Chapter 7
Photoluminescence Spectroscopic Studies on TiO_2 Photocatalyst

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Abstract Photoluminescence is a powerful technique in the study of semiconductor photocatalysts. This chapter deals with the application of photoluminescence techniques to the study of TiO_2 in relation to its photocatalytic performance. The assignment of the visible and the near-infrared luminescence characteristics of TiO_2 are discussed. The influence of the adsorbed molecules, such as H_2O, O_2, H_2, unsaturated hydrocarbons and Pt loaded on TiO_2, on the photoluminescence characteristics of TiO_2 is also discussed. The relationship between the photoluminescence features of TiO_2 and the photo-assisted reaction of water and methanol mixture is also summarized.

1 Introduction

Photoluminescence spectroscopy is a contactless, nondestructive method of probing the electronic structure of materials. Nowadays, the highly sensitive photoluminescence technique is widely used in the investigation of the photophysical and photochemical properties of solid semiconductors (Anpo et al. 1985a, b, 1989; Nakajima et al. 2001, 2004; Nakajima and Mori 2004; Jung et al. 2005; Murakami et al. 2006, 2007). Particularly, it is a powerful technique in the study of photocatalysis, since it can supply meaningful information about the relationship between the nature of the defect sites, such as surface oxygen or metal vacancies, and the efficiencies of charge carrier trapping, immigration and transfer (Jeon et al. 2009; Naito et al. 2009). Application of the photoluminescence to the study of the relationship between the solid surface properties and the efficiency of the photocatalysis has already been reviewed by others (Anpo and Che 2000;

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Jing et al. 2006). And this chapter mainly deals with the application of the photoluminescence techniques to a particular TiO_2 semiconductor photocatalyst.

Because of the high chemical stability and favorable energy band structure for the development of robust and efficient photocatalysts, TiO_2 has been drawing enormous attention over the past decades. Anatase and rutile, the two major crystal structures of TiO_2, are commonly used in photocatalysis. It is well known that the photocatalytic activity of TiO_2 largely depends on its crystal structure (Tsai and Cheng 1997; Tanaka et al. 1991; Nishimoto et al. 1985; Ding et al. 2000; Ohno et al. 2001; Fujihara et al. 1998) and surface properties (Anpo et al. 1989; Yu et al. 2000; Wu et al. 2004), etc. The crystal structures (Tang et al. 1994a; Poznyak et al. 1992; Montoncello et al. 2003; Nakajima et al. 2005) and the surface properties (Anpo et al. 1989; Nakajima et al. 2002, 2004; Nakajima and Mori 2004) of TiO_2 also have essential correlation with the luminescence features of TiO_2. Therefore, photoluminescence spectroscopy study can depict the surface photoactive sites of TiO_2 (Anpo et al. 1985a; Nakajima et al. 2001, 2002; Jung et al. 2005).

This chapter focuses on the review of the application of photoluminescence spectroscopy in the study of TiO_2 photocatalysts. The whole chapter is organized as follows: Sect. 2 will give a brief introduction of the fluorescence spectroscopy, followed by the photoluminescence characteristics of TiO_2 in Sect. 3; the influence of adsorbed molecules and loaded metal Pt on the photoluminescence properties of TiO_2 will be discussed in Sect. 4; the relationship between the photoluminescence features of TiO_2 and its photocatalytic activity will be discussed in Sects. 5 and 6; based on the above extensive discussion, the final conclusion will be made in Sect. 7.

2 Laser-Induced Fluorescence Spectroscopy

Fluorescence spectroscopy is an important spectroscopic technique for the exploration of the electronic structures of materials in a molecular level. It has been extensively applied in biology, pharmacology, and analysis sciences since it is not only sensitively gives the information about the electronic and vibrational states of the luminescent molecule, but also sensitively probes the influence of surrounding environment on the electronic structures of the fluorescent molecules. Fluorescence spectroscopy can help us better understand the mechanism of the chemical reaction and guide us to design efficient photocatalysts. Various kinds of commercially available autocompensating spectrophotofluorometers (photoluminescence instrumentation) have been employed in the study of catalysts. In these spectrophotometers, Mercury or Xenon arc lamps are commonly used as the excitation source. However, laser-induced fluorescence (LIF) spectroscopy, in which laser is used as the excitation source, has been developed in recent years. Compared with the traditional fluorescence spectroscopic technique, in which lamp is used as the excitation source, LIF spectroscopy has some distinguished advantages in terms of higher sensitivity, more facile control of

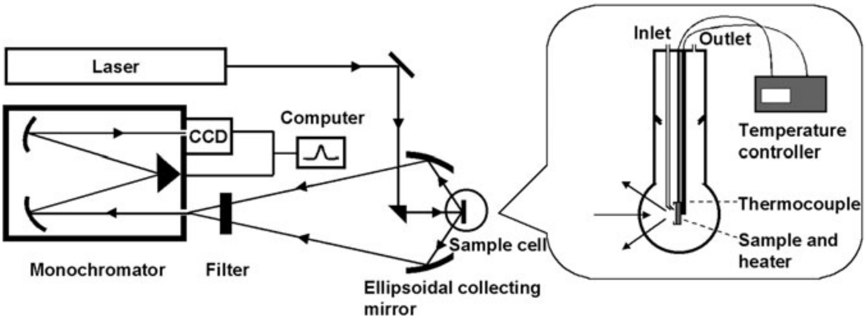


Fig. 1 The schematic diagram of the in situ laser-induced luminescence spectroscopy setup

the light system of the apparatus, and less sample area for luminescence. In literature, there are numerous reports on the application of LIF spectroscopy in biological science. Detection of single molecules using LIF spectroscopy has also been reported. However, this technique has not been well applied in the field of catalysis area.

In order to study heterogeneous catalysis using LIF, we designed and built up an in situ laser-induced fluorescence spectroscopy setup, as shown in Fig. 1. In this setup, continuous wave UV lasers and visible lasers are used as the excitation sources. It is equipped with the home-made ellipsoidal mirror collecting system, which can provide a large space to accommodate the sample treatment system. The CCD is mounted at the focal plane in the exit of the monochromator for efficient detection of the fluorescence signal and collection of the full spectrum simultaneously. A home-made in situ sample cell connected with the gas system is fixed at the focal point of the ellipsoidal mirror. This setup is very convenient to carry out in situ fluorescence studies under various experimental conditions. Using this setup, we have successfully investigated many photoluminescence properties of heterogeneous catalysts in our laboratory (Chen et al. 2004a, b, 2005). By using this technique, we detected the defects in catalyst, which is the crucial subject concerning active sites (Chen et al. 2004a, b). Furthermore, using aniline as the fluorescence probing molecule, this setup also enabled us to study the surface properties of the superacid sulfated zirconia catalysts (Chen et al. 2005).

The photoluminescence has been drawing a great deal of attention in the field of photocatalysis in recent years, because it is proved to be a powerful technique to explore the electron and hole related photocatalytic processes which take place on the surface of solid semiconductors. Indeed, combining the LIF spectroscopy with other spectroscopic techniques, we have successfully obtained some essential information regarding the surface properties of semiconductor photocatalysts as well as the relaxation processes of the photo-induced charge carriers (Shi et al. 2006, 2007a, b).

3 The Photoluminescence Characteristics of TiO_2

As an indirect wide band-gap semiconductor, the band edge luminescence of TiO_2 is difficult to be observed (Emeline et al., 2005). The photoluminescence wavelength of TiO_2 depends on its crystal structure and its particle size, while the photoluminescence intensity depends on the dopants, annealing temperatures and atmospheric conditions during the crystallization of TiO_2, and the ambient temperature and atmospheric environments during the photoluminescence measurements. The main features of TiO_2 are the broad and structureless visible or near-infrared luminescence bands (Anpo et al. 1985a, b, 1989, 1991; Serpone et al. 1995; Tang et al. 1993, 1994b; Zhang et al. 2000a, b; Montoncello et al. 2003; Mochizuki et al. 2003; Poznyak et al. 1992; Hachiya and Kondoh 2003; Nakato et al. 1983, 1986, 1997; Grabner et al. 1970; Ghosh et al. 1969; Fernández et al. 2005; Plugaru et al. 2004; de Haart and Blasse 1986; Forss and Schubnell 1993; Lei et al. 2001; Qian et al. 2005; Knorr et al. 2008).

In photoluminescence spectrum, the anatase TiO_2 has a visible emission with a broad spectral width. In general, the origin of the photoluminescence of anatase TiO_2 can be attributed to different kinds of species: self-trapped excitons, oxygen vacancies and defect sites, impurities or reduced metal ions, etc. The broad visible luminescence band of anatase TiO_2 was interpreted as the emission from the self-trapped excitons localized on TiO_6 octahedra by Tang (Tang et al. 1993, 1994b). Zhang et al. (2000a, b) observed the visible luminescence band at 2.15–2.29 eV and interpreted it as the recombination of the electron/hole pairs via the localized levels within the forbidden gap, which are related to some defect centers resided in the surface region of anatase nanocrystallites. In the study of pristine anatase, Mochizuki and co-workers reported that the broad visible luminescence band was originated from the surface oxygen defects (Mochizuki et al. 2003). Fernández et al. (2005) also observed a complex visible band in different surface orientations of TiO_2 single crystals by the cathodoluminescence spectra and ascribed it to oxygen vacancies accompanied with the formation Ti^{3+}. For rutile TiO_2, a near-infrared luminescence band peaked at about 830 nm has been reported. The luminescence centers of this near-infrared band were identified as the Cr^{3+} impurities (Grabner et al. 1970; Haart et al. 1986), though many other researchers attributed it to the interstitial Ti^{3+} ions (Fernández et al. 2005; Plugaru et al. 2004; Ghosh et al. 1969). In the photoluminescence spectra of rutile electrode in aqueous electrolyte solutions, the near-infrared luminescence band was attributed to the intermediate species generated during the photooxidation reaction of water (Nakato et al. 1983, 1986, 1997). On the contrary, Poznyak et al. (1992) proposed that the near-infrared band was associated with the luminescence centers of the intrinsic defects in TiO_2, which shows more characteristic features of the rutile lattice other than anatase lattice.

In our work, the phase transformation of TiO_2 calcined at different temperatures was systematically studied by the UV-Raman spectroscopy (Zhang et al. 2006). We further studied the photoluminescence properties of TiO_2 in the progress of

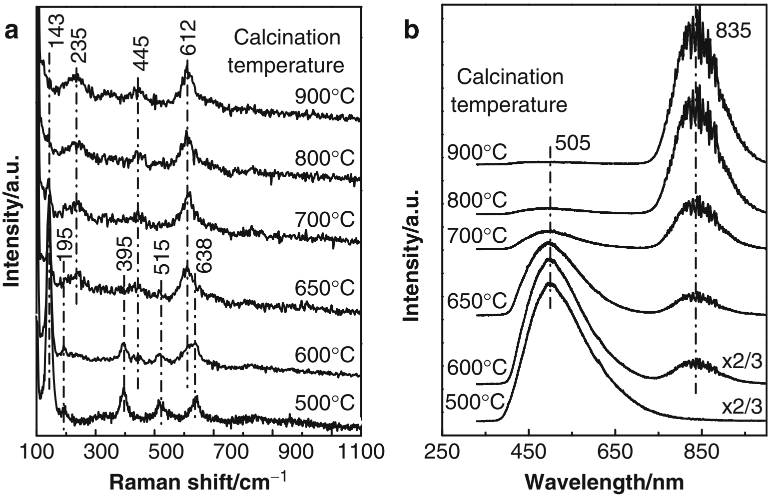


Fig. 2 (**a**) UV-Raman and (**b**) photoluminescence spectra of TiO_2 calcined at different temperatures (Shi et al. 2007a, b)

phase transformation. Interestingly, it was found that the visible luminescence band is related to the anatase structure and the near-infrared luminescence band is associated with the rutile structure (Shi et al. 2007a, b). The photoluminescence spectra and UV-Raman spectra of TiO_2 calcined at different temperatures are shown in Fig. 2. Comparison of the photoluminescence spectra with the UV-Raman spectra of TiO_2 clearly shows that the position of the luminescence bands is related to the crystalline structure of TiO_2. The sample calcined at 500°C is pure anatase phase and displays only the visible luminescence band centered at 505 nm. Elevating the calcination temperature to 600°C, the rutile phase begins to be detected by Raman spectroscopy; accordingly, the near-infrared luminescence band appears in the photoluminescence spectra. With the increase of the calcination temperature, the anatase phase is gradually transformed into the rutile phase, while the visible luminescence band is quenched and the near-infrared luminescence band is prevailed. When anatase phase completely transforms into the rutile phase, the visible luminescence band nearly disappears and the near-infrared luminescence band predominates in the photoluminescence spectra. The results obtained from commercial TiO_2 further indicates that the visible luminescence band located at about 505 nm and the near-infrared luminescence band centered at about 835 nm are respectively relative to anatase structure and rutile structure.

The photoluminescence properties of semiconductors are closely related to the surface stoichiometry and the kinds of surface states, which usually could be changed by annealing processes (Zacharias and Fauchet 1997). Sekiya et al. (2004) reported that the defects states of TiO_2 can be controlled by heat treatments under oxidation or reduction atmospheres. As shown in Fig. 3, the visible and the near-infrared luminescence bands exhibit obviously different characteristics in the in situ

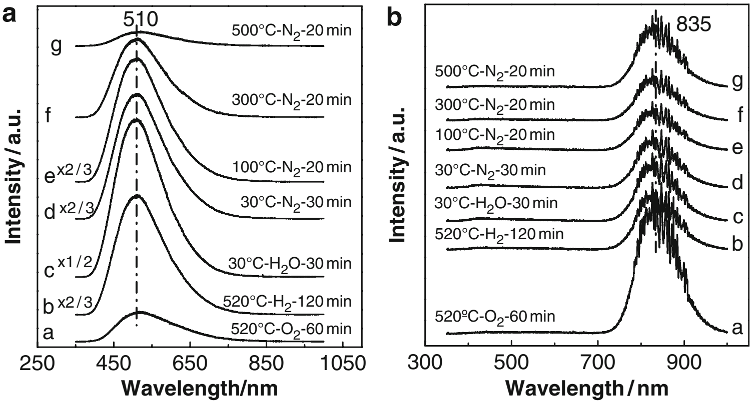


Fig. 3 In situ photoluminescence spectra of TiO_2 calcined at (**a**) 500°C and (**b**) 900°C. The in situ treatment process: (a) after calcined at 520°C for 1 h in O_2 and purged by N_2; (b) after calcined at 520°C for 2 h in H_2 and purged by N_2; (c) after exposure to water vapor for 30 min; (d) after purged water vapor by N_2; and followed by thermal desorption of water in N_2 for 20 min (e) at 100°C; (f) at 300°C; (g) at 500°C (Shi et al. 2007a, b)

photoluminescence experiment of TiO_2. The visible luminescence band is quenched after annealing TiO_2 in O_2 and enhanced in the following reduction treatment in H_2. On the contrary, the near-infrared luminescence band is increased in the oxidation treatment in O_2 and quenched in the reduction treatment in H_2. It has been reported that reducing TiO_2 in hydrogen atmosphere could generate oxygen vacancies (Cronemeyer 1959; Göpel et al. 1983; Salvador and García González 1992), accompanied by the formation of Ti^{3+} ions (Sekiya et al. 2004; Qian et al. 2005; Henderson et al. 1999), while oxidizing TiO_2 in oxygen atmosphere could remove oxygen vacancies and produce the stoichiometry surface (Sekiya et al. 2004; Sanjinés et al. 1994). Numerous spectroscopic studies (Henrich and Cox 1994) have observed isolated oxygen vacancy sites associated with the reduced Ti cations. For example, UPS shows a state located ca. 0.7–0.8 eV below the E_F in the band gap of reduced anatase TiO_2 (Kurtz et al. 1989), which was characterized by the XPS as the defect sites associated with Ti^{3+} ions (Sanjinés et al. 1994). Therefore, it is concluded that the visible luminescence band is originated from the oxygen vacancies associated with Ti^{3+} in anatase TiO_2. For the near-infrared luminescence band, we temporarily ascribe it to the intrinsic defects in rutile TiO_2 and more experiments are needed to confirm the nature of these intrinsic defects.

It is well known that anatase and rutile are the two major crystal structures of TiO_2, which are commonly used as TiO_2 based photocatalysts. The structures of these two crystals can be described as the chains of TiO_6 octahedra differed by the distortion of each octahedra and assembly pattern of the octahedra chains (Linsebigler et al. 1995). The structural differences of these two crystals in the form of anatase and rutile lead to the differences in their electronic and optical properties (Chaves et al. 1974; Plugaru et al. 2004; Diebold 2003). So, it is reasonable to conclude that the different crystalline structures of TiO_2 result in the different luminescence centers in anatase and rutile. This conclusion is obviously supported by our experimental observations, i.e., the oxygen vacancies related to visible emission are prevailed in anatase while the defect states related to near-infrared emission are predominant in rutile. In the mean time, during the phase transformation processes of TiO_2 from anatase to rutile, it was found that the luminescence centers change from the oxygen vacancies in anatase to the intrinsic defects in rutile, evidenced by the visible emission band replaced by the near-infrared band.

4 The Influence of the Adsorbed Molecule on the Photoluminescence Properties of TiO_2

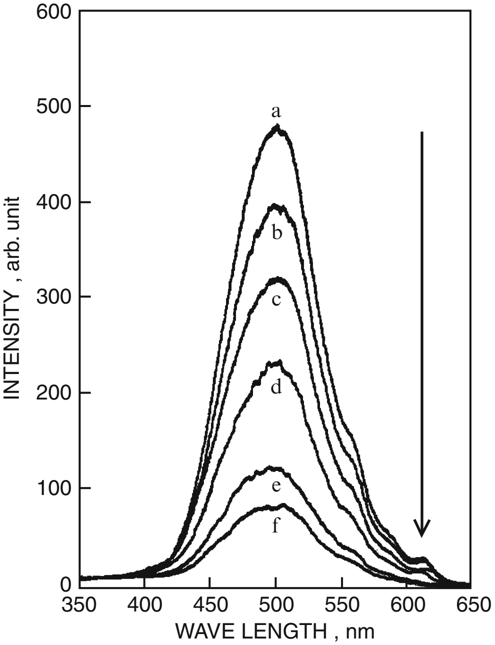
Photoluminescence is basically a kind of surface phenomena of the solid materials, hence the changes of the surface environment will have significant impact on the photoluminescence processes. Study the photoluminescence in the presence of reactant molecules is expected to be a useful approach toward better understanding the relationship between the surface structure and the excited states of the catalysts. Meanwhile, the reactant molecules can also act as molecular probes to explore the detailed photo-induced surface processes generating the electron and hole pairs. The photoluminescence intensity of TiO_2 largely depends on its surrounding chemical and physical environments, such as the nature of the adsorbed molecules. The photoluminescence intensity of TiO_2 depends heavily on its atmosphere. Anpo et al. (1991) had qualitatively depicted the dependence of the photoluminescence intensity of TiO_2 on its surrounding environments by correlating the photoluminescence with the change of the surface band bending.

For the highly dispersed titanium oxide with individual Ti–O sites anchored onto the porous Vycor glass (Anpo et al. 1985a), its photoluminescence peak located at about 485 nm with much higher intensity than that of bulk TiO_2, which is attributed to the radiative deactivation of the charge-transfer excited state of the titanium oxide species:

$$(Ti^{3} - O^{-})* \xrightarrow{hv} (Ti^{4+} - O^{2-})$$

The addition of O_2 led to an efficient quenching of the photoluminescence at -196 or 27°C. The addition of N_2O also led to the quenching of the photoluminescence but with lower quenching efficiency than that of O_2. The efficient quenching of the photoluminescence was attributed to the efficient interaction of the emitting sites with the quencher molecules (O_2 or N_2O here), since the emitting sites were highly dispersed individual sites on the surface of porous Vycor glass. Here, the quenching of the photoluminescence is mainly due to the electron transfer from the excited states of the catalyst to the added O_2 or N_2O molecules.

Fig. 4 Photoluminescence of TiO_2 at −196°C in the absence (spectrum a) and presence of added O_2 (spectra b–f). Excitation wavelength = 300 nm; temperature = −196°C; amounts of added O_2 (in 10^{-6} mol/g of catalyst): (a) 0; (b) 1.1; (c) 4.7; (d) 11.8; (e) 38.2; and (f) 72–150 (Anpo et al. 1989)



Anpo et al. (1989) also systematically studied the influence of the different adsorption molecules on the photoluminescence properties of TiO_2 powder. The TiO_2 powder exhibits a photoluminescence band at 450–550 nm when excited with the light of photon energy larger than the band gap of TiO_2. As shown in Fig. 4, the intensity of the photoluminescence obviously decreases with the increase of the amount of O_2 adsorbed onto TiO_2. However, addition of excessive amount of O_2 cannot quench the photoluminescence completely. In a typical experiment for a sample under 1 bar of O_2 atmosphere, it was found that about 15% of the photoluminescence remains unquenched. And the quenched photoluminescence could not be fully recovered upon evacuation of the sample at 25°C. ESR measurements indicated that addition of O_2 onto TiO_2 at 25°C leads to the formation of O_2^- anion radicals adsorbed onto the Ti^{4+} sites. This confirms that the irreversible quenching of the photoluminescence is due to the formation of thermally stable superoxide anion species which retains tightly on the surface of TiO_2 even after exhaustive evacuation at 25°C. It was also found that addition of N_2O also leads to the photoluminescence quenching but with relatively lower quenching efficiency compared to O_2. The photoluminescence quenching by N_2O was interpreted as the consequence of electron transfer from TiO_2 to N_2O molecules which further decompose into N_2 and O^-. On the contrary, addition of various unsaturated hydrocarbons, such as 1-C_4H_8, C_3H_6, $C_2H_5C{\equiv}CH$, $CH_3C{\equiv}CH$, C_2H_4, and $CH{\equiv}CH$, and small molecules such as H_2O and H_2, can considerably enhance the photoluminescence of TiO_2 powder. Furthermore, the extent of the photoluminescence enhancement strongly depends on the ionization potentials of the added compounds: the lower the ionization potential of the added compound, the higher the photoluminescence intensity. Addition of inert gas, such as N_2, has negligible influence on the photoluminescence. The quenching and enhancement of the photoluminescence intensity of TiO_2 powder can be understood by the changes of the surface band bending in the dead-layer model: the width of the TiO_2 depletion layer becomes larger if the negatively charged adduct species are formed through the electron capture; or it becomes smaller if positive adduct species are formed through the hole trapping. Consequently, the photoluminescence intensity of TiO_2 powder is quenched or enhanced.

Nakajima investigated the influence of C_1–C_3 alcohols on the photoluminescence properties of TiO_2 and discussed the relationship between the properties of the photoluminescence and the adsorbates on the TiO_2 surface (Nakajima et al. 2001, 2002, 2004). The photoluminescence of rutile and anatase TiO_2 powders was measured at room temperature in vacuum, in air, and in air with one of C_1–C_3 alcohols (methanol, ethanol, 1-propanol, and 2-propanol). For rutile TiO_2 powder (Fig. 5), the photoluminescence intensities in air with the C_1–C_3 alcohols and in vacuum increase linearly with $t^{0.5}$, and the time dependence of the photoluminescence intensities agrees with that of the integrated amount of photo-desorbed O_2 from rutile TiO_2 powder. For anatase TiO_2 powder, the photoluminescence intensities in air with methanol and in vacuum also increased linearly with $t^{0.5}$. But this is only the case for methanol, adsorption of other alcohols in air do not increase the photoluminescence intensities. This kind of time dependence of the photoluminescence intensities of TiO_2 in air caused by the interaction with alcohols is elucidated by considering the photo-desorption of O_2 and its effect on the surface band bending of the TiO_2 powder. It is known that the adsorbed O_2 on the rutile TiO_2 powder can be photo-desorbed by the irradiation of the excitation light during the photoluminescence measurement. Adsorption of alcohols inhibits the desorbed O_2 from re-adsorption onto the powder by taking the adsorption vacancies left by the desorbed O_2. Replacement of the adsorbed O_2 by alcohols reduces the surface

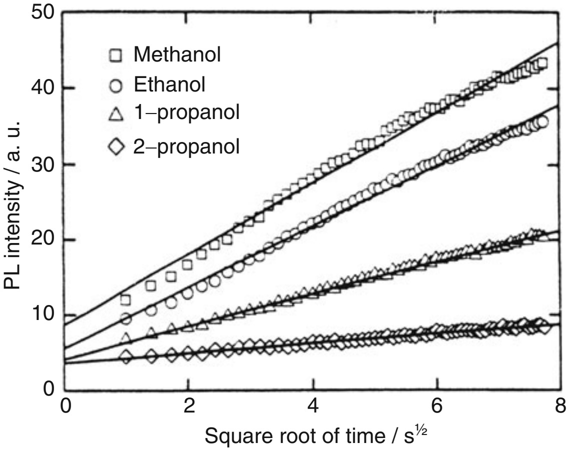


Fig. 5 The relationships between the photoluminescence intensities of rutile TiO_2 powder Kanto-R in air with C_1–C_3 alcohols (methanol, ethanol, 1-propanol, and 2-propanol) and the square root of the UV irradiation time from 1 to 60 s. The squares of the regression coefficients are more than 0.98 (Nakajima et al. 2002)

charge density of the powder and hence the thickness of the space-charge layer linearly with the increase of the $t^{0.5}$. Decrease of the space-charge layer surely facilitates the electron-hole recombination on the surface of the powder, resulting in the increase of the photoluminescence intensity. The inconsistency of the photoluminescence behavior of the anatase TiO_2 upon interaction with different alcohols might be originated from the different photocatalytic activities of anatase TiO_2 toward different alcohols.

The influence of H_2O molecules on the photoluminescence properties of TiO_2 has been studied in our group (Shi et al. 2007a, b). As shown in Fig. 3A, the intensity of the visible luminescence band increases in the presence of water vapor, decreases gradually upon the heat-treatment, and finally declines to the initial level after annealed in the oxygen atmosphere. The interaction between water and the surface of TiO_2 has been studied by a variety of spectroscopic techniques, such as temperature-programmed desorption (TPD), scanning tunneling microscopy (STM), X-ray and ultraviolet photoemission spectroscopy (XPS and UPS). Kurtz et al. (1989) reported that the dissociative adsorption of H_2O onto the TiO_2 surface results in the increase of the amount of the Ti^{3+} defect sites, which also serve as an indication of the increase of the amount of oxygen vacancy sites, since formation of these two sites are the parallel results of the Ti–O bond dissociative cleavages. These fundamental processes can aid us to understand the photoluminescence effect of water upon adsorption onto the TiO_2. It was observed that the visible emission intensity was increased after exposing the surface of TiO_2 to water vapor. The interaction between the water molecules and the TiO_2 surface defect sites actually involves not only the adsorption and dissociation of water on the surface, but also the surface redox reaction such as re-oxidation of the reduced Ti^{3+} to Ti^{4+} by the adsorbed water molecules (Wang et al. 1999; Lu et al. 1994). The oxygen atoms of the water molecules are preferentially extracted by the substrate to fill the surface oxygen vacancies. Therefore, the gradual quenching of the visible luminescence band was observed in the following processes of the thermal treatment. Above the treatment temperature of 500°C, the surface of TiO_2 is fully oxidized by water and accordingly the nearly-perfect surface is formed, as a result, the visible-luminescence intensity decreases to the level of TiO_2 annealed in O_2.

5 The Influence of Platinum Loading on Photoluminescence of TiO_2 Powder

It is well known that the deposited Pt on the surface of TiO_2 plays a vital role in the enhancement of the photocatalytic activity of TiO_2. Excited electrons migrate from the semiconductor of TiO_2 to the metal Pt once the two Fermi levels are aligned (Linsebigler et al. 1995). The Schottky barrier formed at the Pt and TiO_2 interface can serve as an efficient electron trap preventing electron-hole recombination in photocatalysis (Linsebigler et al. 1995).

Nakajima and Mori 2004 compared the photoluminescence characteristic of TiO_2 before and after Pt loading by mixing the TiO_2 powder with platinum black. The photoluminescence intensity of the pure TiO_2 powder was greater than that of the Pt-loaded TiO_2 powder. The result was elucidated as follows: during the photoluminescence measurement, excitation of TiO_2 semiconductor with excitation light generates electron and hole pairs in conduction band and valence band, respectively. The photoinduced electrons in the conduction band will further migrates to the Pt deposited on the surface of TiO_2 by crossing the aligned Fermi energy levels. Because of the interfacial Schottky barrier between TiO_2 and Pt nanoparticles which inhibits back electron transfer from Pt to TiO_2, electron transfer from TiO_2 to Pt generates efficient electron/hole charge separation by the confinement of the excited electrons in the Pt nanoparticles and the holes in the valence band of TiO_2. This will result in the decrease of the photoluminescence intensity of TiO_2. The photoluminescence of two rutile TiO_2 powders with different specific surface areas upon Pt loading (5 wt%) was also investigated (Nakajima and Mori 2006). It was also found that the intensities of the photoluminescence bands observed at around 410 and 800 nm decreased upon Pt loading. The decrease of the photoluminescence intensity was also ascribed to the result of the electron transfer from TiO_2 to Pt nanoparticles.

Our group also investigated the influence of the deposited Pt on the photoluminescence properties of TiO_2 and the photocatalytic activities of TiO_2 for H_2 evolution in a solution of water and methanol mixture (Shi et al. 2007a, b), and the results are shown in Figs. 6 and 7. It can be seen that, upon Pt loading, the visible luminescence band of TiO_2 was obviously quenched while the near-infrared luminescence band was only slightly declined. In the photocatalytic reaction for hydrogen production from water and methanol mixtures, the amount of H_2 production is negligible on the pure TiO_2 samples calcined at various temperatures (500, 650 and 900°C); while hydrogen production were detected in the samples with Pt loaded. The photocatalytic activities of the Pt loaded TiO_2 samples calcined at different

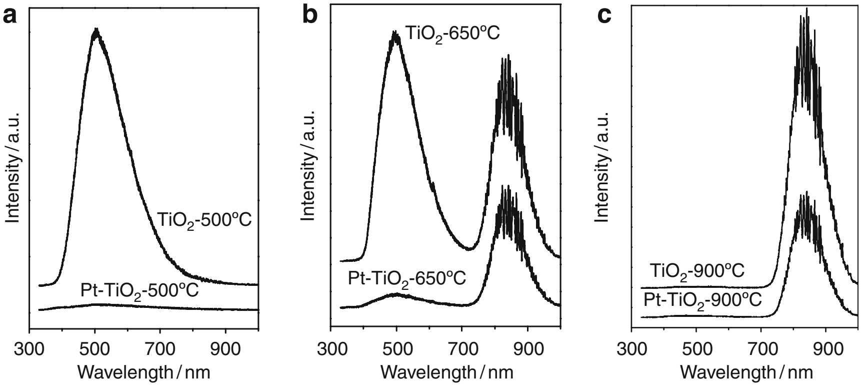
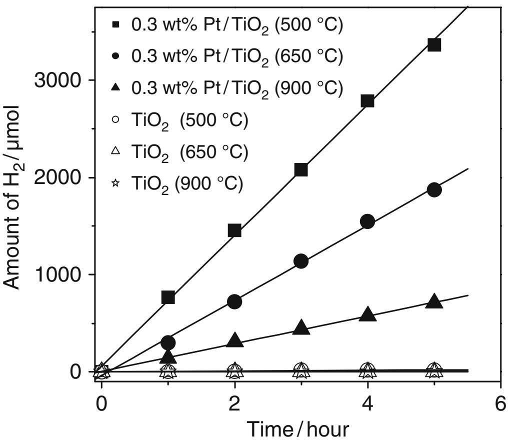


Fig. 6 Photoluminescence spectra of pure TiO_2 and Pt/TiO_2 powders: (**a**) TiO_2 calcined at 500°C; (**b**) TiO_2 calcined at 650°C; (**c**) TiO_2 calcined at 900°C (Shi et al. 2007a, b)

Fig. 7 Photocatalytic H_2 evolutions from methanol-water solution under UV light illumination on pure TiO_2 and Pt/TiO_2 catalysts, and the calcination temperature of TiO_2 are marked in the bracket. Light source, 300 W Xe lamp (Shi et al. 2007a, b)



temperatures follow the order of 500°C > 650°C > 900°C. Since high temperature calcination tends to result in the formation of rutile structure, high photocatalytic activity at relatively low calcination temperature is an indication that anatase TiO_2 has better photocatalytic activity than rutile TiO_2. For TiO_2 alone, the photoinduced charge carriers are mainly deexcited as the luminescence at the recombination centers of the different defects and its photocatalytic activity is negligible. After the deposition of Pt on TiO_2, a large number of photoinduced electrons are further transferred to Pt, which are readily consumed by the photo-assisted reaction. As a consequence, the effective enhancement of H_2 evolution rate is observed for Pt/TiO_2. The obvious quenching of the visible luminescence band and the negligible change of the near-infrared luminescence band indicate that the loading of Pt on the surface of TiO_2 inhibits the recombination of the photoinduced-carriers at the oxygen vacancies in anatase, while it has little influence on the recombination of the photoinduced-carriers at the intrinsic defects in rutile. This may be the reason why photocatalytic activity of anatase TiO_2 is usually higher than that of rutile TiO_2.

6 The Relationship Between the Photocatalytic Performance on TiO_2 and Its Photoluminescence Properties

The photoluminescence spectrum can directly give not only the information about the separation and recombination of the photoinduced charge carriers, but also the information about the surface defects, oxygen vacancies, and surface states, etc. Photoluminescence properties of TiO_2 is useful for monitoring the surface property changes associated with the photocatalytic reactions, for evaluating the photocatalytic activity of TiO_2, and for more thoroughly understanding the mechanism of TiO_2 photocatalysis. The inherent relationships between the photoluminescence

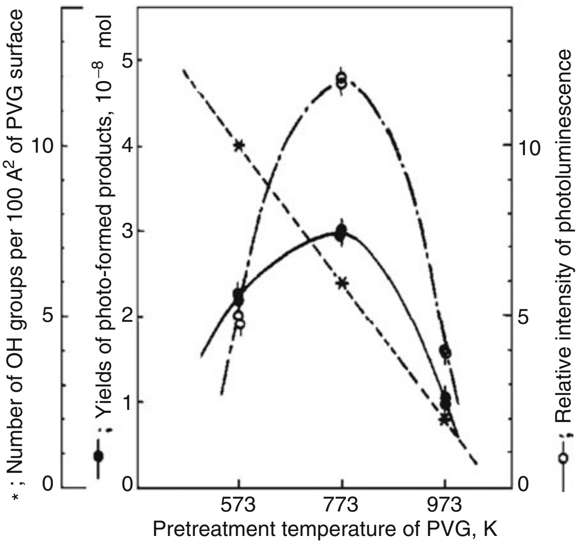


Fig. 8 Effect of the pretreatment temperature of PVG upon the yields of photohydrogenation reaction of CH_3–C≡CH with H_2O and of photoluminescence of the anchored titanium oxide catalyst at 27°C (UV excitation wavelength >290 nm; reaction temperature, 27°C; initial pressure of CH_3–C≡CH, 3.0 torr; initial pressure of H_2O 5.0 torr; excitation wavelength for photoluminescence, 280 ± 10 nm; emission slit width, 7.0 nm), (Anpo et al. 1985a)

intensity and photocatalytic activity have already been investigated and reviewed in detail (Jung et al. 2005; Jing et al. 2006; Jung and Kim 2009).

UV irradiation of the porous Vycor glass anchored with TiO_2 in the presence of H_2O and CH_3–C≡CH at 27°C leads to the photocatalytic hydrogenation of CH_3–C≡CH (Anpo et al. 1985a). As shown in Fig. 8, the yield of the photocatalytic hydrogenation products changes accordingly with the change of the photoluminescence intensity of the anchored titanium oxide. It was proposed that the photoluminescence originates from the charge-transfer excited state of the $(Ti^{3+}–O^{-})^*$, which plays a vital role in the photocatalytic hydrogenation reaction of water with CH_3–C≡CH on the anchored titanium oxide catalyst. UV irradiation of the TiO_2 in the presence of sufficient amount of H_2O and unsaturated hydrocarbon, such as C_3H_6 and C_4H_6, leads to the formation of photocatalytic hydrogenated products and oxygenated products (Anpo 1997; Anpo et al. 1984, 1987). As shown in Fig. 9, the rates of these photocatalytic reactions increase with the decrease of the ionization potential of the reactants (Anpo et al. 1989). There exists a parallel relationship between the enhancement of TiO_2 photoluminescence resulted from the addition of unsaturated hydrocarbons and the photocatalytic reaction rate of these unsaturated hydrocarbons with H_2O on TiO_2, since both of these two processes are closely associated with the electron transfer and the charge separated state. In other words, the initial electron transfer from the reactant molecules to TiO_2 to form cationic derivatives of the hydrocarbons is one of the crucial rate determining steps toward

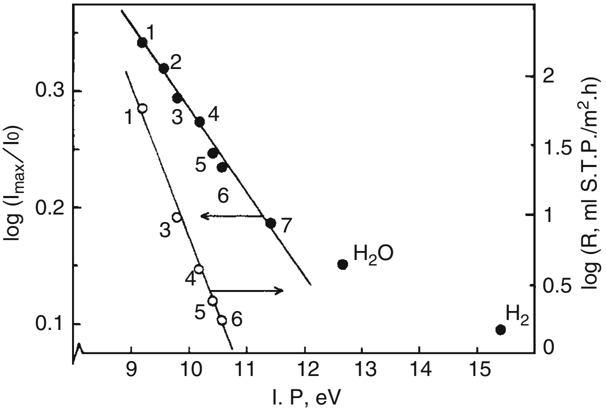


Fig. 9 Effect of additive ionization potentials on the photoluminescence intensity (*filled circle*) and the rate of the photocatalytic hydrogenation of the added unsaturated hydrocarbons with H_2O on TiO_2 (*open circle*). I_0 and I_{max} are maximum photoluminescence intensities, respectively, under vacuum (or in N_2) and in the presence of added compounds: (1) 1,3-butadiene; (2) 1-butene; (3) propene; (4) 1-butyne; (5) 1-propyne; (6) ethylene; and (7) acetylene. Photoluminescence spectra were recorded at −196°C. Photocatalytic reactions were carried out at 25°C (Anpo et al. 1989)

the efficient charge separation of the photoinduced electron/hole pairs, which in turn plays a vital role in determining the yields of the photocatalytic reaction and the intensity of the photoluminescence of the TiO_2 catalyst.

Jung et al. (2005) investigated the photoluminescence characteristics of anatase titania particles prepared by sol–gel method and found good correlations between the photocatalytic behavior and the sample's calcination temperature. They monitored the quenching behavior of the photoluminescence at −196°C by in situ oxygen supply. And Fig. 10 shows the dependence of the quenching intensity (the intensity difference at the peak position of the two photoluminescence spectra measured with and without oxygen) of prepared titania particles on the sample's calcination temperature. The photocatalytic activity of titania toward the decomposition of trichloroethylene (TCE) was measured and plotted as the function of the calcination temperature in Fig. 10. It can be seen that the photocatalytic activity changes in line with the quenching intensity with the variation of the calcination temperatures. The photoluminescence quenching is due to the upward bending of the band edge, which produces thicker space-charge layer for efficient separation of the photoinduced electron/hole pairs. The quenching level largely depends on the quantity of the surface-active sites on which oxygen can be adsorbed. The higher the photoluminescence quenching intensity implies the existence of larger amounts of surface-active sites which readily react with oxygen. Photocatalysis is a surface reaction and the reaction rate is proportional to the quantity of the surface-active sites taken by the electron acceptors or donors. And since titania shows efficient photoluminescence quenching, it is supposed that it should have high photocatalytic activity. The parallel relationship between the quenching intensity of the

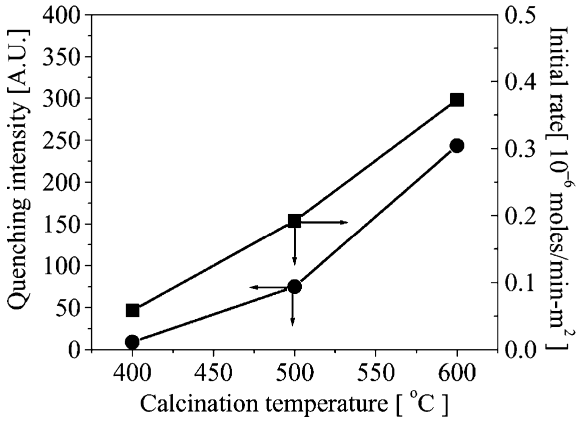


Fig. 10 The effect of the calcination temperature on the quenching intensity of photoluminescence measured at −196°C and the photoactivity of as-prepared titania particles (Jung et al. 2005)

photoluminescence and the photocatalytic activity of TCE decomposition suggests that the increase of the photocatalytic activity of titania particles with the increase of the calcination temperature is due to the formation of surface-active sites.

7 Conclusions

In this chapter, we discussed the application of photoluminescence spectroscopy in the study of TiO_2 photocatalysts. The origin of the TiO_2 photoluminescence, the influence of the adsorbates and loaded Pt on the photoluminescence properties of TiO_2, and the relationship between photoluminescence properties and the photocatalytic activities are summarized. Photoluminescence spectroscopy is an effective way to study the electronic structures, optical and photochemical properties of semiconductor materials. The photoluminescence spectrum applied in photocatalysis fields can provide useful information about the surface oxygen vacancies and defects, the efficiency of charge carrier trapping, immigration and transfer, which are useful for designing and synthesizing new semiconductor photocatalysts with high activity. Better understanding of these processes is crucial for the design and synthesis of new semiconductor photocatalysts with high photocatalytic activity.

It should mention that we haven't included the time-resolved photoluminescence spectroscopic technique in this chapter, though it can provide more direct information about the transfer and separation processes of the photo-induced charge carriers at or near semiconductor surfaces and their effects on photocatalytic activity. Several good studies on TiO_2 have been reported using time-resolved photoluminescence spectroscopy (Fujihara et al. 2000; Harada et al. 2007). Application of the steady-state and time-resolved photoluminescence spectroscopy combined with other related techniques is a powerful tool to nail the nature of the complex photocatalytic processes, which is the main message we would like to deliver in this chapter.

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