

Advanced oxidation processes for water purification: compact vs nanoporous anodic TiO₂

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ABSTRACT

The work herein presented is dedicated to a comparison of photodegradation properties of anodic TiO₂ films, involving the study of both oxides with nanotubular geometry and compact layers. The comparison has been performed both through characterization techniques (SEM, XRD) in order to analyze the influence of anodic oxidation parameters on the oxide structures, morphology and crystal structure, and by evaluating photocatalytic degradation of a dye used in textile industry, known as Acid Orange 7 (AO7).

Different electrolytes and process parameters were used for the fabrication of both compact oxides and nanotubular layers in order to point out the effect of specific anodic parameters on the photodegradation rate.

The characterization of these structures aims to a comparative analysis – between different structures and between similar structures with different features – of photoactivity and related phenomena, which are strongly dependent on the electrolyte used during anodizing, as it influences both morphological features and crystallinity degree.

Keywords: Anodizing, TiO₂, Nanotubes, Compact Layers, Characterization, Photodegradation

1 INTRODUCTION

In the last years, research on the engineering of titanium dioxide has been oriented to the obtaining of compact thin films as well as of more complex nanostructures and architectures, for applications ranging from corrosion resistance to bioengineering, from optical devices to bipolar resistive switching memories, from electrochromic devices to environmental and energetic applications, such as advanced oxidation processes for water purification and

dye-sensitized solar cells [1,2]. In this scenario, anodic oxidation can be a very effective technique in the controlled production of oxide films with high bond strength on the metal, tuning growth kinetics and oxide properties as a function of process parameters. In fact, it is possible to relate the controlling electrochemical parameters (cell voltage, chemical composition of the electrolytic solution, process time) to the thickness, morphology, chemical and structural composition of the growing oxide layer [1,3-5].

In all applications based on exploiting its photoactivated properties, two main features drive titanium dioxide photoefficiency: crystallinity and surface area. The former characteristic is generally achieved either by high voltage anodizing (anodic spark deposition, ASD) where TiO₂ nanocrystals with anatase structure are generated in an otherwise amorphous oxide on account of the onset of localized microplasma surface states; on the other hand, also completely amorphous oxides can be partially converted into crystalline ones by annealing. This is very important when considering the second feature, that is surface area: nanotubular oxides have enhanced surface area but amorphous structure, and annealing enables their successful use in photoactivity-related applications [1,6,7].

Still, few works address a direct comparison between compact oxides of nanoscale thickness, and nanotubular ones. Here we present a comparison among differently obtained anodic titanium oxides, showing either compact or nanoporous morphology, in order to define the most effective and robust treatments for the production of photoactive layers.

Photoactivity of the layers was investigated in terms of photodegradation of an organic dye, (AO7), an azo compound largely used in textile industry. Research in this field has increased in time in order to reduce the content of these compounds in wastewaters, which represent the main source of pollution in this industry. [8,9]. TiO₂ has been identified as an ideal photoactivated catalyst, due to its ability to decompose –N=N– bonds in azo compounds by

formation of OH[•] species or by direct transfer of holes to the adsorbed molecules [10]. Different strategies were developed to improve photocatalytic activity of anodic TiO₂ layers [11,12]; however, a comparison of different nanostructures can help detecting oxide features to be controlled in order to improve photocatalytic performances.

2 EXPERIMENTAL

Several TiO₂ samples were produced during this work in order to investigate the behavior under illumination of oxides with different features. Anodic compact oxides and nanotubular layers were grown on ADVENT Ti foil, (purity 99.6%, max. impurities content: O= 0.15%, N=0.012%, H=0.005%, Fe= 0.15%, C= 0.02%. Foil thickness = 0.1 mm). All the samples were cut in squares with 1.5x1.5 cm² lateral dimensions. After that, dust and surface contaminants were removed by two steps of ultrasonic action, respectively in acetone and in ethanol, rinsing with de-ionized water and then the metallic substrate was dried in N₂ stream. For the production of compact oxides, anodizing was carried out at different voltages in potentiodynamic mode with a sweeping rate of 100 mV/s up to the final voltage, which was maintained, potentiostatically, for 15 minutes. A potentiostat PGU 100V-2A, with an output voltage of 140V, was used. As final voltages 20 V, 50 V and 90 V were investigated. A platinum electrode was used as a cathode while the titanium substrate was anodically polarized by means of a Cu electrode connected to the positive plug of the potentiostat. The chosen electrolyte was 1 M H₂SO₄. After anodic process, samples were rinsed with water and dried in N₂ flow. For the production of nanotubular layers, anodic oxidation was carried out potentiostatically once again with a two-electrode setup where a Pt electrode acted as counter-electrode. The titanium foil was anodized in Ethylene Glycol (EG) +0.1 M NH₄F +1 M H₂O at 35 V for 120 minutes. Then the sample was treated with ultrasonic steps in pure H₂O in order to remove the formed nanotubular layer, followed by cleaning in acetone, ethanol. After being rinsed with water and dried in N₂ flow, the pretreated substrate was used to grow the final oxide layer. For the last step, several electrolytes were used, and depending on the electrolyte, the applied voltage and anodizing time was modified. In Tab.1, the samples investigated in this work are described.

As for morphological and microstructural characterization, a field emission scanning electron microscope (FE-SEM, Hitachi S4800) and a Philips X'Pert MPD PW3040 XRD instrument were used.

Table 1 List of investigated samples

Name	Electrolyte	Sweeping rate	Applied Voltage	Anodizing time
S1	1 M H ₂ SO ₄	100 mV/s	20 V	15 min.
S2			50 V	15 min.
S3			90 V	15 min.
EG-NH ₄ F	EG+0.1 M NH ₄ F+1 M H ₂ O	-	60 V	10 min.
EG-HF 8M	EG+0.2 M HF + 8 M H ₂ O	-	58 V	120 min.
EG-HF 12M	EG+0.2 M HF + 12 M H ₂ O	-	48 V	120 min.

Photodegradation tests were performed in a solution of 2.5×10^{-5} M of AO7 (C₁₆H₁₁N₂O₄SNa, Acros Organics, Belgium) with a measured pH of 5. Samples were immersed in 5 ml of the solution in a quartz cuvette and illuminated by 200 mW He-Cd LASER at 325 nm, Kimmon Electric IK3552R-G with a measured power of 60 mWcm⁻².and an expanded beam to 1 cm². The solution was stirred at 300 RPM during the test. Compact oxides were kept in the solution under illumination for 120 minutes, while the nanotubular layers for 160 minutes. In both cases, the concentration was measured every 20 minutes. The variation in concentration was performed by an UV/Vis machine Perkin Elmer Lambda XLS+ and evaluated by the variation of the orange peak at 485 nm in time. Kinetics of degradation was evaluated by plotting the results as ln(C/C₀) vs time.

3 RESULTS AND DISCUSSION

As shown in Fig.1, representing top morphology of compact oxides S1, S2 and S3 reported in Tab.1 and obtained by anodic oxidation at 20 V, 50 V and 90 V, respectively, SEM images of compact oxides showed occurrence of dielectric breakdown when oxides were produced in 1 M H₂SO₄ at 90 V. This breakdown onset can be observed in the formation of craters in the otherwise smooth oxide, due to sparking which is typically associated to breakdown. No relevant morphological features were noticed on the low voltage compact layers.

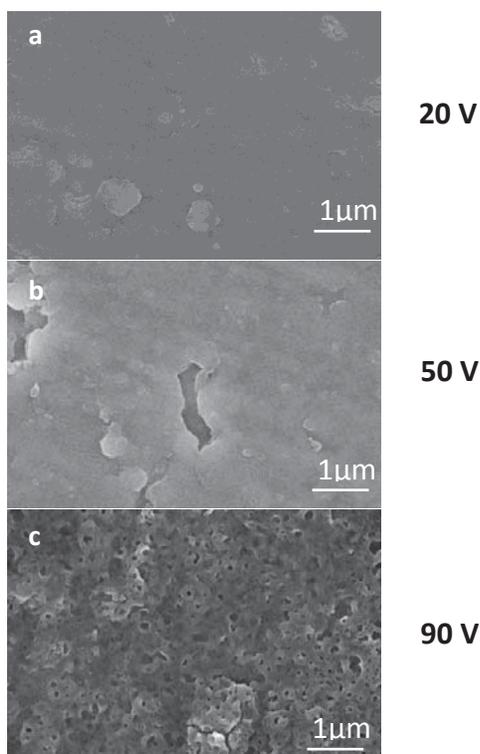


Figure 1: Top morphology of oxides grown in 1 M H₂SO₄. Final applied voltages are a) 20 V, b) 50 V, c) 90 V.

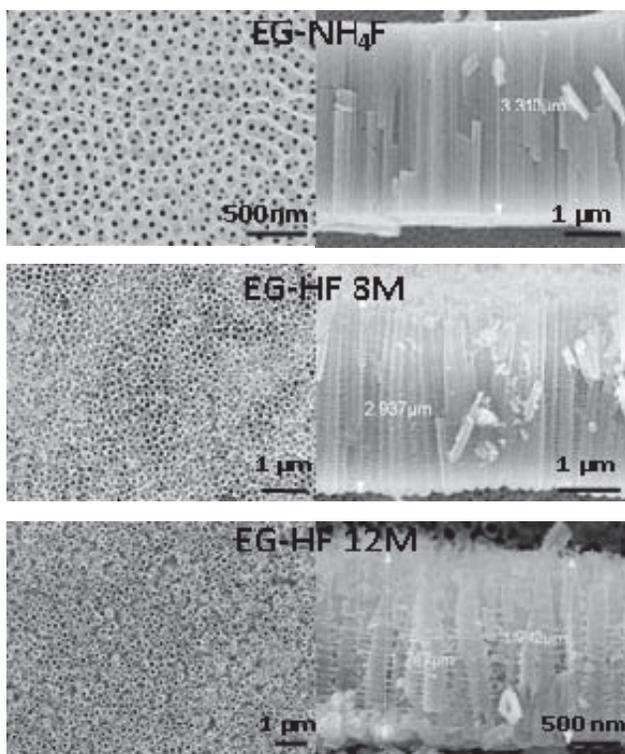


Figure 2: SEM images of nanotubular layers.

Nanotubular layers obtained in the described condition showed different morphologies, dependent on the imposed conditions. Nanotubes grown in NH₄F containing electrolyte are characterized by an initiation layer on top, conversely to oxides layers grown in HF containing electrolytes which show an open tube morphology. As it can be noticed in Fig. 2, the layer thickness ranges between 1.7 and 3.3 μm for the different nanotubular layers. All nanotubes have diameters of ≈95nm, however EG-NH₄F nanotubes are covered with an initiation layer that limits the openings at the top to ≈50nm.

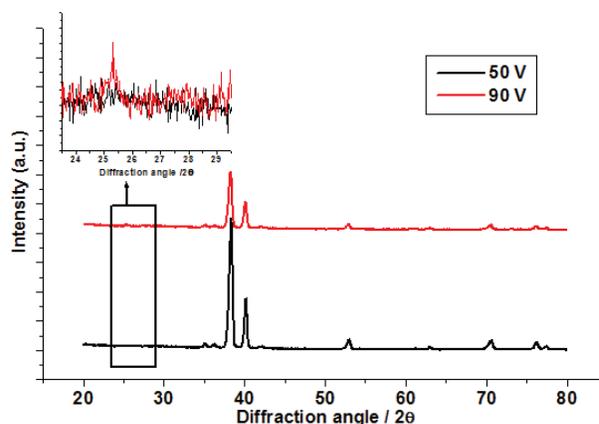


Figure 3: XRD spectra of compact oxides, with a magnification of the diffraction angle range between 23.5° and 29.5° in the inset.

While for nanotubular layers XRD measurements showed no crystalline peaks (amorphous), for compact oxides anatase peaks were recorded for the sample where breakdown occurs (90 V) (Fig 3, in the inset a magnification on the main anatase peak at 25.4°).

Fig. 4 reports the observed values of dye absorbance with irradiation time in the presence of different TiO₂ photocatalysts. In all cases, the dye concentration – which is related to its absorbance by Beer Lambert relationship – decreases under UV irradiation, to different extents depending on the oxide morphology and crystal structure.

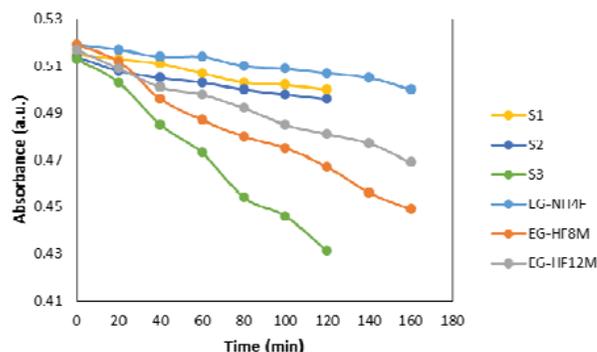


Figure 4: Absorbance of AO7 dye vs irradiation time in presence of different anodic oxides.

Furthermore, a comparison of the kinetics of degradation trends in the photodegradation tests gives interesting results. From Fig.5, in fact, it is possible to notice that concerning compact oxides, even the presence of small amounts of anatase crystals has a fundamental role in improving photocatalytic properties, enhancing photodegradation rate up to almost 10 times with respect to amorphous compact oxides.

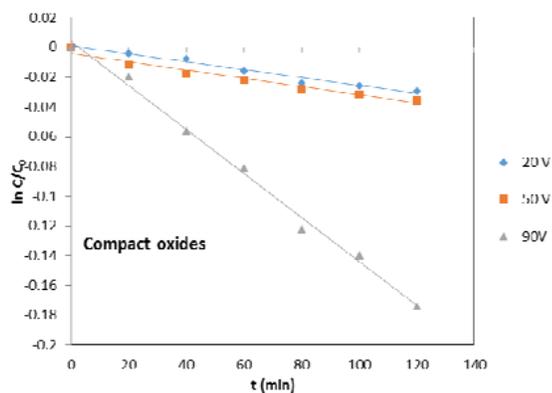


Figure 5: Photodegradation kinetics of AO7 observed in presence of compact titanium oxides.

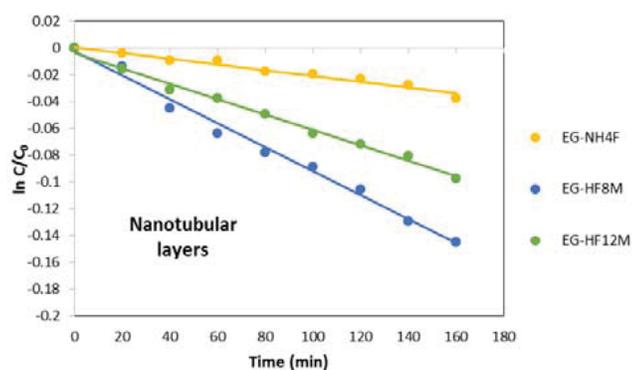


Figure 6: Photodegradation kinetics of AO7 observed in presence of TiO₂ nanotubular layers.

Dye decomposition tests on TiO₂ nanotubes showed that another fundamental factor to be optimized for enhancing photocatalytic activity is the high aspect ratio morphology. In fact, it is possible to notice that nanotubular layers characterized by the presence of an initiation layer present a lower photodegradation rate compared to structures with open tube top morphology, whose efficiency improves with nanotube length, and therefore with available surface area. From numerical evaluation of photodegradation rates, reported in Tab.2, it can be noticed that sample EG-NH₄F has an efficiency comparable to amorphous compact oxides, while longer nanotubes, even at an amorphous state, allow a faster disappearance of the dye, approaching the values presented by the partially crystalline compact oxide.

Table 2 Photodegradation rates.

Name	Photodegradation rate (K) [h ⁻¹]
S1	0.016
S2	0.017
S3	0.089
EG-NH ₄ F	0.013
EG-HF 8M	0.054
EG-HF 12M	0.035

4 CONCLUSIONS

Results presented here can be considered as a first step in the analysis of factors able to enhance TiO₂ photocatalytic activity. Data clearly show the positive effect of dielectric breakdown in improving performances of low aspect ratio structures, related to the presence of anatase crystals, which wasn't detected in any other oxide film. Moreover, nanotubular layers can present different photodegradation rates, not only depending on the layer thickness: more generally, performances are related to oxide morphology. It is clear that the presence of an initiation layer creates a physical barrier for solution intercalation, and thus photodegradation rate is very similar to that measured on amorphous compact oxides. On the other hand, if solutions can penetrate inside nanotubes, an increase in efficiency can be noticed dependent on the nanotubes length.

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