

Characterization of TiO₂ films obtained by a wet chemical process

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TiO₂ has an easily tunable bandgap and a great absorption dye ability being widely used in many fields and in a number of fascinating applications. In this study, a wet chemical route, particularly a sol gel method using spin-coating is adopted to deposit TiO₂ thin films onto soda lime glass and silicon substrates. TiO₂ films were prepared by using an alcoholic solution of analytical reagent grade TiCl₄ as titanium precursor at various experimental conditions. The accent was put on the conditions of preparation (spin time, spin speed, precursor concentration, number of coating layers *etc*), doping and on the post-deposit treatment namely the drying and the crystallization. The results showed a strong dependence on the drying temperature and on the temperature and duration of the crystallization. We found that the solution preparation and its color are important for getting a reproducible final product. The Raman spectra recorded at room temperature, showed the characteristic peaks of anatase which appear at 143 and around 396 cm⁻¹. These peaks confirm the presence of TiO₂. The X-ray diffraction (XRD) was used to identify the crystalline characteristic of TiO₂ while the chemical states and relative amounts of the main elements existing in the samples were investigated by X-ray Photoelectron Spectroscopy (XPS). The morphology of the samples was visualized by AFM. We show by this work the feasibility to obtain different nanostructured TiO₂ by changing the concentration of the solution. Photocatalytic activity of TiO₂ films was evaluated. Rhodamine B is a recalcitrant dye and TiO₂ was successfully tested for its oxidation. An abatement of 60% was obtained under sunlight for an initial concentration of 10 mg/l.

Key words: Titanium oxide, spin-coating, XPS, Raman, XRD

1 Introduction

TiO₂ is a very interesting semiconductor for its chemical and optical properties. Its primary application is as a white pigment in paints, food coloring, cosmetics, tooth-pastes, polymers, and other instances in which white coloration is desired [1,2]. TiO₂ films are widely used in many applications such as easily tunable band gap and great absorption dye ability, gas sensor, sunscreen, in dye-sensitized solar cell as the third generation solar cell [3,4]. On the other hand, they are also used as decontaminants owing to their high thermal and chemical stabilities in hostile environments. The photocatalytic properties of TiO₂ were first realized in the 80s for the detoxication of various harmful compounds both in water and air [5].

However, it has been reported that tested samples of TiO₂ catalyze the photo-oxidation of a representative organic substrate (phenol) and that sunlight-illuminated TiO₂ catalyzes DNA damage both in vitro and in human cells [6]. Despite its probable biological toxicity (not fully proved) in animals and humans TiO₂ NPs have a considerable potential in biomedicines, and a variety of works have been conducted to develop new antibacterial and drug delivery systems based on this nanoparticle due to its photocatalytic properties, which explain its ability to destroy bacteria, viruses, and even cancer cells [7].

They are also widely used in optical thin film device applications owing to their appropriate optical properties like large band gap, high refractive index and the transparency in the visible range [8].

TiO₂ thin films can be obtained with different techniques of deposition such as sputtering, chemical vapor deposition, pulsed laser deposition, spray and sol gel. In this study, a wet chemical route involving a sol gel method is used. The wet chemical method becomes the most favored one due to scalability and cost-effectiveness. Depending of the experimental conditions of preparation, titania crystallizes in three different crystalline structures: anatase (tetragonal), rutile (tetragonal) and brookite (orthorhombic).

2 Experimental procedures

Materials

Analytical reagent grade TiCl₄ (99.99%) from Fluka Company, ErCl₃ · 6H₂O (99.9%) and absolute ethanol purity were purchased from Sigma-Aldrich and Spectro-Scientific companies, respectively, to deposit TiO₂. Soda lime 99 glass pane plates were used as substrates.

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Samples preparation

Prior to the deposition of the TiO₂ thin film, the glass substrates were pre-cleaned with an alkali free detergent then ultrasonically cleaned in distilled water and ethanol. The cleaned substrates were dried for 10 min at 70 °C before use. The solution was prepared by mixing analytical reagent grade TiCl₄; as a titanium containing precursor and ethanol as the solvent, with two titanium ion concentrations namely 0.7 and 0.5 M, stirring for 1 hour at room temperature to get a transparent solution which is a prerequisite for getting a reproducible final product. TiO₂ thin films were deposited by the sol-gel spin coating method onto glass substrates, with different speeds, ranging from 3000 to 6000 rpm, and different duration of deposition (td), ranging from 30 s to 60 s. Also, the precursor concentration, the post-deposit treatment namely the drying and the crystallization time (tc) were studied. TiO₂ films doped with Er were prepared from a mixed solution of ethanol, TiCl₄ and a quantity of (ErCl₃·6H₂O) corresponding to a doping level of 1 %.

The crystallographic structure was examined by means of X-ray diffraction (XRD) technique using a X-ray diffractometer with Cu K α radiation ($\lambda = 1.54056 \text{ \AA}$). The range of measurements was from 20 °C to 80 °C of the angle 2θ . Raman spectroscopy is a powerful tool in the study of microstructure of nanosized materials, and therefore a promising technique for characterization of TiO₂ nanocrystals. It permits the investigation of the structural properties of nanoparticles because the variations in the spectra with the change in the particle sizes can be easily detected. Raman spectroscopy was performed by using a Jobin Yvon R600-10S spectrometer provided with a 633 nm radiation as the excitation source. The Raman spectra were collected in the region 3600-100 cm⁻¹, with a spectral resolution of 0.3 cm⁻¹ and an exposure time of 10 s; all experiments were performed at room temperature. The X-ray photoelectron spectroscopy (XPS) is commonly used as a surface specific analysis technique to characterize the composition of the extreme surface (typically $\leq 10 \text{ nm}$ thick). The qualitative and quantitative analysis of the surface was performed with a XSAM800 spectrometer from KRATOS with non-monochromatic X radiation Al K α (1486.6 eV). Details on spectra acquisition and data treatment were described elsewhere [9]. Quantifications factors were those of Vision 2 library. The morphology of spin-coated TiO₂ films was characterized by a Bruker Innova Atomic Force Microscope (AFM) in tapping mode under ambient conditions with TESP tips, Bruker AFM Probes. The AFM images were analysed with the software NanoScope Analysis 1.5 from Bruker.

The photocatalytic behaviour of the films was studied by degrading Rhodamine-B (RhB) dye. A 3 cm² TiO₂ film was immersed in 10 ml aqueous RhB solution. All solutions were prepared from distilled water (resistivity 0.8 Ωcm). The photocatalytic activity was evaluated by measuring the changes in the optical absorbance of

RhB solution in the wavelength range 400-800 nm. The experiment was conducted with two sets of films annealed at different conditions.

4 Experimental results and discussion

4.1 Structural properties

4.1.1 X-ray diffraction (XRD) analysis

The XRD patterns of the thin films of titania deposited on glass substrates with 5000 rpm and 45 s as spin-speed and as spin-time, respectively and annealed at 500 °C and 550 °C for 1 h are represented in figure 1. The location of the peaks matched with JCPDS 21-1272 of TiO₂ anatase phase, confirming its presence. The diffraction peaks at 2θ with 24.81 deg, 38.3 deg, 48 deg, 53,7 deg, 55,6 deg and 62 deg correspond to anatase crystal planes of (101), (004), (200), (202), (105) and (213) respectively. The peaks of the diffractogram are in good agreement with the literature reports [10-12]. At 550 °C the peaks of the anatase phase became well defined. The films are found to have preferential growth along (101) direction. No peaks corresponding to rutile phase were observed, which is in agreement with the reports that the phase transformation from anatase to rutile occurred at temperature higher than 550 °C.

The average size of the crystallites was calculated from the most intense peak (101), using Scherrer's equation

$$D = \frac{k\lambda}{\beta \cos \theta},$$

where D is the crystallite size, λ is the wavelength of X-ray radiation, K is the constant usually taken as 0.89, β is the peak width at half-maximum height and θ is the Bragg angle taken in radians. The estimated crystallite size of the film calcined at 550 °C about 6.11 nm.

4.1.2 Raman spectroscopy

The recorded Raman spectra, in the range of 50-800 cm⁻¹, of titania thin films deposited onto soda lime glass at 5000 rpm during 45 s and annealed at 550 °C at different crystallization times are represented in Fig. 2. The main features of the spectra of the different samples are very similar. There is no shift in the peaks. As reported in the literature [5, 15-17] the recorded Raman spectrum of tetragonal anatase TiO₂ has six allowed modes that appear at 144 cm⁻¹(Eg), 197 cm⁻¹(Eg), 399 cm⁻¹(B1g), 513 cm⁻¹(A1g), 519 cm⁻¹(B1g), and 639 cm⁻¹(Eg). Figure 2 shows the Raman spectra of the samples of TiO₂ nanoparticles as a function of time of crystallization. The spectra show symmetric modes of vibration A1g + 2B1g + 3Eg of tetragonal anatase phase identified at 142 (Eg), 196 (Eg), 396 (B1g), 512 (A1g) and 637 cm⁻¹(Eg). The observed band positions are in agreement with the previous reports for anatase phase [15, 18, 19]. Raman spectra of the films, crystallized at 1 h, 2 h

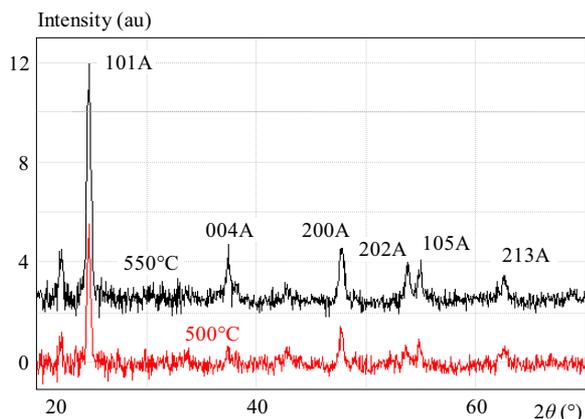


Fig. 1. XRD patterns of thin films of TiO_2 calcined for 1 h at: (a) - 500°C , (b) - 550°C , the concentration of the solution is 0.5 M, A - anatase

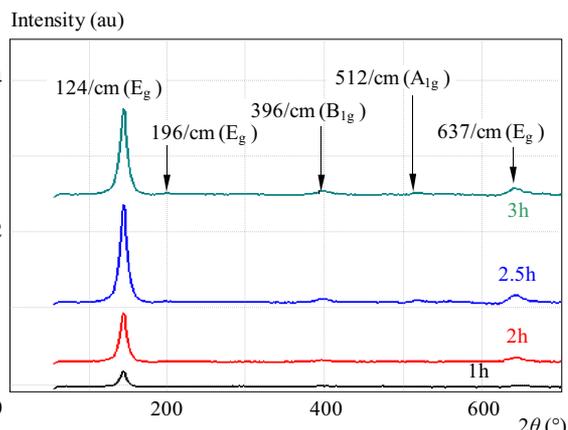


Fig. 2. Raman spectra of TiO_2 thin layers deposited onto glass substrates at 5000 rpm, $t_d = 45$ s and calcined at 550°C versus the time of crystallization

and 2.5 showed a broadening and an increasing intensity of the Raman band at 142 cm^{-1} with crystallization time while the Raman spectrum of the sample crystallized at 3 h exhibit a different dependence. The enhancement of Raman band at 142 cm^{-1} is a characteristic of the TiO_2 crystalline anatase phase

In order to see the differences between the spectra more clearly, the full-widths at half-maximum (FWHM) of the lowest frequency Raman mode band are given in Table 1.

Table 1. Time of crystallization (T), and FWHM of 142 cm^{-1} peak

| Time: | 1 h | 2 h | 2.5 h |
|---------------------------|------|------|-------|
| FWHM (cm^{-1}) | 9.45 | 9.61 | 10.44 |

The FWHM of the main anatase peak (142 cm^{-1}) increased as the time of crystallization increased from 1 to 2.5 h. As reported in the literature [15, 19], this result indicates a decreasing in the particles size.

4.2 Chemical composition of Ti films

The effect of different parameters on the chemical composition of TiO_2 films was studied by XPS. Figure 3 shows the relevant XPS regions of samples prepared with different TiCl_4 concentrations, with distinct times of spin-coating and doped with Er. In (a) and (b) (from bottom to top), films prepared from: a TiCl_4 0.5 m solution spin-coated during 30 s; the same as previous spin-coated during 45 s; a TiCl_4 0.7 m solution spin-coated during 45 s; the same as previous and doped with Erbium. Only the upper spectra are shown with fitted profiles for clarity sake. The remaining spectra have qualitatively the same fitted

$\text{Ti } 2p$ is composed by a doublet with spin-orbit separation of 5.6 eV and $\text{Ti } 2p_{3/2}$ centred at 458.4 ± 0.1 eV, assigned to Ti^{4+} , Fig. 3(a). The oxidation state is the same in the precursor and in titania; to be sure to which element Ti is bound, chlorine (not shown in Fig. 1)

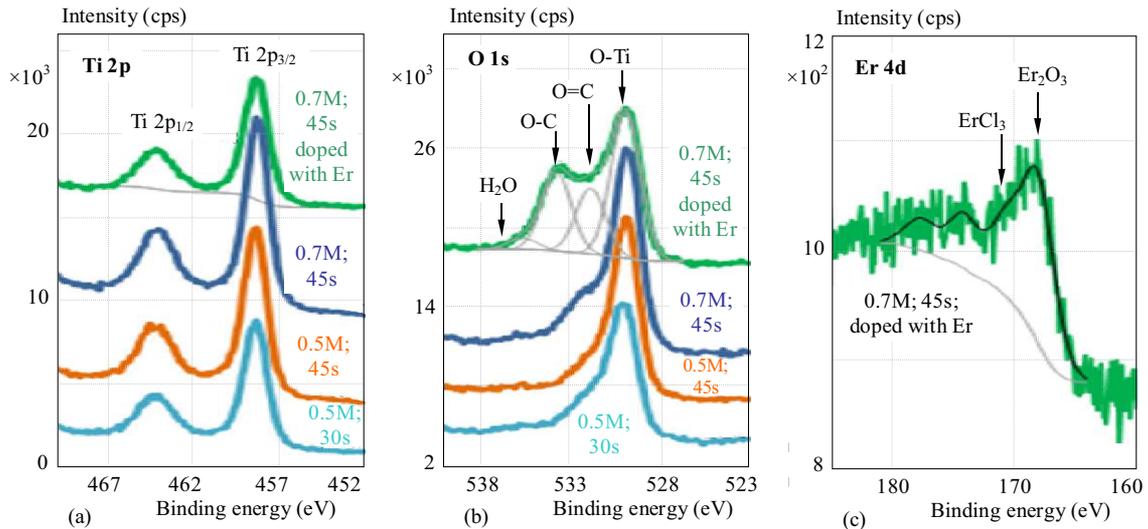
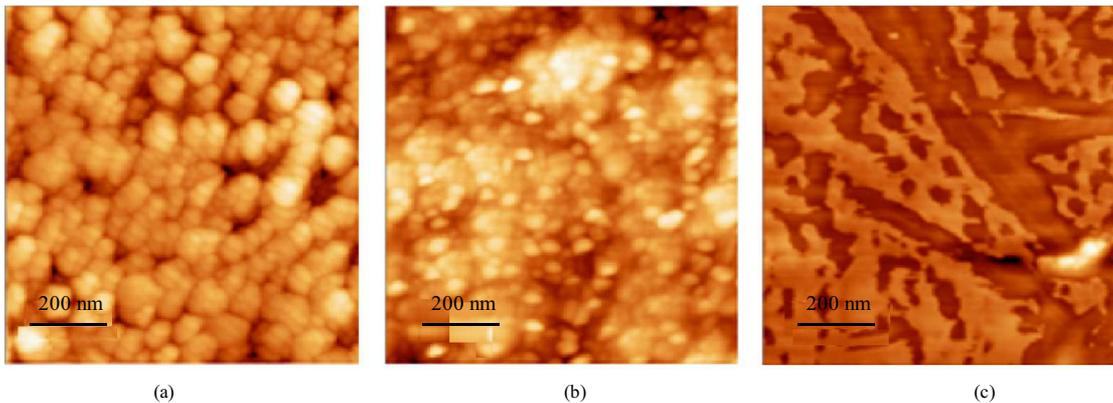
was also analysed (Check quantification below). $\text{Cl } 2p$ is composed by a doublet with the $\text{Cl } 2p_{3/2}$ component, centred at 198.3 ± 0.1 eV, attributed to Cl^- (TiCl_4). $\text{O } 1s$ was fitted with 4 peaks centred at 529.8 ± 0.1 eV, 531.7 ± 0.1 eV, 533.2 ± 0.2 eV and 535.5 ± 0.1 eV, assigned to oxygen in TiO_2 , $\text{O}=\text{C}$, $\text{O}-\text{C}$ and occluded H_2O , respectively, Fig. 3(b). It is interesting to notice that the relative intensities of the peaks fitted in $\text{O } 1s$ of the doped sample, are different from the other samples. Probably, the peak around 533 eV includes also some structured OH from the hydrated Erbium precursor ($\text{ErCl}_3 \cdot 6\text{H}_2\text{O}$). Additionally, this peak can also include, in all samples, oxygen from ethanol OH groups. Er 4d region attests undoubtedly that Erbium is present in the film, Fig. 3(c); however the curve fitting is not a straightforward task, since Er 4d photoelectron region is a complex structure of doublets and satellites not accurately identified at this point. Nevertheless, Er 4d includes the approximate positions of Er_2O_3 , found by Swami *et al*, [13] and ErCl_3 , reported in NIST database [14].

Table 2 shows the XPS quantitative results. Samples indicated as "Not doped" and "45 s" are the samples "0.7 M" and "0.5 M", respectively. They are paired repeatedly for comparison purposes. The ratio $\text{O}529.8/\text{Ti}$ is computed from the $\text{O } 1s$ component centered at lower $\text{BE} = 529.8$ eV, assigned to oxygen bound to titanium, and from $\text{Ti } 2p$ area. This atomic ratio should be 2 if the film was composed only by TiO_2 , but it is slightly larger mainly due to surface hydroxyls or oxyhydroxyls and/or some substrate oxides, which are also included in $\text{O}529.8$. Moreover, XPS attests that most of the TiCl_4 (precursor) reacted producing titania films in all samples, as shown by the atomic ratios $\text{Cl}/\text{Ti} \ll 4$.

As expected, Erbium is detected in the doped sample. Concerning t_d , XPS shows that the relative amount of Ti greatly increases for a longer time of spin-coating as attested by the Ti/Si ratio which increases from 5.5 for 30 s to 14.3 in a film spin-coated during 45 s. Taking in account that all other parameters (speed, solution volume, precursor concentration and temperature of annealing) are kept constant such variation is compatible

Table 2. XPS atomic ratios

| Parameter | [TiCl ₄] | | Doping | | t_d | |
|-----------|----------------------|-------|-----------|---------------|-------|------|
| | 0.5 M | 0.7 M | Not doped | Doped with Er | 30 s | 45 s |
| Cl/Ti | 0.04 | 0.08 | 0.08 | 0.09 | 0.08 | 0.04 |
| O529.8/Ti | 2.5 | 2.7 | 2.7 | 3.1 | 2.7 | 2.5 |
| Ti/Si | 14.3 | - | - | 1.3 | 5.5 | 14.3 |
| Er/Ti | | | | 0.04 | | |

**Fig. 3.** - XPS regions: (a) – Ti 2p, (b) – O 1s, and (c) – Er 4d**Fig. 4.** AFM $1 \times 1 \mu\text{m}^2$ images of TiO₂ thin films covering glass substrates: (a) – TiO₂ spin-coated film with a 0.7 M solution for 45 s, RMS = 6 nm, Z_{max} (white) = 40 nm; (b) – TiO₂ spin-coated film with a 0.5 M solution for 30 s, RMS = 5.3 nm, Z_{max} (white) = 38 nm; (c) TiO₂ film doped with Er, (0.7 M TiCl₄ with 1 % Er, spin-coated for 45 s), RMS = 3.7 nm, Z_{max} (white) = 18 nm

with a much better covered glass substrate with the titania layer when using longer times of spin. Additionally, in a sample spin-coated twice (that is with 2 spin-coatings of 30 s each), no significant changes in the films chemical compositions occur with the additional deposition (not shown).

4.3 AFM: Surface morphology of the TiO₂ films

The AFM was used to study the effect of the time of deposition and precursor concentration, and also of the

doping with Erbium, on the TiO₂ films topography. In Figure 4 the AFM topographic images for TiO₂ undoped (a) and (b) and doped films (c) are shown with the respective surface roughness mean square coefficient (RMS).

While the undoped TiO₂ films, Fig. 4(a),(b) are composed by aggregated nano objects, the TiO₂ film doped with Er, Fig. 4(c) has a completely different topography, with no visible nano objects (at least at this amplification): The doping has also a significant effect on the film roughness: with the addition of Erbium to the spreading solution, the TiO₂ film roughness (RMS) decreases from

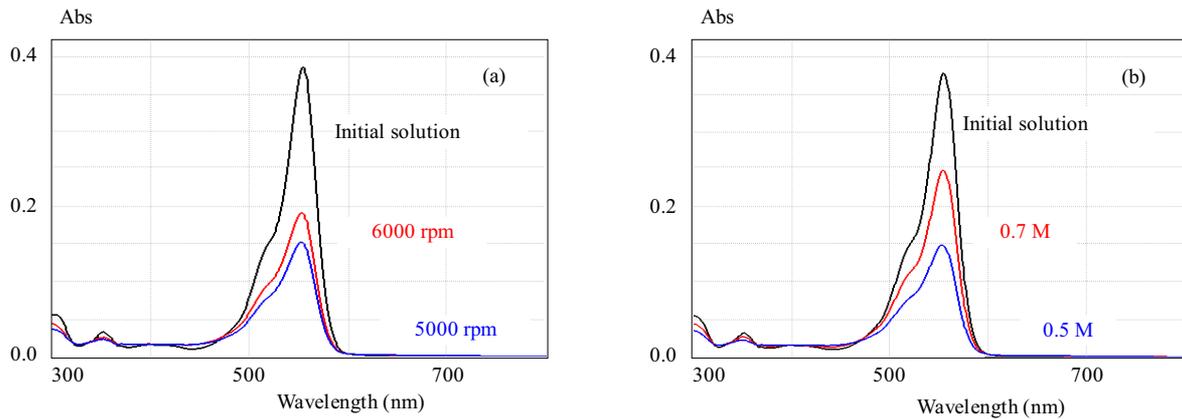


Fig. 5. UV - Visible absorbance spectra of RhB solution after 4 h of illumination in the presence of TiO₂ photocatalyst films: (a) – with spin - coating speed variation, (b) – with TiO₂ precursor concentration variation

6 nm to 3.7 nm, indicating that the surface of the film becomes smoother. The effect of the number of spin-coatings on the layer morphology was also studied by AFM, but no significant differences were detected (not shown).

4.4 Photocatalysis

The photocatalysis is an environmentally friendly alternative for the water treatment [20]. The dyes weaken the light penetration in water and disturb the ecological system by decreasing the photosynthetic activity due to the strong water coloration. Anatase titania (TiO₂) has been studied extensively in the last few decades for its high efficiency photocatalytic properties by using the sunlight for UV source, a cheaper and more ecological alternative. As reported in the literature [19], the anatase phase has better response with ultraviolet photons and for this reason it is used for photocatalysis. The photocatalytic behaviour of the films was studied by degrading Rhodamine-B (RhB) dye which is a typical pollutant in the effluent stream of dye industry. A 3 cm² TiO₂ film was immersed in 10 ml of aqueous RhB solution (10 ppm) and under sunlight irradiation during 4 h (from 11 am to 15 pm). The decomposition testing with and without TiO₂ thin films was carried out using UV-visible absorption as shown in Fig. 5. From this figure it can be observed that RhB dye exhibits a strong absorption at 553 nm which results in a broad asymmetric peak.

The photo-degradation efficiency is defined as

$$\eta = \frac{A_i - A_f}{A_i},$$

where A_i and A_f are respectively the initial and final absorptions of RhB by the solution. In Tab. 3 we report the adequate efficiencies of TiO₂ under different conditions.

Table 3. TiO₂ efficiencies at different conditions

| Sample | 1 | 3 | 4 |
|------------|----------|----------|----------|
| M/rpm | 0.7/5000 | 0.5/6000 | 0.5/5000 |
| Efficiency | 0.342 | 0.526 | 0.608 |

The films with concentration of 0.5 M and speed of 5000 rpm show the maximum degradation efficiency of 60.78% after an irradiation time of 4 h. When we analyze the atomic concentrations (%) and relevant atomic ratios of our thin film by XPS, it can be concluded that the thin film of 5000 rpm of concentration 0.5 M has the highest photoactivity when the atomic ratio O/Ti closer to the stoichiometric ratio for titanium.

5 Conclusion

TiO₂ thin films were prepared by spin-coating sol-gel route at various experimental conditions by using an alcoholic solution of TiCl₄ as titanium precursor. Thin films are advantageous because of their low cost fabrication. The results on the adherence and the uniformity of the layer showed that the optimized speed of spin and td were 5000 rpm and 45 s, respectively. The X-ray diffraction was used to identify the crystalline characteristics of TiO₂ and the chemical states and relative amounts of the main elements existing in the samples were investigated by X-ray Photoelectron Spectroscopy (XPS). XRD results show a dependence on the temperature of crystallization. XPS attests that most of the TiCl₄ (precursor) reacted producing titania films in all samples, although the extreme surface can also be composed by titanium hydroxyls or oxyhydroxyls. Raman spectra show the characteristic peaks of anatase (tetragonal). Moreover, no significant changes occur with an additional deposition, but the relative amount of Ti increases for a longer time of spin-coating. AFM images show that the TiO₂ film has a granular morphology which is very different from the smoother film of doped TiO₂. Rhodamine B is a recalcitrant dye and as application, TiO₂ films were successfully tested for its oxidation under sunlight. An abatement of 60% was obtained under sunlight for an initial concentration of 10 mg/l. The diminishing of the absorbance band at 553 nm is very noticeable indicating good photocatalytic activity. As a main result is the strong degradation of the thin film for 0.5 M and 5000 rpm.

Acknowledgements

The authors would like to thank Fundao para a Cincia e a Tecnologia (FCT), Portugal, for support with project UID/NAN/50024/2013 and fellowships SFRH/BPD/108338/2015 and SFRH/BD/95358/2013. The authors would also like to thank Dr Nadia Saoula from Centre de Developpement des technologies avances (CDTA), Algiers, for the Raman measurements.

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Received 23 April 2017

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