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Article

An Investigation into W or Nb or $ZnFe_2O_4$ Doped Titania Nanocomposites Deposited from Blended Powder Targets for UV/Visible Photocatalysis

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Abstract: The photocatalytic behavior of titania coatings is largely determined by their crystalline structure. Depending on deposition conditions, though, titania may form amorphous, brookite, anatase or rutile structures, with anatase or anatase/rutile mixed phase structures showing the highest levels of activity. Anatase is activated by UV light and, consequently, there is a great deal of interest in doping titania films to both increase activity and extend it into the visible range. In this study, titania and doped titania coatings have been deposited from blended oxide powder targets. This highly versatile and economical technique allows dopant levels to be readily varied. Using this technique, titania coatings doped with W, Nb and $ZnFe_2O_4$ have been deposited onto glass substrates by pulsed magnetron sputtering. The as-deposited coatings were analyzed by scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX) and micro-Raman spectroscopy. Selected coatings were then annealed at temperatures in the range of 400–700 °C and re-analyzed. Structural transformation of the titania coatings was initiated in the 500–600 °C range, with the coatings annealed at 700 °C having predominantly anatase structures. The photocatalytic activity of the coatings was assessed through

measurements of the degradation of organic dyes, such as methyl orange, under the influence of UV and fluorescent light sources. It was found that, after annealing, coatings with photo-active surfaces were produced and that activity varied with dopant content. Activity levels under fluorescent light irradiation were up to 60% of the activity measured under UV irradiation.

Keywords: magnetron sputtering; powder targets; photocatalytic coatings; Raman spectroscopy; methyl orange

1. Introduction

A large number of studies have been published on the use of TiO_2 as a photocatalyst for the decomposition of organic compounds or molecules [1–5]. TiO_2 is favored for use as a photocatalyst because of its moderate band gap, high photoactivity, recyclability, nontoxicity, low cost and its significant chemical and photochemical stability. In semiconducting photocatalysis, no energy is stored and instead an acceleration of a reaction by a photon-assisted mechanism occurs [6].

Titania functions by absorbing ultra-bandgap radiation. This generates electron-hole pairs that can migrate to the surface of the titania and promote oxidation/reduction reactions, creating radical species, which can degrade pollutant organic compounds [7–9]. The highest level of photocatalytic activity of titania is generally exhibited by the anatase phase [1–5]. However, the deposition of coatings with this structure usually requires elevated temperatures (>300 °C) during deposition or post-deposition annealing. Furthermore, the bandgap energy of anatase (around 3.2 eV) means UV light ($\lambda < \sim 380$ nm) is required for activation, which only represents ~3% of the total solar radiation, making anatase titania highly inefficient for visible light applications. If the bandgap of TiO_2 is reduced, lower energy photons may be absorbed by the catalyst and the photocatalytic activity could increase roughly proportional to the increase in the absorbed solar spectrum [10]. Extending the activity into the visible range generally requires doping of the titania with, for example, Fe [9], or N [11], whilst doping with for example; W or Nb increases photocatalytic efficiency [12,13].

Zinc ferrite has also been suggested as a potential semiconductor photocatalyst due to its low band gap (1.9 eV) and also, its ability to absorb visible light of wavelength less than 652 nm [13]. The purpose of this paper, therefore, is to investigate the potential of doping a series of titania coatings with $ZnFe_2O_4$, W or Nb and investigating their impact on photocatalytic activity, in terms of the degradation of organic dyes. The coatings were deposited by mid-frequency pulsed magnetron sputtering directly from blended oxide powder targets [14]. This approach has been demonstrated by the present authors as an efficient way of screening candidate materials and identifying optimum compositions for multi-component coatings. It provides an economic way of testing dopant materials before employing a full size 'solid' sputtering target [14] and has been shown to produce surfaces with photocatalytic activities very close to similar coatings produced by conventional reactive sputtering techniques [15].

2. Experimental Section

In a set of experiments, pure and doped-titania coatings were deposited by directly sputtering oxide powder targets. Initially pure titania coatings were deposited by directly sputtering targets produced from PC105 grade titania powder (Cristal Global) in a purpose built rig fitted with a 180 mm diameter unbalanced magnetron in the 'sputter-up' configuration [14]. This grade of powder has an average crystallite size of 15–25 nm in which the crystals have a predominantly anatase structure. 35 g of PC105 was evenly spread across the surface of a backing plate recessed to a depth of 2 mm and then lightly tamped down. The magnetron was driven in pulsed magnetron sputtering mode at 250 kHz at a duty of 50% using an Advanced Energy Pinnacle Plus power supply. This frequency (250 kHz) was found to be the lowest at which a stable discharge was obtained (previous work by the authors has shown that deposition rate decreases as pulse frequency is increased in this system [16], hence the preference to operate at lower frequencies). The power supply was operated in power regulation mode at 300 W. The operating pressure was fixed at 0.2 Pa using an argon:oxygen flow rate ratio of 2.5:1. It has previously been demonstrated that a low flow rate of oxygen helps maintain coating stoichiometry [14]. The coatings were deposited onto glass microscope slides, which were ultrasonically cleaned in iso-propanol prior to deposition. Run times were varied to produce coatings in the range 450–550 nm thick. Titania coatings doped with $ZnFe_2O_4$, Nb or W were deposited from targets in which the dopant powder was blended with the titania powder in quantities aimed at producing coatings with approximately 1, 3 and 6 atomic% of dopant in the titania coatings. All other operating parameters remained unchanged.

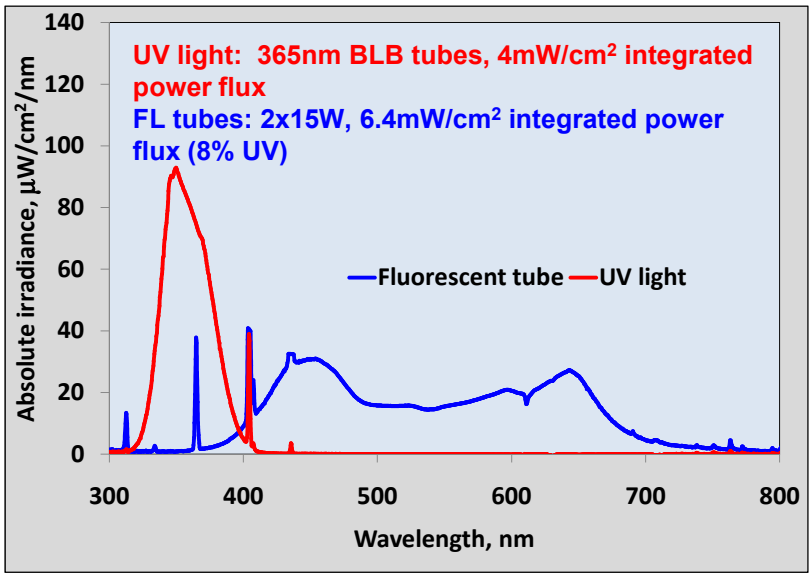
The as-deposited coatings were analyzed by scanning electron microscopy (SEM—Zeiss Supra 40), energy dispersive X-ray spectroscopy (EDX—Edax Trident), and micro-Raman spectroscopy (Renishaw Invia, 514 nm laser). Selected coatings were annealed in air at temperatures in the range 400 to 700 °C and re-analyzed. In addition, the thickness of the coatings was measured by Dektak surface profilometry.

In this study, the photocatalytic activity of the coatings was initially assessed using resazurin (Rz) dye. This test utilizes the photo-reduction reaction of the resazurin [17,18]. Upon irradiation of the ink with ultra-bandgap radiation in the presence of a photocatalytic surface, the photogenerated electrons reduce the blue Rz to the pink resorufin (Rf). This process occurs in minutes on an active surface, making this test particularly suited to "on the spot" tests, but it cannot be readily quantified. Two drops (approximately 5 μL) of resazurin solution were applied to the surface of the film samples (typically 20 mm × 20 mm) using a pipette. Then, a microscope slide (20 mm × 20 mm) was placed onto the dye spot, to spread the dye evenly over the whole sample surface. The coatings were irradiated at an integrated power flux of 4 mW/cm^2 with two 15 W 365 nm BLB lamps (Sankyo Denki) until a blue-to-pink color change was observed for the dye, or for a total period of 40 minutes (bulb to sample separation = 100 mm).

Based on the "pass/fail" resazurin test, selected samples were then re-tested against methyl orange solutions. Methyl orange (MeO 99.9% pure, Alfa Aesar) was used as a simple model of a series of common azo-dyes widely used in industry. When it is dissolved in distilled water, the UV-vis spectrum of MeO shows a strong absorption peak at approximately 464 nm. Fluctuations in the height of this reference peak were used to monitor the photocatalytic degradation of MeO by the titania

coatings. All experiments were carried out at room temperature in air. The coatings were irradiated at 4 mW/cm^2 with 365 nm BLB lamps. Samples of the MeO solution (0.06 M) were taken before testing and then at 30 minutes intervals up to a total time of 4 hours and analyzed using a Perkin-Elmer UV-vis spectrophotometer. Spectra were taken in the range 350–550 nm to monitor the absorption peak in this region. These tests were also carried out using two 15 W fluorescent (Fl) tubes in place of the UV tubes to simulate typical laboratory environments. The integrated power flux to the coatings with the Fl tubes was 6.4 mW/cm^2, of which the UV component (300–400 nm) was 8%. A comparison of the spectra from the two light sources is given in Figure 1.

Figure 1. Spectra from UV and fluorescent tubes used for photocatalytic testing, measured at 100 mm from the light sources.



3. Results

3.1. Coating Structures, Compositions and Deposition Rates

Selected samples were prepared for structural and compositional analysis by SEM, Raman spectroscopy and EDX. Table 1 includes estimates of deposition rates (from SEM micrographs of the fracture sections of the coatings) and R_a roughness values (from the Dektak surface profilometer). For the doped coatings, the atomic percentage of the dopant in the coatings is also included in Table 1. The SEM micrographs of the selected samples in Figure 2a–c show that all samples consisted of dense crystallites with fine features on the surface with slightly columnar fracture sections. However, the presence of larger faceted grains on the surface of sample P4 was also observed in localized regions.

Micro-Raman analysis clearly showed that the as-deposited coatings were amorphous. The selected samples were then re-analyzed after 10 minutes annealing in air at 400–700 °C. Table 1 also shows the predominant structures for the post-annealed coatings. It can be seen that structural evolution was generally observed to initiate after annealing at between 500 and 600 °C, and that the majority of coatings show mixed anatase and rutile structures (the anatase phase is presumed to be the predominant phase based on the relative intensities of the anatase and rutile peaks) with an

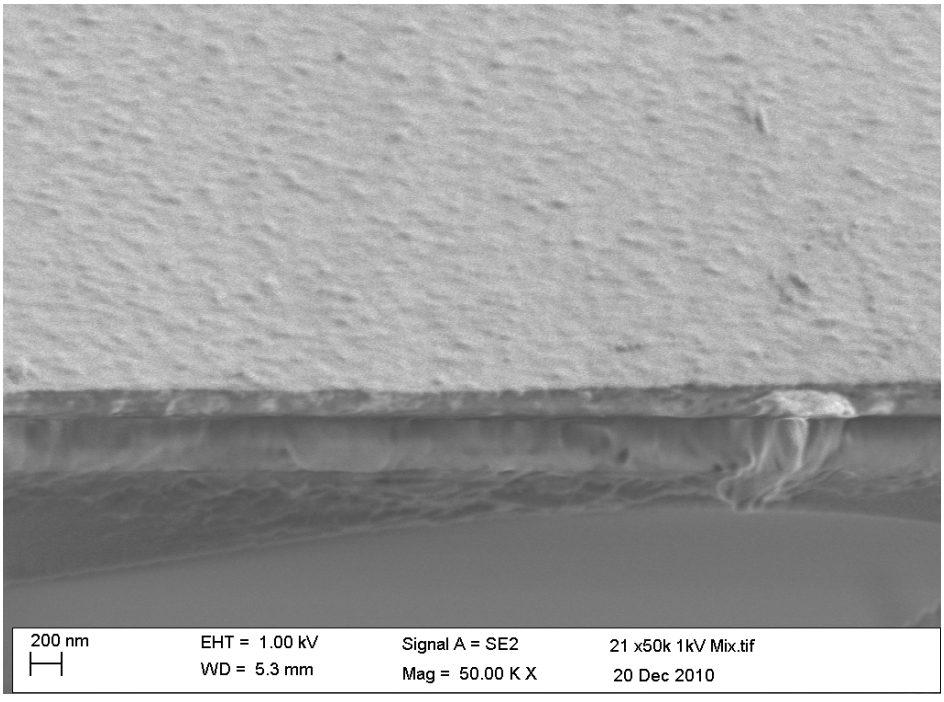
exception of P10 which has a predominantly rutile structure. Raman analyses of samples P4 (TiO_2—6 atomic%W), P7 (TiO_2—6 atomic%Nb) and P10 (TiO_2—6 atomic%$ZnFe_2O_4$) after annealing at 700 °C are shown in Figure 3a–c, respectively, as typical examples of the structures that formed after annealing at this temperature.

Table 1. Compositional and structural properties of titania and doped titania coatings deposited at 250 kHz-50% duty cycle and at various annealing temperature.

Sample	Dopant	Thickness	Dep Rate	R_a Value	Post-annealed Coatings			
No.	at%	nm	nm/min	nm	400 °C	500 °C	600 °C	700 °C
P1	-	486	0.81	25	AM	AM	AN/RU	AN/RU
P2	1 at%W	504	0.84	26	AM	AM	AN/RU	AN/RU
P3	3 at%W	510	0.85	27	AM	AM	AN/RU	AN/RU
P4	6 at%W	528	0.88	29	AM	AM	AN/RU	AN/RU
P5	1 at%Nb	498	0.83	25	AM	AM	AN/RU	AN/RU
P6	3 at%Nb	504	0.84	26	AM	AM	AN/RU	AN/RU
P7	6 at%Nb	510	0.85	27	AM	AM	AN/RU	AN/RU
P8	1 at%ZnFe	468	0.78	21	AM	AM	AN/RU	AN/RU
P9	3 at%ZnFe	474	0.79	24	AM	AM	AN/RU	AN/RU
P10	6 at%ZnFe	480	0.80	22	AM	AM	AN/RU	RU/AN

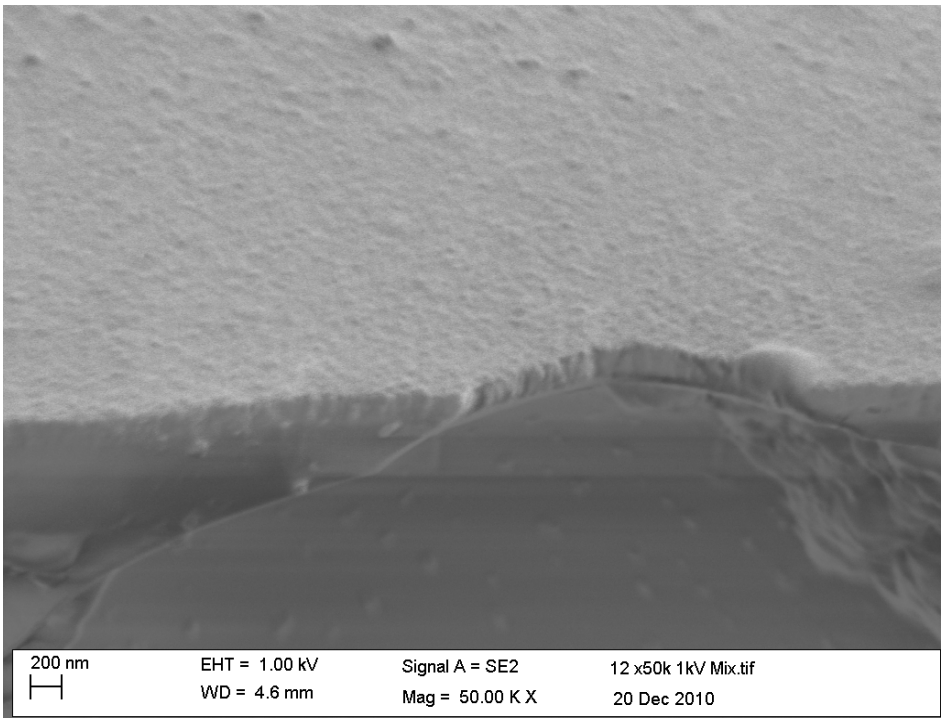
Notes: P: powder targets, directly sputtered; at%: Atomic%; AM: Amorphous; AN: Anatase; RU: Rutile; AN/RU: Mixed films with higher contribution of anatase phase; RU/AN: Mixed films with higher contribution of rutile phase.

Figure 2. SEM micrograph of fracture section of (**a**) titania sample P4 produced at 250 kHz-50% Duty Cycle (dopant content: 6 atomic%W); (**b**) titania sample P7 produced at 250 kHz-50% Duty Cycle (dopant content: 6 atomic%Nb); (**c**) titania sample P10 (dopant content: 6 atomic%$ZnFe_2O_4$).

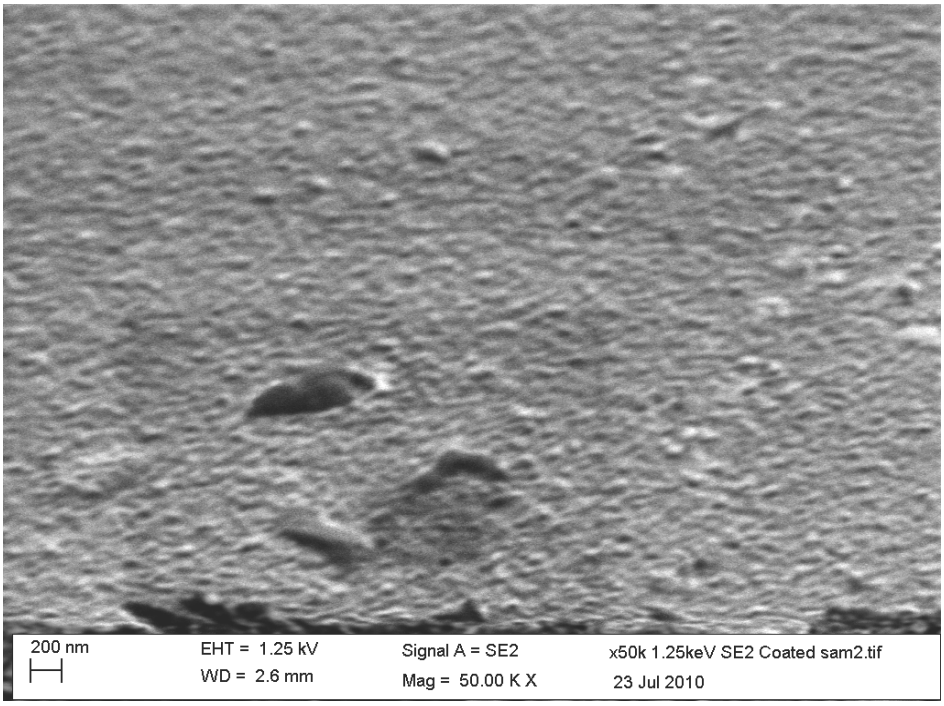


(**a**)

Figure 2. *Cont.*

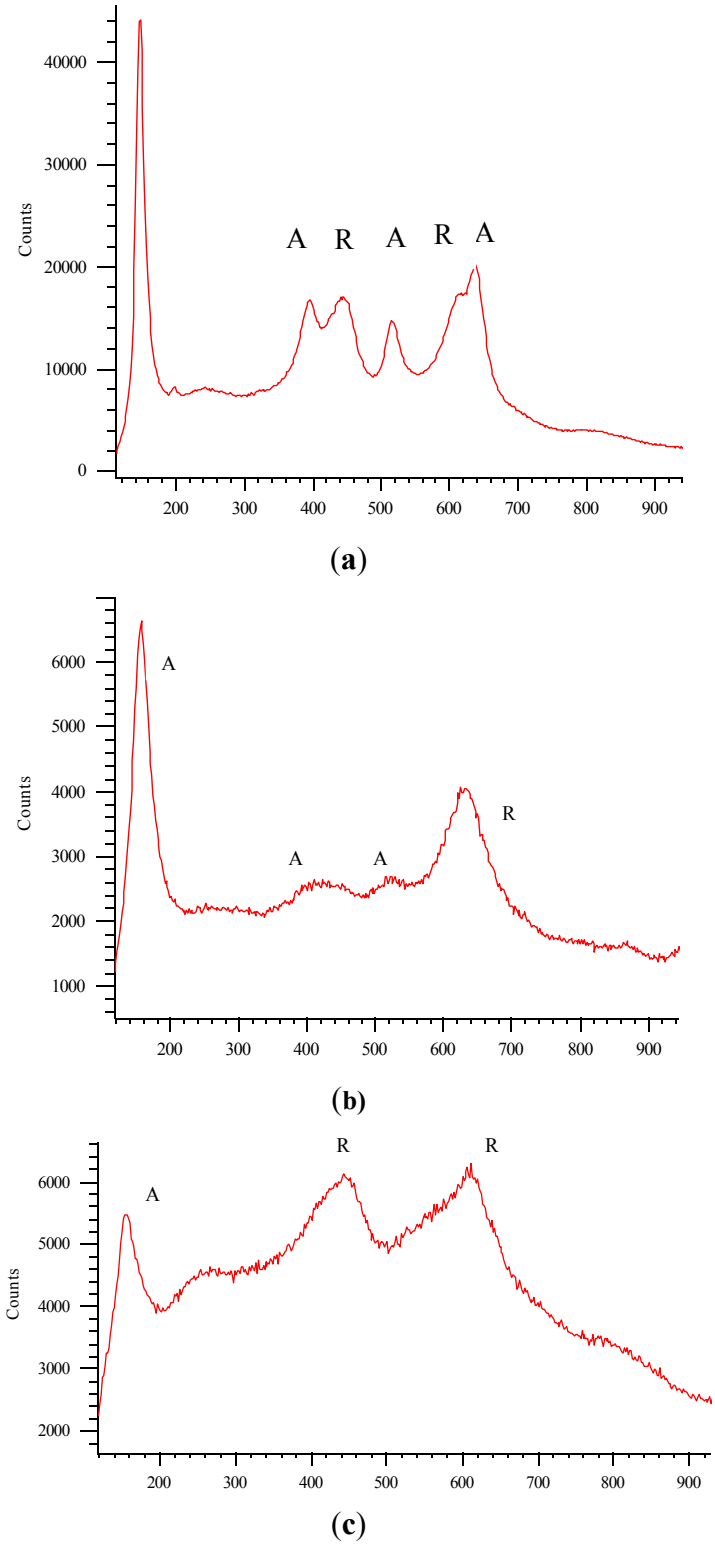


(**b**)



(**c**)

Figure 3. Micro-Raman spectra of (**a**) titania sample P4 produced on glass substrate at 250 kHz-50% Duty Cycle (TiO_2-6 atomic%W) after annealing at 700 °C, showing mixed anatase-rutile structure; (**b**) titania sample P7 produced on glass substrate at 250 kHz-50% Duty Cycle (TiO_2-6 atomic%Nb) after annealing at 700 °C, showing mixed anatase-rutile structure; (**c**) titania sample P10 (TiO_2-6 atomic%$ZnFe_2O_4$) produced on glass substrate after annealing at 700 °C, showing RU/AN structure.



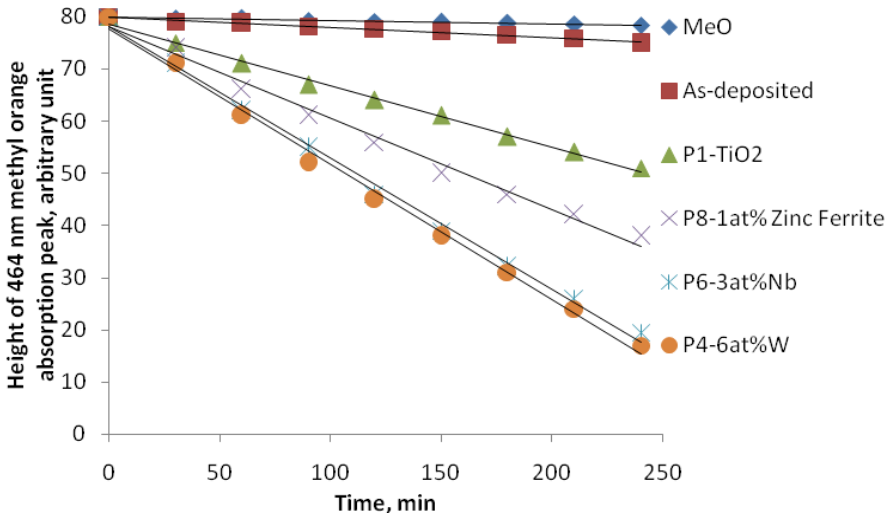
Notes: A: Anatase; R: Rutile.

3.2. Assessment of Photocatalytic Activity

Resazurin tests on the as-deposited coatings showed no color change after 40 min exposure to the UV lamps, indicating no perceptible level of activity for these coatings. For the annealed coatings, based on the structural analysis results, only those heat treated at 700 °C were assessed for photocatalytic activity. After annealing at 700 °C, for the pure TiO_2 coatings and the majority of the doped titania coatings there was a rapid blue to pink color change within 2–3 min of exposure. This indicated that the coatings were photoactive, but the level of activity could not be quantified.

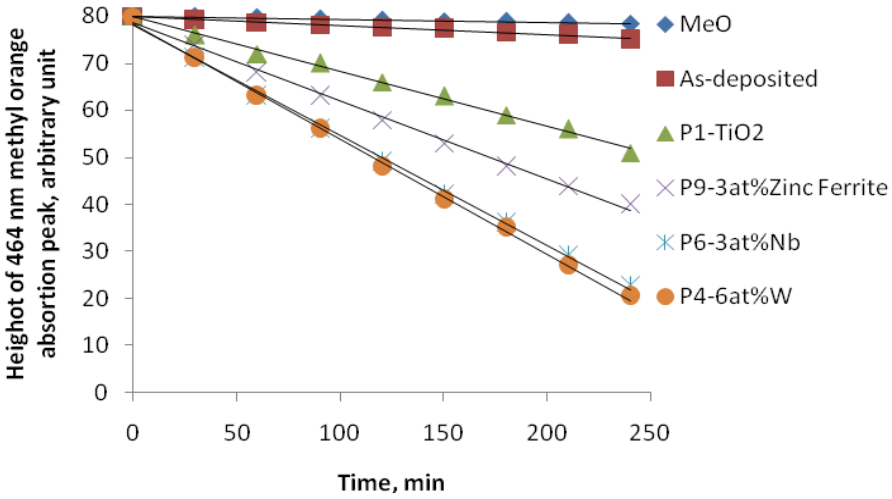
The photocatalytic reaction rate was quantified using methyl orange, as described above. Initially, a sample of MeO was exposed to the UV source to measure the natural rate of degradation of the dye without contact with a photocatalyst. Then, an as-deposited titania coating was also tested to determine a baseline for the level of activity of an amorphous sample. Very low levels of activity were observed for this test. In contrast, the TiO_2 and doped TiO_2 coatings annealed at 700 °C showed significant decreases in the magnitude of the MeO 464 nm absorption peak. All the data were re-plotted to show the height of the peak as a function of exposure time. Figure 4, compares the annealed and the best W, Nb or $ZnFe_2O_4$ doped titania coatings with the amorphous titania sample and MeO without photocatalyst present (Figure 4a shows the results for exposure to UV lamps and 4b shows the results for exposure to fluorescent lamps).

Figure 4. Degradation of 464nm methyl orange (MeO) absorption peak as a function of exposure time to (**a**) UV lamps; (**b**) fluorescent lamps for titania samples P1 (pure titania for comparison), P4, P6 and P8, annealed at 700 °C, compared to an as-deposited coating and MeO without the presence of a photocatalyst. Linear regression analysis trendlines are shown.



(**a**)

Figure 4. *Cont.*



(b)

It can be seen from the Figure 4 that, the degradation rates of methyl orange for the annealed coatings show strong negative correlations of the form "$y = -mx + c$"; where the gradient, m, gives the degradation rate of the methyl orange and the intercept c is the initial concentration of the dye, which was kept constant for all tests. Linear regression analysis was, therefore, used to obtain values for the gradient, m, in each case, which can be used as a comparison of the photocatalytic activity of different coatings. These values are also included in Table 2. For convenience modulus values of m ($|m|$) are given in the tables, and the degradation rates of the 464 nm methyl orange absorption peak following exposure to 365 nm UV lamps and fluorescent (Fl) lamps will be referred to as $|\text{MeO}|_{\text{UV}}$ and $|\text{MeO}|_{\text{Fl}}$, respectively. However, as the power flux to the samples varied for the different bulb types (4 mW/cm^2 for UV and 6.4 mw/cm^2 for the fluorescent tubes), these values have also been normalized to give the rate of decrease of peak height per milliwatt per cm^2 of incident radiation. Normalized values of $|m|$ are presented as a function of dopant content and light source in Figure 5.

Figure 5. Comparison of normalized methyl orange degradation rates by titania coatings as a function of dopant content, sputtering process and lamp type.

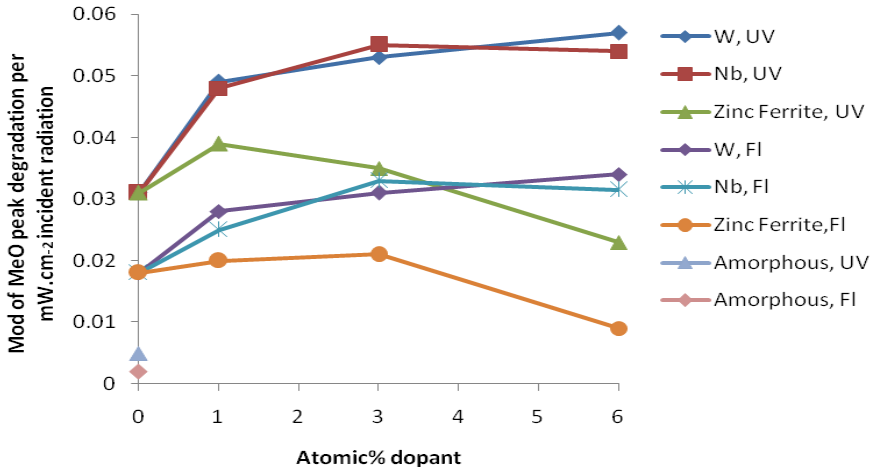


Table 2. Modulus values of degradation rates of 464 nm methyl orange (MeO) absorption peak following exposure to 352 nm UV lamps and fluorescent (Fl) lamps.

Sample No	Dopant at%	MeO UV rate, arbitrary units/min	Normalized MeO UV rate, arbitrary units/min/mW.cm^{-2}	MeO Fl rate, arbitrary units/min	Normalized MeO Fl rate, arbitrary units/min/mW.cm^{-2}
P1	-	0.124	0.031	0.107	0.017
P2	1 at%W	0.193	0.048	0.177	0.028
P3	3 at%W	0.212	0.053	0.198	0.031
P4	6 at%W	0.231	0.058	0.220	0.034
P5	1 at%Nb	0.188	0.047	0.153	0.024
P6	3 at%Nb	0.221	0.055	0.215	0.034
P7	6 at%Nb	0.216	0.054	0.211	0.033
P8	1 at%$ZnFe_2O_4$	0.159	0.040	0.117	0.018
P9	3 at%$ZnFe_2O_4$	0.143	0.036	0.125	0.020
P10	6 at%$ZnFe_2O_4$	0.097	0.024	0.054	0.008
MeO only	-	0.013	0.003	0.010	0.002
TiO_2 As-deposited	-	0.017	0.004	0.014	0.002

Notes: Apart from where indicated the samples were annealed at 700 °C prior to testing; at%: Atomic%.

4. Discussions

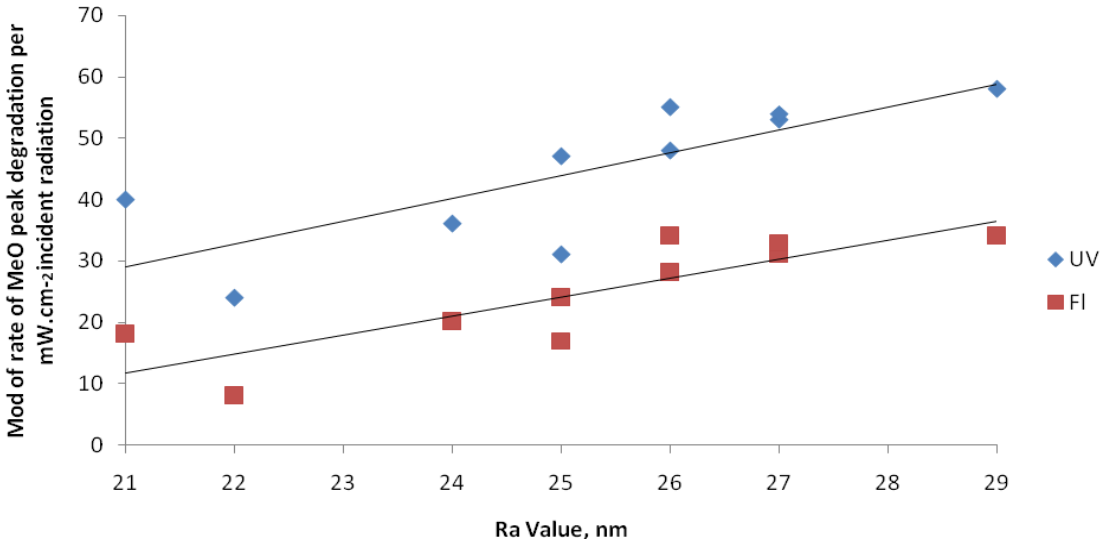
The pulsed magnetron sputtering technique has been used here to produce titania coatings and doped titania coatings directly from oxide powder targets as an economic means of investigating multi-component coating materials. Micro-Raman analysis indicated that the as-deposited coatings were amorphous, whereas the post-annealed coatings formed mixed anatase-rutile structures. For many samples structural transitions from amorphous to a polycrystalline anatase phase occurred over the range of 500–600 °C but it was noticed that there was another structural evolution from anatase to a mixed anatase-rutile structure at annealing temperatures of 600 to 700 °C (See Table 1).

Based on thickness/roughness values from Table 1 it can be noted that the R_a value is weakly dependent on the thickness of the films (deposition rate). There is, though, a clear correlation between R_a value and photocatalytic activity, which is shown in Figure 6. This might be expected, since an increase in R_a value implies an increase in the surface area of the coating in contact with the methyl orange solution. However, the exact contribution of surface area cannot be determined from this data due to the different film compositions.

Considering the assessment of photocatalytic activity in more detail, the resazurin test provided a quick initial indication of whether the surfaces were active or not. In contrast, methyl orange tests provided quantitative assessments of photocatalytic activity on the coatings annealed at 700 °C. The variation in activity with dopant content for the coatings is given in Table 2 and displayed in Figure 5. There are a number of interesting trends in these data. The addition of W or Nb to the coatings has a very similar effect on photocatalytic activity. Activity increases by similar amounts under both UV and fluorescent light sources. Activity levels appear to have reached maximum values for both light sources at 3 atomic%Nb, whereas they are still increasing at 6 atomic% of W, suggesting the optimum

doping level of W may not have been reached in these experiments. Doping at these levels has led to increases of between 87% and 100% in photocatalytic activity, compared to pure titania coatings. The behavior of zinc ferrite as a dopant is somewhat different. At 1% dopant level, a small increase in activity is observed, but increasing the dopant level beyond this actually leads to a decrease in activity under both light sources. Finally, the activity under fluorescent light was found to be between 50% to 60% of the activity under UV light, independent of dopant content. Thus, although the addition of these three dopant materials can significantly improve photocatalytic efficiency, they do not appear to shift the activity into the visible range.

Figure 6. Comparison of normalized methyl orange degradation rates (*1000) with exposure to UV or fluorescent lamps as a function of R_a values for samples listed in Table 1.



5. Conclusions

It was demonstrated that pulsed magnetron sputtering can produce coatings with high photocatalytic activity for the degradation of organic dyes, such as methyl orange, under the influence of UV and fluorescent light sources. In the present study, titania and W, Nb or zinc ferrite-doped titania coatings were deposited by pulsed magnetron sputtering directly from oxide powder targets. Typically, the as-deposited coatings were amorphous, but post-annealed coatings formed mixed anatase-rutile structures. The as-deposited coatings showed very low levels of photocatalytic activity. In contrast, post-annealed coatings with mixed anatase-rutile structures indicated significant activity, in terms of the photo-induced degradation of resazurin and methyl orange organic dyes. The resazurin test provided a quick indication of whether the surfaces were active or not. However, the level of photocatalytic activity was quantitatively assessed by methyl orange tests performed on the coatings annealed at 700 °C. It was found that the photocatalytic activity of the coatings was improved by up to 100% by doping titania films with W, Nb or $ZnFe_2O_4$, compared to undoped titania coatings. In addition, a reasonable level of activity was observed for the coatings exposed to the fluorescent light source. It was shown that the normalized activity level of doped and undoped coatings following exposure to fluorescent tubes was between 55% and 60% of those recorded for the samples exposed to the 365 nm UV tubes.

Conflicts of Interest

The authors declare no conflict of interest.

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