

Formation of smooth and rough TiO₂ thin films on fiberglass by sol-gel method

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Abstract. Substrate dipping in a composite sol-gel solution was used to prepare smooth and rough thin films of TiO₂ on fiberglass. The deposition of films was done using a solution of titanium (IV) isopropoxide as sol-gel precursor and cetyltrimethyl-ammonium bromide as surfactant. The samples were characterized using Raman and Uv-vis spectroscopy, scanning and atomic force microscopy. In some cases, films only consisted of the titanium precursor gel. A TiO₂ 61-nm film was obtained with a short immersion of fiberglass into the sol-gel without surfactant. In other cases, the deposited film consisted of a titanium precursor gel encapsulating micelles of surfactant. In each sample, gel film is converted only to the anatase phase by calcining it at 500 °C. It was found that the TiO₂ film prepared from the sol-gel with surfactant shows a granular microstructure, and is composed of about 2 μm irregular particles. Smooth TiO₂ films could have useful optical and corrosion-protective properties and by other hand, roughness on TiO₂ films can enhance the inherent photocatalytic activity.

Keywords: Sol-gel deposition, fiber-glass, TiO₂, thin films.

Resumen. Se ha usado la inmersión de sustratos en un sol-gel hecho de un compuesto para preparar películas delgadas de TiO₂, ya sean lisas o rugosas sobre fibra de vidrio. La deposición de películas se hizo desde una solución de isopropóxido de titanio (IV) como precursor del sol-gel y bromuro de cetil-trimetil-amonio como surfactante. Las muestras fueron caracterizadas usando las técnicas de espectroscopia Raman y Uv-visible, así como la microscopia electrónica de barrido y de fuerza atómica. En casos especiales, la deposición de película consiste en un gel precursor de titanio que encapsula micelas de surfactante. La película de gel es convertida a la fase anatasa por calcinación a 500 °C, las películas lisas de TiO₂ pueden tener propiedades ópticas y protectoras y la rugosidad de las películas de TiO₂ puede aumentar su inherente actividad foto catalítica.

Palabras clave: Sol-gel depositado, fibra de vidrio, TiO₂, películas delgadas.

Introduction

Metallic oxide films are solid-state systems mainly composed of crystalline layers. Titanium dioxide (TiO₂) films are systems that may have many applications mainly as photocatalytic devices. For example, Robert et al. [1] reported the effective detoxification of benzamide using TiO₂ immobilized on glass fibers. The photocatalytic activity of TiO₂ films was tested by using methyl orange degradation [2]. Recent trends in the modification of TiO₂ films for enhancing the photocatalytic efficiency involve the incorporation of other species or surface treatments. Thus, the activity of a silane agent-TiO₂ film was tested in the photodegradation of salicylic acid in water [3], nanocrystalline TiO₂ thin films were examined in 3,5-dichlorophenol degradation [4], and the activity of mesoporous TiO₂ thin films was evaluated in the decomposition of acetone in air [5].

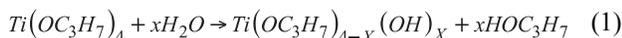
Using conventional methods TiO₂ (anatase) films have been prepared in several ways: Thin amorphous films of titanium prepared by reactive evaporation [6], epitaxial films deposited by a pulsed laser deposition (PLD) technique [7], remote plasma enhanced chemical vapor deposition of precursors such as titanium tetra-isopropoxide [8], the utilization of a

KrF laser [9] and UV radiation [10]. More recently, novel methods have been used to obtain thin films of anatase phases on different substrates: TiO₂ immobilized on glass-tubes of UV lamps by a hydrothermal method [11], amorphous TiO₂ deposited on glass beds using a plasma-CVD reactor [12], TiO₂ supported on ZSM-5 zeolite by a sol method [13], TiO₂ immobilized on a flexible fiberglass cloth using different procedures [14], and transparent films deposited on polymer substrates with crystallization of sol-gel TiO₂ films at low temperatures [15]. In many studies TiO₂ films have been immobilized on glass substrates using the sol-gel technique [4,16] and from the majority of these systems; their photocatalytic activity was used to abate water pollution [17,18].

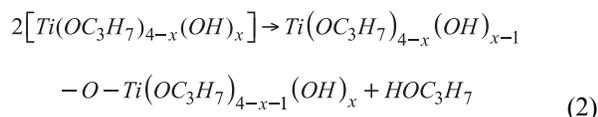
Fiberglass is an interesting material for use as a support of catalytic species since it is economical, flexible, corrosion resistant and easy to handle. In this work, we have prepared TiO₂ films on this material in order to generate mainly a novel photocatalytic material. A detailed preparation process, consisting of a simple immersion method at room temperature, will be described. Moreover, differences between both smooth and rough surfaces and the effect of thickness will be related to the physical properties of TiO₂ films calcined at 500 °C.

Results and discussion

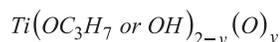
In the sol-gel transition, the precursor powder (TIPO) dissolved in ethanol reacts with water and gives hydrolyzed Titanium(IV) isopropoxide and *i*-propanol. This *initial* step is the hydrolysis of the alkoxide according to the Eq. (1).



The *propagation* step is the condensation of the hydrolyzed species, with the bridging of oxygens. The chemical reaction that takes place is given by Eq. (2). Each new *alcoxolation* step is accompanied by the formation of a *i*-propanol molecule.



The final material before calcining has the following chemical composition, where every titanium atom is forming part of the network.

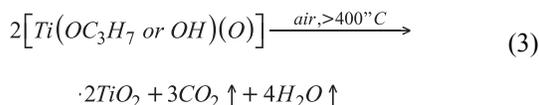


where y can be 1 or 2.

A complete process is conformed by the dip-coating and condensation steps to form a composite layer. A portion of surfactant can be added to give roughness and increase the thickness of the film. Moreover, the addition of surfactants to the titanium alkoxide solution can be effective to diminish the transition temperature of anatase to rutile phase [19].

All films were adhered to the glass substrate and stable for a long period, when they were kept in the ambient atmosphere. The deposited thin film undergoes solvent evaporation, solute condensation and thermal decomposition, thereby resulting in the formation of titanium dioxide films.

After calcination, every oxygen is bonded with a Ti atom and hence a pure and highly homogeneous oxide network is obtained (TiO₂). For this step, Eq. (3) is proposed when every Ti atom is surrounded by three O atoms and one -OH bond or one -OR group, into the network of the hydrolyzed gel.



Without surfactant in the sol-gel, the 61-nm thin film formed is transparent and iridescent. With a [CTAB]/[TIPO] molar ratio of 1/4 in the sol-gel, the TiO₂ remained of white colour after calcining at 500 °C and it gave a thickness of 538 nm (measured on the microscope slide).

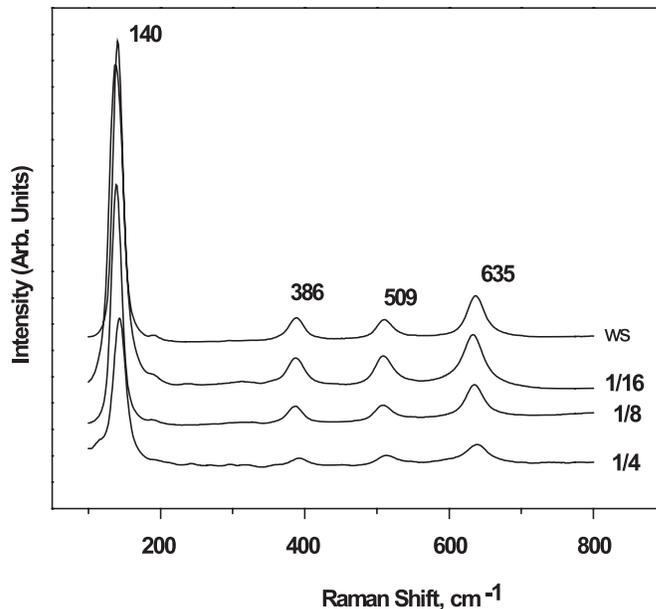


Fig. 1. Raman spectra of the TiO₂ (anatase) films. The molar ratios of [CTAB]/[TIPO] in the sol-gel are shown for each spectrum.

All TiO₂ films deposited on microscope slides approved the adhesion test since they remained unchanged after removing the adhesive tape. The adhesion of the TiO₂ films to the fiberglass was considered to be good since for all these samples, the film coating did not exhibit any peeling after washing with warm ethanol.

Fig. 1 shows Raman spectra of TiO₂ films obtained from a sol-gel without surfactant or with different [CTAB]/[TIPO] molar ratio and heat-treated at 500 °C in air for 1 hr.

The Raman spectrum of the thin film obtained without surfactant is not obscured by the fluorescence signal from the substrate. Therefore, Raman spectra obtained were not interfered by the glass substrate. The 100 -1000 cm⁻¹ Raman spectra region from Fig. 1, shows four well-defined peaks at 140, 386, 509 and 635 cm⁻¹ and they are assigned to the anatase tetragonal-structure in agreement with a previous report [20]. Differences with data reported in the literature are reasonable due to the structural distortions into the thin film or by intra-grain defects in samples. Raman spectra bands for rutile are reported around 144-147, 238-240, 447-448 and 610-612 cm⁻¹ [21, 22]. The spectrum of TiO₂ rutile, prepared from a xerogel and calcined at high temperatures, showed two main peaks at 448 and 612 cm⁻¹ [22]. Therefore, in this work the stronger band around of 448 cm⁻¹ was used to identify a possible signal of rutile phase in the TiO₂ film.

Based on the factor group analysis and regarding the Raman active modes reported in the literature [23, 24], Raman mode characteristics for anatase are given in Table 1.

As can be seen in Fig. 1, TiO₂ film obtained from a sol-gel with a [CTAB]/[TIPO] molar ratio of 1/4 shows peaks with less intensity than those obtained from a solution with a

Table 1. Frequency and assignment of the Raman bands of anatase and rutile TiO₂.

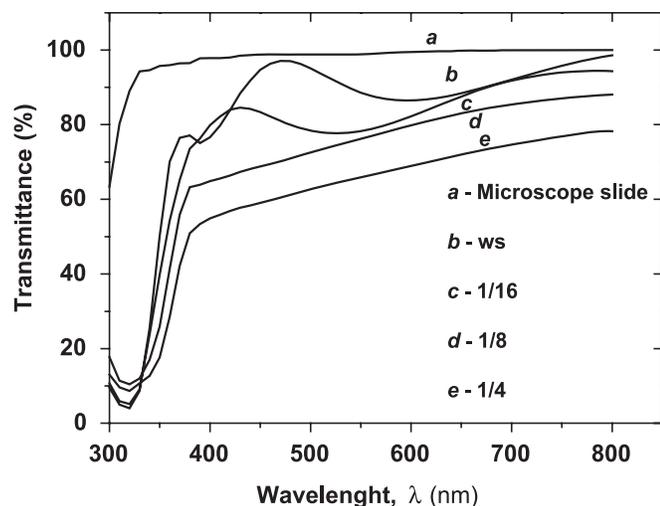
Phase (cm ⁻¹)	Frequency work	In this	Assignment	Signal
Anatase	143	140	B _{1g}	Very intense
	197	198	E _g	Very weak
	398	386	B _{1g}	Intense
	513	509	A _{1g} , B _{1g}	Less intense
	639	635	E _g	Less intense

lower molar ratio. Typically, at higher amount of surfactant in the composite films, the Raman spectra are less intense due mainly to a lower density of TiO₂ in the final film.

The presence of rutile phase was not detected in these Raman spectra since the 448 cm⁻¹ peak cannot be seen even after heat-treatment at 500 °C. This statement agrees with Djaoued [25], who observed only the typical bands of anatase in the spectra of TiO₂ films calcined at 700 °C. In that work, a mixture of anatase and rutile was observed in samples treated at 800 °C. Pure rutile phase was obtained at 900 °C.

Fig. 2 shows the UV-vis transmittance (T %) spectra of TiO₂ films on the microscope slides in the wavelength range 300-800 nm. In the visible region and specifically at 475 nm, transmittance for the TiO₂ film prepared without surfactant was of 95%, while than that of the microscope slide (glass substrate) was of about 98%.

Transmittance values at 600 nm for the TiO₂ films were 85, 81, 78 and 67% for the samples WS, 1/16, 1/8 and 1/4. The difference of transmittance between TiO₂ films in the 500-800 nm range was attributed to the difference in their film thickness. The thickness of these films is 61, 230, 315 and 538 nm, respectively. This parameter can be easily tailored by varying the withdrawal rate and the [TIPO]/[ethanol] ratio in

**Fig. 2.** Optical transmittance (T%) of the TiO₂ thin films. The molar ratios of [CTAB]/[TIPO] in the sol-gel are shown for each spectrum.

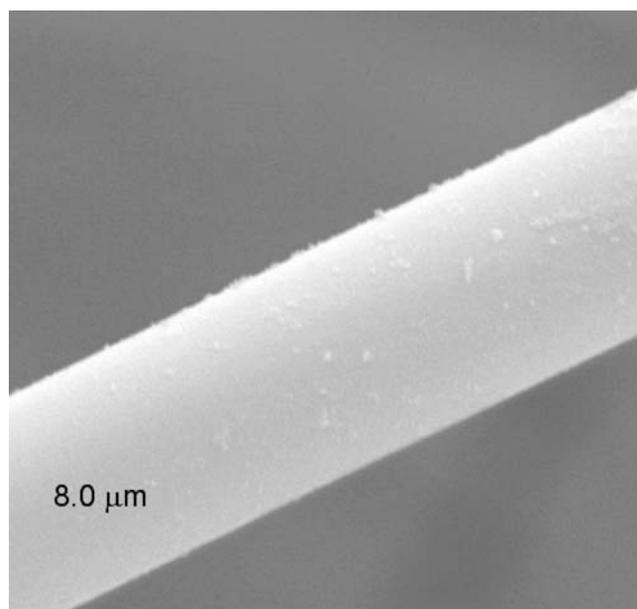
the solution. Thus, a film with a thickness greater than 60 nm can be formed without surfactant if a [TIPO]/[ethanol] ratio higher is used. A film with the thickness less than 538 nm can be formed at [CTAB]/[TIPO] ratio of 1/4 by using a shorter dip-coating time.

At about 380 nm the transmittance decreases quickly for all films and approaches to zero at around 330 nm. This fast decrease in transmittance is due to absorption of light caused by the excitation and migration of electrons from the valence band to the conduction band of TiO₂.

After dissolving the TiO₂ films from the fiberglass, the content of titanium in each coated fiberglass mentioned above was determined to be of 0.28, 0.46, 0.44 and 0.42 wt.% from AAS analysis. With CTAB, micelles formed attract the species that are present in the solution forming aggregates and therefore thickener films. This seems to be the most probable reason for the difference in wt.% Ti between the unmodified and surfactant modified coating.

Surface areas of the TiO₂ thin films on the fiberglass could not be measured directly by the adsorption apparatus because the amount of TiO₂ was too small. Instead surface areas of the powder samples, prepared through the same procedure as the thin films, were measured. The BET surface area of the TiO₂ powder prepared from a sol-gel with a molar ratio of [CTAB]/[TIPO] = 1/4 gave a similar value (54 m² g⁻¹) than that of the commercial material called Degussa P-25 [21]. However, surface areas of the other TiO₂ powders were smaller than that of this commercial titania.

The SEM image of the surface morphology of the TiO₂ film deposited with a molar ratio of [CTAB]/[TIPO] = 1/4 on fiberglass is shown in Fig. 3. As shown on the image, the TiO₂ coating completely covers the substrate and the film reveals a homogeneous granular surface. These grains correspond to

**Fig. 3.** SEM image of the TiO₂ film deposited on fiberglass.

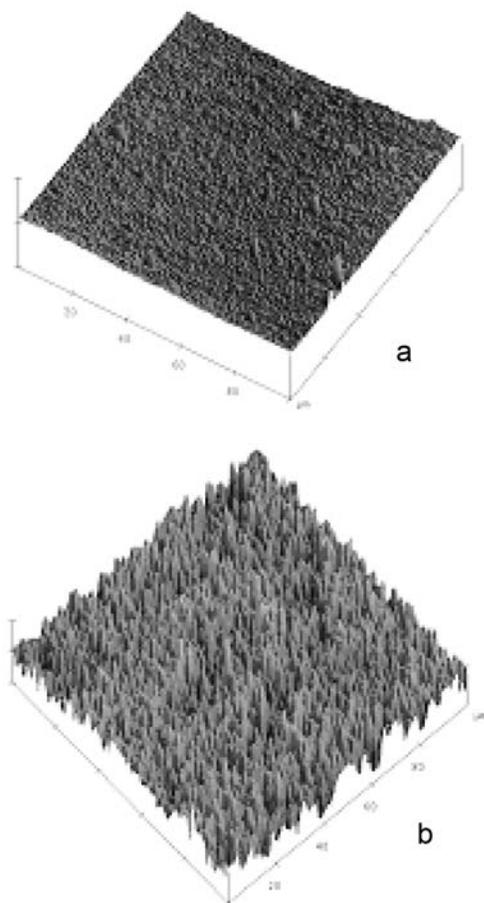


Fig. 4. AFM images of the smooth (a) and rough (b) TiO₂ films deposited on microscope slides.

small aggregates of microcrystallites depicted by AF microscopy.

Three-dimensional AFM images of the smooth (WS) and a rough ([CTAB]/[TIPO] = 1/4) TiO₂ thin films deposited on microscope slides are illustrated in Fig. 4.

At low surfactant concentrations in the micellar solution promotes a mesoporosity into the resultant material, whereas at higher concentrations, appear giving an irregular matrix or a combination of small pores of two different sizes [26]. In this work the high roughness structure observed by AFM can be attributed to the much higher surfactant concentration used. At high surfactant concentration, a coalescence of the ordered clusters of surfactant molecules is favored to produce lamellar lattices or unordered cluster of micelles [19]. Figures 4a and b show that the surface morphology of the modified TiO₂ film is rougher than that of the WS film. Similar roughness surfaces were reported by Yu et al. for mesoporous films [5]. The material in Yu's work presented morphologies with a surface roughness between 0.59 and 1.06 nm. In the present work from the roughness analysis, the R_{ms} values of the samples 1/4 and WS are 16.96 and 0.82 nm. The physical properties of the materials are reported in Table 2.

Table 2. Characterization data of the TiO₂ films and powders

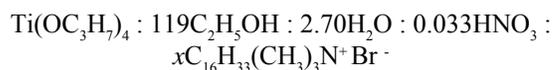
Sample	Crystallite size by XRD (Å)	TiO ₂ Loading (mg/g)	Film thickness (nm)	Surface roughness (nm)	Powders Surface area (m ² /g)
F-WS	240	2.87	61	0.82	< 5
F-1/16	241	4.58	230	1.86	5
F-1/8	244	4.38	315	6.03	9
F-1/4	250	4.21	538	16.96	54

Experimental Methods

The thin films of TiO₂ were deposited by dip-coating in a sol-gel solution according to Wu et al. [3]. The substrate used was a piece of a 8 - mm fiberglass purchased from Corning Inc. Glass microscope slides were also used as substrates for reference samples. The substrates were cleaned for 2 h in an ultrasound bath with isopropanol, and then dried in an oven at 90 °C for 1 h.

The preparation procedure of TiO₂ films by the sol-gel method was as follows: 2.97 mL of titanium (IV) isopropoxide of Aldrich (TIPO) were dissolved in 30 mL of ethanol (J.T. Baker) and stirred for 1 h. In several experiments, a micellar solution was prepared dissolving cetyltrimethyl ammonium bromide (CTAB) in 20 mL of ethanol followed by 30 min in stirring. The TIPO solution was added to the micellar solution by dropping also followed by 30 min in stirring. Then 0.5 mL of diluted HNO₃ (in distilled water, 1/32: v/v) and 12 mL of ethanol were added to induce hydrolysis in the resultant solution.

The molar composition of the starting alkoxide solution was,



The amount (or the factor x) of CTAB was adjusted to obtain a molar ratio of CTAB to TIPO of 1/16, 1/8 and 1/4. The composite films were deposited on the glass substrates by dipping and coating them in the sol-gel solution at room temperature. The concentration of the surfactant used in the different preparations was approximately 20, 40 and 80 times the critical micelle concentrations (cmc) as determined by comparison with the literature [26, 27].

One sample of fiberglass was prepared without surfactant (WS), and three samples more (0.5 g each) with different [CTAB]/[TIPO] molar ratio. After the solution was prepared, the substrates were dipped in the solution for 30 s and withdrawn at a constant rate of 20 cm/min. One side of the microscope slides was covered with removable tape in order to avoid the deposit on it. Coated samples were washed with distilled water and dried at ambient conditions. The substrates coated with composite films were then heat-treated at 500 °C for 3 h in air in a furnace. Powder samples were also prepared

from the same sol-gel which was aged at room temperature for 5 days and then dried at 120° C in air to obtain a gel. The solid was heat-treated in the same way than the film samples and then ground to powder with an agate mortar.

It was found that both WS and 1/16 samples result with a thin, nearly transparent film. With a [CTAB]/[TIPO] molar ratio of 1/8 or 1/4 in the sol-gel, the composite films on the microscope slides and on the fiberglass showed a white colour.

The adhesion of TiO₂ films was tested by immersing the coated fiber in a stirred ethanol bath maintained at 50 °C for 1 h. The adhesions of films on planar surfaces were tested by applying an adhesive tape and removing it abruptly [28].

The TiO₂ films deposited on fiberglass were examined using several techniques. Raman spectra were obtained with an instrumental setup using a He-Ne laser (632.8 nm) and 10 mW of power at the sample. Characteristic peaks for anatase were determined by comparing their relative positions and intensities with that reported previously [23].

A Visible Spectrophotometer (Macbeth model 7000) with a resolution of 0.1 nm was used to get the optical transmittance spectra. In order to obtain better spectra, the optical measurements were carried out in TiO₂ films deposited on microscope slides. A Film Tek 3000 SCI system was coupled to the spectrophotometer to measure film thickness. This system simultaneously solves for refractive index n (λ), extinction coefficient k (λ) and optimises both the reflectance and power density spectrum (FFT). A self-consistent solution is obtained by using a generalised dispersion formula to model fitted values of the dielectric function ϵ (λ). Thickness determination can be done in the range of 5-550nm with a 6% of accuracy.

The surface and pore structure of the result powders were analyzed using nitrogen adsorption measurements with an Accusorb 2100-E porosimeter. The titanium content of the coated fiberglass was determined by atomic absorption spectrophotometry AAS (Perkin Elmer Analyst 100) operating in the flame mode. The TiO₂ coating was dissolved by adding 0.1 g of the coated fiberglass to 5 mL of 50% HCl in deionized water (v/v). This mixture was heated at 60 °C for 30 min to dissolve titanium oxides completely. The final solution was cooled, filtered and transferred to a 50-mL volumetric flask and diluted to volume with deionized water.

A scanning electron microscope (SEM) model JEOL 1100 was used to observe the film surface on the fiberglass. Samples were gold-coated prior to examination. Contact mode atomic force microscopy (AFM) observations of TiO₂ films were carried out at room temperature using a Nanoscope III (Digital Instruments).

Conclusions

One of the most important results is that a TiO₂ 61-nm film can be obtained with a short immersion of fiberglass into the sol-gel without surfactant. In other cases, the deposited film

consisted of a titanium precursor gel encapsulating micelles of surfactant. In all samples, the gel films were converted to the anatase phase by calcining them at 500 °C.

Both smooth and rough anatase thin films were obtained with a short immersion of fiberglass into the sol-gel with or without surfactant. The structural properties of smooth and rough TiO₂ films deposited on fiberglass were characterized by Raman and Uv-vis Spectroscopy, SEM and AFM.

By scanning electron microscopy, we found that all TiO₂ thin films deposited on fiberglass after a short immersion into the sol-gel were homogeneous and continuous.

The gel film deposited on glass changes from a composite structure to TiO₂ when is calcined at 500 °C. The Raman study carried on the TiO₂ films showed that the films are formed predominantly of anatase phase. Nevertheless, this also could depend on the duration of the thermal treatment.

By AFM technique, we found that the TiO₂ film prepared from the sol-gel with surfactant shows a granular microstructure, and is composed of about 2 μ m irregular particles.

Optical sensors or semiconductor wires are potential applications of these fibers with TiO₂ film. Moreover, this novel material could be used as a catalytic material in some oxidation processes or photo degradation reactions.

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