

Titanium dioxide thin films: a study of film morphology and structural changes upon photocatalytic degradation of methylene blue

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TiO₂ thin films were deposited by reactive DC-magnetron sputtering at different Ar/O₂ ratios in the gas mixture. The photocatalytic activity (under UV light irradiation) of these films was evaluated upon degradation of aqueous solutions of methylene blue (MB), a model organic pollutant. Upon photocatalysis, the TiO₂ films showed structural, morphological and compositional changes that were characterized by X-ray diffraction (XRD), Atomic Force Microscopy (AFM), Scanning Electron Microscopy (SEM) and energy dispersive X-ray (EDX).

1. Introduction

Research on TiO₂ and TiO₂-based materials as photocatalysts for decontamination of water and air with UV and visible light has been active since the 1970's. Most of work on the field has focused on transport processes at the semiconductor interface, kinetics of the contaminant removal reactions, and fabrication of reactors for commercial applications [1]. Catalyst lifetime is an important characteristic [2]. However, TiO₂ deactivation is seldom studied presumably because this catalyst is perceived as a low cost material. Although deactivation is often observed in photo-assisted processes at the TiO₂/gas phase interface [3], catalyst deactivation and reactivation have hardly been studied in the TiO₂/aqueous interface probably because it is believed that the competitive adsorption of water and its ability to dissolve degradation intermediates help to keep the TiO₂ surface clean. However, chemical contamination of the TiO₂ surface may prevent photon absorption or inhibit interfacial charge transfer [4, 5]. Therefore, one question that has to be addressed is the modification of the photocatalyst surface and changes in the kinetics of the degradation reactions as a function of the structure of common chemical contaminants. Our aim here is to study the structural, morphological and compositional changes of TiO₂ thin films, obtained by reactive DC-magnetron sputtering, after the photocatalytic degradation of a methylene blue (MB) a model organic pollutant.

2. Experimental procedure

TiO₂ thin films were deposited by reactive DC-magnetron sputtering, on quartz (100) substrates at 400 °C, with a high purity titanium target (99.9%), at 20 W/cm², setting the base pressure to 2x10⁻⁵ mbar and the work pressure in the deposition vacuum chamber to 2.0x10⁻² mbar for 60 minutes. The Ar/O₂ gas mixture ratio was varied (from 80/20 through 50/50) to study the influence of O₂ partial pressure



on the crystallographic structure and catalytic activity of the as deposited TiO₂ films which were used as photocatalysts for the degradation of methylene blue, a model pollutant, under UV radiation.

For photocatalytic experiments, a quartz cell containing the MB test solutions and a TiO₂ film was irradiated with UV light and an incandescent lamp (4 W each) located 4 cm from the cell. Air was bubbled in the solution for 10 min before irradiation. Upon irradiation, the MB concentration was followed by measuring the solution absorbance at 292 nm in a Shimadzu UV-vis 1601 spectrophotometer. Chemical composition of the deposited films was studied in a Philips XL30 SEM with an EDX microprobe for chemical analysis (12 kV), equipped with a window for the detection of light elements. Morphological characterization was made by using an Asylum research Atomic Force Microscopy (AFM) in non-contact mode. AFM image data was processed with a fractal algorithm and the WSxM freeware developed by NanotecElectrónica, Spain [6], to obtain surface parameters like grain size, saturation roughness (σ), correlation length (ϵ) and roughness exponent (α). The crystalline structure of the TiO₂ films was determined by grazing angle X-ray diffraction (GAXRD) at 2° incidence angle, over the range [20 – 80]° using the K α_1 line of Cu ($\lambda = 1.5406$ Å, 45 kV and 40 mA) in a X'pert-Pro Panalytical X ray diffractometer.

3. Results and discussion

3.1 Photocatalytic activity of TiO₂ films

The electronic spectrum of MB in water exhibits two characteristic absorption maxima at 292 and 668 nm, respectively. Upon photocatalytic treatment with UV light, in the presence of O₂, MB is known to decompose into a series of fragments before complete mineralization to produce inorganic acids (HCl, H₂SO₄, and HNO₃), CO₂ and water.

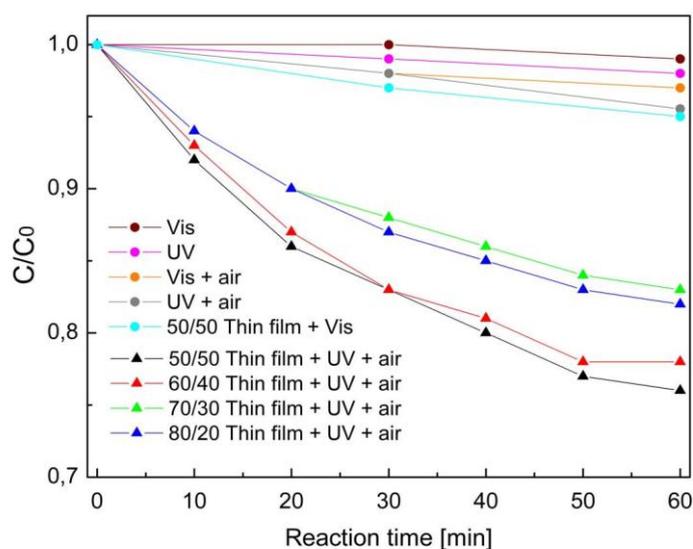


Figure 1. Relative concentration curves of MB aqueous solutions (initial concentration: 2.5×10^{-5} M) upon different experimental conditions.

Figure 1 shows the relative concentration, C/C_0 , (at 292 nm) of 2.5×10^{-5} M MB aerated test solutions subject to UV irradiation in the presence of TiO₂ films prepared in Ar/O₂ mixtures and several control experiments [7]. After 1 h of UV irradiation, in aerated solutions, the best reaction rates are achieved with the 50/50 TiO₂ films, indicated by the 24% decrease in absorbance (black triangles), which, in addition, means that complete mineralization of MB does not happen under our experimental conditions. For the 60/40 films (red triangles), the absorbance change is slightly lower (22%). Apparent reaction rates are lower with the 70/30 and 80/20 films (blue and green triangles, respectively, absorbance decrease of ca. 18%, each). A control experiment, performed by irradiating the test solution with visible light in the presence of a 50/50 TiO₂ film (light blue circles), showed a

total absorbance decrease of 5 %. Other control experiments, including irradiation of the aerated and deaerated test solution with UV and visible light in the absence of TiO₂ showed absorbance changes lower than 5 %. Henceforth, we will use the 50/50 samples to compare the structural, compositional and morphological changes before and after photocatalytic activity in MB solutions.

3.2 Changes of TiO₂ films upon photocatalytic activity

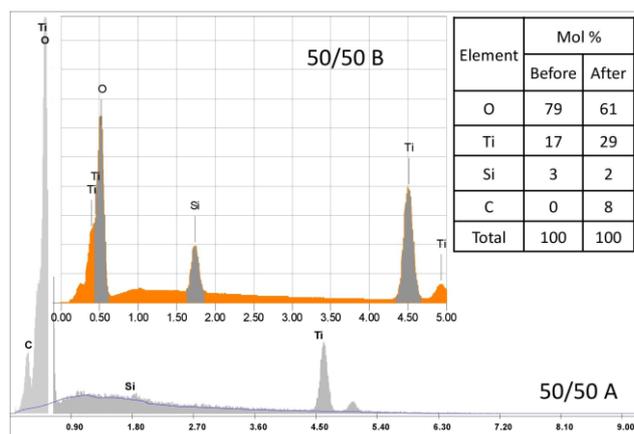


Figure 2. EDX spectra of a 50/50 TiO₂ thin film before and after photocatalytic treatment of MB.

Figure 2 shows the Energy Dispersive X-ray (EDX) analysis of a 50/50 TiO₂ thin film before and after photocatalytic treatment of MB solutions. After reaction, the major spectral change is the appearance of a carbon peak in the 50/50 TiO₂ film, indicating adsorption of MB decomposition intermediates on the film.

The XRD patterns for a 50/50 TiO₂ thin film, before and after photocatalysis, are shown in Figure 3.

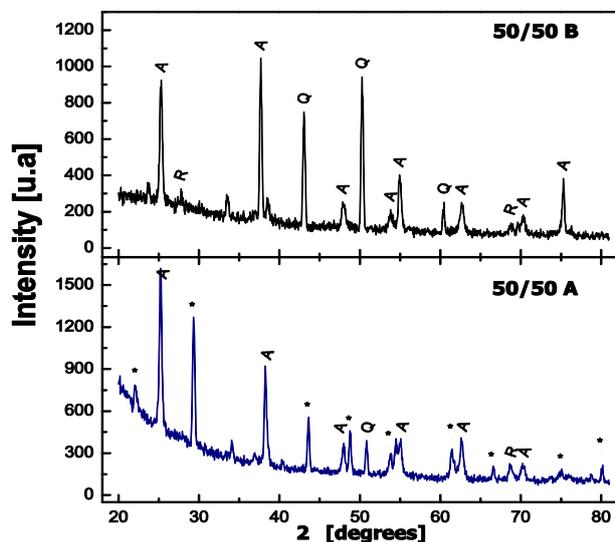


Figure 3. X-ray diffraction patterns of a 50/50 TiO₂ thin film, before and after photocatalytic treatment of MB. A=Anatase, R=Rutile Q=Quartz and* additional phases.

As grown 50/50 TiO₂ thin films exhibit 90% anatase and 9% rutile domains. The diffraction patterns show that, upon photocatalytic activity, the peaks of the quartz substrate (Q) and the rutile (R) phase practically disappear and new diffraction peaks (* at 22.09, 29.35, 43.62, 53.7, 62.49, 75.07, and 80.01 degrees) of other phases emerge, presumably associated to the chemical intermediates of the degradation of MB. In addition, the higher background in the diffraction pattern of the TiO₂ sample after photocatalysis is consistent with the appearance of some amorphous phases in the sample.

Figure 4 shows the changes in roughness and grain size of the TiO₂ films, before and after photocatalysis, studied by atomic force microscopy in noncontact mode.

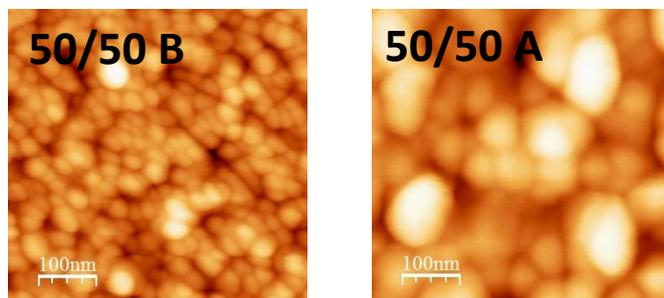


Figure 4. AFM images of a 50/50 TiO₂ film before and after photocatalytic oxidation of methylene blue. Window size: 500 nm.

Figure 4 indicates that particle agglomeration occurs upon photocatalysis. Control experiments show that this phenomenon does not result from exposure to UV or visible light alone. Table 1 summarizes the morphological parameter values obtained from the fit of the size dependent roughness as a function of window size for the 50/50 TiO₂ thin film. The TiO₂ grain size is twice as large, while the saturation roughness decreases, suggesting abrasion of the surface as if the density of the film decreased along the vertical axis.

Table 1. Summarized morphological AFM parameters.

	L=500nm	50/50 B	50/50 A
Grain size [±1nm]		39	81
σ [±0.1nm]		3.1	2.9
ε [±0.01nm]		0.3	0.51
α [±0.02nm]		0.35	0.43

5. Conclusions

Relative concentration curves of MB aqueous solutions in the presence of TiO₂ films deposited at different Ar/O₂, show that the 50/50 TiO₂ thin films, composed of 90% anatase and 9% rutile phases (as determinate from XRD analysis), exhibit the highest photocatalytic activity toward the degradation of MB. In addition, data processing of AFM images indicates that the TiO₂ film grain size doubles upon one single photocatalytic experiment, while the saturation roughness decreases. Further studies on whether rutile to anatase phase conversion and formation of new Ti-C and/or Ti-S phases can occur under the photocatalytic treatment are under way.

6. Acknowledgements

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7. References

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