

Photoactivity of nitrogen-doped anodic TiO₂ under UV and VIS light irradiation

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ABSTRACT

Titanium dioxide in its two main crystal structures, anatase and rutile, is probably the most efficient among the known photocatalysts, and undoubtedly the most studied one. It can be obtained in form of powders or as anodic films on titanium surfaces, which allow to modify surfaces of filters for wastewaters treatment, or buildings external panels, by adding a photocatalytic and self-cleaning layer, or to develop a new generation of solar cells.

In this research photoactive TiO₂ films with different semiconductive properties and morphologies were obtained, by subjecting titanium to Anodic Spark Deposition (ASD) procedures or to anodizing in fluoride-containing electrolytes. Thermal treatments in nitrogen atmosphere were applied to dope TiO₂, and therefore modify its absorption characteristics towards light. The oxides photoactivity under UV and visible light was evaluated in the catalytic decomposition of rhodamine B.

Keywords: anatase, anodizing, doping, photocatalysis, titanium dioxide

1 INTRODUCTION

Titanium dioxide in its two main crystal structures, anatase and rutile, is probably the most efficient among the known photocatalysts, and undoubtedly the most studied one. It is commercially available in powder and suspension forms, which are widely used to modify the surface of components such as filters for wastewaters treatment, or buildings external panels, by adding a photocatalytic and self-cleaning layer, or to develop a new generation of solar cells [1, 2]. In spite of its easy supply and contained price, the high surface areas that most promote photocatalytic efficiency are difficult to obtain and maintain, since crystallites tend to agglomerate [3]. Another route to obtain TiO₂ films with tunable morphology and structure is to exploit the anodizing process to induce the growth of the oxide layer directly on titanium substrates: the higher complexity of this process is rewarded by avoiding problems related to particles dispersion [4, 5].

The parameters that most affect the oxide characteristics are the electrolytic solution (composition, concentration, pH and temperature), the anodic current density and the feeding voltage. High voltages (100 V up to 500 V), combined with high current densities, are used in anodic spark deposition (ASD) processes, which lead to a crystalline or semicrystalline up to a hundred micrometers

thick, showing the presence of either anatase or rutile [6, 7]. Conversely, titanium anodizing in fluoride containing electrolytes grants the achievement of amorphous nanotubular oxides, with enhanced surface area [5, 8].

One reason for the rapid commercialization of TiO₂ for organic compounds photodegradation is that it proved to be effective in the complete mineralization of hundreds of organic materials, including aromatics, pesticides and dyes. Early works on this topic often focused on the removal of organic pollutants from wastewaters; in recent years also the aspect of removing gas phase organic compounds has attracted attention, since volatile organic compounds (VOCs), emitted into the atmosphere by human activities, cause many environmental problems specially concerning air quality degradation, and they are often responsible for malodorous air in buildings [9-11].

Titanium dioxide is a wide band gap semiconductor (3.20 eV for anatase, 3.02 eV for rutile, which corresponds to a wavelength absorption threshold of 384 and 410 nm, respectively). Therefore its optical absorptions lies in the UV range: to increase the percentage of light absorption, TiO₂ doping is performed, to shift absorption towards visible light. Nitrogen doping is the most diffused method to alter TiO₂ electronic structure; the mechanisms that originate the shift of the absorption edge to longer-wavelengths are still under discussion. From a structural point of view, N occupies substitutional and interstitial sites, replacing oxygen in the anatase structure and also generates, even for very low N-content, a vast amount of oxygen vacancies [12].

In the presented research work, undoped and N-doped TiO₂ layers were obtained by means of anodizing techniques: special attention will be given to TiO₂ nanotubes. The photocatalytic activity of differently doped oxides was tested in the decomposition of an organic dye, rhodamine B.

2 EXPERIMENTAL

Titanium sheets 0.5 mm thick (commercial purity, grade 2 ASTM B265) were cut into 30 mm x 20 mm rectangular specimens and subsequently degreased with acetone. Anodizing was carried out in three electrolytic solutions:

- 0.5 M H₂SO₄ (labeled S)
- 0.5 M H₂SO₄ + 0.25 M H₃PO₄ (labeled SP)
- 0.5 wt % NaF + 1 M Na₂SO₄ (labeled F)

As for TiO₂ nanotubes formed in the latter solution, nanotubes length, the crystallization extent and the oxide doping were the process parameters taken into account in the investigation of photocatalytic performance. Nanotubes formation requires the holding of a determined cell voltage (in this case, 20 V) for a prolonged time: by changing the maintenance time (3 h or 6 h) it was possible to modify the nanotubes length, while crystal structure and doping were achieved by thermal treatments: in fact, to convert the amorphous oxide layers to the anatase phase, TiO₂ nanotubes were heated at 400°C (2 h or 4 h treatment) in air atmosphere. The same annealing process was performed in nitrogen atmosphere, as to induce TiO₂ doping. Details about specimens preparation are given in Table 1.

Anodized specimens were characterized through Scanning Electron Microscope (SEM) and X-ray diffraction (XRD), to evidence oxide morphology and crystal structure. XRD spectra were collected in the angular range 2θ 20° to 30°, since it allowed to evidence the main diffraction peaks of both anatase (at 25°) and rutile (at 27°). Glow-discharge optical emission spectroscopy (GD-OES) analyses were performed to attest nitrogen introduction in the TiO₂ layer during annealing in nitrogen atmosphere.

Specimens were used as photocatalysts in the degradation of 10⁻⁵ mol/L rhodamine B (RB) solutions, whose decomposition was measured by means of a UV-Vis spectrophotometer. Since RB exhibits an intense magenta color, with absorbance peak at wavelength of about 550 nm, the degradation of the compound caused the reduction of color intensity due to the breakup of the molecule chromophore groups. Hence, the decrease in the absorbance peak intensity was found to be directly proportional to a decrease in the solution concentration.

The irradiation system consisted of a UV-Vis lamp supplying a UV intensity of either 2500 or 4000 μW/cm², depending on the chosen distance between the lamp and the irradiated specimens.

Label	Electrolyte	Cell voltage	Thermal treatment
S-140V	0.5 M H ₂ SO ₄	140 V	None
SP-200V	0.5 M H ₂ SO ₄ 0.25 M H ₃ PO ₄	200 V	None
F-3h-A2	0.5 wt % NaF 1 M Na ₂ SO ₄	20 V maintained 3 h	Air, 400°C, 2 h
F-6h-A2		20 V maintained 6 h	Air, 400°C, 2 h
F-6h-A4			Air, 400°C, 4 h
F-6h-N4		Nitrogen, 400°C, 4 h	

Table 1: Anodizing conditions and thermal treatments applied on specimens used in photocatalytic tests.

Two beakers, one containing the photoactive specimen and 25 mL of solution and the other containing only the RB solution (reference), were irradiated for 23 hours; periodical measurements of absorbance were performed on both solutions. Moreover, to analyze substrates efficiency under visible light, a solution of 1 mol/L NaNO₂ was used to filter the UV component of the UV-Vis lamp. The shielding effect was demonstrated by measuring UV intensity before and after the interposition of the NaNO₂ solution between the lamp and the beakers, as the intensity measured at about 380 nm dropped from 4000 μW/cm² to less than 1 μW/cm².

RB is a complex organic molecule, containing aromatic rings, nitrogen, chlorine and four ethyl groups: therefore, a partial breakup of the molecule, rather than its total decomposition, was expected. Thus, mass spectroscopy analyses were also performed in order to examine the possible reaction intermediates and products of RB oxidation induced by TiO₂ photocatalysts.

3 RESULTS AND DISCUSSION

3.1 Oxides characterization

As discussed in previous work, ASD conditions were reached by anodizing titanium in sulfuric acid solutions: above a determined voltage threshold (approximately 80 V) the amorphous anodic oxides were found to contain anatase crystals, whose quantity increased with anodizing voltage. Below the given threshold, oxides were found to be completely amorphous. At 150 V the ASD process was completed, and the metal surface was fully covered with a ceramic oxide: it presented craters and cracks due to the establishment of electric sparks on the growing oxide, typical of ASD anodizing [4, 7]. Nevertheless, the increase of cell voltage led to a partial conversion of anatase crystals into the rutile structure, which exhibits lower photoactivity: therefore, a most convenient feeding voltage was chosen, *i.e.*, 140 V, in order to obtain both oxide homogeneity and high anatase content (Fig. 1).

Same considerations apply to anodizing procedures in sulfuric and phosphoric acid mixtures. In this case, the voltage threshold was higher; the process was completed at 200 V, generating a rougher morphology with respect to specimens anodized in sole H₂SO₄, but lower anatase content (Fig. 2).

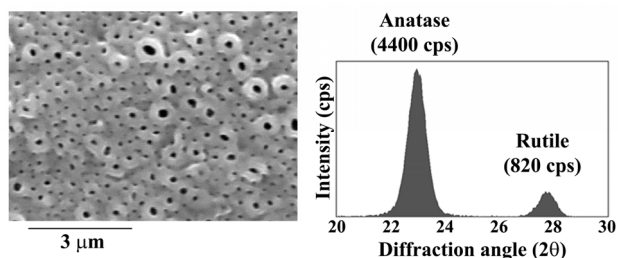


Figure 1: SEM and XRD analyses of sample S-140V.

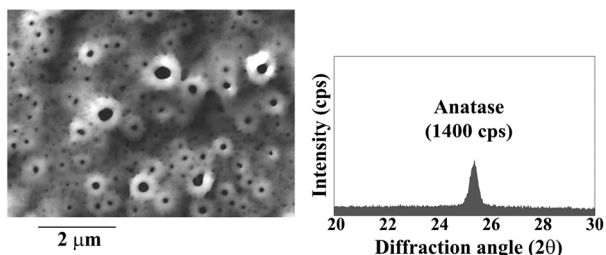


Figure 2: SEM and XRD analyses of sample SP-200V.

Finally, the fluoride containing electrolyte led to the formation of a TiO₂ layer with nanotubular morphology, which granted a particularly enhanced surface area: the nanotubes thickness varied from 1.5 μm to 2 μm by increasing treatment time from 3 h to 6 h. Specimens were then heated in air or nitrogen atmosphere: XRD spectra proved the formation of the anatase structure (Fig. 3).

GD-OES analyses were performed on a specimen anodized in the sulfuric acid and phosphoric acid mixture (100 V cell voltage) and annealed in nitrogen atmosphere for 4 hours, at 400°C. In fact, the elemental analysis provided by this technique was considered to be more reliable if collected on a compact oxide rather than on a nanotubular structure (Fig. 4). The effectiveness of the nitrogen doping treatment was proved by observing the actual detection of nitrogen in the annealed anodic oxide.

From XRD spectra it was possible to evaluate the average dimensions of anatase crystallites formed in the anodic oxides. Scherrer equation, which relates the crystallite diameter *L* to the main diffraction peak of the considered crystal phase, was applied [13]. It was noticed that, while ASD generated oxides have crystallite dimensions of about 25 nm, anatase crystals in nanotubes annealed for 2 h present a 15 nm average diameter: the crystal dimension increase during heating and overcomes 20 nm after 4 h thermal treatment.

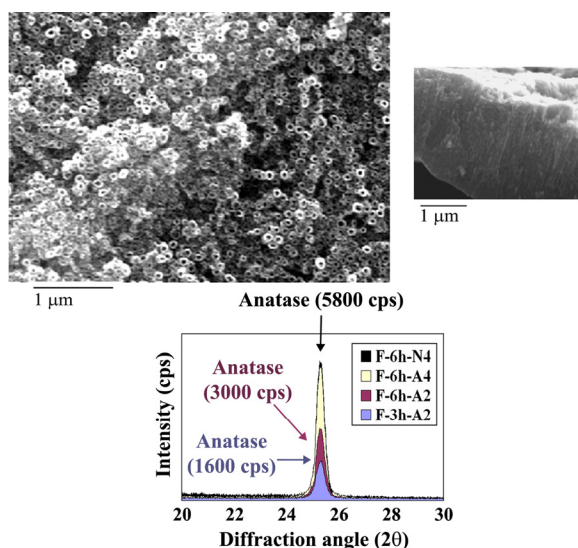


Figure 3: SEM analyses of specimen F-6h (top view, cross section) and XRD spectra of annealed TiO₂ nanotubes.

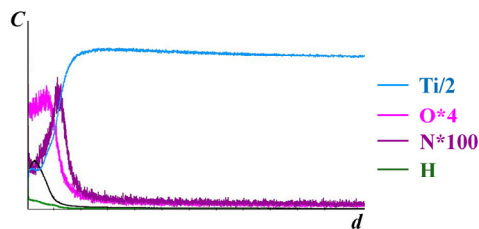


Figure 4: GD-OES analyses of specimen F-6h-N4.

3.2 Photocatalytic tests

To evaluate the reliability of the photocatalytic system, the concentration values of 6 reference beakers were measured after 6 h irradiation: a 0.2% maximum divergence was obtained, thus confirming the effectiveness of the measurements.

The photocatalytic decomposition of RB was found to depend on all considered parameters: light intensity, TiO₂ morphology and crystal structure. Fig. 5 reports the values of RB concentration during UV-VIS irradiation (4000 μW/cm² UV intensity) in the presence of different photocatalytic substrates.

By applying a 2500 μW/cm² UV intensity, a decrease of RB concentration of about 70% was obtained after 23 h irradiation; specimen F-3h-A2 was used as substrate. The increase of UV intensity to 4000 μW/cm² led to an increase of photocatalytic activity: the same photocatalytic substrate allowed the degradation of the 75% of the RB solution. Yet, this photoactivity variation was lower than that expected, considering that UV intensity was almost doubled.

If the crystal structure is considered, by using specimens coated by ASD good efficiencies were obtained, being 46% for specimen SP-200V and almost double, 83%, for specimen S-140V. Hence, the different quantity of anatase formed during anodizing proved to have an outstanding effect on slightly porous specimens. This effect was not evidenced in photocatalytic tests involving differently annealed nanotubular specimens, *i.e.*, F-6h-A2, F-6h-A4 and F-6h-N4: RB degradation was approximately 90% in all cases. The enhanced surface area conferred to TiO₂ by nanotubes formation was found to have a greater influence with respect to differences in anatase quantity.

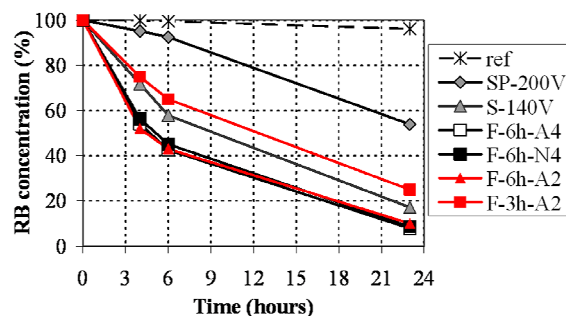


Figure 5: RB concentration as a function of time under UV-VIS irradiation in the presence of different specimens.

The strong influence of oxide morphology was further proved by comparing degradation results obtained by using specimens F-3h-A2 and F-6h-A2: as already mentioned the former, whose oxide thickness was approximately 1.5 μm , only led to the mineralization of 75% RB, while the latter (2.5 μm thick oxide) reached 92%. The variation is not proportional to thickness ratios: this is likely due to the formation of a salt deposit on nanotubes, arising from solution precipitates, which was found to be more consistent with an increase of anodizing time. 6 h anodizing processes caused a higher shielding of nanotubes than 3 h processes, thus limiting the positive effect of increase of nanotubes length on photocatalytic efficiency.

Finally, the RB degradation under visible light was investigated in presence of TiO_2 nanotubes and of specimen SP-200V, as comparison for non-doped TiO_2 . Results were compared with UV-VIS irradiation (Fig. 6).

It is immediately noticed that both nanotubular photocatalytic substrates caused similar RB degradation extent under the two irradiation systems. This was expected in the case of specimen treated in nitrogen atmosphere, whose photoactivity was shifted in the visible light range. Conversely, the high efficiency showed by specimen treated in air atmosphere was surprising, specially considering that non-doped specimen SP-200V didn't maintain its photoactivity under visible light irradiation. A slight difference was observed, *i.e.*, the N-doped specimen showed lower or higher efficiency, under UV-VIS or VIS light respectively, with respect to the non-doped one. This was ascribed either to a high content of oxide defects, or to a doping effect caused by F^- ions included in the oxide during anodizing, which has been demonstrated to slightly decrease the oxide band gap, and therefore to cause a red shift of light absorption [14].

Though, a remarkable difference in the reactions occurring in RB degradation was detected by analyzing the degraded solutions with mass spectrometry. In fact, while under UV-VIS light specimen F-6h-A4 led to a complex ensemble of oxidation reactions giving rise to a wide number of reaction intermediates, the corresponding N-doped specimen only allowed the molecule de-ethylation or the loss of H_2O or CO_2 molecules. Under visible light, reaction pathways further decreased, being RB de-ethylation the only reaction allowed.

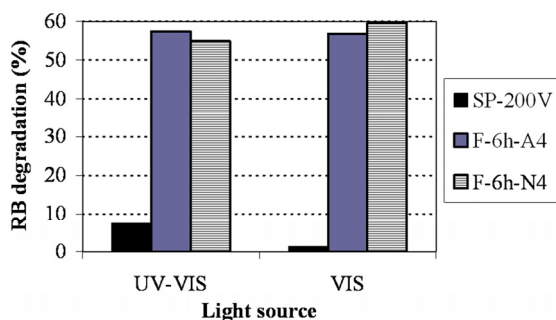


Figure 6: RB degradation under UV-VIS or VIS irradiation.

4 CONCLUSIONS

The presented work showed how to efficiently tune the photocatalytic activity of anodic oxides by choosing correct anodizing and annealing processes, depending on requirements, *e.g.*, a fast production of the photoactive substrate, or an enhanced photocatalytic oxidation, or the obtaining of photocatalytic activity under visible light irradiation.

Among the investigated anodizing techniques, a nanotubular morphology of the TiO_2 layer exhibited higher efficiency than substrates obtained by anodizing in H_2SO_4 or $\text{H}_2\text{SO}_4 + \text{H}_3\text{PO}_4$ mixtures, due to both an enhanced surface area and the emphasized formation of anatase during annealing. The main drawback consisted of a more complex and long lasting preparation, which is not necessary after anodizing in ASD conditions, being the anodic film already semicrystalline. Nitrogen doping gave rise to photoactive oxides, with high efficiency both in the UV and visible light spectrum. Though, some photocatalytic reactions achieved under UV irradiation were impeded by the exclusive use of visible light, since the energy levels of the doped semiconductor could not include the redox potential of some RB reaction products.

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