THE INFLUENCE OF THE PRECURSOR TYPE AND OF THE SUBSTRATE ON THE SPD DEPOSITED TIO₂ PHOTOCATALYTIC THIN FILMS

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Article Info	Abstract
	Photocatalytic degradation of organic pollutants from wastewater using titanium dioxide is recognized as an efficient process. To be feasible, this process needs to be solar- or visible light -activated, but, due to its wide band gap energy, titanium dioxide can only be activated by ultraviolet radiation. In this paper, thin films of titanium dioxide were deposited by Spray Pyrolysis Deposition using organo-metallic (titanium-iso-propoxide) and inorganic (titanium chloride) precursors, as a first step in optimizing the deposition process of titanium dioxide - carbon composite thin films, active in the visible spectral range. The thin films were characterized to outline the differences when using these two precursor solutions, when deposited on Fluorine doped Tin Oxide-glass, regular glass and microscopic glass, in terms of crystallinity (by using X-ray diffraction), elemental composition (using Energy Dispersive X-ray spectrometry), surface morphology (Scanning Electronic Microscopy and Atomic Force Microscopy). The photocatalytic activity of the titanium dioxide thin films was investigated based on the removal efficiencies of methylene blue from a synthetically prepared wastewater. The samples deposited using the inorganic precursor show higher roughness, and this proves to be the most important factor that influences the phocatalytic processes. After 8 hours of ultraviolet irradiation, methylene blue removal efficiencies up to 36% were observed; the highest removal efficiency was registered using the thin titanium dioxide film obtained using the titanium chloride precursor, deposited on fluorine doped tin oxide glass substrate, due to the titanium dioxide-tin dioxide semiconductor tandem formed at the interface, that limits the electron-hole recombination, thus increasing the photoctalytic performance of the substrate.

1. Introduction

During the past decades, wastewater became one of the major problems of humanity. Wastewater treatment represents a serious challenge for the scientists all around the world, particularly considering the aim of re-use that can be a feasible and viable future option. For

this aim, the advanced oxidation processes are intensively studied, especially heterogeneous photocatalysis is recognized to be efficient in the total mineralization of the organic pollutants due to the species produced during the photocatalytic reactions [1]. The photocatalytic process has many advantages, as the pollutants removal at low concentrations, down to ppm and even in the ppb range, complete oxidation of organic pollutants without the formation of toxic by-products and the use of available and low cost catalysts [2]. The mostly reported catalyst used in heterogeneous photocatalysis is titanium dioxide, TiO_2 which fulfills a set of essential proprieties: high stability in various aqueous conditions, rather low-cost, and non-toxicity [3]. The main problem that limits the titanium dioxide large-scale implementation is its band gap of 3.2 eV that makes possible the TiO_2 activation only by UV light, thus increasing the process costs. Significantly lower costs are met when the photocatalyst activation can be done using solar radiation, thus the photocatalytic material is activated by radiation mainly in the VIS spectral range.

To solve the VIS-activation problem, titanium dioxide has to be combined with other compounds. Many papers report on the use dopants to lower the titanium dioxide band gap [4], or on the development of tandem or diode type structures to get a proper energy bands alignment that supports VIS activation.

Recent papers show that TiO_2 can be mixed with various carbon nanostructures to obtain VIS-activated composites; graphene-based compounds are a new type of 2D nanomaterials that improve the electrical conductivity of the charge carriers, thus reducing recombination, and increase the specific surface to support the pollutant adsorption onto the photocatalyst [5]. Regardless the synthesis method, these composites must have the TiO_2 matrix well characterized and optimized.

There are different methods to prepare TiO_2 thin films as the doctor blade method that starts from dispersed powders, dip coating, chemical vapor deposition. Spray pyrolysis deposition (SPD) represents a deposition method that can be used to cover large substrate surfaces, making it efficient in obtaining thin films at industrial scale [6].

Depending on the application, reports mention the use of organo-metallic precursors, such as titanium-iso-propoxide (TTIP) or inorganic precursors (e.g. titanium chloride, $TiCl_4$) for the thin films deposition. Chou et al. [7] studied the TiO_2 thin films deposited using TTIP for solar cell fabrication and noted that this precursor leads to the formation of dense thin films thus, by decreasing the contact resistance, the solar cell efficiency increases. Vivo et al.

[8] reported on the influence of the TiO_2 precursor on the performance of solar cells by comparing thin films deposited using TTIP and $TiCl_4$. They concluded that $TiCl_4$ precursor can be an alternative for solar cell fabrication, because of its higher environmental stability. For photocatalytic structures, $TiCl_4$ precursor is preferred, because of the porous morphology of the resulted thin films, this being a key factor in photocatalytic processes [9,10]. However, when the final aim is the development of TiO_2-graphene derivatives composites, both types of TiO_2 matrixes need to be compared and optimized.

This paper reports on TiO_2 thin films obtained by SPD using TTIP and $TiCl_4$ as precursors, on different substrates. The thin films were further used in methylene blue (MB) removal from synthetic wastewater and the effect of the precursors and substrates was investigated to outline which of the films properties have key influence on the process efficiency.

2. Method and samples

Three different square substrates, of 1.5 cm x 1.5 cm, were used for deposition: (1) glass covered with a thin film of fluorine doped tin oxide, FTO (code F), (2) simple (regular) glass (code S) and (3) microscopic glass (code SM); the substrates were cleaned with water and detergent by ultrasonication, followed by rinsing in ethanol and drying in air.

The TiO_2 thin films were obtained using as precursors:

- Titanium tetra-isopropoxide (TTIP $C_{12}H_{28}O_4Ti$, Sigma Aldrich, 97%) mixed with acetylacetone (AcAc $C_5H_8O_2$, Scharlau, 99%) as ligand and ethanol (C_2H_5OH, Chemical Company, 99.3%) as solvent in the 1:1:15 volume ratio.

- Titanium chloride ($TiCl_4$, Acros Organics, 99.9%) mixed with ethanol (C_2H_5OH, Chemical Company, 99.3%) as solvent in the 1:20 volume ratio.

Table 1. Deposition conditions of the TiO_2 thin films

Sample code	Substrate	Precursor	Deposition temperature	Annealing temperature	Annealing duration
F-Ti-A3h	FTO glass	TTIP	400^oC	450^oC	3h
F-Ti-A6h					6h
S-Ti-A3h	Regular glass				3h
S-Ti-A6h					6h

SM-Ti-A3h	Microscopic glass					3h
SM-Ti-A6h						6h
F-Ti(Cl)-A3h	FTO glass					3h
F-Ti(Cl)-A6h						6h
S-Ti(Cl)-A3h	Regular glass	$TiCl_4$				3h
S-Ti(Cl)-A6h						6h
SM-Ti(Cl)-A3h	Microscopic glass					3h
SM-Ti(Cl)-A6h						6h

The TiO_2 thin films were obtained by SPD using an ABB/IRB5400 robot and a heating plate. After deposition, all the thin films were annealed for 3 and for 6 hours, at 450°C, to increase the crystallinity degree. In Table 1 there are presented the sample codes and the deposition conditions of the thin films.

The thin films crystallinity was investigated by X-ray Diffraction (XRD, Bruker D8 Discover, step size 0.02, scan speed 3 s/step, 2θ range from 20 to 70°). Energy Dispersive X-ray spectrometer (EDX Thermo) was used to evaluate the elemental composition of the thin films while the surface morphology of the thin films was investigated using Scanning Electron Microscopy (SEM, Hitachi model S-3400 N type II) and Atomic Force Microscopy (AFM, NT-MDT model BL222RNTE).

The photocatalytic experiments were run in static regime using a cylindrical photo-reactor equipped with 6 UV light tubes (Philips, TL-D BLB 18W/108). The average irradiance on the beaker containing the dye solution and the photocatalyst plate was G = 20 W/m^2, as measured using a pyranometer (Delta-T Devices, type BF3).

A $1.25 \cdot 10^{-5}$ M (4ppm) methylene blue (MB) solution, prepared using ultra-pure water (Siemens LaboStar) was tested, as recommended by the ISO 10678_2010 standard, [11,12]. During the photocatalytic tests, each sample was immersed in 20 mL MB solutions in a quartz beaker and left 1 h in dark to reach the adsorption/desorption equilibrium. Further on, irradiation was started and samples were taken at t = 1, 2, 4, 6 and 8 h to test the residual concentration of MB. For analyzing the MB concentration, 4mL of solution were taken from the beaker and after the analysis the sample is put back into the beaker. The volume of the

tested solution was maintained rigorously constant, as the evaporated water during the experiment was adjusted by adding ultra-pure water.

The MB removal efficiency, η was calculated according to eq. (1):

$$\eta_t = \frac{A_0 - A_t}{A_0} \cdot 100 \tag{1}$$

where: A_0 is the initial absorbance of the dye solution and A_t is the absorbance after t hours from starting the experiment (1 hour in dark and t-1 hours of irradiation), measured at the maximum absorbance wavelength for MB (λ = 665 nm), using a UV–VIS-NIR spectrophotometer (Perkin Elmer Lambda 950). Similarly, the adsorption efficiency was evaluated after one hour in dark.

3. Results and Discussions

The diffraction patterns for the TiO_2 thin films deposited on all three types of substrates (F, S and SM) and annealed at 3 or 6 h showed anatase as main component (Fig. 1). The samples deposited on FTO (Fig. 1a) also show the characteristic peaks for SnO_2 while the films deposited on microscopic glass in Fig. 1c show also MgO that originates from the substrate composition. Based on the diffraction data, the crystallite sizes were calculated using the Scherrer's equation and the results are included in Table 2 along with the crystallinity degree. The results show that the TiO_2 thin films deposited using the TTIP have smaller crystallites than those obtained using $TiCl_4$, but slightly higher crystallinity degree, suggesting that the films from the organo-metallic precursor are the result of a faster and more extended nucleation of the adsorbed TTIP as compared to the $TiCl_4$ on each substrate. The results also show that a longer annealing duration significantly decreases the crystallite sizes obtained using TiCl4, thus a densification process can be expected, while for the films obtained using TTIP this effect is less obvious, confirming that the films are denser from the beginning. Higher crystallite sizes can make the films more efficient by increasing the charge carriers' mobility; a similar effect can be expected when increasing the crystallinity degree.

Table 2. Crystallite size and crystallinity degree in the TiO$_2$ thin films

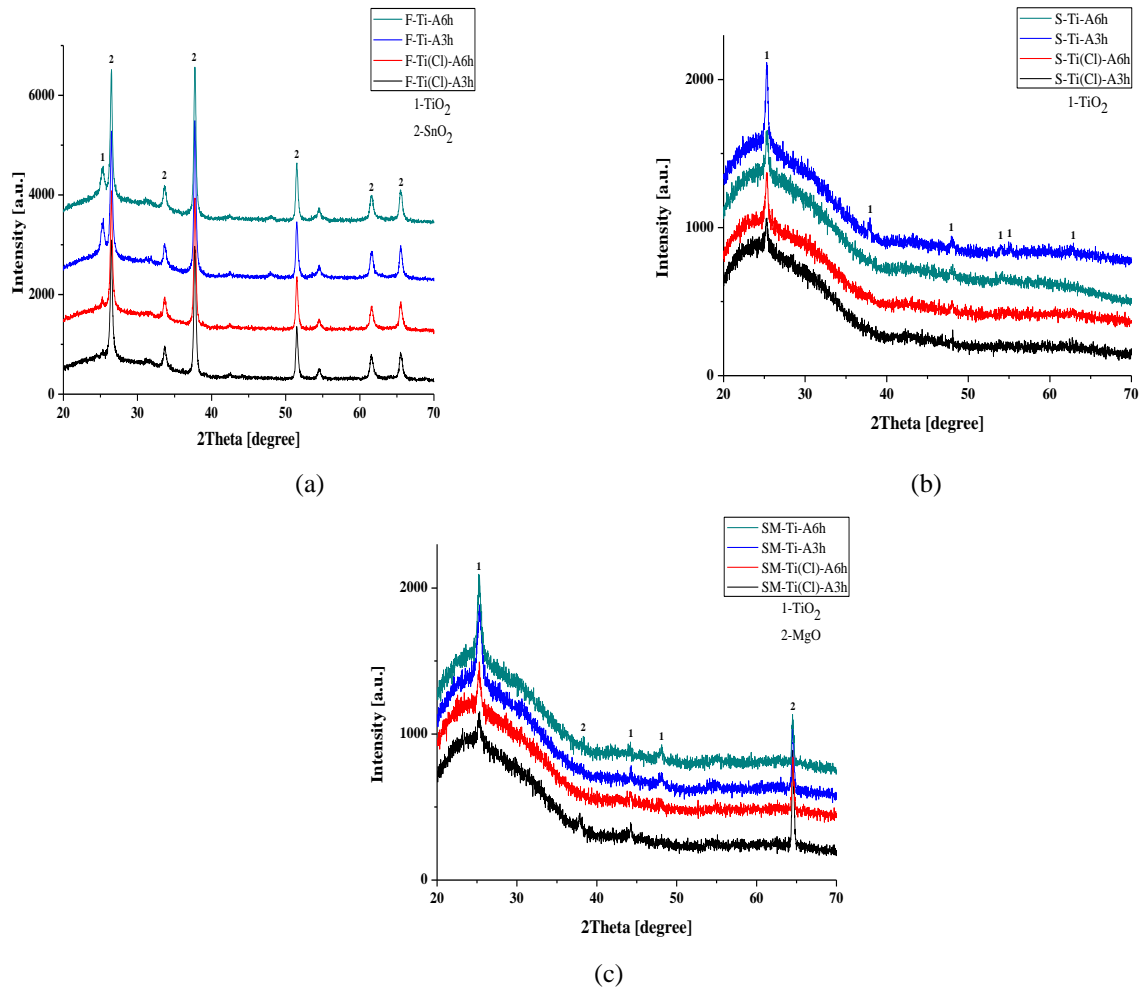| Sample	Crystallite size (Scherrer) [nm]	Crystallinity degree [%]
F-Ti-A3h	18.94	57.2
F-Ti-A6h	19.11	55.8
S-Ti-A3h	24.23	34
S-Ti-A6h	21.98	38.1
SM-Ti-A3h	14.15	38.6
SM-Ti-A6h	15.69	37.9
F-Ti(Cl)-A3h	50.32	56.1
F-Ti(Cl)-A6h	38.65	54.8
S-Ti(Cl)-A3h	32.83	30.4
S-Ti(Cl)-A6h	23.11	33.7
SM-Ti(Cl)-A3h	24.02	40.5
SM-Ti(Cl)-A6h	20,44	37.7

Fig. 1. XRD patterns of the TiO$_2$ thin films deposited on: (a) FTO coated glass; (b) regular glass; (c) microscopic glass substrates

The elemental composition of the films varies depending on the precursor type, as the results of the EDX analysis show, Table 3. The films deposited using TTIP have a more than double atomic percent of titanium then those obtained using $TiCl_4$, and a lower Sn content when deposited on FTO, thus suggesting that the films deposited using TTIP are thicker and/or denser and the crystallites are better organized in the film.

The thin films morphology was investigated using SEM and AFM techniques. The SEM images in Fig.2 show that films contain on the surface TiO_2 aggregates, formed especially when using the inorganic precursor. This can be the result of a less uniform adsorption of the precursor, that runs quite random regardless the type of substrate. However, the largest aggregates are found on the sample obtained using TTIP on microscopic glass (Fig. 2e), while the sample deposited on a similar substrate using $TiCl_4$ (Fig. 2k) has much smaller aggregates, but a more irregular structure. Overall, the thin films obtained using $TiCl_4$ have a larger amount of small aggregates and aggregates clusters, as Fig. 2g - Fig. 2k shows, and this can be the result of the deposition process, when the solvent vaporizes and the concentration of the Ti-precursor in the droplets is increased, supporting a faster reaction that evolves to rougher films than those obtained using TTIP, which needs more time to complete pyrolysis [10]. Because of this, the roughness of TiO_2 films obtained using $TiCl_4$ is significantly higher as it can be observed from the AFM images and roughness values (Fig.3 and Table 4). On the other hand, the films obtained using $TiCl_4$ show many aggregates (Fig. 2g – 2l), mainly consisting of TiO_2 thus, between these agglomerations the titania percent is significantly lower and the films are thinner. These types of aggregates embedded on the film's surface (particularly the small ones distributed all over the surface, e.g. Figs. 2j and 2k and Fig. 3j) can increase the efficiency of the photocatalytic processes by increasing the methylene blue (MB) adsorption.

Table 3. Elemental avearge composition of the TiO_2 thin films

Sample	Element					
	O	Ti	Si	F	Sn	C
F-Ti-A3h	64.58	14.06	2.42	1.13	12.00	5.81
F-Ti-A6h	63.02	13.53	2.99	1.56	14.30	4.60
S-Ti-A3h	63.63	8.82	27.55	-	-	-
S-Ti-A6h	65.41	8.65	25.95	-	-	-
SM-Ti-A3h	62.36	16.46	21.18	-	-	-
SM-Ti-A6h	65.41	8.65	25.95	-	-	-

F-Ti(Cl)-A3h	61.96	6.99	5.11	2.25	18.50	5.18
F-Ti(Cl)-A6h	61.30	7.16	4.99	2.32	19.05	5.17
S-Ti(Cl)-A3h	73.28	3.89	22.83	-	-	-
S-Ti(Cl)-A6h	69.34	3.92	26.75	-	-	-
SM-Ti(Cl)-A3h	61.07	4.62	22.51	-	-	11.80
SM-Ti(Cl)-A6h	58.21	4.40	24.37	-	-	13.02

Table 4. Roughness values of the TiO_2 thin films

Sample	Roughness [nm]	Sample	Roughness [nm]
F-Ti-A3h	7.9	F-Ti(Cl)-A3h	15.8
F-Ti-A6h	7.9	F-Ti(Cl)-A6h	18.1
S-Ti-A3h	4.1	S-Ti(Cl)-A3h	18.9
S-Ti-A6h	2.7	S-Ti(Cl)-A6h	20.4
SM-Ti-A3h	2.3	SM-Ti(Cl)-A3h	13.4
SM-Ti-A6h	4.8	SM-Ti(Cl)-A6h	6.8

The SEM images in Fig. 2 also show that the samples annealed for 6 hours have fewer TiO_2 agglomerations; as the process runs without a significant increase in crystallinity one can conclude that annealing supports the thin films densification, resulting thinner films, as confirmed by the EDX analyses that show the substrate elements in a higher percent, Table 3.

As the results in Table 3 show, the TiO_2 thin film surfaces show a carbon content even when using the inorganic precursor, thus this can be the result of incomplete mineralization of ethanol in the precursors systems. This content is not constant and it may be concluded that the carbon-based compounds are adsorbed by the mostly fractured surfaces.

The thin films were further used for the photocatalytic removal of MB and the results are presented in Fig. 4. The films obtained using $TiCl_4$ lead to slightly higher removal efficiencies after 8 hours of irradiation. The results prove that the surface morphology is the key factor that governs the MB removal process, as the thin films obtained using TTIP, even with a higher crystallinity but with a significantly lower roughness, show a lower MB removal efficiency. The best results are obtained when using TiO_2 thin films deposited on the FTO substrate; due to the fluorine doped SnO_2 content in the FTO layer, tin oxide at the interface can interpenetrate the TiO2 network and the resulted tandem system shows higher photocativity than the pure TiO_2, as already reported in literature, [13], because these tandem structures allows an extended movement of the photogenerated electrons and holes, thus

avoiding the recombination. As the results in Fig. 4 show, the MB removal efficiency has the highest value, close to 36%, when using the F-Ti(Cl)-A3h film.
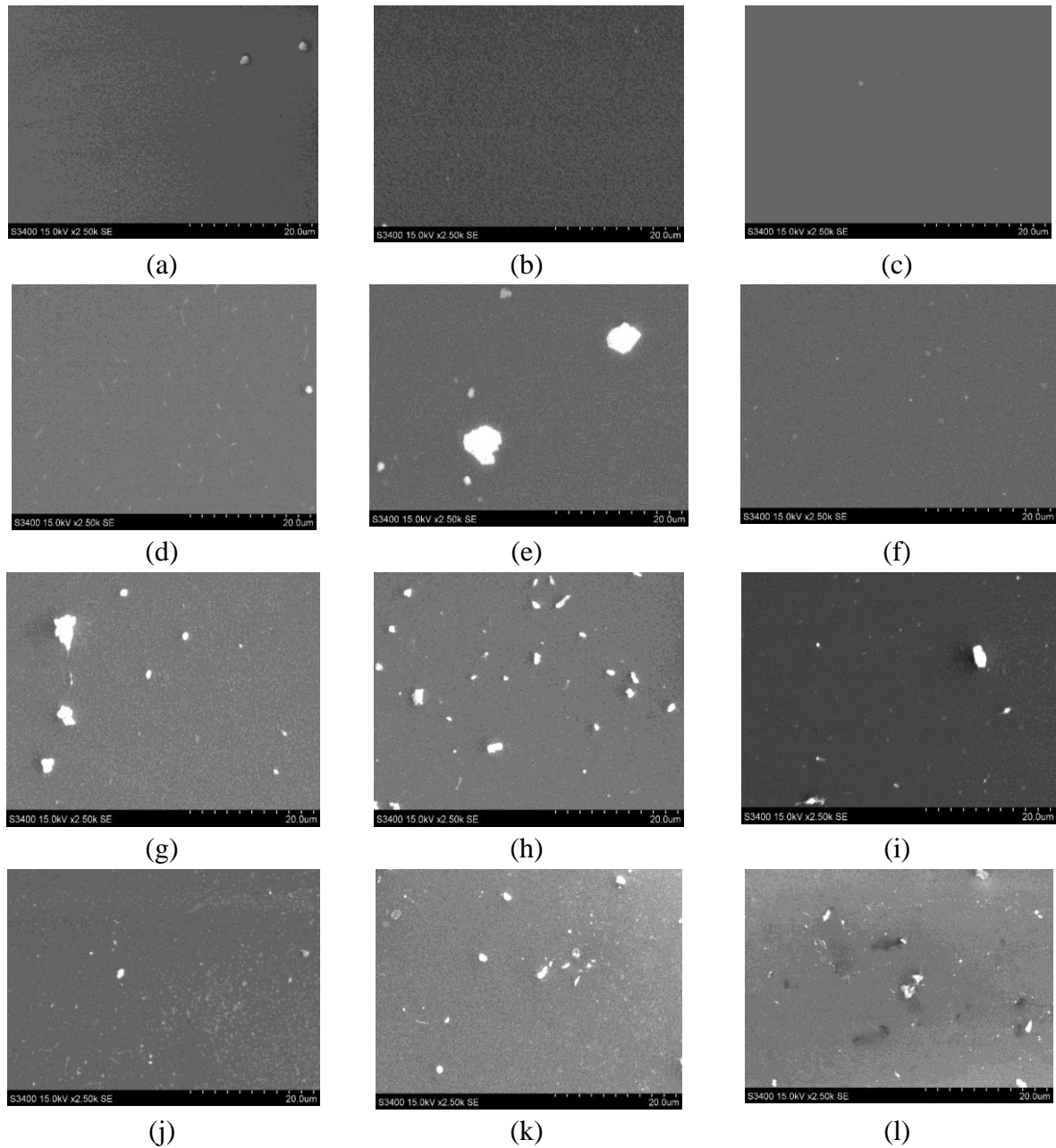

Fig. 2. SEM images of the samples: a. F-Ti-A3h, b. F-Ti-A6h, c. S-Ti-A3h, d. S-Ti-A6h, e. SM-Ti-A3h, f. SM-Ti-A6h, g. F-Ti(Cl)-A3h, h. F-Ti(Cl)-A6h, i. S-Ti(Cl)-A3h, j. S-Ti(Cl)-A6h, k. SM-Ti(Cl)-A3h, l. SM-Ti(Cl)-A6h
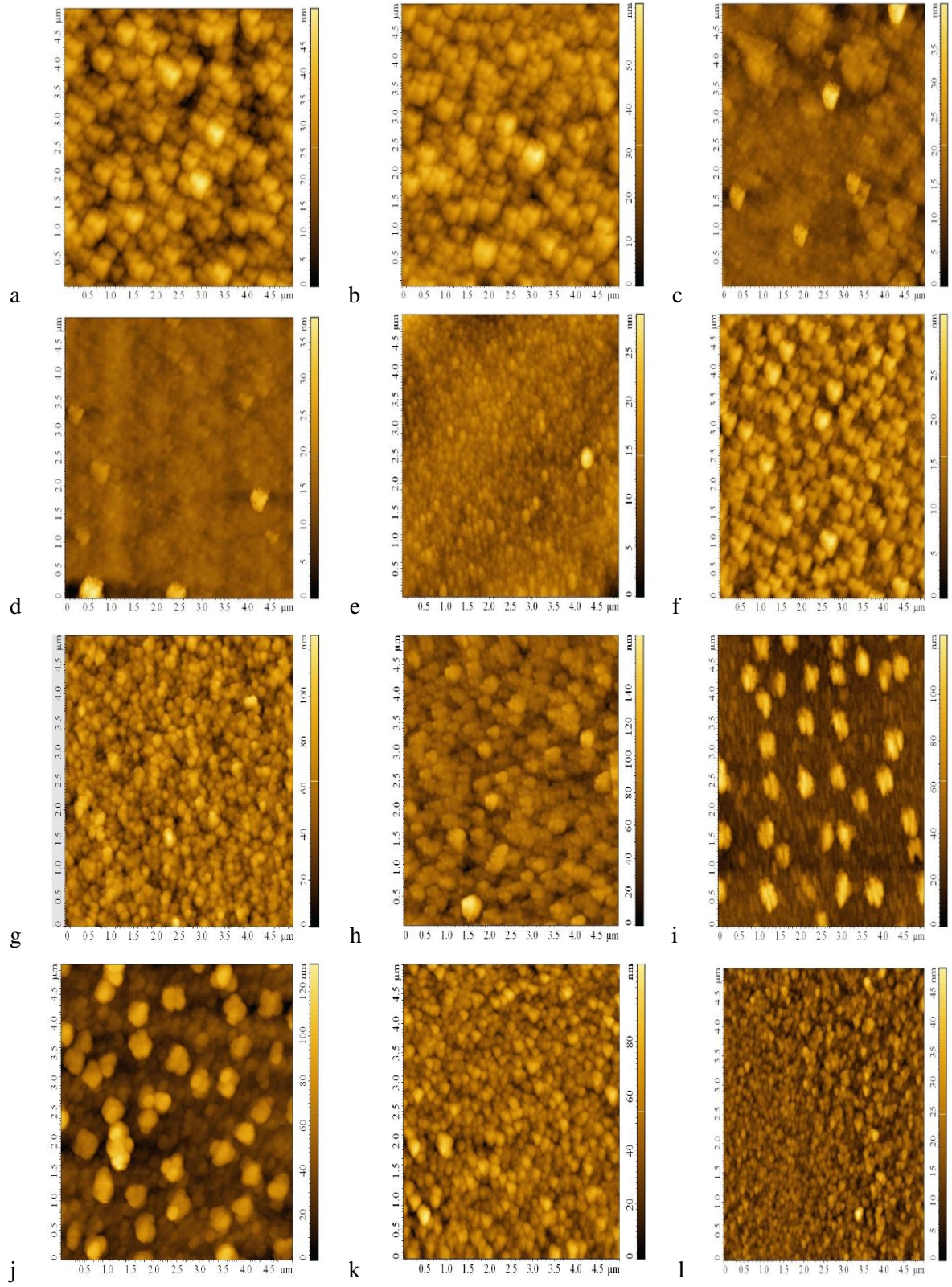
Fig. 3. AFM images of the samples: a. F-Ti-A3h, b. F-Ti-A6h, c. S-Ti-A3h, d. S-Ti-A6h, e. SM-Ti-A3h, f. SM-Ti-A6h, g. F-Ti(Cl)-A3h, h. F-Ti(Cl)-A6h, i. S-Ti(Cl)-A3h, j. S-Ti(Cl)-A6h, k. SM-Ti(Cl)-A3h, l. SM-Ti(Cl)-A6h
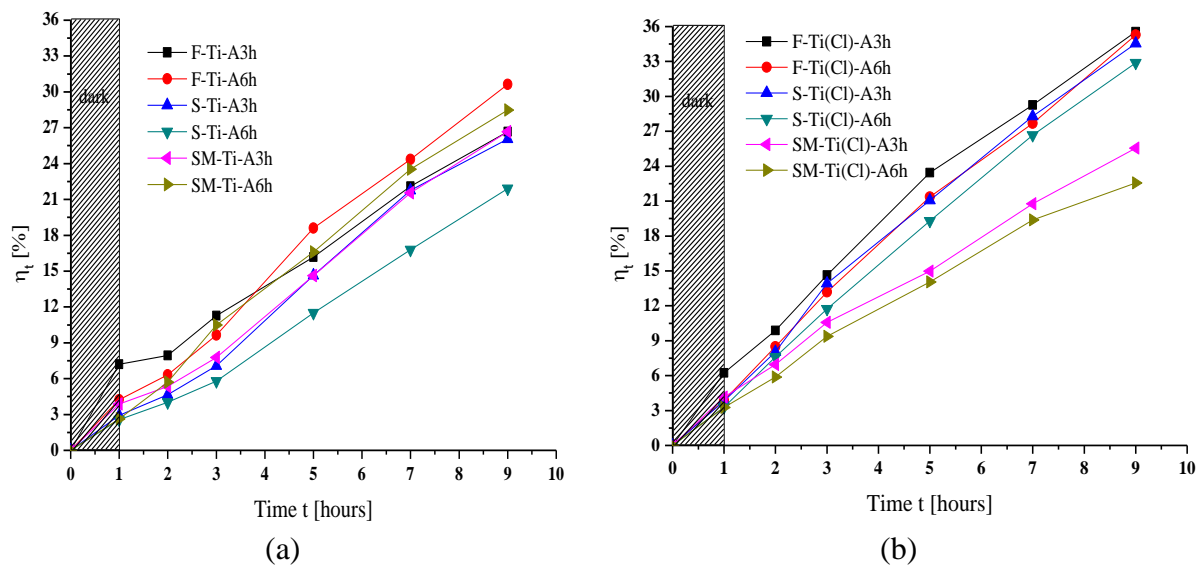
Fig. 4. Efficiency of the photocatalytic removal of MB under UV irradiation on (a) TiO_2 obtained using TTIP and (b) TiO_2 obtained using $TiCl_4$ thin films

The results also outline the differences in the films photoactivity when deposited on microscopic glass (the SM thin films), when the MB removal efficiency on the films obtained using $TiCl_4$ as precursor are smaller when compared to those obtained using TTIP. This is a possible result of the TiO_2 content in the films and of the carbon inserted at the films surface, as the data in Table 3 show.

4. Conclusions

Thin films of TiO_2 deposited by SPD using TTIP and $TiCl_4$ precursors were investigated for methylene blue removal via photo-degradation.

The results allow to formulate the following conclusions:

- Smaller sized anatase TiO_2 crystallites were obtained using the TTIP precursor, as confirmed by the XRD, the SEM and the AFM data; these results also outline that by using the organo-metallic precursor, denser films can be deposited, with lower roughness.

- The methylene blue removal efficiency using TiO_2 thin films depends on the type of substrate and on the type of precursor used to deposit the thin photocatalytic films.

- The highest MB removal efficiency was observed using the TiO_2 thin films deposited on FTO glass using the $TiCl_4$ precursor. Efficiencies close to 36% were observed on both types of films, annealed for 3 and for 6 hours.

- Close removal efficiencies (over 30%) were observed also for the TiO_2 thin films deposited using the inorganic precursor on the glass substrate. This allowed to conclude that the film roughness is

the key factor that governs the removal efficiency of MB from wastewaters at very low concentrations, as the roughness values are significantly higher for these two types of films.

The best performing films can be further used as matrix for Vis-active, TiO_2 - carbon composites.

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