PHOTOCATALITIC ACTIVITY OF N-DOPING TiO2 THIN FILMS DEPOSITED BY THE SOL-GEL TECHNIQUE

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Abstract
Titanium dioxide (TiO₂) is a very stable semiconductor physically and chemically, it is an abundant material and harmless to nature. Currently, TiO₂ is one of the most used photocatalysts to degrade organic molecules in both water and air during purification processes. In this work, we fabricated Nitrogen-doped TiO₂ powders by the Sol-Gel method, the Titanium tetraisopropoxide and urea were as reagents; subsequently, the materials were supported as thin films on glass using the technique of Doctor Blade. The materials were characterized by using different analytical techniques such as Raman spectroscopy, X-Ray Diffraction (XRD), and diffuse reflectance spectroscopy (DRS). The XRD results indicated that TiO₂ films presented a single crystalline phase, corresponding to the anatase. Besides, Raman spectroscopy verified the nitrogen incorporation in the crystal lattice of TiO₂ after the doping process. Furthermore, DRS results showed an improvement in optical photo-response at the visible region of the electromagnetic spectrum, the band-gap narrowing was verified from 3.25 eV for unmodified TiO₂ thin films until 2.84 eV TiO₂–N(5%) thin films. Finally, the photocatalytic activity of materials was studied during methylene blue (MB) degradation, the photocatalytic degradation results indicated the doping process enhanced photocatalytic activity under visible irradiation.

Key words: POA’s, Titanium oxide, anatase, doping with no metals, methylene blue.

1. Introduction
The treatment of liquid waste can be a very complex problem due to the wide variety of chemical compounds and their concentration levels, however, advanced oxidation processes (APOs) have an advantage over the typical techniques, since these processes are not selective and besides, they degrading a large amount of recalcitrant organic substances.

Currently, TiO₂ is the most used semiconductor in photocatalytic processes because it is cheap, safe, has a high resistance to corrosion and has photocatalytic activity [1]. The TiO₂ is found in nature in
several forms: (i) rutile (tetragonal structure), (ii) anatase (octahedral structure) and (iii) brookite (orthorhombic structure). The rutile and anatase-TiO\textsubscript{2} are produced industrially in large quantities and are used as pigments and catalysts, they are also widely used in the production of ceramic materials. TiO\textsubscript{2} is of great importance as a white pigment because of its dispersion properties, its chemical stability and its non-toxicity [2]. The TiO\textsubscript{2} is a light sensitive semiconductor, it absorbs electromagnetic radiation near the UV region, due to this, the TiO\textsubscript{2} cannot use the visible region of solar radiation, it can only take advantage of about 4\% of the solar radiation, this represents a major limitation, since a large amount of solar radiation is abundant energy and without cost [3].

The basic photocatalytic principle relies on the UV photogenerated pair carries (e. i. electrons (\(e^-\)) and holes (\(h^+\))), which can contribute to the organic substrate degradation, the \(h^+\) and the OH• radicals generating by the reaction with hydroxide anions or water adsorbed (on TiO\textsubscript{2} surface) are the major oxidative species for decomposition of organic pollutants [4]. Currently, different strategies are used to extend the TiO\textsubscript{2} photo-response range into the visible region of the electromagnetic spectrum: (a) photosensitization with synthetic and natural dyes, (b) surface modifications, (c) mixing with other semiconductors and (d) doping with metals and nonmetals [5-7]. Among the strategies, the doping process is a very efficient technique, since it significantly improves the electronic properties of the semiconductor and allows to reduce the value of its bandgap improving significantly its photo-response at longer wavelengths [8].

Last decades, different non-metals have been used as for TiO\textsubscript{2} (e.g. N, S, C, B, P, F) [9]. Among non-metal options, N-doped TiO\textsubscript{2} has attracted considerable attention for visible light applications and many reports on this topic have confirmed its visible light activity; last years, research in the field is directed to improve protocols of doping methods [10-12]. The photoactivity at lower wavelengths for N-doped TiO\textsubscript{2} can be explained by the creation of energy levels intra-bandgap, these new energy levels allow electronic excitation with lower energy values to those of the bandgap of pure material, when doping is performed, the effects of electron-hole pair recombination during irradiation are reduced, the decreasing in the recombination of the pair carriers could result in improvement of photoactivity [13].

Finally, the TiO\textsubscript{2} is used for environmental applications in suspension form (dispersing nanoparticles of high surface area); this allows a good mass transfer and direct contact with large amounts of contaminant. However, on a practical level, the use of free nanoparticles in aqueous media makes it necessary to incorporate a rigorous filtration process for subsequent separation from the medium;
besides, the aggregation of particles by electrostatic phenomena could result in an increase in the recombination of the charge carriers in the solid and decrease in the active area for photocatalysis [14]. These drawbacks can be solved for using photocatalyst nanostructures on support; the fixation of the TiO₂ as a thin film eliminates additional steps for recovering the catalyst from the reaction medium after the degradation process.

In this work, we studied the Nitrogen doping process on TiO₂ to fabricate thin films supported on a glass surface for photocatalytic applications.

2. Experimental

2.1. Materials and Methods.

All reagents in this work were analytical grade, urea, (> 99%), Sigma Aldrich titanium isopropoxide, isopropyl alcohol, PEG and water.

2.2. Synthesis of the catalysts and thin films fabrication

The N-doped TiO₂ photocatalyst was prepared by hydrolysis using titanium isopropoxide as a precursor for titanium and urea as a nonmetal source [15]. The titanium isopropoxide was mixed with isopropyl alcohol solution, after that, this solution was added dropwise to deionized water, the was adjusted using ammonia (pH = 10). To this solution was added the required amount of urea (at 1.0%, 3.0% and 5.0% w/w), dissolved in 5 ml of deionized water. The mixture was stirred for 6 h and dried in an oven at 80 °C for 12 h [16-17]. The TiO₂ and N-doped TiO₂ thin films were deposited for using the Doctor Blade technique, the suspension was placed on a soda-lime glass (1 cm x 1 cm), the thin film was heated for 30 minutes at 90 °C to evaporate the solvent, finally, sintering process was performed at 500 °C for 2 hours [18].

2.3. Synthesis of the catalysts and thin films fabrication

The properties of the compounds were studied by Raman spectroscopy, X-Ray Diffraction (XRD), and diffuse reflectance spectroscopy (DRS). The XRD patterns were recorded by X-ray powder diffractometer (MSAL-XDII) using Cu Ka radiation (λ = 1.54056 Å) for operating at voltage of 30 kV and a current of 20 mA. The diffuse reflectance absorption spectrum was measured for using a Lambda 4 PerkinElmer spectrophotometer equipped with an integrating sphere. The Raman spectra were recorded on DRX Raman microscope with laser at 780 nm.
2.4. Photocatalytic Test

The methylene blue (MB) was chosen as the pollutant model in this study. The experiments were carried out in a batch reactor using a LED tape as a source of visible radiation (cold white light 840 lumens). The cylindrical container has a diameter of 20.0 cm and a height of 50 cm, it was made of plastic material because being a bad thermal conductor will prevent heating of the system.

Inside photo-reactor a reflective coating (made of metalized tape) allows the light from the sources to be reflected and prevents it from escaping. We immerse a thin film into MB solution (10 ppm was used as target solution). We reached the adsorption/desorption equilibrium after 1 hour of stirring in darkness, after that, the visible light simulator was turned on, the photo-degradation reaction was following for Spectrophotometric monitoring at 665 nm, during the photo-degradation process, air was injected to the reactor.

3. Results

3.1 structural results

The figure 1 shows the diffraction pattern of the TiO$_2$ and N-doped TiO$_2$ thin films. The diffraction pattern shows different growth planes showing a preferential growth plane located at $2\theta = 25.3$ corresponding to the plane (101) [20]. Figure 1 shows that after the doping process, the diffraction pattern did not change significantly; in addition,
none of the films showed any evidence of the presence of the rutile and brookite phases. Nolan et al. reported that incorporation of N into TiO₂ lattice enhanced transformation of anatase-TiO₂ structure to rutile-TiO₂ structure [21], however, Sun et al. verified that this transformation began N-load of 7%. This result is relevant considering that the anatase phase is the photocatalytically more active phase of the three main polymorphs of TiO₂ [22]. These structural results were confirmed by Raman characterization.

3.2 Raman results

Figure 2. Raman spectra for TiO₂ thin films doped with nitrogen using laser of 780nm. Inside figure is shown the change in E₁g Raman signal intensity for N-doped TiO₂ thin films.

The figure 2 shows the diffraction pattern for TiO₂ thin films. The spectrum for TiO₂ shows signals located at 144 cm⁻¹, 398 cm⁻¹, 520 cm⁻¹, 639 cm⁻¹, they can be assigned to E₁g, B₁g, A₁g/B₁g and E₃g modes respectively, these signals are typical of the tetragonal space group D₄h (I4₁/amd) for anatase-TiO₂ [23]. The Raman spectrum for N-doped N-TiO₂ films showed signals corresponding to anatase-TiO₂ phase and a light shift in E₁g was detected, this result indicates the nitrogen incorporation in the crystal lattice of TiO₂ [24], besides for N-TiO₂ the signals intensity change in comparison with the synthesized pure TiO₂ films (inside figure is shown the change in E₁g signal intensity as the doping load increasing). This rise was directly proportional to the Nitrogen load for 3% and 5% (w/w) doping load, different reports have suggested that Raman intensity of TiO₂ nanoparticles increased with the disorder structure; this change in the intensities of the Raman peaks for increasing disorder has been reported for defects (e.g. vacancies-type) [25, 26]; for N(3%)-TiO₂ films the E₁g signal intensity was smaller than unmodified TiO₂, Kassahun et al reported the decreasing in this signal means a lower crystal size
after doping process [27]. Finally, none of the Raman bands corresponding to the TiO₂ rutile phase or TiN phase were detected in the spectra.

3.3. Optical Results

The figure 3(a) shows the diffuse reflectance spectrum for both the TiO₂ and the N-doped TiO₂ thin films. TiO₂ thin films did not show any optical activity at visible region while N-doped TiO₂ thin films shows optical activity at visible range. Figure 3(a) shows the shift-red for the bands when increasing the dopant load, it shows that TiO₂ films do not have any type of photoresponse at the visible range of the electromagnetic spectrum below 400 nm, this result being expected due to the band gap value TiO₂ (3.25 eV) which is photoactive under UV radiation which has a maximum absorption at 380 nm. For the spectra N-TiO₂ thin films (1%, 3% 5% w/w), they show absorption at wavelength range between 450-700 nm indicating successful insertion of nitrogen into the TiO₂ lattice [28]. The insertion of Nitrogen atoms into the lattice of anatase-TiO₂ induced new band states in the band gap of TiO₂, through replacing the sites of oxygen atoms, the Nitrogen atoms can occupy either interstitial or substitutional sites within the TiO₂ lattice. Both types of Nitrogen insertion are reported to give localized states within the band gap of TiO₂ resulting in visible light absorption [29].

In the visible region, reflectance changes as a function of the doping metal load, the reflectance decrease as the metal load increases, this observation is general for all thin films. The E, value is determined using the function of Kubelka-Munk [30]:

\[
F(R_\alpha) = \frac{(1 - R_\alpha)^2}{2 R_\alpha} \tag{1}
\]

where \(R_\alpha\) is the material reflectance value and \(F(R_\alpha)\) represents the ratio between the absorption and the scattering coefficients, \(F(R_\alpha)\) is proportional to the constant of absorption of the material, an indication of the sample absorbance at a particular wavelength. From equation (2) and the curves shown in figure 3a, an analogue to Tauc plots \((F(R_\alpha)hv)^{1/2}\) against photon energy can be constructed, according to [31]:

\[
(F(R_\alpha)hv)^{1/2} = A(hv - E_g) \tag{2}
\]

Figure 3(b) shows plots of \((F(R_\alpha)hv)^{1/2}\) versus \((hv)\) for the diffuse reflectance spectra shown in figure 3(a). The optical band gap of the films was determined by extrapolating the linear portion of the graph onto the x-axis [32].
The results obtained for the thin films are shown in Figure 3(b). In general, the TiO$_2$ thin films had a band gap value of 3.25 eV, which is according to reports in the literature, the TiO$_2$-N(1%) films had a band gap of 3.1 eV, TiO$_2$-N(3%) films had a band gap of 3.0 eV and TiO$_2$-N(5%) films had a band gap of 2.84 eV, these values being less than the pure TiO$_2$ thin films. It is observed that the reduction of the band gap is made smaller by increasing the N load. The Nitrogen 2p can replace the 2p oxygen position into the TiO$_2$ lattice due to its similar ionic radius causing the bandgap reduction.

3.4. Photocatalytic Results

The photocatalytic activity of TiO$_2$ samples was evaluated for measuring the decomposition rate of methylene blue (MB) under visible light irradiation, the figure 4 shows the MB degradation for samples prepared in this work. As we expected, the MB was suitable under visible irradiation, the TiO$_2$ did not show photocatalytic activity under visible irradiation, and besides, the efficiency of the photocatalytic enhanced after N-doping process. The MB photo-degradation efficiency was increased directly with N-load and besides, the N(5%)-TiO$_2$ thin films showed the best results in the degradation reaching 26.5%. The N incorporation inside TiO$_2$ lattice can reduce the electron–hole recombination effect, which improves its photoactivity [33]. The photocatalytic results verifying the N incorporation into TiO$_2$ lattice after doping process, the band-gap narrowing was verified (figure 3), which facilitate the visible light activity due to the introduction of intra-bands resulting from the mixing of the 2p
states of oxygen from TiO\(_2\) with the 2p states of the dopant, the band-gap narrowing is a reason for increasing photocatalytic activity in visible range [33, 34].

Finally, results indicated that the doping process using non-metals is a suitable technique to improve the TiO\(_2\) properties at visible range of electromagnetic spectrum increasing possibilities to develop potential applications to wastewater treatments.

![Figure 4](image.png)

**Figure 4.** MB photocatalytic degradation by TiO\(_2\) and N-doped TiO\(_2\) thin films after 60 minutes of visible irradiation. Into figure: (i) MB: MB under visible irradiation without catalyst. (ii)TiO\(_2\): MB under visible irradiation on TiO\(_2\) thin films without doping process.

### 4. Conclusions

In this work, N-doped TiO\(_2\) thin films were prepared by a simple sol-gel method in 3 different loads 1%, 3% and 5% (w/w) using urea as the nitrogen source. Their crystalline, optical, spectroscopic and photocatalytic properties were compared. The diffuse reflectance results verified the band-gap narrowing at the visible region of the electromagnetic spectrum verifying the doping process and besides, the Raman results confirming the doping process. The Raman signal (intensity and location) for E\(_{1g}\) Raman mode changed in comparison with the synthesized pure TiO\(_2\) films. Besides the crystalline structure of the films obtained corresponds to the anatase-TiO\(_2\) phase, none of the signals corresponding to the TiO\(_2\) rutile phase or TiN phase were detected. Finally, the N-doped TiO\(_2\) thin films had higher photocatalytic activity than unmodified TiO\(_2\) thin films verifying that N-doping process was effective, the TiO\(_2\)–N(5%) thin films showed the best results in the degradation of MB reaching 26.5%.
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