

Photocatalytic Activity of Nanotubular TiO₂ Films Obtained by Anodic Oxidation: A Comparison in Gas and Liquid Phase

B.E. Sanabria Arenas*, A. Strini***, L. Schiavi***, M.V. Diamanti**, and MP. Pedferri**

* Politecnico di Milano, Department of Chemistry, Materials and Chemical Engineering “G. Natta”
Via Mancinelli 7, Milan, Italy; beatrizeugenia.sanabria@polimi.it; mariavittoria.diamanti@polimi.it;
mariapia.pedferri@polimi.it

**INSTM - National Interuniversity Consortium of Materials Science and Technology
Via G. Giusti 9, Florence, Italy

*** ITC – CNR, Construction Technologies Institute
Viale Lombardia 49, San Giuliano Milanese, Milan, Italy; alberto.strini@itc.cnr.it; luca.schiavi@itc.cnr.it

ABSTRACT

The immobilization of nanostructured photocatalysts is of great importance in the purification of both polluted air and liquids (e.g. industrial wastewaters). Titanium dioxide films with nanotubular morphology and good photocatalytic efficiency in both environments can be produced by anodic oxidation, which avoids release of nanoscale materials in the environment.

Here we evaluate the effect of different anodizing process parameters as electrolyte and anodizing time, in order to identify the most efficient and robust technique for the production of TiO₂ layers with different morphologies with high photocatalytic activity in both gas and liquid phase. In particular, nanoporous layers were optimized to produce nanotubes made of titanium dioxide, whose specific surface area is much larger than that of a nanoporous oxide, therefore allowing more active sites for photocatalytic reactions. Toluene was used as model reactant for gas phase photocatalytic depuration, while an organic dye, rhodamine B, was chosen as model for wastewater purification. It was found that the role of the electrolyte in particular is crucial: nanoporous or nanotubular structures show remarkably different activities, especially in gas phase degradation reactions, and within nanotubular structures, those produced in non aqueous electrolytes display better photocatalytic activity in both phases of study.

Keywords: Photocatalysis; toluene; rhodamine B; titanium dioxide; nanotubes

1 INTRODUCTION

The use of titanium dioxide (TiO₂) for water remediation and air purification by photocatalysis has been subject of a large number of studies in the last decades, concerning the degradation of both inorganic and organic substances. One major issue concerns the use of nanoscale

materials (nanoparticles, nanorods) and their potential dispersion in the gas or liquid phase medium where they are used [1]. In fact, while nanostructured materials present the benefit of increasing process efficiency by increasing the surface area available for reactions, the hazard related to their dispersion in the environment is not negligible.

In this frame, the electrochemical method of anodic oxidation can be a powerful technique to generate photoactive oxides, strongly adherent to a metallic substrate – i.e., titanium, and to modify their chemical composition by inducing doping effects [2]. This process opens the way to the production of nanostructured TiO₂ films immobilized onto a metallic substrate, which is of great advantage to avoid environmental issues in the use and recycle of the photocatalyst [3]. The production of porous ceramic films can be achieved by highly energetic anodic spark deposition (ASD) [2], while the formation of nanotubes relies on a self-organizing process that generates in a fluoride-containing electrolyte, with growth of the oxide and formation of nanometric cavities which rearrange in the form of nanotubes once the oxide has reached a relevant thickness [4]. The shape and thickness of such oxide layers can be tuned as a function of anodic oxidation parameters – mostly based on the electrolyte and voltage applied – while the crystalline structure, if amorphous (as in the case of nanotubes), can be turned into anatase phase by annealing for a suitable time at temperatures from 350°C to 550°C.

Here we present a robust method to obtain immobilized TiO₂ nanostructures by anodic oxidation, in the form of either nanoporous ASD coatings or nanotubes with high aspect ratio and good spatial uniformity. The photocatalytic efficiency of such structures is tested in photocatalytic water remediation, taking as example the degradation of the dye rhodamine B (RhB). Moreover, a comparison is presented between the photocatalytic activity of such structures in liquid phase and in gas phase: VOC degradation, and in particular toluene, is chosen as test reaction.

2 EXPERIMENTAL

Experimental tests were performed on commercial purity titanium sheets, anodized in three different electrolytes: in H₂SO₄ at various voltages (100-150 V), total duration: 2'; in a fluoride containing aqueous electrolyte at 20 V maintained constant for 3, 4.5 or 6 h; in a fluoride containing organic solution at 45 V or 60 V maintained constant for 15, 30 or 45 min. The last two types of samples were then annealed at 400°C for 2 h to promote the crystallization of the amorphous nanotubular oxide to anatase phase TiO₂.

Scanning electron microscopy (SEM) was performed on a Carl Zeiss AG-EVO® Series 50. X-ray diffraction was performed on a Phillips PW 3710 using CuK_α radiation. All the samples were scanned in the 2θ range of 20-30°, where both anatase and rutile crystal structures of titanium dioxide show relevant diffraction peaks.

RhB degradation tests were performed as reported in a previous work, by immersing a 6 cm² sample in a beaker containing 25 ml of 10⁻⁵ M RhB [3] and irradiating samples for 6 h with a solar spectrum lamp (Osram Vitalux, UV-A intensity of 1000 μW/cm²). The photocatalytic efficiency was calculated as a function of the decrease in dye absorbance (*Abs*), measured by spectrophotometry, which is related to a decrease in its concentration, *C*, as described by Beer Lambert equation:

$$Abs = \epsilon l C$$

where ϵ and l are optical constants. Data were then processed to calculate the reaction constant k_{app} , considering a pseudo-first order kinetics:

$$\frac{\ln\left(\frac{C}{C_0}\right)}{A} = -k_{app}t$$

where C_0 is the initial dye concentration, A the surface area of the samples and t the reaction time.

The photocatalytic degradation of toluene (0.75 μmol/m³) in air (25 °C and 50% RH) was assessed in a continuous-flow stirred photoreactor operating at constant toluene concentration, under UV-A irradiation (600 μW/cm²) [5]. Degradation rate in this case (r_a) was calculated as a function of the decrease in toluene concentration, measured by a GC/PID analyzer:

$$r_a = \left(\frac{Q}{A}\right)(C_0 - C)$$

where Q is the volumetric flow rate (m³ s⁻¹); A is the sample area (m²); C_0 is the inlet concentration of toluene (mol m⁻³) and C its concentration in the reactor (mol m⁻³)

3 RESULTS

First, the oxide morphology and crystal structure were analyzed. Figure 1 shows the top view of the nanotubular oxides obtained in aqueous solution as compared to ASD oxides obtained in H₂SO₄.

In the former case a network of self-aligned, vertical nanotubes stem from the substrate; a portion of the tubes is

blocked by a deposit, which may be ascribed to fluoride salts (sodium, titanium) deposited from the electrolyte. In organic solution, the detachment of single nanotubes less pronounced, creating a sort of porous template rather than a nanotubular array, but thickness was higher (2.5 μm vs 1.2 μm). As expected, in both cases the crystal structure after annealing was that of anatase. Conversely, after ASD the oxide showed a glassy appearance and larger pores, typical of anodic spark deposition; the microstructure revealed the presence of both anatase (main phase) and rutile (secondary phase).

After this preliminary characterization, the oxides photocatalytic activity was evaluated.

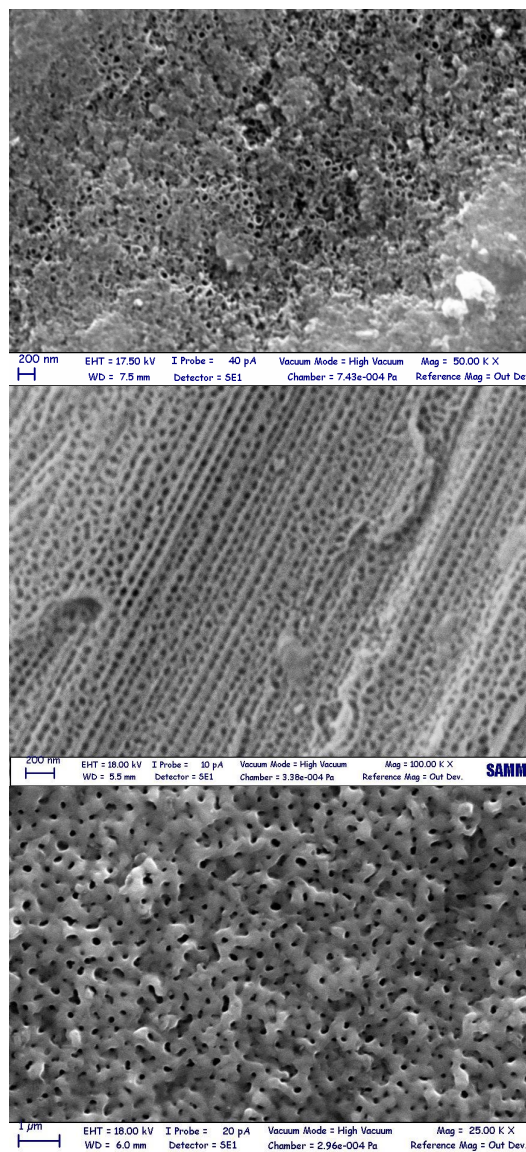


Figure 1: Nanotubes obtained in aqueous solution (top), in organic solution (middle) and morphology deriving from ASD (bottom).

Aqueous nanotubes (A-NT) were produced in a previous work [3] and showed good activity and reproducibility in RhB degradation; therefore, these nanostructures were first considered. Figure 2 reports the photocatalytic degradation rates of both RhB and toluene. Some influence of anodizing time was observed on nanotubes photoactivity, especially in gas phase, where higher time gives higher activity, as expected. Nonetheless, no big difference was observed for A-NT with higher anodizing time in liquid phase. In fact, it seems that photoactivity decreases with increasing anodizing time; this can be due to a partial occlusion of pores in longer anodizing owing to the precipitation of salt deposits, formation of nanograin layer from etching effects, or insignificant change in A-NT length with anodizing time. Yet, the obtained photoactivity in gas phase was low if compared with previous works on TiO₂ nanoparticles [6]; in fact, high irradiance conditions had to be employed in order to see a relevant toluene degradation. Therefore, different electrolytes were also taken into account, as detailed below, growing nanotubes in organic solution or producing ASD-type oxides.

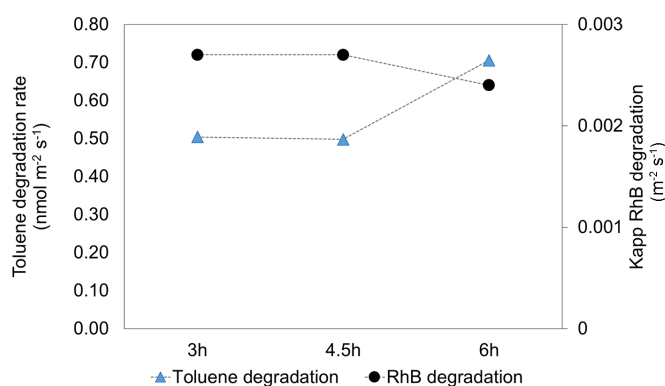


Figure 2: Photocatalytic activity in both liquid and gas phase of TiO₂ nanotubes produced in aqueous solution.

RhB degradation tests showed a relevant activity of all oxides tested, with some singularities (Figure 3). First of all, anodizing in H₂SO₄ produced an increase in crystallinity, and consequently on photoactivity, with increasing voltage up to 150 V; for higher voltages, too much rutile formation reduced the oxide photoactivity. When shifting to a nanotubular oxide, reactivity was increased with respect to the nanoporous structure, in spite of the salts deposit present on the samples surfaces. This was ascribed to the increased surface area available and to the optimal crystallinity achieved by annealing.

Yet, it is necessary to take into account the huge difference in anodizing times – 2' against 30' or even 6 h in the case of nanotubes obtained in aqueous solution which, as abovementioned, also need a post-treatment of annealing to achieve oxide crystallinity.

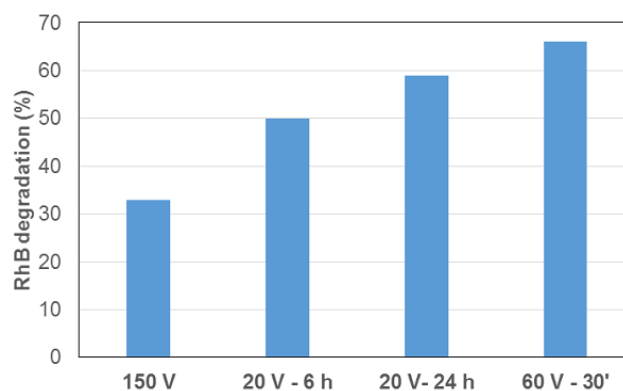


Figure 3: RhB degradation extent in 6 h irradiation with differently anodized samples

Concerning variations among different nanotubular oxides, results clearly indicated an improved reaction efficiency in presence of longer nanotubes with respect to the shorter ones produced in aqueous solution (Figure 4). This proves that actual nanotubes wall detachment is not a strict requirement to produce a large photocatalytic activity, while the oxide thickness impacts more on the efficiency observed.

Unfortunately, nanotubes produced in organic solution also showed a larger dispersion of results, indicating a less controlled process with drawbacks in terms of uniformity and repeatability of the treatment. This was noticed in particular in toluene degradation tests, where a large number of replicates was performed and a variation coefficient of approximately 0.29 was found. Conversely, nanotubes produced in aqueous solution exhibited excellent repeatability, as attested by more than 20 samples examined with less than 0.09 variation coefficient from one sample to another.

For this reason, tests were repeated on samples anodized at 45 V instead of 60 V in organic electrolyte. The decreased voltage allowed lower temperatures to be reached in the production phase, which in turn avoided samples and electrolyte overheating and therefore improve not only oxide quality, but most importantly the repeatability of the treatment. In fact, new tests performed in toluene degradation exhibited higher photocatalytic activity and negligible variability on results, within the error of the measurement method itself. These tests were only preliminary and further work is needed to present the full characterization of the newly produced oxides, which appear to be the most promising ones.

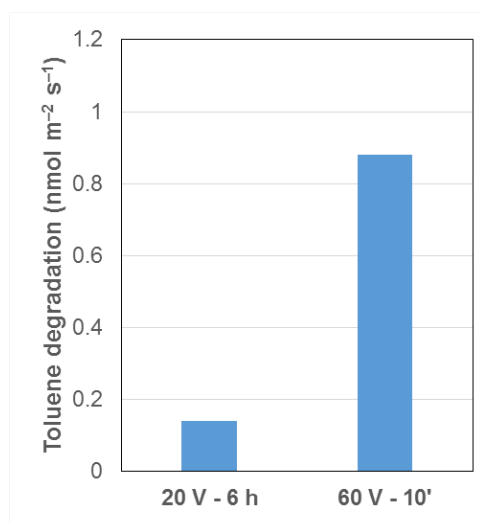


Figure 4: Photocatalytic degradation of toluene on TiO₂ nanotubes (ASD not shown – negligible activity)

The same information could not be derived on ASD oxides, due to the very low reactivity observed in gas phase. This is also interesting, as it points out the increased differentiation among the oxides photocatalytic activities in gas phase, in spite of the lower differences observed in liquid phase reactions. We could therefore identify the ASD treatment as a viable method for fast and reliable production of oxides with moderate photoactivity, which could find applications in water purification, as compared with nanotubular layers, which can be employed both in liquid phase and in gas phase reaction environments with higher yield.

4 CONCLUSIONS

We presented the production and characterization of immobilized, nanostructured titanium dioxide photocatalyst that could be exploited both in gas and liquid phase pollutants removal. The analysis here reported demonstrates how critical is the production stage in terms of choice of electrolyte. While ASD treatments in H₂SO₄ can produce in only 2 minutes very robust and regular oxides, to grow nanotubes with higher photoactivity at least 30' of anodizing are required plus 2 h of annealing.

Finally, it is important to consider that not only high photoactivity is required, but also good reproducibility in order to make the process robust and applicable on a larger scale. For this reason, the identification of other treatments is still ongoing, to improve the overall efficiency together with process reliability.

REFERENCES

- [1] A.O. Ibadon, P. Fitzpatrick, *Catalysts* 3 (2013) 189.
- [2] M.V. Diamanti, M. Ormellese, MP. Pedferri, *J. Exp. Nanosci.* 10 (2015) 1285.
- [3] M.V. Diamanti, M. Ormellese, E. Lanzutti, A. Mele, MP. Pedferri, *J. Haz. Mater.* 186 (2011) 2103.
- [4] X. Zhou, N.T. Nguyen, S. Özkan, P. Schmuki, *Electrochem. Commun.* 46 (2014) 157.
- [5] A. Strini, L. Schiavi, *Appl. Catal. B* 103 (2011) 226.
- [6] A. Strini, A. Sanson, E. Mercadelli, A. Sangiorgi, L. Schiavi, *Thin Solid Films* 545 (2013) 537.