

SYNTHESIS AND PHOTOCATALYTIC PROPERTIES OF NITROGEN MODIFIED TITANIUM DIOXIDE

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Summary

Pure and nitrogen-doped titanium dioxide (N-doped TiO₂) photocatalysts were prepared by non-aqueous sol-gel method by means of the reaction between titanium (IV) chloride (TiCl₄) and C₆H₅CH₂OH (benzyl alcohol), used as precursors and urea serving as a nitrogen source. The phase formation and short-range order of the resulting particles were characterized by X-ray powder diffraction (XRD) and infrared (IR) spectroscopy. The crystallite size of as-prepared composite powders was in the range 12-35 nm. The aim of this work was to investigate the efficiency of N-doped TiO₂ as a photocatalyst in degradation of model organic pollutants - dyes Reactive Black 5 (RB5) and Malachite Green (MG), under ultraviolet (UV) and visible (Vis) irradiation. Our results indicated that synthesized N-TiO₂ nanocomposites slightly improved the photocatalytic activity under UV irradiation, compared to the pure titanium dioxide (TiO₂), and had no effect under Vis light illumination.

Key words: nonhydrolytic, sol-gel method, N-modified TiO₂

Introduction

Titanium dioxide (TiO₂) is one of the most researched semiconductor materials because of its excellent properties: it is cheap, nontoxic, possesses good stability and is a highly efficient photocatalyst and has many promising applications in the fields of renewable energy and environmental protection [1-4].

It is well known that TiO₂ is a wide band semiconductor (3.2 eV) and its photocatalytic activation requires ultraviolet (UV) irradiation. There are some theoretical calculations suggesting that anionic doping of TiO₂ has a significant impact on its photocatalytic efficiency [1-5]. In recent years, N-doped TiO₂ (N-TiO₂) has become one of the most investigated non-metallic doping systems. The presence of a non-toxic additive and the reported activity are the main reasons why N-TiO₂ is chosen as a promising photo-catalyst for use in sunlight/visible (Vis) light [6]. Two main reasons could explain the improved photocatalytic activity of nitrogen-modified TiO₂: i) the bandwidth reduction due to the mixing of the nitrogen states 2p with oxygen 2p conditions in the valence band; ii) the appearance of the N-induced intermediate level as well

as some types of impurities [4]. The atomic size of nitrogen, its small ionization energy and high stability favor its easy including in the TiO_2 structure [7]. So far, a number of methods - sol-gel, chemical vapor deposition, decomposition of N-containing metal organic precursors, etc., have been used to prepare nitrogen modified TiO_2 [8].

The sol-gel method is assumed to contribute for the better control of the level of nitrogen doping and particle size by simple variations in experimental conditions – pH value, hydrolysis rate, or the solvent used [9].

There are contradictory views concerning the photocatalytic capability of TiO_2 doped with nitrogen. According to some studies, N-doped TiO_2 has a higher photocatalytic activity in the Vis region, as compared with the non-doped TiO_2 [10]. However, some authors have argued that doping with nitrogen lowers photocatalytic activity [11, 12]. Obviously, more research is needed to clarify the photocatalytic properties of TiO_2 modified with nitrogen.

Here we present synthesis, characterization and photocatalytic activity of N-modified TiO_2 prepared by the non-aqueous sol-gel method. Our team has experience with the sol-gel synthesis of pure and modified nanosized TiO_2 catalysts, and this study continues the investigations in this area [13]. Two different nitrogen concentrations were selected for modification of TiO_2 in the synthesized samples - 1.3 and 13 mol %.

Materials and Methods

The reagents used in this study were titanium tetrachloride (Fluka), titanium (IV) oxide (Aldrich), $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$ (benzyl alcohol, $\geq 99.5\%$), $\text{C}_2\text{H}_5\text{OH}$ (absolute ethanol) and $\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$ (diethyl ether) from Merck. The organic dye Malachite Green (MG) oxalate ($\text{C}_{46}\text{H}_{50}\text{N}_4 \cdot 3\text{C}_2\text{H}_2\text{O}_4$) was supplied from Sigma. Reactive Black 5 (RB5) dye ($\text{C}_{26}\text{H}_{21}\text{N}_5\text{Na}_4\text{O}_{19}\text{S}_6$, dye content, 55%) were supplied by Sigma-Aldrich. Commercial Degussa P-25 TiO_2 powder was kindly donated by Evonik Industries AG. All the chemicals were used without further purification.

Preparation of titania catalysts

The N-doped TiO_2 nanoparticles were synthesized by non-aqueous sol-gel method

using the reaction between benzyl alcohol and TiCl_4 . The urea was added as nitrogen source as shown Figure 1.

The precursors were mixed and the mixtures

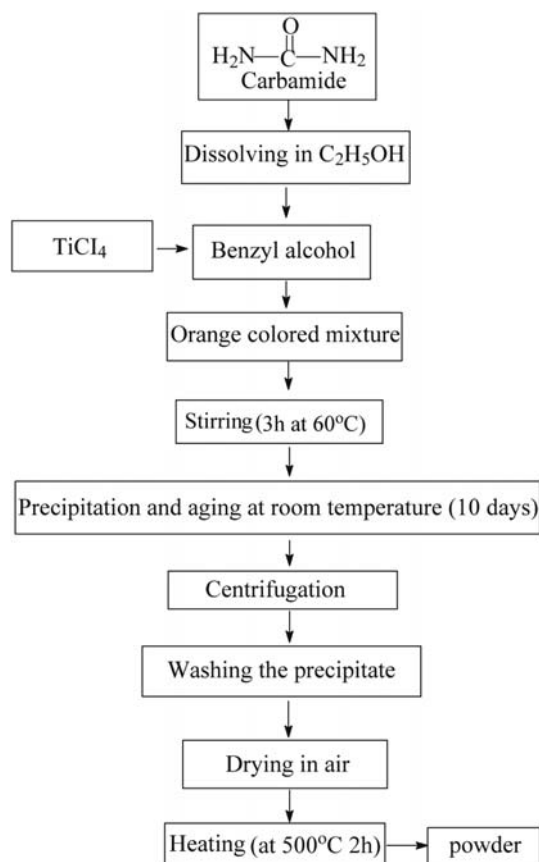


Figure 1. Scheme of nonhydrolytic synthesis of N-doped TiO_2

obtained were aged at room temperature for 10 days.

The next step was centrifugation of the obtained white suspensions at 4500 rpm for 15 minutes, followed by removal of the precipitate by decantation. The precipitates were washed 3 or more times with diethyl ether. After each washing step, the solvent was separated by centrifugation.

The collected materials were air-dried and subsequently calcinated at 500°C for 2 hours.

Thus, fine N-doped titania composite powders were obtained with assumed content of nitrogen – 1.3 and 13 mol%, labeled as 1.3N/ TiO_2 and 13N/ TiO_2 , respectively. For comparison, pure TiO_2 was also synthesized under the same preparation procedure but without adding urea.

Characterization of the prepared samples

Data on the structure and morphology of the resulting powders were obtained by X-ray diffraction (XRD, Bruker D8 Advance X-ray apparatus), infrared (IR), using the KBr pellets method (Nicolet-320, FTIR spectrometer with a resolution of $\pm 1 \text{ cm}^{-1}$, by collecting 64 scans in the range $1600\text{--}400 \text{ cm}^{-1}$) and UV-Vis spectroscopy (Spectrophotometer Evolution 300).

Studies of photocatalytic activity

The photocatalytic activity of the obtained powders was determined by measuring the rate of decoloration of water solutions of the dyes Malachite Green (MG) and RB5 under UV/Vis illumination. These two organic dyes were selected as model pollutants because of their intensive use in industrial processes. The initial concentrations of MG and RB5 aqueous solutions were $5 \times 10^{-6} \text{ M}$ and $11 \times 10^{-6} \text{ M}$, respectively. The applied experimental set up for investigation of photocatalytic activity was composed of a 500 ml borosilicate beaker, magnetic stirrer, and UV lamp.

This procedure included mixing a certain amount of dye solution with a titanium sample, followed by sonication for 10 min and then magnetical stirring in dark for 30 mins to ensure the establishment of an adsorption-desorption equilibrium on the catalyst surface. After adsorption, the light was turned on and this time was accepted as the starting point ($t=0$) of the reaction, at which the concentration of the dye was denoted as C_0 .

The UV-light irradiation was provided by a black light blue UV-lamp (Sylvania BLB 50 Hz 8W T5) emitting UV light with a wavelength of

365 nm. The distance of this lamp from the top level of the paint solution was kept at 10 cm, as in our previous investigations [13, 14]. The Vis light source was a 500W halogen lamp (Sylvania) fixed at 40 cm above the treated solution. The intensities of UV and Vis light reaching the solution surface were measured by a numeric Luxmeter (LM 37, Dostmann electronic) and were estimated to be 150 Lx (UV) and 14000 Lx (Vis). All photocatalytic measurements were carried out under constant stirring (450 rpm) and at room temperature (25°C). Aliquots (3 ml) were taken at regular time intervals of illumination and centrifuged to separate the catalyst from the solution. The progress of the photocatalytic degradation of the dyes was monitored by a Jenway 6505 UV-Vis spectrophotometer at the dyes maximum absorption wavelengths – 618 nm for MG and 597 nm for RB5.

Results

The XRD measurements were performed to identify the crystalline phases in the synthesized N doped TiO_2 powdered samples. The XRD patterns of pure TiO_2 and Degussa P25 as well as of undoped and N-doped TiO_2 powders prepared with two molar ratios of nitrogen to titanium are shown in Figures 2 and 3, respectively.

As a more sensitive method, the IR spectroscopy was used to verify the short range order of the obtained N-doped TiO_2 submicron powders (Figure 4). As can be seen in the figure, vibrations of the inorganic building units were recognized only in the range $1600\text{--}400 \text{ cm}^{-1}$. Several bands centered at $470\text{--}430 \text{ cm}^{-1}$, $650\text{--}590 \text{ cm}^{-1}$ and about 800 cm^{-1} were observed.

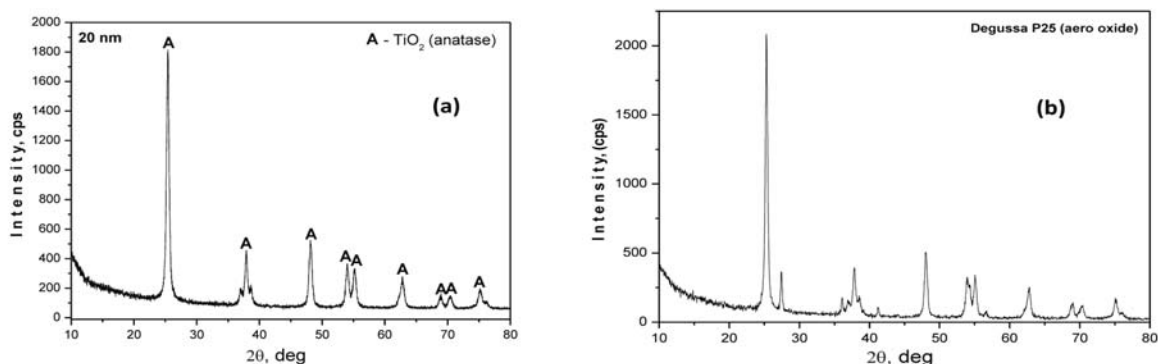


Figure 2. XRD patterns of pure TiO_2 (a) and Degussa P25 (b)

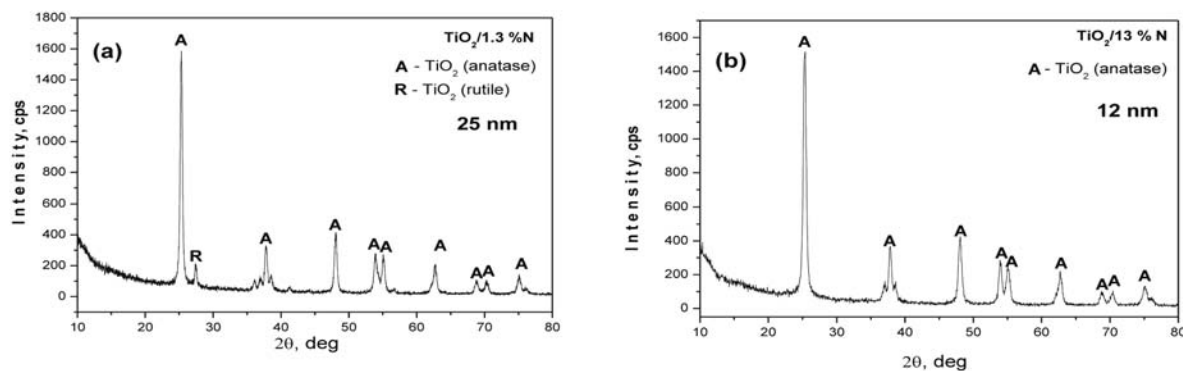


Figure 3. XRD patterns of TiO₂/1.3%N (a) and TiO₂/13%N (b)

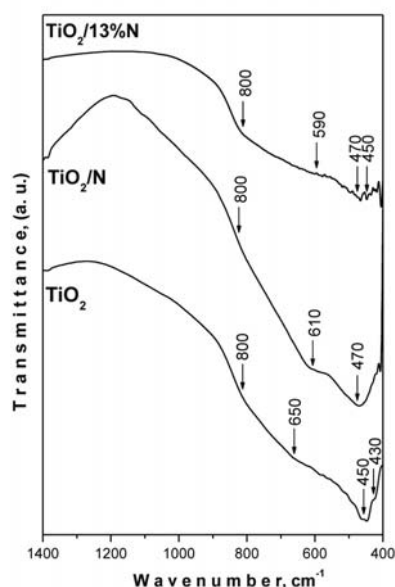


Figure 4. IR spectra of pure TiO₂, TiO₂/1.3%N and TiO₂/13%N

Figure 5 illustrates the photocatalytic activities of synthesized pure TiO₂, commercial Degussa P25 and N-modified with 1.3 and 13 mol % nitrogen TiO₂ on degradation of the organic pollutant MG, when irradiated with UV light. As it can be seen, complete decoloration of MG solution was achieved for different time by various photocatalysts.

Figure 6 illustrates photocatalytic activities of catalysts on decomposition of the dye RB5 under UV illumination.

When irradiated with Vis light, as shown in Figures 7 and 8, all four photocatalysts demonstrated similar photocatalytic activity and N-doping slightly affected the photocatalytic performance.

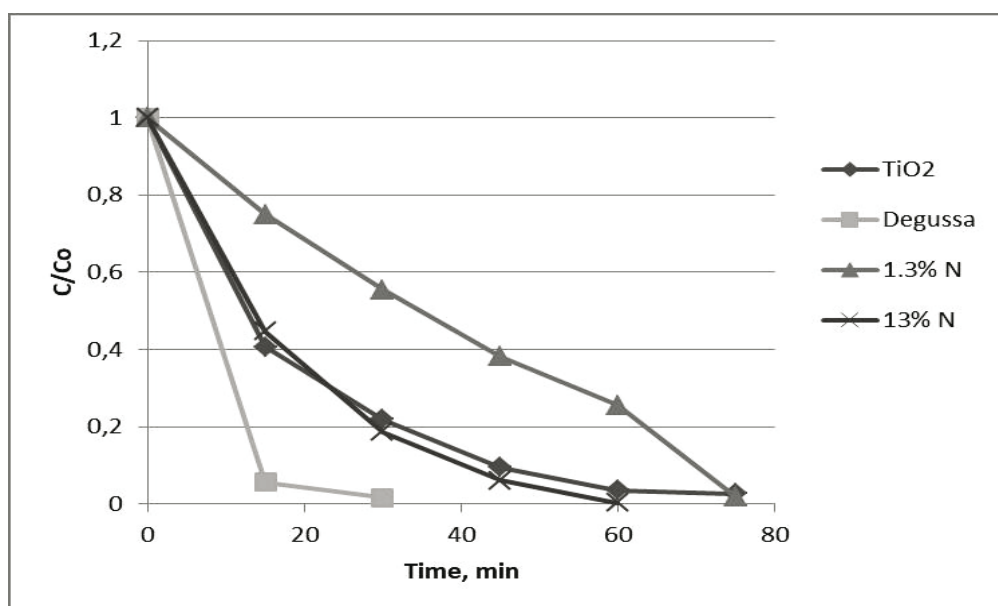


Figure 5. Photocatalytic activities of pure TiO₂, commercial Degussa P25 and N-modified with 1.3 and 13 mol % nitrogen TiO₂ on degradation of the organic pollutant MG, when irradiated with UV light

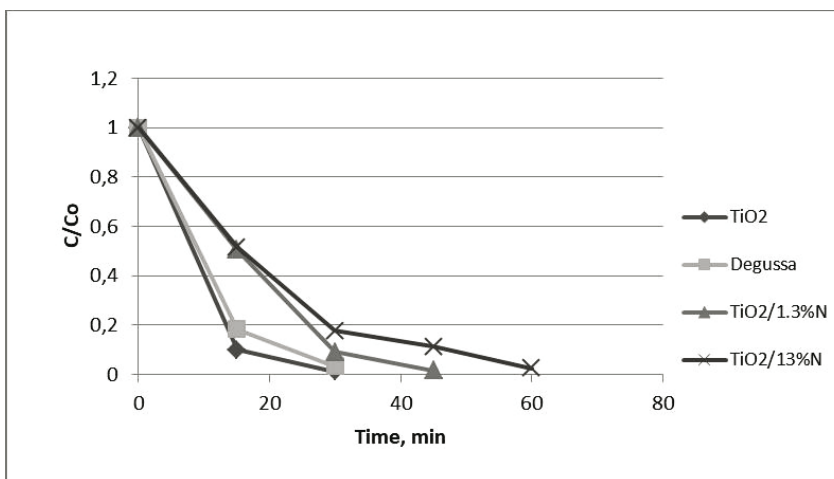


Figure 6. Photocatalytic activities of pure TiO₂, commercial Degussa P25 and N-modified with 1.3 and 13 mol% nitrogen TiO₂ on degradation of the organic pollutant RB5, when irradiated with UV light

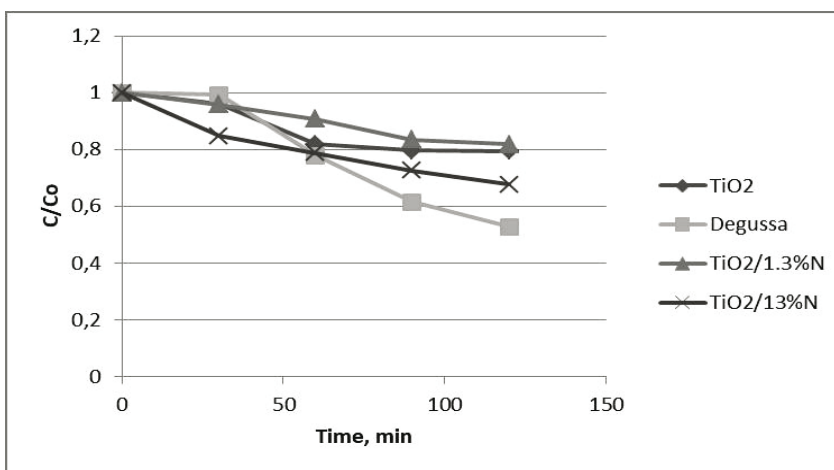


Figure 7. Photocatalytic activities of pure TiO₂, commercial Degussa P25 and N-modified with 1.3 and 13 mol% nitrogen TiO₂ on degradation of the organic pollutant MG, when irradiated with Vis light

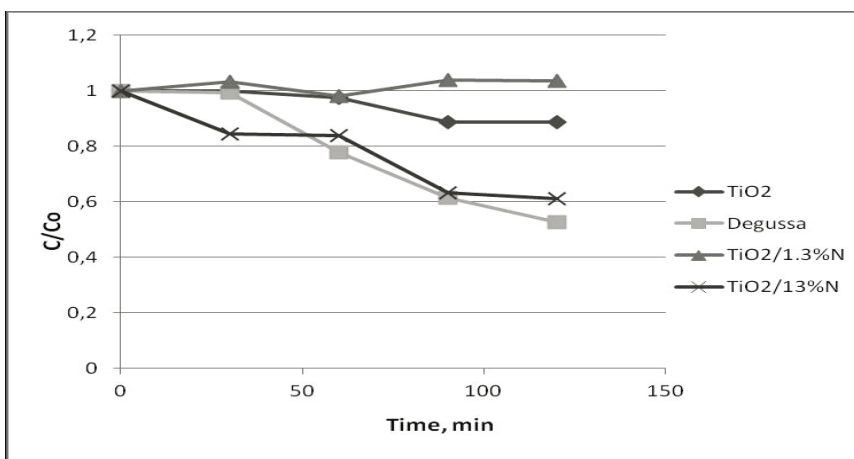


Figure 8. Photocatalytic activities of pure TiO₂, commercial Degussa P25 and N-modified with 1.3 and 13 mol% nitrogen TiO₂ on degradation of the organic pollutant RB5, when irradiated with Vis light

Discussion

Characterization of titania samples

The obtained XRD data for undoped pure TiO₂ and Degussa P25 (mixture of anatase and rutile

phases) were used as a reference (Figure 2). As can be seen in Figure 3, anatase (TiO₂) is the dominating crystalline phase and its three strongest interplanar distances appeared at 3.51; 1.89 and 1.66 Å (JCPDS 78-2486). It is

noteworthy that in the XRD patterns of sample 1.3N/TiO₂ small amount of rutile was observed as well. Obviously, the N doping in small concentrations enhances the crystallization of rutile-TiO₂. In the other sample, doped with 13% N (Figure 3b), rutile was not identified. As expected, no new diffraction peaks were observed in the N containing samples. The average crystallite size of as prepared undoped TiO₂ and Degussa P25 was about 20 nm and calculated using the Scherrer equation [15]. The nitrogen doped samples exhibited different crystallite size, depending on its content (Figure 3). As is seen from the figure, the crystallite size of 1.3N/TiO₂ was larger (25 nm) than those of 13N/TiO₂ (12 nm). Thus, the increase in N content led to decrease of the particles size. Obviously, the level of nitrogen doping has a significant impact on the TiO₂ particle size. Our results correspond well to those obtained by other authors [16] but differ from those obtained by Yang et al. (2010) who established that N doping led to increasing of the crystallite size of the obtained products [17]. This experimental fact could be explained by several reasons such as precursors used, experimental conditions applied, and the type of sol-gel method.

As was mentioned above, the IR spectrum analysis of as-prepared samples (Figure 4) recognized only inorganic building units. Bands in the range 470-430 cm⁻¹, 650-590 cm⁻¹ and about 800 cm⁻¹ were observed, which could be related to the vibrations of TiO₆ units [14, 18]. The doping with nitrogen resulted in the appearance of a broad band, centered at about 610 cm⁻¹.

Photocatalytic activity

The photocatalytic performance of pure and N-doped TiO₂ nanoparticles was investigated by observing bleaching of the dyes MG and RB5 in an aqueous solution irradiated by UV/Vis light. Synthesized pure TiO₂ and Degussa P25 were used as a reference system. No degradation of MG or RB5 was observed in the absence of photocatalyst or illumination. The results of photodegradation in the absence of photocatalyst indicate that the photolysis can be ignored as only 0.5 % of RB5 and 2 % of MG removed after 2 h illumination under UV/Vis light.

Figure 5 shows that the complete decoloration

of MG solution under UV irradiation was achieved for different time by various photocatalysts. As it can be seen, the best results were observed with Degussa P25 – 30 min, followed by that of 13N/TiO₂ – 60 min, pure TiO₂ and 1.3N/TiO₂ – 75 min. Some studies explain high photoreactivity of Degussa P25 by its phase composition (existence of rutile phase), morphology and slow electron/hole recombination rate [19, 20].

Rutile by itself has low photodegradation ability, but according to some studies, samples containing mixtures of rutile and anatase have exhibited greater photocatalytic activity than pure rutile and anatase [19, 21]. Obviously, a small amount of rutile present in sample 1.3N/TiO₂ (Figure 3) was not sufficient to achieve the optimum ratio between phases and to affect photocatalytic activity.

According to the results obtained for decomposition of the RB5 dye under UV illumination (Figure 6), the performance of pure TiO₂ was comparable to that of Degussa P25 and it expressed a better photoactivity than the N-doped TiO₂ samples, following the order TiO₂ > Degussa P25 > 1.3N/TiO₂ > 13N/TiO₂.

The data presented in Figures 5 and 6 show that, in UV light, the modification of TiO₂ with 13 mol% N led to improved decoloration activity against MG dye (Figure 5), while doping with nitrogen was not beneficial for the photocatalytic degradation of the dye RB5 (Figure 6).

According to Figures 7 and 8, all four photocatalysts demonstrated similar photocatalytic activity in Vis light and N-doping slightly affected their photocatalytic performance.

It is well known that the material properties and photocatalytic activities of titania samples are defined by synthesis procedure, type of precursors and nature and amount of dopants. On the other hand, in photodegradation of organic compounds various other parameters should be considered such as light source, particle size, surface area, initial concentration of organic material, amount of catalyst, temperature, etc. The existence of so many determining factors makes it very difficult to compare the results reported in different studies, and can be a source of controversy.

Doping with nitrogen at our experimental conditions slightly improved the photocatalytic

performance under UV light illumination and did not change it in Vis light. As already stated, similar results about no or even negative effect of N-doping have been obtained in other studies [12-19]. Some authors have reported that the impurities of N can act as recombination centers, especially at high N content [22, 23]. It is supposed that N doping can create defect levels in the deep region of the band gap and that these defects disturb the charge transfer in the TiO₂ nanoparticles [11, 24].

Conclusions

Pure and doped with nitrogen nanosized TiO₂ (12-35 nm) was synthesized by a non-hydrolytic sol-gel route. XRD analysis established that TiO₂ (anatase) was the dominant crystalline phase. It was found that the photocatalytic behavior of pure TiO₂ was similar to that of the Degussa P25, when irradiated with UV light. In UV light, the sample containing 1.3% N exhibited slightly improved activity in decolorizing RB5 dye, while its photocatalytic activity against MG dye did not change. When irradiated with Vis light under the same reaction conditions, the rate of photodegradation of nitrogen modified TiO₂ was not improved.

Acknowledgements

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