TiO₂-based photocatalytic and antimicrobial coatings: comparison between sol-gel and electrodeposited silver/TiO₂ nano-composites

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ABSTRACT

The work here presented proposes a comparison between two different immobilization systems: the deposition of nanostructured TiO_2 coatings on glass and polymeric substrates via acid sol-gel, alkaline sol-gel and silver doped acid sol-gel, and the electrodeposition of Ag/TiO_2 nanocomposites on metallic substrates. The presence of silver is beneficial to increase the bioactivity of the film in disinfection processes, but it is important to verify that its presence shows beneficial, or in the worst case nil, effects on photocatalytic decomposition of non-biological contaminants. An organic dye (rhodamine B) was first considered as model reactant; the antibacterial effect was also studied on the most promising films, through the evaluation of total bacterial counts in the presence of TiO_2 on PMMA pellets and Ag-doped TiO_2 films on glass. The doped films demonstrated to produce an improved abatement of bacteria, but improvements are still needed to improve the effectiveness of these systems.

Keywords: titanium dioxide, photocatalysis, antimicrobial, silver

1   INTRODUCTION

The issues arising from low air quality in urban atmospheres, as well as indoor, is more and more stringent and many attempts are made to reduce pollution levels. Among the possible remedies, the use of nanostructured TiO_2 films as photocatalysts has been studied in depth, as it is still an excellent way to mitigate the problem, although it cannot offer a complete solution. Besides this field of application, TiO_2 also induces significant photocatalytic degradation of liquid phase contaminants and for disinfection, which also offers interesting scenarios for its application in the treatment of wastewaters. Yet, it is important to find a suitable immobilization technique for TiO_2 on different substrates, in order to exploit its potential in the cited areas [1,2].

Several studies also investigate the efficiency of silver-modified TiO_2, taking into account the deposition of the metal on the catalyst surface or the production of Ag/TiO_2 composites. Silver itself has a broad-spectrum bactericidal activity: its efficiency is due to the leaching of Ag^+ ions into bacteria cells, which minimizes the risks of microbial contamination of treated surfaces [3,4]. Silver can be immobilized on different substrates, such as porous carbon materials (mesoporous activated carbon fibres, activated carbon aerogels) or bioactive glasses; a few works have been published on the production of mixed Ag/TiO_2 systems.

Metal deposition on the surface of titanium dioxide can enhance photocatalytic reactions by accelerating the transfer of electrons to the surrounding reactive species (*i.e.*, water and oxygen molecules adsorbed on the surface), improving electron-hole separation. An optimum loading value must be respected, above which a detrimental effect on charge separation arises due to electron attraction by metal particles and scarce availability of active sites for the photoreaction [5]. As for silver, in some cases its presence was observed to decrease the TiO_2 photocatalytic activity in aqueous solution towards a certain number of reactions [6], but in most cases the doped system exhibits an enhanced photoactivity, both towards the degradation of organic compounds and in the form of an improved antimicrobial activity [2,7]. The physical form of both the sole catalyst and of the Ag/TiO_2 composite retains a great importance, since any dispersed system (powders, nanoparticles, fibres…) has the drawback of post-separation from the reaction slurry [8]. Hence, novel methods must be optimized in order to achieve a highly active photocatalyst and bactericide, possibly immobilized on a proper support.

In this attempt, a previous work was presented on the immobilization of TiO_2 films on different substrates, considering several types of glass and polymers and chosing Pyrex and PMMA as best candidates of the two classes [9]. Different TiO_2 sol formulations were tested to understand their adhesion to the substrate and the possible photocatalytic efficiency that the oxide layer would exhibit. In this study, this experimental work was further extended, considering the addition of silver to previous sol-gel films or co-depositing silver and TiO_2 by electrodeposition.

2   EXPERIMENTAL

2.1   Production of coatings

Sol-gel. Sol-gel coated glass (Pyrex) and polymeric (PMMA) substrates were obtained by applying two sol compositions: the A1 (acetic acid-based acidic sol) optimized in previous work [9] and Ag (A1 sol modified with the addition of silver). The films were produced by dip-coating, with a dipping rate of 200 mm/min, and consolidated at different temperatures: 60°C or 200°C for glass substrates and 60°C for PMMA substrates.

Electrodeposition. Silver nanoparticles were deposited on brass substrates by electrodeposition (Ag ED); the same technique was also used to obtain the co-deposition of Ag and TiO_2 nanoparticles (Ag/TiO_2 ED).

Before film deposition, brass substrates were ultrasonically cleaned sequentially in acetone and doubly distilled water. A two-electrode system was prepared in an electrochemical cell volume of 300 mL, using the brass plate as working electrode for deposition and a platinum mesh as anode. Electrodeposition was carried out galvanostatically with a potentiogalvanostat (AMEL 549 model). Coatings consisted of sole silver nanoparticles or codeposition of TiO_2 and Ag. Degussa P25 TiO_2 particles (anatase and rutile phases in a ratio of about 3:1, average particle sizes of 85 and 25 nm respectively) and Ag metallic precursors were cathodically electrocodeposited onto the brass substrates from an alkaline bath, with procedure described elsewhere [10]. Electrodeposition was performed with constant current density at 10 mA/cm^2 and deposition time of 3 h at room temperature. TiO_2 nanoparticles were estimated to occupy approximately 5% of the coating volume.

2.2   Characterization

Rhodamine B (RhB) was first considered as model reactant, as presented previously and further extended in the present work [9]. The antibacterial effect of TiO_2 was studied on the most promising films, through the evaluation of total bacterial counts in the presence of the different samples.

Rhodamine B. A flat batch reactor is used to investigate the degradation rate the organic dye rhodamine B, 10^{-5} M concentration; the reactor was equipped with a UV-Vis light source of 3.6 mW/cm^2 intensity in the UVA range (fig. 1). Dye degradation was monitored with spectrophotometric measurements of the solution absorbance *Abs*, which is linearly correlated to its concentration *C* as given by Beer Lambert equation:

$$Abs = \varepsilon \, l \, C \tag{1}$$

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. 2 cm x 3 cm sheets were used (thickness 1 mm). The percent degradation was then calculated as the percent decrease of absorption at the peak wavelength of RhB, that is, 550 nm.
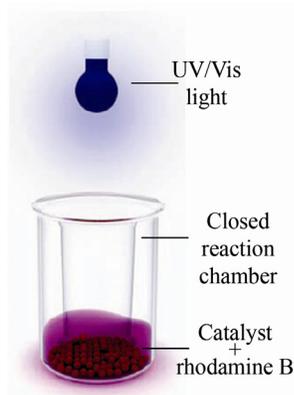

Figure 1: Rhodamine B degradation setup.

Antibacterial effect. The setup consisted of two filtering channels filled with PMMA pellets, followed by a sampling system (Petri dish), as shown in Figure 2. The Petri dish was provided with a suitable culture medium. A UV lamp was mounted inside each filtering channel. This experimental setup allowed a direct analysis of bacteria commonly present in indoor air, and of their possible inactivation through a photocatalytic and antibacterial filter.

External air passed through the PMMA pellets covered with photocatalytic TiO_2 nanofilms and reached the Petri dish, where the bacterial load contained in the environmental air was collected.

Figure 2: Antibacterial activity setup.

3 RESULTS AND DISCUSSION

Figures 3 and 4 report the degradation percentage of RhB in the presence of the tested substrates and the absorbance spectra of degraded solutions in the visible light range provided by the UV-Vis spectrophotometer. From these graphs it is possible to observe a higher photocatalytic efficiency for films produced at lower consolidation temperatures. This effect was ascribed to possible damaging of the TiO_2 nanostructured film at high temperature due to a too fast evaporation of the sol-gel solvent.
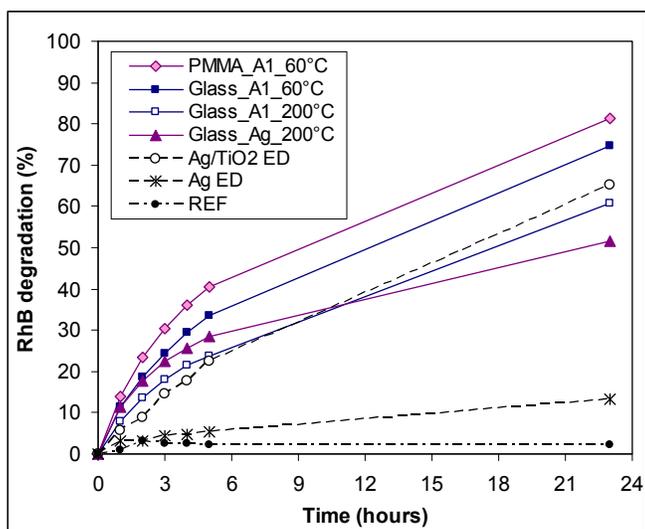

Figure 3: RhB degradation extent.

The type of substrate has a slight influence on photoactivity, being films produced on PMMA more efficient than those produced on glass. Still, the effect is almost negligible. Same considerations arise from the addition of silver to the sol composition: almost no effect was noticed, neither positive nor negative. This was expected and wished because, as stated in the introductory section, the presence of metal nanoparticles in the oxide film can induce the recombination of photoactivated holes and electrons, thus reducing the photoefficiency.

Electrodeposition of sole silver nanoparticles didn't lead to significant onset of photocatalytic reactions, since the curve describing RhB degradation in the presence of electrodeposited silver is very close to the degradation of a reference solution, that is, RhB exposed to UV without any catalyst. This proves the absence of any photocatalytic effect by sole silver. On the contrary, the co-electrochemical deposition of Ag/TiO_2 nanoparticles produced a photocatalytic effect similar to that obtained with sol-gel TiO_2 films.

Color loss may be due not only to the actual degradation of RhB molecules, but also to the simple alteration of the molecular structure: in the case of RhB, deethylation (i.e., the loss of ethyl side groups from the molecule) produces changes of color from magenta to yellow, while leaving the conjugated structure of the organic molecule untouched. Therefore, the full spectrum of the molecule in the visible range was recorded. In Figure 4 some of the spectra of degraded solutions are reported, together with a reference solution (spectrum before photocatalysis tests): in all cases, the spectrum was not shifted to shorter wavelengths (deethylation) and a decrease of intensity was observed at all wavelengths, thus confinrming the actual degradation of the molecule.
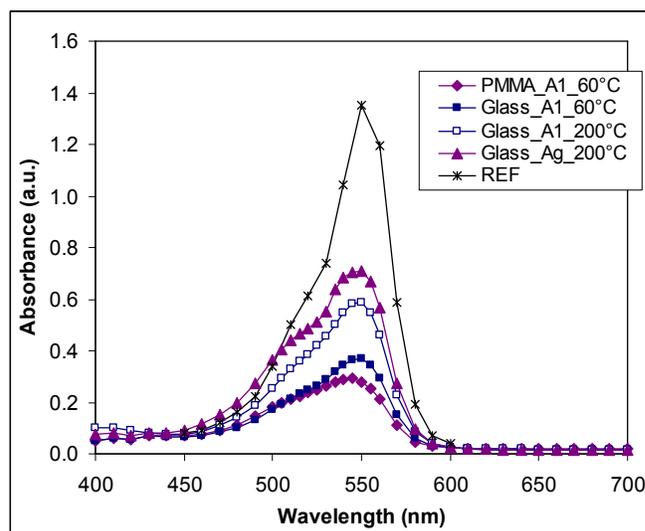

Figure 4: RhB absorbance spectra.

Antibacterial activity was evaluated by performing six tests for each material and by considering the following conditions: PMMA pellets coated with A1 sol or with Ag sol, with or without UV irradiation. Results are presented in figure 5. Error bars are presented together with the mean values of the six tests.

An actual decrease of cell counts can be observed in Ag-containing sol formulations, and specially under UV irradiation. This implies both a biocidal effect induced by sole Ag, and a photokilling effect developed by irradiated TiO_2. Still, the antibacterial activity obtained is far from being optimized.

Electrodeposited films were not subjected to antibacterial activity tests. In fact, electrodeposition requires the use of a conducting substrate, which in this case was brass. While in photocatalysis tests the presence of a metallic substrate had no effect on the progress of degradation reactions, an influence can be exerted by the presence of metals on bacteria, and generally speaking on

living organisms, due to possible ionic release. Moreover, the setup defined for antibacterial tests involved the use of trasparent substrates as key requirement for a full irradiation of the filter volume. Therefore, a different antibacterial test setup should be designed to evaluate electrodeposited coatings: this will be subject of future studies.
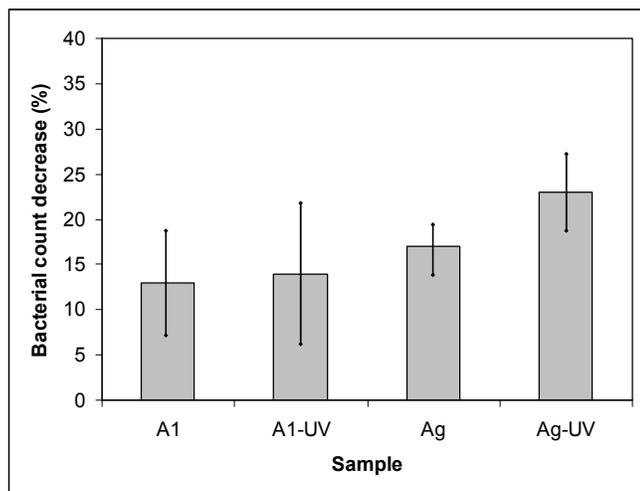

Figure 5: Antibacterial activity of selected coatings.

4   CONCLUSIONS

This work presented a comparative analysis of the photoactivated properties of TiO_2-containing coatings on different substrates. Attention was paid to the photocatalytic degradation of organic contaminants and to antibacterial activity, both induced by UV irradiation. The performances of sol-gel deposited films of TiO_2 and Ag-doped TiO_2, with different deposition parameters, as well as of Ag or Ag-TiO_2 coelectrodeposited films, were compared. Sol-gel and electrodeposition formulations were optimized previously.

The highest photocatalytic activity was observed for sol-gel films deposited on PMMA, which was chosen as test material for antibacterial activity evaluations; the presence of silver in the coating was not observed to produce a reduction of photoactivity, which is important to assure an optimal combination of photocatalytic and antibacterial properties. Finally, a decrease in cell counts, indicating a biocidal activity, was actually observed, but the effect still needs to be optimized.

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