Photocatalytic and antibacterial properties of titanium dioxide flat film.

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Keywords: Atomic Layer Deposition, Photocatalytic activity, Antibacterial activity, Titanium dioxide

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 bekilled by the contact with a TiO_2–Pt catalyst under illuminationwith 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 •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 hydroxylradical would be the most important oxidant species responsiblefor the attack of the bacterial cell wall, leading to modifications ofmembrane permeability and cell death [11,12,13].

It is known that holes and electrons, generated throughUV illumination, have to be separated and have to reach the surfacein order to allow the electrochemical reaction with pollutants and water to proceed. Photocatalyticactivity strongly depends on the synthesis method of the material [14].

Atomic layer deposition (ALD) is a technique that allowsa very precise film thickness control,which is uniform even on nanostructured substrates [15]. Moreover, it allowsto grow films

at relatively low temperatures [16]. Changing growth temperature alsoenables thedeposition offilms 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-negativebacterium, through CFUs count. *E. coli* is a representative of coliforms and it is considered to be an indicator of fecal contaminationin drinking water [18].

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 difractometer at an angle of incidence of 0.8º, and Θ-2Θ from 20 to 60º. 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 hours and a half. Every 30 minutes 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 50ml 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 600nm. Bacteria were diluted up to 10^5 CFU/ml in phosphate buffer saline (PBS) and 100µl 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 photo-catalysis was the same as for MB degradation analysis. Aliquots were collected at 15, 30 and 60 minutes, 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 the Lambert-Beer law [21]) and thus its decreases with UV irradiation time is a measure of the photocatalytic decomposition of the MB molecules.

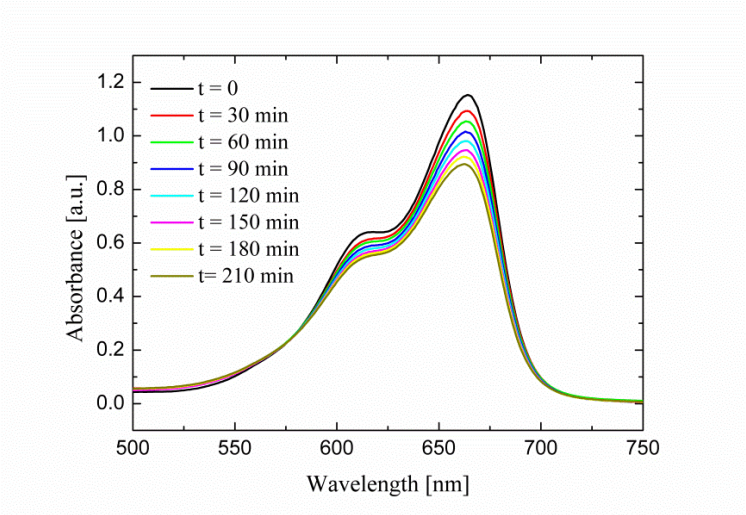

Figure 1: Absorption spectra for the MB solution for different irradiation times for the TiO_2 film grown at 300°C.

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_2sample 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°Chas 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].

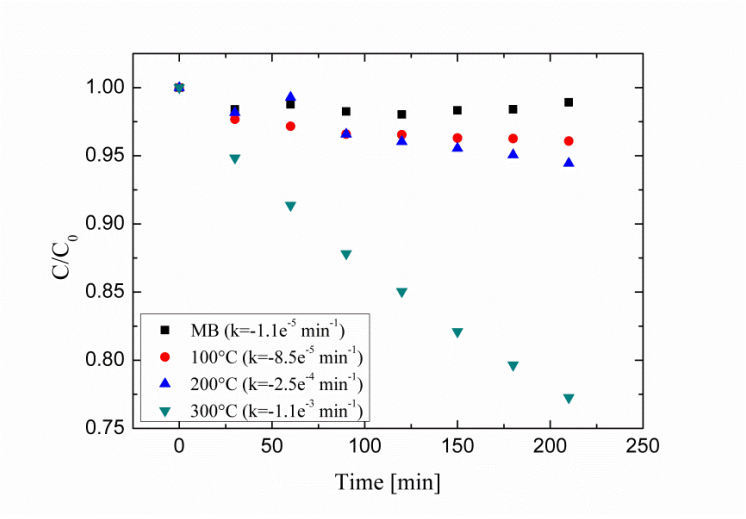

Figure 2:MB degradation under UV-irradiation for four samples: MB (squares), MB with TiO_2grown at 100°C (circles), MB with TiO_2grown at 200°C (triangles) and MB with TiO_2grown at 300°C (diamonds).

These results can be understood considering the change in phase composition from amorphous film to crystalline anatase film. The X-ray diffraction patterns of the three TiO_2 films are shown in Fig. 3. The film grown at 100°C is amorphous. Whereas the films grown at temperature of 200°C and 300°C consist of crystalline anatase phase only. In particular, its amount increased with deposition temperature. In fact, as reported in literature, crystalline anatase phase appeared at a growth temperature ≥ 150°C,at the expenses of the amorphous phase. It can be considered complete at around 300°C, for film deposited by ALD [22].

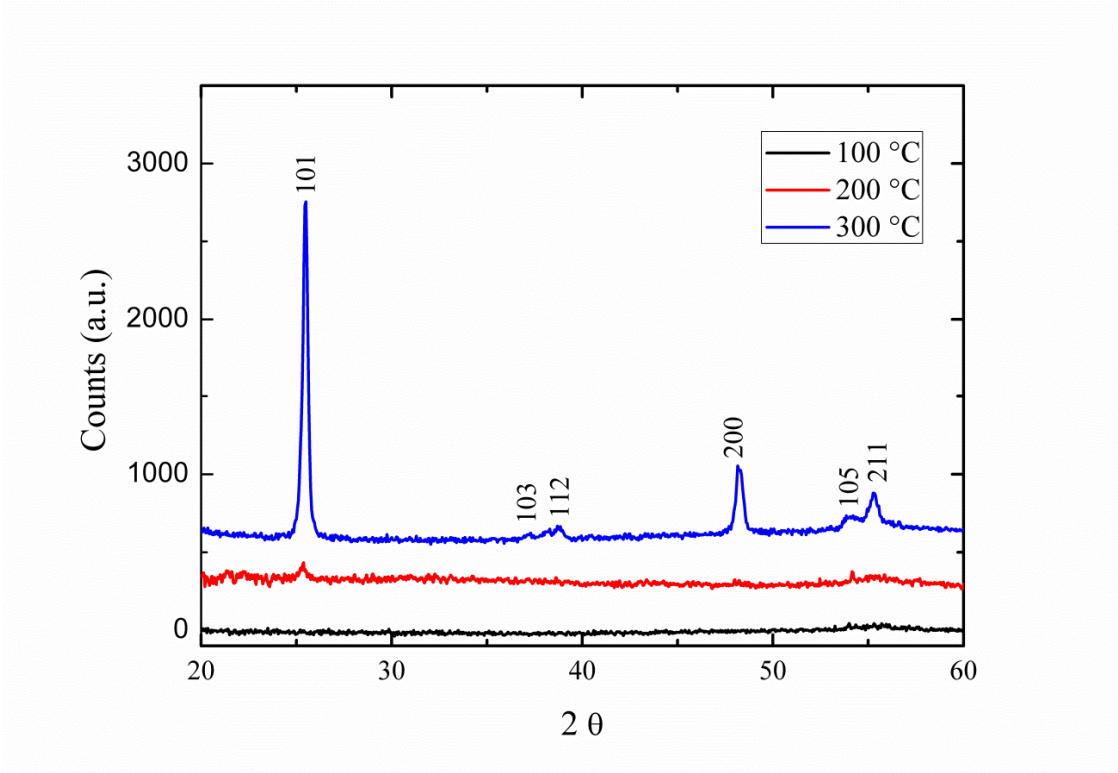

Fig. 3: XRD patterns of the TiO_2 films deposited at different temperature.

TiO_2 films antibacterial activity was tested by measuring the survival rate of *E. coli* after exposure to films and UV light. Best results were obtained after one hour exposure. As shown in Fig. 4, after one hour exposure to the film deposited at 200°C, bacterial survival dropped down to 61% while after exposure to the film deposited at 300°C it is reduced up to 66%. Results were normalized

toward initial bacterial concentration. The statistical error of the test is 5% . The difference among the two results is not significant, as assessed by a Chi-Square test performed on raw data. Thus, the two films display the same antibacterial activity.

At a first glance, the result may look surprising, considered the enhanced photocatalytic activity showed by the film deposited at 300°C. However, different reasons may lie behind these results.

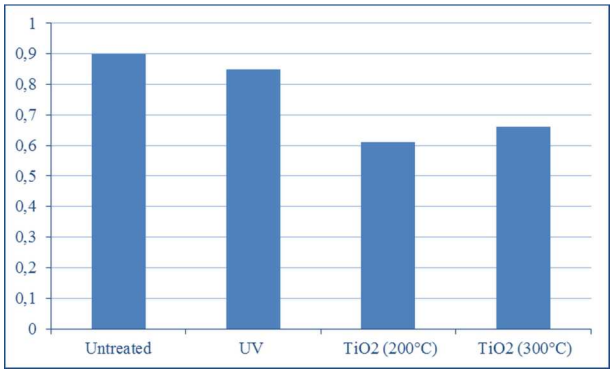

Figure 4: *E.coli* survival after exposure to TiO_2 sample grown at 200°C and TiO_2 grown at 300°C. Untreated and exposed to UV only bacteria were run as controls.

The increase in crystallinitydemonstrates to be beneficial in improving thephotocatalytical activity. In a first instance, although it is expected that the higher degree in crystallinity would generate a higher amount of hydroxyl radicals, it may be reasoned that, possibly, not all hydroxyl radicals will be able of interacting with the bacterial membrane.In fact, hydroxyl radicals have a very short half-life, thus they are likely to travel only very short distances in the extracellular environment before encountering oxidizable substrates such as fatty acids of the bacterial membrane [24]. Thus, in order for the disinfection reaction to occur, microbes, like molecular reactants, are required to be in contact with or in very close proximity to the photocatalyst surface. Possibly, an increase of the contact surface between the nanomaterials and the bacteria or an important nano-structuration of the surface could prove to be of help, as shown in Sanz,R. et al. [25].

Furthermore, a bacterial surface is much more complex than soluble molecules. The reaction pathways through which TiO_2 is able to inactivate organisms are complex, and mechanism based modeling of photocatalytic inactivation has not been fully explored yet.Still to be determined is the relation between photocatalytically induced lipid peroxidation and cell death. It is possible that bacterial inactivation would occur at some threshold of peroxidation (critical level of lipid damage).Even though peroxidation may continue, further damage has no effect on an already inactivated organisms[24].

In addition, bacteria are able to put in place resistance mechanisms to external stress which may influence the reaction to TiO_2 films. Further investigations would be required to disentangle the mechanisms behind bacterial inactivation and thus to improve key features to enhance antibacterial properties.

However, the same antibacterial displayed by films deposited at 200°C and at 300°C could be really interesting for deposition on polymeric substrates or nanostructured samples, where high temperature is detrimental.

4. Conclusion

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. Thus, surface nano-structuration and proper synthesis technique or synthesis parameters have to be chosen according to desired final applications. With the goal in mind of degrading

organic compounds, ALD performed at 300°C results in a more efficient TiO_2 film, if compared to other titania films synthesized at lower temperatures.

Acknowledgments

This research has been supported by the FP7 European Project WATER (Grant Agreement 316082).Authors are grateful to Prof. Stefania Stefani, Laboratory of Medical Microbiology and Antibiotic Resistance (MMAR), Università di Catania, Italia, for the *E.coli* strain.

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