted dramatically by Cr doping. In the research by Ozcan et al. [39] which tried to extend the photoresponse extension of TiO<sub>2</sub> to the visible spectrum by Pt loading, the amount of product from CO<sub>2</sub> reforming with illumination of Xe lamp without UV light was 10<sup>4</sup> times less than what we produced that is, 1.89 mmol/g-catalyst. Therefore, Cr doping by sol-gel and dip-coating method is effective to promote the CO<sub>2</sub> reforming performance of TiO<sub>2</sub>.

## 4. Conclusions

Based on the above experimental results and discussion, the following conclusions can be drawn.

- (i) For the highest actual doping amount of Cr and the best CO<sub>2</sub> reforming performance, the optimum  $R$  when  $N = 1$  is 70 wt% under the experimental conditions in this study.
- (ii) When  $N = 1$ ,  $R$  is also confirmed to be equal to 70 wt% to achieve the highest photoresponse extension of TiO<sub>2</sub> to the visible spectrum.
- (iii) The CO<sub>2</sub> reforming performance of Cr-doped TiO<sub>2</sub> film is promoted with the increase in  $N$ , especially under the coating condition of  $N_{\text{top}}$ .
- (iv) The photoresponsibility of visible spectrum of Cr-doped TiO<sub>2</sub> film as well as CO<sub>2</sub> reforming performance both are promoted in the case of  $N_{\text{top}} = 7$ .
- (v) It has been proved that Cr doping by sol-gel and dip-coating method is an effective way, comparing with Pt loading, to promote the CO<sub>2</sub> reforming performance with TiO<sub>2</sub>.

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