

VOCs Removal by Oxidation/Reduction Reaction of Cu-Doped Photocatalyst

K. W. Nam, H. R. Jeong, and S. H. Ahn

Abstract—Photocatalytic TiO_2 is widely used in many devices and applications in our lives and its usefulness has been significantly evaluated. Nevertheless, as has been demonstrated, TiO_2 has low efficiency as it only reacts in the UV-A region. In order to address this problem, this study attempted to develop photocatalytic materials that can be used in many situations by doping a relatively low energy gap. The photoactive and the photocatalyst characteristics were evaluated to develop a photocatalyst. The photoactive characteristic was analyzed with the FT/IR using TCE. While pure TiO_2 showed photoactivity only in the UV-A region, Cu/TiO_2 showed photoactivity in both the UV region and the visible region. Unlike pure TiO_2 , dichloroacetyl chloride (DCAC) was not found on the detected reaction product with Cu/TiO_2 photocatalytic reaction. At oxidation, the degradation of TiO_2 was greater than that of Cu/TiO_2 . However, the degradation of Cu/TiO_2 was greater than that of TiO_2 at reduction.

Index Terms—Cu-doped photocatalyst, oxidation/reduction, volatile organic compounds (VOCs).

I. INTRODUCTION

Photocatalytic material, TiO_2 , reacts in UV light (200~380 nm), and has the characteristic of degrading volatile organic compounds (VOCs) [1]. This can effectively absorb short wavelength UV light because of the large band gap of 3.0~3.2 eV. However, less than 5% of UV light from the sun reaches the earth's surface [2]. For this reason, with the TiO_2 photocatalyst, it is difficult to expect a large effect on the degradation of VOCs. A real-life application has many problems because the photodegradation reactions of photocatalytic materials do not occur where there is no sunlight. In order to address this problem, TiO_2 reduces the band gap with the doping of a variety of materials, and attempts have been made to change the position of the valence band and the conduction band [3]. For this, many researchers use the transition metal as a doping material [4].

Among the various transition metals, doped Cu forms Cu compounds. Cu compounds can react in the visible light zone (380~800 nm) as a narrow band (2.0~2.2 eV). In the case of Cu oxide, electrons that are generated from light cannot be utilized, and we can determine the oxidation and reduction

reaction mechanism of Cu oxide because of the phenomenon of the reduction to copper [5]. TCE, a volatile organic compound, is an environmental pollutant, and is commonly used as an industrial solvent. TCE is an effective solvent for a variety of organic materials. TCE solvents have various applications in the chemical, pharmaceutical, oil, and gas industries, including in chemical syntheses and purification processes. They are suspected to be carcinogenic pollutants and the increase in TCE usage may therefore affect the air, soil, and water [6].

This study was evaluated by TCE degradation about the oxidation reaction and the reduction reaction using TiO_2 sol and Cu doped TiO_2 sol.

II. MATERIALS AND EXPERIMENTAL METHOD

The photocatalytic material used in the present study is anatase TiO_2 , which has excellent light absorbing properties [7]. The manufacturing processes of the TiO_2 sol are as follows. First, titanium propoxide, distilled water, ethanol, and acid catalyst were mixed. The mixture was then stirred for 60 minutes at 70~80 °C. TiO_2 was then added and the mixture was prepared by stirring at room temperature for 30 minutes [8], [9]. The amounts of TiO_2 used were 1.5 wt.% and 3.0 wt.%. The manufacturing process of the Cu/TiO_2 sol is the same as that of TiO_2 . Cu/TiO_2 sol was used as a doping material with a Cu precursor, copper acetylacetonate. This was prepared by enclosing the form on the TiO_2 with Cu of a colloid state. The amount of Cu and TiO_2 used is 1.9 wt.% and 3.0 wt.%, respectively. Fig. 1 and Fig. 2 show the flow chart of the manufacturing processes of TiO_2 sol and Cu/TiO_2 sol, respectively.

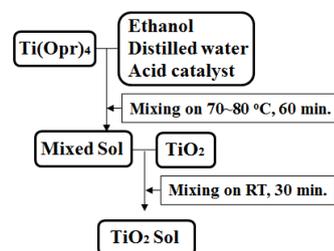


Fig. 1. Manufacture process of TiO_2 sol.

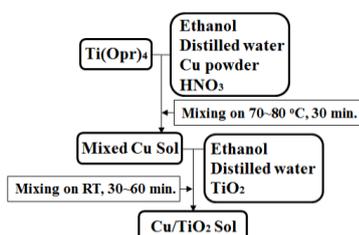


Fig. 2. Manufacture process of Cu/TiO_2 sol.

Manuscript received April 5, 2016; revised July 18, 2016. This work (Grants No. C0268714) was supported by Business for Academic-industrial Cooperative establishments funded Korea Small and Medium Business Administration in 2015.

K. W. Nam is with Pukyong National University, Busan, 48547 Korea (e-mail: namkw@pknu.ac.kr).

H. R. Jeong is with Prepoll Co. Ltd., Busan, 46719 Korea (e-mail: prepoll5208@gmail.com).

S. H. Ahn is with Jungwon University, Chungbuk, 28024 Korea (e-mail: shahn@jwu.ac.kr).

The materials for the coating of a photocatalyst sol were used with a glass plate and a nonwoven fabric of $60 \times 25 \times 1$ mm. The glass plate and the nonwoven fabric were used to observe the photoreaction and the color transition, respectively. The glass plate and the nonwoven fabric were dried in a drying oven for 40 minutes at 100°C after dip coating with SiO_2 sol (20 wt.%) in order to prevent deterioration due to the photocatalytic reaction of TiO_2 and Cu/TiO_2 . Thereafter, the glass plate and the nonwoven fabric were coated with TiO_2 sol and Cu/TiO_2 sol; these were then formed into TiO_2 and Cu/TiO_2 samples by drying for 10 minutes at 100°C . The glass plate and the nonwoven fabric were coated with 0.1g and 1.0 g, respectively.

The characteristics of TiO_2 and Cu/TiO_2 were analyzed using Transmission electron microscopy (TEM), X-ray diffractometer (XRD), and energy dispersive x-ray spectroscopy (EDS). The powder state and crystals were observed using TEM (JEOL, JEM-2010). The structures of the crystals were analyzed using XRD (PHILIPS, X'Pert-MPD System). The components were determined using EDS (HITACHI, S-2700).

The active evaluation of the oxidation reaction and the reduction reaction was measured using a Fourier transform infrared spectroscopy (FT/IR) (JASCO, FT/IR4100) [10]. At this time, the two light sources of UV-A 20W (320~380 nm) was used. In addition, a fluorescent lamp 27W (380~800 nm) was used for the active evaluation of the visible light region. For the active evaluation by the oxidation reaction, the sample is placed into a reaction vessel of 100 mL and tightly sealed. The distance of the light source to the sample is 50 mm, and the sacrificial reagents used were TCE at a concentration of 850 ppm. On the other hand, for the active evaluation of the reduction reaction, TiO_2 was oxidized for 3 hours, and Cu/TiO_2 was oxidized for 1 hour and 3 hours. The evaluation method is the same as that for the oxidation reaction.

The photoreaction of TiO_2 and Cu/TiO_2 was measured with a light absorbing reaction using an ultraviolet-visible spectrometer (JASCO, V670). The active analysis of the photocatalytic material was measured using the FT/IR by injecting about $0.3 \mu\text{L}$ of 850 ppm of TCE in the reaction vessel. The concentration is measured in the area of the spectrum, and the reaction process in the vessel can be seen as a change in the spectrum.

III. RESULTS AND DISCUSSION

A. Particles and Composition Analysis

TiO_2 sol and Cu/TiO_2 sol are dried and made into a powder. Fig. 3 shows an observation of the powder by TEM, wherein Fig. 3(a) and 3(c) present the particles, and Fig. 3(b) and 3(d) show the crystals. The size of the TiO_2 particles shown in Fig. 3(a) is about 20 nm. The Cu/TiO_2 in Fig. 3(c) shows a shape that is surrounded by particles of a diameter of about 2 nm around the TiO_2 . Compared to Fig. 3(a), the small particles show a form surrounding the periphery of TiO_2 . The transition metal-doped crystal shown in Fig. 3(d) is clearer than the crystals shown in Fig. 3(b).

Fig. 4 shows the structure of TiO_2 according to the XRD analysis, illustrating the reflection intensity due to the Cu-K α

radiation of TiO_2 . The maximum intensity of the anatase crystalline structure appeared at 25.3° , and also appeared at 37.8° , 48.0° , 54.2° , 55.1° , and 62.6° . However, while Cu/TiO_2 was detected the anatase TiO_2 , the crystal structure of Cu was not detected. It is determined that the X-ray is not diffracted since the Cu particles are fine (about 2 nm). Cu/TiO_2 was analyzed to identify the Cu component using EDS.

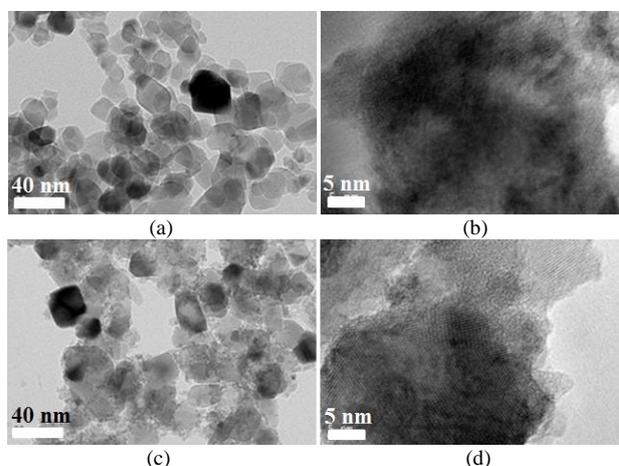


Fig. 3. TEM analysis of TiO_2 and Cu/TiO_2 , (a) particle of TiO_2 , (b) crystal of TiO_2 , (c) particle of Cu/TiO_2 , (d) crystal of Cu/TiO_2 .

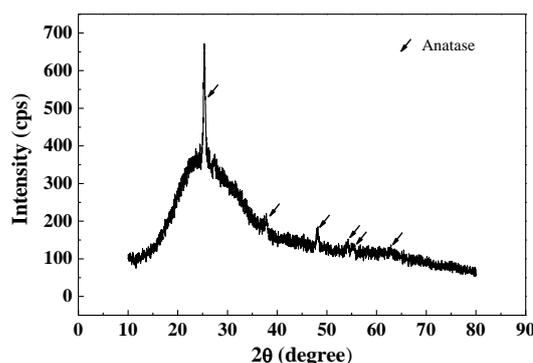


Fig. 4. X-ray diffraction pattern of TiO_2 .

Table I and Table II show the components of TiO_2 and Cu/TiO_2 , respectively, using EDS analysis. Ti of 34.08 wt.% and O of 65.92 wt.% were detected in TiO_2 , while Ti of 25.70 wt.%, O of 36.93 wt.%, and Cu of 37.37 wt.% were detected in Cu/TiO_2 . It can therefore be seen that small particles of Cu occur around anatase TiO_2 as shown in Fig. 3(c) and 3(d). It was confirmed that the Cu in Cu/TiO_2 is completely doped.

TABLE I: INGREDIENT ANALYSIS OF TiO_2

| Element | wt.% | at.% |
|---------|-------|-------|
| O | 65.92 | 85.28 |
| Ti | 34.08 | 14.72 |

TABLE II: INGREDIENT ANALYSIS OF Cu/TiO_2

| Element | wt.% | at.% |
|---------|-------|-------|
| O | 36.93 | 67.24 |
| Ti | 25.70 | 15.63 |
| Cu | 37.37 | 17.13 |

B. Absorbance

To confirm the wavelength region that can cause the photoreaction, TiO_2 (3 wt.%) and Cu/TiO_2 analyzed the ultraviolet visible (UV visible region). Fig. 5 shows an

analysis result. While it can be seen that the absorbance of TiO_2 gradually increases in the visible region, it abruptly increases in the UV-A region. The point at which the absorption reaction rapidly occurs is the boundary point of 380 nm in the visible region and the UV-A region. In other words, Catalytic reaction in the visible area almost didn't show up at TiO_2 . On the other hand, the absorbance of Cu/TiO_2 was much smaller than that of TiO_2 in the visible light region of 450~800 nm, but was higher than TiO_2 in the visible light region and UV-A region under 450 nm. Thus, since the light reaction occurs even in the visible light region, Cu/TiO_2 is judged to be used as a photocatalyst.

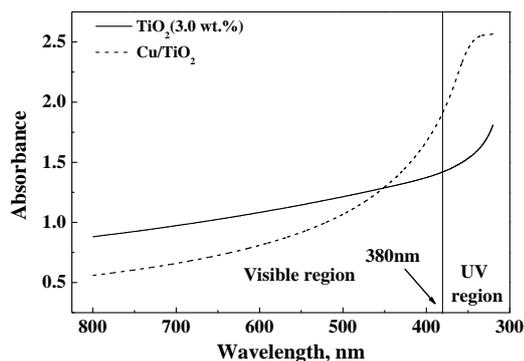


Fig. 5. Absorbance of TiO_2 and Cu/TiO_2 .

C. Oxidation Reaction Mechanism

Fig. 6 shows TCE degradation in the ultraviolet region. TCE was completely degraded in 7 minutes by TiO_2 . In the figure, after injection of the TCE, the shapes of the spectra measured in 0 minutes, 3 minutes, and 7 minutes can be compared. The TCE concentration in the reaction vessel reduces with the TCE degradation, and other reaction products were formed in the degradation process. The reaction products are dichloroacetyl chloride (DCAC) and phosgene (COCl_2) gas. The phosgene gas is again reacted with the water, and is degraded into CO_2 and HCl .

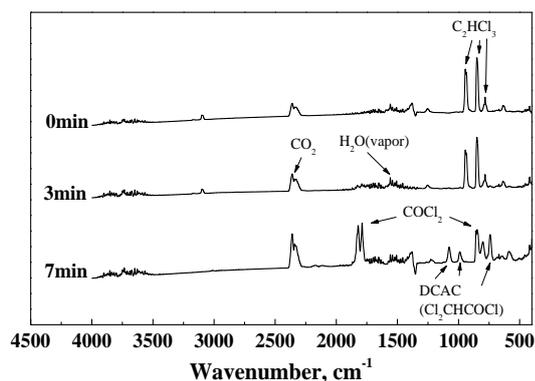


Fig. 6. TCE degradation process by TiO_2 under UV region.

Fig. 7 shows the degradation of TCE by TiO_2 in the visible light region. TCE takes a long time to degrade due to the low photoactivity of TiO_2 in the visible light region. Therefore, the TCE degradation process was observed for 180 minutes. A small amount of TCE is degraded in the visible light region. The reaction product is therefore not detected and only water vapor (H_2O) and CO_2 were detected.

Fig. 8 shows the degradation process by Cu/TiO_2 in the UV region. TCE was completely degraded in 60 minutes. DCAC was not detected in Cu/TiO_2 , and only phosgene gas was detected. Thus, the difference in the reaction products occurs due to the difference in the transport of holes and electrons according to the transition metal.

Fig. 9 shows the TCE degradation process by Cu/TiO_2 at the visible region. The oxidation reaction of Cu/TiO_2 in the visible light has low photoactivity. Therefore, the complete degradation of TCE is very slow and was observed for 180 minutes. The reaction products, DCAC and COCl_2 , were not detected and only water vapor (H_2O) and CO_2 were detected. This is the same as the visible reaction of TiO_2 .

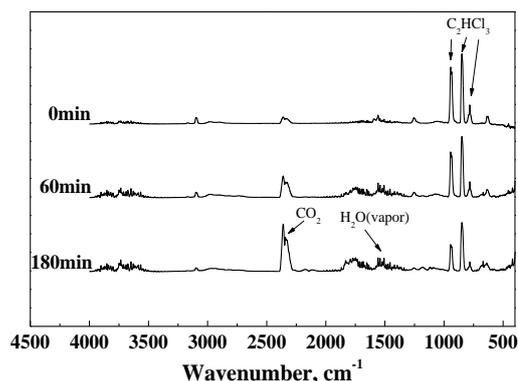


Fig. 7. TCE degradation process by TiO_2 under visible region.

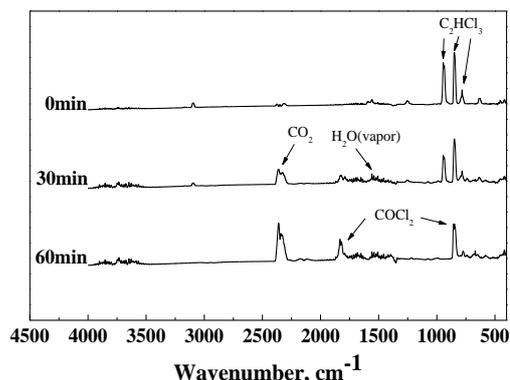


Fig. 8. TCE degradation process by Cu/TiO_2 under UV region.

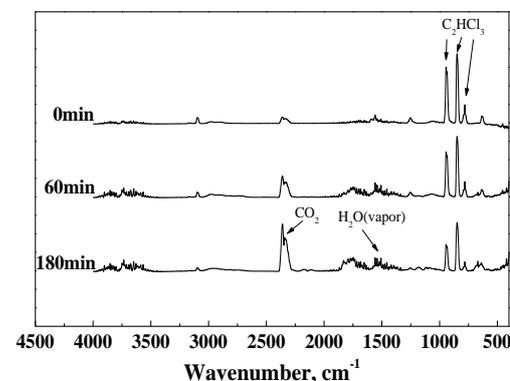


Fig. 9. TCE degradation process by Cu/TiO_2 under visible region.

D. Reduction Reaction Mechanism

Fig. 10 shows the TCE degradation process under a dark atmosphere using oxidized Cu/TiO_2 for 60 minutes in a UV-A region. The figure indicates the reduction reaction of Cu/TiO_2 .

The reaction product detected was water (H₂O), and the other reaction product was not observed. However, TCE was slightly degraded with time. As such, it is determined that TCE degradation is caused by the reduction. That is, the electron and the hole of CuO are formed by reduction. Electrons and holes are made of OH radicals, and degrade the TCE. The OH radical performs a catalytic role in the process of reduction. However, the TCE degradation decreased according to the passage of time. This is because the amount of Cu is limited. This reduces the speed of the formation of the electron and hole, and TCE degradation decreased since the CuO is reduced in the reduction reaction. In other words, the TCE degradation of the reduction reaction is in accordance with the formation and movement of the electrons and holes.

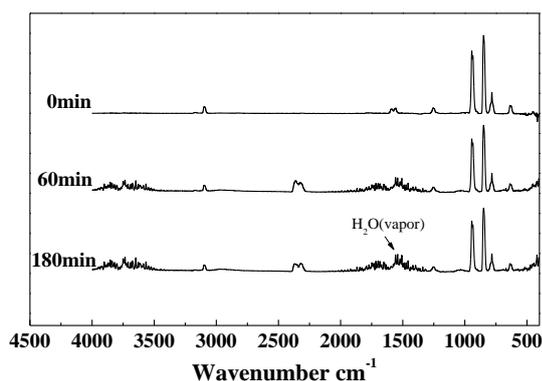


Fig. 10. TCE degradation process under dark atmosphere using oxidized Cu/TiO₂ under UV region.

E. TCE Degradation of TiO₂ and Cu/TiO₂

TCE degradation was analyzed using FT/IR according to the oxidation reaction of TiO₂ and Cu/TiO₂ under UV-A. Fig. 11 shows the TCE degradation of TiO₂ and Cu/TiO₂ by oxidation reaction under UV-A (320~380 nm). TCE was completely degraded (100%) in about 9 and 7 minutes by TiO₂ at 1.5 wt.% and 3.0 wt.%, respectively. However, Cu/TiO₂ was completely degraded (100%) in approximately 60 minutes. The degradation of the Cu/TiO₂ was low due to the Cu surrounding the TiO₂. The light energy reaching Cu/TiO₂ is small compared to that reaching TiO₂.

Fig. 12 shows the TCE degradation for the dark reaction (reduction reaction) of Cu/TiO₂ in a dark region without light energy. Although a small amount of TCE was degraded, Cu/TiO₂ was degraded by the dark reaction (reduction reaction).

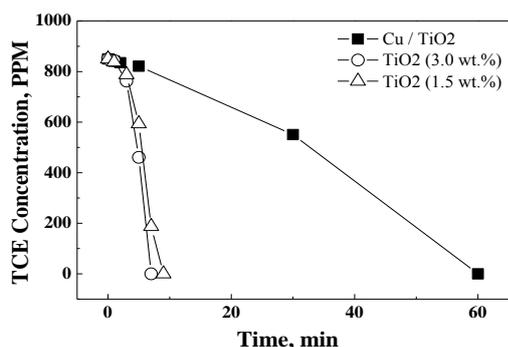


Fig. 11. TCE Resolution of TiO₂ and Cu/TiO₂ by oxidation reaction under UV region.

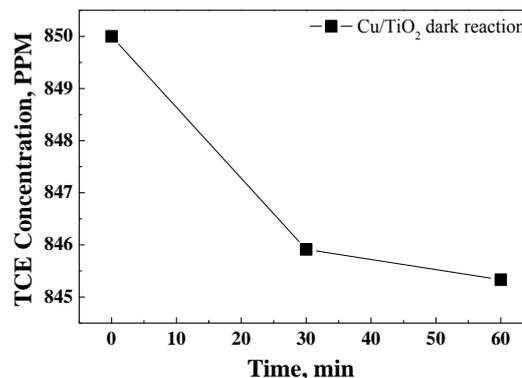


Fig. 12. TCE Resolution of Cu/TiO₂ by dark reaction under dark region.

Fig. 13 shows the degradation of TiO₂ and Cu/TiO₂ for the oxidation reaction in the visible region (380~800 nm). A 20 W fluorescent lamp was used as the visible light. The degradation of the visible light region was compared at 30 minutes because degradation takes longer in the visible light region than in the UV-A region. TCE was degraded by about 4.2% and 8.5% with 1.5 wt.% and 3.0 wt.% TiO₂, respectively. On the other hand, TCE was degraded by 9.3% with Cu/TiO₂. The greater Cu/TiO₂ degradation is because electrons are generated more easily in the visible area of a large wavelength (λ) since the band gap of the transition metal Cu (2.0~2.2 eV) is narrower than TiO₂ (3.0~3.2 eV).

Fig. 14 shows the TCE degradation for the reduction reaction in a dark atmosphere using TiO₂ and Cu/TiO₂ oxidized in the UV-A region. Degradation by reduction reaction in the dark atmosphere was compared at 30 minutes. The TCE degradation of TiO₂ at the oxidation reaction of the UV-A region is much better than that of Cu/TiO₂. However, the degradation by the reduction reaction of TiO₂ and Cu/TiO₂ was low because the reaction rate is slower than the oxidation reaction. Reduction of oxidized TiO₂ (3 wt.%) and Cu/TiO₂ for 3 hours showed a degradation of about 5.8% and 12.0%, respectively. The degradation of Cu/TiO₂ was about 2 times greater than that of TiO₂. Degradation of the oxidized Cu/TiO₂ for 1 hour showed about 6.6%, showing a slightly better degradation than the oxidized TiO₂ (3 wt.%) for 3 hours. Further, the Cu/TiO₂ oxidized for 3 hours was degraded about 2 times more than that of Cu/TiO₂ oxidized for one hour. Thus, Cu/TiO₂ was superior to TiO₂ (3 wt.%) in the degradation of the reduction reaction. In the same Cu/TiO₂, the Cu/TiO₂ oxidized for a long time was superior to that oxidized for a short time.

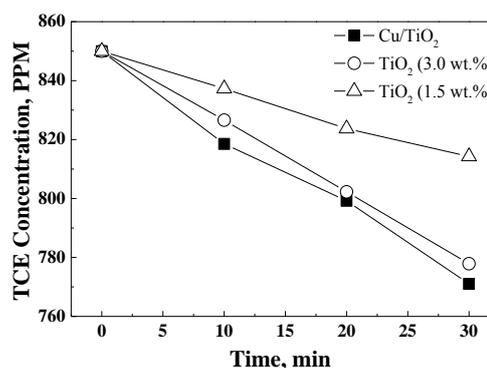


Fig. 13. TCE Resolution of TiO₂ and Cu/TiO₂ by oxidation reaction under visible region.

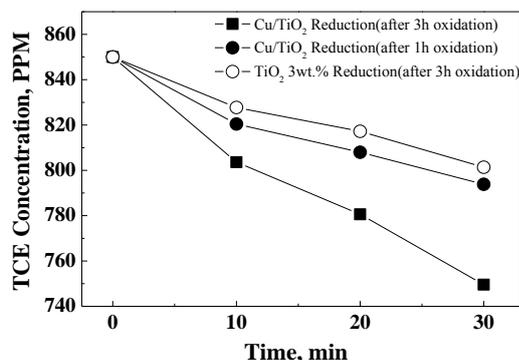


Fig. 14. TCE Resolution by reduction reaction under dark atmosphere using oxidized TiO₂ and Cu/TiO₂ under UV region.

F. Colour Change of Cu/TiO₂ by Oxidation and Reduction Reactions

Because it is difficult to observe color change on the glass plate, felt was placed under the glass to help in the macroscopic observation of the reaction of Cu/TiO₂ by UV-A. Fig. 15 shows the color change due to the oxidation and reduction of Cu/TiO₂. Fig. 15(a) and 15(b) show the color change due to oxidation and reduction reactions, respectively. The color change shown in Fig. 15(a) was observed for 60 minutes. It can be seen that the color becomes black with the increase in oxidation reaction time. On the other hand, it can be seen that the color in Fig. 15(b) brightened with the increase of the time of reduction reaction in a dark area after oxidation reaction for 60 minutes. Oxidation reaction shows a faster color change by up to 60 minutes. However, the reduction reaction took 300 minutes, which was five times slower than the oxidation reaction. In the oxidation reaction, the color of Cu/TiO₂ changed because Cu was oxidized to CuO. It is determined that the reduction reaction made an ionization according to the reduction from oxidized CuO.

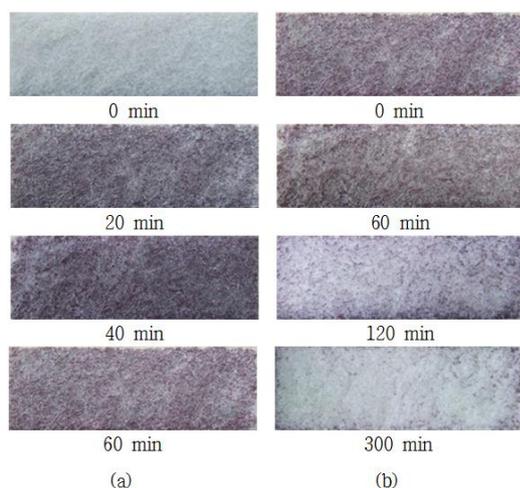


Fig. 15. Color transition of Cu/TiO₂ by (a) oxidation and (b) reduction.

Fig. 16 shows the TCE degradation with time of the oxidation and reduction reactions of the non-woven fabric. This also shows the color change of the non-woven fabric seen in Fig. 15. These were carried out the oxidation reactions for 60 minutes, followed by the reduction reaction for 300 minutes after oxidation reaction of 60 minutes. In oxidation reaction, the TCE was degraded according to change to black. On the other hand, the TCE was degraded according to

change to brighten in the reduction reaction. However, the degradation of the oxidation reaction was superior to that of the reduction reaction. It is determined that the TCE is degraded by OH radicals generated from the reduction reaction of CuO. The oxidation reaction of Cu/TiO₂ coated on the nonwoven fabric in UV-A was carried out for 60 minutes. However, TCE was degraded by a concentration of 395 ppm and a concentration of 455 ppm remained. This was a slower degradation rate in spite of a large amount of coating of 10 times than the glass, as shown in Fig. 11. Cu/TiO₂ was coated on the inside of the nonwoven fabric. However, the light energy does not reach the inner parts of the nonwoven fabric, and the oxidation reaction took place on the surface. On the other hand, the reduction reaction degraded TCE by a concentration of about 150 ppm. TCE was degraded by the dark reaction of Cu/TiO₂ in the dark atmosphere. That is, the surface of nonwoven fabric degraded the TCE by the reduction of the oxidized CuO, and the inside is degraded by dark reaction. Therefore, the reduction reaction of Cu/TiO₂ with the coating on the non-woven fabric was superior to the TCE degradation than the coating on the glass.

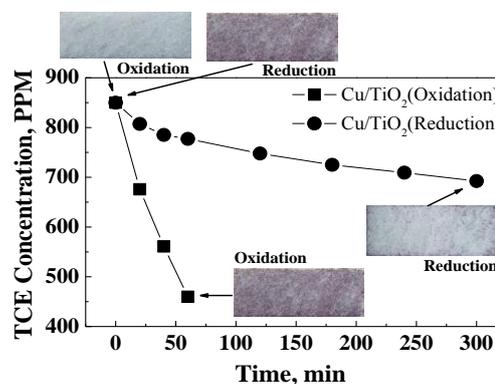


Fig. 16. TCE resolution of oxidation and reduction due to color transition.

IV. CONCLUSIONS

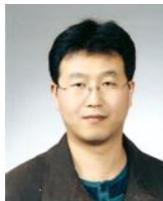
The photoactive characteristics of TiO₂ sol and Cu doped Cu/TiO₂ sol were evaluated using UV-A and visible light. Cu/TiO₂ is surrounded by Cu particles of a diameter of about 2 nm around the TiO₂. Cu/TiO₂ showed absorption reaction in the UV-A region and some part of the visible region. In the oxidation reaction of the ultraviolet region, TiO₂ was detected in the toxic reaction product (DCAC) in the TCE degradation process, and Cu/TiO₂ was not detected in DCAC. However, the TCE degradation of TiO₂ is faster than that of Cu/TiO₂. In the reduction reaction, oxidized Cu/TiO₂ was not detected with any other reaction product except water (H₂O). The TCE degradation of oxidized Cu/TiO₂ was faster than that of oxidized TiO₂. This is because the OH radical was made according to the formation and movement of electrons and holes. The TCE degradation of Cu/TiO₂ was superior to that of TiO₂ in the visible region. This is because electrons are generated more easily in the visible area since the band gap of the transition metal Cu (2.0~2.2 eV) is narrower than that of TiO₂ (3.0~3.2 eV). Even though the TCE degradation of Cu/TiO₂ is worse than that of TiO₂ in the oxidation reaction, oxidized Cu/TiO₂ exhibited better degradation properties than TiO₂ in the reduction reaction.

REFERENCES

- [1] X. Huang and Z. Liu, "Heterogeneous deposition of Cu₂O nanoparticles on TiO₂ nanotube array films in organic solvent," *Journal of Nanomaterials*, vol. 51, pp. 648-655, 2013.
- [2] H. K. Yoo, J. K. Lee, K. H. Hwang, D. S. Seo, H. S. Kang, H. S. Bae, and W. W. Kim, "Characteristics of Ag Ions photoadsorption using photocatalytic TiO₂ nanocrystalline powder," *Journal of the Korean Ceramic Society*, vol. 39, pp. 535-539, 2002.
- [3] K. Y. Song, Y. T. Kwon, G. J. Choi, and W. I. Lee, "Photocatalytic activity of Cu/TiO₂ with oxidation state of surface-loaded copper," *Bull. Korean Chem. Soc.*, vol. 20, pp. 957-960, 1999.
- [4] J. B. Varley, A. Janotti, and C. G. Van de Walle, "Mechanism of visible-light photocatalysis in nitrogen-doped TiO₂," *Advanced Materials*, vol. 23, pp. 2343-2347, 2011.
- [5] J. H. Kim, "Photocatalysts for hydrogen production from solar water splitting," *Clean Technology*, vol. 19, pp. 191-200, 2013.
- [6] M. G. Ha, P. A. Ghorpade, and J. J. Kim, "Trichloroethylene(TCE) removal capacity of synthesized calcium sulfoaluminate minerals in hydrated cement-based materials," *Journal of the Korean Society of Civil Engineers*, vol. 33, pp. 1463-1469, 2013.
- [7] M. J. Hwang, T. B. Nguyen, and K. S. Ryu, "A study on photocatalytic decomposition of methylene blue by crystal structures of anatase/rutile TiO₂," *Chem. Eng.*, vol. 23, pp. 148-152, 2012.
- [8] Y. I. Lee, M. H. Jung, and M. C. Lee, "Improvement of photo-stability for p-Aramid fibers by SiO₂/TiO₂ sol-gel method," *Textile Coloration and Finishing*, vol. 25, pp. 172-180, 2013.
- [9] S. Sakka, "Handbook of sol-gel science and technology: Processing, characterization and applications," Kluwer Academic Pub., 2004.
- [10] TS Science, *FT/IR Spectrometer*, 2005.



K. W. Nam was born on November 11, 1958 in Changwon. He graduated from Yokohama National University in Japan. He is working with the Department of Materials Science and Engineering, Pukyong National University, Busan, Korea since 1990. He has an interest in strength of ceramics, development and evaluation of organic/inorganic hybrid coating solution.



J. R. Jeong was born on September 14, 1973 in Geochang. He graduated on February 2015 from Pukyong National University. He is now developing and producing products that are using filter for home appliances. Especially, He has been producing eco-friendly products. He is currently working as CEO of Prepoll Co. Ltd.



S. H. Ahn was born on February 10, 1966 in Busan. He graduated from Yokohama National University in Japan. He is working with the Department of Mechatronics Engineering, Jungwon University, Goesan-gun, Chungbuk, Korea. He has an interest in various materials and its characteristic evaluation.