

## Research Article

# N-TiO<sub>2</sub>: Chemical Synthesis and Photocatalysis

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The chemical synthesis of nitrogen-doped titanium dioxide (N-TiO<sub>2</sub>) is explored in an attempt to understand the mechanisms of doping. Urea is used as precursor in a sol gel synthesis of N-TiO<sub>2</sub>. Chemical and structural changes during thermal treatment of the precursors were followed by several techniques. The effect of doping on band gap, morphology, and microstructure was also determined. The byproducts produced during firing correspond to those obtained during urea thermal decomposition. Polynitrogenated colored compounds produced at temperatures below 400°C may act as sensitizer. Incorporation of N in the TiO<sub>2</sub> structure is possible at higher temperatures. Degradation experiments of salicylic acid under UVA and visible light ( $\lambda > 400$  nm) in the presence of TiO<sub>2</sub> or N-TiO<sub>2</sub> indicate that doping decreases the activity under UVA light, while stable byproducts are produced under visible light.

## 1. Introduction

The development of novel materials capable of solar-driven chemical transformation or electricity production is one of the more important challenges for now and the following years. Oxide semiconductors are an interesting family of semiconductors that can use solar light to catalyze several chemical processes and/or produce electricity. In this sense, TiO<sub>2</sub> is a noble material due to its chemical stability, photo-corrosion resistance, and low toxicity [1, 2]. However, TiO<sub>2</sub> can absorb only the relatively small part of the solar spectrum that includes the  $300 < \lambda < 390$  nm range (around 5% of the solar light). In an attempt to improve light absorption in the visible range, TiO<sub>2</sub> was modified by incorporation of transition metals, noble metals and recently by nonmetallic elements [3–7].

During recent years, N-TiO<sub>2</sub> became one of the more studied nonmetal-doped systems. The presence of a nontoxic dopant and the reported activity are the principal reasons why N-TiO<sub>2</sub> is chosen as a promising photocatalyst to be used under solar light illumination.

The methods to prepare N-TiO<sub>2</sub> can be summarized as follows:

- (1) sputtering and implantation techniques [8–10]: these techniques are adequate for the preparation of films;
- (2) calcinations of TiO<sub>2</sub> or Ti(OH)<sub>4</sub> under N-containing atmospheres generated by nitrogen compounds like ammonia [11–13]: these techniques are principally used to prepare powders;
- (3) sol-gel process [5, 14–16] which can be used to prepare powders or films.

The preparation method has an important role in determining the final properties of the products, because different ways to incorporate N lead to systems with dopant located in different positions of the TiO<sub>2</sub> structure and with different activities [15, 17, 18].

N-TiO<sub>2</sub> can be synthesized by chemical method if an appropriate N containing precursor is selected. This methodology is attractive because there is no expensive equipment involved, which helps to reduce costs for the massive

synthesis of the product. Coprecipitation of TiO<sub>2</sub> with urea followed by thermal treatment is one of the most popular procedures to prepare N-TiO<sub>2</sub> [14, 19, 20]. However, the mechanism of doping is still not well understood and is a challenge for chemists to determine how TiO<sub>2</sub> is doped by N under those conditions. Besides, the synthesis is sometimes difficult to reproduce; so a better understanding of the process is necessary in order to develop reliable synthesis.

In this paper, we present the results of studies designed to understand the mechanisms involved in the synthesis and in the determination of the photocatalytic activity of the materials under black and white light illumination.

## 2. Materials and Methods

**2.1. N-TiO<sub>2</sub> Synthesis and Characterization.** The synthesis procedure is based on what was reported by Ohno [19]. Three solutions containing Ti-isopropoxide, Ti(C<sub>3</sub>H<sub>7</sub>O)<sub>4</sub> (Aldrich), urea (Anedra PA), or water dissolved in absolute ethanol (Merck, PA) were prepared: solution (a) Ti(C<sub>3</sub>H<sub>7</sub>O)<sub>4</sub> 0.40 mol dm<sup>-3</sup>, solution (b) urea 0.80 mol dm<sup>-3</sup>, and solution (c) water 0.40 mol dm<sup>-3</sup>. Solution (a) was incorporated into solution (b) under stirring and mixed during 15 minutes. After the stirring period, solution (c) was slowly incorporated to the mixture under stirring. A white slurry was obtained, which was stirred for another 60 minutes. Finally, the slurry was evaporated under vacuum at 40°C until a white precursor powder, with a 4 : 1 N : Ti molar ratio, was obtained. In order to determine the effect of N doping on microstructure, precursor powders with N:Ti ratios 2:1 and 8:1 were prepared following the same protocol, but using solutions (b) with 0.40 and 1.6 mol dm<sup>-3</sup> urea, respectively. The product was air-dried and fired under air at 175, 250, 375, 412, 450, or 500°C, during 15 min with a 10°C/min ramp. The precursor powders used in photocatalysis experiments and those with N:Ti ratios 2:1 and 8:1 were fired at 250°C for 3 h, heated to 500°C with a 10°C/min ramp, and immediately cooled down in the oven. Finally, they were washed with water to remove possible soluble impurities and dried at 60°C. As control, pure TiO<sub>2</sub> was synthesized in a similar way, but without the incorporation of urea.

The evolution of the powder precursor during firing was followed by thermal gravimetric analysis (TGA; Shimadzu TG-50) and differential thermal analysis (DTA; Shimadzu DTA-50) under air atmosphere. The nature of the byproducts obtained at the different firing temperatures was determined by Fourier transformed infrared spectroscopy (FTIR, Thermo Nicolet 8700). The crystalline phases predominant at each temperature were determined by X-ray diffraction (XRD; Siemens D-5000) using the Cu K $\alpha$  wavelength. The bandgap of the different samples was determined by reflectance spectroscopy (Shimadzu UV-3101PC), using BaSO<sub>4</sub> as reference. Surface area and porosity of the powders were measured by N<sub>2</sub> sorptometry, using the BET formalism (Micromeritics ASAP 2020 V3.00 H). The morphology of the particles of powders was determined by Field Emission Scanning Electron Microscopy (FEGSEM Zeiss LEO 982 GEMINI).

**2.2. Photocatalytic Activity.** The photocatalytic activity of the different photocatalysts was determined through the degradation of salicylic acid (Fluka, PA, USA) as model contaminant. Salicylic acid is a nice target because the presence of aromatic and phenol functionality, with negligible toxicity at the used concentrations (2.5 × 10<sup>-4</sup> M). A homemade photoreactor was used for all the experiments. A borosilicate glass cylindrical container (200 mL) was surrounded by four 12 W light tubes, symmetrically placed at 15 cm from the axis of the cylinder. The photocatalyst was incorporated to the salicylic acid solution and suspended with the application of ultrasound for 10 minutes. The final concentration of photocatalyst was 1.0 g/L. The suspension was magnetically stirred, and O<sub>2</sub> was bubbled during all the experiment. The system was stirred in the dark during 30 minutes to reach adsorption equilibrium. The lamps were warmed up during 15 minutes. Once the reactor was under illumination, 5 mL samples were taken at regular periods. The samples were filtered through a 0.45  $\mu$ m pore diameter polycarbonate membrane (Sartorius) and stored in glass containers at -20°C until analysis was performed.

The experiments run under UVA light were carried out using 12 W black light tubes, while for the experiments with visible light 12 W, white tubes were used. In the latter case, a 4 mm thick Plexiglas cylinder was placed surrounding the borosilicate glass reactor to eliminate all the emissions with wavelength lower than 400 nm. The intensity of light inside the photoreactor was determined with a radiometer at 360 nm, using a combination of two filters: WG 335 and UG 11. The radiance was calculated through:

$$\frac{\text{Photons}}{\text{s} \cdot \text{cm}^2} = \frac{P}{A \cdot E} \cdot f, \quad (1)$$

where P is luminic potency; A is photodiode area; E is photon energy (h $\nu$ /360 nm); h is Planck's constant; f is correction factor due to filter attenuation (f = 13.43).

The concentration of the remaining salicylic acid in the irradiated samples was determined by High-Performance Liquid Chromatography (HPLC), Shimadzu, equipped with an Econosphere C-18, 150 mm × 4 mm, column, and UV-Vis detector. The solvent carrier was a 25 : 75 methanol:acetic acid (2% in water), with a flow rate of 1.4 mL/min. Salicylic acid was detected at 298 nm. To detect the presence of byproducts, standards of dihydroxybenzoic acid and hydroquinone were analyzed by HPLC with UV detection.

## 3. Results

Figures 1(a), 1(b) and, 1(c) show TGA and DTA plots of urea, TiO<sub>2</sub> powder, and coprecipitated TiO<sub>2</sub>-urea powder, respectively. As shown in Figure 1(a), decomposition of pure urea starts after melting, characterized by a sharp endothermic peak at 133°C, with a steep loss of mass that involves at least two processes, as indicated by the endothermic peaks at 191 and 230°C. There is a small plateau in the 260–300°C range, followed by another steep loss of mass that ends at 360°C and corresponds with one endothermic process centered at 330°C. Finally, there is another endothermic process centered at 395°C, associated with a smooth loss of mass in the

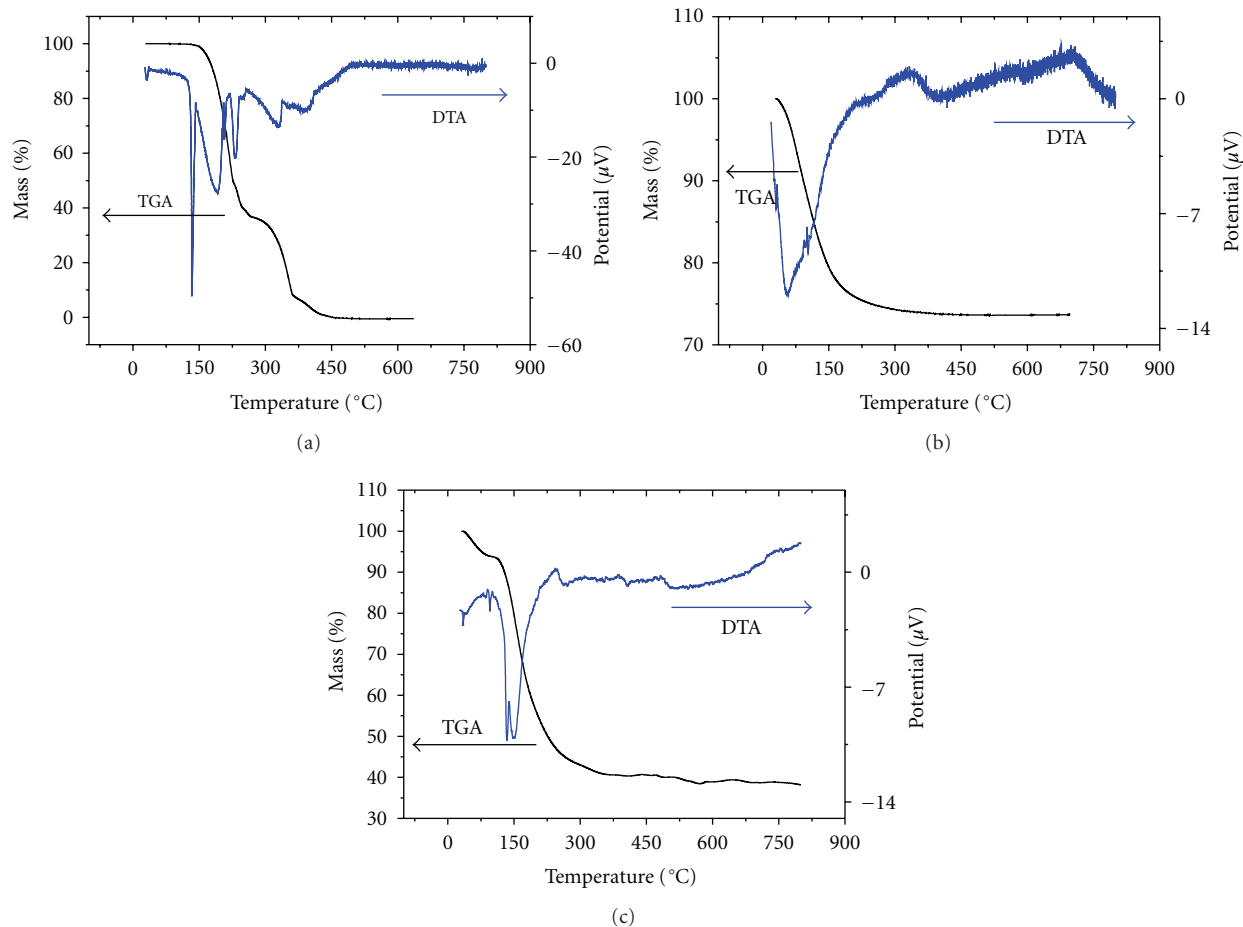


FIGURE 1: TGA (left vertical axe) and DTA (right vertical axe) analysis of samples: (a) urea, (b) TiO<sub>2</sub>, and (c) TiO<sub>2</sub> + urea (N:Ti, 4:1).

range 330–450°C. In the case of pure TiO<sub>2</sub>, synthesized as explained previously, the thermal behavior is much simpler. There is a steep loss of mass in the range 33–300°C that corresponds with a broad endothermic process that likely contains, at least, two superimposed processes centered at 56 and 110°C. The coprecipitated mix of urea and TiO<sub>2</sub> displays similar behavior to pure TiO<sub>2</sub>. As shown in Figure 1(c), mass is lost from the beginning of the heating, with a steep loss at 115°C. The slope of the curve decreases as the temperature rises. DTA indicates that decomposition starts immediately after urea melting (133°C); probably the different processes observed in Figure 1(a) are superimposed in the peak centered at 150°C in Figure 1(c). It should be considered that the mass of urea is lower than in the experiment shown in Figure 1(a), because in the case of Figure 1(c), there is a mixture of urea and TiO<sub>2</sub>. Consequently, some processes that involve small losses of mass may be hidden.

Figure 2 shows FTIR spectra of raw coprecipitated TiO<sub>2</sub>-urea and fired at different temperatures. As can be seen in the figure, the raw mixture displays the typical features of urea corresponding to N-H stretching (3450 and 3300 cm<sup>-1</sup>), C=O (1600 cm<sup>-1</sup>), and N-C (1340–1250 cm<sup>-1</sup>) [21]. After firing at different temperatures, new features can be characterized and others disappear. The more important changes

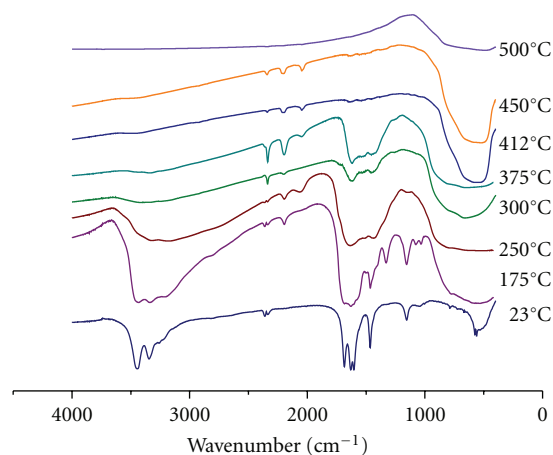


FIGURE 2: FTIR spectra of TiO<sub>2</sub>-urea (N:Ti, 4:1) samples fired at the indicated temperature during 10 minutes. Heating ramp: 10°C/min. Samples were cooled down to room temperature in the oven.

take place in two ranges: 175–375°C and 375–500°C. In the first range, the typical peaks of urea are replaced by others typical of biuret (see also Figure 7), (1405 cm<sup>-1</sup>, 1330 cm<sup>-1</sup>,

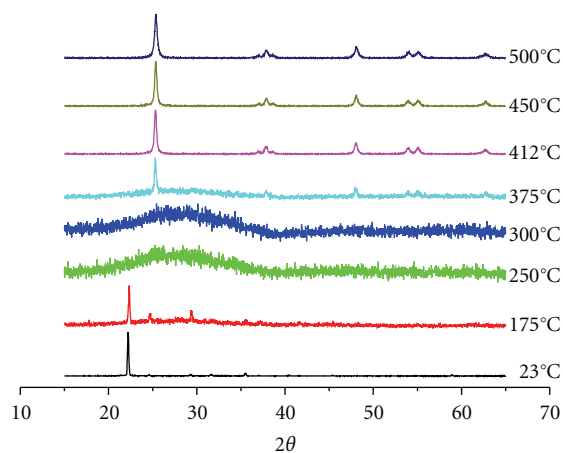


FIGURE 3: XRD patterns of  $\text{TiO}_2$ -urea (N:Ti, 4:1) samples fired at the indicated temperature during 10 minutes. Heating ramp:  $10^\circ\text{C}/\text{min}$ . Samples were cooled down to room temperature in the oven.

TABLE 1: Surface area, pore volume, and pore size of samples prepared from precursors with different N:Ti molar ratios, fired at  $250^\circ\text{C}$ , 3 h, and  $500^\circ\text{C}$  1 min. Ramp:  $10^\circ\text{C}/\text{min}$ .

Sample	Surface area $\text{m}^2/\text{g}$	Pore volume $\text{cm}^3/\text{g}$	Pore size $\text{\AA}$
N:Ti, 0 ( $\text{TiO}_2$ )	52	0.088	66
N:Ti, 2:1	40	0.068	56
N:Ti, 4:1	26	0.051	63
N:Ti, 8:1	17	0.034	64

$1075\text{ cm}^{-1}$ , and  $1025\text{ cm}^{-1}$ ), cyanuric acid ( $1158\text{ cm}^{-1}$ ), ammeline, and melanine with typical bands in the  $1800\text{--}1300\text{ cm}^{-1}$  range among others (see [22] and references cited therein). There are also bands at  $2048$ ,  $2195$ , and  $2340\text{ cm}^{-1}$  that correspond with cyanides and cyanates; these bands increase as the other decrease with the temperature. In the range  $412\text{--}500^\circ\text{C}$ , only the bands typical of cyanates and cyanides remain in the spectra in the range  $3500\text{--}1000\text{ cm}^{-1}$ , and the bands corresponding to O-Ti-O stretching, in the range  $400\text{--}600\text{ cm}^{-1}$ , increase with the temperature.

Figure 3 shows X-Ray diffractograms of  $\text{TiO}_2$ -urea coprecipitated samples fired at different temperatures. The raw sample displays features that correspond to crystalline urea. As the temperature increases, the peaks become less intense, until in the range  $250\text{--}300^\circ\text{C}$  the samples are noncrystalline. At  $375^\circ\text{C}$ , the sample is slightly crystalline, while at higher temperatures, it becomes crystalline. Anatase is the only crystalline phase present in the range  $375\text{--}500^\circ\text{C}$ . It is noteworthy that when the solid starts to crystallize, polynitrogenated cyclic compounds, such as ammeline, ammeline, and melanine are present on the  $\text{TiO}_2$  particles, as determined by FTIR (see Figure 2).

Figure 4 shows SEM images of pure  $\text{TiO}_2$  and N- $\text{TiO}_2$  samples prepared from different N:Ti ratios. In all the cases, the particles that form the aggregates are nanometric, with an average size of approximately 10 nm. As the urea/Ti ratio

increases, the morphology of the systems notably changes. The particles seem bigger and the porosity decreases. The  $\text{N}_2$  sorption experiments displayed in Table 1 agree with the SEM images. The surface area and the pore volume decrease as the urea/Ti ratio in the synthesis increases.

Figure 5 shows the reflectance spectra and the band gap of  $\text{TiO}_2$ , N- $\text{TiO}_2$ , and a commercial sample (Finnit by Kemira). The remission function was calculated from the reflectance data through the Kubelka-Munk function:

$$F(R) = \frac{(1 - R)^2}{2R}, \quad (2)$$

where  $F(R)$  is the remission function and  $R$  is the measured reflectance.

The band-gap energy can be obtained by extrapolation to zero of a plot of  $(F(R) \times E)^{1/2}$  versus  $E$ , where  $E$  is the energy of the incident light in eV. The band gap of the commercial sample corresponds with anatase ( $3.26\text{ eV}$ ). The  $\text{TiO}_2$  synthesized in the laboratory has a band gap shifted to lower energies, compared with pure anatase. N- $\text{TiO}_2$  displays a shoulder at  $2.5\text{--}2.7\text{ eV}$ , which can be associated with the deep yellow color displayed by the N-doped samples.

Analysis of the surface chemical composition by XPS shown in Table 2 indicates the presence of N in all the studied samples. The presence of N in the bare  $\text{TiO}_2$  sample can be assigned to physisorbed N ( $400.9\text{ eV}$ ). The concentration of N increases with the urea/Ti ratio. The binding energies can be assigned to substitutional N ( $396\text{--}397\text{ eV}$ ), interstitial N ( $400\text{ eV}$ ) [18], graphite-like phases: ( $400.6\text{ eV}$ , N-Csp<sup>2</sup>), or polycyanogen ( $399.0\text{--}400.5\text{ eV}$ ,  $(\text{-C=N-})_x$ ) [23], due to polycyclic nitrogenated compounds. Table 2 also shows that C is present in all the samples.

Photocatalytic activity of  $\text{TiO}_2$  and N- $\text{TiO}_2$  was determined under UVA ( $360\text{ nm}$ ) and visible light ( $\lambda \geq 400\text{ nm}$ ). When black lights were used, the photon flux at  $360\text{ nm}$  inside the reactor was  $1.67 \times 10^{16}$  photons/(s  $\text{cm}^2$ ). In the case of white lamps, the  $360\text{ nm}$  emission was removed by the Plexiglas filter; the photon flux at different wavelength was  $4.65 \times 10^{15}$  ( $400\text{ nm}$ ),  $1.37 \times 10^{16}$  ( $436\text{ nm}$ ),  $1.19 \times 10^{16}$  ( $492\text{ nm}$ ),  $2.22 \times 10^{16}$  ( $547\text{ nm}$ ), and  $1.77 \times 10^{16}$  photons/(s  $\text{cm}^2$ ) ( $579\text{ nm}$ ). As the band-gap energy for  $\text{TiO}_2$  synthesized in the laboratory is  $3.03\text{ eV}$  and for N- $\text{TiO}_2$  is  $2.38\text{ eV}$ , only the emissions with wavelengths shorter than  $400$  or  $547\text{ nm}$  can be, respectively, absorbed by the photocatalysts.

Salicylic acid was used as target contaminant; Figure 6(a) shows the temporal evolution of the concentration when a  $2.5 \times 10^{-4}\text{ M}$  solution containing  $1.0\text{ g/L}$  of catalyst is illuminated with black or white light. Under UVA illumination, N- $\text{TiO}_2$  displayed much lower efficiency than  $\text{TiO}_2$  synthesized under similar conditions. Under visible light, N- $\text{TiO}_2$  was slightly more efficient than  $\text{TiO}_2$  and, in both cases, the degradation rate decreases with the time. Figure 6(b) shows the concentration of dihydroxybenzoic acid (DHB) relative to the remnant salicylic acid at different illumination times. It is clear that the highest accumulation of DHB is observed with N- $\text{TiO}_2$ , followed by  $\text{TiO}_2$ , in both cases under visible light. Direct photolysis of salicylic acid by UVA illumination, as shown in Figure 6(a), or visible light illumination (not shown) was negligible during the studied period. Adsorption



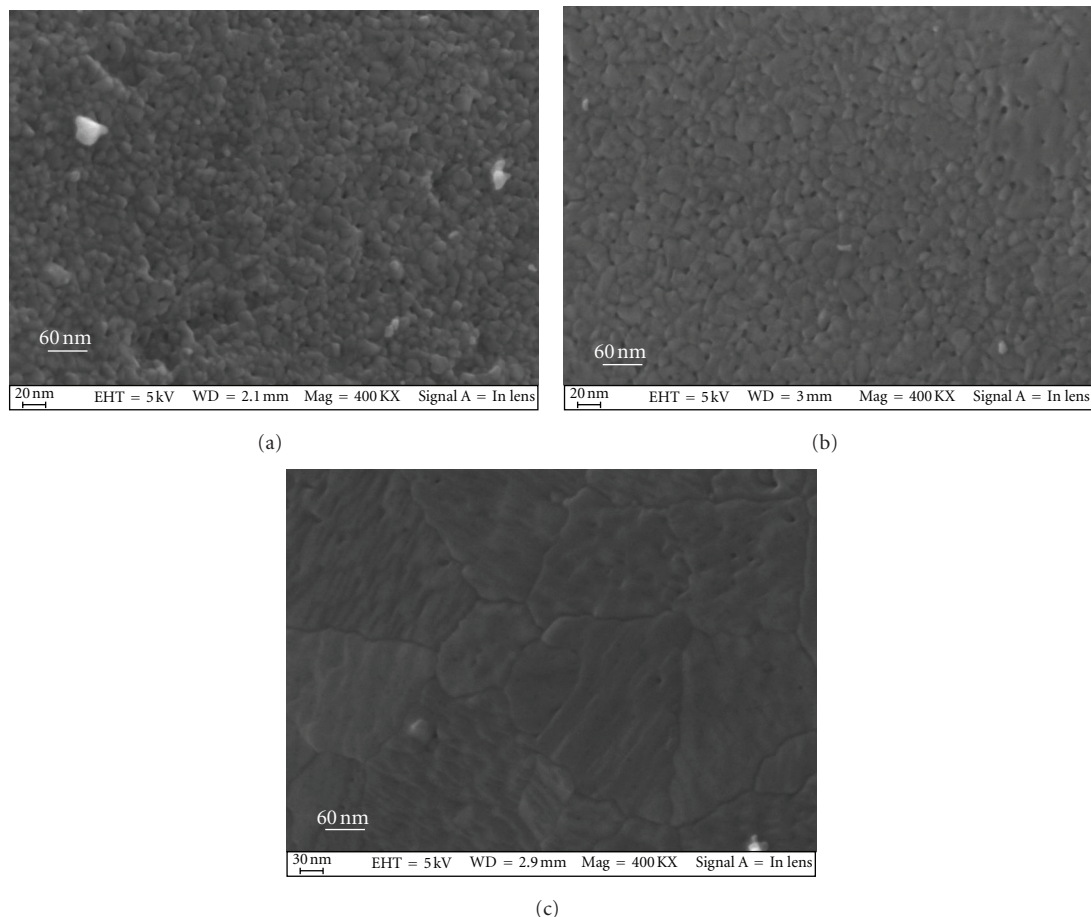


FIGURE 4: SEM images of N-TiO<sub>2</sub> samples prepared from precursors with different N : Ti molar ratios, fired at 250°C, 3 h, and 500°C 1 min. Ramp: 10°C/min. (a) N : Ti, 0 (TiO<sub>2</sub>); (b) N : Ti, 4 : 1; (c) N : Ti, 8 : 1.

TABLE 2: Surface % at/at for Ti, O, C, and N determined by XPS. Samples are prepared from precursors with different N : Ti molar ratios, fired at 250°C, 3 h, and 500°C 1 min. Ramp: 10°C/min.

Sample	Titanium%	Oxygen%	Carbon%	Nitrogen%	N/Ti × 100%
TiO <sub>2</sub> N:Ti, 0	24	63	11	1.7	7.0
N-TiO <sub>2</sub> N:Ti, 4:1	24	62	10	4.0	17
N-TiO <sub>2</sub> N:Ti, 8:1	22	59	15	3.9	18

of salicylic acid on TiO<sub>2</sub> and N-TiO<sub>2</sub> was 12–25% of the initial concentration.

#### 4. Discussion

The transformation of the coprecipitated urea-TiO<sub>2</sub> system during thermal treatment starts after the melting of urea, as can be seen in Figures 1(c) and 2. The byproducts detected in samples fired at different temperatures are coincident with that reported by Schaber et al. [22]. The decomposition reaction begins with the condensation of urea yielding biuret. Figure 7 compares FTIR spectra of urea, biuret, and a sample fired at 175°C. Clearly, the sample contains

both urea and biuret as shown by the characteristic peaks indicated with arrows “u” or “b,” respectively. The heating at higher temperatures produces further condensation leading to more complex polynitrogenated compounds as melamine. Cyanates and cyanides are also present in the fired samples. It can be noticed in Figure 2 that as the temperature increases, the intensity of the features corresponding to polynitrogenated compounds (1300–1800 cm<sup>-1</sup>) decreases in comparison with those of cyanates and cyanides (2048–2340 cm<sup>-1</sup>). As the firing temperature gets close to 500°C, all the features disappear and eventually the samples become white. The synthesis of polynitrogenated compounds on the surface of TiO<sub>2</sub> can be a consequence of the condensation

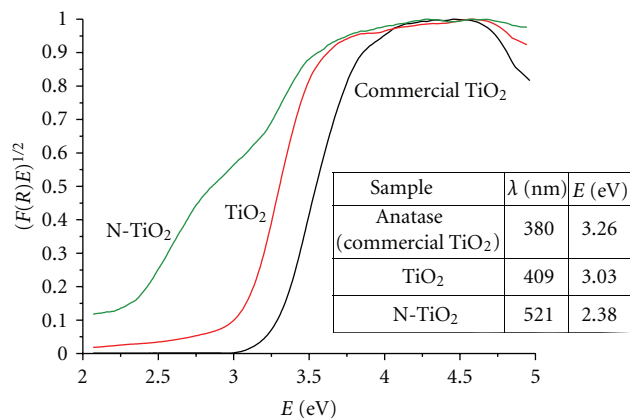
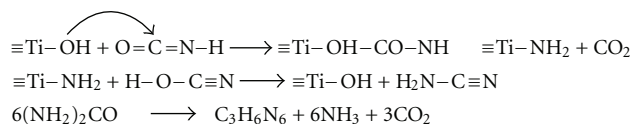


FIGURE 5: Plot of the product  $[F(R) \times E]^{1/2}$  versus  $E$ , where  $F(R)$  is the remission function, and  $E$  is the energy in eV, for different samples. The band-gap values of each sample, determined by extrapolation of the linear part of the plot until intersection with the  $E$  axis, are shown in the inset.

reaction as postulated by Mitoraj and Kisch [23, 24], which starts with the synthesis of melamine:



Further condensation of melamine leads to melam, melon, and so forth. All these compounds are dyes that withstand temperatures close to 400°C, which turn the N-TiO<sub>2</sub> system yellow. The presence of these compounds or their firing byproducts may be responsible of the reduction of surface area in the N-TiO<sub>2</sub> samples, as indicated in Table 1 and Figure 4.

Crystallization begins in the range 300–375°C, where polynitrogenated compounds are still present in the samples. N may be incorporated into the TiO<sub>2</sub> structure as the samples crystallize with the increase of the firing temperature. Buha et al. reported that nitrides can be formed from oxides by thermal treatment in the presence of urea or cyanamide at 800 C [25]. The conversion to titanium nitride is total with 5 nm TiO<sub>2</sub> particles, while for 20 nm particles titanium nitride and titanium oxide coexist. The particle size of the systems studied in this work is close to 20 nm; so based on the previous report, the substitution of oxides by nitrides seems to be possible.

The incorporation of N into the TiO<sub>2</sub> structure might explain the shift in the band gap determined by diffuse reflectance (Figure 5). Carbon can also act as a dopant, helping in the shift of the band gap to lower energy. It should be noticed that in the TiO<sub>2</sub> sample synthesized following a similar procedure as for N-TiO<sub>2</sub> the band gap is lower than in pure anatase. Carbon doping can be the reason of the band-gap shift in this case. Figure 5 shows a shoulder in the visible range, which indicates the presence of surface or intraband-gap states in the samples. Mitoraj et al. [26] proposed that

nitrogen-carbon-doped TiO<sub>2</sub> (N,C-TiO<sub>2</sub>) displays an energy band-like structure of intraband-gap states, while N-TiO<sub>2</sub> has a manifold of discrete levels. Hole ( $h^+$ ) stabilization by charge delocalization is more likely in N,C-TiO<sub>2</sub>. Our results do not allow to discriminate between doping or sensitization produced by the polynitrogenated dyes, but it is clear that both effects are related with the band-gap shift and the shoulder observed by diffuse reflectance in the visible range.

The photocatalytic activity of TiO<sub>2</sub> is notably affected by doping as shown in Figure 6. N-TiO<sub>2</sub> under UVA light displays the lowest activity for the degradation of salicylic acid, while TiO<sub>2</sub> displays the highest. The presence of surface states may enhance hole electron recombination in N-TiO<sub>2</sub> leading to low activity. When visible light was used in the experiments, degradation of salicylic acid was observed with both photocatalysts. The degradation rate notably decreases after 250 minutes and almost stops completely in the case of N-TiO<sub>2</sub>. Figure 6(b) shows that DHB acid was detected in these experiments and that its concentration, relative to the remnant salicylic concentration, was higher than in other cases. When the system is illuminated with visible light, the polynitrogenated compounds inject electrons into the TiO<sub>2</sub> conducting band, generating excited dye radicals on the surface. Górska et al. proposed that in N,C-TiO<sub>2</sub>, superoxide radicals or direct charge transfer to the adsorbed organic are involved in degradation paths [27]. The oxidation power of these species is lower than that of  $\text{OH}^\bullet$  or  $h^+$ , leading to less oxidized byproducts which can poisoned the surface of the catalyst.

The degradation of salicylic acid on TiO<sub>2</sub> can be a consequence of C doping, which shifts the band gap to 3.03 eV, allowing the absorption of light with 400 nm wavelength. The light source has a moderate emission at 400 nm which can be used to activate the catalyst. However, another effect should be considered. Salicylic acid can be absorbed on the TiO<sub>2</sub> surface in the form of different surface complexes [28]. These complexes display an absorption band in the visible range and can act as sensitizers of TiO<sub>2</sub> [29], leading to the self-degradation of salicylic acid. Both phenomena may be responsible for the target degradation, and it is not possible to discriminate which is the most important.

## 5. Conclusions

Byproducts generated during urea thermal decomposition are key in the synthesis of N-TiO<sub>2</sub>. Some byproducts, such as biuret, might be used as precursors themselves. Sol-gel synthesis with urea as N-precursor leads to the production of crystalline N-TiO<sub>2</sub> sensitized with polycyclic nitrogen compounds at firing temperatures lower than 400 C. At firing temperatures higher than 400 C, N doping is related with the presence of simpler nitrogenated species or N incorporation. N-TiO<sub>2</sub> photocatalytic activity is higher under *vis* light than under UVA illumination. Accumulation of byproducts was detected in TiO<sub>2</sub> and N-TiO<sub>2</sub> systems illuminated with white light. Target compounds chemisorbed on TiO<sub>2</sub> surface can be degraded by *vis* light. Both phenomena may be superimposed in N-TiO<sub>2</sub> photocatalysis.

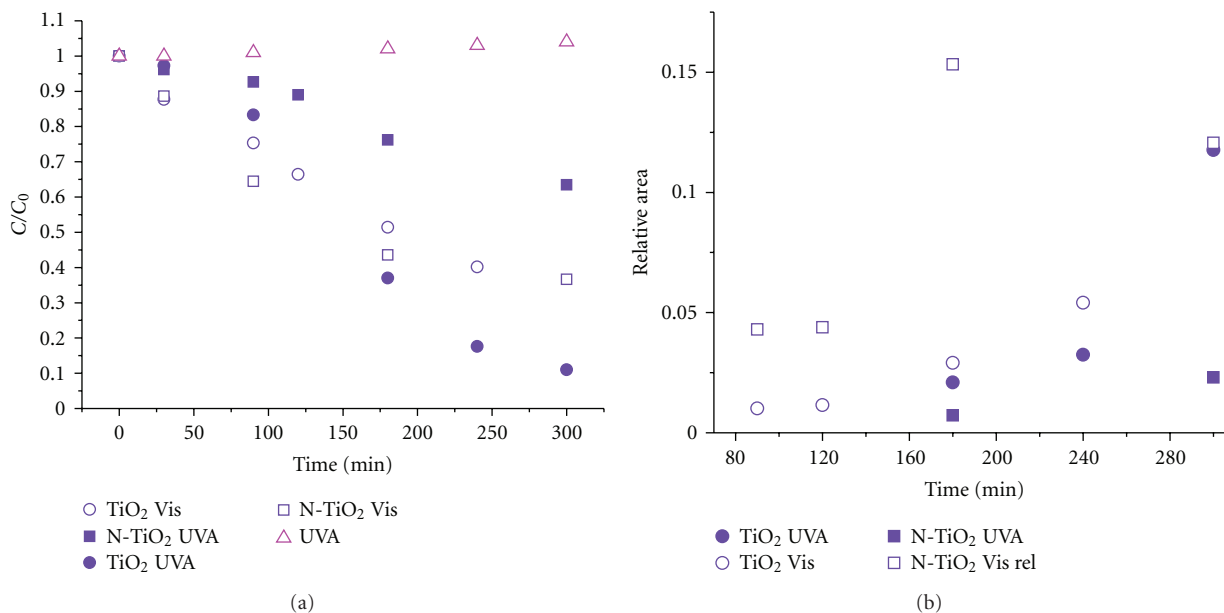


FIGURE 6: (a) Evolution of salicylic acid concentration versus irradiation time, in solution containing  $2.5 \times 10^{-4}$  M salicylic acid and 1.0 g/L of photocatalyst. UVA and Vis correspond to experiments performed under black light (360 nm) or filtered white light ( $\lambda > 400$  nm), respectively. (b) Evolution of DHB/salicylic ratio versus irradiation time for different catalysts and light (DHB: dihydroxybenzoic acid).  $\text{TiO}_2$  and  $\text{N-TiO}_2$  samples are prepared from precursors with N : Ti, 0 and N : Ti, 4 : 1, respectively, fired at 250°C, 3 h, and 500°C 1 min. Ramp: 10°C/min.

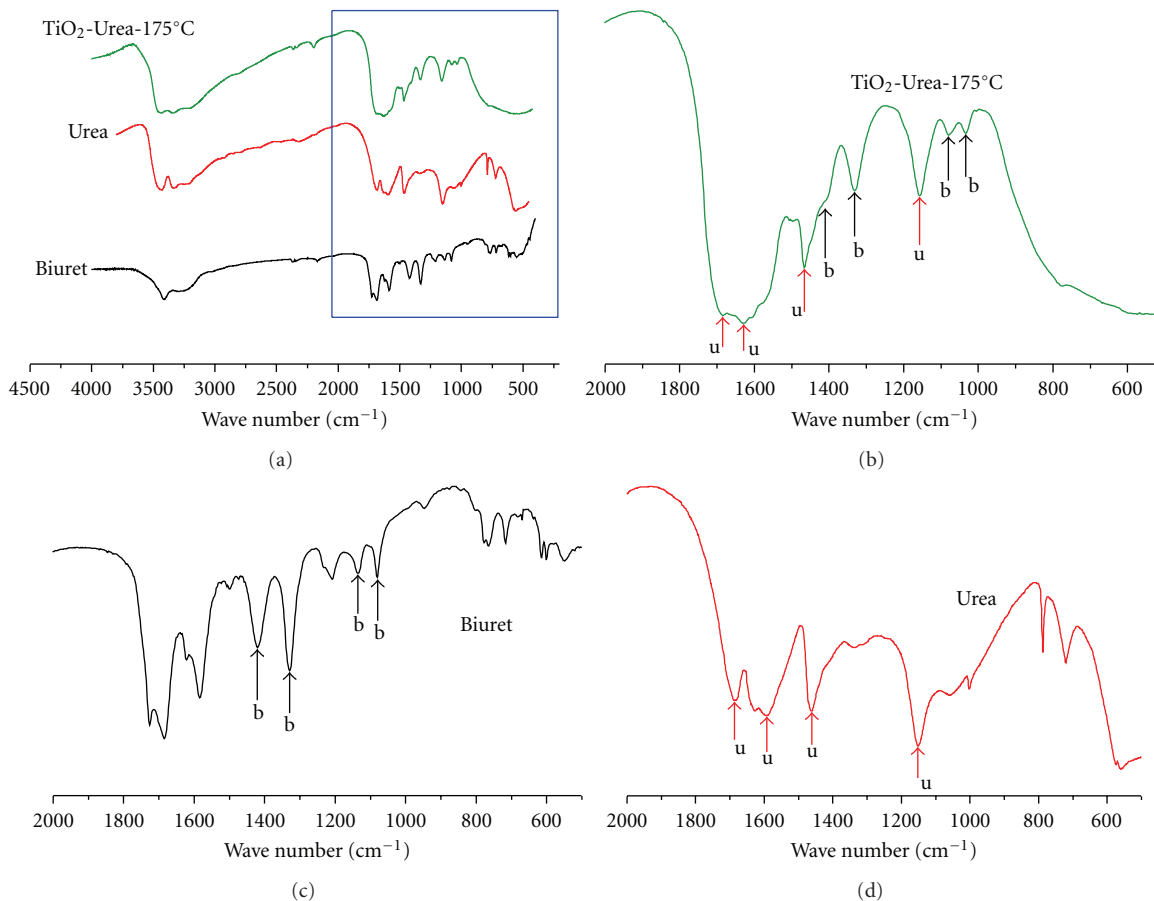


FIGURE 7: FTIR spectra of urea, biuret, and a sample of urea- $\text{TiO}_2$  (N : Ti, 4 : 1) fired at 175°C.

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