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Tantalum doped titania photocatalysts: Preparation by dc reactive sputtering and catalytic behavior

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Abstract

TiO_2 thin film photocatalysts doped with various Ta amounts were deposited on glass slides by the sputtering method, in Ar/O_2 atmosphere. They were characterized by XRD, UV–vis spectroscopy, AFM and EPMA. XRD patterns showed that the films were crystalline and consisted mainly of anatase. The doping with Ta enhanced the crystallinity and determined, for high Ta loadings, the phase transition into rutile. The large blue shift of the bandgap energy absorption in the UV–vis spectra, which is a quantum size effect, shows that the dimensions of the crystallites are smaller than 10 nm. The photocatalytic activity of the sputtered films was tested in the acetone degradation. Depending on the preparation conditions, two optimum Ta loadings were found (0.60 and 1.61 at.%, respectively), which ensure rather high conversions. A direct correlation between the bandgap of the catalysts and the catalytic activity was found. Ta doping was found to improve the ability of the titania photocatalysts to use UV radiations of lower energy, when compared to undoped samples.

Keywords: Titania photocatalysts; Acetone photodegradation; Tantalum ions doping

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1. Introduction

In the area of advanced oxidation technology, titanium dioxide semiconductor photocatalysis has been widely studied because of its potential application in air clean-up and water purification [1,2]. TiO_2 is largely used as photocatalyst due to its beneficial characteristics: high photocatalytic efficiency, physical and chemical stability, low cost and low toxicity. In addition to its wide bandgap, titania exhibits many other interesting properties, such as transparency to visible light, a high refractive index and a low absorption coefficient. All these characteristics make it very useful in a wide range of applications [3–6], including photo-decomposition of noxious compounds found in the atmosphere and in water [3,7,8].

The possibility to produce photocatalysts by deposition of titania thin films on low-cost materials, such as glasses, makes it even more attractive for various applications [9–11]. TiO_2 films have already been prepared by various vacuum and chemical techniques such as chemical vapor deposition [12], vacuum arc deposition [13], flame synthesis [14], reactive electron beam evaporation [15] and reactive dc magnetron sputtering [16,17], glass coating [18], precipitation [19], and alkoxide sol–gel process [20]. Low processing temperatures are desirable in order to minimize interfacial interactions at the film–substrate interface. Unfortunately, TiO_2 thin films prepared using alkoxides or other titanium precursors require processing temperatures higher than 573 K for the crystallization of TiO_2 particles and removal of organic materials.

Experiments carried out by deposition of TiO_2 on glass, polycarbonate, polymethyl methacrylate, and aluminum via a sol–gel process using different alkoxide precursors evidenced the role of the carrier [11]. Decomposition of a methylene

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blue solution over these TiO_2 thin films photocatalysts indicated that TiO_2 thin films deposited on glass substrate exhibited better photocatalytic decomposition activity than those deposited on polycarbonate and polymethyl methacrylate because of a different surface morphology. The lower rate of the decomposition reaction of films deposited on aluminum was explained by the fact that the film substrate captures the holes generated in the bulk of the TiO_2 and thereby decreases the photocatalytic efficiency.

The aim of the present study is to investigate the properties of Ta-doped titania catalysts prepared by dc reactive sputtering. In this process, atoms from a target (cathode) connected to a voltage source are sputtered off by positively charged ions originating in the plasma created between the cathode and the anode (substrate holder). These atoms further react with the particles of the reactive gas and deposit on the substrate in oxidized form. The sputtering technique is a versatile deposition method, allowing the preparation of thin films with controlled crystallinity, composition (including ion doping) and thickness. By this procedure, titania films can be obtained as pure anatase [21,22], pure rutile [23] or a mixture of these two crystallographic modifications [16,17,24].

These photocatalysts were tested in the photocatalytic decomposition of acetone, a volatile organic compound that creates serious problems in insufficiently aerated indoor environments. The adsorption and the photocatalytic degradation of acetone on pure TiO_2 have been previously studied. The titania catalysts used in these studies were either those available on the market (as Degussa P25) or prepared by titanium precursors precipitation [25,26]. Kinetic studies [26] indicated that the gas-phase photocatalytic oxidation of acetone is thermally activated up to 373 K and the reaction rate obeys a Langmuir–Hinshelwood expression.

2. Experimental part

2.1. Catalysts preparation

Titania-based thin films were prepared by reactive dc-magnetron sputtering, using a Sputtron II (Balzers) equipment. The distance between the substrate holder and the titanium target, inside the deposition chamber, was 7 cm. The titanium (99.7% titanium, from Lesker) disk-shaped target was of 10 cm diameter and allowed the modification with 1 up to 6 Ta inserts (99.9% purity). The size of one tantalum insert corresponded to 0.25% of the total area of the target. The titanium target was connected to a negative dc bias source, such that it was bombarded by positively charged ions present in the plasma. The plasma discharge was generated under a current intensity of 0.2 A, and a tension of 450 V. Before each preparation, the deposition chamber was evacuated to a pressure of 5×10^{-6} mbar and the target surface was cleaned using plasma generated in pure argon atmosphere. The reactive gas consisted of oxygen (Carbagas, purity 48, without oils and fats), while argon was used as inert gas (Carbagas, purity 48, oil and fats free). The total operating pressure was fixed at 5×10^{-3} mbar and the reactive gas pressure at 50% of the total operating pressure. Microscope glass slides (REWA Lehmann-Schmidt) were used as substrates. The glass slides were degreased by rinsing with isopropylic alcohol in an ultrasonic bath and then dried using a N_2 gun. The temperature of the substrates during the depositions was maintained at 573 ± 10 K, or at 500 ± 10 K for the sample Ta-1.61. The denomination of the samples includes the name of the dopant and its atomic percentage in the film composition (x), as Ta-x.

2.2. Catalysts characterization

The film thickness was measured with an Alphastep 500 Surface profiler (Tencor Instruments) coupled to a computer. X-ray diffraction (XRD) patterns were obtained using a Rigaku diffractometer, the Cu Kα radiation ($\lambda = 1.5418$ Å) being provided by a Philips X-ray source. The measurements were made in grazing incidence geometry, with an angle of 5° between the X-ray direction and the film surface. Atomic force microscopy (AFM) measurements were made by a Topometrix Explorer AFM in the non-contact mode. UV–vis spectra were collected using a Cary 500 Scan (Varian) spectrometer. For the determination of the E_g values, the wavenumbers at which light absorption became zero was taken into account. The composition of the films was determined by electron probe microanalysis (EPMA). Electrochemical measurements were carried out in a three-electrode cell under argon. As reference, an Ag/AgCl/KCl (3 M) electrode has been used, and as electrolyte a solution of 0.2 M lithium triflate in 3-methoxypropionitrile. The voltammetric and impedance measurements were performed using a potentiostat PGSTAT 30 model from AUTOLAB (Eco Chemie, Netherlands), for a potential modulation of 10 mV, and a frequency between 1 kHz and 5 mHz. To determine the Fermi level, these experiments followed the methodology proposed by Garcia-Cañadas et al. [27] in which this was estimated from the redox level of viologen. To obtain these values, redox capacitance of viologen was determined by subtraction of the value of non-covered and viologen covered TiO_2 and tantalum modified TiO_2 films.

2.3. Photocatalytic tests

Photocatalytic tests were performed in a flow system, using a water-cooled quartz reactor. The catalysts were irradiated using a Philips HPK 125 W UV-lamp. Catalyst platelets of 1.60–2.30 cm^2 surface area were placed inside the reactor, perpendicular to the light propagation direction, the titania-based film being exposed to the UV radiation.

Purified and dried air, containing 34% acetone, was sent to the reactor at a flow rate of 13.3 $cm^3\,min^{-1}$. The gas flow circulation rate was maintained constant during the experiments using a pump. The reactor was coupled on line to a Fisher-Rosemount gas analyzer, equipped with a CO_2 detector. The gas analyzer was calibrated before each test.

Before the UV irradiation, the acetone containing air stream was purged through the reactor over the catalysts for 20 min. No catalytic reaction products were detected in the absence of the UV radiation. The initial moment of each catalytic experiment was considered the moment when the UV lamp was turned on.

The activity was expressed as steady-state conversion % per surface area of the platelets. The conversion was calculated as the number of moles of acetone transformed in CO_2 relative to the number of moles of acetone present in the gas mixture. The exposure time was at least 200 min.

3. Results

3.1. Catalysts composition

Table 1 presents the amount of tantalum ions incorporated in the titania films, as obtained from EPMA analyses. Under similar preparation conditions, the tantalum content depended on the number of tantalum insertions, varying from 0.28 at.% (for one insertion) to 1.42 at.% (for 6 insertions). The sample Ta-1.61 (for which the substrate temperature during the deposition was about 100 K smaller than for the other catalysts) incorporated a tantalum amount (1.61 at.%) higher than all the other samples. This result shows that the substrate temperature plays an important role too in controlling the composition of the films: the lower the temperature the higher the tantalum amount incorporated in the films.

3.2. Film morphology

The thickness of the deposited films, as measured with the Alphastep profiler, varied between 150 and 300 nm. The deposition rate, measured on a microbalance placed near the support holder, was 0.2 Å/s.

AFM revealed the polycrystalline structure of the investigated catalysts. The top view image for all the samples reveals a superposition of round-shape grains. The morphology of the surface does not seem to depend either on the deposition conditions or on the tantalum content. Fig. 1 shows the top view image obtained for the sample Ta-1.42 scanning a surface of 25,000 nm^2.

Table 1
The tantalum content of the investigated cataysts, as given by EPMA

Catalyst	Number of tantalum insertions	Ta at.%
Ta-0	–	–
Ta-0.28	1	0.28
Ta-0.46	2	0.46
Ta-1.61	3	1.61
Ta-0.60	3	0.60
Ta-1.31	4	1.31
Ta-1.26	5	1.26
Ta-1.42	6	1.42

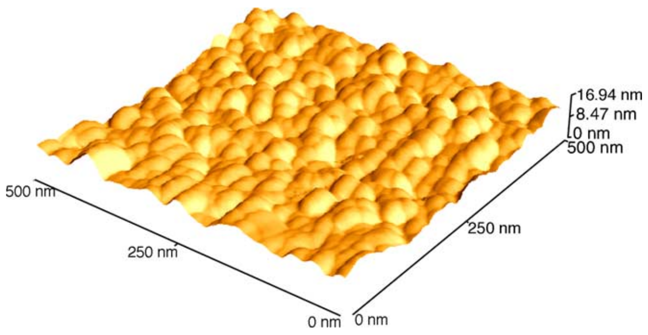

Fig. 1. AFM image of sample Ta-1.42 on a scale 25,000 nm^2.

3.3. Crystalline structure

Fig. 2 shows the XRD patterns of the investigated samples. They indicate that all the samples were crystalline, irrespective to the tantalum content, and consisted mainly of anatase. The intensity of the diffraction peaks was very low for the undoped sample, Ta-0, which may correspond to the existence of an amorphous titania phase, too. The doped samples present more intense peaks, which may suggest that the Ta addition improved the TiO_2 crystallinity. However, the diffraction peaks remained broad, indicating that the resulted thin films are made of small crystallites. The presence of amorphous TiO_2 cannot be excluded in these samples.

The presence of rutile is difficult to observe, because the broad boss associated with the amorphous SiO_2 substrate (in the range $2\theta = 10$–$40°$) hides the range where the most intense rutile diffraction peak results. However, for the samples Ta-1.61 and Ta-1.42, the intensity of this peak is high enough to allow its assignment to the presence of rutile in the composition of these samples.

3.4. UV–vis spectra

Typical UV–vis spectra of the investigated samples are given in Fig. 3. UV–vis spectra of the thin films prepared by sputtering exhibit a shoulder in the range

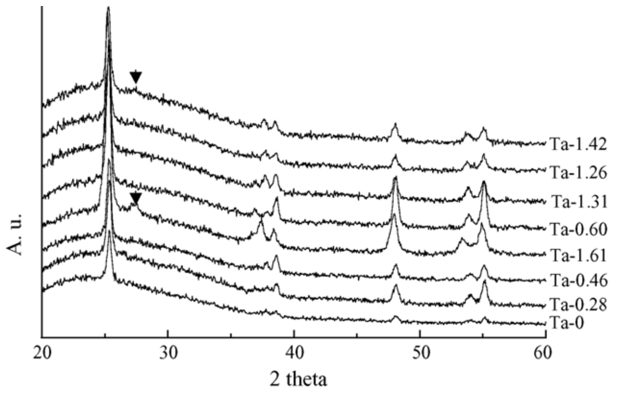

Fig. 2. XRD patterns of the investigated samples. All the peaks correspond to anatase diffraction planes, except those marked with an arrow, which are attributed to rutile.

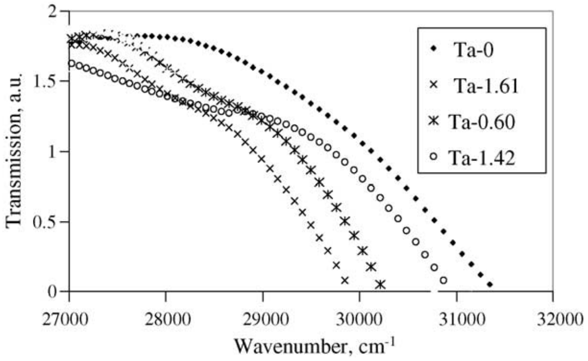

Fig. 3. Superposition of UV–vis spectra of the investigated catalysts.

28,250–28,550 cm^{-1}, which, according to the literature data, can be assigned to nanosized anatase particles [28].

The light absorption corresponding to the bandgap of the semiconductors is observed at wavenumbers in the range 29,850–31,350 cm^{-1} (see Fig. 3), values slightly higher than that corresponding to powder anatase, 28,514 cm^{-1} [29]. It is interesting to note that even the sample containing undoped anatase presented an E_g of 3.9 eV, larger than the bandgap energies of both rutile and anatase in powder form. This is also the highest bandgap energy value in this catalysts series. Doping with Ta ions resulted in a slight decrease of the semiconductor E_g, which, for the doped samples, ranged between 3.71 eV (sample Ta-1.61) and 3.87 eV (sample Ta-1.26). The large blue shift observed for these catalysts is due to the quantum-size effect, produced by the small dimensions of the titania crystallites. The results of the UV–vis spectroscopy are confirmed by the XRD patterns, the broadened peaks present there being a proof of the low crystallinity of titania films.

3.5. Electrochemical measurements of the redox capacitance

Fig. 4 shows the redox capacitance of viologen determined by the subtraction of the value of pure films and viologen covered films. Changes in the Ta composition led to a shift in the potential corresponding to the maximum in capacitance. Till a tantalum content of 0.60 the shift was occurring to lower values than that of pure titania, while a larger amount of tantalum determined a shift in an inverse sense. However, it is very speculative to assign these changes only to the modification in the tantalum content. Tantalum generates these changes, but the increase of the Ta content was also accompanied by changes in the structural characteristics.

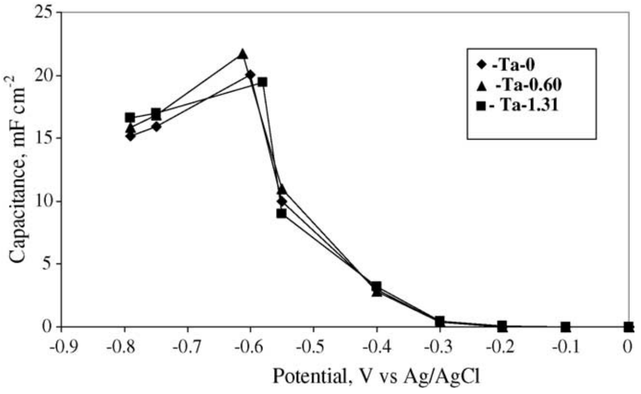

Fig. 4. Catalytic activity of the investigated photocatalysts, after reaching the steady state.

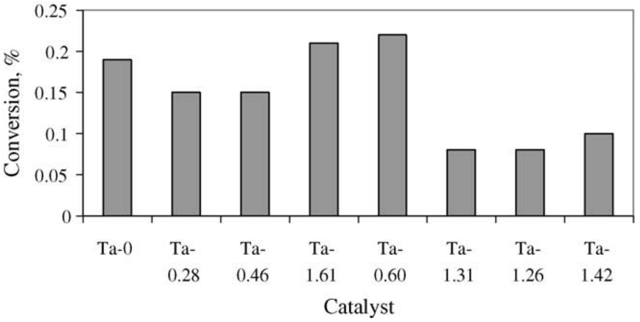

Fig. 5. Activity of the sample Ta-0.28 during 200 min of run. The steady state is attained after 110 min from the beginning of the reaction.

3.6. Catalytic activity

Fig. 5 presents the conversions obtained at steady state in the photocatalytic decomposition of acetone, as a function of the tantalum content. The catalysts reached the steady state after approximately 100 min from the beginning of the reaction (see Fig. 6). The conversion increased rather fast in the first 50 min, and then reached slowly a constant value. Mass spectrometric analysis of gases and residual liquid in the photoreactor indicated that under the investigated conditions CO_2 was the only product. No CO or intermediate decomposition products of acetone have been detected.

Data presented in Fig. 5 show that the samples doped under the same conditions exhibit a volcano-type dependence of the conversion on tantalum content with a maximum corresponding to 0.60 at.% Ta (sample Ta-0.60). Lower and even higher Ta loadings led to a photocatalytic activity inferior to

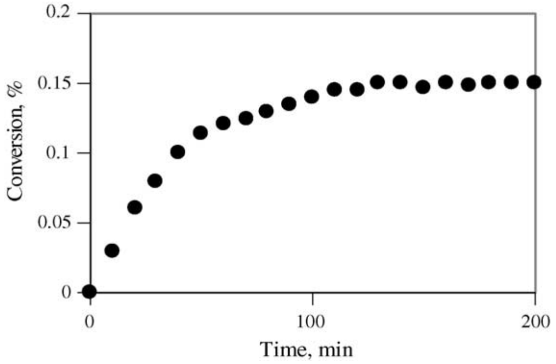

Fig. 6. Correlation between the photocatalytic activity of Ta-doped samples and bandgap energy of the photocatalysts.

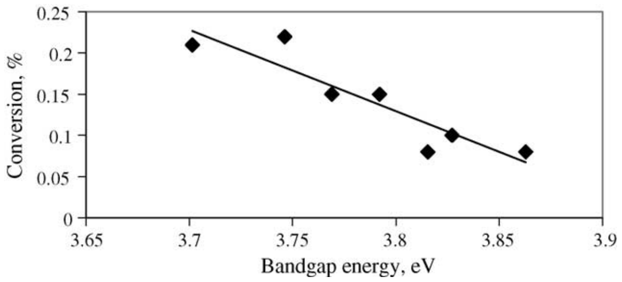

Fig. 7. Correlation between the photocatalytic activity of Ta-doped samples and bandgap energy of the photocatalysts.

that of the undoped sample. The decrease of the conversion for further increases in the Ta amount may be associated to the formation of Ta aggregates.

A different situation was determined for the sample Ta-1.61. Although this catalyst contains a higher amount of Ta (1.61 at.% Ta), it exhibits an activity comparable to that of samples Ta-0 and Ta-0.60. The preparative conditions (respectively a lower substrate temperature) seem to have a strong influence on the catalytic properties of the sample.

Fig. 7 presents the plot of the conversion vs. bandgap energy of the catalysts. These indicate an inverse correlation, namely, the increase of the bandgap energy leads to a decrease of the photocatalytic activity. The best photocatalytic activities are exhibited by samples with the lowest E_g values. The catalytic performance is proportional to the catalyst capacity to use UV–vis radiation of lower energy.

The reuse of the catalysts in five successive cycles of 20 h resulted in no change of the conversion compared with the fresh catalysts.

4. Discussion

The dc reactive sputtering deposition method led to thin titania films made of nanosized crystallites, as demonstrated by the blue shift of the bandgap absorption and the broadening of the diffraction peaks. The resulted films are composed mainly of anatase, but doping the titania crystallites with Ta ions over a concentration of 1.42 at.% led to the apparition of the rutile peaks in the diffraction patterns. A similar phenomenon was observed also in the case of titania doped with Nb and Fe [30,31], while doping with Ce in amounts higher than 1.2 at.% led to a complete amorphisation of the anatase films [32].

As opposed to these studies, doping of TiO_2 with Ta ions using reactive dc-magnetron sputtering was found to enhance the crystallinity of the thin films, the intensity of the diffraction peaks increasing parallel to the Ta doping. The Ta-ions doping influenced the surface morphology of the thin films, and exhibited an obvious influence on the photocatalytic activity.

The role played by the Ta ions in the modification of titania photocatalytic properties it is still unclear, as is that of other ions with higher valence than Ti^{4+}. The electronic theory of semiconductors stipulates that doping titania with ions of valence higher than 4 leads to an upward shift of the Fermi level. As the dopant concentration increases, the surface barrier becomes higher and the space charge region narrower. The electron–hole pairs photogenerated within this region are efficiently separated by the large electric field across the barrier, before having the chance to recombine [33]. Thus, it would appear that increasing the doping ion amount would result in a continuous improvement of the photocatalytic activity, by increasing the lifetime of the electron/hole pairs. This is not the case experimentally observed. Moreover, Wilke and Breuer [34] demonstrated that doping TiO_2 with 0.5 at.% Mo^{5+} ions, using a synthesis method based on the sol–gel process, reduced the lifetime of the electrone/hole pairs from 89.3 μs (TiO_2) to about 30 μs. Further increase of Mo^{5+} concentration, up to 1 at.%, decreased even more the lifetime, to a value of 20 μs. At low molybdenum concentrations (less than 1 at.%), the course of the photodegradation of Rhodamine B followed the decreasing tendency of the charge carriers lifetime, the activity decreasing from 80% photodegraded amount of Rhodamine B (after 60 min of experiment, pure titania catalyst) to 35% (1 at.% Mo^{5+}). However, doping with Mo concentrations beyond 1% led to an increase in the activity. This value became comparable to that of the undoped titania. The authors suggested that if the molybdenum concentration increases beyond 1 at.% the influence of the adsorption becomes predominant, and, since there is a higher surface coverage of the dye, more charge carriers reaching the surface can contribute to the degradation process. From the data reported in the literature [34,35], it appears that this volcano-type curve observed for the photocatalytic activity as a function of the doping ions amount is a rather typical behavior for the titania catalysts doped with ions of valence higher than 4 and it was observed in our case too, for the catalysts prepared under similar conditions (samples Ta-0–Ta-1.42). The sample Ta-1.61, which was prepared using a substrate temperature of approximately 70 K, lower than the temperature used for the other samples, exhibits a behavior comparable to that of Ta-0.60. As a function of the preparation conditions, there is an optimum amount of Ta ions, which ensures the highest photoactivity. The dependence of the capacitance vs. potential after subtraction of pure- and viologen covered films followed the same order as that determined for the photocatalytic activity indicating small changes in the Fermi level.

The crystallinity of the films and the anatase to rutile ratio seem to have also an influence on the photocatalytic properties of the doped titania. The most active doped samples, Ta-0.60 and Ta-1.61, present a higher crystallinity degree than the other samples, as can be appreciated by the intensity of the diffraction peaks (Fig. 2). Although it is generally assumed that anatase is the photocatalytically active phase, in the case of the sample Ta-1.61 the presence of rutile in a small amount seems to have a beneficial influence over the activity. Ohno et al. [36] also observed a synergetic effect in the photocatalytic decomposition of naphtalene when anatase and rutile particles were in contact. The attempts to prepare photocatalysts with the same anatase phase content for different Ta loadings were unsuccessful. Changes in the Ta loadings led to changes in the anatase content. However, since these films are not very large it would be difficult to distinguish between bulk and surface effects.

The highest conversions are exhibited by the samples with the smoothest surface, as given by AFM. Indeed, for samples Ta-0.60 and Ta-1.61, the differences between the lowest and the highest points of the surface were 11.91 and 10.54 nm, respectively, while for the other samples the surface roughness was at least 50% higher. An increased roughness of the surface, correlated with narrow pores, seems to be unfavorable, in this case, for the acetone access to the active sites of the surface. This may be due to pore blocking by capillary condensation of the water vapors resulting from the reaction.

The photoactivity in the acetone degradation was found to be directly proportional to the width of the bandgap of these semiconductors. However, no correlation between the Ta loading and the magnitude of the bandgap could be established. Although the activity of the most active doped samples (Ta-0.60 and Ta-1.61) is only slightly higher than that of the undoped sample, the doped samples exhibit a better ability to use UV light of lower energy. However, in our case, the absorption displacement to lower wavenumbers was counterbalanced by the blue shift, typical for *Q*-sized particles. An increase in the particle size would probably lead to the disappearance of this *Q*-size related phenomenon and will make the object of future investigations.

5. Conclusions

The doping with Ta ions was found to have a beneficial influence on the crystallinity of titania thin films prepared by dc reactive sputtering. With respect to the photocatalytic activity of these films, as a function of the deposition conditions, there is an optimum of Ta loading, which ensures high conversions. The highest conversions realized by the doped samples Ta-0.60 and Ta-1.61 exceed only slightly the conversion realized by the undoped sample, Ta-0, but the Ta doping improves the capacity of the photocatalysts to use UV radiation of lower energy. The surface morphology too has an influence on the photocatalytic activity, an advanced roughness being unfavorable for the acetone decomposition, probably due to the blocking of the pores by the capillary condensation of water vapors formed in the reaction. Another advantage of this preparation technique is the possibility to recycle the catalysts without any loss in activity.

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