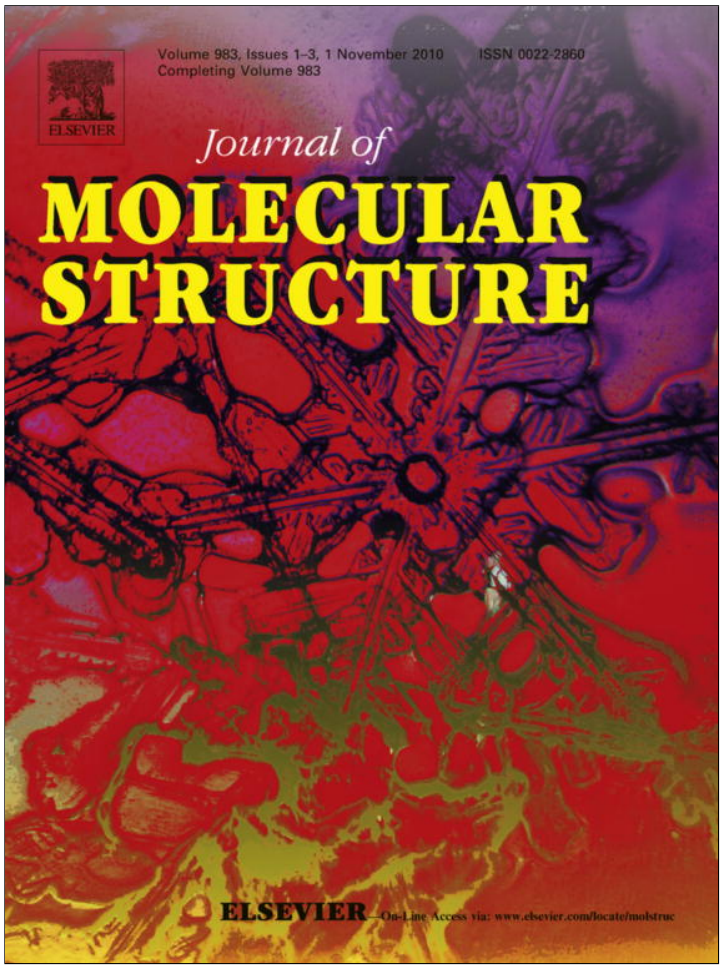
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Photocatalytic degradation of C.I. Reactive Blue 19 with nitrogen-doped TiO_2 catalysts thin films under UV/visible light

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ABSTRACT

Nitrogen-doped titania semiconductor thin films, with photocatalytic properties and a high transmittance in the visible range, have been deposited by unbalanced reactive magnetron sputtering on glass substrates, using d.c. pulsed power supplies. In order to increase the photocatalytic efficiency of the titania coatings the authors optimized the sputtering process, namely by using d.c. pulsed currents for better optimization of reactive gas consumption, and doped the coatings with nitrogen. With this combined and synergistic effect it was possible to enhance the catalysts absorption of visible light, by reducing its semiconductor indirect band-gap. By slightly doping the titania films with 0.7–0.9 at.% nitrogen the photocatalytic performance is ameliorated with almost one order of magnitude. This has been achieved by using nitrogen as a co-reactive gas, together with oxygen, when sputtering from a pure titanium target. The as-deposited thin films on glass are mostly amorphous; however, upon a thermal annealing in vacuum at 500 °C, the crystalline phases of anatase and rutile are developed, being anatase the most prominent polymorph. The photocatalytic performance of the N-doped titania films was evaluated by the decomposition of an organic dye (C.I. Reactive Blue 19) with combined UV/visible light irradiation. Furthermore, a mechanism for the degradation of this dye is proposed. The hydrophilic properties of these films have also been studied by means of water contact angle measurements after varied illumination periods; a minimum contact angle of ~10° was achieved for optimized wettability conditions.

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1. Introduction

Over the last few years, the titanium dioxide (titania) self-cleaning effect has been largely studied, since it is a well known photocatalyst used in the coating's industry, due its efficiency in decomposing organic pollutants upon ultra-violet (UV) irradiation [1–4]. With the development of organic chemical industry, more and more new organic compounds have been synthesized [5]; some of them cause serious environmental problems. The intrinsic colour due to commercial dyes diluted in the wastewater is extremely difficult to remove [6]. Therefore, chemical oxidation methods have been extensively studied because they can provide the ultimate solution for the destruction of commercial dyes in wastewaters [7]. Some textile dyes are refractory towards chemical oxidation and this renders them resistant towards decoloration by conventional biochemical and physicochemical methods. The combination of UV irradiation with photocatalysts such as TiO_2 is one of such methods that attracted considerable attention in recent years, due to its effectiveness in mineralization of organic compounds. This has included removal of dye pollutants from residual textile treatment waters [8–10].

The photocatalytic properties of the titania thin films rely on the inter-band transition induced by the UV light illumination of its surface. For UV light with a higher energy than the titania band-gap, electron–hole pairs are generated and diffuse to the surface. The diffusion of these charges originates the radical or ion generation that, in turn, will decompose organic compounds adsorbed on the catalyst surface. This material yields most of its photocatalytic activity under UV-A light irradiation, because anatase has a band-gap value of 3.2 eV and rutile has a band-gap value of 3.0 eV. In order to utilize the economical and ecological sunlight, many attempts have been made to shift the onset of TiO_2 absorption edge from the ultra-violet to visible region, such as doping with transition metal ions or non-metallic ions, coupling with small band-gap semiconductors. Doping with non-metallic elements has been considered as one of the most promising methods to develop visible light sensitive TiO_2 photocatalyst, since it does not create undesired defects in the semiconductor band-gap that might enhance electron–hole recombination and thus reduce the photocatalyst's efficiency. Titanium oxide anionic doping with nitrogen, in particular, is considered as one of the best visible light photocatalyst known to date [11].

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The photocatalytic behaviour of the titania coatings was determined by combined ultra-violet irradiation and absorption measurements of a particular dye, acting as an organic pollutant. The observed photo-decomposition of the dye was measured in the UV/visible spectrum by the decrease of the maximum absorbance of the dye with irradiation time. The photocatalytic decoloration of C.I. Reactive Blue 19, a textile anthraquinone dye, has been already reported in the literature in aqueous suspensions containing TiO_2 or ZnO as nano-particles catalysts [12] and by ozonation [13]. The choice for using this dye is that it is commonly used in the textile industry and can have a prejudicial impact on the environment when the residual waters are not treated. In this work, we describe the photocatalytic degradation of the same dye when adsorbed on the surface of nitrogen-doped TiO_2 thin films.

2. Experimental procedure

Titania films with a thickness of ~450 nm, were deposited at room temperature on glass slides (76 mm × 26 mm and 1 mm thick), by unbalanced d.c. pulsed reactive magnetron sputtering, from a high purity Ti target in an Ar/O_2 atmosphere, while introducing a little amount of N_2:O_2 mixture for nitrogen doping. A turbo molecular pump was used to achieve a base pressure of $\sim 10^{-4}$ Pa (before introducing the gas mixture). The argon flow rate was set to 60 sccm (working gas), the oxygen flow rate set to 8 sccm, while the N_2:O_2 flow rate (85:15) varied from 1.5 to 2 sccm. The cathode power density and substrate bias voltage was set to 7.5 W/cm^2 (50 kHz) and −50 V, respectively. By using d.c. pulsed power supplies the advantages are threefold: there is less chance of target poisoning, comparing to diode or direct d.c. sputtering, since the oxygen consumption is optimized by regulating the pulse frequency; the deposition rate is increased due to better target performance; the ionization of argon is enhanced near the substrate holder due to the alternating attraction of either electrons or Ar^+ ions, providing a more efficient ionic bombardment of the substrate and enhancing the nucleation density of the growing film [14]. The target-to-substrate distance was kept constant at 75 mm and the working pressure during the sputter deposition was 0.3 Pa. No external substrate heating was used during the deposition. Prior to deposition, the glass substrates were first boiled in a 200 ml solution of H_2SO_4 and H_2O_2 (1:3) for 30 min, in order to eliminate Ca^+ and Na^+ ions, which can diminish the photocatalytic efficiency of the film since the interactions of those ions with the TiO_2 molecules can decrease the deposition rate, then ultrasonically cleaned in acetone.

The surface properties of titania are of extreme importance in order to evaluate and study its photocatalytic performance. Thermal annealing treatments, in a vacuum furnace, were performed on the titania samples in order to enhance crystalline growth. The temperature was ramped from room temperature to 500 °C in 1.5 h, remained at that temperature for 2 h and subsequently it was naturally cooled to room temperature during 12 h. The background pressure prior to the annealing was of the order of 10^{-4} Pa. The crystallinity of the titania films was characterized by X-ray diffraction, using Cu Kα radiation with a wavelength of 1.54 Å, $\Delta\theta = 0.01°$ and integration time of 1.5 s, from a Bruker AXS D8 X-ray diffractometer, in the conventional Bragg–Brentano geometry.

In order to study the photocatalytic performance of the titania films, a solution of an extremely robust organic dye, C.I. Reactive Blue 19 (Sigma–Aldrich, R8001), was prepared with a concentration of 2.84 mg/L and pH ≈ 7. Blue 19 is one of the textile industrial dyes most difficult to degrade in the absence of catalyst and thus it was chosen for this study. The titania films were immersed in this solution in a 4 × 4 × 1 cm^3 quartz cell with the irradiation perpendicular to the surface. No oxygen was artificially introduced in the solution during the irradiation experiments. A 150 W xenon discharge lamp was used as the radiation source. For UV-only irradiation experiments, a broadband filter (Schott UG11) was mounted between the lamp and cell in order to select the spectral UV-A light range between 280 and 380 nm. In this case the total irradiance on the catalyst surface was 1 mW/cm^2. For the full spectra irradiation experiments, the total irradiance was 10 mW/cm^2. After the irradiation experiments, performed for a particular period of time, the solution concentration was monitored by recording the absorbance spectrum, through the 4 cm optical path of the cell, using a Shimadzu UV-2501 spectrophotometer.

Contact angle measurements were performed by measuring the angles at which the liquid/vapour interface from a 20 μl water droplet meets the liquid/solid sample surface. A method based on B-spline snakes (active contours) for measuring high-accuracy contact angles was employed [15]. The tests were performed for samples in the dark (t = 0 min) and for different intervals of illumination with the full spectra of a Xe 150 W arc lamp with an irradiance of 10 mW/cm^2; the spectra of this lamp closely resembles the sun's spectra. A set of four 20 μl droplets were dropped on the surface after each illumination procedure, being their results averaged. The measurements of absorbance, transmittance and reflectance of the glass substrates coated with the titania thin films, were made in the Shimadzu UV-2501 spectrophotometer coupled with an integrating sphere.

3. Results and discussion

3.1. Optimization of the sputtering process

Fig. 1a and b explains the choice of pulsed d.c. frequency of 50 kHz. Combined with bipolar pulsed d.c. substrate bias polarization (−100 V), the inherent ionic bombardment provides defect centres on the surface of the growing film that will enhance the nucleation and coalescence of the deposited species [15]. For this frequency, the films are thicker (260 nm) due to the higher deposition rate, as seen in Fig. 1b, and presents also a better first-order dye degradation rate constant (k) (see Section 3.4.). As the TiO_2 crystals coalesce in the growing film, their shape and size will stabilise upon reaching a certain thickness. Normally, the crystal size increases up to a threshold that will further inhibit its growth, despite increasing film thickness [15]. This maximum grain size is important for the inherent surface area of the surface crystalline grains; the larger the better the adsorption of the pollutants and subsequent degradation. It can be seen from the transmittance data in Fig. 2 that for the samples deposited with a pulsed frequency of 50 kHz the respective absorption edge is slightly shifted to the visible spectrum, resulting in better conditions for UV-A/visible light photocatalysis.

3.2. Structural analysis

X-ray diffraction scans provided evidence that anatase is the primary crystalline phase that develops in the thin films after thermal annealing in a vacuum furnace at 500 °C. This result can be observed in Fig. 3. In this figure, the large band that is observed at lower angles is attributed to the amorphous glass substrate, while the labels A and R refers to anatase and rutile polymorph phases, respectively. There is a slight decrease in the anatase phase and increase in development of the rutile phase by changing the level of atomic nitrogen doping from 0.72% to 0.84%; resulting from different N_2:O_2 reactive mixture flows during the sputtering process, 1.5 and 2 sccm, respectively. The level of N-doping was determined from previous Rutherford Backscattering Spectroscopy experiments [16]. Furthermore, the compositions of these films indicate a O/Ti ratio of 2:2.

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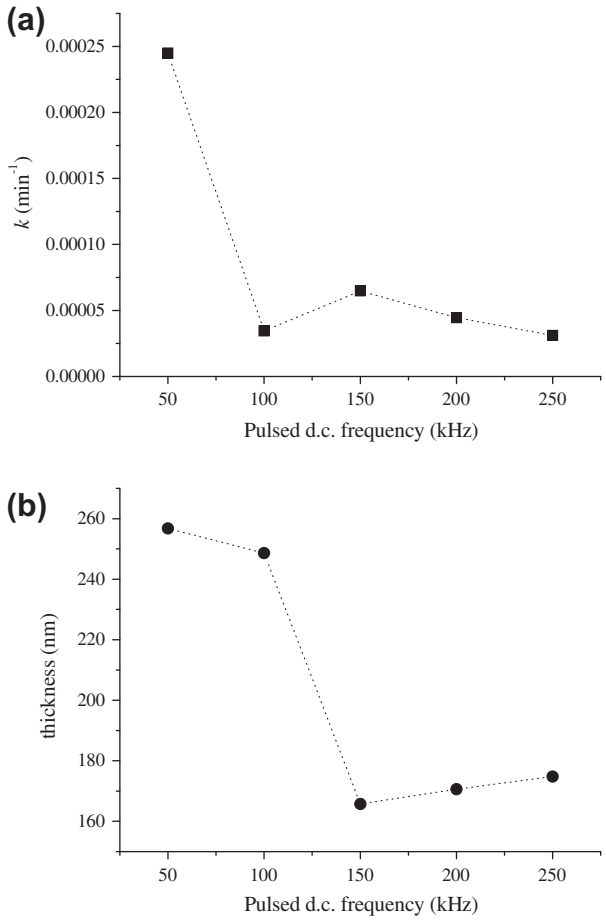


Fig. 1. Relationship between the (a) relative 1st-order dye degradation rate constant (k) and the (b) thickness with the pulsed d.c. frequency used during deposition, for a set of undoped TiO_2 thin films.

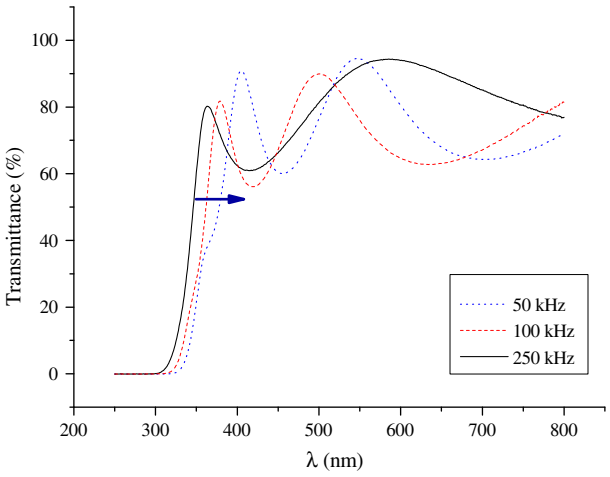


Fig. 2. Transmittance spectra of three TiO_2 films, using different pulsed d.c. frequency.

3.3. Contact angle measurements

As it can be seen from Fig. 4, the hydrophilicity of the TiO_2:N surface (for this particular case, with 0.72 at.% of N) is enhanced with the exposure of combined UV–visible light. This illumination yields through a redox process the generation of OH radicals that initiates the photo-oxidation of the water droplet, leading to a larger wetting of the surface. In this process, as the illumination exposure time is increased, the contact angle decreases from an initial value of ~52° (in the dark) to a final value of ~10° after 2 h of illumination of the sample in the absence of droplets. For the longest exposure time, the hydrophilicity does not vary more than 5% for the TiO_2:N samples doped with 0.72–0.9 at.%.

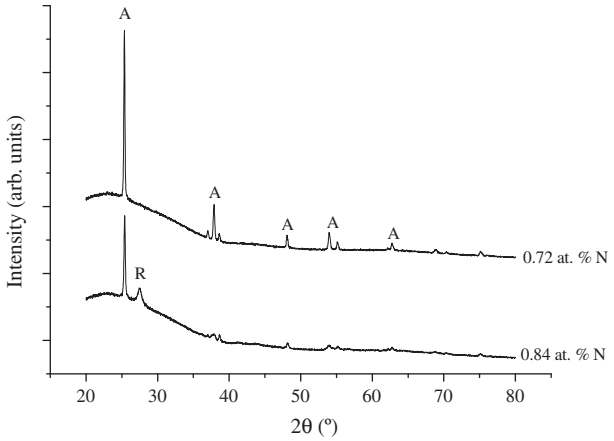


Fig. 3. X-ray diffraction pattern for two distinct TiO_2:N thin films, revealing a dominant anatase crystalline phase.

3.4. Photocatalysis

The observed photo-decomposition of the aqueous solution of Blue 19 (organic dye), acting as a pollutant, was measured in the UV/vis spectrum by the decrease of its maximum absorbance with irradiation time. For relatively small concentrations, the absorbance (A) is related to the solution concentration through the Beer–Lambert law:

$$A = \varepsilon l c \tag{1}$$

where ε is the molar extinction coefficient, l is the path length of the quartz cell, and c is the concentration of the absorbing compound in the solution. Since l and ε are constant, we have:

$$\frac{A}{A_o} = \frac{c}{c_o} \tag{2}$$

where the o subscript is related to time zero ($t = 0$). The rate constant for this process, k, can be calculated by means of a pseudo-first-order reaction:

$$\ln\left(\frac{c}{c_o}\right) = -kt \tag{3}$$

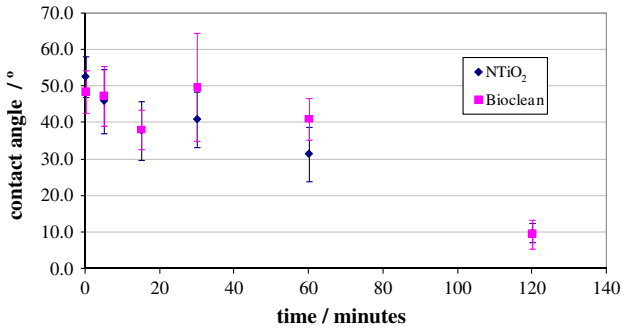


Fig. 4. Contact angle measurements experiments performed on the surfaces of a TiO_2:N (0.72 at.% of N) sample and a Saint-Gobain BioClean® reference sample (for the sake of comparison) after different intervals of illumination with the full spectra of a Xe 150 W arc lamp, using an irradiance of 10 mW/cm^2.

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The values of k in the plots present in Figs. 1a and 5 were obtained using this Beer–Lambert law.

Several photocatalytic experiences were performed with other textile dyes, such as Yellow 27, Black 5, Red 41 and Red 158, with the same concentration. To perform further studies, C.I. Blue 19 dye was chosen, since, comparing to the previous lot of dyes, it proved to be the most difficult to degrade in the absence of catalyst, as it is shown in Fig. 5.

The absorbance decay of the Blue 19 dye when adsorbed on the photocatalyst surface is monitored as a function of time in Fig. 6. For this experiment, the sample was exposed to the lamp's full spectral range, due to the higher absorption in the visible range for this particular N-doped titania film. Since the colour of the dye solution changed from bright blue to colourless during this process, it indicates that an oxidation–reduction mechanism took place on the surface of the titania thin films; subsequently degrading the organic chromophore with time. Even after prolonged irradiation, the dye presents a relatively high absorbance in the UV-C region ($\lambda \approx 260$ nm), which may suggest that organic aromatic intermediates such as quinones and phenols are still present. This is a consequence of the choice of an anthraquinone dye, which is known to be highly resistant to this type of radiation.

Fig. 7 shows the relative decrease in Blue 19 dye concentration as function of irradiation time for two titania thin films with different at.% of N-doping, 0.72 and 0.84. For sake of comparison, data has also been included for an undoped sample, deposited in the same conditions, albeit without N_2:O_2 mixture. The calculated 1st-order rate constant (k) is for undoped, 0.72 and 0.84 at.% N-doped, 5.1×10^{-5}, 1.8×10^{-4} and 2.0×10^{-4} min^{-1}, being the associated experimental error ±6%, ±2% and ±4%, respectively. As it can be seen, doping of the titania thin films with nitrogen clearly enhances the photocatalytic activity. Moreover, the sample with higher amount of N yields a slightly faster dye degradation rate; the difference in k for both doped samples exceeds the experimental error. In order to aid the observation, in Figs. 5 and 7, the vertical axis is in $\log_{10}$, but as in a ln scale, the experimental data follows a first-order linear tendency.

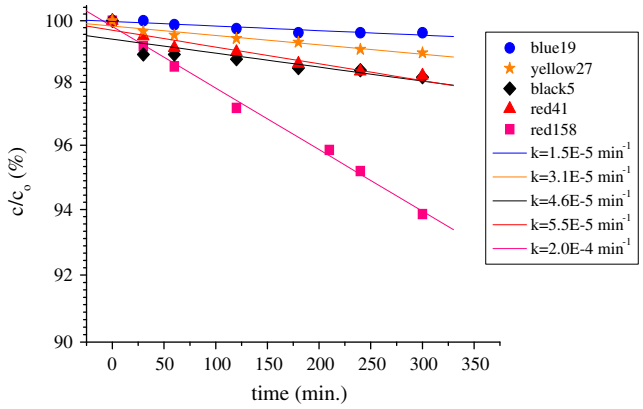


Fig. 5. Degradation of various dyes in the absence of catalyst upon selected UV-A irradiation.

3.5. Optical properties

In Fig. 8 one can observe the transmittance and reflectance spectra of the same N-doped titania sample used on the photo-decomposition tests shown in Figs. 6 and 7 (with 0.72 at.% N-doping). From these curves it is clear that the film has a very high transmittance in the visible range and that the maxima and minima occur for the same wavelengths of the reflectance minima and maxima, respectively. This information indicates there is a coherent optical pathway inside the thin films, resulting from a dense and homogeneous structure, due to the inherent homogeneity in the crystallite texture distribution and nitrogen doping.

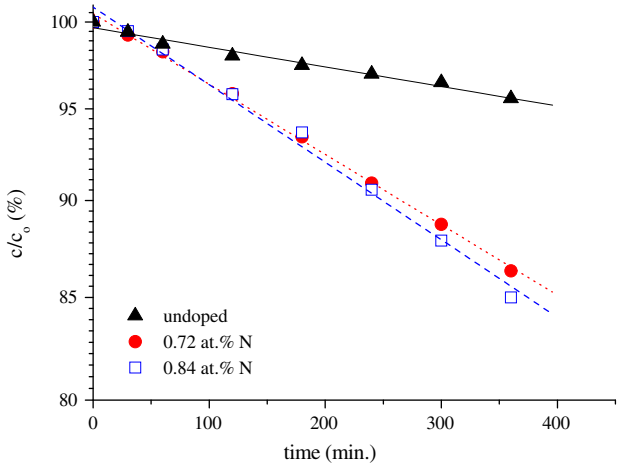


Fig. 7. Relative decrease in Blue 19 dye concentration as function of time, upon irradiation with a Xe lamp with a UV-A filter, in the presence of two titania thin films with different at.% of nitrogen doping.

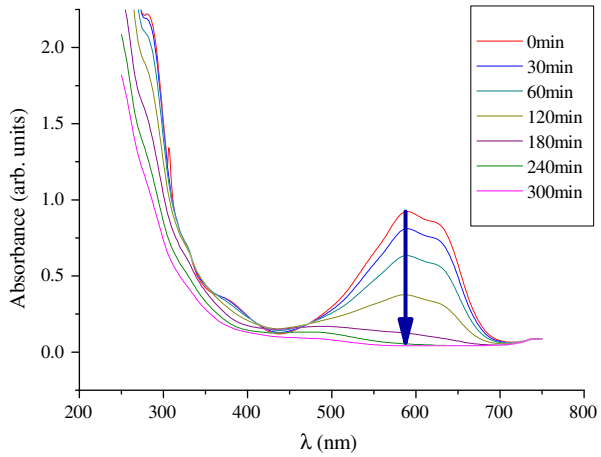


Fig. 6. Absorbance spectra of Blue 19 dye as a function of time upon being adsorbed to a TiO_2:N (0.72 at.% of N) thin film.

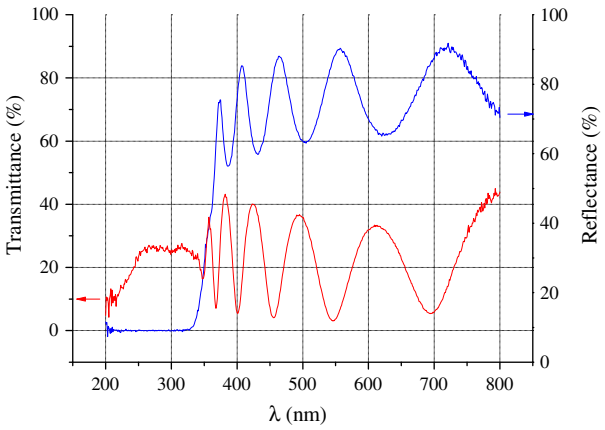


Fig. 8. Reflectance and transmittance curves for a TiO_2:N thin film, doped with 0.72 at.% of nitrogen.

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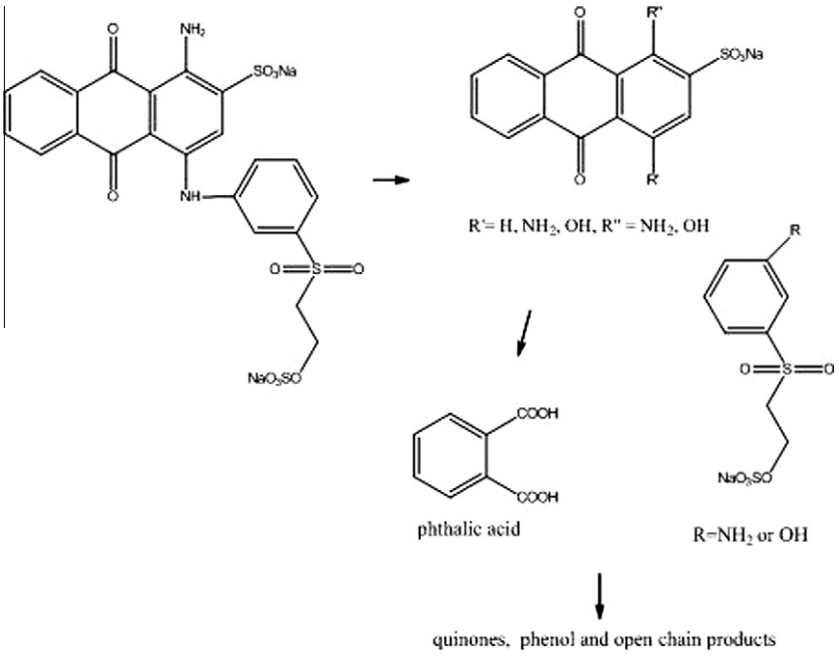


Fig. 9. Reaction pathway of photocatalytic degradation of the Reactive Blue 19 dye.

3.6. Reaction pathway

Anthraquinone dyes are characterized by their high light fastness. The blue colour of C.I. Reactive Blue 19 (also known as Remazol Brilliant, RBBR) is due to electron-donating substituent such as $-NH_2$ and –NH–Ar forming hydrogen bonds with C=O bond within the molecule, which increases the maximum absorbance wavelength in the visible range of the UV–visible absorption spectra. The mechanism that initiates the photocatalytic degradation of Blue 19 is related to the hydroxyl radicals attack to the C–N bond of the side chain on anthraquinone [7]. Studies with anthraquinone dyes have shown that the early steps of the degradation process mainly involve C–N bonds breaking and substrate hydroxylation [17,18]. When the experimental conditions are mild the degradation may stop at the stage of phthalic acid [19].

In the study of mineralization of C.I. Reactive Blue 19 by ozonation, the authors show the end products as quinones, phenols and diacids, such as maleic, oxalic and acetic acids [13]. Based on the results of other authors on anthraquinone dyes, just described, the overall reaction pathway can be theoretically postulated as shown in Fig. 9.

4. Conclusion

Nitrogen-doped titania thin films have been deposited by reactive pulsed d.c. magnetron sputtering on glass substrates. The as-deposited photocatalytic films deposited at room temperature are predominantly amorphous. However, upon thermal annealing in vacuum at 500 °C, both anatase and rutile crystalline phases are developed; depending on the level of N-doping. These films developed very good photocatalytic efficiency by degrading a chosen organic pollutant (C.I. Reactive Blue 19) via irradiation with UV-A light. In order for the N-doping to be effective, and for the decrease of the indirect band-gap, N must be substitutional in the TiO_2 lattice, as it has been reported [16]; otherwise, it will create defects in the band-gap of TiO_2 and hence yield electron–hole recombination, which has the adverse side of decreasing the photocatalytic efficiency. By slightly doping the titania films with 0.7–0.9 at.% nitrogen the photocatalytic performance is ameliorated with almost one order of magnitude. Additionally, from water contact angle experiments, it was found that these films developed hydrophilic properties upon UV-A/vis illumination.

Furthermore, transmittance and diffuse reflectance spectra recording of these anionic N-doped films yielded proof of a small absorption shift to the visible part of the solar spectra, thus evidencing a band-gap narrowing and absorption increase of joint UV–visible light irradiation, clearly justifying the observed photocatalytic efficiency enhancement.

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References

[1] M.R. Hoffmann, S.T. Martin, W. Choi, D.W. Bahnemann, Chemical Reviews 95 (1995) 69–96.
[2] Andrew Mills, Jishun Wang, Matthew Crow, Giovanni Taglioni, Luca Novella, Journal of Photochemistry and Photobiology A: Chemistry 187 (2007) 370–376.
[3] A. Fujishima, Xintong Zhang, Donald A. Tryk, Surface Science Reports 63 (2008) 515–582.
[4] M. Kitano, M. Matsuoka, M. Ueshima, Masakazu Anpo, Applied Catalysis A: General 325 (1) (2007) 1–14.
[5] N. Guettaï, H. Ait Amar, Desalination 185 (2005) 427–437.
[6] J. Grzechulska-Damszel, M. Tomaszewska, A.W. Morawski, Desalination 241 (2009) 118–126.
[7] W.Z. Tang, H. An, Chemosphere 31 (9) (1995) 4171–4183.
[8] Tim Robinson, Geoff McMullan, Roger Marchant, Poonam Nigam, Bioresource Technology 77 (2001) 247–255.
[9] B. Van der Bruggen, B. Daems, D. Wilms, C. Vandecasteele, Separation and Purification Technology 22–23 (2001) 519–528.
[10] Marco S. Lucasa, José A. Peresa, Gianluca Li Puma, Separation and Purification Technology 72 (2010) 235–241.
[11] R. Asahi, T. Morikawa, T. Ohwaki, K. Aoki, Y. Taga, Science 293 (2001) 269–271.
[12] C. Lizama, J. Freer, J. Baeza, H.D. Mansilla, Catalysis Today 76 (2002) 235–246.
[13] Z. He, L. Lin, S. Song, M. Xia, L. Xu, H. Ying, J. Chen, Separation and Purification Technology 62 (2008) 376–381.
[14] P. Yashar, J. Rechner, M.S. Wong, W.D. Sproul, S.A. Barnett, Surface and Coatings Technology 94–95 (1997) 333–338.
[15] A.F. Stalder, G. Kulik, D. Sage, L. Barbieri, P. Hoffmann, Colloids and Surfaces A: Physicochemical and Engineering Aspects 286 (1–3) (2006) 92–103.

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[16] C.J. Tavares, S.M. Marques, S. Lanceros-Méndez, L. Rebouta, E. Alves, N.P. Barradas, F. Munnik, T. Girardeu, J.P. Rivière, Journal of Nanoscience and Nanotechnology 10 (2010) 1072–1077.
[17] A.B. Prevot, C. Baiocchi, M.C. Brussino, E. Pramauro, P. Savarino, V. Augugliaro, G. Marcí, L. Palmisano, Environmental Science Technology 35 (2001) 971–976.
[18] I. Bouzaida, C. Ferronato, J.M. Chovelon, M.E. Rammah, J.M. Herrmann, Journal of Photochemistry and Photobiology A: Chemistry 168 (2004) 23–30.
[19] P. Zucca, C. Vinci, F. Sollai, A. Rescigno, E. Sanjust, Journal of Molecular Catalysis A: Chemical 288 (2008) 97–102.