

Photoluminescence of La/Ti mixed oxides prepared using sol–gel process and their pCBA photodecomposition

Hong Rok Kim, Tai Gyu Lee, Yong-Gun Shul*

Yonsei Center for Clean Technology, Yonsei University, 134 Sinchon-dong, Seodaemun-gu, Seoul 120-749, Republic of Korea

Received 29 December 2005; received in revised form 5 April 2006; accepted 29 May 2006

Available online 11 July 2006

Abstract

La/Ti mixed oxides with weight ratios of 1:9, 2:8, 3:7, and 4:6 were prepared by sol–gel method. The photocatalytic activity of La/Ti oxides was evaluated based on the pCBA photodecomposition. The catalyst samples were characterized by XRD, TEM, DRS, BET, and photoluminescence (PL) spectra. Particles of the La/Ti-mixed oxides showed the diameter of about 7 nm. We found that 30% doping of lanthanum ions on the TiO₂ powders induced the highest pCBA (4-chlorobenzonic acid) photodecomposition in these experimental conditions. The order of its photoactivity was as following: 30 > 20 > 0 > 10 > 40 wt%, which was the same for PL tendency. Also, PL spectra intensity increased with calcination temperature from 500 to 600 °C, then decreased at 700 °C. Photocatalytic activity followed the trend of the PL spectra intensity. The modification of TiO₂ surface by lanthanum ion made it possible to enhance the photoactivity by retarding the recombination of photoexcited electron/hole pairs, in the result of the higher photoactivity in the stronger PL intensity.

© 2006 Elsevier B.V. All rights reserved.

Keywords: TiO₂; Photocatalysis; La doping; Photoluminescence; pCBA

1. Introduction

Currently, titanium dioxide (TiO₂) has been used enormously in many products and in different processes, such as pigments in foodstuffs, paint, and cosmetics, due to its broad functionality, long-term stability, and non-toxicity. The oxidizing power of the photogenerated holes in TiO₂ has been proved to be sufficient in decomposing the pollutants in water and air, about 30 years ago [1]. The photocatalytic activity of TiO₂ strongly depends on its crystal structure, particle size, surface area, and porosity. When the TiO₂ particle size is decreased to the nanometer scale, the optical band gap has been widened due to the effect of quantum size, combined with the increased surface area, resulting in the enhancement of catalytic activity [2,3]. Doping of ions has been employed as one of TiO₂ powder modification methods. The activity of TiO₂ as photocatalyst can be improved by using rare earth metal as dopant can improve the activity of TiO₂ photocatalyst [4,5]. It is well known that the activity of the photocatalysts can be greatly influenced by the surface composition

and structure of them. Due to the recombination between excited electron/hole pairs at the surface of the oxides, PL spectrum has been strongly affected [6–8]. Liqiang et al. [9], Toyoda et al. [10], and Rahman et al. [11] observed surface oxygen vacancies and defects of La, Ce, and Pb doped TiO₂ with PL spectra.

The purposes of this study are to prepare the pure and La/Ti nanoparticles using sol–gel process, and to characterize them with XRD, TEM, DRS, BET, and PL spectra. Furthermore, the photoluminescence results have been connected to the photocatalytic behavior for the decomposition of pCBA (4-chlorobenzonic acid) as with varying the lanthanum dopant and calcination temperature.

2. Experimental

La-doped TiO₂ nanoparticles were prepared by the sol–gel method. Thirteen millilitres of tetraisopropyl titanate, Ti[OCH(CH₃)₂]₄, was dissolved in 50 ml of absolute isopropyl alcohol, and then this Ti[OCH(CH₃)₂] solution was added under vigorous stirring into the appropriate amount of La₂O₃ dissolved in 20 ml of 35% HCl. The resulting transparent solution was stirred for 6 h at room temperature and dried at 110 °C for 12 h. The obtained sample was calcined at various temperatures

* Corresponding author. Tel.: +82 2 2123 2758; fax: +82 2 312 6401.

E-mail address: shulyg@yonsei.ac.kr (Y.-G. Shul).

between 500 and 800 °C for 2 h. The crystal phase composition of the prepared La-doped TiO₂ nanoparticles was determined from X-ray diffraction patterns (XRD) obtained by using a Rigaku Denki (4057A2, Japan) diffractometer. Optical properties were analyzed by UV-diffuse reflectance spectrometer (V 650, Jasco). Surface area was evaluated by N₂ adsorption in a constant volume adsorption apparatus (ASAP 2010, Micrometrics). The particle sizes and morphology of photocatalyst powder were investigated with a transmission electron microscopy (JEM 2010, Jeol). The photoluminescence (PL) measurements of prepared photocatalysts have been conducted under the excitation of a 325 nm line from a 50 mW He–Cd laser. The PL spectra have been analyzed by employing conventional photon-counting technique.

The photocatalytic experiments were carried out using a 6-W BLB lamp with a main emission peak at 365 nm, which was surrounded by a circulating water jacket to maintain a constant temperature during the reaction. The reaction suspensions were prepared by adding 1 g of photocatalyst powder into 500 ml of pCBA aqueous solution with an initial concentration of 0.15 mg l⁻¹. The pCBA aqueous solution was continuously stirred for 15 min after 1 g of photocatalyst powder was added into the reaction system. The analytical samples were taken from the suspension and passed through a 0.45 μm Milipore filter. The concentration of pCBA was measured with HPLC (P580A, Dionex) equipped with an ODS-23Micron. The mobile phase was a mixture of water and acetonitrile. The flow rate of the mobile phase was in 1.0 ml min⁻¹ at 30 °C.

3. Results and discussion

Table 1 summarizes the BET surface area of the photocatalyst used in this study. BET surface area increases with the amount of La in TiO₂ catalyst up to the low 30% La/Ti. The BET surface area suddenly drops in 40% La/Ti. The pure TiO₂ shows the low surface area in comparison with the mixture oxides. Fig. 1 shows the XRD patterns of mixed oxides of various La/Ti ratios after heat treatment at 600 °C. Up to 20% of La, anatase phase is dominant without showing any crystalline peak consequent from lanthanum ion. At 30% of La, rutile and La₂Ti₂O₇ phase are observed and those phases are increased with the La contents as showing 40% La sample. It implies that La doping affects the phase transition behavior of TiO₂ during the calcinations process. Fig. 2 shows the X-ray diffraction patterns of 30% La/Ti calcined sample at various temperatures. The peak intensity for La₂Ti₂O₇ increased with the calcination temperature indicating

Table 1
Summary of BET surface area of the photocatalyst used in this study

Samples (calcined at 600 °C)	BET surface area (m ² g ⁻¹)
TiO ₂	28.2
10% La/Ti	56.1
20% La/Ti	54.7
30% La/Ti	56.5
40% La/Ti	32.9

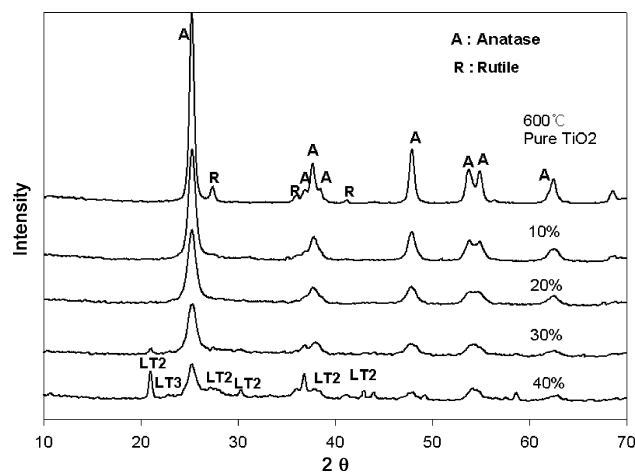


Fig. 1. XRD patterns of doped TiO₂ with various La content (LT2: La₂Ti₂O₇, LT3: La₂Ti₃O₉).

crystal growth of La₂Ti₂O₇. The XRD pattern after heat treatment at 800 °C shows that the sample is a mixture of anatase, rutile, and binary oxide phase. Therefore, it can be concluded from these results that delaying the phase transformation of titania from anatase to rutile has been performed due to lanthanum doping and may hinder the increase of the crystallite size.

Fig. 3 shows the TEM images of pure TiO₂ and 30% La/Ti samples calcined at 600 °C. The average particle sizes of pure and 30% La/Ti samples were about 12 and 7 nm, respectively. This suggests that doped La may prohibit the primary particle growth.

UV–vis diffuse reflectance spectra of the samples are shown in Figs. 4 and 5. Although, the curve shape of the DRS spectrum of pure TiO₂ was similar to that of La/Ti mixture oxides, it was found that the increase of La³⁺ contents shifted the light absorption of the specimens to the visible region. In terms of the red shift, effect of La ion was more distinctive than that of calcination temperature; this observed red shift of the absorption edge was probably due to the increment of the particle size from varying La contents. Fournier et al. [12] previously reported that

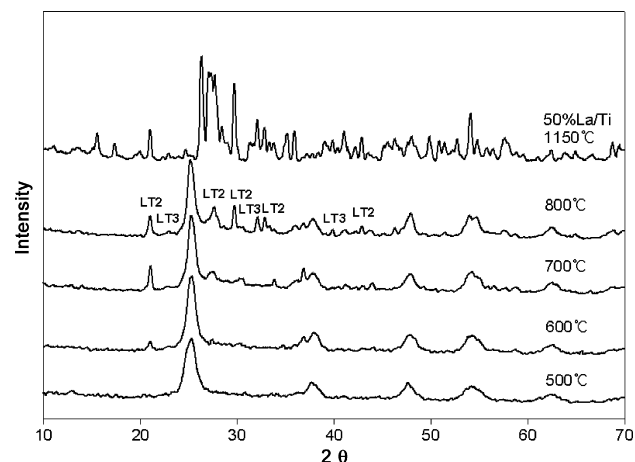
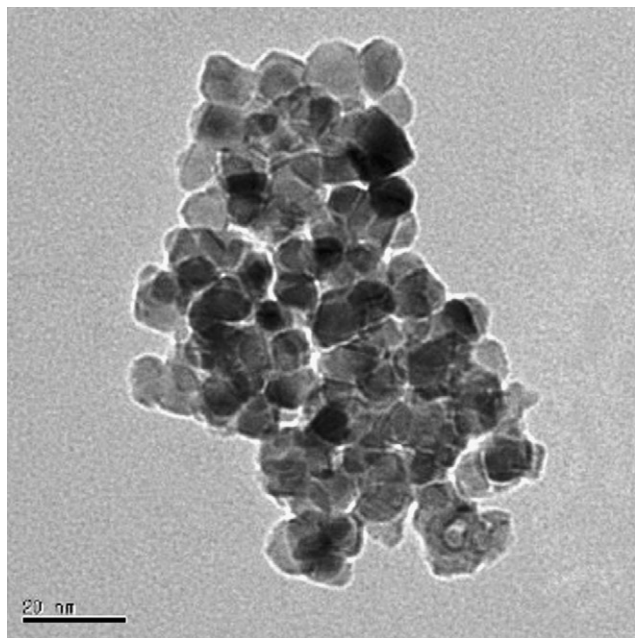
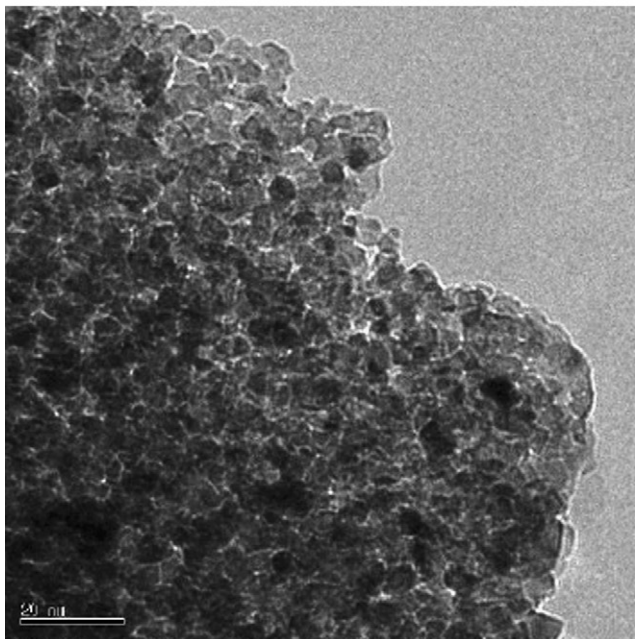


Fig. 2. XRD patterns of doped TiO₂ (30% La) calcined at various temperatures (LT2: La₂Ti₂O₇, LT3: La₂Ti₃O₉).



(A)



(B)

Fig. 3. TEM photographs of (A) pure TiO₂ and (B) 30% La-doped TiO₂ calcined at 600 °C.

band position of DRS spectrum is mainly dependent on structural characteristics, e.g. cluster size and its dispersion pattern over the support. In our study, the average particle sizes were 6.6, 5.4, 7.0, and 16.0 nm for 10, 20, 30, and 40 wt% La/Ti mixture oxide indicating that the increment of the particle size is responsible for the edge position shift of the absorption spectrum towards the longer wavelength.

PL spectrum can provide the information about the surface oxygen vacancies and defects based on the electronic structure and optical characteristics [13–16]. Fig. 6 shows the PL spectra of La/Ti mixture oxides with varying the lanthanum dopant.

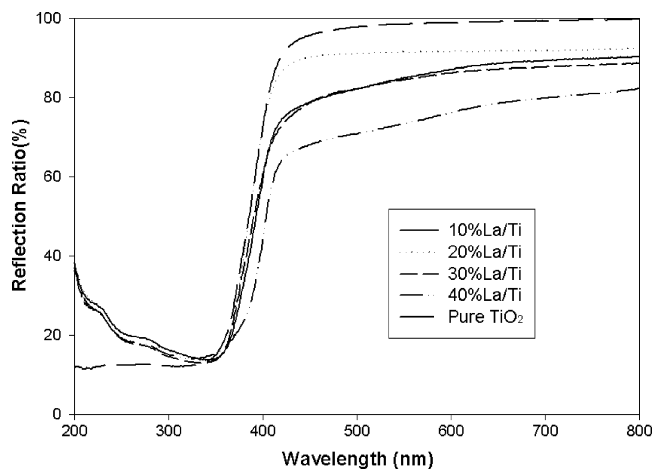


Fig. 4. DRS spectra of La-doped TiO₂ calcined at 600 °C with various La contents.

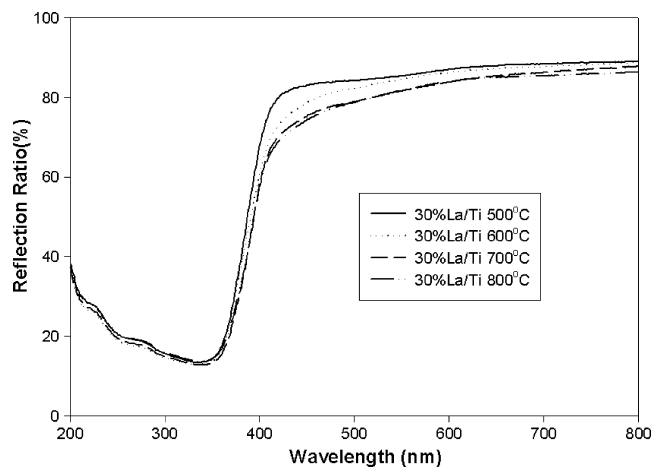


Fig. 5. DRS spectra of doped TiO₂ (30% La) calcined at various temperatures.

The PL intensity gradually increases as La content increases, and arrives at the highest degree when La dopant is 30 wt%. In the case of 50 wt% La/Ti calcined at 1150 °C, the PL intensity is more conspicuous than other La/Ti mixed oxides. The change

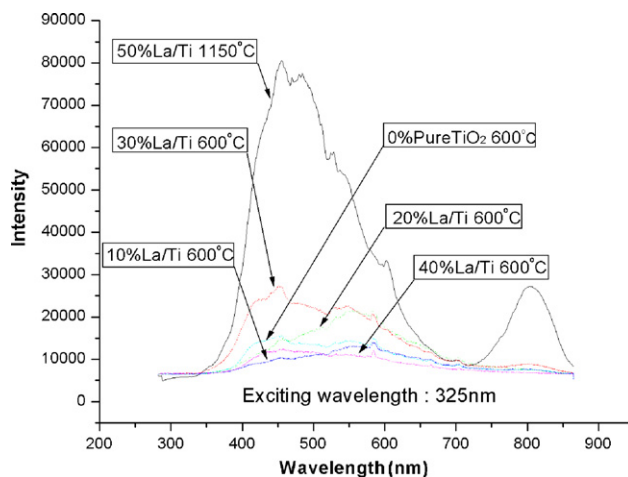


Fig. 6. PL spectra of doped TiO₂ calcined at 600 °C with various La content (excitation: 325 nm).

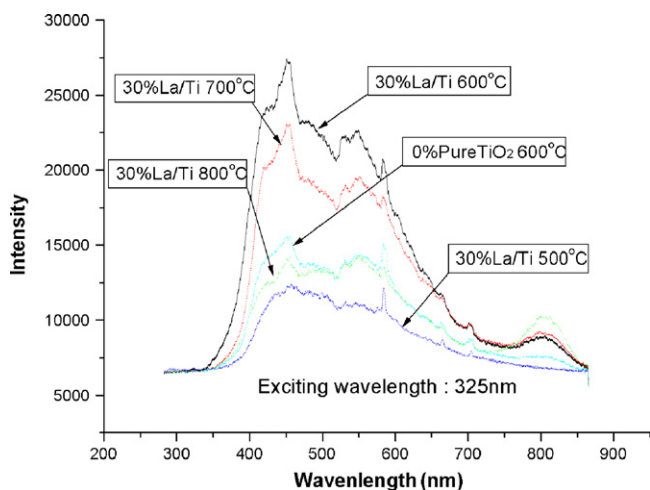


Fig. 7. PL spectra of doped TiO_2 (30% La) calcined at various temperatures (excitation: 325 nm).

of PL intensity as a function of the calcinations temperature is shown in Fig. 7. PL spectra intensity increases with calcination temperature from 500 to 600 °C, then decreases at 700 °C. It was found that that an appropriate change by lanthanum ion and calcination temperature affected the increase of PL intensity for pure TiO_2 . The increase of PL intensity was responsible for the surface content of oxygen vacancy or defect. In general, with decrease in the particle size of the catalysts the oxygen vacancy will be enhanced and probability of exciton occurrence will also increase, resulting the stronger PL signal [17].

The photocatalytic degradation rate of pCBA on La/Ti mixed oxides (calcined at 600 °C for 2 h) is shown in Fig. 8. The order of photoactivity was as following: 30 > 20 > 0 > 10 > 40 wt%. The 50% La loading in TiO_2 showed the lowest performance. This may be due to the existence of lower active phases of $\text{La}_2\text{Ti}_2\text{O}_7$ and $\text{La}_2\text{Ti}_3\text{O}_9$. The order of photocatalytic activity was the same as that of PL intensity, indicating that the high number of oxygen vacancies and defects might be beneficial to pCBA decomposition by La/Ti mixed oxides. Similar observation on the close relationship between PL intensity and photocatalytic activity

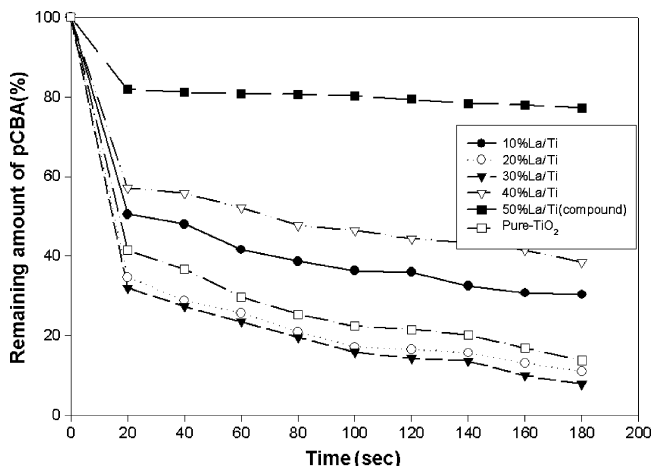


Fig. 8. Decomposition of pCBA by La-doped TiO_2 calcined at 600 °C with various La contents.

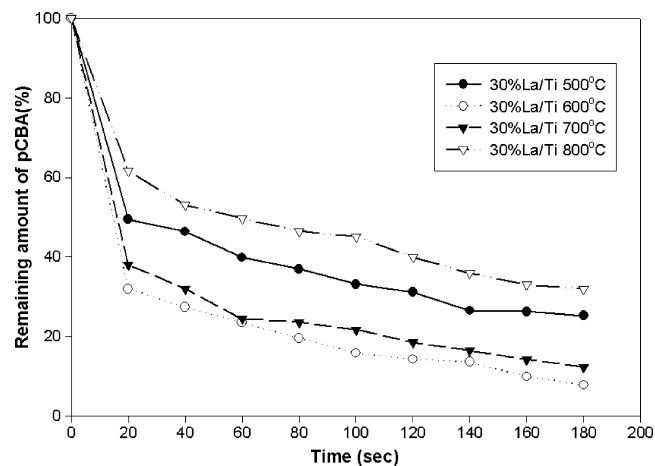


Fig. 9. Decomposition of pCBA by doped TiO_2 (30% La) calcined at various temperatures.

was previously reported by Liqiang et al. [9]; during the photocatalytic reaction, the oxygen vacancies and defects effectively capture the photoinduced electron preventing electron/hole pairs from any possible recombination. Also, the oxygen vacancies promote the adsorption of O_2 and capture the photoinduced electrons of the adsorbed O_2 to produce $\cdot\text{O}_2$ group, which then oxidize the target organic substances.

Fig. 9 shows the photocatalytic degradation curves of pCBA on 30% La/Ti mixture oxides calcined at various temperatures. The photocatalytic activity gradually decreased with increasing calcination temperature. This behavior may be explained by the particles agglomeration and growing of $\text{La}_2\text{Ti}_2\text{O}_7$ and $\text{La}_2\text{Ti}_3\text{O}_9$ phase, which was observed from SEM and XRD. The order of photocatalytic activity was the same as that of PL intensity measured, except for the 30% La/Ti mixed oxide calcined at 800 °C; the PL intensity of 30% La/Ti mixed oxide calcined at 800 °C might be affected by $\text{La}_2\text{Ti}_2\text{O}_7$ and $\text{La}_2\text{Ti}_3\text{O}_9$, which were not the case for the pCBA decomposition.

The change in the decomposition rate of pCBA as a function of the quenching area is shown in Fig. 10. As discussed previously, Jung et al. [18] and Anpo et al. [19], the quenching phenomenon by the addition of oxygen can be explained

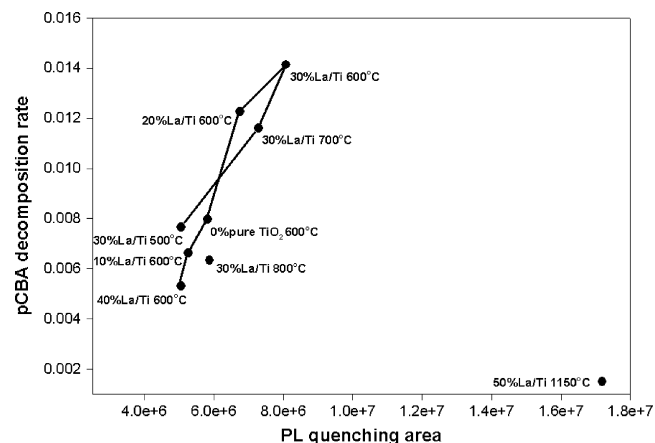


Fig. 10. Photoreactivity of as-prepared La–Ti mixed oxides w.r.t. the PL quenching area.

by the band bending—upward bending of the band edge, which produces thicker space charge layer and effectively separates the photogenerated electron/hole pairs is mainly responsible for the quenching of the photoluminescence. The degree of quenching has a relation with the availability of surface-active sites on which oxygen can be adsorbed. Thus, increasing number of oxygen vacancies and defects means increasing amount of adsorbed O_2 . In other words, the stronger the PL intensity, the more the oxygen vacancies and defects, and the more the oxygen vacancies and defects, the higher the photocatalytic activity. In this study, with the exception of 30% La/Ti (800 °C) and 50% La/Ti (1150 °C), the PL quenching area increased monotonously with the pCBA decomposition rate. According to the XRD patterns of La/Ti mixed oxide, increasing the calcination temperature resulted in the increased portion of $La_2Ti_2O_7$ and $La_2Ti_3O_9$ in the La/Ti mixed oxide. It was also found that more of $La_2Ti_2O_7$ and $La_2Ti_3O_9$ were generated for the case of 30% La/Ti (800 °C) and 50% La/Ti (1150 °C) than any other tested cases (La/Ti ratio: calcination temperature). The photocatalytic activity of pCBA decomposition in La/Ti oxides, which calcined at below 800 °C, was investigated using the PL intensity measurement. The photocatalytic activity increased with PL intensity for catalysts with various La compositions calcined at 600 °C and catalysts with added TiO_2 (30% La) calcined at the temperatures between 500 and 700 °C.

4. Conclusions

La/Ti mixture oxides with various La contents and calcination temperatures were examined and compared to pure TiO_2 . The presence of La^{3+} enhanced the light absorption of the specimens in the visible region hindering the TiO_2 phase transformation. The modification of TiO_2 surface by appropriate lanthanum ion and calcination temperature improves the increase of PL intensity, which was relative to the quantity of the surface oxygen vacancy and/or defect reported by researchers [9]. The relationship between PL spectra and photocatalytic activity was discussed. The order of photocatalytic activity of La/Ti mixture oxides calcined at 600 °C with various La contents was the same as that of the corresponding PL intensity. For 30% La-doped TiO_2 calcined at various temperatures from 500 to 800 °C, the photocatalytic activity showed the same tendency with the intensity of PL intensity except for the one calcined at 800 °C. This may be affected by $La_2Ti_2O_7$ and $La_2Ti_3O_9$ phase from

30% La/Ti (800 °C). The change in photocatalytic surface with lanthanum dopant and calcination temperature was measured by PL spectra. The experimental results showed a linear relationship between the PL intensity and the photocatalytic activity of the tested La/Ti oxides; photocatalytic activity followed the trend of the PL spectra intensity.

Acknowledgement

This work was supported by KRF (R08-2-3-000-10214-0, KRF-2004-003-D00135) and KOSEF through NCRC for Nanomedical Technology (R15-2004-024-00000-0).

References

- [1] D.F. Ollis, H. Al-Ekabi, Photocatalysis Purification and Treatment of Water and Air, Elsevier, New York, 1993.
- [2] A. Mills, S. Le Hunte, J. Photochem. Photobiol. A 108 (1997) 1–35.
- [3] K.M. Reddy, C.V.G. Reddy, S.V. Manorama, J. Solid State Chem. 158 (2001) 180–186.
- [4] K. Wilke, H.D. Breue, J. Photochem. Photobiol. A 121 (1999) 49–53.
- [5] L. Jinsheng, J. Zongzhe, W. Jing, J. Chin. Ceram. Soc. 27 (5) (1999) 601–604.
- [6] M. Anpo, N. Aikawa, Y. Kubokawa, M. Che, C. Louis, E. Giamello, J. Phys. Chem. 89 (1985) 5017–5021.
- [7] M. Anpo, Y. Yamada, Y. Kuubokawa, S. Coluccia, A. Zecchina, M. Che, J. Chem. Soc. Faraday Trans. 84 (1988) 751–764.
- [8] M. Anpo, M. Tomonari, M.A. Fox, J. Phys. Chem. 93 (1989) 7300–7302.
- [9] J. Liqiang, S. Xiaojun, X. Baifu, J. Solid State Chem. 177 (2004) 3375–3382.
- [10] T. Toyoda, T. Hayakawa, Q. Shen, Mater. Sci. Eng. B78 (2000) 84–89.
- [11] M.M. Rahman, K.M. Krishna, T. Soga, T. Jimbo, M. Umeno, J. Phys. Chem. Solids 60 (1999) 201–210.
- [12] M. Fournier, C. Louis, M. Che, P. Chaquin, D. Masure, J. Catal. 119 (1989) 400–414.
- [13] W.F. Zhang, M.S. Zhang, Z. Yin, Q. Chen, Appl. Phys. B 70 (2000) 261–265.
- [14] H. Yamashita, Y. Ichihashi, S.G. Zhang, Appl. Surf. Sci. 121 (1997) 305–311.
- [15] X.Z. Li, F.B. Li, C.L. Yang, J. Photochem. Photobiol. A: Chem. 141 (2001) 209–217.
- [16] L.Q. Jing, X.J. Sun, W.M. Cai, J. Phys. Chem. Solid 64 (2003) 615–623.
- [17] Z. Lide, M. Jimei, Nanomaterials and Nanostructure, Science Press, Beijing, 2001, p. 312.
- [18] K.Y. Jung, S.B. Park, M. Anpo, J. Photochem. Photobiol. A: Chem. 170 (2005) 247–252.
- [19] M. Anpo, K. Chiba, M. Tomonari, S. Coluccia, M. Che, M.A. Fox, Bull. Chem. Soc. Jpn. 64 (1991) 543–551.