

Nb-doped TiO₂ thin films as photocatalytic materials

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Abstract. Amorphous undoped and Nb-doped films were obtained by the spin coating method. The films have a compact structure, as revealed by scanning electron microscopy, and are very thin, with thickness values under 100 nm. The photocatalytic activity of the films was evaluated by observing the decomposition of an oleic acid solution under UV irradiation, and by studying the change in the optical transmittance of an aqueous solution containing methylene blue, in the presence of the UV-irradiated films. More than 30 h, depending on doping, are needed to recover their initial contact angles before applying oleic acid. The increase of the optical transmittance of the methylene blue solution confirms the photocatalytic degradation of methylene blue on the Nb-doped TiO₂ films. X-ray photoelectron spectroscopy studies, performed to detect the presence of the carbon on the irradiated surface of the films, drive to the conclusion that at the surface of the films, even for contact angles close to 0°, the presence of carbon still can be detected, which demonstrates that hydrophilicity is ruled by a different mechanism than photocatalysis.

Keywords. Nb-doped TiO₂ thin films; oleic acid decomposition; hydrophilicity; photocatalysis.

1. Introduction

TiO₂ thin films are non-toxic and economical materials that can be used in the benefit of the environment, being studied for a large area of applications: solar cells,^{1–3} hydrogen production,^{4,5} sensors,⁶ photocatalysis,⁷ etc. Photocatalytic performance of a material can be greatly influenced by the deposition method and by the chosen parameters during the deposition process. To obtain TiO₂ thin films with the desired properties, they were deposited by using different techniques, with certain parameters: spray pyrolysis,⁸ reactive magnetron sputtering,⁹ sol–gel.¹⁰ The sol–gel method, more precisely spin coating (the method used to obtain undoped and Nb-doped films discussed in this paper), provides a number of advantages such as easy to use, relatively low cost of technology and materials, precise control of the composition in the obtained films, adhesion to the substrate, etc.¹¹ While previous studies dealt with the hydrophilic properties of similar samples, which proved to be excellent for the Nb-doped films compared with the undoped one,¹² in this study it was investigated how doping influences their oxidation power and they also show good photocatalytic performances.

2. Experimental

TiO₂ and Nb-doped TiO₂ thin films were obtained by the spin coating method. In preparing the necessary solutions, titanium tetraisopropoxide was used as the source for TiO₂, while different quantities of niobium pentaethoxide were used to obtain solutions with increasing Nb content. The solutions were deposited on unheated glass substrates by using spinner speeds of 2000–3000 rotations min⁻¹. The obtained films were subjected to an annealing process, for 1 h, at 500°C. Details are given elsewhere.¹³

X-ray photoelectron spectroscopy (XPS) studies have been performed to detect the presence of the carbon on the irradiated film's surface. A Physical Electronics-Ulvac (PHI 5000 VersaProbe) instrument was used for this purpose. The monochromatic X-ray radiation AlK α ($h\nu = 1486.7$ eV) was the excitation source.

Scanning electron microscopy (SEM) analysis was carried out to investigate the surface morphology of the films, by using a Hitachi S-3400N microscope. Before obtaining the SEM images, the surfaces of the samples were covered with a 15 nm gold layer, to avoid charging. Cross-sectional images were also acquired to obtain the thickness of the films. The obtained values confirm the previous results determined by ellipsometry,¹² that the films are very thin, with thickness under 100 nm.

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The photocatalytic activity of the films was evaluated by observing the decomposition of an oleic acid solution under UV irradiation, according to the route described in ISO/DIS 27448-1 standard. In this purpose, a thin layer of oleic acid solution (0.5 vol% oleic acid, diluted in *n*-heptane) was deposited on the surfaces of the films, by the dip coating method, using a picked up speed of 60 cm min⁻¹, followed by a drying process at a temperature of 70°C, for 15 min.¹⁴ Further, the samples were subjected to UV irradiation, and the contact angles between deionized water and the surface of the films were recorded with a Data Physics OCA 15EC goniometer, in a sessile drop arrangement (at room temperature – 22°C and at 65% relative humidity). The final contact angle values were obtained by averaging five values measured at different locations on the films surface. A mercury lamp (150 W, 1 mW cm⁻²) with emission lines in both UV and visible ranges was utilized.

The photocatalytic properties of the studied films were evaluated, by observing the change in the optical transmittance of an aqueous solution containing methylene blue (C₁₆H₁₈N₃S·Cl·3H₂O) and the film, during the UV irradiation. The aqueous solution (10 ml, 0.05 mmol l⁻¹) was located in a 15 ml quartz cuvette. Optical transmittance through the solution was measured at intervals of 24 h, for 18 days, using a double beam UV–vis Lambda 3 Perkin Elmer spectrophotometer, at 660 nm.

3. Results and discussion

The Nb-doped films are labelled as S1, S2 and S3, as Nb increases, while the undoped film is labelled S0. Some of the properties of these films were already discussed in our previous work.^{12,13} Results show that all the films are amorphous and they are very smooth, with roughness values under 5 nm. The films are slightly overoxidized and the ratio Ti/Nb derived from XPS was found to decrease from 11.4 to 0.46 with the increase of the dopant concentration. It was observed that Nb-doped films could be photoactivated with UV radiation of higher energy, as Nb percentage increases, which contradicts some results in the literature,¹⁵ while they are in good agreement with others.¹⁶ The explanation made from a polaronic point of view was given in Mardare *et al.*¹² The Nb-doped films present excellent hydrophilic properties under UV irradiation, comparing with the undoped one.¹² It has been already shown that Mo-doped titania films with higher hydrophilic performances are also good photocatalysts, confirming the idea that investigating the hydrophilic properties constitutes a much simpler way to obtain information on their photocatalytic activity.⁸ Further, the properties of these Nb-doped films, namely, their oxidizing power, have been discussed in the present paper.

A typical SEM image is presented in figure 1a, representing the surface of one of the doped sample (S3), together with the cross-sectional SEM image (figure 1b), which estimates its thickness to be around 70 nm. They reveal a very compact structure, which normally does not allow to affirm that the films have good hydrophilic properties, as the Wenzel model¹⁷ evidences that a high surface roughness induces a good surface wettability in the case of hydrophilic films. Still, as seen from the contact angle measurements presented in ref. 12, the initial contact angles of the Nb-doped films have values lower than 5°, being highly superhydrophilic even in the absence of the UV irradiation. This might be related to the presence of the Ti³⁺ states in the non-irradiated films. The Ti³⁺ peaks area increases with the Nb content, as revealed by XPS.¹² The increase of the Ti³⁺ states at films surface has the effect on decrease of the electron–hole recombination, and thus, the improvement of the hydrophilic properties.

On the highly hydrophilic surfaces of the Nb-doped films, as well as on the surface of the undoped one, a fatty acid was deposited. As seen from figure 2, the initial contact angles of all the covered films increase from ~5° till ~57°. By beginning the UV irradiation, the contact angles start to decrease, as a result of the oxidation process of the oleic acid. Two of the studied films recover their initial contact angles before applying oleic acid, after 30 and 50 h of UV irradiation respectively, and their contact angle values continue to decrease reaching values around 29° for the undoped film (after 90 h), and around 1° for the sample S3 (after 65 h).

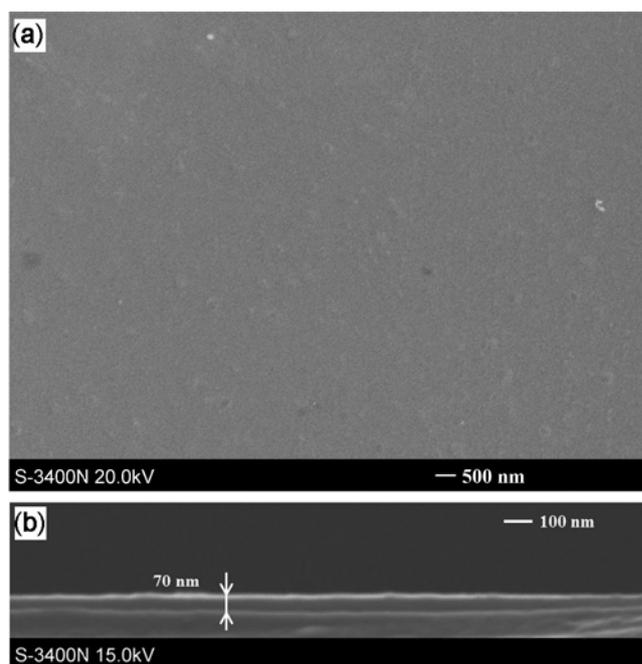


Figure 1. (a) Typical SEM image acquired for the film S3 and (b) cross-sectional SEM image corresponding to the film S3.

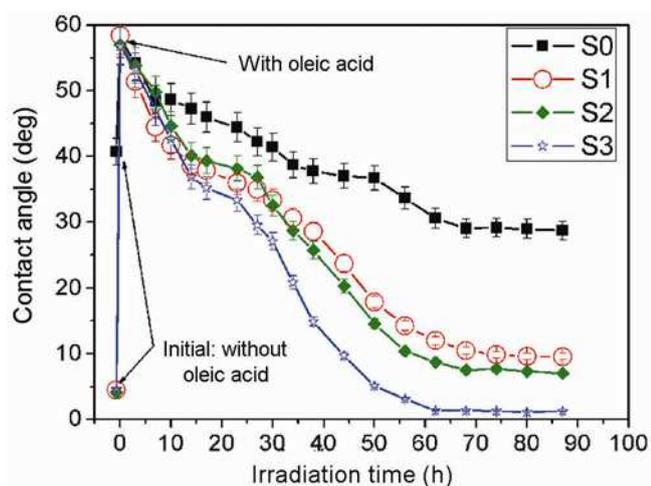


Figure 2. Modification of the contact angle after depositing the oleic acid layer, and its variation as a function of the irradiation time.

The decrease tendency of the contact angle is evident for the other two films, but obviously need longer times to reach the contact angles corresponding to the saturation of the photoactivation observed in ref. 12 (close to 0°), much longer times of irradiation than found in the case of Mo-doped TiO₂ films (20–27 h as a function of doping).⁸ Anyhow, these studies confirm again that hydrophilicity is ruled by a different mechanism than photocatalysis. It has been shown that, even for a superhydrophilic film under UV, such as sample S3, the presence of carbon on its surface was still detected. It was registered that the C 1s peak of the film S3 covered with oleic acid, before irradiation (contact angle of about 57°) and at different intervals of UV irradiation (50 and 65 h), knowing that all the Nb-doped films have reached contact angles close to 0° after only 10 min of UV irradiation,¹² while they needed hours to decompose the oleic acid, as observed above. Previously it was observed that after 50 h of UV irradiation, the film S3 recovered its initial contact angle that it had before applying oleic acid, and after 15 h more, the contact angle reaches the saturation, with a value of 1°. Thus it was proved that carbon is still present at the S3 film surface, even in its superhydrophilic state of 1° (figure 3), confirming the idea of Hashimoto *et al.*,¹⁸ that superhydrophilic surfaces are not simple clean surfaces. The explanation is related to a possible change in the surface structure of TiO₂, namely, metastable photoinduced states with large surface energies can be generated when the films are UV irradiated, determining the conversion to a superhydrophilic surface.¹⁸

To confirm the level of the oxidation power of the Nb-doped TiO₂ thin films, we have measured the optical transmittance through an aqueous solution containing methylene blue and one of the UV irradiated film (S3). One can observe that the optical transmittance slowly increases from 64% till 97%, in 18 days (figure 4). This

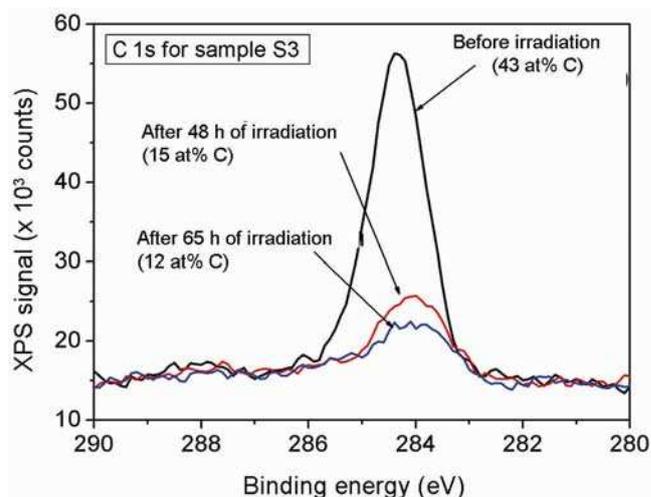


Figure 3. C 1s XPS spectra of the film S3 covered with oleic acid, before the UV irradiation, and after 50 and 65 h after irradiation.

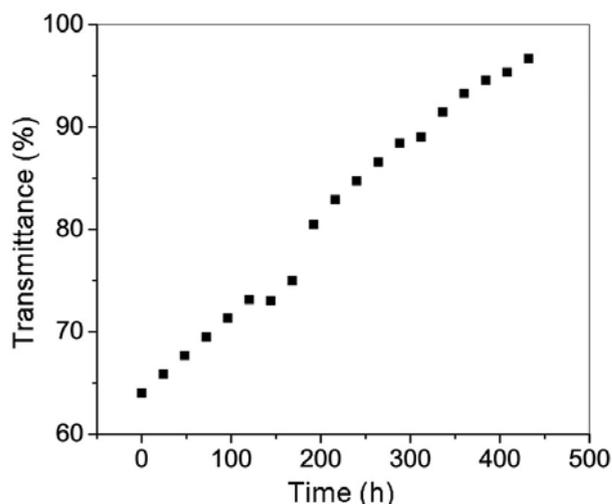


Figure 4. Optical transmittance vs. time, for an aqueous methylene blue solution containing the UV-irradiated film S3.

method was applied only for one Nb-doped film, which presents promising hydrophilic properties according to our previous investigations,¹² in order to show that the evaluation of the decomposition of an oleic acid solution by contact angle measurements is a much simpler method (less time consumer) than by observing the change in the optical transmittance of an aqueous solution containing a dye.

Knowing that the light absorption is proportional to the concentration of methylene blue,^{9,19} the ratio C/C_0 between the actual (C) and the initial (C_0) methylene blue concentrations was derived. The kinetics of methylene blue decolorization, where the logarithm of the normalized dye concentration is plotted against the irradiation time, is presented in figure 5. For a low concentration of

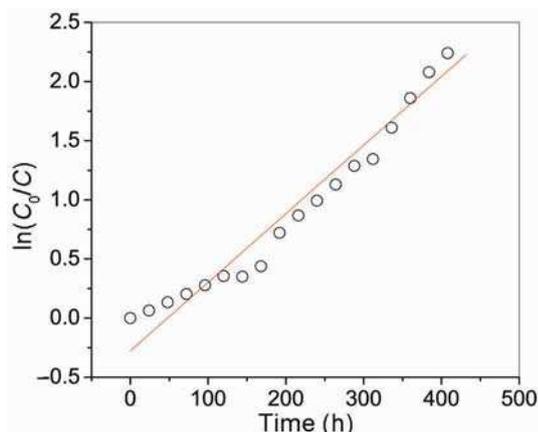


Figure 5. Photocatalytic degradation of methylene blue on the Nb-doped TiO₂ film (S3).

methylene blue as in the present study (0.05 mmol l⁻¹), the reaction followed the first-order kinetics²⁰

$$\ln \frac{C_0}{C} = kt, \quad (1)$$

From the linear dependence (1) (0.95 – the correlation coefficient) the apparent reaction rate $k = 0.006 \text{ h}^{-1}$ was found.

The results obtained from the acid oleic decomposition at the surface of the studied films and from the decomposition of methylene blue in aqueous solution clearly show that the photocatalytic degradation of the organic compounds takes place.

4. Conclusions

Undoped and Nb-doped TiO₂ thin films were obtained by the spin coating method. The films are amorphous and have a compact structure.

Studies of the decomposition of the oleic acid applied on the films surface show that the films needed more than 30 h to recover their initial contact angles in the absence of the oleic acid. By continuing the UV irradiation, the contact angles decrease, tending to reach the values corresponding to the saturation of the photoactivation previously observed when investigated the hydrophilic properties of these films.

The optical transmittance through an aqueous solution containing methylene blue increases till 97%, in 18 days, in the presence of the UV-irradiated sample S3, and the reaction rate was found to be 0.006 h^{-1} .

These Nb-doped films, even highly superhydrophilic in the presence of the UV radiation, decompose the organic compounds in much higher times. This observation, together with the carbon can still be detected on the surface of the film, even in its superhydrophilic state with a contact angle close to 0°, shows that hydrophilicity is ruled by a different mechanism than photocatalysis, even

if it can provide information on the oxidation power of TiO₂.

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