Lanthanide oxide doped titania photocatalysts for degradation of organic pollutants under UV and visible light illumination

D. Tz. Dimitrov*, M. M. Milanova, R. P. Kralshevska

Department of General and Inorganic Chemistry, Faculty of Chemistry, University of Sofia, 1, J. Bourchier Blvd., Sofia 1164, Bulgaria

Received November 2, 2010; Revised January 5, 2011

The main goal of this short review is to present the most valuable attempts that have been made in the past decades to shift the absorption of TiO$_2$ from UV- to the visible-light region by lanthanide doping. In order to understand the other factors by which doping of TiO$_2$ with lanthanides can increase the photocatalytic activity under solar irradiation, the first short chapter is devoted to the physical mechanisms responsible for the degradation of organic pollutants by lanthanide oxide doped titania under UV-light exposure. This aspect has been studied for a long time and is better understood. The second chapter deals with the same features, but extended for the visible-light exposure of catalysts. The most typical observations for bathochromic shift, effect of co-doping and organic dye sensitizing on the photocatalytic activity of lanthanide oxide doped titania are considered in detail.

Key words: photocatalysts, titania, lanthanides-doped titania, visible light.

INTRODUCTION

The heterogeneous photocatalysis based on oxide semiconductors is a promising technology for remediating environmental pollution and solving energy depletion and has become one of the most active research fields in recent years. So far, researchers have developed many materials that have the potential to act as photocatalysts for a wide range of applications including TiO$_2$, WO$_3$, SrTiO$_3$, $\alpha$-Fe$_2$O$_3$, ZnO and NaBiO$_3$. Among them, TiO$_2$ has proven to be a benchmark catalyst for detoxification of organic pollutants [1-4]. The photoexcitation of a semiconductor leads to the formation of an electron-hole pair. The excited-state conduction band electrons can: recombine with the holes and dissipate the input energy; get trapped in surface states; react with electron donors and electron acceptors adsorbed on the semiconductor surface [5].

In particular, because of their unique 4$\mu$-electronic configuration and spectral characteristics, lanthanides are ideal dopants for modifying the crystal structure, electronic structure, optical properties and surface adsorption of TiO$_2$ and forming a series of novel promising photocatalysts. On the other hand, as a group of elements that both resemble each other and show particular differences between them, lanthanides provide an opportunity for an in-depth study of the electronic structure that can influence the performance of TiO$_2$ photocatalysts [6]. However, as a wide band gap oxide semiconductor ($E_g = 3.23$ eV), anatase TiO$_2$ shows a photocatalytic activity only under UV-light irradiation ($\lambda < 384$ nm), which accounts for only a small fraction of the solar energy (~5%). The sun is an abundant source of photons, where visible light accounts for a large fraction of spectrum (~45%) [7]. Therefore, how to effectively utilize sunlight is the most challenging subject for extensive application of TiO$_2$. The main goal of the present article is to consider the most important attempts that have been made in past decades to shift the TiO$_2$ absorption from the UV region to the visible-light region. In order to understand all factors that can increase the photocatalytic activity under solar irradiation, the first short part of this review is devoted to the physical mechanisms responsible for the degradation of organic pollutants by lanthanide oxide doped titania under UV-light exposure.

1. PHYSICAL MECHANISMS RESPONSIBLE FOR THE DEGRADATION OF ORGANIC POLLUTANTS BY LANTHANIDE OXIDE DOPED TITANIA UNDER UV-LIGHT EXPOSURE

1.1 Enhancing of the photocatalytic activity of TiO$_2$ powder by suppressing electron-hole
recombination with trapping of photogenerated electrons at the interface.

Li et al. [8] have studied the effect of electrons, shallowly trapped by Gd$^{3+}$ in nanocrystalline La$_{1.5}$Gd$_{0.5}$Ti$_2$O$_7$ solid solution and in Gd$^{3+}$-doped TiO$_2$, on the photocatalytic activity in the liquid phase. They claim that the half-filled $f$-shells of Gd$^{3+}$ ions play a mechanistic role because it is more stable and when such a configuration is destroyed, it has a strong tendency to return to the original stable state. This particular characteristic of a dopant ion has a strong tendency to return to the original stable configuration and when such a configuration is destroyed, it has a strong tendency to return to the original stable state. This particular characteristic of a dopant ion has a strong tendency to return to the original stable configuration.

Rengaraj et al. [9] have discovered the synergetic effect of neodymium ions deposited on the TiO$_2$ surface, which behave as sites where electrons and sacrificial electron donors such as formic acid accumulate. The transfer of photo-induced electrons from the TiO$_2$ conduction band to the metallic Nd particles at the interface is thermodynamically possible because the Fermi level of TiO$_2$ is higher than that of Nd metal [10]. The proposed mechanism of the effect of both Nd particles and formic acid added as a hole scavenger is shown in Fig. 1.

Fig. 1. Mechanism of the photocatalytic reaction on a Nd–TiO$_2$ catalyst under UV [9].

The metallic Nd particles at the interface will act as electron traps, enhancing the electron–hole separation and the subsequent transfer of trapped electrons to the adsorbed O$_2$ or Cr(VI) acting as an electron acceptor. This can be explained by the surface electronic effect induced by neodymium. This reaction enables the positive photoholes p$^+$ to react with adsorbed OH$^-$ species in order to create •OH radical, as shown in the sequence of Eqs. (1-3):

$$(\text{TiO}_2)+\text{h}v\rightarrow\text{e}^-+p^+ (1)$$

$$\text{Nd}+\text{e}^-\rightarrow\text{e}_{\text{Nd}} (2)$$

$$\text{OH}^-+p^+\rightarrow•\text{OH} (3)$$

The •OH species formed from the holes will be accepted by HCOOH specially added for that purpose (Eq. (4)):

$•\text{OH}+\text{HCOOH}\rightarrow\text{intermediates}\rightarrow\text{CO}_2+\text{H}_2\text{O} (4)$

By this way HCOOH suppresses the electron–hole recombination process and increases the reduction efficiency. In the presence of formic acid, the Cr(VI) reduction reaction can be described as follows:

$$\text{Cr}_2\text{O}_7^{2-}+14\text{H}^++6\text{e}^-\rightarrow2\text{Cr}^{3+}+7\text{H}_2\text{O} (5)$$

In this reaction, 1 mol of Cr(VI) requires 3 mol of electrons to be reduced to Cr(III), which needs an equivalent of 3 mol of HCOOH to scavenge the holes. The enhanced reduction of oxygen through better electron-hole separation in Nd–TiO$_2$ particles compared to pure TiO$_2$ increases the rate of HCOOH degradation while simultaneously increasing the rate of reduction of Cr(VI).

Yang et al. [11] have studied the photocatalytic activity of CeO$_2$/TiO$_2$ mixed oxide nanoparticles. They claim that the Ce$^{4+}$/Ce$^{3+}$ redox couple increases the separation of electron-hole pairs. Doped cerium only may be present as the so-called second phase on the surface of TiO$_2$. CeO$_2$ can trap photo-generated electrons at the interface while reducing to Ce$^{3+}$ according to the reaction (6):

$$\text{e}^-+\text{Ce}^{4+}\rightarrow\text{Ce}^{3+} (6)$$

In this case, the role of Ce$^{4+}$ is the removal of electrons from electron–hole recombination sites with simultaneous production of oxidizable species.

Mele et al. [12] have used lanthanide diphthalocyanine sensitizers on a polycrystalline anatase TiO$_2$ surface. These sensitizers work because of the positions of conduction and valence band energy levels of anatase TiO$_2$ relative to the redox potentials of the sensitizers allow charge transfer by injection of an electron from the excited sensitizers to the conduction band of TiO$_2$ and from the conduction band of TiO$_2$ to the sensitizers.

Jiang et al. [13] have studied TiO$_2$ composite nanoparticles doped with low amount of Yb$^{3+}$; the doping increases the number of hydroxyl groups on the TiO$_2$ surface because Ti$^{4+}$ replaces Yb$^{3+}$ in the
Yb₂O₃ crystal lattice and creates a charge imbalance. In order to restore the charge balance, more hydroxide ions will be adsorbed on the surface, which could enhance the lifetime of electron-hole pairs.

Ökte and Yılmaz [14] have investigated the synergy between ZSM-5, TiO₂, and La₂O₃ of lanthanum loaded TiO₂-ZSM-5 photocatalysts where TiO₂ and La₂O₃ nanoparticles are dispersed on the support surface. The benefit of La⁺ ion incorporation is due to the capability of these ions to trap electrons, inhibit electron–hole recombination reactions and concentrate pollutant molecules on the catalyst surface. ZSM-5 acts as a hole trap (ZSM is abbreviation for Zeolite Sieve of Molecular porosity). This is possible because the high Si/Al ratio in ZSM-5 presents a limited number of Lewis acid sites in the framework. This property decreases the electron-delocalizing ability, but simultaneously allows capturing of photogenerated holes of TiO₂.

1.2 Enhancing of the photocatalytic activity of TiO₂ powder caused by the different effect of mesoporous walls

Peng et al. [15] have suggested that the presence of lanthanum ions in the TiO₂ mesostructure increases the photoactivity due to the larger surface area and more active sites for combining with molecules of the pollutant. The high degree of crystallinity also plays an important role in the photoactivity of TiO₂.

Zhao et al. [16] have shown that the absorption edge of TiO₂ shifts to the visible light range and the band-gap narrows, when TiO₂ is doped with Nd³⁺. The Nd species are distributed in the bulk of nanoparticle instead of concentrating on its surface. Density functional theory calculations are used to interpret the narrowing of the band-gap. The density of states (DOS) profiles of the undoped TiO₂ and Nd³⁺-doped anatase TiO₂ are shown in Fig. 2. The calculated value of the band-gap for undoped TiO₂ is 3.20 eV, which is in good agreement with the experimental value of 3.22 eV. The band-gap is formed between the O 2p orbitals and Ti 3d orbitals.

The main contribution to the valence band comes from O 2p orbitals, while the states at the conduction band are predominantly Ti 3d orbitals. A NdTiO₆ super cell models the Nd³⁺-doped anatase with Nd atoms in the substitutional sites. The DOS for this structure is shown in Fig. 2 b with a much smaller band-gap value (1.93 eV) calculated. Obviously, the existence of DOS of Nd 4f orbitals means that some electronic states are introduced into the band-gap of TiO₂ by Nd 4f electron levels located close to the lower edge of conduction band to form new LUMO (lowest unoccupied molecular orbitals). Consequently, the photoexcited electron for Nd-doped material can be transferred from O 2p to Nd 4f instead of Ti 3d, which is different from the situation of undoped TiO₂.

1.3 The effect of co-doping on the photocatalytic activity

Shi et al. [17] have found a marked improvement of the photocatalytic activity of TiO₂ by co-doping with Fe³⁺ and Ho³⁺. Fe³⁺-doping improves the photoutilization of TiO₂ and generates more electron–hole pairs under photoirradiation, which helps to improve the photocatalytic activity of TiO₂.
The crystal expansion and matrix distortion of TiO\(_2\) caused by Ho\(^{3+}\)-doping creates oxygen vacancies, which generate shallow energy states in the bottom of conduction band and serve as electron trap sites in nanocrystalline TiO\(_2\). Meanwhile, shallow energy states introduced by the rare earth ions in the top valence band serve as hole trap sites. The separation of charge carriers is attributed to such trapping. Subsequently, the charge carriers transfer to the surface of photocatalyst to cause there redox reactions so that the photocatalytic activity of doped TiO\(_2\) is promoted. When both Fe\(^{3+}\) and Ho\(^{3+}\) are co-doped into the nanocrystalline TiO\(_2\) particles, a synergistic effect will be produced. Fe\(^{3+}\)-doping broadens the absorption profile, improves the photoutilization of TiO\(_2\), and thereby generates more electron–hole pairs. Ho\(^{3+}\)-doping prevents the increase of grain sizes, leads to a crystal expansion and matrix distortion and retards the recombination of photoexcited charge carriers. The photocatalytic activity of TiO\(_2\) co-doped with Fe\(^{3+}\) and Ho\(^{3+}\) is markedly improved.

1.4 The effect of intrinsic surface properties on the photocatalytic activity

Zhang et al. [18] have investigated the properties of Dy\(_2\)Ti\(_3\)O\(_7\) prepared by two different methods: citric-acid sol–gel soft chemistry and solid state reaction route. Dy\(_2\)Ti\(_3\)O\(_7\) nanocrystals prepared by the citric acid method have an oxygen content that is much lower than the theoretical value; the oxygen-deficiency on the Dy\(_2\)Ti\(_3\)O\(_7\) surface is about 40%. This oxygen deficiency helps the catalyst to absorb more O\(_2\) and is very beneficial to achieve a good photocatalytic activity. Both the morphology and the degree, by which it can be dispersed, are quite different from those of samples produced by the solid state reaction. The Dy\(_2\)Ti\(_3\)O\(_7\) crystals of samples obtained by the citric acid method are quadrilateral and have a good dispersibility, while the average crystal size is about 50 nm. It is very difficult to identify the morphology of Dy\(_2\)Ti\(_3\)O\(_7\) produced by the solid state reaction and its dispersibility is quite low. The BET surface area of Dy\(_2\)Ti\(_3\)O\(_7\) prepared by the citric acid method is 25 m\(^2\)/g, which is much larger than that of samples prepared by traditional solid state reaction (2 m\(^2\)/g) and other soft chemistry routes. The good physical properties of the sample obtained by the citric acid method result in a better photoactivity than that of the sample prepared by solid state reaction. For the first, the photodegradation of methyl orange is 98.6% within 60 min, whereas for the second, the degree of decomposition is only 16.0%.

2. PHYSICAL MECHANISMS RESPONSIBLE FOR THE DEGRADATION OF ORGANIC POLLUTANTS BY LANTHANIDE OXIDE DOPED TITANIA UNDER VISIBLE-LIGHT EXPOSURE

The effects of lanthanide doping on the electronic structures and optical properties of anatase TiO\(_2\) are studied by Zhao and Liu [6]. They presented electronic structures and optical properties of pure anatase TiO\(_2\) and lanthanide-doped TiO\(_2\), based on calculations of the crystal structures. The results indicate that the lanthanide doping could remarkably improve the photocatalytic activity of TiO\(_2\), and that the effect of improvement is sensitive to the atomic electronic configuration and ionic radius. Most lanthanide doping could narrow the band gap of TiO\(_2\), so the fundamental absorption edges shift to the visible light region and simultaneously maintain strong redox potentials. In terms of the correlation of electronic structure and optical properties, the ref. [6] describes that there are three kinds of electronic transitions in lanthanide-doped TiO\(_2\): intraband transition in lanthanide 4\(f\) states, interband transition between O\(_2\) states and lanthanide 4\(f\) states and interband transition between IELs and valance band maximum or conduction band minimum (IELs is abbreviation for impurity energy levels).

2.1 Shift of the absorption from UV-light region to visible-light region by lanthanide doping

Parida and Sahu [19] have found a high photocatalytic activity for the reduction of hexavalent chromium and methylene blue degradation under visible light by La\(^{3+}\)-TiO\(_2\) containing 0.4 mol% lanthanum, prepared by incipient wetness impregnation method and activated at 400°C. The photocatalytic activity of TiO\(_2\) doped with lanthanides is shifted to the visible part of the spectrum (bathochromic shift). It was observed (see Fig. 3) that the absorption edges of La\(^{3+}\) doped TiO\(_2\) shift slightly towards a longer wavelength (red shift) compared to that of pure TiO\(_2\), for which the samples are active under visible light of the solar spectrum.
D. Tz. Dimitrov et al.: Lanthanide oxide doped titania photocatalysts for degradation of organic pollutants...

Fig. 3. UV–vis spectra of pure and La$^{3+}$ doped TiO$_2$ [19].

Xiao et al. [20] have studied the visible light photocatalytic decomposition of methylene blue by 0.5 mol% Sm$^{3+}$ doped TiO$_2$ produced by sol-gel auto-combustion synthesis. To investigate the optical absorption properties of their catalysts, they have examined the diffuse reflectance spectra (DRS) of TiO$_2$ and Sm$^{3+}$-doped TiO$_2$ in the range of 220–850 nm. They have found that while TiO$_2$ has no absorption in the visible region (>400 nm), Sm$^{3+}$-doped TiO$_2$ shows a significant absorption between 400 and 500 nm, which increases with increasing the samarium ion content. The photocatalytic activity of Sm$^{3+}$-TiO$_2$ is higher than that of undoped TiO$_2$, which is consistent with the larger specific surface area of Sm$^{3+}$-TiO$_2$ compared to undoped TiO$_2$. However, it is noticeable that the larger specific surface area of Sm$^{3+}$-TiO$_2$, resulting from a higher samarium ion dosage does not lead to a higher photocatalytic activity, which might be limited by a lower separation efficiency of electron–hole pairs.

Fig. 4. The photoluminescence emission mechanisms of TiO$_2$ and Ce$^{3+}$–TiO$_2$ catalysts at 77 K [21].

Li et al. [21] have found enhanced photocatalytic activity of Ce$^{3+}$–TiO$_2$ prepared by a sol–gel process for the degradation of 2-mercaptobenzothiazole in aqueous suspension for odor control. They have investigated the optical absorption properties of TiO$_2$ and Ce$^{3+}$–TiO$_2$ catalysts in the range of 220–850 nm and have found that while TiO$_2$ has no absorption in the visible region (>400 nm), Ce$^{3+}$–TiO$_2$ has a significant absorption between 400 and 500 nm, which increases with increasing the cerium content. CeO$_2$ is a n-type semiconductor with a band gap of about 3.2 eV [22,23]. Therefore, the absorption at 400–500 nm can not be attributed to CeO$_2$, but should rather be due to Ce$_2$O$_3$. In contrast to the closed shell of Ce$^{4+}$-ion ($4f^0$), the Ce$^{3+}$-ion possesses a single optically active electron with the ground-state configuration in the $4f^1$-orbital. Within this configuration, there are only two electronic levels, the $^2F_{7/2}$ excited state and the $^2F_{5/2}$ ground state. The $4f-4f$ transitions attributed to Ce$^{3+}$ can only be observed in the infrared spectral region. However, Ce$^{3+}$ has a first state configuration $5d^1$ that is rather close in energy. The electronic dipole transitions $4f \leftrightarrow 5d^1$ may occur in either the UV or visible region. Based on the valence band of Ce$^{3+}$–TiO$_2$ as determined by XPS, the authors propose that electron hole pairs are generated in both types of catalysts (Ce$^{3+}$–TiO$_2$ and Ce$_2$O$_3$) by two mechanisms shown in Fig. 4. According to Eq. (7), an electron can be excited from the valence band of Ce$^{3+}$–TiO$_2$ into the Ce $4f$-level when the energy of the photon is more than ($E_{\text{Ce}^{4f}} - E_v$). Equation (8) shows the excitation of an electron from the ground state of Ce$_2$O$_3$ into the Ce $4f$-level.

Therefore, the red shift of the absorption edge for Ce$^{3+}$–TiO$_2$ is explained by the following two reactions. The Ce $4f$ levels may play a crucial role in generating electron-hole pairs under visible light illumination.

\[
Ce^{3+} - TiO_2 + h\nu \rightarrow e^- + h^+ \quad (7)
\]
\[
Ce_2O_3 + h\nu \rightarrow e^- + h^+ \quad (8)
\]

The optimal dosage of cerium under visible light illumination is found to be 0.7%, while for UV illumination it is 1.2%. Ikeda et al. [24] have proposed that the rate of electron-holes escaping from their recombination should be proportional to the light flux of excitation and to the probability of light absorption to produce an electron-hole couple (F). This means that the optimal dosage may be
dependent on the reaction conditions. The value of $F$ under visible light illumination is much lower than that under UV illumination in this study. The lower $F$ value might lead to a lower Ti$^{3+}$ content. Therefore, the optimal dosage of ceria under visible light illumination is lower than that under UV illumination at these experimental conditions.

2.2 The effect of co-doping on the photocatalytic activity

Xu et al. [25] have prepared Ce, C-codoped TiO$_2$ nanoparticles through a modified sol–gel method under mild conditions and have studied their photocatalytic activity under visible light. The UV–vis spectra of the TiO$_2$ samples (plotted in Fig. 5) show that Ce, C-codoped titania has a greatly improved absorption of visible light.

![Fig. 5. UV-Vis spectra of Ce, C-codoped titania particles [25].](image)

The authors claim that the distance of charge transfer between the $f$-electrons of the cerium ions (or the C dopant) and the conduction or valence band of TiO$_2$ is narrowed, thus allowing visible light absorption. The energy level of Ce$^{4+}$/Ce$^{3+}$ is 1.8 eV. The introduction of such energy level in the band-gap can give rise to the red-shift in the band-gap transition. The Ce 4$f$ level also plays an important role in the interfacial charge transfer and elimination of the electron-hole recombination.

2.3 Shift of the absorption from the UV region to the visible light region by organic dye sensitizing

Xie and Yuan [26] have demonstrated an effective photodegradation of reactive brilliant red dye (X-3B) with the reaction system dye/Ce$^{4+}$-TiO$_2$/visible-light prepared by chemical coprecipitation–peptization and hydrothermal synthesis. The optical band gap energy of TiO$_2$ sol is estimated to be 350 nm by measuring the UV-Vis spectra for TiO$_2$ and Ce$^{4+}$-TiO$_2$ sol. Both TiO$_2$ and Ce$^{4+}$-TiO$_2$ s have similar UV-Vis absorption spectra except for the absorption intensity at the maximum wavelength ($\lambda$ = 202 nm). There was no apparent absorption in the visible-light range ($\lambda$ > 400 nm). This means that the sol–sol system cannot be directly excited by visible light irradiation. The absorption band shows a blue shift, which is due to the quantum size effect of sol nanoparticles. The experimental results, however, show that the dye photobleaching reaction occurs on Ce$^{4+}$-TiO$_2$ (both sol and nanocrystalline system) under visible light. The photosensitized photocatalysis reaction mechanism of dye bleaching in the Ce$^{4+}$-TiO$_2$ sol system is shown in Fig. 6.

![Fig. 6. Photosensitized photocatalysis mechanism of the Ce$^{4+}$-TiO$_2$ sol system [26].](image)
It can be seen from Fig. 6 that the Ce$^{4+}$-TiO$_2$ sol particles are physically adsorbed on the surface of sol particles and a dye molecule is excited by the absorption of a visible-light photon. The dye molecule in the excited state can then transfer electrons to the Ce$^{4+}$ ion. Meanwhile, the positively charged vacancies (h$^+$) remaining on the dye molecule can extract electrons from hydroxyl species in the solution to produce hydroxyl radicals (HO') These radicals are strong electrophiles capable of oxidizing and destroying organic molecules in aqueous media. In this process, the Ce$^{4+}$ species act as electron scavengers to trap electron transfer is the key step to inhibit electron–cation radical recombination. The cation radical (dye•+) produced by the electron injection is less stable than the ground state of the compound (dye). As a result, the unstable cation radical of dye may either directly degrade to products or react with superoxide radical anion (O$_2$•−) to produce degradation products. The photocatalysis of TiO$_2$ sol and P25 TiO$_2$ powder can be explained by the above reaction mechanism. However, in the photocatalysis with Nd$^{3+}$–TiO$_2$ sol system, the Nd$^{3+}$ species can act as effective electron scavengers to trap the conduction band electrons of TiO$_2$ that have been injected from the excited dye molecules. Nd$^{3+}$ ions, as a Lewis acid, apparently are superior to oxygen molecules (O$_2$) in their ability to trap electrons. The electrons trapped

**Fig. 7.** Sensitized photocatalysis mechanism in the Nd$^{3+}$–TiO$_2$ sol system (S$_0$ = singlet ground state, S$_1$ = first excited singlet, T$_1$ = first excited triplet state, ISC = intersystem crossing) [27].
on Nd$^{3+}$ sites (Nd$^{3+}$) are subsequently transferred to the surrounding adsorbed O$_2$ by an oxidation process. The presence of Nd$^{3+}$ on the surface of TiO$_2$ sol nanoparticle may promote the following processes: Nd$^{3+}$ + e$^{-}$ → Nd$^{2+}$ and Nd$^{2+}$ + O$_2$ → Nd$^{3+}$ + O$_2^•$. More effective electron trapping and transferring will produce more cation radicals, which are more active to undergo degradation. Therefore, Nd$^{3+}$ TiO$_2$ sol shows a superior photocatalytic activity in comparison with the TiO$_2$ sol and P25 TiO$_2$ powder.

Xie and Yuan [28] have also studied the activity of Nd$^{3+}$–TiO$_2$ nanocolloids for the photodegradation of phenol in water solution by visibile light, and have explained the observed enhancement with self-sensitization and sub-band gap overlapping. The AFM micrograph and XRD show that sol particles (10 nm in size) are well developed in the whole dispersion system and have a semicrystalline structure. The difference in ion radius (1.13 nm for Nd$^{3+}$ and 0.64 nm for Ti$^{4+}$) means that the neodymium(III) ion is unlikely to be built effectively into the crystal lattice of bulk TiO$_2$ when the Nd$^{3+}$–TiO$_2$ sol crystallizes at 62$^\circ$C. However, during the peptizing and digesting processes, Nd$^{3+}$ can bond with non-bridging oxygen ions at the surface of –Ti–O–Ti–O– bulk network structure. After crystallization, the sol system forms with individual TiO$_2$ particles crosslinked with neodymium cations at the surface, which form NdOCl molecules. NdOCl is sensitive to visible light, but its discrete energy levels cannot be split into well divided band gaps. Due to the character of electronic arrangement of neodymium with partially filled atomic d or f shells, electrons can be excited and transferred from the Nd$^{3+}$ 4f-orbitals by absorbing visible-light photons of the right energy. The surrounding Nd$^{3+}$ ions may react with the Nd$^{4+}$ produced by a self-sensitization process, thus forming a positively charged neodymium cluster (Nd$_m$)$^{3n}$ (m > 3n). This neodymium cluster has empty multi energy levels below the conduction band of crystalline TiO$_2$. Their presence allows a new electronic transition from the TiO$_2$ valence band to the empty energy levels of neodymium cluster known as a sub-band gap. This transition requires less energy than the TiO$_2$ valence-conduction band transition (3.2 eV) and can be induced by visible light. Simultaneously, the positively charged vacancies (h$^+$) in the TiO$_2$ valence band can extract electrons from the hydroxyl species to produce hydroxyl radicals (•OH), by which organic molecules as well as other oxidizable species can be degraded. Figure 8 shows the photocatalytic reaction mechanism in the Nd$^{3+}$–TiO$_2$ sol system.

Xie et al. [29] have then studied photosensitized and photocatalyzed degradation of azo dye using Ln$^{n+}$–TiO$_2$ sol in aqueous solution under visible light irradiation. They have developed a new method of chemical coprecipitation–peptization to synthesize a crystalline TiO$_2$ sol at a low temperature (<100$^\circ$C), which is attractive to further improve the photocatalytic activity of TiO$_2$ catalysts. Compared to most TiO$_2$ powders, these TiO$_2$ sol catalysts have several advantages: (1) finer particle size with more uniform distribution and better dispersion in water; (2) stronger interfacial adsorption ability; and (3) easy coating on different supporting materials including substrates with a poor heat resistance such as polymers, optical fibers, plastics, wood, and paper.

It is generally believed that pure TiO$_2$ cannot be directly excited by visible light due to its high band-gap of 3.2 eV. The system X-3B dye/Ln$^{n+}$–TiO$_2$ has an entirely different mechanism of photo-excitation under visible light illumination. The X-3B dye sensitization process involves the excitation of dye
molecules by absorbing visible light photons, followed by the electron injection from excited dye molecules to the TiO₂ conduction band. Then the electrons are transferred from the conduction band to the working electrode (ITO conductive film) and finally form out-circuit. In such as system (dye/Ln³⁺-TiO₂/vis hydrosol), the Ln³⁺-TiO₂ particles act as a bridge band connecting the X-3B dye and the working electrode. Some key reactions are shown in Eqs. (9–14):

\[
\text{Dye} + h\nu \rightarrow \text{dye}^* \quad (9)
\]
\[
\text{Dye}^* + \text{TiO}_2 \rightarrow \text{TiO}_2(\text{e}^-) + \text{dye}^+ \quad (10)
\]
\[
\text{TiO}_2(\text{e}^-) + \text{O}_2 \rightarrow \text{O}_2^{*-} + \text{TiO}_2 \quad (11)
\]
\[
\text{Ln}^{n+} + \text{TiO}_2(\text{e}^-) \rightarrow \text{Ln}^{(n-1)+} + \text{TiO}_2 \quad (12)
\]
\[
\text{Ln}^{(n-1)+} + \text{O}_2 \rightarrow \text{O}_2^{*-} + \text{Ln}^{n+} \quad (13)
\]
\[
\text{O}_2^{*-} + \text{dye}^{++} \rightarrow \text{intermediates or final products} \quad (14)
\]

In the above reactions, the dye can be excited under visible light illumination (Eq. 9). The dye molecule in the excited state can then transfer electrons into the conduction band of TiO₂ (Eq. 10) that may be trapped by the electron scavengers such as oxygen molecule that usually surround the sample (Eq. 11). If the transferred electrons accumulate in the conduction band of TiO₂, recombination between cationic radicals and the electrons is extremely likely. Therefore, the electron trapping (Eq. 12) and electron transfer (Eq. 13) are two key steps to inhibit electron-cationic radical recombination. The cationic radical (dye⁺⁺) produced by electron injection is less stable than the probe molecule in the ground state. As a result, the unstable dye cationic radicals can be directly degraded into decomposition products by reacting with super-oxidizing anionic radicals or other active oxygen (HO*, HOO* and O₂−) (Eq. 14). The lanthanide ion that TiO₂ is doped with plays an important role in promoting significantly the electron trapping and electron transfer in the dye/Ln³⁺-TiO₂ hydrosol system. The photosensitization reaction mechanism and potential states in the dye/Ln³⁺-TiO₂/vis system are further illustrated in Figs. 9 and 10.

Su et al. [30] have studied the visible light photocatalysis on praseodymium(III)-nitrate-modified nanocrystalline TiO₂ 5 nm in particle diameter, that is prepared by an ultrasound method in a sol–gel process at low temperature. The UV–vis diffuse reflectance spectra of the Pr(NO₃)₃-TiO₂ and undoped TiO₂ samples show that both samples have a strong absorption at wavelengths below 400 nm, which is attributed to the transitions of electrons from the valence band to the conduction band of TiO₂. Visible light absorptions at 444, 469, 482 and 590 nm are observed for Pr(NO₃)₃-TiO₂ only, which are attributed to the 4f-transitions \( ^3\text{H}_4 \rightarrow ^3\text{P}_2 \), \( ^3\text{H}_4 \rightarrow ^3\text{P}_1 \), \( ^3\text{H}_4 \rightarrow ^3\text{P}_0 \) and \( ^3\text{H}_4 \rightarrow ^1\text{D}_2 \) of praseodymium(III) ions. This absorption feature suggests that the photocatalyst can be activated throughout the visible wavelengths where the light absorption occurs. The sample shows a high activity and stability in the decomposition of rhodamine-B (RhB) and 4-chlorophenol (4-CP) under visible light.

**Fig. 9.** Proposed mechanism of photosensitization reaction in the system dye/Ln³⁺-TiO₂/vis [29].
Fig. 10. Schematic illustration of the valence and conduction band potentials of TiO_2 and excitation and ground state potentials of the X-3B molecule along with the standard reduction potentials of lanthanide ion pairs [29].

Fig. 11. Postulated mechanism for the visible light-induced oxidative degradation of RhB in aerobic aqueous media on TiO_2 (A) and Pr(NO_3)_3-TiO_2 (B) surfaces [30].

irradiation. From the investigation of photoinduced conversion of RhB, carried out under visible light illumination at wavelengths greater than 420 nm in aqueous Pr(NO_3)_3-TiO_2 dispersions, one can conclude that RhB photodegrades by a pathway that is distinct from the pathway prevailing in the pure TiO_2 dispersion. The latter pathway is related to self-photosensitization of RhB as shown in Fig. 11A.

The results presented above reveal that a completely different mechanism of charge generation must operate for the Pr(NO_3)_3-TiO_2 photocatalysts. The authors postulate as a working hypothesis a simple mechanism depicted in Fig. 11B. The local excitation of praseodymium(III) nitrate under visible light irradiation yields a metal-to-ligand charge-transfer transition 4f(Pr^{3+})(^1H_4 → 3P_2, 3P_1, 3P_0 and 1D_2) → π* (NO_3^2−), which produces Pr^{4+} and NO_3^2−-intermediates. The labile NO_3^2− anion intermediate will rapidly transfer electrons to the conduction band of TiO_2. The strong oxidizing Pr^{4+} ions (standard redox potentials of E^0(Pr^{4+}/Pr^{3+}) = +2.86 V, and E^vb(TiO_2) = +2.7 V) attract electrons from either the surface OH groups and/or the surface H_2O molecules to produce hydroxyl radicals through the reaction depicted in Fig. 11B (evidence for this is found in the ESR spectrum). This electron transfer leads to efficient charge separation and effectively suppresses the recombination between Pr(IV) and NO_3^2− by the surrounding TiO_2 matrix. In the absence of Pr(NO_3)_3, the titania cannot be directly excited by visible light due to its 3.2 eV band-gap, but the photobleaching reaction still occurs in the TiO_2/dye/visible light system due to the dye molecule acting as a photosensitizer. Molecular O_2 adsorbed on TiO_2 acts as an electron scavenger to trap the excitation electrons of the excited dye molecules, thus producing superoxide radical (O_2•−) and the extent of photoactivity is somewhat lessened. The difference in ESR spectra observed with respect to the kind of active oxygen species produced between the Pr(NO_3)_3-TiO_2 and TiO_2 dispersions is then understandable. In addition to the local excited photocatalysis, the dye assisted photosensitization also plays an important role in the photo-oxidative degradation of RhB in the dye/TiO_2 system. The produced superoxide radical is reduced by the electron from NO_3^2− to form •OH,
as shown in Fig. 11B. Therefore, the photocatalysis and photosensitization simultaneously occur under visible light irradiation. It is clearly shown that the photocatalytic oxidation is superior to the photosensitized oxidation, and the photocatalytic process will surely help to improve the overall photodegradation efficiency and make the bleaching reaction more feasible.

Mele et al. [12] have compared the photocatalytic activity of TiO$_2$ samples impregnated with lanthanide diphthalocyanines with those impregnated with Cu(II)-porphyrin. The photocatalytic degradation of 4-nitrophenol (4-NP) in aqueous suspension is used as a probe reaction. Commercial anatase TiO$_2$ is impregnated with home-prepared double-decker phthalocyanine complexes of the lanthanide metals, such as Ce, Pr, Nd, Sm, Ho, and Gd. In particular, the impregnation with Ho, Sm, and Nd complexes, acting as sensitizers, proves beneficial for the photoactivity of studied systems. Significant improvements of the TiO$_2$-based catalytic system seem possible in terms of lower impregnation loading, enhanced photoreactivity under solar light irradiation, as well as chemical, thermal, and photochemical stability of the sensitizers in comparison with those using Cu(II)-porphyrin.

No appreciable shift of the band gap edge of TiO$_2$ can be observed for all of the samples from the diffuse reflectance spectra of bare TiO$_2$ and some LnPc$_2$-loaded TiO$_2$ photocatalysts recorded in the range of 250-800 nm. Nevertheless, all of them reflect less light than the bare support, and the absorption increases with increasing of loading. All of the spectra of the LnPc$_2$-TiO$_2$ samples present quite similar patterns, independent of the coordinated lanthanide metal, showing absorption maxima at nearly the same $\lambda$-value. The characteristic bands are due to the strong absorption, particularly within the Q-range (ca. 650-680 nm), by the LnPc$_2$ particles deposited on the TiO$_2$ grains. The bands are relatively broad compared to the respective solution spectra, and all of the studied samples show similar large absorptions that cover the visible range fairly well. Moreover, the spectra of SmPc$_2$, GdPc$_2$, and HoPc$_2$ show distinct absorption peaks at ca. 460 nm, similar to the pesaks in dichloromethane and in nujol suspension. The LnPc$_2$ sensitizers probably enhance the absorption of studied samples also within the near-UV range (ca. 300-350 nm, B band).

Figure 12 shows the conduction band and the valence band energy levels of anatase TiO$_2$ at neutral pH and redox potentials of the various sensitizers considered in this study [12].

The presence of two phthalocyanine macrocycles in LnPc$_2$ favors probably a better delocalization of the positive charges during certain stages of the radical photocatalytic mechanism compared to “classic” porphyrins and phthalocyanine systems previously used as sensitizers. However, it is not easy to obtain a direct experimental evidence for this hypothesis. In addition, the formation of singlet oxygen [${}^1\text{O}_2(\Delta)$] in higher quantities, promoted by the photoexcited LnPc$_2$ sensitizers (sens), as shown bellow by eqs 15 and 16, and suggested elsewhere, may not be excluded.


3. CONCLUSIONS

This review presents a summary of the attempts made by different researchers in the past decades to shift the absorption of TiO$_2$ from UV-light to the visible light region by lanthanide doping. To understand the factors, by which TiO$_2$ doping by lanthanides can increase the photocatalytic activity under solar irradiation, the first chapter presents briefly the physical mechanisms responsible for the degradation of organic pollutants by lanthanide oxide doped titania under UV-light exposure. Some typical examples are presented, where the enhancement of photocatalytic activity of TiO$_2$ powder is due to the suppression of electron-hole recombination with trapping of photogenerated electrons at the interface, the different effects of mesoporous wall, the co-doping and the intrinsic surface properties. Based on these findings, the second chapter presents the ways of increasing the photocatalytic activity of catalysts towards visible-light by bathochromic shift, co-doping and organic dye sensitizing of lanthanide oxide doped titania are presented.

Acknowledgments. This study was performed with the financial support of the NATO “Science for Peace” Programme (Contract SJP 982835) as well of project DO02-252 of the National Science Fund of Bulgaria. The authors are thankful to Dr. C. Dushkin (Faculty of Chemistry, University of Sofia) and Dr. R. Smits (Catalysis Services International, Sofia) for the valuable discussions.

REFERENCES

D. Tz. Dimitrov et al: Lanthanide oxide doped titania photocatalysts for degradation of organic pollutants...

ТИТАНОВ ДИОКСИД С ДОБАВКИ ОТ ЛАНТАНОИДИ КАТО ФОТОКАТАЛИЗАТОР ЗА РАЗГРАЖДАНЕ НА ОРГАНИЧНИ ЗАМЪРСИТЕЛИ ПРИ ОБЛЪЧВАНЕ С УЛТРАВИОЛЕТОВА И ВИДИМА СВЕЛИНА

Д. Ц. Димитров*, М. М. Миланова, Р. П. Кралчевска

Катедра Обща и неорганична химия, Химически факултет, Софийски университет, бул. Джеймс Бауър 1, София 1164, България

Постъпила на 2 Ноември 2010 г.; Преработена на 5 януари 2011 г.

(Резюме)

Основната цел поставена при написването на този кратък обзор е да представи най-значимите изследвания, които бяха проведени през последните десетилетия, свързани с изместването на поглъщането на TiO₂ от ултравиолетовата във видимата област чрез добавки от лантаноиди. С цел да се внесе ясност в другите фактори, чрез които внасянето на лантаноиди в TiO₂ увеличава неговата фотокатализична активност при облъчването му с видима светлина, първата част на обзора е посветена на физическите механизми, причиняващи разграждането на органични замърсители от модифициран с лантаноиди TiO₂ при облъчването му с ултравиолетова светлина. Тази тема е изследвана много по-отдавна и по-добра изучена. Втората част на представения обзор представя отново тези механизми, но при облъчване на катализатора с видима светлина. Там подробно са разгледани най-типичните изследвания свързани с намаляването на ширината на забранената зона на TiO₂, ефекта на съвмесното модифициране едновременно с две добавки и ефекта на сенситизирането с помощта на органични оцветители при модифицираният с лантаноиди титанов диоксид.