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Photoluminescence and photoactivity of titania particles prepared by the sol–gel technique: effect of calcination temperature

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Abstract

The photoluminescence (PL) characteristics of anatase titania particles prepared by the sol–gel method were investigated and correlated to their photocatalytic behavior with respect to the change of calcination temperature. It was found that the photoluminescence intensity measured at 77 K was gradually increased by increasing the calcination temperature due to the reduction of the internal defects which are responsible for the radiationless recombination of photoexcited electron/hole pairs. Also, the calcination temperature was found to influence the maximum peak position (λ) of the photoluminescence spectra of titania. That is, a blue shift of the photoluminescence spectrum occurs as a consequence of the enlargement of the energy-gap between the lowest excited state and the ground state of titania as increasing the calcination temperature. The quenching behavior of the photoluminescence at 77 K was monitored by in situ supplying oxygen at 77 K in order to investigate what happened to the surface of titania by the calcination. The quenching intensity was monotonically increased with increasing the calcinations temperature. Based on the above results, we concluded that the calcination of titania at higher temperature produces more surface-active sites easily reacting with oxygen molecules as well as improving the crystallinity of anatase phase. Consequently, higher temperature heat treatment of anatase titania particles makes it possible to get higher photoactivity as long as no significant rutile phase is formed.

Keywords: Titania; Photocatalysis; Photoluminescence; Calcination effect; Sol–gel

1. Introduction

Titania is well known as a good photocatalyst in the field of water and air treatment [1–6]. The preparation temperature or the post-heat-treatment condition greatly affects the photoactivity of titania [7–9]. The effect of post-heat-treatment temperature on the photoactivity becomes more significant factor, especially when titania is prepared by a liquid-phase reaction route [9]. The increase of crystallinity is considered as the major reason why the photoactivity is improved by elevating the calcination temperature [9–11].

Simultaneously with the crystallinity, the changes in the surface area and the surface property of titania as varying the calcination temperature also play a key role in determining the photoactivity because the heterogeneous photocatalysis is a surface phenomenon. To get a high photoactivity, the photoexcited electron/hole pairs should be effectively separated and take part in the oxidation/reduction reaction after they reach the titania surface. So, the surface-bounded species greatly affect the destiny of photoexcited electron/hole pairs. The surface OH group has been known as a major hole consumer of heterogeneous photoreaction [12]. Unfortunately, the surface OH group is generally reduced as elevating the calcination temperature which is essentially needed to get high crystallinity. Therefore, one can surmise that some use-

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ful changes for the photoactivity occur by the heat treatment, so that the loss of surface OH groups and the surface area could be compensated. So, a systematic study of what happens to the surface of titania by the heat treatment is urgently required for the better understanding of photocatalysis.

In resent, the application of photoluminescence (PL) as a technique to characterize solid surface in relation to adsorption, catalysis, and photocatalysis was reported [13]. Photoluminescence spectrum is strongly affected by the surface state of oxides because it results from the recombination between excited electron/hole pairs. For example, photoluminescence can be quenched by oxygen [14–16]. Therefore, the change of surface-active sites of titania can be monitored successfully by measuring the photoluminescence characteristics with changing the calcination temperature.

In this work, anatase phase titania was prepared by the sol–gel method. Photoluminescence technique was used to characterize the change of titania surface and bulk. Finally, the photoluminescence results were connected to the photocatalytic behavior for the decomposition of trichloroethylene (TCE) as varying the calcination temperature.

2. Experimental

Titania particles were synthesized by the conventional sol–gel technique. Titanium ethoxide ($Ti(OC_2H_5)_4$, Ti-20%, Aldrich) was used as a precursor of titania. The precursor alkoxide was hydrolyzed in excess water ($H_2O/M^+ = 100$ in mole ratio) containing acid catalyst of HCl ($H^+/M^+ = 0.2$). The ratio of alcohol (C_2H_5OH, Aldrich) to alkoxide was kept as 1. Titanium precursor was added slowly in purified water containing dosed HCl and alcohol with vigorous stirring by a magnetic stirrer at room temperature. After mixing for 24 h, the sol solution was heated at 80 °C for 5 h to remove the added and produced alcohol and dried in an oven of 100 °C. The obtained titania xerogel was calcined at the temperature between 400 °C and 600 °C for 5 h.

The major phase of the prepared titanium-based photocatalyst was determined from X-ray diffraction patterns obtained by using a Rigaku D/MAX-III (3 kW) diffractometer. Surface area of the prepared titanium-based photocatalyst was determined by nitrogen physisorption data at 77 K using a Micrometritics ASAP 2400.

The photoluminescence spectra of prepared photocatalysts were measured at 298 K and 77 K using a Shimadzu RF-5000 spectrophotofluorometer. To investigate the quenching of photoluminescence for as-prepared photocatalysts, titania powder is treated thermally as shown in Fig. 1. First, some powder is loaded in a quartz tube connected with a vacuum pump and heated at 300 °C for 3 h to remove water or weakly bounded surface OH groups into air. Next, it was evacuated up to 10^{-5} Torr, maintained for 1 h, and cooled down to the room temperature. Then, it was refilled with oxygen of 200 Torr and maintained at 200 °C for 2 h to oxidize organic compounds remaining on the surface of prepared photocatalysts. It was

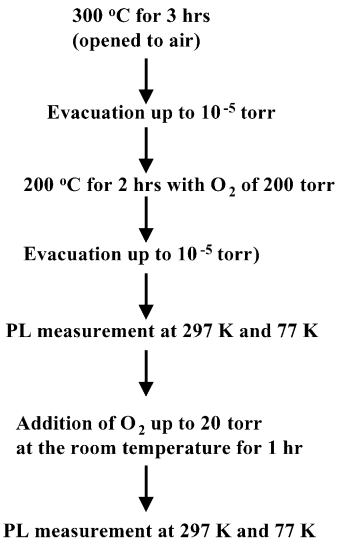

Fig. 1. The pretreatment procedure for the measurement of photoluminescence.

evacuated again and analyzed at 298 K and 77 K. To investigate the quenching characteristics of photoluminescence, oxygen of 20 Torr was in situ filled again at room temperature in the sample tubes.

A semi-circulation batch reactor of annular shape was used to test the photoactivity of as-prepared titania particles. Each prepared titania particle (1 g/l) was dispersed into purified water of 750 ml. Before the reactant (TCE) is loaded, the titania-containing solution was sonicated for 5 min to separate the aggregated particles. The initial concentration of TCE was 37 ppm. The solution was irradiated by ultraviolet light (black light, 15 W, 3.08×10^{-4} Einstein min^{-1}) with the wavelength range from 300 nm to 400 nm. The TCE concentration was monitored by Cl^- electrode (Orion, model 96-17B) as a function of reaction time. Then, the curve showing the change of TCE concentration versus time was obtained and the initial rate was determined from the slope (dC/dt) at $t = 0$.

3. Results and discussion

Fig. 2 shows the XRD spectra of titania particles prepared by the sol–gel method. Up to 500 °C, no rutile phase was observed. Some rutile phase was formed at the calcination temperature of 600 °C. From these XRD results, it was confirmed that the major phase of as-prepared titania is anatase phase in all calcination temperatures. Photoluminescence spectra measured at 298 K and 77 K under vacuum condition for titania calcined at 400 °C are shown in Fig. 3. At room temperature, a very weak PL spectrum was observed due to the rapid recombination rate of photoexcited electron/hole pairs, whereas the intensive PL spectrum around 540 nm was obtained at 77 K. So, all following photoluminescence spectra were measured at 77 K. The unique peak in Fig. 3 means there

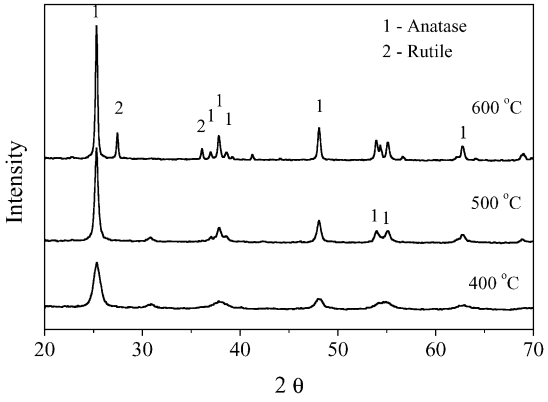

Fig. 2. XRD patterns of titania particles prepared by the sol–gel method. The temperature labeled in the figure denotes the calcination temperature.

is only one kind of photoluminescence site (i.e., low coordinated titanium site). Referring to the previous study [14], high intense photoluminescence is observed when titania is highly dispersed on vycor glass. Bulk anatase titania has very low intensity of photoluminescence. In addition, the peak point in the reference [14] was around 440 nm. In 1989, Anpo et al. reported the photoluminescence spectrum for pure titania at the same measuring conditions we used in this work except for the crystal phase (their catalyst was rutile phase) [16]. According to their reports, a clear photoluminescence spectrum was exhibited at 450–550 nm. This is similar with that shown in Fig. 3. Therefore, it was confirmed that the obtained photoluminescence is due to the bulk anatase.

The photoluminescence spectra in Fig. 3 result from not the fluorescence but the phosphorescence. The successive steps involved in phosphorescence are schematically shown in Fig. 4. First, an excitation occurs from the ground singlet state to the excited singlet state by the absorption of light coming form the external source. The excited triplet state is necessary and plays a key role in obtaining phosphorescence. For every exciton reaching the lowest energy boundary of the excited singlet state, if only the radiationless decay is preceded to the ground singlet state, there is no way to obtain the phosphorescence spectrum. Therefore, the excitons decaying without radiation should jump into the triplet state at a moment. This process is called 'intersystem crossing'. It is well known that the intersystem crossing occurs efficiently in molecules with heavy metal atoms or ion pairs in a solid oxide because their spin orbital coupling is large and electron is easy to be the same spin of the excited triplet state [13].

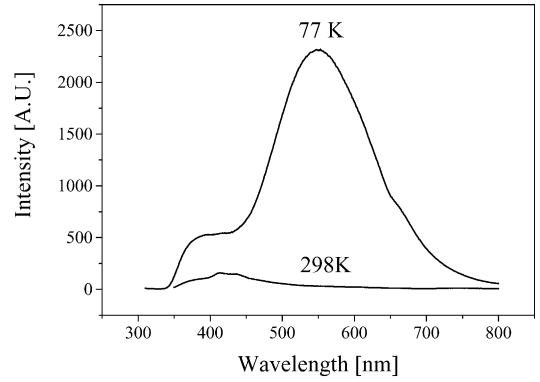

Fig. 3. Photoluminescence spectra measured at a vacuum condition without O_2 for anatase-phase titania calcined at 400 °C. The excitation wavelength was 300 nm. The temperature in the figure denotes the measuring temperature.

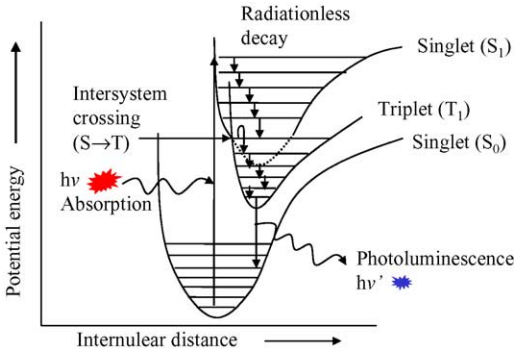

Fig. 4. The sequencing step leading to photoluminescence [14].

Fig. 5 shows the PL spectra measured at 77 K under vacuum condition with changing the calcination temperature for titania particles prepared by the sol–gel method. The PL intensities of pure titania particles were increased by elevating the calcination temperature. The increase in the photoluminescence intensity means that the intersystem crossing of excitons is facilitated as a consequence of the enhancement of the spin orbital coupling by increasing the calcination temperature simultaneously with suppressing the radiationless decay or the deactivation process for excitons. That is, the enlargement of the crossing area between the excited singlet state and the excited triplet state could be achieved by widening the energy gap. As a result, more electrons in the excited singlet easily jump into the triplet

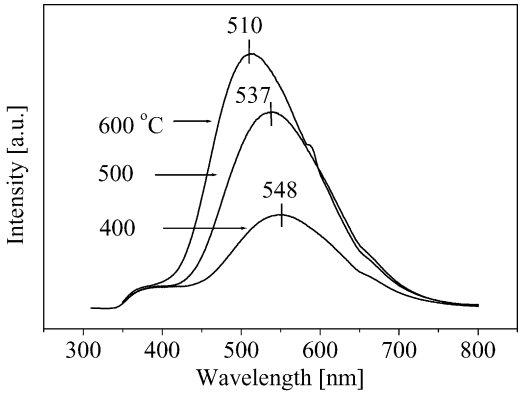

Fig. 5. Photoluminescence spectra measured at 77 K under a vacuum condition without O_2 for titania particles calcined at several temperatures. The excitation wavelength was 300 nm. The temperature in the figure indicates the calcination temperature. The labeled number (i.e., 510, 537, 548) is the wavelength at the maximum peak in photoluminescence.

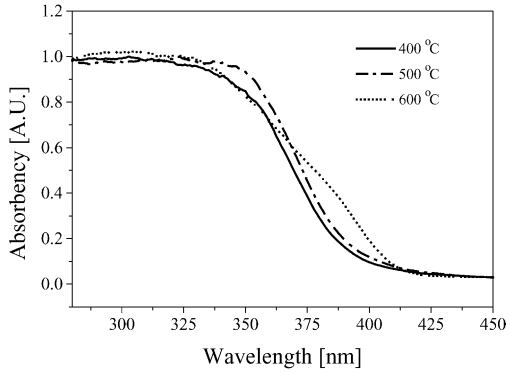

Fig. 6. UV/vis absorbance spectra of titania particle.

state by the intersystem crossing, which leads to more efficient photoluminescence.

The notable phenomenon in Fig. 5 is in the peak position of photoluminescence which shifted toward shorter wavelength as increasing the calcination temperatures. The wavelength of PL is related to the energy position of triplet state relative to the ground state. Consequently, the shift of maximum peak positions to the short wavelength means that the energy gap between the lowest triplet state and the ground singlet state becomes enlarged. Anatase phase generally emits PL of longer wavelength than rutile one. Fujihara et al. [17] reported that the less dense structure of anatase phase than rutile one is favorable for stabilizing the excited state of the TiO_6^{8-}-like species by the lattice deformation which is responsible for the long-wavelength photoluminescence of anatase phase. So, the shift in the peak position of photoluminescence spectra may be related to the change in the structural irregularity of titania, i.e., the structural ordering by elevating the calcination temperature reduces the lattice deformation and leads to shortening of the wavelength of the photoluminescence. This argument is in good agreement with the experimental results that anatase titania particles are changed to more dense and ordered structure as increasing the calcination temperature. The fact that the anatase phase grows and becomes bulky by the increase of the calcination temperature was also identified from the change of UV/vis absorption spectra which are shown in Fig. 6. On increasing the calcination temperature, the edge position of the absorption spectrum moved toward longer wavelength, which is called 'red shift', because of the enlargement of crystallite size.

A similar result with this work is found from the PL study of MgO. According to the literature [15], the λ_{max} of the photoluminescence for MgO shifts toward shorter wavelength with increasing the degassing temperature. It was also reported that the photoluminescence intensity of MgO increases as the degassing temperature goes up to 700 °C and decreases again over 700 °C. The removal of surface-bounded water or OH groups by increasing the degassing temperature is mainly contributed to the increase of photoluminescence intensity. In our measurement, all samples were degassed at the fixed temperature of 300 °C, but the calcination temperature of each sample is different. So, it is speculated that the changes in the intensity and peak position of the photoluminescence occur due to the different calcination temperature. Therefore, the observed changes in the photoluminescence intensity and the λ_{max} for prepared titania particles absolutely reflect the changes of titania itself such as crystallinity and local defects in the calcination process.

The in situ investigation of the quenching phenomena for all prepared titania particles was carried out using oxygen as an electron scavenger. Fig. 7 shows photoluminescence spectra measured at 77 K with and without oxygen quencher. When about 20 Torr of oxygen was supplied, the considerable quenching in the photoluminescence intensity occurred

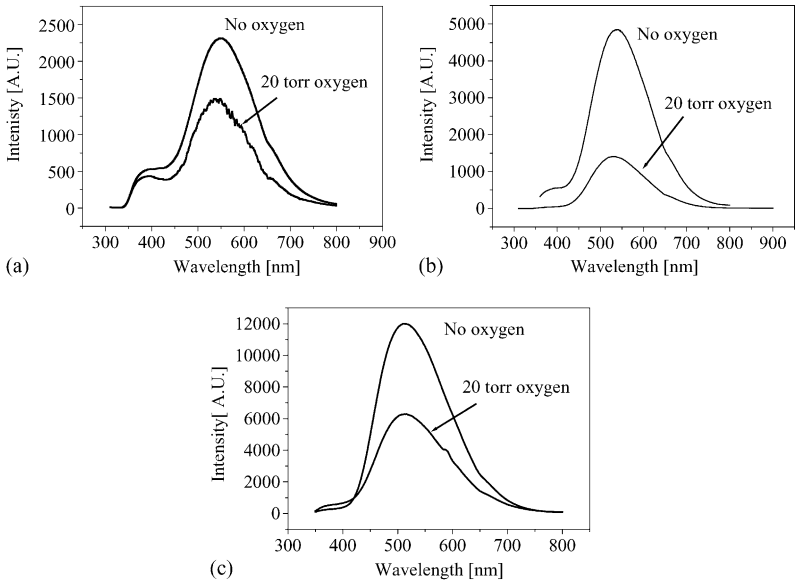

Fig. 7. The quenching phenomena in photoluminescence of titania particles (excitation: 300 nm, measuring temperature: 77 K, used quencher-O_2 of 20 Torr) calcined at (a) 400 °C, (b) 500 °C, and (c) 600 °C.

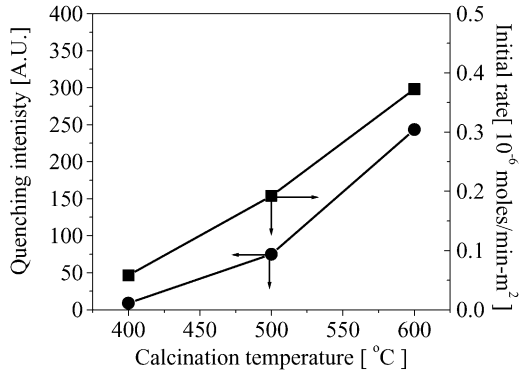

Fig. 8. The effect of the calcination temperature on the quenching intensity of photoluminescence measured at 77 K and the photoactivity of as-prepared titania particles.

in all samples. The quenching phenomenon by the addition of oxygen is explained by the band bending. Referring to reference [18], the quenching of photoluminescence is due to the upward bending of the band edge, which produces thicker space charge layer and effectively separates the photogenerated electron/hole pairs. The degree of quenching is related to the quantity of surface-active sites on which oxygen can be adsorbed. Larger quenching in the photoluminescence intensity means larger amounts of surface-active sites easily reacting with the oxygen. Also, titania showing larger quenching in the photoluminescence is supposed to have higher photoactivity because the photocatalysis is a surface reaction and proportional to the quantity of surface-active sites which are taken by the electron acceptor or donor.

The quenching intensity of prepared titania particles, which is the intensity difference at the peak position of two photoluminescence spectra measured with and without the oxygen in Fig. 7, is shown in Fig. 8. The change in the photoactivity (g mole/(m^2 min)) as a function of the calcination temperature is also plotted in Fig. 8. According to the BET analysis for the titania samples prepared, elevating the calcination temperature reduced the surface area that was 93.6 m^2/g, 45.9 m^2/g, and 23.5 m^2/g at 400 °C, 500 °C, and 600 °C, respectively. The reduction of surface area means the decrease of active sites on which the reactants can adsorb. So, the increase of the calcination temperature seems to be not helpful for the photoactivity. In order to remove the influence of the surface-area reduction on the photoactivity, the initial rate unit surface area is used in Fig. 8. Then, the surface-normalized photoactivity (g mole/(m^2 min)) should be constant under the assumption that all surface area has taken part in the photocatalytic reaction. The photoactivity per unit surface area was, however, increased gradually by increasing the calcination temperature as shown in Fig. 8. This means that increasing the calcination temperature makes the surface of titania particles more active for the decomposition of TCE. In Fig. 8, it is notable that the quenching intensity of titania particles increases monotonically with increasing the calcination temperature. This result supports that the increase of the calcination temperature produces more surface-active sites although the surface area is reduced according to the result of BET analysis. This situation is expected to be helpful for the photoactivity of titania. This expectation is in good agreement with the experimental result for the photoactivity of titania with changing the calcination temperature as shown in Fig. 8. The photoactivity was changed in coherence with that of the quenching intensity as increasing the calcination temperature. From this result, it was proved that the increase of photoactivity for prepared titania particles as increasing the calcination temperature is due to the formation of surface-active sites as well as the enhancement of crystallinity. Therefore, it is concluded that titania showing larger quenching intensity in photoluminescence is promised to have higher photoactivity.

4. Conclusions

The calcination temperature greatly affected the photoluminescence behavior and the photoactivity of titania for TCE decomposition. The photoluminescence intensity was enhanced gradually as increasing the calcination temperature due to the efficient intersystem crossing of photoexcited electrons from the excited singlet state to the excited triplet states. It was also observed that the calcination temperature has an influence on the peak position of photoluminescence spectrum, which was shifted toward short wavelength with increasing the calcination temperature due to the reduction of structural irregularity, which means that the prepared titania is turned into more ordered crystalline. It was also found that the calcination temperature affects the quenching intensity of photoluminescence by the addition of oxygen. The quenching intensity increased monotonically with increasing the calcination temperature. Larger quenching intensity means larger amount of surface-active sites. Based on these results, we experimentally proved that the increase of the calcination temperature produces more surface-active sites as well as increasing the crystallinity, which are the major reasons why the enhancement in the photoactivity of anatase titania can be achieved by elevating the calcination temperature as long as no significant rutile phase is formed.

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