A Markedly Controllable Adhesion of Superhydrophobic Spongelike Nanostructure TiO$_2$ films

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ABSTRACT

A simple electrochemical and self-assembled method was adopted for the fabrication of superhydrophobic sponge-like nanostructured TiO$_2$ surface with markedly controllable adhesions. Water adhesion ranged from ultra-low (5.0 μN) to very high (76.6 μN) can be tuned through adjusting the nitro cellulose dosage concentrations. The detailed experiments and analyses have indicated that the significant increase of adhesion by the introducing of nitro cellulose is ascribed to the combination of hydrogen bonding between the nitro groups and the hydroxyl groups at the solid/liquid interfaces and the disruption of the dense packed hydrophobic PTES molecule. A mechanism has been proposed to explain the formation of superhydrophobic TiO$_2$ films with distinct adhesion.

Keywords: superhydrophobic, titanium dioxide, nanostructures, adhesion, hydrogen bonding

1 INTRODUCTION

In recent years, superhydrophobic surfaces, with a water contact angle (CA) greater than 150°, have attracted much interest due to their importance in theoretical research and practical application.[1-3] It is well-known that the preparation of superhydrophobic surfaces is the combination of rough structure and the coating of low surface energy materials.[4-9] There are two extremely superhydrophobic cases in nature, that is, superhydrophobic lotus leaves with a sliding angle (SA) lower than 10° and superhydrophobic gecko feet with highly adhesive force. These findings have inspired the creation of functional materials with self-cleaning and novel adhesive by mimicking their special structures.[10-12] However, the research on superhydrophobic surfaces with ultra-low or highly adhesive force to water droplet was always neglected and only had been theoretically or experimentally discussed to a very limited extent.[13-15] It is expected that superhydrophobic surface with ultra-low or highly adhesion to water will have many potential applications, such as microanalysis and liquid transportation without loss.

In this work, we fabricated sponge-like structure TiO$_2$ films by a simple electrochemical method, and then modified the as-prepared samples with 1*H*，1*H*，2*H*，2*H*-perfluorooctyltriethoxysilane (PTES) and certain concentration of nitro cellulose (NC) to obtain superhydrophobicity with highly distinct adhesive forces by self-assembled technique. The sponge-like film with superhydrophobic and ultra-low adhesive force was achieved by sole PTES modification. However, when a certain NC was added into the PTES modified solution, the films not only retain superhydrophobicity but also have highly adhesive forces to water droplet. Extensive experimental results indicate that NC concentration has a great effect on both the contact angles and adhesive force for water droplet. This remarkable phenomenon and further mechanism analysis offer us an insight into how to control the surface chemical compositions to regulate the superhydrophobicity with a markedly controllable adhesive force that varies a wide range (5.0-76.6 μN). This simple method on the control of water adhesion under ambient condition without resorting to other special coating processes may be conveniently applied to other superhydrophobic surfaces.

The sponge-like nanostructure TiO$_2$ films were fabricated by electrochemical anodizing purity titanium sheets in 0.5 wt % HF electrolyte with Pt counter electrode. The anodizing was carried out at 50 V for 20 min. The TiO$_2$ film was then rinsed with deionized water and dried with dry N$_2$. The as-prepared TiO$_2$ films were then treated with a methanolic solution of hydrolyzed 1 wt % PTES (Degussa Co.) for 3 h and subsequently baked at 140 $^{\circ}$C for 1 h.

2 RESULTS AND DISCUSSION

Figure 1a, b show the typical top and cross-sectional SEM images of the as-anodized samples, respectively. It can be seen that the surface has a uniformly-distributed sponge-like nanostructure, and the thickness of nanostructured TiO$_2$ film is approximately 500 nm. Water rapidly spreads and wets this as-anodized sponge-like film without PTES modification due to side penetration of the liquid by capillary forces, indicating such sample is superhydrophilic. However, it is observed that the droplets with spherical shapes slide spontaneously, and hardly come to rest even when it is placed gently onto the PTES modified sponge-like TiO$_2$ surface. The water CA on such sponge-like structure film is as high as 160° (shown in the inset of Figure 1a), while that on a regular flat TiO$_2$ surface is only 115°, which is in good agreement with the results of

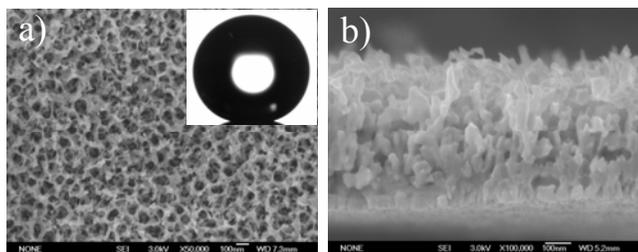coating fluorocarbon hydrophobic layer on smooth surface by self-assembly.

Figure 1. A typical top (a) and cross-sectional (b) SEM images of the as-prepared TiO_2 sponge-like structure film by 50 V. The inset shows the shape of water droplet on the corresponding PTES modified film.

To understand the superhydrophobicity of the sponge-like TiO_2 surface, we describe the contact angle in terms of the Cassie equation:[16] $\cos\theta_r = f_1 \cos\theta - f_2$. Here, f_1 and f_2 are the interfacial area fractions of the sponge-like TiO_2 surface and of the air in the interspaces surrounding the TiO_2 material, respectively (i.e., $f_1 + f_2 = 1$); θ_r (160°) and θ (115°) are the contact angles on the rough sponge-like TiO_2 surface and on the self-assembled monolayer of PTES on a flat TiO_2 surface, respectively. It is easy to deduce from this equation that contact angle of the rough surface (θ_r) increases with increasing the air fraction (f_2). According to the equation, the f_2 value of the rough, sponge-like TiO_2 surface is estimated to be 0.90. Therefore, we can realize that the large fraction of air trapped in the rough surface (i.e., to prevent water from penetrating) is important to the superhydrophobicity. These results demonstrate that the combination of a uniquely rough structure with large air fraction and a low surface energy coating modification are definitively vital for the superhydrophobicity.

The roll-off behavior was recorded with a high-speed photography as shown in Figure 2a. The white arrow heads at the bottom of the figures show the sliding direction of water droplet on the sponge-like TiO_2 thin film. The sliding behavior indicates that this film has an exceptionally low resistance to water droplet rolling. It is also interesting to note that the water droplet bounces off this sponge-like structure film when it is dropped from a certain height above the surface. The mean advancing and receding angles of water droplet on the surface are 160.1° and 159.3°, respectively, indicating that this unique structure film has an ultra-low CA hysteresis (only about 0.8°). Up to now, only limited information on the ultra-low water hysteresis phenomenon has been reported.[17] The reason for such ultra-low hysteresis can be attributed to the large fraction of air trapped in the rough sponge-like nanostructure TiO_2 surface, which significantly decreases the contact area. On the other hand, it has been suggested that the unstable discontinuous three-phase (solid-liquid-air) contact line of the rough TiO_2 surface can lead to a smaller hysteresis than the well-ordered two-dimensional surface.[18]

In contrast to the rolling behavior of water droplet on the sole PTES-modified sponge-like structure film, the behavior of water droplet on the surface of the same film that was modified by a mixture of PTES and NC is totally different. Figure 2b shows the shape of a water droplet on the PTES and 0.2 mg/mL NC (PTES-NC) modified sponge-like structure film with different tilt angles. The static water CA on the horizontal surface of this material is also very high, approximately 153.6°, indicating that these films retain their superhydrophobicity after the incorporation of NC. For these films, the water droplet adheres firmly to the surface and can resist against its gravitational forces when the sample is tilted vertically (90°) or even turned upside down (180°), indicating a strong adhesive effect exists between the water droplet and the "sticky" TiO_2 sponge-like structure surface.
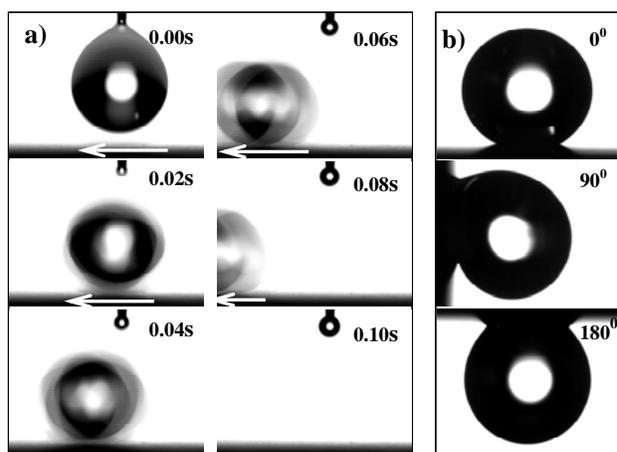

Figure 2. (a) Behaviors of water droplet on the PTES-modified 50 V sponge-like structure surface. In right top of images show the time sequence. (b) Shapes of water droplet on the PTES and 0.2 mg/mL NC modified 50 V sponge-like structure surface with different tilt angles: 0°, 90° and 180°.

Figure 3 shows the typical results of X-ray photoelectron spectroscopy (XPS, VG ESCALAB MK II) for sponge-like TiO_2 films before and after NC modification. It is indicated that the strong F 1s peak along with a C 1s peak due to C-F in addition to that of C-H and the attenuation of the Ti 2p and Ti 2s peaks comfirm the presence of PTES monolayer. This is in good agreement with the report by Wang et al.[19] However, the further addition of NC, which damages the uniform arrangement of PTES molecule and leads to the decrease of the C-F on surface, result in the slightly CA decrease and highly adhesive force of the superhydrophobic nanostructure surface with water droplet. The detailed XPS spectra for the corresponding N 1s region of the sponge-like TiO_2 films with and without adsorbed NC are shown in the inset of Figure 3. Without NC modification, there is only one peak in the N 1s spectrum at a binding energy (BE) about 400.5 eV, which could be assigned to adsorbed nitrogen gas. However, another peak attributed to nitrate is observed at a BE about 407.2 eV with PTES-NC mixed modification. This indicates the presence of NC on the sponge-like TiO_2 surface.[20]
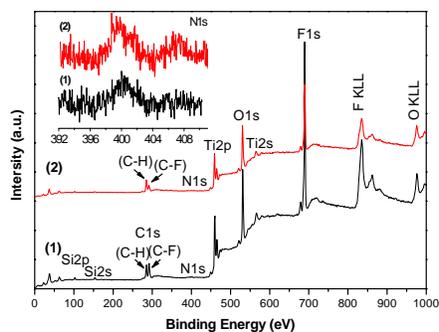
Figure 3. XPS spectra of the sponge-like surface with PTES modification (1) and PTES and 0.2 mg/mL NC mixed modification (2). The inset shows the coresponding N 1s XPS detail spectra.

Figure 4a shows a typical force-distance curve of the sole PTES-modified sponge-like structure film when it approaches and retracts from the water droplet. From the linear force-distance relationship during the contacting and retracting processes, it reveals that the water droplet always maintains a spherical shape without any noticeable distortion. The adhesive force the water droplet is subjected to pull down by the sponge-like structure surface is only approximately 5.0 μN. The low value is attributed to the large fraction of air trapped beneath the water droplet. This effect greatly reduces the solid-liquid interface and the rolling resistance and, thus, cannot create a high adhesive force to water droplet. The force-distance curve shows a marked change when the sponge-like structure TiO$_2$ nanostructure was co-assembled with PTES and 0.2 mg/mL NC under identical experimental conditions (Figure 4b). It is obvious that an attractive force is created as soon as this sticky, superhydrophobic surface makes contact with the water droplet. When the sample was withdrawn from the droplet, the adhesive force gradually increases and the droplet shape changes from spherical to elliptical. Then, just before the detachment, it yields the highest adhesive force of approximately of 76.6 μN. To our surprise, no any detectable water remained on the PTES-NC modified film surface is observed. The final balance force comes back to nearly zero also confirms that there is no water abrupt loss, except a faint evaporation of the water droplet during the measurement process under ambient environment. This high adhesive force is fifteen times stronger than that required to remove a 3 mg water droplet away from the sole PTES-modified sponge-like TiO$_2$ nanostructure surface.
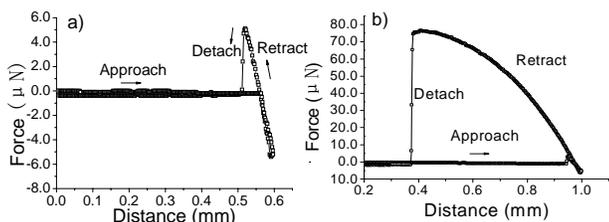

Figure 4. Typical force-distance curve of the sponge-like structure TiO$_2$ film approaches and retracts a 3 mg water droplet: (a) PTES modification; (b) PTES and 0.2 mg/mL NC mixed modification. The arrows represent the sample's moving direction to water droplet.

To determine the effects of NC concentration on the adhesion of PTES-NC modified TiO$_2$ nanostructure surfaces, other samples of superhydrophobic, sponge-like TiO$_2$ nanostructure modified with different NC concentrations were fabricated. The experimental results indicate that NC concentration has a drastic effect on adhesive force change. Figure 5 shows the influence of NC concentration in the sample on water CA and adhesive force. When the amount of NC increases from nothing to 0.04 mg/mL and 0.067 mg/mL, the adhesive forces between the water droplet and the sponge-like structure film increase sharply from 5.0 μN to 19.8 μN and 70.7 μN, respectively. It is noted that the largest deviation of the adhesion values measured in this study is ± 4.2 μN, indicating that the superhydrophobicity of the modified sponge-like surface is uniform and highly reproducible. In contrast, the water CA decreases gradually and then reaches a minimum near 153.5° with an increase of the NC concentration. This difference in the behavior between CA and adhesion suggests that other factors besides the wettability may be involved in the adhesion with water of these PTES-NC modified samples.
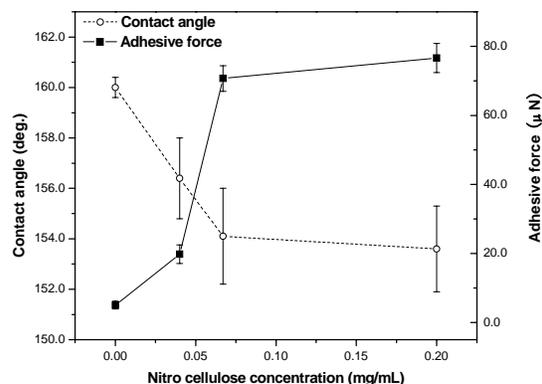

Figure 5. The inter-relationships between water CA and adhesive force with the NC concentration on the sponge-like structure TiO$_2$ surface.

A possible model for surface chemical composition change during the self-assembled process of mixed PTES-NC on hydroxylated sponge-like TiO$_2$ surfaces and the formation of hydrogen bonding between NC nitro group and water hydroxyl is shown in Figure 6. When NC is introduced into the PTES system, a competition occurs between NC and PTES molecules for the hydroxyl on hydroxylated TiO$_2$ surfaces (Figure 6a). This would lead to a disruption of the dense packed hydrophobic PTES molecule and thus a decrease of CA to some extent.[21] The hydrophilic nitro groups on the self-assembled layer surface

can readily form hydrogen bonding with water (Figure 6b), which directly provides a good adhesion between the PTES-NC modified, sponge-like TiO$_2$ layer and water. Therefore, a combination of the hydrogen bonding offered by the nitro groups on the surface and the disruption of the dense packed hydrophobic PTES molecule is the primary factor responsible for the significant increase of the adhesion between PTES-NC modified, sponge-like TiO$_2$ film and water
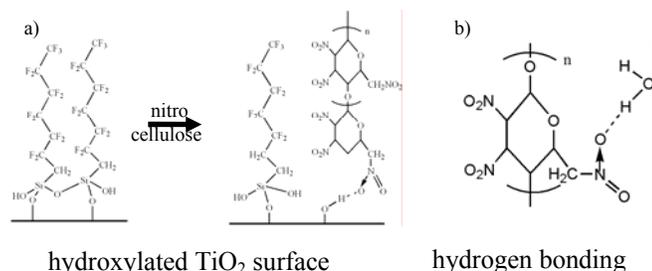

hydroxylated TiO$_2$ surface   hydrogen bonding

Figure 6. A model of surface chemical composition change during the PTES-NC mixed self-assembled layer on the hydroxylated sponge-like TiO$_2$ surfaces (a) and the conformation of hydrogen bonding association between nitro group and hydroxyl group of the water droplet (b).

3   CONCULSIONS

By using a facile electrochemical oxidation and mixed self-assembled processes with proper control of the nitrocellulose concentration, we have fabricated a sponge-like nanostructure of superhydrophobic TiO$_2$ thin films that have a wide range of the adhesive force. The results provide new insights into how to vary the wettability and adhesion of superhydropbobic surfaces. These stable TiO$_2$ nanostructure superhydrophobic films with exceptional adhesion effect can potentially be used in many industries, and be further extended to control the adhesion of a wide variety of superhydrophobic functional materials.

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