

A comparative study over the photocatalytic activity of nanostructured TiO₂ layers for air purifiers

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ABSTRACT

The research here described presents an investigation over the efficiency of nanostructured TiO₂ films as photocatalysts either in air purification systems or to be integrated in light devices, based on the exploitation of UV or Vis irradiation to induce the degradation of hazardous chemical compounds. Gas pollutants (NO) and dyes (rhodamine B) will be considered as model reactants.

Several oxides were tested as photocatalytic substrates: nanostructured TiO₂ films on metallic titanium were produced by different anodizing processes (crystalline oxides obtained by Anodic Spark Deposition, TiO₂ nanotubes). The oxides activity was compared with that of different substrates (polymers, glasses) functionalized by depositing nanostructured TiO₂ layers via sol-gel: commercial sol-gel solutions were used, provided by an industrial partner.

Keywords: anodizing, NO_x, photocatalysis, sol-gel, titanium dioxide

1 INTRODUCTION

Surface modifications induced on titanium by means of anodizing processes deserve great attention, because of the properties these treatments can confer to titanium: from photocatalytic and self-cleaning behavior, to a strong biocompatibility, to the increase of corrosion resistance and the generation of interference colors at the metal surface, which are exploited in architectural and design applications. In particular, the most renowned among the engineered properties of TiO₂ is by far its photocatalytic activity, which allows the decomposition of organic compounds and removal of harmful gases: in fact, in the last decades Advanced Oxidation Processes (AOPs) have been thoroughly investigated as methods to solve the major problems of air and water pollution [1-3].

More in detail, AOPs exploit the synergetic use of UV irradiation and oxidizing compounds to increase the degradation efficiency of hazardous chemical compounds in wastewaters or in air. Its main uses range from the mineralization of organic substances in air and in wastewaters, for environmental clean-up and deodorizing, to the removal of metal ions from wastewaters, from

photovoltaic cells to the creation of antifouling, antibacterial, self-cleaning and antifogging surfaces [1-8].

The mechanism of photocatalytic reactions involves the absorption of light by a semiconductor (in our case, TiO₂): the absorbed energy generates a highly reactive electron/hole couple across the TiO₂ band gap, by moving an electron from the valence band to the conduction band. These species react with surrounding water and oxygen molecules to form hydroxyl and superoxide radicals, which in turn cause the decomposition of harmful organic and inorganic substances adsorbed on the semiconductor surface to water, CO₂ and harmless mineral acids through a chain mechanism [1, 2].

Attention has been paid by researchers on the potential of TiO₂ structures both in the cleansing of wastewaters, focusing on the degradation of organic dyes [5, 6], and in the purification of air from harmful NO_x gases, which can be emitted either from natural sources (biological degradation in soil, lightning thunder), artificial ones (traffic, coal burning boilers, thermal power plants, and from industrial/chemical processes [7, 8].

Due to the wide range of working conditions that could be applied in TiO₂-assisted photocatalysis, different substrates were adopted. TiO₂ films were obtained on titanium by means of anodic oxidation, performed either in diluted H₂SO₄ solutions, to produce partially crystalline oxides (Anodic Spark Deposition process), or in NaF/Na₂SO₄ mixture, to produce nanotubular oxides [9, 10]. Results obtained on anodic titanium dioxide were compared to the degradation efficiencies produced by TiO₂ layers deposited on glass or polymer substrates *via* sol-gel: three sols were tested, provided by an industrial partner.

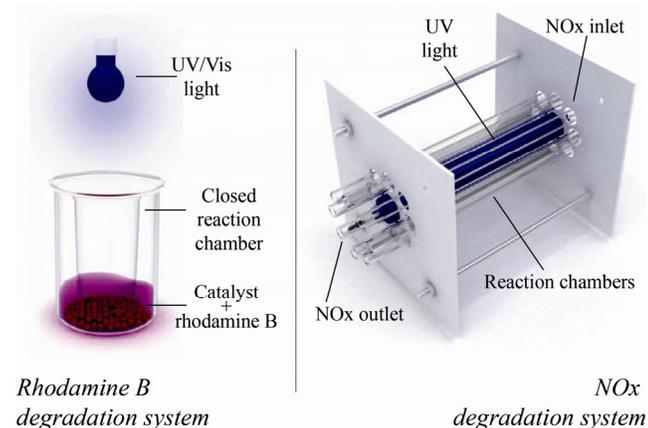
2 EXPERIMENTAL

In the presented experimental work, the degradation efficiency of differently obtained photocatalytic surfaces is explored in liquid and gas phase reactions. In the former case, a flat batch reactor is used to investigate the degradation rate of an organic dye, rhodamine B, 10⁻⁵ M concentration; the reactor was equipped with a UV-Vis light source of 3.6 mW/cm² intensity in the UVA range (fig. 1a). In the latter, an annular flow reactor is used to understand the reaction kinetics of a 45 ppm NO and 5 ppm O₂ gas flow with 100 cc/min flow rate. A 8 W Wood lamp

was used to activate the photocatalyst (fig. 1b). Dye degradation was monitored with spectrophotometric measurements of the solution absorbance, which is linearly correlated to its concentration as given by Beer Lambert equation:

$$Abs = \epsilon l C \quad (1)$$

where ϵ is the molar absorption coefficient of the solution and l the optic path, in both cases assumed to be constant values in the operating conditions. NO_x degradation was observed by measuring the variations in NO and NO_2 concentration by chemiluminescence.



Rhodamine B degradation system

NO_x degradation system

Figure 1: Reaction setups for rhodamine B and NO_x .

As anticipated, titanium specimens were anodized in two conditions: in a 0.5 M H_2SO_4 solution, by imposing a current density of 80 mA/cm^2 and a cell voltage of 140 V, and in a $\text{NaF}/\text{Na}_2\text{SO}_4$ electrolyte, by imposing an oxidation rate of 1 V/min up to a final cell voltage equal to 20 which was maintained constant for 4 h 30. The oxides morphology, obtained by SEM analyses, is shown in fig. 2. In the first anodizing treatment the anodic oxide resulted to be partially crystalline, with the presence of both anatase and rutile TiO_2 allotropic forms. Conversely, titanium dioxide nanotubes produced in fluoride-containing electrolyte were amorphous and required an annealing treatment (2 h, 400°C) to induce the formation of anatase.

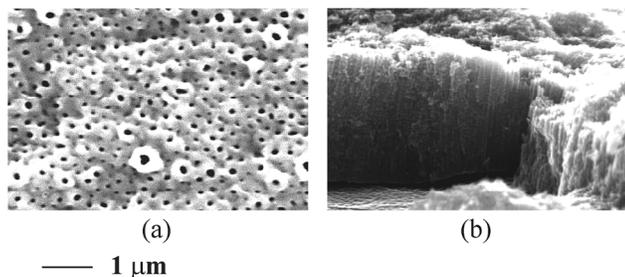


Figure 2: SEM micrographs of titanium anodized in H_2SO_4 (left) and $\text{NaF}/\text{Na}_2\text{SO}_4$ (right).

Sol-gel coated glass (Pyrex) and polymeric (PMMA) substrates were obtained by applying three sol compositions: A1 (acetic acid-based acidic sol), A2 (acetic and nitric acid-based acidic sol) and B1 (amine-based alkaline sol).

In the two reactor setups different photocatalyst shapes were required. In the flat reactor, 2 cm x 3 cm sheets were used (thickness 0.5 to 1 mm), while in the annular one the reaction chamber dimensions (a tube of 8 mm diameter and 5 cm length) required the use of glass/PMMA pellets and titanium wire, which was cut into pieces and bent to increase the chamber filling (fig. 3). Anodizing procedures were identical for titanium sheet and wire; conversely, sol-gel was applied by dip-coating on sheets and by rotary evaporation on pellets. To compare the two deposition processes, both sheets and pellets were tested in rhodamine B degradation for glass coated by sol A1.

All specimens used in the presented experimental work are listed in table 1.



Figure 3: From left to right: Pyrex pellets, PMMA pellets, cut titanium wire.

Sample	Substrate	Coating
T-140	Titanium	Anodizing: 140 V in H_2SO_4
T-N	Titanium	Anodizing: 20 V in $\text{NaF}/\text{Na}_2\text{SO}_4$
G-A1	Pyrex	Sol-gel: A1
G-A2	Pyrex	Sol-gel: A2
G-B1	Pyrex	Sol-gel: B1
P-A1	PMMA	Sol-gel: A1
P-A2	PMMA	Sol-gel: A2
P-B1	PMMA	Sol-gel: B1

Table 1: Coating conditions of the titanium, Pyrex and PMMA substrates.

3 RESULTS AND DISCUSSION

3.1 Dye degradation

All results of rhodamine B degradation tests are provided in fig. 5 in the form of degradation percentage, which was calculated as proportional to the percent decrease of the dye absorbance.

The degradation extent of rhodamine B induced by 30 min exposure of the solution to UV-Vis light was first tested in the presence of anodized titanium. It is clear that

both oxides exhibit a good photoactivity, since the dye concentration was strongly reduced. Nevertheless, a deeper investigation proved that specimen T-140 activity was slightly lower, since the color loss was only partially due to a complete mineralization of the dye, while the remaining part only underwent a deethylation process. On the contrary, sample T-N caused the total decomposition of the rhodamine B molecule.

As for tests performed on sol-gel coated glass and polymer, two situations were observed. PMMA pellets coated by rotary evaporator induced a fast decrease of the dye concentration, owing to the higher surface area involved in the reaction compared to the same weight in the form of sheet (*i.e.*, the fracture surfaces, covered by sol-gel as well). The sol-gel coated sheets also caused rhodamine B degradation, but to a lower extent (60 % final degradation after 23 h) No dramatic difference was noticed between Pyrex and PMMA substrates. A higher photocatalytic activity was exhibited by sol A1 compared with A2.

Unfortunately, the characterization of the three sols could not be completed since the alkaline sol, B1, proved to be incompatible with the organic dye, which caused its detachment from the substrate.

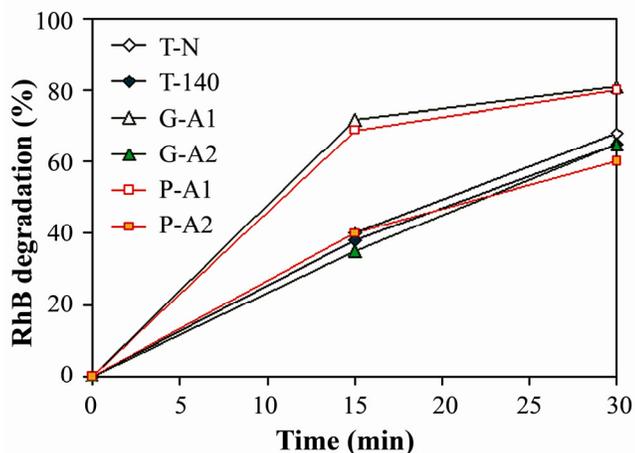


Figure 4: Photocatalytic degradation of rhodamine B induced by anodized titanium and by sol-gel coated Pyrex and PMMA (labels as in table 1).

3.2 NO_x removal

Fig. 5 contains the NO removal extent obtained by flowing a mixture of NO and oxygen in reaction chambers containing either non-treated PMMA or sol-gel coated PMMA. Among the sol formulations tested, once again the alkaline sol didn't produce appreciable degradation of NO, and was therefore discarded owing to its insufficient photoactivity.

Surprisingly, the acetic and nitric acid sol exhibited a much lower degradation efficiency compared to the sole acetic acid sol, while in rhodamine B degradation the difference was not so marked. This effect was therefore imputed to the presence of residual nitric acid in the coating

after drying which would interfere with the photocatalytic reaction over NO, being the reaction product nitric acid as well.

Tests performed on glass substrate led to identical behaviors of the different sol-gel coatings.

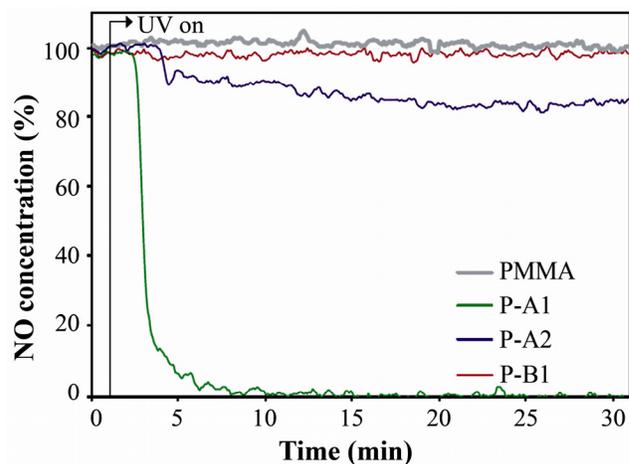


Figure 5: NO concentration observed after flowing the gas mixture in reactor chambers containing PMMA either non treated or coated by sol-gel (labels as in table 1).

Finally, tests performed on anodized titanium didn't lead to the high photocatalytic efficiencies observed in the dye mineralization, as reported in the NO tests summary (fig. 6). This was ascribed to the poor filling of the reaction chamber obtained with cut wires, which caused a strong reduction in contact time between the gas flow and the photocatalytic surface. Moreover, while PMMA and Pyrex substrates allowed the transmission of light from the inner surface of the cylindrical chamber to the back, promoting the surface activation of all pellets inserted into the reaction chamber, titanium is opaque and only the surfaces of wires exposed towards the inside of the reactor could be activated, thus losing a considerable quantity of photoactive surface (fig. 7).

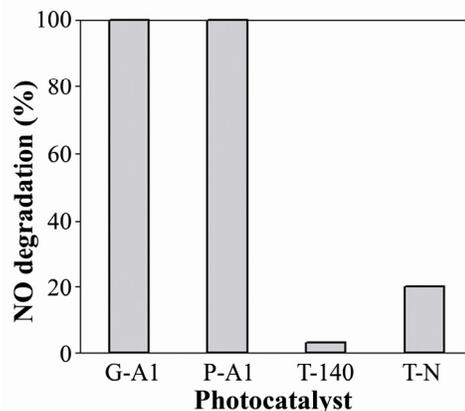


Figure 6: Degradation of NO promoted by the different substrates tested after 30 min test.

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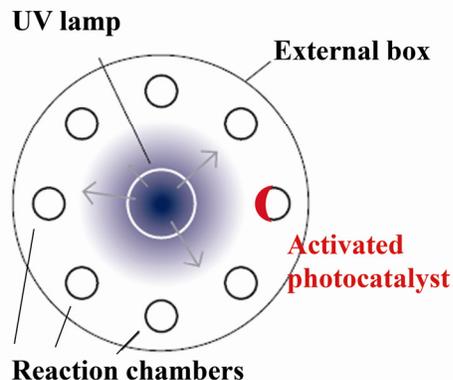


Figure 7: Cross-section of the reactor showing the possible irradiation extent of opaque substrates.

4 CONCLUSIONS

The presented work was aimed at considering different photoactive substrates for liquid and gas phase AOP, and exploring their photocatalytic efficiency in organic dyes mineralization and in NO removal. To meet this aim, two experimental setups were prepared, in order to address the possible working conditions of the photocatalysts in wastewaters and air decontamination, respectively.

From the experimental results obtained it is possible to assume that anodized titanium can be efficiently integrated into AOP flat bed purifiers, in which radiation is provided directly to the whole catalytic surface. On the contrary, it would yield a negligible photocatalytic effect in annular reactors in spite of its excellent performances in the first reactor type. Opposite considerations can be drawn concerning the TiO₂ films deposited by sol-gel on transparent substrates, since the overlapping of multiple pellets layers would not hinder the lower layers activation, while increasing the exposed surface area. Among transparent substrates, PMMA and Pyrex exhibited similar photocatalytic efficiency: the choice would therefore fall on the lighter and cheaper polymeric substrate.

Therefore, to summarize the obtained results in possible devices to be implemented, a configuration considering polymeric pellets coated with TiO₂ by sol-gel route results to be particularly suitable for air purifiers preset to shield the UV radiation. Conversely, light devices including anodized titanium can be studied, which would assure an improved degradation of liquid pollutants in flat-type reactors exposed to artificial UV light (where a shielding would be needed, to prevent the diffusion of the UV component in the environment) or to less harmful lamps simulating solar light.

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