

Photoinduced hydrophilic and photocatalytic response of hydrothermally grown TiO₂ nanostructured thin films

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ABSTRACT

It is demonstrated that nanostructured titanium (IV) oxide (TiO₂) films can be deposited on glass substrates at 95 °C using hydrothermal growth, their properties being greatly affected by the substrate materials. Anatase TiO₂ films grown on ITO for deposition period of 50 h were observed to exhibit a very efficient, reversible light-induced transition to super-hydrophilicity, reaching a nearly zero contact angle. Enhanced photocatalytic activity (65%) was found for the rutile TiO₂ samples grown on microscope glass, possibly due to their higher roughness with respect to anatase grown on ITO. The effect of the substrate material used is discussed in terms of the TiO₂ phase and morphology control, for the best photoinduced hydrophilic and photocatalytic performance of the samples.

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1. Introduction

Self-cleaning TiO₂ films have a high potential for practical applications such as mirrors, window glasses and windshields of automobile [1]. The self-cleaning mechanism is based on a unique dual-action. The photocatalytic action, in which the coating reacts with daylight to break down organic dirt and the hydrophilic action in which the rainwater hits the glass and spreads evenly, running off in a 'sheet', and taking the loosened dirt with it, drying quickly without leaving streaks. Hence, the synergetic effect of these two mechanisms is quite important in sustaining the self-cleaning effect [2].

TiO₂ exists in three polymorphs: rutile and anatase (both tetragonal) and brookite (orthorhombic) [3]. Anatase and rutile have been widely studied as photocatalyst semiconductors, since pure brookite is cumbersome to prepare and amorphous TiO₂ has no photocatalytic activity at all [4]. It is generally known that

anatase is more efficient as a photocatalyst than rutile, because of its higher energetic level, which enables an efficient reduction potential [5]. However, the existence of the anatase phase seems to be a necessary, but not a sufficient condition for high efficiency.

In addition, the performance of TiO₂ in photoinduced applications depends on its roughness, which enhances the adsorption of more molecules, therefore resulting in a higher efficiency [6]. Hence, it is important to develop deposition methods by which these properties can be controlled. The most common routes include the chemical vapour deposition (CVD) [7], the sol–gel [8] and the hydrothermal growth [9–11], some of them requiring high temperatures, and/or toxic chemicals and/or expensive equipment. Hydrothermal growth is based on a 'one-pot' process, requiring low temperatures, no toxic chemicals and atmospheric pressure. In such a procedure, the morphological and structural properties can simply be controlled by the growth temperature and time, the substrate and the precursor solutions [12].

The aim of the present work is the hydrothermal growth of TiO₂ on ITO (Indium Tin Oxide) and microscope glass substrates at 95 °C for a range of deposition periods. It is found that under appropriate conditions, it is possible to grow rutile or anatase TiO₂ exhibiting reversible photoactive properties.

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2. Experimental

The growth of TiO₂ on ITO and microscope glass was performed by hydrothermal growth, using TTIP (Ti[(OCH(CH₃)₂)₄]), i-PrOH (CH₃CH(OH)CH₃) and MilliQ H₂O as precursors. Before deposition, all substrates were ultrasonically cleaned with propanol, acetone and MilliQ H₂O and dried with N₂. The solution preparation involved the stirring of 12 M i-PrOH with 0.1 M MilliQ H₂O, followed by the addition of 0.03 M TTIP. Finally, the solution was placed in a Pyrex glass bottle with polypropylene autoclavable screw cap, with the substrate positioned on the bottom, and heated at 95 °C under atmospheric pressure for deposition periods of 20, 30, 40 and 50 h in a regular laboratory oven. After growth, the samples were thoroughly washed with i-PrOH in order to eliminate residual salts, and dried in air at 95 °C.

X-ray diffraction (XRD) measurements were performed using a Rigaku (RINT 2000) Diffractometer with Cu K α X-rays for $2\theta = 20.00\text{--}40.00^\circ$, a range of step sizes and time step 30 s/ $^\circ$ with various glancing angles, 0.5, 1, 1.5 and 2 $^\circ$. Raman measurements were carried out in the wavenumber range 100–700 cm⁻¹, using a Raman Spectrometer (Nicolet Almega XR) with 473 nm excitation. UV–vis transmittance measurements were performed using a Perkin–Elmer Lambda 950 spectrometer over the wavelength range of 250–1000 nm. Surface imaging was carried out on an atomic force microscopy (AFM) in tapping mode (Digital Instruments – Nanoscope IIIa) using Si cantilevers. The thickness of the samples was determined from cross-sectional scanning electron microscopy (SEM) images. Contact angle measurements were performed by positioning a 10 μ l distilled, deionised Millipore H₂O droplet on the surface of the samples. Contact angles were determined from the corresponding pictures (obtained from a CCD camera-lens optical system) using an image-processing algorithm. The mean value was calculated from at least five individual measurements. Photoinduced hydrophilicity was evaluated by irradiating the samples at certain time intervals a light intensity of 4 mW cm⁻² UV using a Hamamatsu, ozone free silica Xe lamp, centred at 365 nm, in atmospheric air and a temperature of 25 °C. Following irradiation, the samples were stored in the dark at room temperature for seven days and then the respective contact angles were measured again. Finally, stearic acid testing was performed after spin coating the samples using a 30 μ l droplet of stearic acid in chloroform (0.1 M solution), spun at a rotation speed of 2000 rpm for 30 s. Samples were then dried at 80 °C in air for 10 min. The IR absorbance of the C–H stretching region of the stearic acid spectrum (2800–3000 cm⁻¹) was recorded by a Fourier transform infrared spectrometer (FTIR) (IRPRESTIGE-21, Shimadzu), in transmission mode before and after illumination using a UV lamp centred at 365 nm (black light blue lamps) with a light intensity of 2 mW cm⁻² at certain time intervals.

Each characterization method was completed on at least three samples prepared under the same conditions for consistency and reproducibility.

3. Results and discussion

The TiO₂ samples were grown for the deposition period of 20–50 h, based on consideration of similar procedures reported in the literature [13,14] and since the deposition period below 20 h would result in the films exhibiting poor or no photoinduced response. In addition, the growth temperature was kept constant at 95 °C because at higher temperatures (>95 °C), evaporation of i-PrOH was observed, while at lower temperatures (<95 °C), no photoactivity was recorded. The thickness of the samples was found to range 30–50 nm for the deposition periods 20–50 h. All deposited TiO₂ films were found to exhibit very good adhesion passing the

Scotch tape test (removal of an X shaped piece of sticking tape) [15]. Moreover, the stability of our films was investigated by comparing their phase, morphology and photoinduced properties just after deposition and after six months. As we have seen during similar tests, films presenting similar characteristics after six months, they remain stable for long periods after deposition. Finally, all films presented an almost flat transparency, exhibiting 60–80% transmittance in the spectral range from 380 nm up to NIR.

Regarding the film crystallinity, XRD of the as-deposited TiO₂ films showed no evidence of diffraction peaks, indicating that the films were largely amorphous. Thus, on the basis of XRD results, it may be concluded that the films are not crystalline and as a consequence, no photoinduced properties can be expected.

Fig. 1 shows the Raman spectra of the as-deposited films grown on (a) ITO and (b) microscope glass for deposition time of 50 h. As can be seen, for TiO₂ samples deposited on ITO, the anatase phase is obtained, with phonon frequencies, matching within ± 2 cm⁻¹ with literature: 144 cm⁻¹ (E_g), 398 cm⁻¹ (B_{1g}), 516 cm⁻¹ (A_{1g}) and 638 cm⁻¹ (E_g) [16]. In contrast, for TiO₂ samples grown on microscope glass, the rutile phase is obtained with respective phonon frequencies: 146 cm⁻¹ (B_{1g}), 443 cm⁻¹ (E_g) and 609 cm⁻¹ (A_{1g}). In addition, for the rutile case, there is second-order scattering feature at 243 cm⁻¹ [17]. Moreover, with decreasing deposition period, the peaks were lower in intensity and broader, for both substrates studied. Therefore, it is of great significance that the phase of the TiO₂ films can be controlled by using different substrates and simply keeping the other conditions constant.

Although XRD results gave no indication for the characteristic phase of the TiO₂ films, at least in the as-deposited state, Raman analysis proved the presence of anatase or rutile TiO₂, depending on the substrate used. XRD is known to probe the long range order crystallinity of materials, while Raman is a probe of the influence of even localized short-range order to the vibrational modes of bond configurations [18,19]. Therefore, the simultaneous presence of well-identified Raman signatures with the absence of XRD peaks in our films suggests that they are mainly amorphous retaining however a short-range crystalline ordering.

As a next step, we investigated the surface morphology of the TiO₂ films, which can clearly affect their photoinduced properties. Fig. 2 presents a high resolution AFM image of an as-deposited sample grown on microscope glass for a deposition period of 50 h at 95 °C, the results being similar for TiO₂ grown on ITO. The image

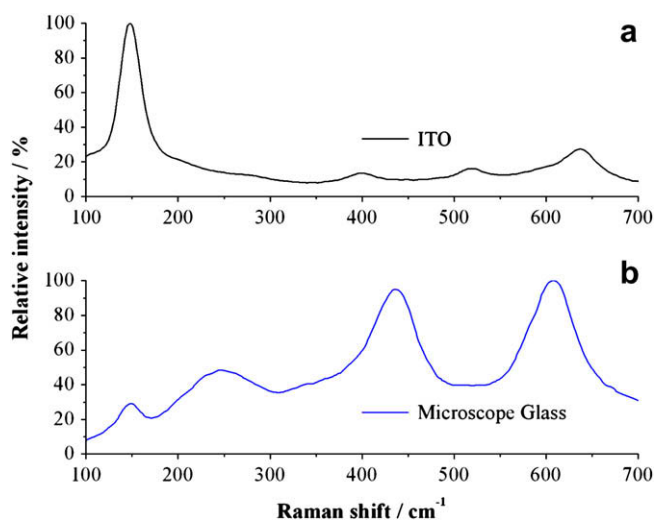


Fig. 1. Raman spectra of as-deposited TiO₂ films grown on (a) ITO and (b) microscope glass substrates by hydrothermal growth for deposition time of 50 h.

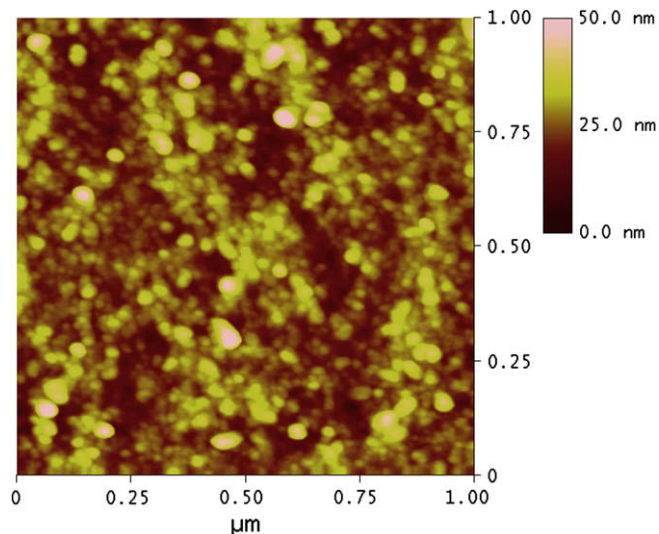


Fig. 2. AFM image of rutile TiO_2 film deposited on microscope glass for a deposition time of 50 h at 95°C .

indicates the formation of fine agglomerations consisting of compact nanoparticles with non-uniform size. The roughness of the as-deposited TiO_2 on microscope glass was determined to be approximately 10.5 nm, while for the ITO case, this was half, approaching a value of 5 nm. This difference can be very important, since it can affect the photoinduced properties of the samples due to the enhancement of the adsorption of water molecules [6], which can increase the photocatalytic response. Finally, it is interesting to note that for short deposition period, the agglomerations were found to be larger, while, with increasing deposition time, they were becoming smaller in size.

The dependence of the surface roughness ($1 \times 1 \mu\text{m}$) on the deposition period for TiO_2 samples grown on ITO and microscope glass is shown in Fig. 3. It is indicated that the roughness is almost constant for the samples grown on ITO (being approximately 5 nm) for the whole range of deposition periods. While, it is shown that there is an abrupt increase in surface roughness for films grown on microscope glass at 50 h (approaching 10.5 nm). This increase could be related to the different substrate adsorption properties

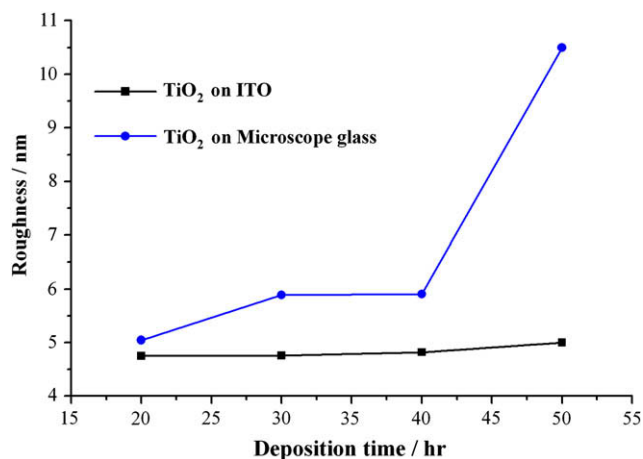


Fig. 3. Roughness ($1 \times 1 \mu\text{m}$) dependence on deposition time for TiO_2 samples grown on ITO and microscope glass substrates for deposition periods 20, 30, 40 and 50 h at 95°C .

and the morphological characteristics (size, shape, specific surface area, surface hydroxylation, etc.) of the TiO_2 particles being deposited under the particular conditions. However, the corresponding growth mechanisms are still under investigation.

The water contact angle of all as-deposited films before UV-light illumination was determined to be in the range of $85\text{--}100^\circ$, values indicating hydrophobicity (Fig. 4). The photoinduced hydrophilic response of samples grown for deposition periods of 20, 30 and 40 h, was found to cause changes in the water contact angle from 90 to 15° . For the samples grown for 50 h, the water droplet spreads out on the film surface after approximately 20 min of UV irradiation, yielding a nearly zero contact angle, which indicates superhydrophilicity. The water contact angle was observed to return to its initial value after storing the samples in dark for seven days at room temperature. Therefore, the photoinduced hydrophilic response of the TiO_2 films is improved with increasing growth time, a behaviour which is mainly consistent with a corresponding enhancement of the anatase TiO_2 phase as indicated by Raman measurements (Fig. 1).

The mechanism of the photoinduced hydrophilic conversion and its reversibility have been intensively studied [20–22]. It is assumed that surface Ti^{+4} sites were reduced to Ti^{+3} states via the photogenerated electrons, and oxygen vacancies were generated through the oxidation of the bridging O^{2-} species to oxygen via the photogenerated holes. Successively, dissociated water adsorption on the vacancy sites, created hydrophilic OH groups on the surface. This photoinduced hydrophilic process is always reversed slowly in the dark, since contaminants are gradually adsorbing at the surface, thus, making it more hydrophobic. Oxygen in the air is responsible for oxidizing of the hydrophilic surface via Ti^{+3} to Ti^{+4} states during storage in the dark [23]. Hence, it can be assumed that during dark storage oxygen healing could be a possible candidate for hydrophilic/hydrophobic conversion mechanism.

Thus, the 50 h sample grown on ITO, which showed the highest photoinduced hydrophilic response, exhibited the best-defined, among our samples, anatase TiO_2 phase, as shown from Raman spectroscopy. The thickness of the samples may not be the most important parameter for the observed behaviour, since it does not vary significantly for the whole range of deposition periods.

Regarding the rutile TiO_2 samples grown on microscope glass, the initial water contact angle of all films was measured to be 88° .

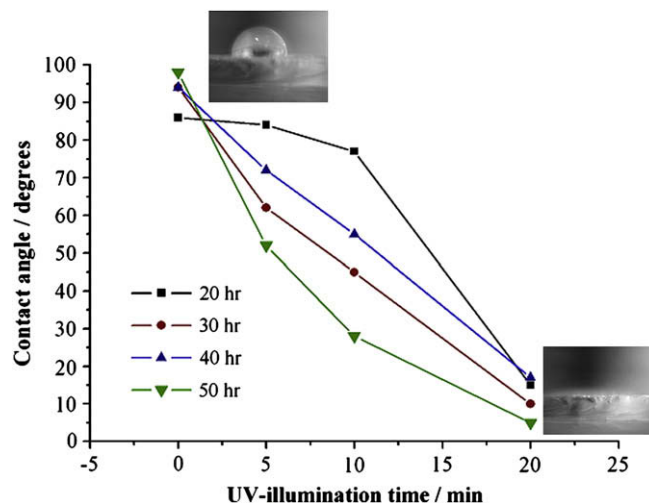


Fig. 4. Water contact angle dependence on UV illumination time of anatase TiO_2 thin films grown on ITO for a range of deposition periods using 4 mW cm^{-2} UV-light of a Hg lamp, in atmospheric air and a temperature of 25°C .

Only the sample grown at 50 h showed reversible photoinduced change in the water contact angle varying from 88 to 32°, for a 20 min exposure period to UV-light irradiation. The origin of this behaviour may be the high surface roughness of the film, which results in efficient absorption of UV energy and promotion of the transportation of charge carriers [24]. This observation needs however further investigation for a better understanding of the corresponding mechanism. Therefore, the contact angle cannot be modified appreciably under UV illumination, a behaviour that can be attributed to the presence of rutile TiO₂, which, according to the literature [25], does not present significant photoinduced hydrophilic response.

A measure of photocatalytic activity that is commonly used for the films is the degradation rate of stearic acid [26].

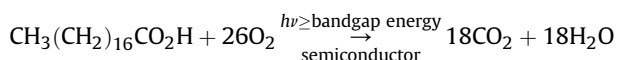


Fig. 5 clearly demonstrates that the rutile TiO₂ samples grown on microscope glass for a deposition time of 50 h present quite efficient photocatalytic activity, degrading stearic acid by almost 65%. In contrast, the stearic acid was not appreciably degraded (24%) for the samples grown on ITO, despite the presence of anatase TiO₂, which is known to be a more efficient photocatalyst than rutile [5]. Therefore, our results indicate that the presence of anatase TiO₂ is not sufficient to ensure effective photocatalytic activity of TiO₂ samples. Regarding the observed behaviour of rutile TiO₂, this can possibly be attributed to its higher surface roughness, which provides more active sites and results in the adsorption of more reactive species [6,25]. In addition, it could shorten the route for an electron migration from the conduction band of the rutile TiO₂ to its surface [27]. However, further studies for a better understanding of the photoactive behaviour of the TiO₂ catalysts are in progress.

Samples grown on ITO and microscope glass for deposition periods lower than 50 h were found to exhibit similar (24%) and lower photocatalytic activities (approximately 40%), respectively. This behaviour may be attributed to the surface roughness differences among the films. In the case of anatase TiO₂ grown on ITO, constant roughness resulted in constant activity, whereas, decreased activity was recorded for decreasing roughness for the rutile TiO₂ grown on microscope glass (Fig. 3).

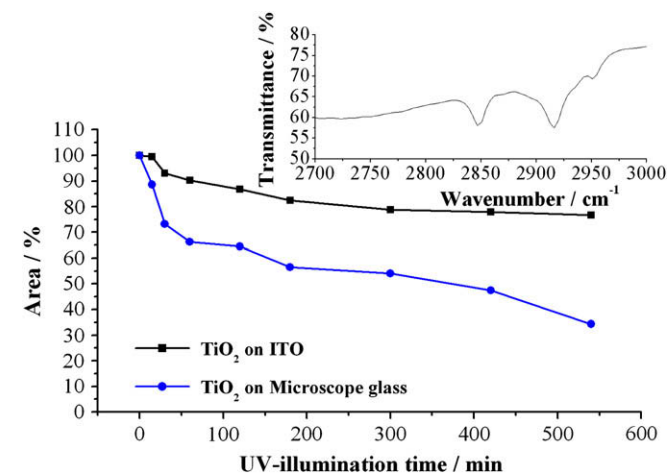


Fig. 5. Variation of the area under the C–H stretching region of the stearic spectrum (inset) as a function of the UV illumination time of TiO₂ thin films grown on ITO and microscope glass, using 2 mW cm⁻² UV-light, in atmospheric air and temperature of 25 °C.

Experimentally, we have established that the photoinduced hydrophilicity is higher for the samples grown on ITO for a deposition period of 50 h due to the enhanced crystalline anatase TiO₂, according to Raman spectroscopy (high intensity and narrow peaks). In contrast, the best photocatalytic activity was observed for the rutile TiO₂ films grown on microscope glass for a deposition period 50 h, possibly due to the higher roughness, which is beneficial for the adsorption of water on the surface [6]. Our observations indicate that the presence of anatase TiO₂ is not sufficient for the presence of both photoinduced hydrophilic and photocatalytic response.

4. Conclusion

The results presented in this paper reveal that under suitable deposition conditions, it is possible to control the phase, morphology and consequently the photoinduced properties of TiO₂ samples. It was demonstrated that photoactive rutile or anatase TiO₂ nanostructured thin films can be produced, depending on the substrate material. Moreover, it was shown that the presence of anatase TiO₂ is not sufficient to get both photoinduced hydrophilic and photocatalytic responses, since the surface morphology of the films can also play a very significant role. Finally, it may be concluded that a cheap and environmentally friendly method can be used for the deposition of photoactive nanostructured TiO₂ thin films that can be used in self-cleaning or anti-bacterial applications.

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