Promoting Effect of MgO in the Photodegradation of Methylene Blue Over MgO/MWCNT/TiO₂ Photocatalyst

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Abstract For the present paper, we prepared MgO/MWCNT/TiO₂ photocatalyst by using multi-walled carbon nanotubes (MWCNTs) pre-oxidized by *m*-chlorperbenzoic acid (MCPBA) with magnesium acetate tetrahydrate (Mg(CH₃COO)₂·4H₂O) and titanium *n*-butoxide (Ti{OC(CH₃)₃}₄) as magnesium and titanium precursors. The prepared photocatalyst was analyzed by X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) analysis. The decomposition of methylene blue (MB) solution was determined under irradiation of ultraviolet (UV) light. The XRD results show that the MgO/MWCNT/TiO₂ photocatalyst have cubic MgO structure and anatase TiO₂ structure. The porous structure and the TiO₂ agglomerate coated on the MgO/MWCNT composite can be observed in SEM images. The Mg, O, Ti and C elements can be also observed in MgO/MWCNT/TiO₂ photocatalyst from EDX results. The results of photodegradation of MB solution under UV light show that the concentration of MB solution decreased with an increase of UV irradiation time for all of the samples. Also, the MgO/MWCNT/TiO₂ photocatalyst has the best photocatalytic activity among these samples. It can be considered that the MgO/MWCNT/TiO₂ photocatalyst had a combined effect, the effect of MWCNT, which could absorb UV light to create photo-induced electrons (e⁻), and the electron trapping effect of MgO, which resulted in an increase of the photocatalytic activity of TiO₂.

Key words MWCNT, magnesium oxide, titanium *n*-butoxide, photodegradation.

1. Introduction

Photocatalytic purification of water and air has been considered as one the promising methods. Particularly, the photocatalytic purification of water by irradiated TiO₂ particles has proven to be a very effective process which leads to complete mineralization of pollutants.^{1,2)} TiO₂ having a crystal form of anatase is expected as the most promising photocatalyst. However, the use of TiO₂ as photocatalysts is limited mainly to the recombination of the generated photo-holes and photo-electrons. Photocatalysis involves the oxidation of a chemical by photo-holes from the semiconductor, so every recombination event involves the loss of holes that might otherwise have promoted degradation. Therefore, the victoria transfer of photogenerated electrons and holes between the valence and conduction bands of semiconductors is important to photocatalysis.

Various methods have been reported to improve photocatalytic efficiency by the modification of surface or bulk properties, i.e. doping, codeposition of metals, surface chelating, mixing of two semiconductors, coating of an

insulating oxide layer, etc.³⁻⁷⁾ In our previous works,⁸⁻¹⁰⁾ the photocatalytic efficiency of TiO₂ could be increased by introduced multi-walled carbon nanotube (MWCNT) to prepare MWCNT/TiO₂ composites. MWCNT is 1D carbon-based ideal molecule with the nano cylinders, which can conduct electricity at room temperature with essentially no resistance. This phenomenon is known as ballistic transport,^{11,12)} by which the electrons are considered to move freely through the structure, without any scattering from atoms or defects. While the electrons formed by the UV irradiation migrate to the surface of MWCNT, they are easily transported into conduction band (CB) of TiO₂ which are bound with MWCNT. Hence, the increased amount of generated photo-electrons could be decreased the high rate of electron/hole pair recombination, which reduces the quantum yield of the TiO₂ process.

Magnesium oxide (MgO) is a promising material with potential applications in a variety of field. Recently, it has been exploited as catalyst support, reinforcing agent, and a component in superconductors.¹³⁻¹⁵⁾ Furthermore, MgO is a typical wide bandgap insulator; thus, the electronic and optical properties of bulk MgO has been intensively studied.¹⁶⁻¹⁸⁾ Tada et al. showed the coating of SiO₂ or MgO on TiO₂ results in threefold increase in catalytic activ-

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ity of TiO_2 for the degradation of cationic surfactants.^{19–22)} Bandara et al. showed that the coating of MgO on TiO_2 increases chlorophenol degradation by three to four times compared to uncoated TiO_2 .²³⁾

In this report, we combined both advantages of introduced MWCNT and MgO to design an effective photocatalyst (MgO/MWCNT/TiO_2) for methylene blue (MB, $\text{C}_{16}\text{H}_{18}\text{N}_3\text{S}\cdot\text{Cl}\cdot 3\text{H}_2\text{O}$) decomposition. The magnesium acetate tetrahydrate ($\text{Mg}(\text{CH}_3\text{COO})_2\cdot 4\text{H}_2\text{O}$) and titanium *n*-butoxide ($\text{Ti}\{\text{OC}(\text{CH}_3)_3\}_4$) were used as MgO and TiO_2 precursor. The properties of prepared photocatalyst (MgO/MWCNT/TiO_2) were analyzed by X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) analysis. The MB decomposition was determined under irradiation of UV light.

2. Experimental Procedure

2.1 Materials

The titanium *n*-butoxide (99%) as titanium alkoxide precursor to form the TiO_2 was purchased from Acros Organics, New Jersey, USA. Crystalline MWCNT (95.9%) powder with diameter of 20 nm and length of 5 μm was purchased from Carbon Nano-material Technology Co., Ltd, Korea. For the oxidization the surface of MWCNT, *m*-chlorperbenzoic acid, used as an oxidized reagent, was also purchased from Acros Organics, New Jersey, USA. Benzene (99.5%), used as solvents, was purchased from Samchun Pure Chemical Co., Ltd, Korea. Magnesium acetate tetrahydrate (99%) were used as organometallic compounds precursors which purchased from Daejung Chemicals & Metals Co., Ltd, Korea. The methylene blue was used as analytical grade which purchased from Duksan Pure Chemical Co., Ltd, Korea. The pure TiO_2 and MWCNT/TiO_2 photocatalysts are used as compare materials for photo-degradation effect of MB solution. The pure TiO_2 , with anatase structure, is obtained from Duksan Pure Chemical Co., LTD, Korea. The MWCNT/TiO_2 photocatalyst was prepared in our previous work.¹⁰⁾

2.2 Synthesis of MgO/MWCNT/TiO_2 photocatalyst

Due to the MWCNT is very stable, it needs to be treated with strong acids to introduce active function groups on their surface. We took 1.0 g MCPBA melted in 60 mL Benzene to prepare oxidizing agent. And then 0.2 g MWCNT was put into the oxidizing agent. The mixture was stirred with a magnet for 6 h at 343 K. Then the MWCNT was dried at 373 K and spared.

Magnesium acetate tetrahydrate was melted in distilled water to prepare 0.01 M solution. The oxidized MWCNT was put into a certain volume of solution. And then the solution was homogenized at 343 K for 5 h using a shaking water bath (Lab house, Korea) with a shaking rate of 120

rpm/min. After reaction for 5 h, the solution was transformed to the MgO/MWCNT gels, and these gels were heat treated at 873 K for 1 h with a heating rate of 279 K/min. Finally, MgO/MWCNT composite was obtained.

On the other hand, 2 mL of TNB was dissolved in 50 mL of benzene to get the sol. The MgO/MWCNT composite was put into the sol, after homogenized at 343 K for 5 h using a shaking water bath (Lab house, Korea) with a shaking rate of 120 rpm/min, the MgO/MWCNT/TiO_2 gels were obtained. These gels were heat treated at 873 K for 1 h to form the MgO/MWCNT/TiO_2 photocatalyst.

2.3 Characterization

Synthesized MgO/MWCNT/TiO_2 photocatalyst was characterized by various techniques. XRD was used for crystal phase identification and estimation of the anatase-to-rutile ratio. XRD patterns were obtained at room temperature by using an X-ray generator (Shimata XD-D1, Japan) using $\text{CuK}\alpha$ radiation. SEM (JSM-5200 JOEL, Japan) used to observe the surface state and structure of MgO/MWCNT/TiO_2 photocatalyst was carried out. EDX was used to measure the elemental analysis of MgO/MWCNT/TiO_2 photocatalyst. The light absorption spectra of the samples were recorded with a UV-VIS spectrophotometer (Optizen POP, Mecasys Co., Ltd, Korea) in a range of 200–750 nm.

2.4 Photocatalytic activity of metal oxide/CNT catalysts

The photocatalytic activity of MgO/MWCNT/TiO_2 photocatalyst was taken out by decomposition of MB solution under irradiation of UV light. In an ordinary photocatalytic test performed at 25°C, 0.05 g photocatalyst was added to 50 mL of 1.0×10^{-5} mol/L MB solution and maintained in suspension by magnetic stirring. After stirring continuously in the dark for 2 h to ensure establishment of adsorption/desorption equilibrium of MB, the suspension was irradiated by UV lamp (20W, 365 nm, 1.2 mW/cm²) and it was treated as the starting point ($t = 0$) of the reaction, where the concentration of MB was designated as c_0 . At specific time (30 min, 60 min, 90 min and 120 min) intervals a certain volume of the sample was withdrawn and centrifuged to remove the catalyst before analysis. The concentration of MB (c) solution during the photocatalytic degradation reaction was monitored through measuring the absorbance of the solution samples with UV-VIS spectrophotometer at $\lambda_{\text{max}} = 660$ nm.^{24,25)}

3. Results and Discussion

3.1 Characterization results

Fig. 1 shows the X-ray diffraction patterns of MgO/MWCNT and MgO/MWCNT/TiO_2 photocatalysts. The strong (002) diffractions of the hexagonal graphite at 2θ

Fig. 1. The XRD patterns of MgO/MWCNT and MgO/MWCNT/TiO₂ photocatalysts.

of about 25.88° indicate that the graphite structure of CNT supports was not destroyed after deposition of MgO for MgO/MWCNT.²⁶⁾ However, the graphite structure cannot be observed in MgO/MWCNT/TiO₂ photocatalyst, due to the lower C content and the overlapping of diffraction peaks attributed to TiO₂. Apart from the (111) and (200) diffraction peaks of cubic MgO structure from the substrate (JCPDS: 04-0829), all recognizable reflection peaks, including (101), (004), (200) and (204), can be well indexed to the anatase TiO₂ structure (JCPDS: 21-1272). No reflection peaks from impurities (*i.e.*, unreacted Mg, other magnesium oxides or mixed oxides of magnesium and titanium) are observed, indicating the high purity of the products.

Fig. 2 shows the SEM images of MgO/MWCNT and MgO/MWCNT/TiO₂ photocatalysts. It can be observed that the MWCNT was homogeneously distributed with

Fig. 3. Photocatalytic activity of different samples evaluated by the decomposition of MB solution under UV light irradiation for 120 min.

MgO which has fluffy structure from the Fig. 1(a). From Fig. 2(b), the porous structure can be observed, and the TiO₂ agglomerate is coated on the MgO/MWCNT composite. EDX is carried out to probe the composition of the MgO/MWCNT and MgO/MWCNT/TiO₂ photocatalysts, as shown in Fig. 2(a) and (b), respectively. It reveals the presence of Mg, O and C, which confirms the existence of MgO and C particles in the MgO/MWCNT composite. Meanwhile, a new element Ti is observed in MgO/MWCNT/TiO₂ photocatalyst, which confirms not only the MgO and C particles are existed, but TiO₂ is also existed in MgO/MWCNT/TiO₂ photocatalyst.

3.2 Photocatalytic degradation of MB

Fig. 3 shows the photocatalytic activity of pure TiO₂, MWCNT/TiO₂, MgO/MWCNT and MgO/MWCNT/TiO₂

Fig. 2. SEM images and EDX spectra of MgO/MWCNT (a) and MgO/MWCNT/TiO₂ photocatalysts (b).

Fig. 4. Apparent first-order linear transform $-\ln(c/c_0)$ against $f(t)$ of MB degradation kinetic plots for different samples under irradiation of UV light.

photocatalysts evaluated by the decomposition of MB solution under UV light irradiation for 120 min. It has been indicated that the photocatalytic activity of MWCNT/TiO₂ is higher than that of pure TiO₂, due to the MWCNT can absorb UV light to create photo-induced electron (e^-) into the conduction band (CB) of the TiO₂ particles, thus increase the amount of electron.⁸⁻¹⁰ After UV light irradiation for 120 min, the photocatalytic activity of MgO/MWCNT is lower than that of pure TiO₂. Since the MgO have too high band gap to absorb UV light. As described above, when introduced with MWCNT, the MWCNT can absorb UV light to create photo-induced electron (e^-) into the conduction band (CB) of the MgO particles, thus MgO has photocatalytic activity. Furthermore, the MgO/MWCNT/TiO₂ photocatalyst exhibits the highest photocatalytic activity among all of samples.

The photodegradation experiments by UV light irradiation of MB solution follow the pseudo-first-order kinetics²⁷⁻²⁹) with respect to the concentration of dyestuff in the bulk solution (c):

$$-dc/dt = k_{app}c \quad (1)$$

Integration of this equation (with the restriction of $c = c_0$ at $t = 0$, with c_0 being the initial concentration in the bulk solution after dark adsorption and t the reaction time)

Table 1. The apparent kinetic constant (k_{app}) of pure TiO₂, MgO/MWCNT, MgO/MWCNT/TiO₂ and MWCNT/TiO₂

Samples	k_{app} (min ⁻¹)	R
Pure TiO ₂	3.1×10^{-3}	1
MgO/MWCNT	2.8×10^{-3}	0.9
MgO/MWCNT/TiO ₂	1.3×10^{-2}	4.2
MWCNT/TiO ₂	3.8×10^{-3}	1.2

Fig. 5. The schematic illustration of the mechanism of photocatalytic activity for MgO/MWCNT/TiO₂.

will lead to the following expected relation:

$$-\ln(c/c_0) = k_{app}t \quad (2)$$

where c and c_0 are the reactant concentration at time $t = t$ and $t = 0$, respectively, k_{app} and t are the apparent reaction rate constant and time, respectively. A plot of $-\ln(c/c_0)$ versus t for MB degradation with pure TiO₂, MgO/MWCNT, MgO/MWCNT/TiO₂ and MWCNT/TiO₂ photocatalysts is presented in Fig. 4. The value of k_{app} can be obtained directly from the slopes of the respective linear curves in the plot, which shows in Table 1. A combination factor (R) is defined as $R = k_{app}(\text{sample})/k_{app}(\text{TiO}_2)$ to quantify the combination effect, is also showed in Table 1. Pure TiO₂, MWCNT/TiO₂, MgO/MWCNT and MgO/MWCNT/TiO₂ photocatalysts give apparent rate constant of 3.1×10^{-3} , 3.8×10^{-3} , 2.8×10^{-3} and 1.3×10^{-2} , respectively. It can be indicated that the MgO/MWCNT/TiO₂ photocatalyst have best efficiency for photodegradation of MB solution. The introduction of MWCNT and MgO into matrix obviously creates kinetic combination effect in MB degradation with an increase in the rate constant by the combination factor of 4.2. It can be indicated that the rate for photodegradation of MB solution is 4.2 times than pure TiO₂.

Fig. 5 shows the mechanism of photocatalytic activity for MgO/MWCNT/TiO₂. Apart from the photocatalytic activity of TiO₂, the photocatalytic activity of MgO/MWCNT/TiO₂ photocatalyst can be consisted from three kinds of photocatalytic activities: the photocatalytic activity of MWCNT/TiO₂, the photocatalytic activity of MgO/MWCNT and the photocatalytic activity of MgO/TiO₂. In our previous works,^{30,32}) we described the mechanism of photocatalytic activity for MWCNT/TiO₂ photocatalyst detailedly. For the photocatalytic activity of MgO/MWCNT, since the MgO have too high band gap to absorb UV light. As described above, when introduced with MWCNT, the MWCNT can

absorb UV light to create photo-induced electron (e^-) into the conduction band (CB) of the MgO particles, thus MgO has photocatalytic activity. And the photocatalytic activity of MgO/TiO₂ can be showed in Fig. 5, when MgO/MWCNT/TiO₂ photocatalyst is exposed to light, TiO₂ particles absorb light to generate electron-hole pairs (reaction (3)).

Photoexcited electrons in the CB of TiO₂ particle are not energetic enough to inject into the CB of MgO particle, as the CB edge of MgO particle lies far above the CB level of TiO₂. Also the injection of energetic electrons (the hot carrier which has not relaxed to the CB of TiO₂ particle) from TiO₂ to CB of MgO particle can be ruled out considering the band gap energy and energy levels of both MgO (~9 eV) and TiO₂ (~3.1 eV).³³⁾

Nevertheless, electron deficient anion vacancies present on the MgO surface are capable of trapping these excited electrons.³⁴⁾ Those electrons trapped in electron defect sites may become localized in trap sites to form $[Mg^{2+}-O^{2-}]^-$ while photogenerated holes remained on the TiO₂ particles generate Ti-OH• species (reactions (4) and (5)). As a result, photogenerated negative and positive charges are widely separated and recombination is suppressed. The holes remain on the TiO₂ crystalline particles eventually participate for the oxidation of MB via direct reaction with the substrate or the formation of OH radicals and electrons trapped on MgO can react with molecular O₂ to form O₂•⁻ radicals which eventually oxidize MB as explained in Fig. 5.

4. Conclusion

X-ray diffraction, SEM, EDX analysis and spectrophotometer are employed to investigate the enhancement of photocatalytic activity of TiO₂ by MWCNT and MgO for degradation of MB solution under irradiation of UV light. The XRD results show that MgO/MWCNT/TiO₂ photocatalyst have cubic MgO structure and anatase TiO₂ structure. The porous structure and the TiO₂ agglomerate coated on the MgO/MWCNT composite can be observed from SEM images. And the Mg, O, Ti and C elements can be also observed from EDX results. According to the results of photodegradation of MB solution, apart from the effect of MWCNT, the MgO can also promote the photocatalytic activity for MWCNT/TiO₂ photocatalyst.

References

1. P. V. Kamat, *Chem. Rev.*, **93**, 267 (1993).
2. Y. Nakaoka and Y. Nosaka, *J. Photochem. Photobiol. A*, **110**, 299 (1997).
3. J. Zhao, T. Wu, K. Wu, K. Oikawa, H. Hidaka and N. Serpone, *Environ. Sci. Technol.*, **32**, 2394 (1998).
4. H. Park and W. Choi, *J. Phys. Chem. B*, **108**, 4086 (2004).
5. P. V. Kamat, *J. Phys. Chem. B*, **106**, 7729 (2002).
6. K. Nagaveni, M. S. Hegde, N. Ravishankar, G. N. Subbanna and G. Madrad, *Langmuir*, **20**, 2900 (2004).
7. Z. Zou, J. Ye, K. Sayama and H. Arakawa, *Nature*, **414**, 625 (2001).
8. M. L. Chen and W. C. Oh, *Analytical Science & Technology*, **21**, 229 (2008).
9. M. L. Chen, F. J. Zhang and W. C. Oh, *Analytical Science & Technology*, **21**, 553 (2008).
10. M. L. Chen, F. J. Zhang and W. C. Oh, *J. Kor. Ceram. Soc.*, **45**, 651 (2008).
11. J. C. Charlier, *Acc. Chem. Res.*, **35**, 1063 (2002).
12. X. Z. Li, F. B. Li, C. L. Yang and W. K. Ge, *J. Photochem. Photobiol. A: Chem.*, **141**, 209 (2001).
13. S. H. C. Liang and I. D. Gay, *J. Catal.*, **101**, 293 (1986).
14. A. N. Copp, *Am. Ceram. Soc. Bull.*, **74**, 135 (1995).
15. P. D. Yang and C. M. Lieber, *Science*, **273**, 1836 (1996).
16. G. P. Summers, T. M. Wilson, B. T. Jeffries, H. T. Tohver, Y. Chen and M. M. Abraham, *Phys. Rev. B*, **27**, 1283 (1983).
17. G. H. Rosenblatt, M. W. Rowe, G. P. Williams, Jr., R. T. Williams and Y. Chen, *Phys. Rev. B*, **39**, 10309 (1989).
18. J. L. Grant, R. Cooper, P. Zeglinski and J. F. Boas, *J. Chem. Phys.*, **90**, 807 (1989).
19. Z. S. Wang, C. H. Huang, Y. Y. Huang, Y. J. Hou, P. H. Xie, B. W. Zhang and B. W. Cheng, *Chem. Mater.*, **13**, 678 (2001).
20. H. Tada, M. Yamamoto and S. Ito, *Langmuir*, **14**, 2936 (1998).
21. H. Tada, Y. Kubo, M. Akazawa and S. Ito, *Langmuir*, **15**, 3699 (1999).
22. H. Tada, Y. Kubo, M. Akazawa and S. Ito, *J. Electrochem. Soc.*, **147**, 613 (2000).
23. J. Bandara, C. C. Hadapangoda and W. G. Jayasekera, *Appl. Catal. B: Environ.*, **50**, 83 (2004).
24. M. L. Chen, J. S. Bae and W. C. Oh, *Bull. Kor. Chem. Soc.*, **27**, 1423 (2006).
25. M. L. Chen, C. S. Lim and W. C. Oh, *J. Ceram. Process. Res.*, **8**, 119 (2007).
26. W. C. Oh, F. J. Zhang and M. L. Chen, *J. Ind. Eng. Chem.*, **16**, 321 (2010).
27. Y. Yu, J. C. Yu, C. Y. Chan, Y. K. Che, J. C. Zhao, L. Ding, W. K. Ge and P. K. Wong, *Appl. Catal. B: Environ.*, **61**, 1 (2005).
28. S. Ghasemi, S. Rahimnejad, S. Rahman Setayesh, S.

- Rohani and M. R. Gholami, *J. Hazard. Mater.*, **172**, 1573 (2009).
29. S. Ghasemi, S. Rahimnejad, S. Rahman Setayesh, M. Hosseini and M.R. Gholami, *Prog. React. Kinet. Mech.*, **34**, 55 (2009).
30. W. C. Oh and M. L. Chen, *Bull. Kor. Chem. Soc.*, **29**, 159 (2008).
31. M. L. Chen, F. J. Zhang and W. C. Oh, *New Carbon Materials*, **24**, 159 (2009).
32. F. J. Zhang, M. L. Chen and W. C. Oh, *Kor. J. Mater. Res.*, **18**, 583 (2008).
33. M. Che and A. J. Tench, *Adv. Catal.*, **31**, 77 (1982).
34. G. Pacchioni and A. M. Ferrari, *Catal. Today*, **50**, 533 (1999).