MICRO-WRITING UNDER WATER DROPLET USING PHOTO-SWITCHABLE TITANIUM OXIDE ON NANOCELLULOSE COATED MICRO-HOODOOS

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ABSTRACT

In this work we develop fast and locally photo-switching transition between rolling state (Cassie-Baxter (CB)) and sticky state (Wenzel (W)) using photo-switchable titanium dioxide (TiO_2) deposited by atomic layer deposition (ALD). It takes 1 min of UV exposure for switching from CB to W and 5 min of dark storage in oven (200°C) to recover the surface energy. We use crystal nanocellulose (CNC) on T-shaped micro-pillars (micro-hoodoos [1] Figure1-j) to make hierarchical structures. Photo-masked UV exposure causes the locally transition from CB to W.

KEYWORDS: Photo-switching, Superhydrophobic, Nanocellulose

INTRODUCTION

There are two superhydrophobic states reported for surfaces: state with low hysteresis (rolling state or the so called "Cassie-Baxter" state), and state with high hysteresis (sticky state or "Wenzel" state). Locally transition between these two states is in our interest. We showed how to locally control the wetting properties of surface using photo-switchable TiO_2. Hierarchical micro/nano structuring of the surface is the key for fast switching. We introduce a new structure that causes fast photo-switching of TiO_2 in its superhydrophobic states. There are many reports on the wetting engineering of ALD TiO_2 but there is no report in fast reversible or local photo-switching CB to W. The re-entrant structure of hoodoos causes water droplet suspended on top of hoodoos while wetting properties of TiO_2 is tunable by UV exposure. We used a photo-masked UV exposure to locally change the wetting properties of the superhydrophobic TiO_2 and make the contrast visible under water droplet for micro-writing.

EXPERIMENTAL

Figure 1 is sketch of the fabrication process. The fabrication of micro-hoodoos started with ALD deposition of thin layer aluminum oxide (Al_2O_3) 25 nm ± 1 % thick at 300°C temperature. Aluminum oxide layer was grown in a Beneq TFS-500 reactor using trimethylaluminum (TMA) as a metal precursor and water as a precursor for oxidation. The pressure in the reactor was kept at about 4 Torr. Nitrogen was used as a carrier gas and to purge reaction gases from the reactor during each reaction half cycle. 250 ms precursor pulses and 1 s purge pulses (the same for both precursors) were used. Trimethylsilyl (HMDS) is used to improve the adhesion of photoresist during the photolithography. To pattern the aluminum oxide layer, 1.5 µm of AZ5214 photoresist is spin coated on it. After photolithography, aluminum oxide layer was wet etched at 50°C (Fig1c). Etchant contains 80 wt% phosphoric acid, 5 wt% nitric acid and remaining 15 wt% water. Pattern consists of 10 µm squares with 10 µm spacing. Then two step isotropic and anisotropic cryogenic deep reactive ion etching process (ICP-RIE, Plasmalab System 100, Oxford Instruments) at -120°C is done to make the neck and body of hoodoos respectively (Fig 1d and 1e). A mixture of SF_6/O_2 was used as the anisotropic etching gas and their flows were set to 40 sccm / 6.5 sccm, while the powers of inductively and capacitively coupled power sources were 1000 W and 2 W, respectively. For isotropic etching no oxygen flow is used. To make nanostructures on top of our pillars we dip the sample in 1% solution of CNC diluted in water for 1 hour to get homogeneous distribution of CNC nanorods on surface. It turns out CNC is pleasant scaffold to growth photo-switchable ALD TiO_2 [2] due to high amount of hydroxyl groups which is favorable for ALD process, and also causes more hierarchy on top of hoodoos. Then 5 nm layer of TiO_2 deposited using the same ALD system for surface passivation. $TiCl_4$ and water are two precursors used for ALD of TiO_2. 250 ms precursor pulses and 250 ms purge pulses (the same for both precursors) were used. TiO_2 deposition took place in two steps, first 2 nm thick in low temperature at 70°C to passivate the CNC and then 3 nm thick at 300°C to make the photo-switchable film.

A UV lamp with 105 mW/cm^2 and 365 nm wavelength (ECE 2000 Modular DYMAX) was used for UV exposure. Advancing and receding contact angle measurement of the films has been studied by an optical goniometer (THETA, Biolin Scientific). Recovery of the samples is done in an oven at 220°C.

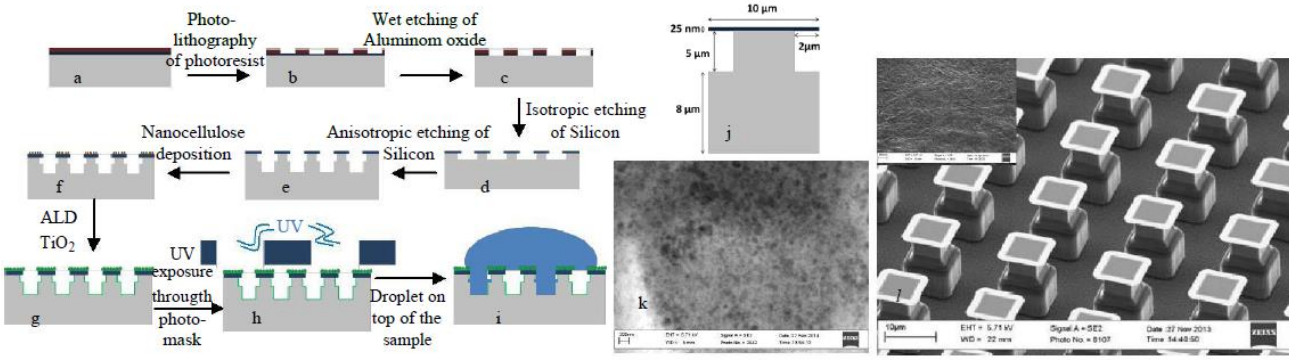

Figure 1: Fabrication process of micro-hoodoos. a-c) Photolithography and etching the aluminum oxide. d) Isotropic etching of silicon. e) Anisotropic etching of silicon. f) CNC deposition to make nano-structures on top of hoodoos. g) ALD TiO_2 on CNC. h) Photo-masked UV exposure to make locally transition from CB to W. i) Water drop on sample after UV exposure, water locally penetrate through pillars on places which get exposed. j) Dimensions of a hoodoo. SEM micrographs of k) highly porous CNC on hoodoos before TiO_2 deposition, l) hoodoos before CNC deposition, inset is 5 nm TiO_2 coated on CNC on top of hoodoos

RESULTS AND DISCUSSION

We program the surface by locally changing the surface wetting properties. As a demonstration a micro-sized logo of Aalto University is written under a water droplet. It takes 1 min photo-masked UV exposure on sample for transition from CB to W. The resulting contrast is invisible in solid-air interface but becomes visible in presence of water droplet (Figure 2b). When a droplet dispenses on top of the exposed sample, water can locally penetrate between hoodoos which were exposed while water remains on top of pillars on unexposed areas (Figure 1-i). Recovery of the surface energy is done by keeping the sample for 5 min in oven (erasing the patterns).

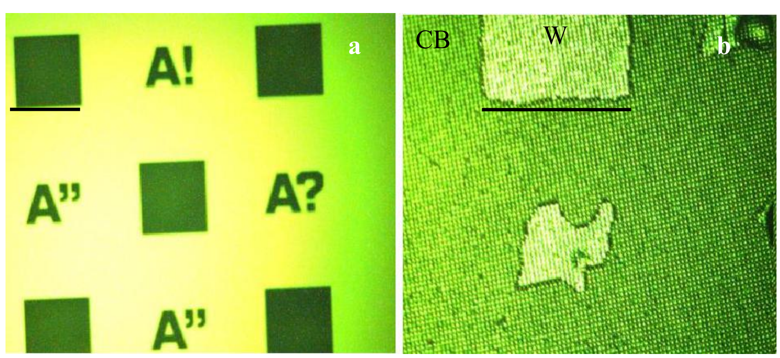

Figure 2: Microscope images, a) Glass photo-mask used during UV exposure (dark part is opening), b) Sample under water droplet after photo-masked UV exposure. Scale bars are 600 µm.

Contact angle measurements are collected in Table 1. It shows sample is in CB state (low hysteresis) before UV exposure and is in W (high hysteresis) state after. Hysteresis contact angle is plotted in Figure 3 confirms fast reversible transition of CB and W.

Table 1 contact angle measurements

contact angle measurement of CNC on hoodoos	before UV exposure	after 1 min UV exposure	after 5 min dark hot oven
Advancing	156°	150°	156°
Receding	151°	110°	151°
Hysteresis	5°(CB)	40°(W)	5°(CB)

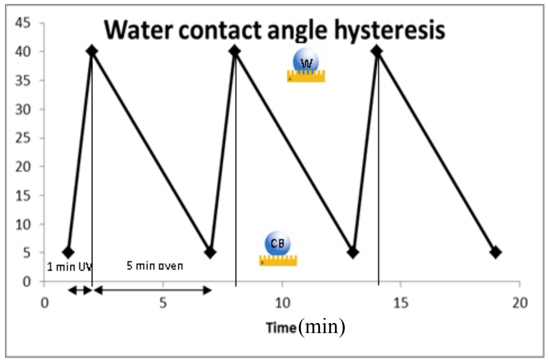

Figure 3: Hysteresis contact angle measurement shows reversible transition from CB to W after 1 min UV exposure and from W to CB after 5 min dark hot storage.

CONCLUSION

Switching between CB and W was reported before but instead of photo-switching they used water jet to locally force water penetrate through pillars [3]. Water jet switching is more complex for in situ applications. We showed how to make fast photo-switching of rolling and sticky states of superhydrophobic materials using a new hierarchical structures. We also introduce a way to locally program the wetting properties of superhydrophobic material. Fast photo-switching of TiO_2 can open many applications such as valves and pumps in microfluidic and biosensing devices. Faster switching, and also increasing the resolution of writing (nano-writing) by decreasing the pitches of hoodoos remain to be improved for future.

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