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Photocatalytic and antibacterial properties of titanium dioxide flat film

V. Scuderi [a], M.A. Buccheri [a,*], G. Impellizzeri [a], A. Di Mauro [a], G. Rappazzo [b], Kristin Bergum [c], Bengt G. Svensson [c], V. Privitera [a]

[a] CNR-IMM, Via S. Sofia 64, I-95123 Catania, Italy
[b] Università degli Studi di Catania, Dip. Di Scienze Biologiche Geologiche e Ambientali, Via Androne 81, I-95124 Catania, Italy
[c] Oslo University, Department of Physics/Centre for Materials Science and Nanotechnology, N-0318 Oslo, Norway

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ABSTRACT

Today, one of the biggest problems of humanity is the inadequate access to clean water. For this reason, much effort is devoted to study new effective methods of purifying water, efficiently, at low cost and with less energy. Titanium dioxide (TiO_2) plays a central role in energy and environmental research. Several methods have been developed for the realization of TiO_2 films for developing very efficient photo-catalytic filters for water purification.

In this work, we characterize the photocatalytic and antibacterial activity of TiO_2 films deposited by ALD at different temperatures. In particular, the variation of the growth temperature influences film properties. Here we demonstrate that increasing growth temperature up to 300 °C clearly improves TiO_2 film photocatalytic activity. However, the process does not show to have an impact on antibacterial activity. Different routes have to be followed in order to obtain enhanced antibacterial properties.

1. Introduction

Titanium dioxide (TiO_2) plays a central role in energy and environmental research, finding applications in dye-sensitized solar cells [1], lithium ion batteries [2], as an active layer in chemical sensors [3], as a catalyst [4,5], in self-cleaning coatings [6], and for water purification [7,8].

In 1985, Matsunaga and colleagues observed the antimicrobial activity of TiO_2 [9]. In particular, microbial cells could be killed by the contact with a TiO_2–Pt catalyst under illumination with near UV light. When TiO_2 is irradiated with photons of energy equal to or higher than its band-gap (3.15 eV for anatase, 3.05 eV for rutile crystalline phase [10]), electron–hole pairs are generated. They can induce the formation of reactive oxygen species (ROS), such as $\cdot OH$, O_2^- and H_2O_2 on its surface (in contact with water). These species are directly involved in the oxidation processes that remove organic compounds and microorganisms in water. All three ROS exhibit bactericidal activity but some studies have emphasized that the hydroxyl radical would be the most important oxidant species responsible for the attack of the bacterial cell wall, leading to modifications of membrane permeability and cell death [11–13].

It is known that holes and electrons, generated through UV illumination, have to be separated and have to reach the surface in order to allow the electrochemical reaction with pollutants and water to proceed. Photocatalytic activity strongly depends on the synthesis method of the material [14].

Atomic layer deposition (ALD) is a technique that allows a very precise film thickness control, which is uniform even on nanostructured substrates [15]. Moreover, it allows to grow films at relatively low temperatures [16]. Changing growth temperature also enables the deposition of films with different structure and surface roughness [17].

In this work, we characterize the photocatalytic and antibacterial activity of TiO_2 films deposited by ALD at different temperatures. Photocatalytic activity was evaluated by the degradation of the organic compounds Methylene-Blue (MB) in water under UV light irradiation. The antibacterial activity was tested on *Escherichia coli*, a well-known Gram-negative bacterium, through CFUs count. *E. coli* is a representative of coliforms and it is considered to be an indicator of fecal contamination in drinking water [18].

* Corresponding author.
E-mail address: mariaantonietta.buccheri@cnr.it (M.A. Buccheri).

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2. Experimental methods

The ALD film were deposited on Si substrate with a Beneq TFS-200 system, using $TiCl_4$ (Sigma Aldrich, 99.9%) and de-ionized water as precursors, at deposition temperature of 100, 200 and 300 °C. Nitrogen (> 99.999%) from a Sirocco N_2 generator was used as carrier gas, with a combined flow rate of 550 sccm, maintaining a reactor pressure of approximately 1.3 mbar. The films thickness (~ 50 nm) was evaluated by the M-2000 spectroscopic ellipsometer by Woollam (Lincoln, Nebraska, U. S.).

The structural characterization was achieved by scanning electron microscopy (SEM).The analyses were performed in plan-view by a field emission Zeiss Supra 25 microscope. However the SEM analysis does not give relevant information. In fact, only the grain of the TiO_2 film is visible.

XRD measurements were acquired by Bruker D-500 diffractometer at an angle of incidence of 0.8°, and Θ-2Θ from 20° to 60°. Acquired spectrum were analyzed by Bruker software suite, including ICSD structure database.

The photocatalytic activity of the investigated materials was evaluated by the degradation of the MB organic compound. The samples, 1 cm × 1 cm in size, were immersed in a solution (2 ml) containing MB and de-ionized water (starting concentration: 1.5×10^{-5} M). The mixture was irradiated by an UV lamp (peaked at 365 nm with 20 nm of full width at half maximum) with a irradiance of 1.1 mW/cm^2 for a total time of 3 h and a half. Every 30 min of irradiation the solution was measured with a UV–vis spectrophotometer (Perkin-Elmer Lambda 35) in a wavelength range between 500 and 800 nm. The degradation of MB was evaluated by the absorbance of the MB peak at 664 nm, thanks to the Lambert-Beer law ($A = \varepsilon \times l \times C$, where A is the absorbance of the solution at 664 nm, ε is the molar extinction coefficient, l is the width of the cuvette, C is the concentration of the MB) [19]. The UV lamp used for the irradiation does not emit in the region of absorbance of the MB, as a consequence the measured degradation of the MB can be only ascribed to the presence of the catalyst. The decomposition of the MB in absence of any catalyst materials was also checked as a reference. Before the measurements, the samples were irradiated by the UV lamp for 30 min in order to remove the hydrocarbons localized on the sample surface [20].

Antibacterial activity was tested on the *Escherichia coli* ATCC25922 strain. Bacteria were routinely maintained by spreading on McConkey agar. To run tests, a single colony was inoculated in 50 ml of Luria-Bertani (LB) broth and grown overnight at 37 °C by constant agitation at 180 rpm under aerobic conditions. The following day, the bacterial growth was measured by optical density at 600 nm. Bacteria were diluted up to 10^5 CFU/ml in phosphate buffer saline (PBS) and 100 µl were added onto the TiO_2 samples. Untreated bacteria and bacteria exposed to UV only were run in parallel as controls. The UV source utilized to induce photocatalysis was the same as for MB degradation analysis. Aliquots were collected at 15, 30 and 60 min, conveniently diluted by serial dilutions 1:10 and plated in LB Agar Petri dishes. Plates were incubated overnight at 37 °C. CFU were counted the following day. Experiments were made in triplicates.

3. Results and discussion

The photocatalytic activity of the samples in the degradation of an organic compound dissolved in water under UV irradiation was confirmed by Methylene blue. Fig. 1 illustrates a typical measurement of MB discoloration. In detail, Fig. 1 reports the absorption spectra for the MB solution for different irradiation time for the TiO_2 samples deposited at 300 °C. The absorbance peak at 664 nm is a direct measurement of the MB concentration (through

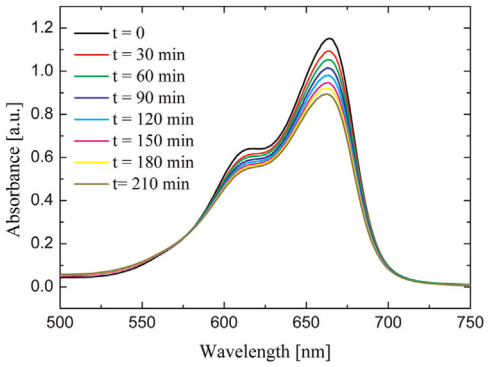

Fig. 1. Absorption spectra for the MB solution for different irradiation times for the TiO_2 film grown at 300 °C.

the Lambert–Beer law [21]) and thus its decreases with UV irradiation time is a measure of the photocatalytic decomposition of the MB molecules.

The photocatalytic response of all TiO_2 samples was performed first in the presence of the catalysts under dark condition, in order to estimate the degree of adsorption of MB on the catalysts surface. The starting and final concentration of MB were equal within the experimental error (2%), for the three types of samples, indicating that the investigated materials do not adsorb the MB. Fig. 2 reports the residual concentration C/C_0 of MB, where C is the concentration of MB after the irradiation, C_0 is the starting concentration of MB, versus the irradiation time. We tested four samples: MB in absence of any catalyst materials (squares), with TiO_2 sample deposited at 100 °C (circles), at 200 °C (triangles) and at 300 °C (diamonds). While there is not any decomposition of the MB without any photocatalyst materials, as expected, a more significant decrease in the MB concentration is clearly observed when the photocatalytic materials are added to the solution. It is interesting that the TiO_2 sample deposited at 200 °C has a photo-response almost equal to the TiO_2 sample deposited at 100 °C. The TiO_2 film deposited at 300 °C, instead, exhibits a remarkable increase in MB degradation by more than 15%, after 210 min, compared to the TiO_2film deposited at 200 °C (compare diamonds to triangles in Fig. 2). In Fig. 2, we also reported reaction rates, k, for all the analyzed samples. The observed reaction rate, k, follows a Lagmuir-Hinshelwood model kinetics, which can be expressed by a first-order reaction kinetic:

$$\ln\left(\frac{C}{C_0}\right) = -kt$$

where C is the concentration of organic species, C_0 is the initial concentration of organic species, t is the irradiation time [23].

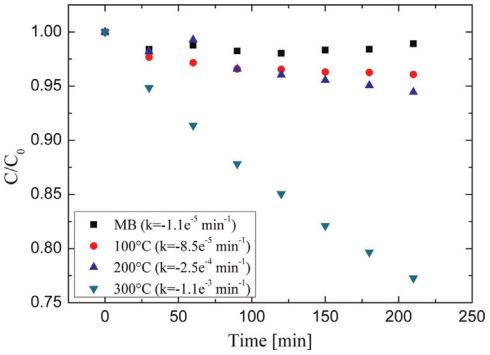

Fig. 2. MB degradation under UV-irradiation for four samples: MB (squares), MB with TiO_2 grown at 100 °C (circles), MB with TiO_2 grown at 200 °C (triangles) and MB with TiO_2 grown at 300 °C (diamonds).