



Effect of Surface Roughness of 316 L Stainless Steel Substrate on the Morphological and Super-Hydrophobic Property of TiO₂ Thin Films Coatings

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Abstract

In this study, TiO₂ was coated on 316L stainless steel substrates via sol–gel/ dip coating method. The effects of surface roughness on the physical properties have been investigated. Scanning electron microscopy (FE-SEM), FTIR and X-ray diffraction (XRD) were used to investigate the morphological properties, identification of simple mixtures of organic and inorganic compounds and structure of crystal, respectively. Also, the effect of roughness on the hydrophobic property of coating measured by water contact angle. Water contact angle increased from 142.5° to 168.5° by increasing the roughness. From wettability results indicated that roughness had significant effect on the hydrophobic property of thin films.

Keywords TiO₂ · Sol–gel · Hydrophobic property · Thin film

1 Introduction

Wetting phenomenon on solid materials plays important roles in biology [1], chemistry [2], physics [3, 4], materials and applied sciences, engineering technology [5]; and it is governed by both chemical composition and geometric structure of the surface [6, 7]. A surface with a water contact angle (WCA) of more than 150° that extremely repels water is called a superhydrophobic surface [8]. This strategy is perfectly exhibited by the lotus leaf whose surface has two scales (micron and nano-sized) wax protrusions [9–11]. The development of various fabrication techniques for superhydrophobic surfaces by simulating the surface of the lotus leaf is a pertinent subject. Super-hydrophobicity can be achieved by combination of surface roughening and lowering surface energy [12, 13]. Self-cleaning glass is used in automotive industry [14]. It was found that a certain percentage of SiO₂ doped to TiO₂ thin film can enhance the super-hydrophilic effect after UV irradiation. Mixed oxides have been widely produced by sol-gel process to improve photo-catalytic reaction [15]. Yu and Zhao reported

that the hydrophilicity can be enhanced by processing the TiO₂ surface with acids resulting in the decrease of water contact angle of porous TiO₂ coating film by increasing the absorbed content of hydroxyl, capillary force and roughness of coatings [16, 17]. Barabasi, evaluated photo-induced hydrophilic conversion on different crystal faces of single crystal rutile and polycrystalline anatase to clarify the effect of the crystal structure on photo-induced hydrophilic conversions [18]. The super-hydrophilicity of TiO₂ thin films is obtained only under UV light irradiation. Therefore, it is necessary to extend the photo-response of the TiO₂ thin film from UV to the visible region by modification of its optical properties. Extensive studies have been conducted to shift the TiO₂ absorption edge from the UV to the visible light region by ion doping with transition metals [17–19].

Today, surface roughness has a vast consideration in science and technology [20, 21], it has an important effect in some physical phenomena such as: friction, degrees of hydrophilicity and hydrophobicity, self-cleaning, [22, 23] and also improving the mass throughput in microchannel and Nano channel flows [24]. The substrate roughness might alter the interfacial energy and the wetting mechanism. Early modeling carried out by Wenzel [25] to discuss thermodynamic approach in which the additional surface area produced by roughening the substrate was regarded as effectively causing an increase in its surface energy. To the best of our knowledge this is the first

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Table 1 Chemical analysis of 316L stainless steel (in weight percent)

Fe	C	Si	Mn	P	S	Cr	Mo	Ni	Al	Co	Cu	Nb	Ti	V	W
67.7	0.031	0.44	1.36	<0.005	<0.005	17.2	1.95	10.69	0.0119	0.266	0.102	0.019	<0.005	0.0872	<0.005

report studying on the effect of roughness of 316L stainless steel substrate on the superhydrophobicity of TiO₂ coating prepared by sol-gel method. Also, the results obtained in the synthesis and characterization of nanostructured thin films of TiO₂ which were prepared by dip coating method are reported. Results from Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (FESEM) and contact angle measurement (CA) studies are discussed.

2 Experimental Procedures

2.1 Preparation of Thin Films

The preparation of precursor solution for TiO₂ thin films is described as follows. For the preparation of TiO₂ sol, Titanium (IV) iso-propoxide (TTIP = TiO₄H₂₈Cl₂, Sigma) was selected as titanium source. First, 0.35 mol ethanol (EtOH, Merck) and 0.04 mol ethyl acetoacetate (EAcAc is as a sol stabilizer during preparation of sol and also chelating agent during coating, Merck,) were mixed, and then 0.01 mol TTIP was added by the rate of 1 mL/min to the mixture at the ambient temperature (25 °C). The solution was continuously stirred for 45 min, followed by the dropping of 2ml of HNO₃ as catalyst to the solution until pH = 3. 3ml of De-ionized water was added to the

solution slowly to initiate hydrolysis process, finally volume of solution achieved to 50ml. Solution was aged for 24 h in order to complete all reactions. The substrate were degreased in HNO₃ and NaOH in de-ionized water for 35 min then in acetone. Thin films were applied on the 316L stainless steel substrates (its chemical analysis shown in Table 1) with the prepared sol solutions by dipping-withdrawing at room temperature with withdrawal speed of 10 mm/min. Substrate dimensions were 10× 10× 1 mm. After that substrate were dried at 100 °C for 1 h after each coating cycle and finally heated at a rate of 10 °C/min and annealed at 400 °C for 1h.

2.2 Characterization Methods

Roughness measurements were obtained on a Taylor–Hobson Surtronic 25 instrument with the inclusion of 50 mm stylus lift and right-angle attachment 70 mm stylus. Roughness was measured perpendicular to the grinding scratches, and each measurement is a mean of five measurements on each specimen.

Morphology of the thin films was observed using scanning electron microscope (FESEM, MIRA3 TESCAN) with an accelerating voltage of 10–30 kV. FTIR absorption spectra were measured using Bruker Tensor 27 (Bruker-Germany) over the range of 4000–400cm⁻¹ at room temperature. The contact angles (CA) were measured by a

Fig. 1 XRD pattern of dip-coated pure TiO₂ thin film calcined at 400 °C

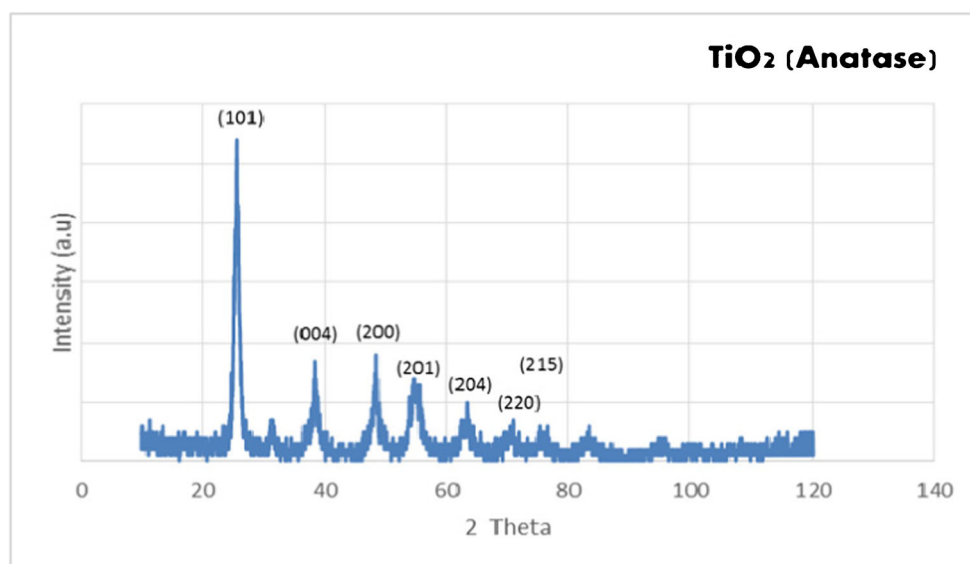
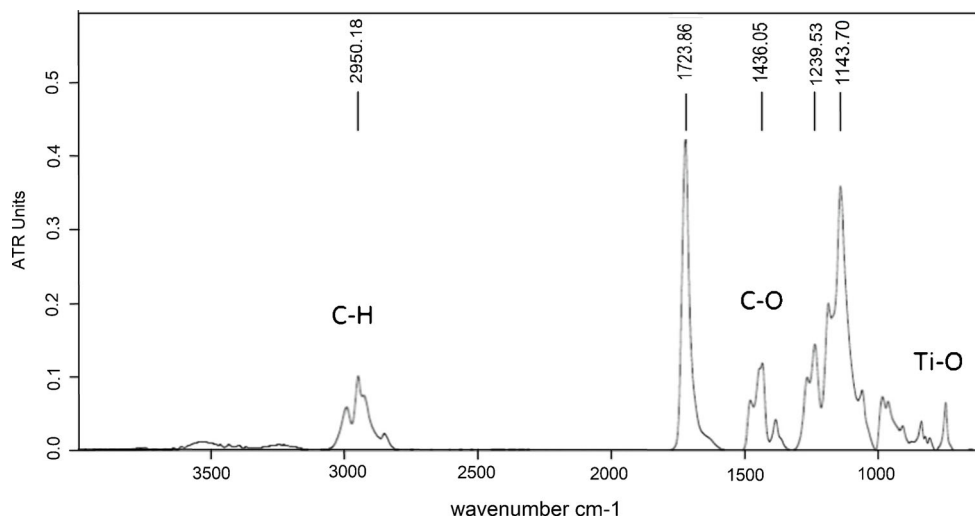


Fig. 2 FTIR spectra of pure TiO₂ thin film calcined at 400 °C



Dataphysics (OCA 15 Plus) static dynamic contact angle instrument, after dropping several water drops on the film surface of each sample.

3 Results and Discussion

3.1 X-ray Diffraction and FTIR Studies of TiO₂ Thin Films

Figure 1 shows the XRD patterns of TiO₂ thin film heat treated at 400 °C for 1 h. X-Ray diffraction peak at 25.5° corresponds to characteristic peak of crystal plane (1 0 1) of anatase in film. According to XRD pattern, the pure TiO₂ constituted of pure anatase phase.

Figure 2 shows FTIR spectra for TiO₂ thin films in the range of 400–4000 cm⁻¹. Metal oxides generally give absorption bands in fingerprint region below 1000 cm⁻¹ arising from inter-atomic vibrations.

The infrared spectra (Fig. 2) of TiO₂ thin films exhibited the following bands:

- (i) 2924.25 cm⁻¹ related to band C₂H₅-O band
- (ii) 3442.27cm⁻¹ and 3332.02 cm⁻¹ related to inter molecular structure and the O-H band(respectively) low intense peak at 1645 cm⁻¹ attributed to the δ- mode of the O-H groups of the adsorbed water molecules
- (iii) weak bands around 1384 cm⁻¹ corresponded to the C-O vibration.
- (iv) 511.02 cm⁻¹and 511.04cm⁻¹which can be attributed to the Ti-O stretching and Ti-O-Ti binding stretching modes (respectively)

Results of FTIR Spectroscopy, confirmed the existence of mixtures of organic and inorganic compounds on the surface.

3.2 Study of the Surface Morphology of TiO₂ Thin Films

The morphologies of TiO₂ thin films were studied by SEM as illustrated in Fig. 2. There are changes in the size, shape and amount of clusters on the surfaces, as the surface roughness varies. Accordingly, Fig. 3a clearly shows a uniform and delimited thin film on surface of the 316L stainless steel with surface roughness of 0.2μm. Figure. 3b shows non porous uniform TiO₂ substrate coating with some agglomerated particles which are randomly. From Fig. 3c one can see very much agglomerated particles which are attached to the surface to form an uneven surface. In Fig. 3d TiO₂ coating was applied on a highly roughened substrate. This figure also shows a uniform thin film on the surface. It should be noted that with increase in roughness, the Surface was consisted of highly dense and uniform nanocrystalline TiO₂ coating.

3.3 Surface Wettability of TiO₂ Thin Films

Wettability is depend on both surface chemical composition and surface geometric structure. Wettability is classified as hydrophobic and hydrophilic due to the contact angle of a fluid such as water with a solid surface. If the contact angle is higher than 90°, the surface is hydrophobic and the surface is hydrophilic when the angle lower is than 90° Fig. 4 shows the evolution of the water contact angle of TiO₂ thin films with the substrate roughness. The images of water droplets have been included in Fig 4. As observed, all thin films showed the hydrophobic behavior with static contact angles in the range of 142.5–168.5° for TiO₂ thin films, where the contact angle for the bare 316L stainless steel slide was 72°. The water contact angle of TiO₂ thin film

Fig. 3 FE-SEM micrographs of TiO_2 at different roughness of the thin film calcined at 400°C **a** $0.2\mu\text{m}$ **b** $0.26\mu\text{m}$ **c** $0.33\mu\text{m}$ **d** $0.45\mu\text{m}$

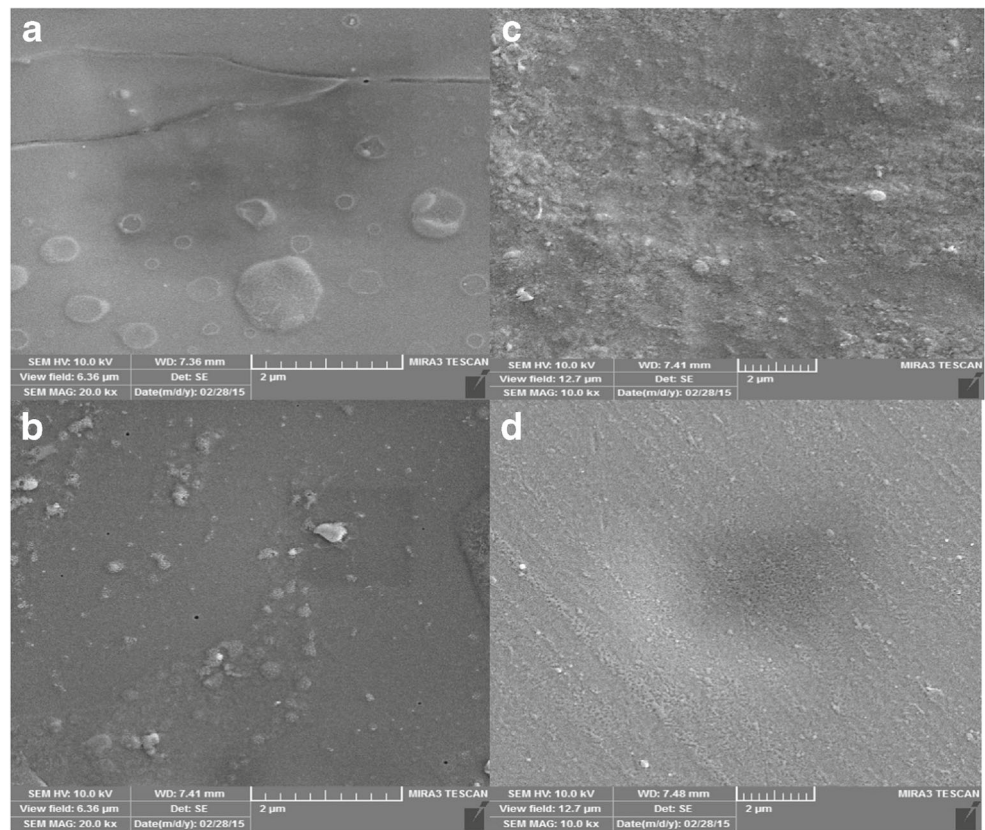
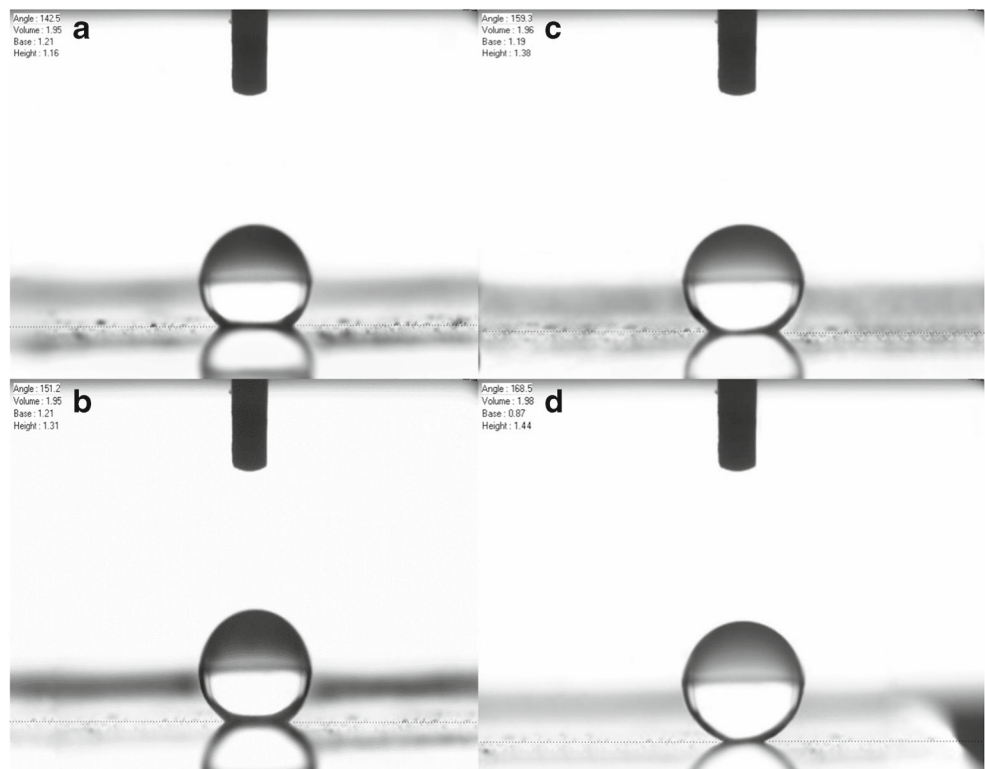


Fig. 4 Contact angle images of surfaces of the samples with water at different roughness: **a** $0.2\mu\text{m}$ **b** $0.26\mu\text{m}$ **c** $0.33\mu\text{m}$ **d** $0.45\mu\text{m}$



was 142.5° , which reveals lower wettability for this sample (roughness = $0.20\mu\text{m}$) compared to that of the bare 316L stainless steel. Also, for the TiO_2 sample with roughness of $0.26\mu\text{m}$, the contact angle was measured as 151.2° . By increasing roughness up to $0.33\mu\text{m}$, the wettability decreased to 159.3° . Hence, increasing of roughness of the substrate led to a valuable increase in hydrophobicity behavior and decrease wettability properties. Nevertheless, the wettability decreased with further increase in the surface roughness of 316L stainless steel substrate. Generally, due to the same chemical compositions of TiO_2 thin films, the difference in wettability among all of the samples is dependent on the amount of surface roughness. Therefore, in agreement with SEM images, the wettability is the lowest for TiO_2 with the highest surface roughness.

4 Conclusions

1. An easy and cost-effective method for fabricating TiO_2 thin films on the surface of 316L stainless steel substrate was demonstrated
2. XRD spectrum confirmed the formation of pure anatase on the 316L stainless steel substrate after heat treating of the thin film in 400°C for 1h.
3. FTIR results represented two peaks at 511.02 and 511.04 attributed to Ti-O and Ti-O-Ti bands respectively. So the existence of TiO_2 on the surface is evident.
4. The FESEM images indicated that the increase of the substrate roughness affected thin film morphology
5. The water contact angle thin films increased from 142.5° to 168.5° with change in the surface roughness from $0.2\mu\text{m}$ to $0.45\mu\text{m}$ respectively.
6. Furthermore, as thin films have received considerable attention for their application in various industries, this

cheap and easy to make method may be used to produce various metallic and metal oxide thin films.

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