Photocatalytic degradation of Rhodamine B under UV irradiation over anatase TiO$_2$:Ln$^{3+}$ nanoparticles

R Domínguez-Flores$^1$, L N Palacios-Grijalva$^1$ and A Martínez$^2$$^*$

$^1$División de Estudios de Posgrado e Investigación, Instituto Tecnológico de Tlalnepantla, Av. Instituto Tecnológico s/n, Col. La Comunidad, Tlalnepantla de Baz, Estado de México, C.P. 54070

$^2$Area de Física Atómica Molecular Aplicada, Ciencias Básicas – DCBI, Universidad Autónoma Metropolitana - Unidad Azcapotzalco, San Pablo 180, Col. Reynosa Tamaulipas, Ciudad de México, C.P. 02200

$^*$E-mail: amartinez@azc.uam.mx

Abstract. TiO$_2$:Ln$^{3+}$ (Ln$^{3+}$: Ce$^{3+}$, Yb$^{3+}$ and Sm$^{3+}$) nanoparticles were prepared by sol-gel method under laboratory ambient conditions by using titanium tetraisopropoxide (C$_{12}$H$_{28}$O$_4$Ti) as the TiO$_2$ source and template, and the as-synthetized samples were characterized by XRD and UV-vis DRS techniques. XRD patterns shows that the as-prepared nanomaterials exhibit tetragonal anatase-phase. The photoactivity of the synthesized catalysts was tested in the photocatalytic degradation of a Rhodamine B solution exposed to the following radiation wavelengths (254 nm, 350 nm, 365 nm, and 385 nm). UV-vis spectroscopy analysis of the samples was used to estimate the band gap energy of the samples.

1. Introduction
Wastewater management is a very important issue in several industrialized countries who employ organic dyes to give color to a great variety of finished products. This kind of industries is of main concern to environment safeguard as the wastewater contain many non-biodegradable organic dyes. Rhodamine B (RhB) is a synthetic water-soluble xanthene organic dye. It is widely used as colorant in textile, paper, plastic, cosmetics, leather, food, and many other industries as a result a large discharge of dye effluents is generated. When the wastewater effluents are not properly treated, they become a serious environmental hazard affecting not only flora and fauna ecosystems but also human health. The carcinogenic behavior of RhB dye can irritate the eyes and skin, may damage the respiratory, reproductive and nervous systems. Besides, rhodamine B is potentially dangerous even at very low concentrations for these reasons the treatment of the RhB effluents becomes a priority for environment protection [1-3].

Lately, visible light induced photocatalysis has gained growing attention because of its usefulness in making the most of sunlight to eliminate organic pollutants such as organic dyes [4-6]. In addition, conventional methods of wastewater treatment can not eliminate this type of contaminants, they only transfer the non-biodegradable matter into sludge, giving rise to a new type of pollution, which needs further treatment. This situation has generated the need of developing new economical and effective
technologies capable of efficiently solve the challenge of achieving an enough supply of potable water for human consume [7-10]. Titanium dioxide is one of the most widely investigated photocatalysts because of its high activity, low cost and availability. Yet its large band gap ($E_g = 3.2$ eV) harshly decreases efficient absorption of sunlight and restricts practical application in visible light driven catalytic reactions [11,12]. Chemical modification of TiO$_2$ is a viable approach to narrow the wide band gap, allowing the active photocatalysts to work in visible light region [13-16].

Specifically, multiple studies have been realized on doping nanostructured titanium dioxide with rare earth (RE) ions to improve its photocatalytic activity. In virtue of the ability of TiO$_2$ to form complexes with the lanthanides f-orbital, it will adsorb external ions around the surface, then amplifying the photocatalytic activity or other optoelectronic characteristics [17-19]. The RE ions forms complexion RE–O–Ti bond on the inner sphere surface. This chemical bond will inhibit the transformation from anatase to rutile, plus formed complexation will enhance the ability of the photocatalyst to absorb foreign ions [20-21]. Furthermore, the absorption of TiO$_2$ nanomaterials doped with RE ions may be tuned from UV to visible region because the RE ions can absorb photons in the visible region [20-24].

This study is focused in the comparison on the photodegradation activity of these titania based photocatalysts on an analytical grade RhB dye diluted in water. Also, photodegradation performance has been studied to measure the efficiency of each catalyst. The photocatalytic reactions are initiated when the TiO$_2$ semiconductor absorbs energy ($a$ photon or $h\nu \geq E_g$) [24] and an electron is excited from the valence band to the conduction band then a hole is formed in the valence band, this charge carriers are the responsible species of redox process and shift the $E_g$ to visible region. In this study a series of RE$^{3+}$/TiO$_2$ semiconductors were synthetized.

2. Experimental

2.1. Materials and synthesis
Titanium dioxide and materials TiO$_2$:Ln$^{3+}$ ($Ln^{3+}$: Ce$^{3+}$, Yb$^{3+}$ and Sm$^{3+}$), were synthesized using titanium tetraisopropoxide (TIP, C$_{12}$H$_{28}$O$_4$Ti), cerium nitrate (III) hexahydrate [Ce(NO$_3$)$_3$:6H$_2$O], ytterbium (III) chloride hexahydrate [YbCl$_3$:6H$_2$O], samarium nitrate (III) hexahydrate [Sm(NO$_3$)$_3$:6H$_2$O], ethanol (EtOH), Rhodamine B dye, the aforementioned chemicals were of analytical grade and purchased from Sigma Aldrich; nitric acid (HNO$_3$) and hydrochloric acid (HCl) were purchase from JT Baker, and deionized water (H$_2$O). All reagents were used without additional purification procedures. Titania nanoparticles were obtained by hydrolysis of TIP in a mixture of anhydrous EtOH, HCl, HNO$_3$ and H$_2$O, by sol-gel method, followed by 2 h calcination at 500 °C with a temperature rate of 5 °C / min in air atmosphere; in the case of the TiO$_2$:Ln$^{3+}$ materials, the corresponding lanthanide compound was added in the step prior to hydrolysis.

2.2. Structural characterization
The resulting nanomaterials were characterized by X-Ray Diffraction on a Philips XPert Diffractometer using Cu Kα radiation of 1.5045 Å operating at 40 kV and 25 mA, in a scanning range of 10-80° (20).

2.3. UV-Vis spectroscopy analysis
A UV–Vis spectrophotometer (Varian Cary 1G) with an integrating sphere attachment DRA-CA-30I for diffuse reflectance measurements was used to establish the optical band gap. The optical absorption was measured in the 190–900 nm range.

2.4. Photoluminescence spectroscopy
RhB was chosen as a model pollutant to evaluate the photocatalytic activities of the undoped and doped TiO$_2$ samples under UV and near visible light at room temperature. The reaction was carried out with natural air diffusion, and thus oxygen was involved in the reaction, 5 mg photocatalyst was added to 50
mL of RhB solution with an initial concentration of 10 ppm under constant stirring. The solution was stirred for 60 min in a glass reactor with UV radiation (254 nm, 350 nm, 365 nm, 385 nm and 405 nm). The distance between the irradiation source and the reactor containing the dye suspension was 12 cm. The photodegradation performance of each material was evaluated by fluorescence spectroscopy technique in a Varian Cary Eclipse equipment with a PMT detector at 540 V operating with λ<sub>ex</sub> = 573 nm and λ<sub>em</sub> = 545 – 700 nm, 5 mL aliquots were taken every 10 min for one hour.

3. Results and discussion

3.1. Structural analysis

The XRD patterns of the prepared powders are shown in Figure 1, the diffraction peaks displayed the predominant presence of the tetragonal anatase phase in all the samples with the diffraction peaks at 2θ of 25.48°, 37.70°, 38.87°, 48.17°, 53.88°, 55.26°, 62.46°, 69.29°, 70.07° and 75.23° which can be indexed as the (1 0 1), (1 0 3), (0 0 4), (2 0 0), (1 0 5), (2 1 1), (2 0 4), (1 1 6), (2 2 0) and (2 1 5) planes which were confirmed by means of the diffraction chart (JCPDS number 21-1272) and other XRD patterns of TiO<sub>2</sub> nanoparticles available in the literature [12,18,21].

In diffractograms can be observed that the presence of the rare earth ions (Ce<sup>3+</sup>, Yb<sup>3+</sup> and Sm<sup>3+</sup>) favors the stability of the anatase phase, as can be seen from the presence of relatively weak peaks of the rutile (1 1 0) and brookite (1 2 1) phases in pure titanium dioxide at 2θ of 27.6° and 30.89° respectively, which did not appear in the doped materials.

Figure 1. XRD patterns of the titanium dioxide prepared powders.

Crystallite size was calculated by Scherrer’s equation using three XRD peaks for each sample. MATCH! Phase Identification from Powder Diffraction, Crystal Impact software was used to made crystallite size calculation and the results can be seen in Table 1.

| Nanoparticles       | Mean crystallite size (nm) |
|---------------------|----------------------------|
| TiO<sub>2</sub>     | 57                         |
| 1% Ce<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> | 39                         |
| 1% Yb<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> | 47                         |
| 1% Sm<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> | 30                         |

3.2. Band gap calculations

To calculate the band gap of the RE<sup>3+</sup>/TiO<sub>2</sub> prepared samples, the use of the Indirect Transition Model [25-28] is employed in this study because of the nanostructured nature of the synthetized materials. The equation for this model is:

\[(a h ν)^{1/2} = B(h ν - E_g)\]  

(1)
Where $\alpha$ is the absorbance or diffuse reflectance (in this study we used the absorbance), $h\nu$ is photon energy in eV, $B$ is an independent parameter of the photon’s energy for the respective transitions in eV; $E_g$ is the band gap in eV. Determination of $E_g$ was made by the following equation:

$$E = h\nu = \frac{hc}{\lambda}$$  \hspace{1cm} (2)

Where $E$ is photon energy in eV, $h$ is Planck’s constant = 4.136x10^{-15} eV·s, $c$ is light velocity in vacuum = 2.998x10^{17} nm/s and $\lambda$ is wavelength in nm.

Then Equation 1 can be rewritten as follows:

$$ (\alpha E)^{1/2} = B(E - E_g) $$  \hspace{1cm} (3)

Finally if $(\alpha E)^{1/2}$ is plotted against $E$, the optical $E_g$ can be calculated from the intersection to $(\alpha E)^{1/2} = 0$, on the corresponding graphic by extrapolating a region apparently linear. According to the above-mentioned methodology indirect transitions were chosen in accordance with the linear adjustments shown in Figure 2, tendency of the obtained spectra suggests the activation of the material by the action of the photo induced photons on the sample during the measurements with the UV-Vis spectrophotometer.

The UV-Vis analysis of absorbance is showed in Figure 2, in the absorbance spectrum of the samples (Figure 2a) it can be observed that almost all of the samples, excluding the cerium doped one, have an absorbance maximum peak at 365 nm which corresponds to the near UV region and the cerium doped one have its maximum at 405 nm which corresponds to a red shift in the visible region, this result means that the electronic structure of titanium dioxide has been effectively modified by cerium dopant. The Figure 2 also shows the linear regression of the flat part of the absorbance spectrum (Figure 2a) and the Equation 3 absorbance function (Figure 2b) of the cerium doped sample and from this mathematical expressions the $E_g$ value can be estimated for the mentioned material, the same treatment was made for the estimation of the $E_g$ values of each material and the results are summarized in Table 2.

### Table 2. Experimental $E_g$ values obtained from absorbance spectra of the samples

| K-M function | TiO$_2$ | TiO$_2$:(1%)Ce$^{3+}$ | TiO$_2$:(1%)Yb$^{3+}$ | TiO$_2$:(1%)Sm$^{3+}$ |
|--------------|--------|----------------------|----------------------|----------------------|
| Abs.         | 2.94   | 2.09                 | 2.98                 | 3.02                 |
| $(\text{Absxh}\nu)^{1/2}$ | 2.70   | 1.50                 | 2.67                 | 2.70                 |
From the obtained results, it is suggested that the cerium doped material has an ideal value of \( E_g = 2.09 \text{ eV} \) for photocatalytic applications \((1.6 \text{ eV} \leq \Delta E_g \leq 2.2 \text{ eV})\) [29]. The results of the \( E_g \) values listed on Table 2 are in good agreement with the nanometric nature of the prepared materials, because the band gap can be adjusted due to electronic confinement that occurs in nanometric systems [30] and the effect of the RE\(^{3+}\) dopants used [17-19].

3.3. Photocatalytic experiments

In Figure 3, by exciting the materials at different wavelengths each one showed a distinct response depending on the irradiation wavelength and the intrinsic properties of each rare earth ion, at 254 nm (Figure 3a) the photocatalyst that presented best photodegradation performance was TiO\(_2\):(1\%)Yb\(^{3+}\) followed by un-doped TiO\(_2\), at 350 nm (Figure 3b) the powder that displayed best photodegradation activity was TiO\(_2\):(1\%)Yb\(^{3+}\) followed by TiO\(_2\):(1\%)Sm\(^{3+}\), at 365 nm (Figure 3c) the best material was the un-doped TiO\(_2\) this result may be explained by the absorbance spectra (Figure 2) in which the maximum peak its located precisely at 365 nm, for this is reasonable to think that the prepared material absorbs strongly at this wavelength. Finally, at 385 nm (Figure 3d), closer to the visible region the best photoactivity is associated with the TiO\(_2\):(1\%)Sm\(^{3+}\) photocatalyst.

Figure 3. Concentration vs time graphics of the RhB photodegradation experiments at different wavelengths

4. Conclusions

X-ray diffraction patterns confirmed that TiO\(_2\):Ln\(^{3+}\) (Ln\(^{3+}\): Ce\(^{3+}\), Yb\(^{3+}\) and Sm\(^{3+}\)) photocatalysts has been effectively synthetized with a tetragonal crystalline structure typical of the anatase phase of titanium dioxide. The UV-Vis spectroscopy analysis revealed an absorbance maximum peak at 365 nm which
corresponds to the near UV region for the un-doped TiO$_2$, the ytterbium doped material and the samarium doped one, as for the cerium doped catalyst the maximum appears at 405 nm which corresponds to a red shift in the visible region and this result means that the electronic structure of titanium dioxide has been effectively modified by cerium oxide dopant. From the Indirect Transition Model the $E_g$ values were estimated for each material and the lowest $E_g$ value who is optimal for visible light driven photodegradation of Rhodamine B correspond to photocatalyst TiO$_2$:(1%)Ce$^{3+}$, as for the effect of lanthanide doping the best material for the photodegradation process in the UV region was TiO$_2$:(1%)Yb$^{3+}$ at 350 nm because the Rh B dye was practically degraded in 1 hour.

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