Reversible switching on superhydrophobic TiO_2 nano-strawberry films fabricated at low temperature†

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Received (in Cambridge, UK) 12th October 2007, Accepted 15th November 2007
First published as an Advance Article on the web 26th November 2007
DOI: 10.1039/b715805j

Superhydrophobic TiO_2 nano-strawberry rutile films, on which superhydrophobicity and superhydrophilicity can be reversibly switched by alternation of ultraviolet (UV) irradiation and dark storage, were fabricated on a large scale from aqueous solution *via* a seeded growth method at low temperature without any pressure equipment.

The ability to control surface wettability of solid substrates is important in many situations. Superhydrophobic surfaces[1] with a water contact angle (CA) larger than 150° and superhydrophilic surfaces[2] (CA equal to 0°) have been extensively investigated due to their importance for both fundamental research and industrial applications. Recently stimuli-responsive smart materials that can be switched between superhydrophobicity and superhydrophilicity have generated great interest.[3]

Titanium dioxide is one of the most important semiconductors and is widely used in a great variety of applications[1] such as photocatalysis, solar energy conversion, sensors, and photovoltaic cells. Furthermore, the photo-induced superhydrophilicity[2] on TiO_2 thin films has attracted much interest in extending the applications of the material. However, little work has been done on the fabrication of superhydrophobic TiO_2 surfaces.[4] Feng[5] reported a superhydrophobic TiO_2 nanorod film fabricated by a hydrothermal method at 160 °C in an autoclave. Recently, efforts have been made to produce films by chemical routes directly from aqueous solution, which are less energy consuming and low cost.[6–8] Herein we report a superhydrophobic nano-strawberry TiO_2 surface (CA = 163.0°) fabricated at low temperature (80 °C) without any pressure equipment, on which the transition from superhydrophobicity to superhydrophilicity can be reversibly switched by alternation of ultraviolet (UV) irradiation and dark storage.

The aligned TiO_2 nano-strawberries were grown *via* a simple seeded growth method which is similar to Weng's.[8] First, a slide was dipped into the TiO_2 sol and annealed at 500 °C to prepare a 50–100 nm thick film of crystalline TiO_2 seeds. The sol–gel method was adopted here because of its simplicity and low cost. The TiO_2 sol was prepared by the method reported previously.[9] In a typical experiment, hydrochloric acid (2 ml) was first added dropwise into a solution of tetrabutyl titanate (2 ml) in 20 ml ethanol at room temperature with continuous stirring for 2 h. The resulting spherical nanoparticles were then stable for at least a day in solution.

After the glass slide had been uniformly coated with TiO_2 nanocrystals, the titania nanostructure growth was carried out by suspending the slide upside down in a beaker filled with 50 ml of an aqueous solution of tetrabutyl titanate (0.024 mol) and urea (0.15 mol) at 80 °C. Reaction times ranged from 10 to 15 h. The wafer was then removed from the solution, rinsed with deionized water, and dried. A field-emission scanning electron microscope (FESEM) was used to examine the morphology of the seeds film and the array across the entire slide, while the crystallinity and growth direction were analyzed by X-ray diffraction (XRD) techniques. The wettability of the films was investigated by a contact angle instrument.

Three SEM images of the as-prepared nano-strawberry films taken at different magnifications are shown in Fig. 1a–c. Fig. 1a is a rather low magnification SEM image of the as-prepared product, showing that the sample looks like a kind of flat and continuous film product. Closer inspection indicates that the morphology of the titania film is indeed composed of some nano-strawberries aligned together, as shown in Fig. 1b. Fig. 1c is a higher magnification of the part of the sample shown in Fig 1b, showing that the TiO_2 nano-strawberry is composed of two parts: the leaves at the bottom and the berries growing among the leaves. The leaves are 100–300 nm in length and the berries are 100–200 nm in width and a little larger in height. The leaves are relatively smooth

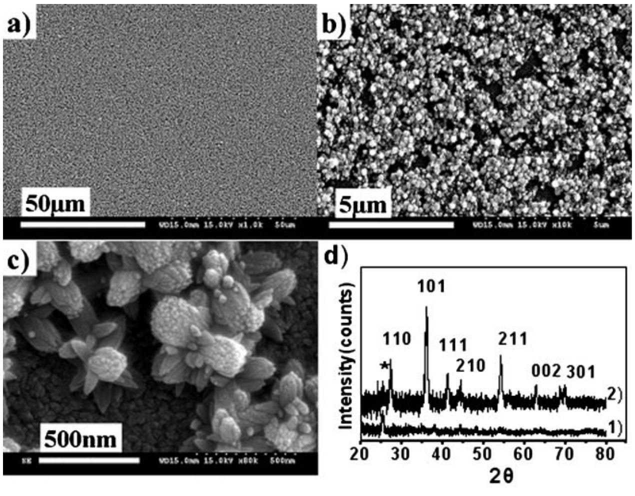

Fig. 1 (a, b and c) Typical top view SEM images of the as-fabricated TiO_2 nano-strawberry film taken at different magnifications. (d) The XRD pattern of the seed film (1) and the as-prepared nano-strawberry film (2). Peak *: anatase, the others: rutile.

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† Electronic supplementary information (ESI) available: The advancing/receding contact angle (CA), contact angle hysteresis, and sliding angle of the superhydrophobic TiO_2 film. Video of advancing/receding CA. See DOI: 10.1039/b715805j

and grainless, while the grain-berries are composed of grains of about 10 nm. Fig. 1d gives the XRD pattern of the seed film and the as-prepared titania nano-strawberry film. The X-ray diffraction analysis shows that the seeds are composed of mainly anatase nano-crystals and a little rutile phase (Fig. 1d(1)) and the crystalline phase of the as-prepared titania nanostructure film is mainly rutile with an enhanced 101 face. It is interesting to form rutile titania film through such a simple process at low temperature. The rutile film fabricated here is mainly dominated by the solution conditions[8] such as temperature, concentration, pH value and so on. The seed layer is important for the film growth. Films with or without a seed layer in low $Ti(OC_4H_9)_4$ concentration were investigated and the results are shown in Fig. 2. It can be seen that on the surface without a seed layer (Fig. 2a) there were almost no products growing which adhered to the substrate. As shown in Fig. 2b only a few parts of the surface with a seed layer were covered with nanostructures, which suggests that the nanostructures grow mainly on the rutile parts of the seed layer. Because most of the seed layer is anatase phase, if the nanostructures grew on the anatase parts, most of the surface would be covered with the products.

The wettability was evaluated by the water contact angle measurement of the as-prepared films. Fig. 3Aa (left) shows the water CA on the smooth film surface (the seed film) of about 70°, and when the surface was irradiated with UV (obtained from a 500 W Hg lamp) for 60 min, it showed high hydrophilicity with a water CA of about 7° (Fig. 3Aa (right)). Fig. 3Ab (left) shows the shape of a water droplet on the titania nano-strawberry film surface, where the water CA is 163.0°, showing that the nano-strawberry film surface has obvious superhydrophobic properties (see ESI†). The superhydrophobic surface was then irradiated, and water droplets spread out thoroughly on the surface immediately, resulting in a water contact angle of 0° shown in Fig. 3Ab (right). After the UV irradiation the film was stored in the dark for several weeks, a new water droplet was used to measure the surface wettability, and the superhydrophobicity of the nano-strawberry films was obtained again. That is, by dark storage and UV irradiation the superhydrophilicity and superhydrophobicity on the surfaces can be reversibly switched. This process has been repeated several times, and good reversibility of the surface wettability was observed (shown in Fig. 3B).

The results confirm that nanostructure has a profound effect on superhydrophobic properties and superhydrophobic surfaces can be obtained by hydrophilic materials. Cassie and Baxter derived the heterogeneous wetting equation,[10]

$$\cos\theta = f_1\cos\theta_1 + f_2\cos\theta_2 \qquad (1)$$

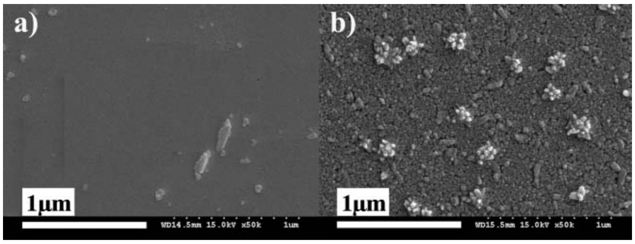

Fig. 2 Rutile nanostructures growth on glass without (a) and with (b) a seed layer.

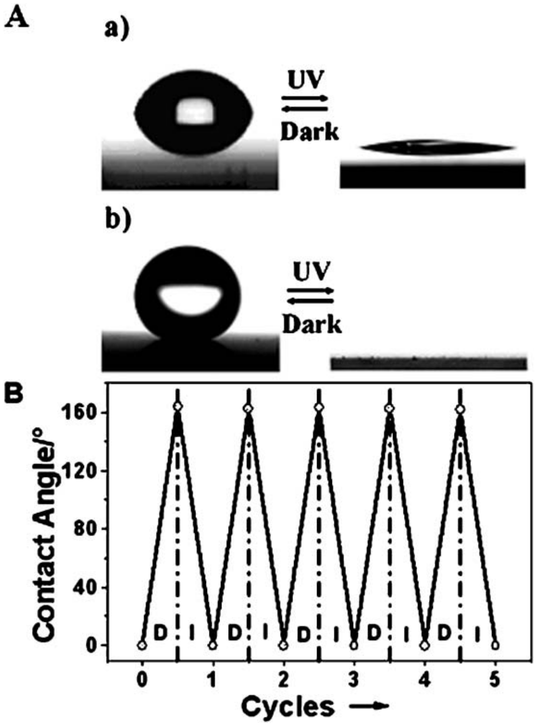

Fig. 3 (A) Photographs of water droplet shape on the smooth (a) and nano-strawberry (b) TiO_2 films before (left) and after (right) UV illumination. (B) Reversible superhydrophobic–superhydrophilic transition of the as-prepared films under the alternation of UV irradiation and dark storage.

Here, f_1 and f_2 are the fractions of surface 1 and surface 2 in contact with liquid, respectively ($f_1 + f_2 = 1$). θ_1 and θ_2 are the corresponding CAs on each surface. Conventionally, it is believed that when a water droplet contacts the rough surface of a hydrophilic material, the interface is composed of solid and liquid surfaces and a highly hydrophilic surface can be gained using the hydrophilic material, which is called the hemi-wicking state[10] as shown in Fig. 4a. TiO_2 is a photosensitive material,[2] and when the film is irradiated with UV light the surface hydrophilicity can be improved greatly (Fig. 3Aa (right)) because the photogenerated hole reacts with lattice oxygen to form surface oxygen vacancies, to which water molecules kinetically coordinate. For the as-prepared surface, the water droplet will fill the grooves and replace the

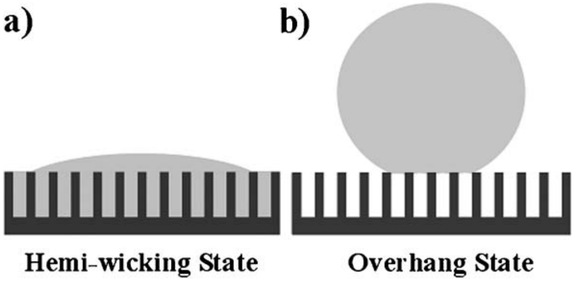

Fig. 4 A schematic model for the two cases when a water droplet contacts a rough surface made by a hydrophilic material. (a) Hemi-wicking state resulting in a highly hydrophilic surface; (b) overhang state resulting in a hydrophobic surface.

trapped air (hemi-wicking state), which can account for the enhanced superhydrophilic phenomenon (CA = 0°, Fig. 3Ab (right)) shown on the TiO_2 nano-strawberry surface.

In some cases, air can be trapped below the drop if the native material is not hydrophilic enough,[11] that is, the water droplet is suspended over the indentations or curves of the rough surface, which can be called the overhang state (Fig. 4b). Thus, the contact surface turns out to be the composite surface of solid and air, that is, $\theta_2 = \pi$. Eqn (2) was derived from eqn (1),

$$\cos\theta = f_1\cos\theta_1 - f_2 \tag{2}$$

It can be easily verified that for a θ_1 ($0 < \theta_1 < \pi/2$) there is a certain f_2 to make $\theta > \pi/2$ (hydrophobic) and $\theta > 5\pi/6$ (superhydrophobic). In our experimental conditions, given the water CA of a native TiO_2 surface θ_1 (70°) and the composite surface θ (163°), f_2 is calculated to be about 0.97, which indicates that the achievement of superhydrophobicity on the composite surface is mainly a result of the air trapped in the rough surface by the nano-strawberries and cavities. On storage in the dark, the adsorbed hydroxy groups on the TiO_2 surface can gradually be replaced by atmospheric oxygen and the TiO_2 becomes less hydrophilic.[2] After a time, the water will not be able to fill in the grooves of the as-prepared surface and some air will remain, with the material becoming gradually less hydrophilic (for example, the native contact angle reaches 70°). The contact face changes to the composite face of air and the solid material. According to the Cassie–Baxter equation, the apparent water CA becomes larger than 90°, showing a hydrophobic then a superhydrophobic state. Thus the surface evolves back to its original state, and the surface wettability converts from superhydrophilic to superhydrophobic again.

In conclusion, nano-strawberry TiO_2 surfaces were fabricated *via* a simple seeded growth method at low temperature without any pressure equipment. Superhydrophobicity shown on the surface indicated that hydrophilic materials with certain structures can display a superhydrophobic state, which is beyond the traditional concept. Furthermore, reversible switching between superhydrophilicity and superhydrophobicity is observed on the film. The special structure and the native wettability are considered as the key factors for the behaviors.

This work was supported by the National Nature Science Foundation of China (Grant No. 20033010).

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