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Synthesis of N-TiO₂ Effect of the Concentration of Nitrogen in the Band Gap

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Abstract

In this work TiO₂ modified with nitrogen was synthesized by sol-gel method from the hydrolysis of titanium isopropoxide with urea solution in different concentrations so that the theoretical N/Ti molar ratio was equal to 0, 0.5, 1 and 2, calcined at 400°C. The samples were characterized by diffuse reflectance spectroscopy, thermo differential analysis and Raman spectroscopy. The TiO₂ synthesized without nitrogen are active only under ultraviolet radiation, while samples containing nitrogen absorbed in the visible range. In Raman spectra the characteristic peaks of the crystalline anatase phase were observed with a slight shift and a decrease of the crystallization grade with the increase of the N/Ti ratio. The analysis of photoactivity of the modified catalyst in the degradation of tartrazine under visible light is analyzed.

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Keywords: TiO₂ doped; visible absorption.

Nomenclature

K	absorption coefficients of TiO ₂
S	scattering coefficients of TiO ₂
R _∞	is the diffuse reflectance to given wavelength

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1. Introduction

Titanium dioxide (TiO_2) is the most used semiconductor as photocatalyst because of chemical stability, no toxicity and low cost. It is employed in environmental remediation, for example, air purification and treatment of polluted waters according to Ochiai (2012), Ao (2003), Pichat (2000) and Choi (2010). However, this photocatalyst has two important drawbacks, the high value of band gap (3.2 eV for anatase phase and 3.0 eV. for rutile phase) that prevent the use of the solar light and a low quantic efficiency related to the high recombination rate of photogenerated electrons and holes. With the object to extent the response of TiO_2 at the visible region various technics were developed as for example the introduction of sensitizer like dyes, doping with metals and no metals like S, B, C and N according to Zyoud (2011), Jaimy (2012), Wang (2008), Zaleska (2008), Dolat (2012) and Dong (2009).

In particularly, the modification of TiO_2 with nitrogen ($\text{TiO}_2\text{-N}$), was very studied since the work of Asahi (2001), which produces TiO_2 with a lower band gap energy, which allow the use of this catalyst under solar light.

In this work TiO_2 modified with nitrogen was synthetized trough the sol-gel technic from titanium isopropoxide and urea as precursors of TiO_2 and nitrogen respectively.

2. Experimental method

2.1. Reagents

Titanium isopropoxide ($\text{Ti}[\text{OCH}(\text{CH}_3)_2]_4$) of Aldrich Argentina and urea (NH_2CONH_2) of Cicarelli were used as titania and nitrogen precursors respectively. Isopropyl alcohol of Cicarelli laboratory was used as solvent and tartrazine dye as target compound in the photocatalytic tests.

2.2. Characterization

The spectrums of diffuse reflectance of the samples $\text{TiO}_2\text{-N}$ and TiO_2 were measured in a spectrophotometer UV-vis equipped with a sphere of integration and using BaSO_4 as reference. The range of analysis was from 200 to 800 nm. The function of Kubelka Munk was used to convert the diffuse reflectance to coefficient of absorption and to obtain the value of band gap energy. The Raman spectra were acquired on a Perkin Elmer FT-IR GX spectrometer with a laser excitation source. The thermo differentials studies were performed in static air in a Rigaku TAS 1100.

2.3. Synthesis of $\text{TiO}_2\text{-N}$ solids

The sol-gel technic was used to prepare $\text{TiO}_2\text{-N}$. A determined urea mass was dissolved in water and stirred until complete dissolution. Titanium isopropoxide was dissolved in isopropanol alcohol to obtain a 1 M solution. Then a determined volume of urea solution was dropwise added to the titanium isopropoxide under vigorous stirring, to obtain N/Ti molar ratios of 0,5; 1 and 2. After one of reaction, the obtained solid was separated and dried at 80°C overnight. Then the solids were calcined at 400°C in air for 3 hours. After calcinations pale yellow solids were produced with an increasing in the intensity of color as the N/Ti molar ratio increases. The catalysts prepared under this procedure are named $\text{TiO}_2\text{-N}$ 0,5; 1 and 2 according to the N/Ti ratio used.

TiO_2 without nitrogen was also synthesized by the same procedure using water instead of urea to produce the hydrolysis of the alkoxide.

2.4. Photocatalytic activity

The photocatalytic degradation of tartrazine was studied using the prepared catalysts under visible radiation. All experiments were developed at constant temperature in a batch reactor. A metal halogen lamp was used as light source and a UV-filter was employed to eliminate spectral range radiation below 400 nm.

A tartrazine solution 1.10^{-5} M and a catalyst concentration of 1,0 g/L were used in the photocatalytic tests. The suspensions were stirred in the darkness for 30 minutes to establish adsorption/desorption equilibrium. During the tests suspensions were maintained under mechanical stirring to avoid agglomeration of catalyst.

At predetermined time intervals, some mL of suspension was sampled and filtered using a membrane of regenerated cellulose acetate. The filtrates were analyzed by means of UV-vis spectroscopy at 427.25 nm.

3. Results and discuss

3.1. Diffuse reflectance

The UV-vis diffuse reflectance spectra of TiO_2 and $\text{TiO}_2\text{-N}$ are shown in Fig.1. In the DRS experiments, UV-vis reflectance data cannot be used directly to measure the absorption coefficients because of the large scattering contribution to the reflectance spectra. Normally it is assumed that there is only a weak dependence of the scattering coefficient S on the wavelength. The value of K/S is assumed to be proportional to the absorption coefficient within the narrow range of energy containing the absorption edge features. The Kubelka-Munk relations measuring K/S for thick samples were used to convert reflectance measurements into the equivalent absorption spectra. The reflectance of BaSO_4 was used as reference.

$$R'\infty = \frac{R\infty(\text{muestra})}{R\infty(\text{referencia})} \quad (1)$$

$$F(R'\infty) = \frac{K}{S} = \frac{(1-R'\infty)^2}{2R'\infty} \quad (2)$$

Where $R\infty$ is the diffuse reflectance for a given wavelength, $R\infty(\text{sample})$ is the sample diffuse reflectance and $R\infty(\text{reference})$ is the BaSO_4 diffuse reflectance. $R'\infty$ is the diffuse reflectance of sample with respect to reference.

TiO_2 present edge absorption around 380 nm and do not absorb in the visible light range, whereas $\text{TiO}_2\text{-N}$ samples extend the absorption edges in the visible light region, consistent with the yellow color observed.

Generally the absorption in the visible range increase with the increasing of the theoretical ratio N/Ti from 0.5 to 2, although the $\text{TiO}_2\text{-N}$ 1 catalyst a lower absorption than that observed for $\text{TiO}_2\text{-N}$ 0.5, as shown in Fig. 2. This difference in behavior is perhaps related to the fact that the $\text{TiO}_2\text{-N}$ 1 solid behave different to the others catalysts because it presents two absorption edges. The first absorption edge corresponds to unmodified TiO_2 , whereas the second edge is due to nitrogen introduced in TiO_2 structure.

$\text{TiO}_2\text{-N}$ 0.5 sample absorb in all visible range, as showed in Fig. 2, in contrast with the sample with the higher N/Ti ratio, probably due to the presence of carbon rests associated with the incomplete hydrolysis process, which leaves alkyl residues in the lattice of TiO_2 that during calcination lead to the coke formation.

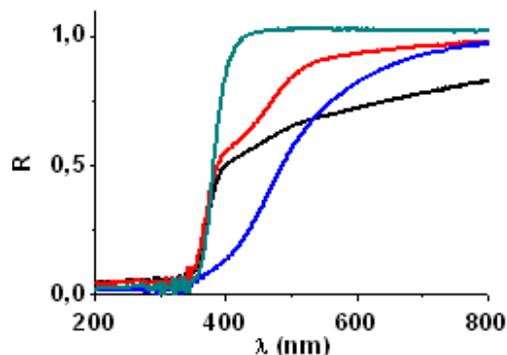


Fig. 1. UV-vis diffuse reflectance spectra of samples, black for N-TiO₂ 0.5, red for TiO₂-N 1, blue for TiO₂-N 2 and green for TiO₂.

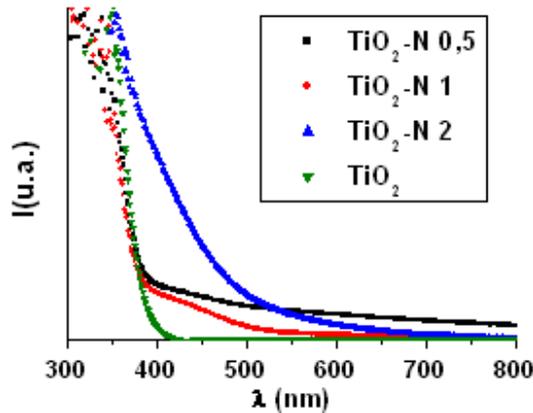


Fig.2. UV-vis absorbance spectra of TiO_2 and $\text{TiO}_2\text{-N}$.

The extrapolation, in the plots of $[F(R'\infty)]^{1/2}$ versus photon energy $h\nu$, of the linear portion of the modified spectra to zero absorption determines the band gap energies of the photocatalysts.

Band gap energies and related wavelength are presented in the table 1.

Table 1. Band gaps and wavelengths values.

Sample	E_g (eV)	λ (nm)
TiO_2	3.24	383
$\text{TiO}_2\text{-N 0.5}$	3.19	389
$\text{TiO}_2\text{-N 1}$	3.18-2.28	390-544
$\text{TiO}_2\text{-N 2}$	2.51	494

The values of band gap energies developed shows that effectively the doped of TiO_2 with nitrogen produced a decrease of band gap as expected. The band gap for unmodified TiO_2 was 3.24 eV whereas for modified samples the values were 3.19, 3.18, 2.28 y 2.51 eV.

3.2. Raman studies

Fig. 3 shows the Raman spectra of TiO_2 and $\text{TiO}_2\text{-N}$ catalysts. The Raman spectrum of the unmodified TiO_2 is provided for comparison. The observed peaks at 396, 515, and 640 cm^{-1} can be attributed to the characteristics of the anatase phase, represented as (B_{1g}), ($A_{1g} + B_{1g}$) and (E_g), which indicates that the anatase is the predominant phase structure of the TiO_2 . $\text{TiO}_2\text{-N 0.5}$ and $\text{TiO}_2\text{-N 1}$ present also the characteristics peaks of anatase, but in this case a light shift to lower values indicate the nitrogen incorporation in the crystal lattice of TiO_2 , that is in agreement with the reported observations by Gurkan (2012). In contrast $\text{TiO}_2\text{-N 2}$ solid presents a series of resolved little bands with great fluorescence effect, that may indicate that crystallization process is retarded in this case probably due to high concentration of nitrogen.

By comparing of the intensity of peaks, note that unmodified sample presents peaks with higher intensity that modified samples and that as nitrogen content increase the decrease of peaks intensity belonging to the anatase phase is more noticeable.

$\text{TiO}_2\text{-N 0.5}$ sample unlike $\text{TiO}_2\text{-N 1}$ present bands of minor intensity lightly shifted respect to actives modes of TiO_2 unmodified.

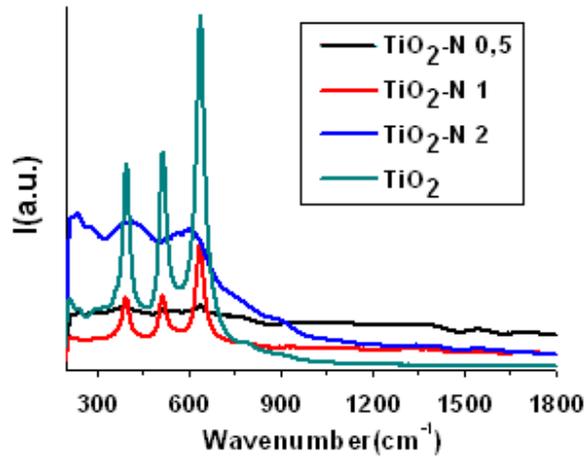


Fig. 3. Raman spectra of TiO_2 and $\text{TiO}_2\text{-N}$.

3.3. Thermo differential Analysis

Fig. 4 shows DTA curves of nitrogen modified samples. We can observe an exothermic peak at 400°C in all curves. The intensity of this peak decrease with the increase of N/Ti ratio. This behavior could be attributed to the crystallization degree.

We can also observe that the peak at 400°C for $\text{TiO}_2\text{-N 0.5}$ is the most intense, indicating that this solid is crystallized more easily to anatase phase. By the contrary $\text{TiO}_2\text{-N 2}$ presents peaks with very low resolution, showing that in this case the crystallization process to anatase is not favor, which is in agreement with the observations of Raman spectroscopy.

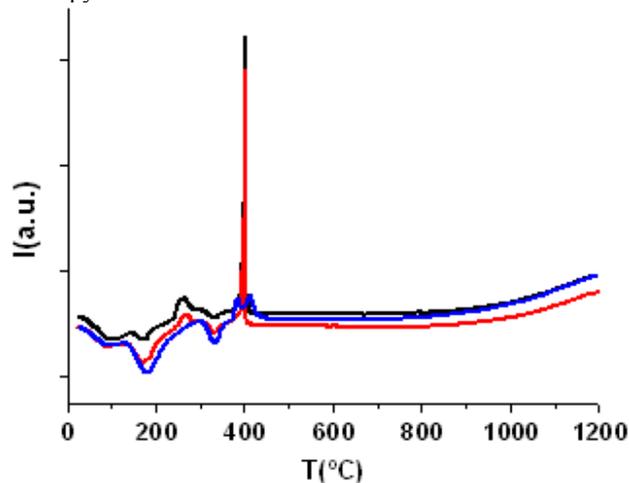


Fig. 4. DTA of nitrogen modified samples, black for N-TiO₂ 0.5, red for TiO₂-N 1 and blue for TiO₂-N 2.

3.4. Photocatalytic test

Fig. 5 shows degradation curves, expressed as percentage of tartrazine degradation in function of time.

$$\text{Deg}(\%) = \frac{(C_0 - C)}{C_0} \times 100 \quad (3)$$

Where C_0 is the initial concentration of solution after to reach adsorption-desorption equilibrium in darkness and C is the solution concentration in the reaction time t .

The order of photocatalytic activity is: $\text{TiO}_2\text{-N } 1 > \text{TiO}_2\text{-N } 0.5 > \text{TiO}_2\text{-N } 2$. The best photoactivity showed for $\text{TiO}_2\text{-N } 1$ in tartrazine degradation may be attributed to its major crystallization grade and low band gap value, as should be expected, given that active phase to photodegradation is anatase phase, presenting also the lower band gap value. Although we can expect that $\text{TiO}_2\text{-N } 0.5$ solid, which extend its absorption to visible range presents a similar behavior, the major band gap value decrease its activity in the presence of visible light. Also, the carbon presents in this solid can produce a decrease of the photocatalytic performance.

$\text{TiO}_2\text{-N } 2$ presents a negligible activity for the dye degradation in spite of its absorption capacity in the visible range due to its lower crystallinity.

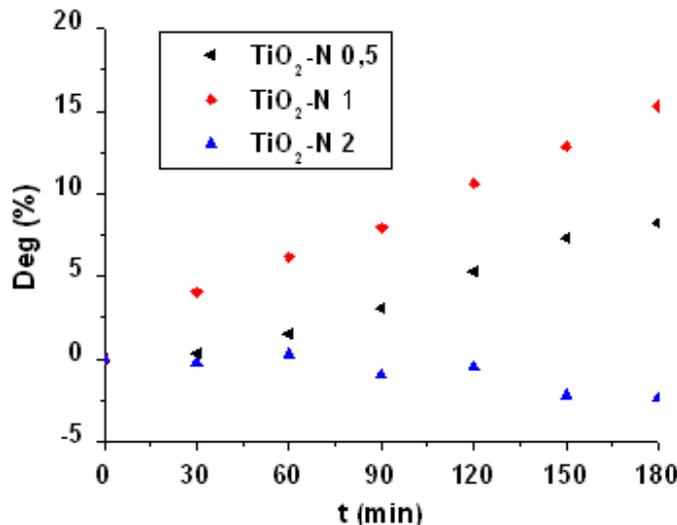


Fig.5. Degradation curves of tartrazine for $\text{TiO}_2\text{-N}$.

4. Conclusions

Nitrogen modified TiO_2 were synthesized through the sol-gel synthesis method, using as reagents titanium isopropoxide and urea as precursors of TiO_2 and nitrogen. The obtained solids present a yellow color, and their diffuse reflectance spectra show that effectively the absorption was extended to visible range. The incorporation of nitrogen in the crystal lattice of TiO_2 produce shifts in the characteristic peaks of anatase phase of TiO_2 and decrease the intensity of these, indicating an influence on the degree of crystallization, this is also shown in the thermodifferential studies.

The modified sample with theoretical ratio N/Ti equal to 1 has greater activity in the degradation of tartrazine. This can be attributed to presence of anatase phase associated with a lower band gap energy which promotes photodegradation in the presence of visible light. The catalyst with lower nitrogen content, $\text{TiO}_2\text{-N } 0.5$ presents intermediate conversion values because in this case despite having anatase phase, it has a band gap energy value higher which affects its efficiency in the presence of visible light. On the other hand, the solid $\text{TiO}_2\text{-N } 2$ solid has the smallest band gap value but in this case the active anatase phase is not completely crystallized, therefore this catalyst presents the lowest efficiency in the process of photodegradation.

Consequently we can conclude that it is important to decrease the value of band gap energy to develop photocatalytic activity in the presence of visible light, but at the same time catalysts must also develop an optimum degree of crystallization of the anatase phase, which means that there is a critical N/Ti ratio to obtain the best results.

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