

# Micropatterned Superhydrophobicity by Photocatalytic Lithography and its Application as Template

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## ABSTRACT

We describe an unconventional approach to fabricate octacalcium phosphate (OCP) pattern based on the superhydrophilic-superhydrophobic template on the TiO<sub>2</sub> nanotube structured film by a combination of electrochemical anodization and photocatalytic lithography. The resultant OCP micropattern has been characterized with scanning electron microscopy, optical microscopy, and X-ray photoelectron spectroscopy. It is shown that the ribbon-like OCP crystals possess a highly ordered and hierarchically porous structure at nano-micro scales. They can be selectively grown at superhydrophilic areas which are confined by the hydrophobic regions. The high wetting contrast template proves to be useful for constructing well-defined dual scale OCP film with porous structure biomimetic to natural bone. A mechanism has been proposed to explain the formation of the OCP patterned film with hierarchically porous structure and distinct selectivity.

**Keywords:** superhydrophilic-superhydrophobic micropattern, TiO<sub>2</sub> nanotube, photocatalytic lithography, octacalcium phosphate, electrochemical deposition

## 1 INTRODUCTION

Wettability of solid surfaces is an important property governed by not only chemical composition, but also geometrical structure as well [1-3]. Two extremely cases, superhydrophobicity with a water contact angle (CA) above 150° and superhydrophilicity with CA below 5°, have attracted much interest due to their importance in both theoretical research and practical application [4-7]. Micropatterns with different physical or chemical properties have frequently been acted as microtemplates for fabricating various functional materials. Micropatterns can be formed by printing self-assembled monolayers (SAMs) using soft lithography [8], or by decomposing SAMs through electron beams [9], photocatalytic lithography [10], atomic force microscopy [11] and so on. Among these methods, photocatalytic lithography is one of the most

practical techniques because it is able to accurately transfer an entire photomask pattern to a sample substrate at a single exposure time. Till now, only a few reports on the fabrication of superhydrophilic-superhydrophobic micropatterns have been reported [12-14].

Upon UV irradiation, the electron-hole pairs in TiO<sub>2</sub> can be generated and migrated to its surface, where the hole reacts with OH<sup>-</sup> or adsorbed water to produce highly reactive hydroxyl radicals [15,16]. These hydroxyl radicals can further oxidize and decompose most organic compounds. Recently, we found that the pollutant solution can be rapidly decomposed on a nanotube array TiO<sub>2</sub> film with UV irradiation [17-19]. Considering its effectiveness for the photocatalytic decomposition of organic compounds, the photocatalysis of such TiO<sub>2</sub> nanotube film can be a promising way to decompose the hydrophobic fluoroalkyl chains. By using a patterned photomask to control the site-selective decomposition, it is possible to achieve a conversion from superhydrophobicity to superhydrophilicity due to the amplification effect of the rough aligned nanotube structure. Therefore, these two types of extreme wettability coexist on the surface directly to make up of superhydrophilic-superhydrophobic pattern.

Various ways of preparing TiO<sub>2</sub> films on the different solid substrates have been developed, including sol-gel technique [20], sputtering [21], chemical vapor deposition [22] and liquid phase deposition [23]. Among them, the electrochemical anodizing is verified to be a convenient technique for fabricating nanostructured TiO<sub>2</sub> films on titanium substrates [24-26]. Moreover, the conductive titanium support substrate can be an advantage for fabricating multifunctional micropatterned functional materials through electrochemical depositions, such as octacalcium phosphate (OCP) coating, an important biomaterial, to enhance its bioproperties [27].

## 2 EXPERIMENTAL SECTION

TiO<sub>2</sub> nanotube array film was fabricated by electrochemical anodizing of titanium sheets (purity 99.5 %) in 0.5 wt % HF electrolyte with Pt counter electrode

under certain voltage for 1 h [28-30]. The as-prepared amorphous TiO<sub>2</sub> nanotubes were calcinated at 450°C to form anatase phase under air ambient for 2 h, then treated with a methanolic solution of hydrolyzed 1 wt % 1*H*,1*H*,2*H*,2*H*-perfluorooctyl-triethoxysilane (PTES, Degussa Co., Ltd.) for 1 h and subsequently heated at 140°C for 1 h. In a word, the fabrication procedure (Figure 1) of superhydrophobic-superhydrophilic micropattern includes that, at the first step, the superhydrophobic nanotube structure TiO<sub>2</sub> film is prepared by using the above mentioned electrochemical oxidation and self-assembled monolayer technique, and at the second step, the superhydrophobic film is selectively exposed to UV light for 20 min through a copper grid (photomask) to photocatalytically cleave the fluoroalkyl chain. Then the superhydrophobic-superhydrophilic micropatterned TiO<sub>2</sub> on titanium sheet used as a microtemplate to selectively deposit nano-OCP crystals on the superhydrophilic regions by an electrochemical deposition to form a special micropatterned nano-OCP. The deposition electrolyte was consisted of 0.042 mol/L Ca(NO<sub>3</sub>)<sub>2</sub> and 0.025 mol/L NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub>. The pH value was adjusted to approximately 4.2 with 0.05 mol/L NaOH solution. The precipitation was carried out galvanostatically at a cathodic current of 0.5 mA cm<sup>-2</sup> under 67.5°C for a certain time [31,32].

The morphology of the TiO<sub>2</sub> nanotube films and OCP micropatterns were investigated by field-emission scanning electron microscope (FESEM, JEOL JSM-6700F) and environmental scanning electron microscope (ESEM, Phillips XL-30), respectively. The water CA was measured with an optical contact angle meter system (DataPhysics, OCA-20). The chemical compositions were determined by X-ray photoelectron spectroscopy (XPS, VG ESCALAB MKII) with Al K $\alpha$  X-ray source (1486.6 eV). The binding energies were referenced to the C 1s hydrocarbon peak at 285.0 eV. For fluorescence experiments, the obtained patterns were stained with fluorescein sodium, and observed by Karl Zeiss fluorescence microscope (Axioskop2, MAT).

### 3 RESULTS AND DISCUSSION

It is noteworthy, from the characterization of chemical composition before and after UV irradiation by X-ray photoelectron spectroscopy, that the intensities of the F1s and FKLL are decreased greatly and those of the Ti2p and O1s are increased after exposing the PTES modified surface to UV light for 20 min (Fig. 2a). From the inset high-resolution spectra (Fig. 2b), the peaks of -CF<sub>2</sub> (at 291.8 eV) and -CF<sub>3</sub> (at 294.1 eV) are obviously vanished after UV light irradiation, while the strength of silicon peaks in the XPS spectra remains unchanged but shifts from 102.8 to 103.3 eV, suggesting that Si-O-Si networks have already formed due to UV irradiation. According to these results, we believe that the hydrophobic fluoroalkyl chains have been completely decomposed and removed by the photocatalytic reactions at TiO<sub>2</sub> nanotube films.

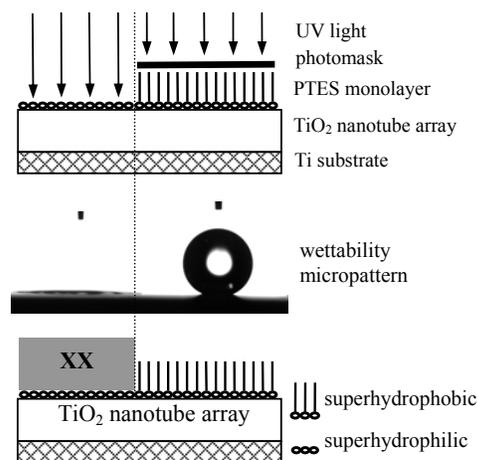


Figure 1: Schematic outline of the procedures to fabricate nanostructured OCP patterning film by electrochemical deposition based on superhydrophilic-superhydrophobic micropattern.

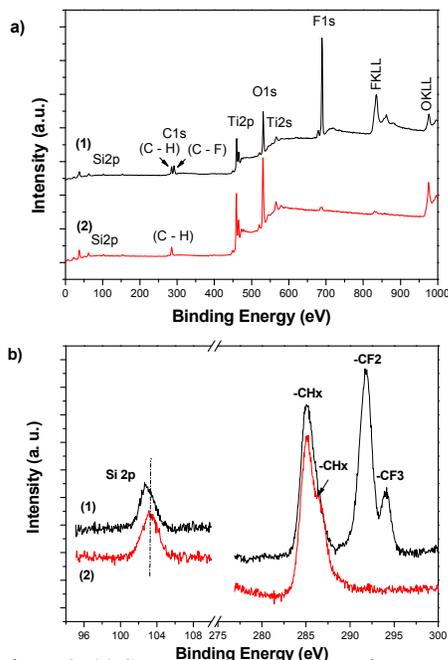


Figure 2: (a) Survey-scan X-ray photoelectron spectra of the PTES modified nanotube TiO<sub>2</sub> films before (1) and after (2) 20 min UV irradiation. (b) The high-resolution spectra of Si 2p and C 1s regions.

Fig. 3a shows the top view SEM image of the typical nanostructured TiO<sub>2</sub> film by anodizing Ti sheet under 20 V for 20 min. The surface consists of vertical aligned TiO<sub>2</sub> nanotubes with a single tube diameter of about 80 nm and

an average center-to-center spacing of 150 nm. Water droplet can quickly spread and wet the as-grown vertically aligned TiO<sub>2</sub> nanotube array film due to capillary effect caused by the rough tubular structure, indicating such TiO<sub>2</sub> nanotube array film is superhydrophilic [33,34]. The typical SEM image of OCP composited film on TiO<sub>2</sub> nanotube array surface by electrochemical deposition for 5 min is shown in Fig. 3b. It can see that quasi-perpendicular ribbon-like crystals of several hundred nanometers in width are uniformly grown on the TiO<sub>2</sub> nanotube array surface.

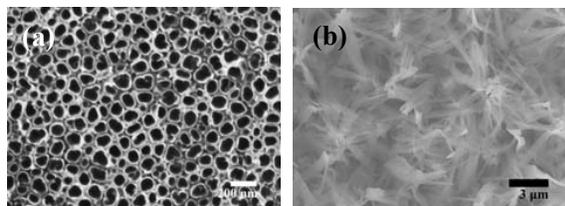


Figure 3: SEM images of the (a) TiO<sub>2</sub> nanotube array film fabricated by electrochemical anodization; (b) OCP nanostructure layer on TiO<sub>2</sub> nanotube array film by electrochemical deposition for 5 min.

Fig. 4a shows a typical fluorescence microscope of the superhydrophilic-superhydrophobic micropattern on TiO<sub>2</sub> nanotube surface. As can be seen, the green dot patterns are clearly imaged through the fluorescence contrast between the UV-irradiated superhydrophilic and photomasked superhydrophobic regions. The photoirradiated dot exhibiting a uniformly stronger fluorescence against the surrounding dark background is due to the highly affinity to solution resulting in the absorption of fluorescent probes into the irradiated nanotube array films. Therefore, a clear well-defined fluorescence pattern based on the superhydrophobic-superhydrophilic pattern is obtained. Fig. 4b displays the identical patterning of OCP biomaterials deposited on the superhydrophilic-superhydrophobic patterns on TiO<sub>2</sub> nanotube array surface. It is obvious that the size of the white OCP dots is equal to that of the superhydrophilic area on template, indicating the deposited regions were only located within the superhydrophilic dots where photocatalytic degradation of PTES SAMs was performed [35].

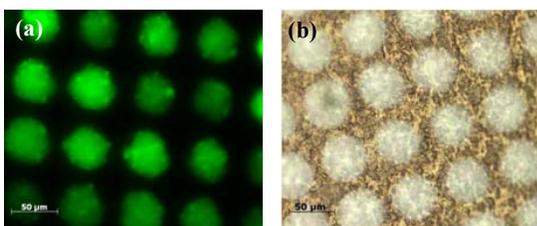


Figure 4: Optical micrographies of the superhydrophilic-superhydrophobic template and patterned OCP thin films selectively deposited in pre-defined superhydrophilic

regions by electrochemical deposition for 5 min. (a) fluorescence pattern; (b) OCP pattern.

On the basis of this patterning technique, the as-prepared superhydrophilic-superhydrophobic pattern is applied to direct and guide the selective deposition of bioactive calcium phosphate onto the TiO<sub>2</sub> nanotube film by a facile electrochemical deposition. Fig. 5 shows the ESEM image of micropatterned OCP crystals selectively deposited onto TiO<sub>2</sub> nanotube array film by electrochemical deposition. It is of interest to note that the nano-OCP crystals were preferentially deposited on superhydrophilic regions generated by photocatalytic lithography (Fig. 5a). On the center of the superhydrophobic region, one can clearly see several micro concaves (indicated by the arrow) of the substrate without the cover of deposited nano-OCP crystals (Fig. 5b). This is due to the superhydrophobic regions assembled with the PTES monolayers are able to strongly prevent from any aqueous solution with air trapped in the liquid/solid interface. It has been reported that such orderly structured nano-OCP coating on Ti possess of much better bio-properties [31,32], based on the biomimic point of view. The EDX spectrum also verified that it only contains Ti and O elements within the superhydrophobic region. This result indicated the superhydrophobicity can effectively suppress the nucleation and growth of the OCP nanocrystals due to the air trapped between the electrode/electrolyte interfaces [3]. The polygonal microstructure shape could be a result of anisotropic etching of the underlying Ti grains [36]. Mechanical stresses due to electrostriction and volume expansion from metal to oxide at the metal/oxide interface might also be a contributing factor [37].

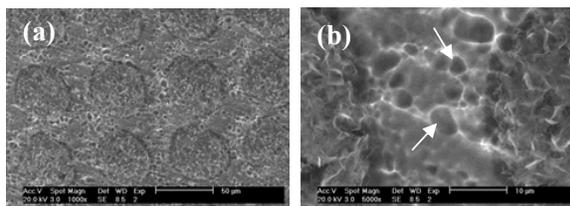


Figure 5: Typical SEM image of the patterned OCP thin films selectively deposited in predefined superhydrophilic regions on TiO<sub>2</sub> nanotube films by electrochemical deposition (a) and (b) the corresponding higher magnified image.

## 4 CONCLUSION

In summary, we have developed an unconventional approach for constructing superhydrophilic-superhydrophobic micropattern on the nanotube structured TiO<sub>2</sub> films by using electrochemically self-assembly and photocatalytic lithography. This micropatterned wettability is based on a SAM process on the special nanostructured TiO<sub>2</sub> film to achieve superhydrophobicity and the region-

optional photocatalytic decomposition of PTES SAM to obtain superhydrophilicity. Furthermore, the superhydrophilic-superhydrophobic micropatterns have been further developed, as a novel template, to fabricate a define micropatterned coating of nano-octacalcium phosphate by electrochemical deposition. It is indicated that the combined processes of electrochemically self-assembly and photocatalytic lithography reveal a promising approach for constructing well-defined micropatterns of various functional materials and micro-nano devices [38-41].

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