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# Influence of the OH groups on the photocatalytic activity and photoinduced hydrophilicity of microwave assisted sol–gel TiO<sub>2</sub> film

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## ABSTRACT

In the present work the influence of the OH groups on the photocatalytic activity and the photoinduced hydrophilicity of microwave assisted sol–gel TiO<sub>2</sub> films was investigated. The prepared TiO<sub>2</sub> films were characterized using XRD and AFM. Furthermore, the surface of the TiO<sub>2</sub> films was examined by help of XPS in order to determine the amount of OH groups before and after UV irradiation at different humidities. The activity of the TiO<sub>2</sub> films was determined using stearic acid as a model compound and the photoinduced superhydrophilicity was investigated through contact angle measurements.

The results of this investigation showed that the microwave assisted sol–gel technique produces highly homogeneous and efficient TiO<sub>2</sub> films without the need for heat treatment for crystallization. Based on the conducted experiments it is suggested that the amount of OH groups on the TiO<sub>2</sub> surface highly influence the photocatalytic activity and the photoinduced superhydrophilicity and that the two mechanisms may be closely related. It is suggested that the superhydrophilicity is obtained through a combination of photocatalytic degradation of organic contaminants and surface structural changes in form of an increased amount of OH-groups.

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## 1. Introduction

Heterogeneous photocatalysis is one of the advanced oxidation processes that couples low-energy ultraviolet light with semiconductors acting as photocatalysts. In this process completely mineralization of the organic pollutants to carbon dioxide and mineral acids is achieved [1,2]. TiO<sub>2</sub> is the most often used semiconductor in photocatalysis due to high activity, chemical stability and it is not subject to photocorrosion [2].

In the field of photocatalysis, most applications are concerned with water and air purification or self-cleaning properties of different materials [3,4]. Considerable amount of work has been done on TiO<sub>2</sub>-modified materials for self-cleaning windows [5,6] and building surfaces [7,8].

The photocatalytic activity of TiO<sub>2</sub> has been found to be tied to the surface properties of the catalyst. Some of the particle properties which are known to affect the photocatalytic activity are particle size, crystal structure, amounts and the identity of defects and preparation method [3,9–11]. In addition to titanium dioxide ability to photodegrade organic contaminants, it has been found that UV irradiation of the titanium dioxide surface will

induce superhydrophilicity, which changes the nature of a surface from hydrophobic to hydrophilic.

The mechanism for the photomineralization capability of titanium dioxide films is well recognized, however, different models have been proposed for the mechanism leading to superhydrophilicity.

One model for the photoinduced superhydrophilicity is based on surface structural changes caused by the photogenerated electron–hole pair. Hashimoto and co-workers [12,13] has suggested the following mechanism for the photoinduced superhydrophilicity. The photogenerated holes are assumed to be trapped at lattice oxygen at the surface of the TiO<sub>2</sub> film. The trapped holes are thought to weaken the bond between the titanium atoms and the lattice oxygen. As a result such oxygen is liberated to create oxygen vacancies. At these defect sites water molecules are dissociatively absorbed creating a more hydroxylated surface. The photogenerated electrons are assumed to be trapped by Ti(IV) sites, as Ti(III), which are subsequently oxidized by oxygen. After the superhydrophilic state has been obtained through UV irradiation prolonged irradiation will not lead to any changes in this property. However, if the TiO<sub>2</sub> film is stored in the dark, the surface of the TiO<sub>2</sub> film will convert back to its initial more hydrophobic state. The recovery of the film is thought to be due to relaxation of the surface where the weakly bonded hydroxyl groups desorb and the initial surface is recreated [14].

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A second model suggesting that the superhydrophilicity is obtained by photocatalytic removal of organic contaminants from the surface has been proposed [15–17]. This model suggests that photocatalysis and the photoinduced hydrophilicity are directly related. In this case the regeneration of the hydrophobic surface in the dark is thought to be caused by re-contamination by air-borne hydrophobic organics.

Evidence supporting both mechanisms for the photoinduced superhydrophilicity has been reported. An investigation into superhydrophilicity conducted by Watanabe and co-workers [18] on a range of semiconductors suggests that the ability to undergo photoinduced superhydrophilicity is connected to surface structural changes. Fujishima and co-workers [14,19–21] and Watanabe et al. [22] have shown that water is reversibly adsorbed on TiO<sub>2</sub> during UV irradiation using FT-IR and XPS analysis. AFM studies have shown roughening of the TiO<sub>2</sub> surface as a result of UV irradiation presumably due to formation of defect sites [23]. Furthermore, Irie and Hashimoto have shown that superhydrophilic samples recovered their hydrophobic characteristic at increased rates in the dark in vacuum [24]. Increased rates of recovery have also been reported at increasing temperatures up to 150 °C suggesting desorption of hydroxyl groups [25].

In contrast, other groups have reported evidence for the photomineralization mechanism for the photoinduced superhydrophilicity. White [15] and Zubkov [16] have studied the hydrophobic/hydrophilic change occurring during UV irradiation using a model organic layer of trimethyl acetate and hexane, respectively, and reported an induction period, presumably during which the organic layer are photooxidized, followed by rapid wetting of the surface. Mills and Crow has reported that samples of Pilkington Activ and plain glass both obtained superhydrophilic properties after heat treatment at 550 °C suggesting that the superhydrophilicity is attributed to removal of organic contaminants [26]. In the same study similar results were obtained using UVC/O<sub>3</sub> treatment and chemical oxidation using aqua regia [26]. Sum frequency generation (SFG) analysis has been used to demonstrate that the intensity from C–H stretches decreased upon UV irradiation of an apparently pristine but hydrophobic sample of titania on glass but was regenerated under ambient dark conditions [27].

In the present work the influence of the OH groups on the photocatalytic activity and the photoinduced hydrophilicity of TiO<sub>2</sub> films were investigated by varying the experimental conditions.

The prepared TiO<sub>2</sub> films were characterized using X-ray diffraction (XRD) and atomic force microscopy (AFM). Furthermore, the surface of the TiO<sub>2</sub> films were examined by help of X-ray photoelectron spectroscopy (XPS) in order to determine the amount of OH groups before and after UV irradiation in different humidity in order to reveal the surface changes occurring during photocatalysis. The activity of the TiO<sub>2</sub> films was determined by stearic acid degradation. The photoinduced superhydrophilicity of the TiO<sub>2</sub> films was investigated through contact angle (CA) measurements.

## 2. Materials and methods

Microwave assisted sol–gel TiO<sub>2</sub> films were prepared from a modified sol–gel method initially described by Barbé et al. and Mills et al. [28,29]. The sol–gel method produces a TiO<sub>2</sub> paste which can be coated onto different substrates. The TiO<sub>2</sub> paste was prepared by adding 5 ml titanium (IV) tetraisopropoxide to 1 ml glacial acetic acid which was mixed with 30 ml 0.1 M nitric acid solution. The solution was placed in a microwave reactor (Anton Paar, Multiwave 3000) in order to control the sol–gel synthesis. A temperature ramp of 100 min was used to reach the final temperature of 220 °C and a pressure of 60 bar. The final conditions were held for 100 min before allowing the system to cool down.

The solution in the microwave reactor was stirred at 400 rpm during the entire process. After synthesis the particles were redispersed using ultrasound. The solution was rotary evaporated until the TiO<sub>2</sub> content was 10 wt.%. TiO<sub>2</sub> films on glass plates were prepared by applying a doctor blade technique described in [29]. After drying for 30 min the films were heat treated of 25–550 °C for 1 h in order to investigate the influence of calcination.

The crystallinity of TiO<sub>2</sub> is normally determined by XRD analysis from the relative intensities of the peaks corresponding to the anatase and rutile phase [30]. In the present work the absolute crystallinity of the films was determined by transmission X-ray powder diffraction using a STOE Stadi P transmission diffractometer with CuKα<sub>1</sub> X-ray tube ( $\lambda = 1.5406 \text{ \AA}$ ). The determination of the crystallinity of the TiO<sub>2</sub> samples was made with reference to CaF<sub>2</sub>, which is 100% crystalline. The method for determining the absolute crystallinity is described elsewhere [30]. The crystal size was determined from the broadening of the (1 0 1) reflection of anatase by Scherrer's formula.

XPS analysis of the TiO<sub>2</sub> films was carried out in a UHV chamber on a SX700 at the synchrotron source at the Institute for Storage Ring Facilities (ISA) in Aarhus, employing a Zeiss SX700 plane grating monochromator. The chamber was equipped with a VG CLAM2 electron spectrometer running with a pass energy of 30 eV and a slit width of 2 mm. The base pressure was around  $8 \times 10^{-10}$  mbar. The TiO<sub>2</sub> films used in the XPS analysis were cast onto stainless steel in order to prevent charging of the sample. The TiO<sub>2</sub> films were UV irradiated in a climate chamber in order to obtain controlled humidity during the experiments. In the experiments the set points of the climate chamber was temperature: 25 °C, air circulation: 6 m<sup>3</sup>/h, and the relative humidity: 35%, 50%, 75% and 95%. The samples were UV irradiated using one 9 W germinal bulb (254 nm) with an aluminium reflector placed 5 cm above the samples. The UV light intensity at the surface of the TiO<sub>2</sub> film was measured using a UV-meter to 10 mW/cm<sup>2</sup>. The obtained XPS spectra were fitted using XPS Peak software (available for download from <http://www.phy.cuhk.edu.hk/~surface/> [31]). The atomic concentration was determined by dividing the integrated intensities by the relative sensitivity factors, which for titanium 2p<sub>3/2</sub> is 1.1 and 0.63 for oxygen 1s [32].

AFM imaging was performed with a Ntegra Aura AFM instrument under ambient conditions. AFM images were obtained in semi contact mode. The sample used in the measurement was coated onto glass. The roughness was determined using an image analyzing program (ImageAnalysis2).

The photocatalytic activity of the TiO<sub>2</sub> films was investigated using stearic acid as a model compound. A stearic acid solution was made from 0.5 g stearic acid dissolved in 100 ml chloroform. The stearic acid solution was deposited by a pipette until the whole surface of the film was covered and then spun at 1000 rpm for 10 s using a spin coater. The samples were UV irradiated in a climate chamber at constant temperature (25 °C) and airflow (6 m<sup>3</sup>/h) and varying the relative humidity (20–95% RH). The samples were UV irradiated using one 9 W germinal bulb (254 nm) with an intensity of 10 mW/cm<sup>2</sup>. The degradation of stearic acid was monitored by FT-IR absorbance spectroscopy, through the disappearance of the peak at 2957.5 cm<sup>-1</sup> corresponding to the asymmetric C–H stretching of the CH<sub>3</sub> group, and the peaks at 2922.8 cm<sup>-1</sup> and 2853.4 cm<sup>-1</sup> corresponding to the asymmetric and symmetric C–H stretching of the CH<sub>2</sub> group. In the present work the integrated area under these peaks (2800–3000 cm<sup>-1</sup>) was used to measure the concentration of stearic acid as a function of irradiation time. The FT-IR measurements were carried out using a FT-IR spectrometer (Thermo Nicolet Spectrometer, AVATAR 370 FT-IR).

Contact angle measurements were performed on the TiO<sub>2</sub> films under the same conditions as described under the evaluation of the photocatalytic activity. The instrument allows the shape of a water

**Table 1**

Chemical and physical properties of the prepared TiO<sub>2</sub> film heat treated at 25–550 °C.

	25 °C	150 °C	300 °C	450 °C	550 °C
<b>XRD</b>					
Anatase (%)	69.2	69.5	61.9	69.1	68.7
Rutile	–	–	–	–	–
Amorphous (%)	30.8	30.5	38.1	30.9	31.3
Crystallite size (nm)	9.1	8.9	10.0	10.9	15.9
<b>AFM</b>					
Surface roughness (nm)	21.2	24.5	23.3	26.4	32.8
<b>XPS</b>					
Area <sub>Ti–OH</sub> (%)	41.3	41.1	42.3	44.0	35.4
Area <sub>Ti–O–Ti</sub> (%)	58.7	58.9	57.7	56.0	64.6

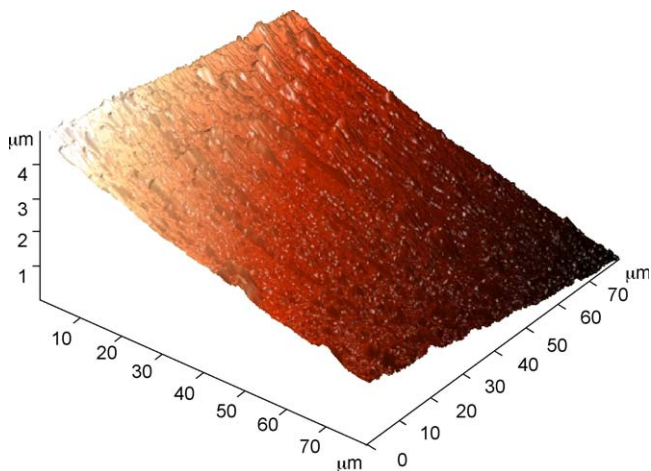
droplet deposited on the surface of the TiO<sub>2</sub> film under test to be recorded by a CMOS camera and analyzed using a computer program. This analysis provides an accurate value for the contact angle made by the water drop with the test substrate. In this work, the reported contact angle for the TiO<sub>2</sub> film refers to the contact angle made by a drop of water on its surface 20 s after the drop first falls on the test substrate. In the investigation the same TiO<sub>2</sub> film was used throughout a single experiment.

### 3. Results

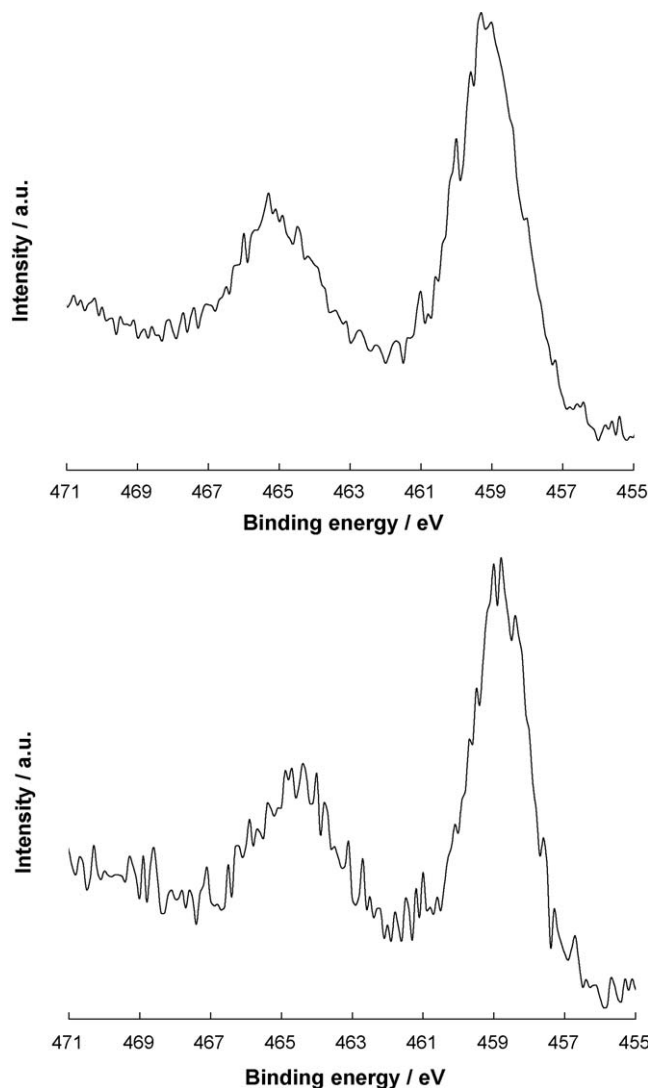
#### 3.1. Crystallinity and surface roughness

The absolute crystallinity of the TiO<sub>2</sub> produced by the microwave assisted sol–gel method was found to consist of about 70% anatase without further treatment. Moreover it was found that further heat treatment or calcination of the produced TiO<sub>2</sub> up to 550 °C did not result in greater crystallinity. The crystallinity data are presented in Table 1 together with the crystal size data. From the data shown in Table 1 it is seen, that the heat treatment at elevated temperatures leads to crystal growth. The crystal size of the anatase crystals increases from about 9 nm up to 16 nm after heat treatment at 550 °C for 1 h.

AFM imaging of the films confirmed that the produced TiO<sub>2</sub> films were highly homogeneous. The AFM analysis of the TiO<sub>2</sub> films showed that the surface roughness of the films increased after heat treatment as shown in Table 1. An AFM image of a TiO<sub>2</sub> film produced without further treatment is shown in Fig. 1.



**Fig. 1.** AFM image of a film produced from the microwave assisted sol–gel method without further treatment.



**Fig. 2.** Representative Ti spectra for the TiO<sub>2</sub> film before and after UV irradiation in the climate chamber (50% RH).

#### 3.2. Surface analysis using XPS

##### 3.2.1. Ti 2p

Representative Ti 2p spectra for the TiO<sub>2</sub> film before and after UV irradiation in the climate chamber are shown in Fig. 2. From the figure it is seen that the titanium peaks of the films are located at 458.7 eV (Ti 2p<sub>3/2</sub>) and 464.4 eV (Ti 2p<sub>1/2</sub>). No significant changes between the Ti 2p spectra before and after UV irradiation were observed in the present investigation.

##### 3.2.2. O 1s

The O 1s spectra obtained from XPS analysis of the sol–gel film before and after UV irradiation at 50% RH is shown in Fig. 3. From the XPS spectra it is seen that the oxygen peak is asymmetric indicating that at least two different chemical states of oxygen are present. In literature the O 1s peak has been proposed to consist of 4–5 contributing species such as Ti–O in TiO<sub>2</sub> and Ti<sub>2</sub>O<sub>3</sub>, hydroxyl groups, C–O bonds, and adsorbed H<sub>2</sub>O [33]. Although H<sub>2</sub>O is adsorbed on the surface of TiO<sub>2</sub> films the physically adsorbed H<sub>2</sub>O on TiO<sub>2</sub> desorb under the ultrahigh vacuum condition of the XPS system. Thus only negligible amounts of physisorbed water remains on the surface of the TiO<sub>2</sub> films. The peaks located at 529.9 eV and 531.9 eV are assigned to Ti–O in TiO<sub>2</sub> and hydroxyl groups (Ti–OH), respectively

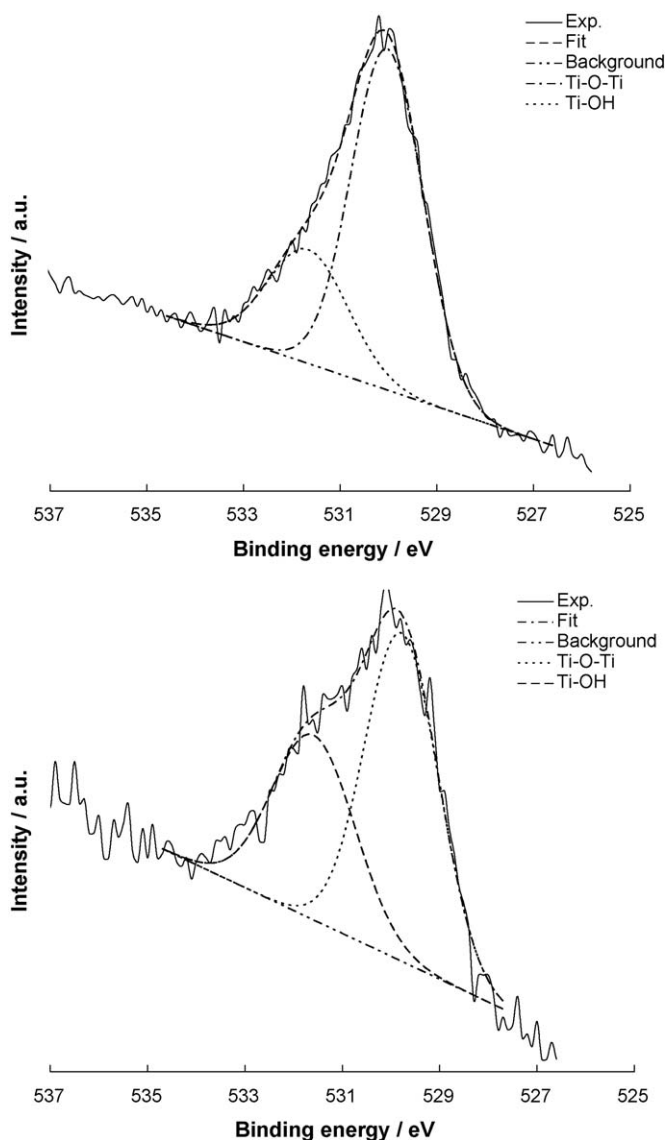


Fig. 3. O 1s spectra obtained from XPS analysis of the sol-gel film before and after UV irradiation in an atmosphere of 50% RH (25 °C).

[34]. In this work the O 1s peak is modeled using two gaussian functions corresponding to hydroxyl groups (Ti–OH) and lattice oxygen (Ti–O–Ti), respectively.

The modeled peak data for the O 1s spectra of the TiO<sub>2</sub> films obtained before and after UV irradiation under different atmospheric conditions (35–95% RH) are shown in Table 2. The peak data in Table 2 shows that the amount of surface OH groups on the

Table 2

Fitted XPS peak data for the microwave assisted Sol-gel TiO<sub>2</sub> films before and after UV irradiation in different humidity.

	35% RH	50% RH	75% RH	95% RH
O 1s peak data				
Area <sub>Ti-OH</sub> (%)	27.1	32.2	37.3	38.5
Area <sub>Ti-O-Ti</sub> (%)	72.8	67.8	62.7	61.5
Area <sub>Ti-O-Ti</sub> /area <sub>Ti-OH</sub>	2.7	2.1	1.7	1.6
O 1s peak data after UV				
Area <sub>Ti-OH</sub> (%)	35.8	43.5	47.1	49.2
Area <sub>Ti-O-Ti</sub> (%)	64.2	56.5	52.9	50.9
Area <sub>Ti-O-Ti</sub> /area <sub>Ti-OH</sub>	1.8	1.3	1.1	1.0

Table 3

Fitted XPS peak data for the microwave assisted Sol-gel TiO<sub>2</sub> film.

	Atomic ratio O <sub>lattice</sub> -Ti	Atomic ratio O <sub>total</sub> -Ti
TiO <sub>2</sub> films before UV irradiation		
35% RH	1.9	2.6
50% RH	2.1	3.1
75% RH	1.8	3.2
95% RH	1.9	3.4
TiO <sub>2</sub> films after UV irradiation		
35% RH	1.9	3.0
50% RH	1.9	3.5
75% RH	2.0	4.1
95% RH	2.2	4.2

TiO<sub>2</sub> films increase with an increase in the RH both prior and after UV irradiation.

In order to compare the amount of OH groups on the TiO<sub>2</sub> films under the different experimental conditions the atomic ratio between the crystal lattice oxygen and Ti was calculated and presented in Table 3. However, without a standard TiO<sub>2</sub> reference surface, it is not possible to use these ratios quantitatively, the ratios is therefore only used semi-quantitatively to obtain knowledge about changes in surface and lattice oxygen. From Table 3 it is seen that the atomic ratio between crystal lattice oxygen and Ti were found to be around 2 both before and after UV irradiation. In comparison the ratios between total amount of oxygen and Ti were found to vary significantly between the TiO<sub>2</sub> films investigated under different humidity both before and after UV irradiation.

In addition the amount of OH groups on TiO<sub>2</sub> films calcinated at temperatures from 25 °C to 550 °C was determined and the results are shown in Table 1 (Experimental conditions 50%RH, UV irradiation). It was found that the amount of surface OH groups increased a little for the films calcinated up to 450 °C. However, a significant drop in the OH concentration was observed for the TiO<sub>2</sub> films calcinated at 550 °C.

### 3.3. Photocatalytic activity

The photocatalytic activity of the microwave assisted TiO<sub>2</sub> films was investigated using stearic acid degradation. In Fig. 4 the photocatalytic degradation profiles of stearic acid on the

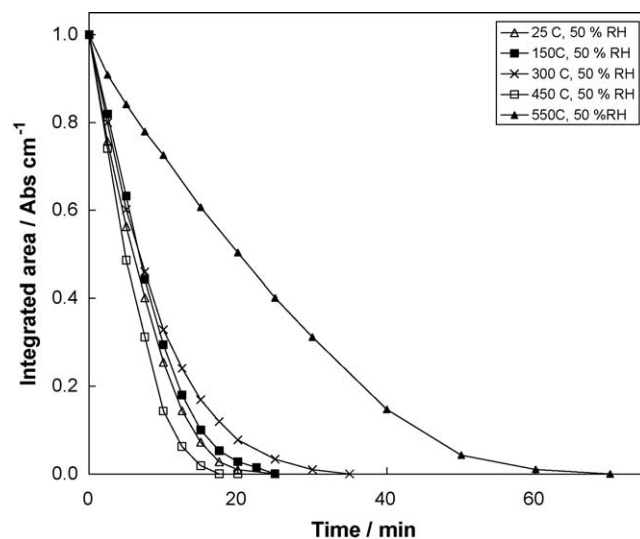


Fig. 4. Degradation profiles of stearic acid at different sintering temperatures. In the experiments the initial area of stearic acid varied between 6.2–7 Abs cm<sup>-1</sup>.

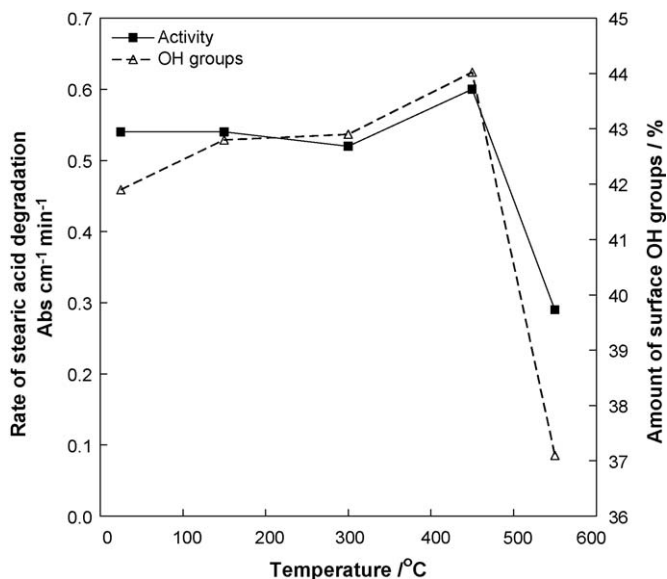


Fig. 5. Initial rate of stearic acid degradation as a function of the treatment temperature.

TiO<sub>2</sub> films heat treated at temperatures up to 550 °C are shown. The degradation profiles show that the rate of degradation of stearic acid of the TiO<sub>2</sub> films heat treated at a temperature up to 450 °C do not vary significantly. However, it was observed that the rate of degradation was considerably lower for TiO<sub>2</sub> films heat treated at 550 °C. In Fig. 5 the initial rate of degradation of stearic acid is shown as a function of the treatment temperature, which clearly shows a drop in activity of the TiO<sub>2</sub> films heat treated at 550 °C.

In Fig. 6 the degradation profiles of stearic acid on TiO<sub>2</sub> films at different humidity (20–95% RH) is shown. From the figure it is seen that the rate of degradation of stearic acid is highly influenced by the amount of water vapor in the air. It should be noted that the degradation of stearic acid on the TiO<sub>2</sub> films produced by the microwave assisted sol–gel method is highly reproducible. In Fig. 7 the rate of degradation of stearic acid is given by the initial rate of degradation from the degradation profiles in Fig. 6. From Fig. 7 it is seen that there is nearly a linear dependence between the rate of

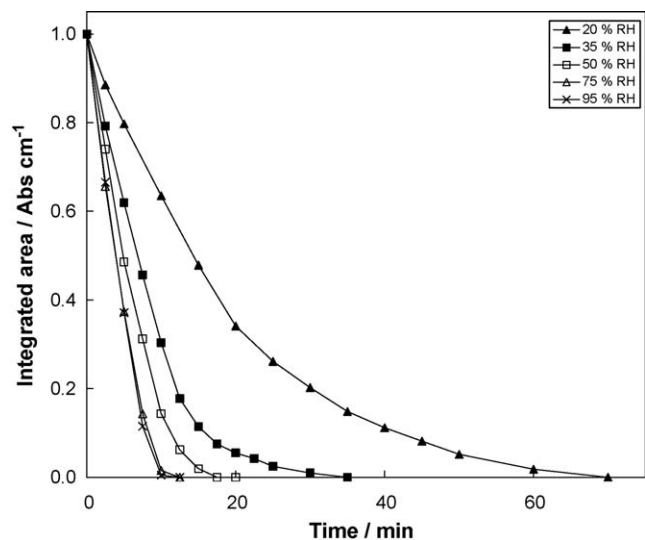


Fig. 6. Degradation profiles of stearic acid under varying humidity (20–95% RH). In the experiments the initial area of stearic acid varied between 6.2 Abs cm<sup>-1</sup> and 7 Abs cm<sup>-1</sup>.

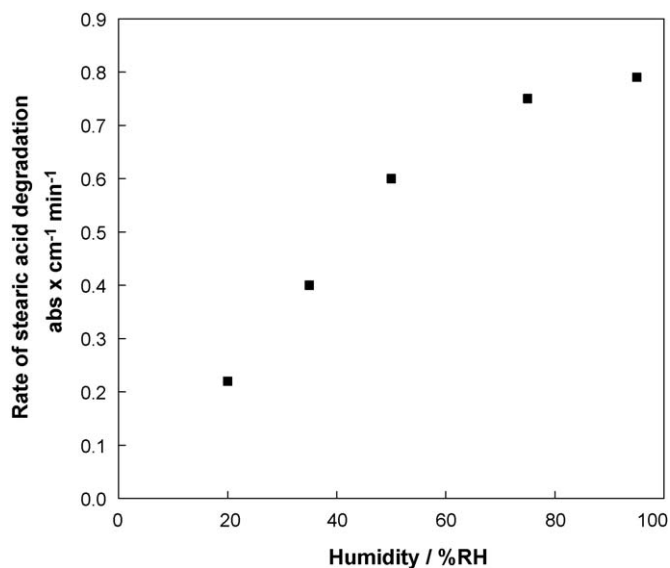


Fig. 7. Initial rate of degradation of stearic acid as a function of humidity.

degradation and the humidity up to about 60% RH. Above 60% RH the surface of the TiO<sub>2</sub> film may become saturated with OH groups and further increase in the RH up to 95% only leads to an increase in the rate by 15%.

In Fig. 8 the photocatalytic activity determined by stearic acid degradation is plotted against the amount of OH groups determined by XPS analysis. From the figure it is seen that there is a very good correlation between the activity and the percentage of OH groups on the TiO<sub>2</sub> films.

#### 3.4. Photoinduced superhydrophilicity

Fig. 9 shows the variation in the water contact angle (CA) on TiO<sub>2</sub> films as a function of irradiation time. The initial CA was found to be in an interval between 35° and 40°. After the UV irradiation was initiated the CA dropped to a value close to zero within 30 min. The conversion rates for the TiO<sub>2</sub> film used in this work were found to be highly reproducible. Although the

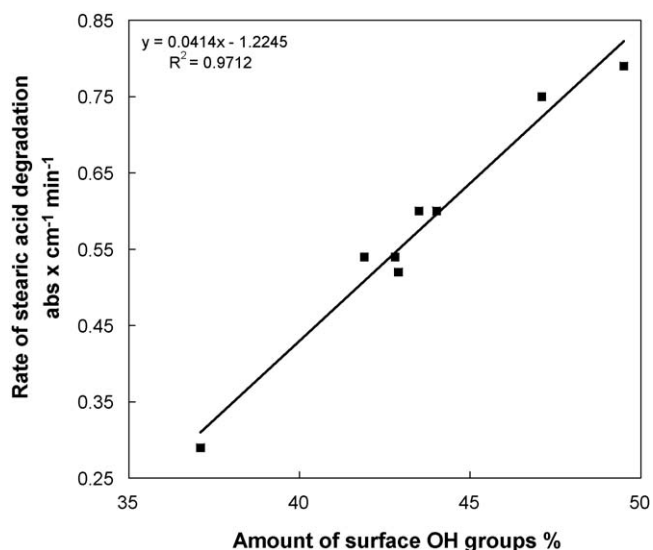


Fig. 8. Correlation between the photocatalytic activity and the percentage of OH groups on the surface of the TiO<sub>2</sub> films.

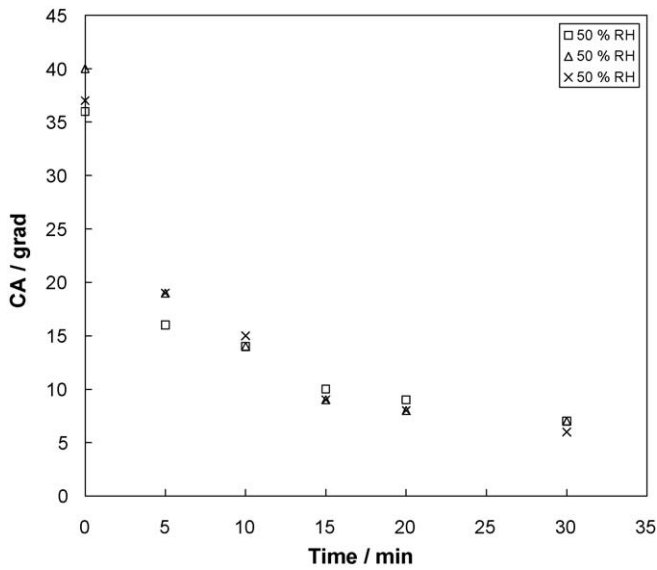


Fig. 9. Contact angle of water as a function of irradiation time.

conversion rate can be defined by the slope, it does not give a constant value because it depends on the initial value of the contact angle. The difference in the initial values of the CA is considered to be due to the difference in the amount of OH groups on the surface of the TiO<sub>2</sub> films under the different experimental conditions. In this work the conversion rate is given by the plot of CA<sup>-1</sup> as a function of UV irradiation time which has been suggested by Hashimoto and co-workers [14]. In Fig. 10 CA<sup>-1</sup> vs. UV irradiation time is shown for the hydrophilic conversion of TiO<sub>2</sub> films obtained at different humidity. The plot resulted in straight lines with correlation coefficient between 0.97 and 0.99. From Fig. 11 it is seen that the conversion rate increase nearly linear with increasing humidity. The conversion rates found in this work range from  $1.8 \times 10^{-3}$  degree<sup>-1</sup> min<sup>-1</sup> at 20% RH and up to  $11.3 \times 10^{-3}$  degree<sup>-1</sup> min<sup>-1</sup> at 95% RH.

In Fig. 12 the rate of conversion of the TiO<sub>2</sub> films as a function of treatment temperature is shown. It was found that the TiO<sub>2</sub> films heat treated at 25–450 °C showed similar conversion rates. In

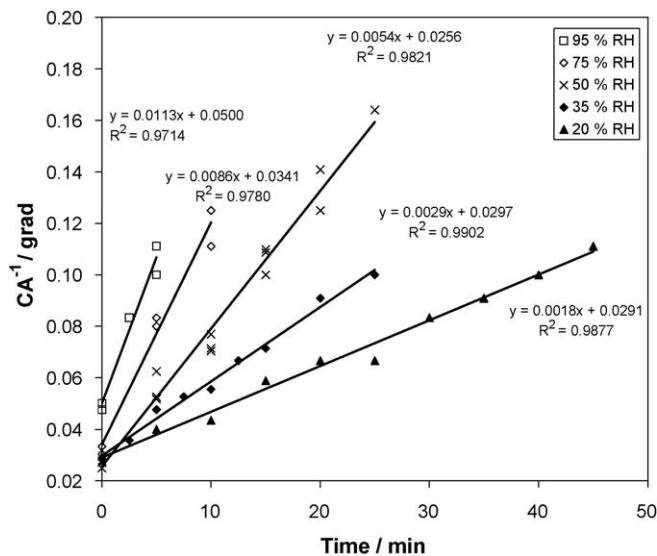


Fig. 10. Reciprocal contact angle of water as a function of irradiation time in different relative humidity.

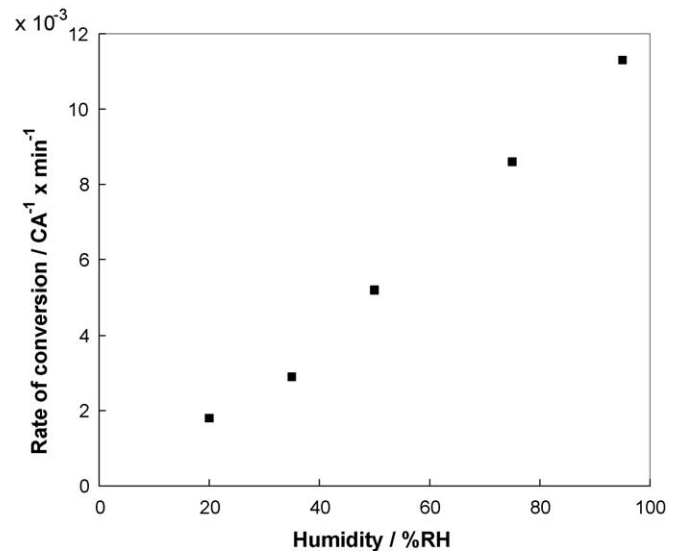


Fig. 11. Conversion rate as a function of humidity.

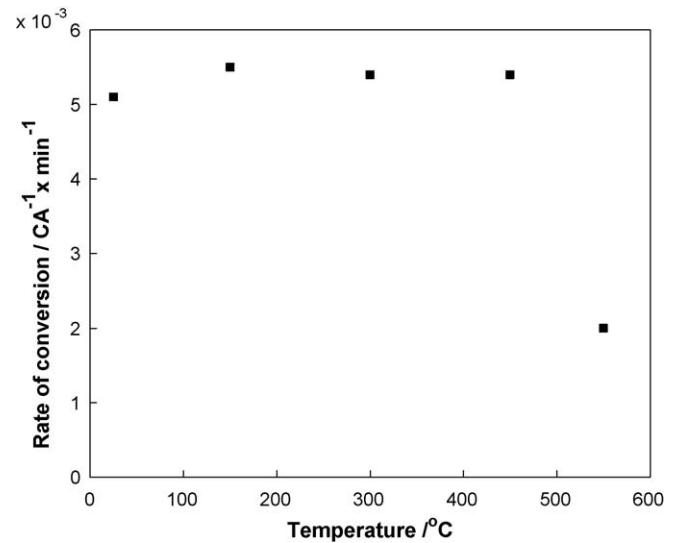


Fig. 12. Rate of conversion of the TiO<sub>2</sub> films heat treated at temperatures between 25 °C and 550 °C.

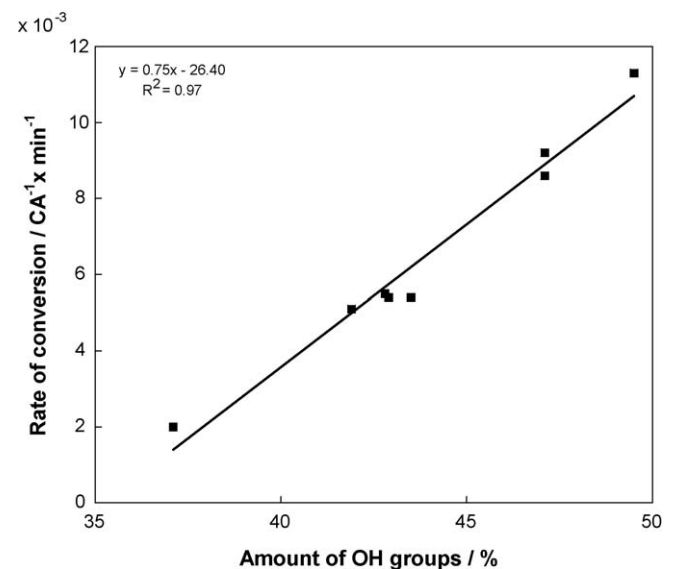


Fig. 13. Correlation between the amount of surface OH groups and the conversion rate.

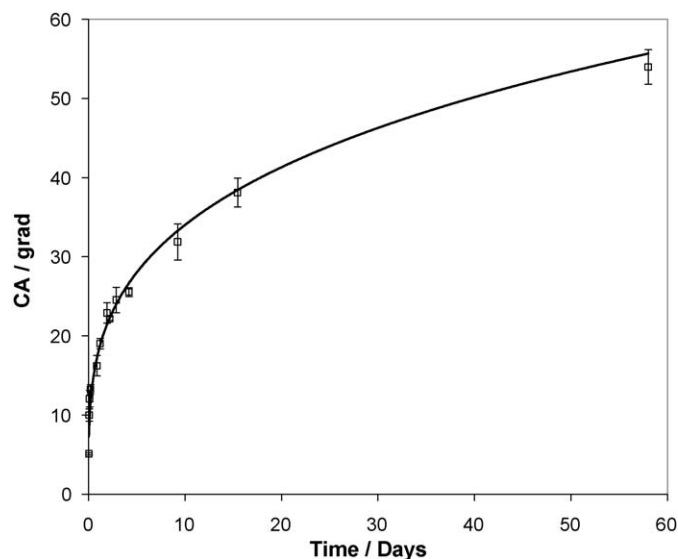


Fig. 14. Recovery of the TiO<sub>2</sub> films measures by the water contact angle as a function of time in ambient atmosphere (dark).

comparison a significant decrease in the rate of conversion was observed when the calcination temperature was increased to 550 °C.

In the present work a linear correlation between the amount of surface OH groups and the conversion rate was found (Fig. 13). From Fig. 13 it is seen that the amount of surface OH groups of the investigated TiO<sub>2</sub> films varied from 37% to 49% corresponding to a conversion rate of  $2 \times 10^{-3}$  degree<sup>-1</sup> min<sup>-1</sup> and  $11 \times 10^{-3}$  degree<sup>-1</sup> min<sup>-1</sup>, respectively.

Fig. 14 shows the recovery of the TiO<sub>2</sub> films measured as an increase in CA as a function of the dark storage time. From the figure it is seen that the recovery of the TiO<sub>2</sub> film proceeds over a period of up to 60 days.

#### 4. Discussion

Synchrotron X-ray photoelectron spectroscopy (XPS) was used in this work to investigate the changes occurring during UV irradiation of TiO<sub>2</sub> films in different humidities. The sharp and strong peak located at 458.7 eV in the Ti 2p spectrum Fig. 2 indicates that the Ti element mainly existed as Ti(IV) both before and after UV irradiation [35,36]. In photocatalysis the photogenerated electrons are assumed to be trapped by Ti(IV) sites, as Ti(III), which are subsequently oxidized by oxygen. In this case it should be possible to observe Ti(III) as a small shoulder at 1.6 eV lower bindings energies. However, the XPS spectra obtained in this work do not show any significant difference indicating that UV irradiation under these conditions induce a significant change in the Ti chemical states resulting in the formation of Ti(III) and Ti(II), which have been suggested by other groups [37,38].

From the O 1s spectrum of the TiO<sub>2</sub> films before UV irradiation in Fig. 3 it is seen that most of the oxygen is present as lattice oxygen. In comparison the XPS spectrum after 1 h of UV irradiation shows a significant change in the amount of surface oxygen. After UV illumination, the area of the peak due to the hydroxyl groups increases, indicating that the chemisorption of water molecules on the surface of the TiO<sub>2</sub> films is enhanced by UV irradiation. From the calculated atomic ratios in Table 3 it is seen that the atomic ratio of lattice oxygen and titanium was found to be around 2 corresponding to the general composition of TiO<sub>2</sub>. In comparison the atomic ratio of total amount of oxygen present and titanium

was found to be considerable higher. Comparing the atomic ratios in Table 3 shows that an increase in the RH leads to an increase in the amount of surface OH-groups (atomic ratio 0.7–1.5). In comparison an even higher increase in the amount of surface OH groups was observed when the TiO<sub>2</sub> films were UV irradiated under the same conditions (atomic ratio 1.1–2.1). These results are similar to the results reported by Yu et al. who also observed an increase in the OH group content after UV irradiation using high resolution XPS analysis [34].

Attenuated total reflection FT-IR was used in the study of the surface changes induced by UV irradiation of the TiO<sub>2</sub> films. The FT-IR investigation showed that UV irradiation induced an increase in the amount of adsorbed water on the TiO<sub>2</sub> films, however the observed increase was difficult to quantify due to physically adsorbed water.

The increase in the amount of OH groups is suggested to be caused by dissociative adsorption of water in vacancies. The photogenerated holes are assumed to be trapped at lattice oxygen at the surface of the TiO<sub>2</sub> film [12,13]. The trapped holes are thought to weaken the bond between the titanium atoms and the lattice oxygen. As a result such oxygen is liberated to create oxygen vacancies. It has been reported that UV irradiation of TiO<sub>2</sub> films in UHV creates lattice oxygen vacancies [39] and that subsequent water exsoria heals the TiO<sub>2</sub> surface by producing surface hydroxyl groups [40].

Besenbacher and co-workers has conducted a detailed study of the interaction of oxygen and water with the vacancies on rutile TiO<sub>2</sub> single crystals using STM [41]. The investigation showed that after interaction between dioxygen and the vacancies lattice oxygen was observed at the original vacancy site and a second oxygen atom was found in a five-coordinated position on top of a titanium atom indicating that a splitting of the dioxygen molecule has occurred. Interaction between water and the vacancies resulted in chemisorbed hydroxyl groups located in the original vacancy position. A second hydroxyl group was found very close to this indicating a transfer of a proton from the chemisorbed water molecule to a neighbouring bridging oxygen.

Our group believes that the increase in the amount of hydroxyl groups observed by the XPS investigation of the TiO<sub>2</sub> films after UV irradiation at different humidities has two origins. First existing oxygen vacancies in the TiO<sub>2</sub> films were occupied by water molecules after pretreatment of the films. Water is adsorbed easily on the TiO<sub>2</sub> films and occupies the vacancies even if it is present in almost negligible amounts [41]. Interaction between the vacancy and the water molecule leads to diffusion of a proton to a neighbour oxygen atom thereby creating two hydroxyl groups. According to the DFT calculation conducted by Besenbacher and co-workers the system is stabilized by diffusion of a proton to a more distant oxygen atom [41]. Furthermore, the diffusion to distant oxygen atoms is catalyzed by the presence of water molecules [42]. The DFT calculations also showed that the adsorption of dioxygen can stabilize the system even further. However, this process is not believed to occur to a greater extent if the principle part of the vacancies is already occupied by hydroxyl groups. That dioxygen did not occupy these vacancies immediately after creation is suggested to be a result of the difference in kinetics between the two competing molecules (dioxygen and water) during interaction with the oxygen vacancies. The increase in the total oxygen/titanium ratio at higher humidities is suggested to be due to adsorption of H<sub>2</sub>O leading to the formation of OH groups which are chemisorbed in the surface of the TiO<sub>2</sub> film and not only to be found in the vacancies [43,44]. Secondly, an increased amount of oxygen vacancies are induced by the UV irradiation. These vacancies are yet again believed to interact with water molecules resulting in an increase in the amount of hydroxyl groups.



In the photocatalytic process the hydroxyl groups on the surface are active in the oxidation process of organics by capturing a hole ( $h^+$ ) from the excited crystal resulting in formation for hydroxyl radicals. Usually, an increase in the hydroxyl content on the surface of  $TiO_2$  films enhances both the photocatalytic activity and the superhydrophilicity [34].

In the present study the rate of degradation of stearic acid on the  $TiO_2$  films heat treated at 550 °C was found to be considerable lower than films heat treated below 550 °C. In literature heat treatment at 550 °C has been reported to reduce the photocatalytic activity of  $TiO_2$  film due to the conversion of anatase to rutile. XRD investigation of the prepared films did however not show any evidence of formation of rutile. In recent work reported by Lim et al. [45] the amount of X-ray amorphous material was found to increase at temperatures from 500 °C to 700 °C due to the way of conversion of anatase to rutile in nanotitania. However, in the present work it was found that the amount of crystalline material (Anatase) did not change due to heat treatment at temperatures up to 550 °C. The crystal size of the anatase crystals determined by XRD was found to increase from 9 nm to 16 nm as the temperature was increased from 25 °C to 550 °C. This increase in crystalline size of the anatase may lead to a reduction of the active surface area (number of active sites) and thus a decrease in the photocatalytic activity. Surface roughness measurements of the  $TiO_2$  films suggested that the surface roughness increased with higher heat treatment. The observed increase in surface roughness is suggested to be caused by elimination of residual carbon originating from the sol-gel synthesis. Results obtained from DSC analysis of the produced  $TiO_2$  show that residual carbon is eliminated at temperatures between 200 °C and 450 °C (data not published) correlating with the observed increase in surface roughness at 450 °C and 550 °C. Usually a small increase in the surface roughness will result in an increase in the surface area and thus higher activity. However, depending on the surface composition (ratio between amorphous and crystalline material) the activity may vary. In this case the anatase crystals were found to increase in size suggesting that the surface area of the anatase crystals decrease. In addition XPS analysis of the surface of the  $TiO_2$  films showed that the films heat treated at 550 °C have the lowest amount of surface hydroxyl groups compared to the films calcined at 25–450 °C. Previous investigations conducted by this group have shown that there is a correlation between the photocatalytic activity and the amount of OH groups on the surface of the  $TiO_2$  films [46]. An increase in the amount of chemisorbed OH groups enhances not only the photocatalytic activity but also the polar properties and hydrophilicity of the surface [34]. Investigation of the photoinduced superhydrophilicity of the  $TiO_2$  film heat treated at different temperatures showed that the rate of conversion displayed a similar trend as for the photocatalytic activity indicating the importance of surface OH groups on the  $TiO_2$  film. Usually, the wettability of a solid surface is determined not only by the chemical properties of the surface, but also by its geometry. The hydrophilic properties of a surface are enhanced by fine roughness [34]. Thus, an increase in surface roughness will usually enhance the hydrophilic properties. In this investigation it was found that the surface roughness increased as the treatment temperature exceeded 300 °C (Table 1). However, in comparison the rate of conversion was found to decrease above 300 °C. The effect of the increase in surface roughness was most likely overshadowed by the change in the amount of surface OH groups.

The effect of humidity on the photocatalytic reactions in the gas phase has been well studied [47–50]. In these studies a competitive adsorption model between water molecules and contaminants on available sites and changes in hydroxyl radical population levels was suggested leading to a decrease in the degradation rate at high humidities.

The effect of humidity on the photocatalytic degradation of stearic acid deposited on  $TiO_2$  films is shown in Fig. 7. It was found that increasing humidity has a positive effect on the photocatalytic activity. The photocatalytic activity of the  $TiO_2$  films was found to increase linearly in the humidity interval from 20% to 75% RH resulting in an increase in the rate of degradation by a factor of 4. Hence, when assessing the photocatalytic activity of  $TiO_2$  films it is of great importance that the evaluation is conducted under the same atmospheric conditions and not just under ambient conditions. The increase in activity is suggested to be caused by increased amount of OH groups on the  $TiO_2$  films observed by XPS analysis. In Fig. 8 it is seen that there is a very good correlation between the photocatalytic activity and the amount of OH groups on the  $TiO_2$  film. Nizard et al. has also reported the existence of a high dependency of the photocatalytic activity on the humidity for the degradation of stearic acid on Solaronix™ anatase films [51].

In the present investigation the photoinduced superhydrophilicity was investigated through contact angle measurements at different humidity. The results of this investigation showed that there was a linear relation between the rate of conversion given by the reciprocal CA and the RH. Additionally, it was found that there was a linear relation between the conversion rate and the amount of OH groups on the  $TiO_2$  film determined by XPS analysis.

In regard to the two models suggested for the photoinduced superhydrophilicity described in the introduction the results of the present investigation supports the surface structural change model in the sense that UV irradiation was found to increase the amount of hydroxyl groups on the surface the investigated  $TiO_2$  films creating a more hydrophilic surface. However, it was also found that even though the samples were superhydrophilic the amount of OH groups on the surface varied significantly which may suggest that the difference in time required in order to obtain superhydrophilicity may be due to the difference in the photomineralization rate of organics contaminants on the  $TiO_2$  surface. As it was found that higher amount of OH groups on the  $TiO_2$  surface enhance the photocatalytic activity. Based on the conducted experiments it is suggested that the amount of OH groups on the  $TiO_2$  surface highly influence the photocatalytic activity and the photoinduced superhydrophilicity and that the two mechanisms may be closely related. It is suggested that UV irradiation of the  $TiO_2$  films lead to the formation of vacancies which in turn will react with  $H_2O$  and lead to the formation of OH groups. These OH groups is then thought to react with photogenerated holes leading to the formation hydroxyl radicals which will mediate the destruction of organics on the  $TiO_2$ . This mechanism suggests that the superhydrophilicity is obtained through a combination of the photocatalytic and surface structural change model.

Lee et al. has in their investigation of the role of water adsorption on the photoinduced superhydrophilicity on  $TiO_2$  films arrived at similar conclusions, in which the formation of hydroxyl groups and the removal of contaminants by photocatalysis together form the necessary conditions for superhydrophilicity [52].

The recovery of the  $TiO_2$  film is ascribed to the fact that the surface is contaminated by adsorbing gaseous contaminants from the air and that the surface defect sites can be healed or replaced gradually by oxygen atoms, which changes the surface wettability from hydrophilic to hydrophobic [34].

## 5. Conclusion

The results of this investigation showed that the microwave assisted sol-gel technique produces highly homogeneous and efficient  $TiO_2$  thin films without the need for treatment or calcination at high temperature for crystallization. It was found that the amount of crystalline material (anatase) did not change

due to heat treatment at temperatures up to 550 °C. Moreover, it was found that the rate of degradation of stearic acid on the TiO<sub>2</sub> films heat treated at 550 °C was considerable lower than on films heat treated below 550 °C. XRD analysis of the crystallite size showed that the crystalline size of anatase in the film increased from 9 nm to 16 nm as the temperature was increased from 25 °C to 550 °C indicating a decrease in surface area. In addition XPS analysis of the surface of the TiO<sub>2</sub> films showed that the films heat treated at 550 °C have the lowest amount of surface hydroxyl groups compared to the films calcined at 25–450 °C. Investigation of the photoinduced superhydrophilicity of the heat treated TiO<sub>2</sub> film showed that the rate of conversion displayed a similar trend as for the photocatalytic activity indicating the importance of surface OH groups on the TiO<sub>2</sub> film.

It was found that increasing humidity has a positive effect on the photocatalytic activity. The photocatalytic activity of the TiO<sub>2</sub> films was found to increase linearly in the humidity interval from 20% to 75% RH resulting in an increasing rate of degradation by a factor of 4. The increase in activity is suggested to be caused by increasing amount of OH groups on the TiO<sub>2</sub> films as observed by XPS analysis. There was found a very good correlation between the photocatalytic activity and the amount of OH groups on the TiO<sub>2</sub> film.

Investigations of the photoinduced superhydrophilic conversion rate showed that there was a linear relation between the rate of conversion given by the reciprocal CA and the RH. Additionally, it was found that there was a linear relation between the conversion rate and the amount of OH groups on the TiO<sub>2</sub> film determined by XPS analysis.

Based on the conducted experiments it is suggested that the amount of OH groups on the TiO<sub>2</sub> surface highly influence the photocatalytic activity and the photoinduced superhydrophilicity and that the two mechanisms may be closely related. It is suggested that UV irradiation of the TiO<sub>2</sub> films will lead to the formation of vacancies which in turn will react with H<sub>2</sub>O and lead to the formation of OH groups. These OH groups are believed to react with photogenerated holes leading to the formation of hydroxyl radicals who will mediate the destruction of organics on the TiO<sub>2</sub>. This mechanism suggests that the superhydrophilicity is obtained through a combination of the photocatalytic and surface structural change model. Absorbed organic contaminants are removed by photogenerated hydroxyl radicals creating a pristine TiO<sub>2</sub> surface and an increasing number of OH groups on the surface induced by UV irradiation will result in a hydrophilic surface.

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