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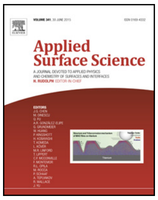

# Photocatalytic activity of $TiO_2$ thin films by hydrogen DC plasma

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ABSTRACT

Thin layers of anatase titanium dioxide were coated on glass by spray pyrolysis method. The layers were hydrogenated by DC plasma from room temperature up to 350 °C. Hydrogen plasma treatment at low temperatures, leads to decrease the surface roughness, while surface roughness is increased by enhancing plasma temperature. Layers' band gap was decreased 0.13 eV by plasma treatment at highest temperature. Hydrophilicity and photocatalytic properties of the layers under plasma treatment at 150 and 200 °C, were improved noticeably. However, plasma treatment at temperatures above 200 °C was lead to decrease hydrophilicity and photocatalytic activity of $TiO_2$ layers. The reason seems formation of oxygen vacancies in the interior layers that act as charge carriers' recombination centers.

## 1. Introduction

Due to its property as a semiconductor, when we apply ultraviolet light to titanium dioxide, it generates electron–hole pairs which are applicable in some processes such as photocatalytic activity, self-cleaning [1–6], solar cells [7,8], water and air purification, and antibacterial products [9–11]. The main disadvantage of $TiO_2$ is its large band gap (3.2 eV for anatase phase), so that its absorption edge is in ultraviolet region [12,13], which cause only about 5% of sunlight intensity. $TiO_2$ has three stable phases, anatase, rutile, and brookite, which structural, electronic, and vibrational properties of these phases have already been investigated by *ab-initio* calculations too [14]. There have been several attempts for increasing the benefits of this substance, by hydrogen treatment which some of them are; using hydrogen atmosphere at high pressures [15–20], hydrogen plasma and atmosphere treatment [21–26], and using hydrogen at high temperatures [27,28], to reduce its band gap and to increase its photocatalytic activity in visible region. Recently, Chen et al. have shown that the pressurizing $TiO_2$ powder under hydrogen atmosphere creates some engineered disorders along with remarkable reduction of band gap which leads to increased $TiO_2$ optical activity in visible region and its improved photocatalytic and photoelectrochemical properties [15]. In addition, the study of hydrogen adsorption and desorption on two dominant surfaces (1 0 1) and (0 0 1) of anatase phase have shown that in equal conditions of hydrogenation, (1 0 1) surface stores 40% more hydrogen than (0 0 1) surface [29].

Due to hydrogenation by plasma treatment and pressurizing methods, improving photocatalytic property of $TiO_2$ has been investigated greatly in recent years. It has already been shown that nanowires and nanoparticles of treated $TiO_2$ at hot hydrogen atmosphere have better photoelectrochemical and photocatalytic properties, because of formation of mid-levels due to presence of oxygen vacancy and $Ti^{3+}$, surface modification, and morphology improvement [21,22]. Application of hydrogen, argon, oxygen, and nitrogen's plasma lead to reduction of $TiO_2$ powder and producing middle states resulted in increasing its optical activity in visible region. In addition, it reduces the rate of electron–hole recombination because of charge carriers trapping [24,30–33].

As a computational view, many precise studies have been performed about the method of hydrogen's configuration in nano clusters [34,35], nanotubes [36], different surfaces of $TiO_2$, and also hydrogen adsorption [37–41]. In anatase phase, the (1 0 1) surface, due to its high thermodynamics stability, and (0 0 1) surface, due to high optical activity have drawn great attention [42,43]. It has been shown that, desorption of hydrogen and hydrogen diffusion into the bulk are energetically at the same level on (1 0 1) surface and oxygen vacancies are proper places for hydrogen attraction [44]. Concerted contamination of nitrogen and hydrogen in anatase $TiO_2$ has shown that if nitrogen is placed interstitially and hydrogen is connected to nitrogen, then, due to reduction of formation energy and band gap, increasing mobility, and reduction of recombination centers, photocatalytic property will be improved [45,46].

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In this research, thin layers of $TiO_2$ in anatase phase were coated by spray pyrolysis method and results lead to formation of dominant (1 0 1) surface. Hydrogenation of samples was performed by hydrogen plasma treatment and structural properties were studied by AFM and XRD (normal and grazing) experiments. We studied optical properties by measuring band gap, hydrophilicity by contact angle survey and photocatalytic activity by methylene blue degradation analysis under ultraviolet light.

## 2. Experimental details

In order to grow thin layers of $TiO_2$, we prepared precursor on magnetic stirrer. The composition of precursor was as follows: Titanium tetrachloride ($TiCl_4$, Merck, 99.9%) and Ethanol ($C_2H_5OH$, Merck, 99.9%) with the ratio 1:10. The precursor was mixed an hour in ice bath due to degasing of HCl from solution. Coatings were performed on the glass substrates (TEGET). To remove any pollutions, substrates were washed 24 h in HCl and 20 min in water and ethanol solution under ultrasound. The prepared solution was coated on glass by spray pyrolysis. We have used nebulizer (Omron–NE–C28E) as atomizer and substrate temperature was kept at 350 ± 5 °C. Distance between atomizer's nozzle and substrate was set to 10 cm. The period of coating was 60 s with 30 s delay between 2 pitches, so that it prevented excess temperature drop of substrate. At the end of coating and cooling to room temperature, in order to form the anatase crystal structure, the samples were annealed at 300 and 450 °C each one for 60 min. Sample hydrogenation was performed by hydrogen DC plasma. Quartz tube vacuum was set at 20 mTorr and entering hydrogen flow was set at 0.2 l/min. Applied voltage was 300 V and produced hydrogen plasma current was set at 50 mA. Hydrogenation temperature was changed for samples from room temperature until 350 °C.

Samples photospectrometry was done by Avantes-2048 spectrometer. Structural properties and roughness was measured by X-ray diffraction (Philips) and atomic force microscopy (NT-MDT), respectively. XRD data were collected with angular step of 0.02 degree and time step of 0.7 s in normal and angular step of 0.01 degree and time step of 100 s in grazing XRD. Thickness of layers was measured by profilometry method (Dektak 3 version 2.13 instrument). Droplets' contact survey was measured by CCD camera (Proline-UK). Each contact angle is average of five measurements. The experimental error of the measurements is ±1°. The photocatalytic activity was tested by degradation of 0.01 molar methylene blue (MB) using photospectrometer at wavelength of 660 nm under 2.5 $mW/cm^2$ ultraviolet light.

## 3. Results and discussions

At first, we have studied the effect of hydrogen plasma on surface and crystal structure of $TiO_2$ layers. For better observation of hydrogen plasma effect, we chose similar growth conditions for all the samples to get maximum similarity. We have shown AFM images of the samples in Fig. 1. According to Table 1, non-hydrogenated layer has mean roughness of 7.5 nm, which the magnitude was decreased about 3 nm by applying hydrogen plasma at room temperature. Roughness magnitude was increased by increasing hydrogen plasma temperature. It is seen that hydrogen plasma has decreased the roughness exclusively, but along with increasing temperature, has increased the roughness although these changes are not considerable.

In chemical synthesis methods, different structures may be grown in coating of $TiO_2$ on glass. The results of XRD analysis show (in Fig. 2) that for layers grown by spray pyrolysis method, the crystal structure of anatase is formed in the following manners: along (1 0 1) surface at angle 25.34 degree, along (2 0 0) surface at angle 48.07 degree, and along (2 1 1) surface at angle 55.07 degree [16,20]. With respect to peak intensity, (1 0 1) surface of anatase which is thermodynamically the most stable surface [42], has the most frequent grown surface. During H-doping of different surfaces of anatase and rutile $TiO_2$, calculations have shown that penetration of hydrogen into the bulk and bonding with $O_{2c}$ is the most preferred situation [39,44]. XRD of the layers show that by increasing the hydrogenation temperature from room temperature to 350 °C, there is no considerable change in peak intensities (Fig. 2). The considerable point is the presence of a new peak at angle 29.45 degree which can be assigned to hydrogen penetration into the layer and formation of $H_2Ti_8O_{17}$ structure along $(2\,0\,\bar{4})$ planes [47]. The intensity of this new peak increases until 250 °C and it decreases by increasing plasma temperature up to 350 °C.

Regarding to peaks intensities, it seems that hydrogen penetration (diffusion) into the structure takes place at the temperatures up to 400 °C. By increasing the temperature from 200 to 350 °C, hydrogen atoms may is desorbed from the surface and the structure is relaxed and returned to its initial form. The normal and grazing XRD (Fig. 3) for the sample 4 was performed three months after hydrogenation, to study the presence of hydrogen in bulk and surface of the layer, separately. Presence of anatase phase peaks was approved by the results of normal analysis. The (0 0 4) peak of anatase phase at angle 37.92 degree and $(2\,0\,\bar{4})$ peak of $H_2Ti_8O_{17}$ structure at angle 29.57 degree were also seen with lower intensities. While in results of grazing XRD analysis only (2 0 4) and (0 0 4) peaks of anatase were observed and $(2\,0\,\bar{4})$ peak of $H_2Ti_8O_{17}$ structure was not observed, it seems that $H_2Ti_8O_{17}$ structure has the maximum forming amount at 200 °C and decreases after 3 months desorption of hydrogen atoms from the structure due to its instability. By comparing the normal and grazing XRD results, it seems hydrogen absorption and forming of $H_2Ti_8O_{17}$ structure was performed at interior layers (not surface layers) of the hydrogenated samples.

Transmission and reflection spectrum of the layers before and after hydrogenation were measured to determine band gap changes due to hydrogenation (Fig. 4). The effect of atomic hydrogen doping in the bulk of $TiO_2$ has already been shown that anatase band gap decreases about 0.12 eV, which was corresponded to presence of Ti–OH–Ti bonds and donor states under conduction band [27,48]. In addition, presence of oxygen vacancy in different $TiO_2$ phases and reduction of band gap due to middle states, have already been reported [49]. Application of hydrogen plasma at room temperature (sample 2) leads to 7 nm red shift of absorption edge, which is about 15 nm at 350 °C (sample 7). Optical band gap of thin films was calculated from fit on linear relation of $(\alpha h\nu)^{0.5}$ versus incident photon energy ($h\nu$) plot. Thickness of films was 1518 ± 8 nm for hydrogenated and non-hydrogenated samples. Based on the results (Fig. 5 and Table 1), hydrogen plasma at room temperature decreases the band gap only 0.02 eV, while increasing the temperature of hydrogen plasma reduces the band gap up to 0.13 eV at 350 °C. For better resolution, only transmission, reflection, and absorbance of samples 1, 2, 4, and 7 have been plotted.

It seems that application of hydrogen plasma leads to a hydrogen doping or/and oxygen vacancy creation. In addition, reduction of absorption edge to visible region with increasing plasma temperature may be due to forming of oxygen vacancies [30]. It has been shown that, in synchronous doping of hydrogen and oxygen vacancy, the hydrogen atoms locate on oxygen vacancies [44]. In this work, application of plasma at higher temperatures, may increase bulk oxygen vacancies and also decreases the amount of newly formed structure, $H_2Ti_8O_{17}$, which is due to relaxation of hydrogen atoms and diffusion inside bulk of the thin films.

Contact angle survey (Fig. 6) showed that the contact angle of water droplet on $TiO_2$ layer decreases by UV illumination time.

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