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A geometry controllable approach for the fabrication of biomimetic hierarchical structure and its superhydrophobicity with near-zero sliding angle

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Abstract

A simple, geometry controllable method is presented for fabricating multiscale hierarchical polymer structures that exhibit superhydrophobic water-repellent properties with near-zero sliding angle over a large area. A UV-assisted micromolding technique is used to create a microtexture with an ultraviolet (UV)-curable resin containing Al₂O₃ nanoparticles. A subsequent treatment of ultraviolet ozone (UVO) leads to the formation of nanoscale roughness over the as-formed microstructured surface, resulting in a dual-scale surface texture similar to a lotus leaf, in a reproducible manner. After hydrophobization with a self-assembled monolayer (SAM) in the liquid phase, this hierarchical surface exhibits stable superhydrophobic characteristics, having a water contact angle close to 160° and a contact angle (CA) hysteresis as low as 1°. These characteristics did not change even after exposure to ambient conditions for 6 months.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Control over the wettability of a solid surface through surface chemistry and geometric surface structure has been pursued for technological applications and for the fundamental understanding of surface physics. Various nature-inspired surfaces suggest that a simple modification of surface topography to a multiscale hierarchical structure could be useful in manipulating important surface properties such as wettability, friction and adhesion for electronic, optical and biological applications [1]. For example, the surface of a lotus leaf, where the surface is covered by a branch-like nanostructure on top of micropapillae, revealed that the hierarchical structure is very effective for a superhydrophobic surface with an heterogeneous wetting property [2, 3]. Another extreme is the gecko's foot structured with micro-

to nanometer-sized hairs with particular dimensions and geometries, which also plays an important role in many biological dry attachment systems [4].

On the other hand, many useful methods have been introduced to produce superhydrophobic surfaces either by roughening a hydrophobic surface or modifying a rough surface with a low surface energy material [5]. These include various bottom-up [6–8] and top-down approaches [9–11] for fabrication of superhydrophobic surfaces with a hierarchical architecture, but the former lacks the designing capability of length scale in a highly reproducible manner, while the usefulness of the latter could be limited due to the costs involved in the complicated processing. Furthermore, use of alternating processes, rigorous process conditions or limited adoptability to various substrates could restrict the widespread use of these methods for large-area fabrication.

Here, we present a controllable and reproducible method for fabricating a superhydrophobic hierarchical structure,

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which does not require sophisticated equipment or harsh chemicals. The method utilizes a UV-assisted micromolding and subsequent hydrophobization of nanoparticles. As a consequence, stable superhydrophobic surfaces are created with a water contact angle higher than 150° and a near-zero water sliding angle at all droplet sizes. Moreover, this method captures the advantages that both a top-down pattern transfer and a bottom-up assembly can offer: micropatterns formed with stringent pattern fidelity and precise control over geometrical structures, and facile hydrophobization of nanoparticles by a self-assembled monolayer in a liquid phase.

2. Experiment

The UV curable precursor used for UV-assisted micromolding in this work is a mixture of photoinitiator and acrylate functionalized prepolymer dispersed with aluminum oxide nanoparticles (Al_2O_3). The acrylate functionalized prepolymer containing nanoparticles was used as received from BYK Chemie (product number NANOBYK-3602), which consists of 1,4-hexanediol diacrylate (70 wt%) and 40 nm Al_2O_3 particles (30 wt%). Additionally, Darocur 1173 (2-hydro-2-methyl-1-phenyl-1-propane, Ciba Specialty Chemicals, Switzerland) as a photoinitiator was simply blended with the composite prepolymer for UV curability in a weight ratio of 5.

A schematic diagram for the fabrication of a dual-scale hierarchical structure is illustrated in figure 1. A UV curable liquid precursor was first drop-cast onto a glass substrate or a flexible poly(ethylene terephthalate) (PET) film and then a rigiflex poly(urethane acrylate) (PUA) mold with a desired pattern was placed on the liquid film. The prepared rigiflex mold having a designed micro-scale pattern was then placed on the coated layer, while ensuring conformal contact by slightly pressing at less than 1 bar. The rigiflex poly(urethane acrylate) (PUA) molds, which were an array of regular prisms or pyramids to provide a base micropattern, were prepared according to the procedure reported earlier [12]. The mold size used for the UV-assisted replica molding was around $25 \times 20 \text{ cm}^2$. After micropatterning by replica molding, the replicated substrate was cut into $4 \times 6 \text{ cm}^2$ pieces for the characterization of surface properties. After conformal contact of the mold with the liquid precursor layer containing nanoparticles, UV light ($\lambda = 250\text{--}400 \text{ nm}$) was illuminated for several tens of seconds (dose = 200 mJ cm^{-2}) through the backside of the transparent rigiflex mold for solidification by crosslinking between acrylate functional groups so as to preserve the desirable surface features with physical integrity throughout the subsequent processing steps, followed by removal of the mold from the cured layer. Then, the micro-scaled patterned surface was exposed to ultraviolet ozone (UVO). Upon exposure, the crosslinked polymer decomposes to be eventually evaporated by oxidation reaction with activated oxygen radicals, which is generated from the illumination of deep ultraviolet (DUV), having two beams at wavelengths of 254 and 185 nm using a low pressure mercury lamp under an ambient atmosphere including oxygen, in effect etching the polymer. This selective etching of polymer causes the alumina nanoparticles to be exposed on

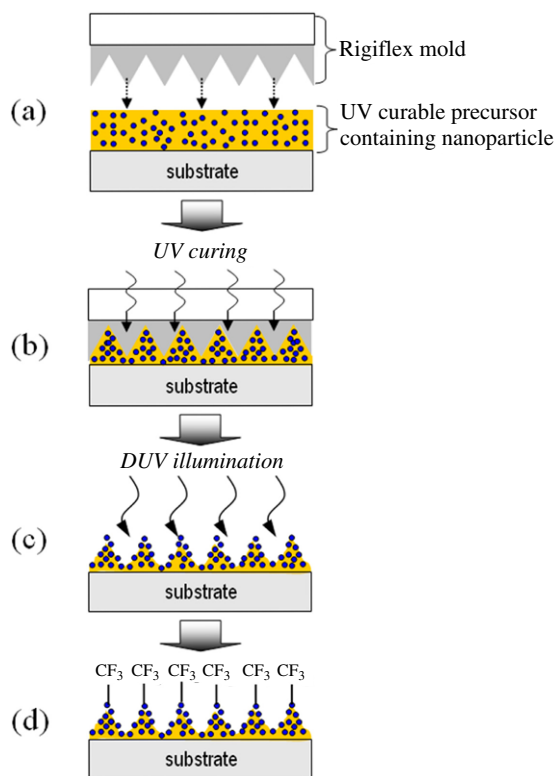


Figure 1. Schematic illustration for creating a dual-scale hierarchical structure by the UV-assisted micromolding method.

(a) Micromolding by a rigiflex curing; (b) UV curing followed by demolding; (c) deep UV (DUV) illumination for etching; (d) liquid-phase SAM treatment for passivation with CF_3 mold.

the outermost surface of the patterned micro-scale structure, yielding a multiscale hierarchical structure with the nanoscale roughness on the surface of the micro-scale structure.

The prepared multiscale rough surface can be transformed into a super water-repellent surface by treating with a liquid-phase self-assembled monolayer (SAM) with fluoroalkylsilane under an ambient atmosphere. For creation of a superhydrophobic water-repellent surface, the patterned substrate was dipped for 10 min into tridecafluoro-1,1,2,2-tetrahydrooctyl-1-triethoxysilane that was mixed with perfluorocarbon fluid, FC-40, (3M Co., Ltd, USA) as a diluent. Subsequently the substrate was placed in an oven at 120°C for 10 min to remove excess diluent completely as well as to ensure bonding of Al_2O_3 nanoparticles with fluoroalkylsilane, finally forming a stable surface with a low surface energy.

For examination of superhydrophobicity, advancing and receding contact angles (CAs) of water droplets were measured at ambient atmosphere using a contact angle analyzer (DSA100, Kruss GmbH., Germany) by the sessile-drop method with $5 \mu\text{l}$ and $20 \mu\text{l}$, respectively. All CA values presented in this experiment were averaged over five different positions. In this experiment, more than 10 specimens were fabricated and the CA deviation was within $\pm 1^\circ$ in all cases. The surface textured morphology of the prepared layer was observed using a high-resolution scanning electron microscope (SEM, XL30FEG, Philips Electron Co., Netherlands) after deposition of 3 nm platinum layer to prevent charging. The

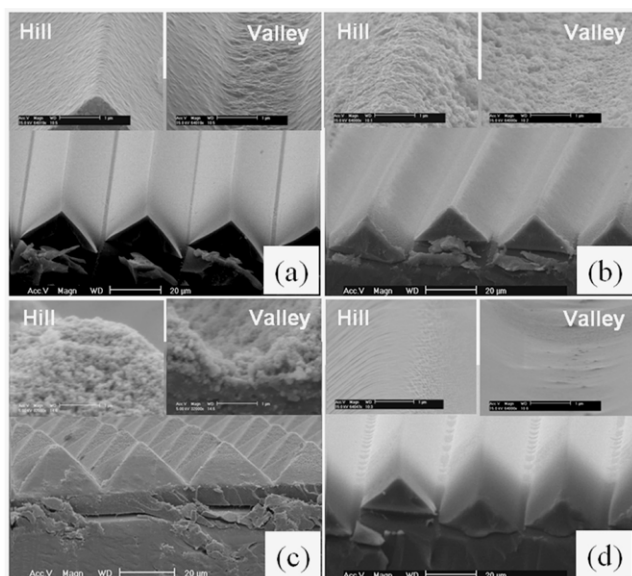


Figure 2. SEM images of patterned surfaces for (a) a prism-like microtexture with nanoparticles prior to UVO treatment, (b) the same microtexture after UVO treatment for 60 min, (c) a pyramid-like microtexture with nanoparticles after UVO treatment for 60 min, and (d) a prism-like microtexture without nanoparticles after UVO treatment for 60 min.

surface roughness was analyzed by atomic force microscopy (AFM, Veeco Dimension 3100, Digital instrument Ltd., USA) in tapping mode and the root-mean-square roughness was obtained by the image analyzer.

3. Results and discussion

Scanning electron microscopy (SEM) images of the patterned surface in the form of an array of prisms or pyramids are shown in figure 2. As shown in figure 2(a), the microfabricated surface prior to UVO treatment does not show any significant nanoscale roughness. After UVO treatment for 60 min, the surface on the pre-formed micro-scale prism pattern exhibits a nanoscale texture of the order of several tens of nanometers after selective etching of the resin at a rate of $1 \mu\text{m h}^{-1}$ (figure 2(b)). Overall, the surface possesses a dual micro- and nanoscale hierarchical structure. The entire surface (including hills and valleys) of the micro-scale pattern formed by the micromolding method is covered with a nanoscale texture of Al_2O_3 nanoparticles that were exposed to air in the course of UVO etching. Such a dual-scale hierarchical structure is not limited to a particular micropattern. As shown in figure 2(c), a pyramid-like base microtexture can also be replicated by the same method, indicating the capability of precise control and pattern transfer of various geometrical dimensions. The hierarchical surface thus formed is very similar to the structural characteristics of a lotus leaf where the micro-scale papillae on the surface are covered by nanoscale papillae. For the UV curable resin without nanoparticles, a smooth surface was found even after UVO treatment for 60 min (figure 2(d)).

Shown in figure 3(a) is the change of contact angle as a function of UVO treatment time for the prism micropattern with nanoparticles, along with some roughness values

measured by atomic force microscopy (AFM). As shown, the root-mean-square (RMS) roughness of the surface prepared with an Al_2O_3 -containing UV curable precursor increases with increasing time of UVO treatment. This RMS roughness increased to 52.8 nm after UVO treatment for 60 min (initially, 11.7 nm prior to the treatment). In contrast, the same surface without Al_2O_3 was less than 1 nm even after UVO treatment for 60 min (not shown). To further evaluate the hydrophobicity of the dual-scale hierarchical structures, CA hysteresis was measured by dynamic contact angle measurements since the hysteresis is an indication of how easily a water droplet can roll off over a surface (e.g. 2° – 3° for the lotus leaf [13]). After liquid-phase hydrophobization of different surfaces with a fluorine-containing self-assembled monolayer, the CA hysteresis was monitored in terms of the difference between advancing and receding CAs. The CAs were measured by the sessile-drop method in which water was added to and withdrawn from the drop for advancing and receding CAs, respectively. It is noted that any efforts to measure the static CA by the sessile-drop method failed because a water droplet immediately rolled off over the surface as soon as it was separated from a syringe.

As shown in figure 3(a), the contact angle increases to 160° from 139° and the CA hysteresis decreases from more than 20° to as low as 1° when the UVO treatment time is increased from 0 to 60 min. In this regard, the contact angle and the hysteresis are of interest for comparison when only one of the dual-scale hierarchical structures is present. Without the nanostructure but with the microstructure present, the contact angle is 124° and the hysteresis is 6° , as shown in figure 3(b). When only the nanostructure is present with the nanoparticles, figure 3(c) shows that the contact angle is 151° and the hysteresis is 6° . These results suggest that the combination of micro-scale patterning by micromolding and nanoscale roughening by selective etching is necessary to ensure the Cassie wetting state, in which a water droplet is in partial contact with the surface due to trapped air and then effectively sits on a surface of air pockets. Because high surface roughness enables a transition from a non-composite to a composite wetting state that is described by Cassie's equation [14], the droplet in contact with such a surface can move freely without any adhesion to the surface, exhibiting a very low CA hysteresis.

The sliding behavior of a water droplet on the prepared dual-scale hierarchical surface was also investigated. As shown in figures 4(a) and (b), both 30 mg and 10 μg water droplets rolled quickly off over the surface even when placed horizontally without any tilting as soon as they were dispensed through the syringe, indicating a near-zero sliding angle, regardless of the weight of water droplet. There appears to be no resistance to the sliding of a water droplet on the hierarchical surface presented in this study. Remarkably, such a superhydrophobic surface was extremely stable for a long period of time. The contact angle and sliding-off property of a water droplet did not change even after exposure to ambient conditions (relative humidity: 25–50%, temperature range: 5– 35°C) for 6 months. Furthermore, this surface exhibited stable anti-adhesion behavior even after sitting on the surface

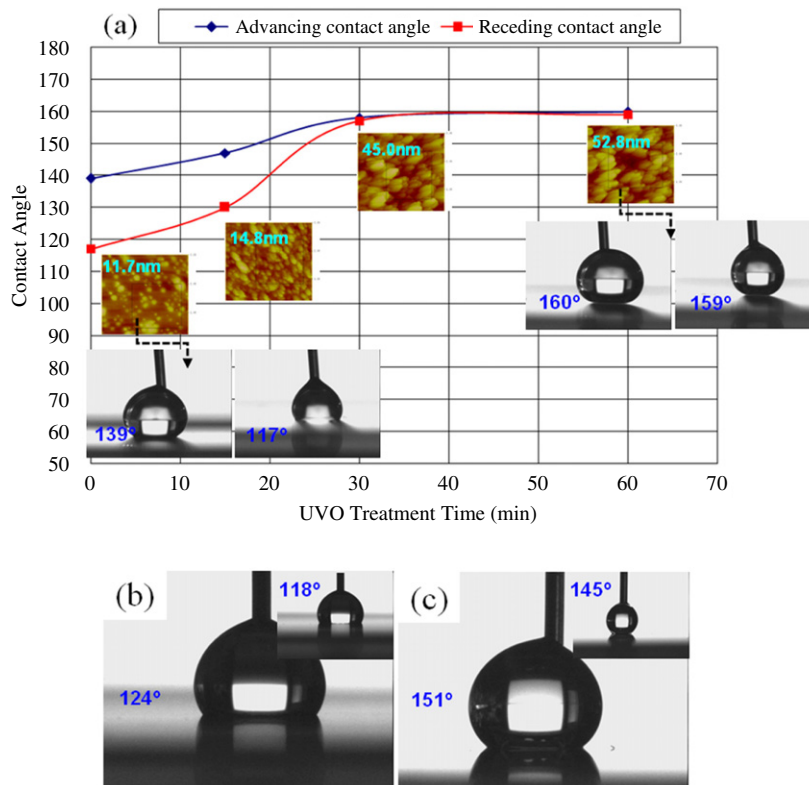


Figure 3. (a) Advancing and receding CAs as a function of UVO treatment time for pre-formed prism-like texture and some examples of surface roughness measured by AFM. (b) Advancing CA on the prism-like texture without nanoparticles after UVO treatment. (c) Advancing CA on the nanoscale surface roughened with a nanoparticle-containing resin (without a micro-scale texture) after UVO treatment. In (b), (c), the inset images show the receding CAs.

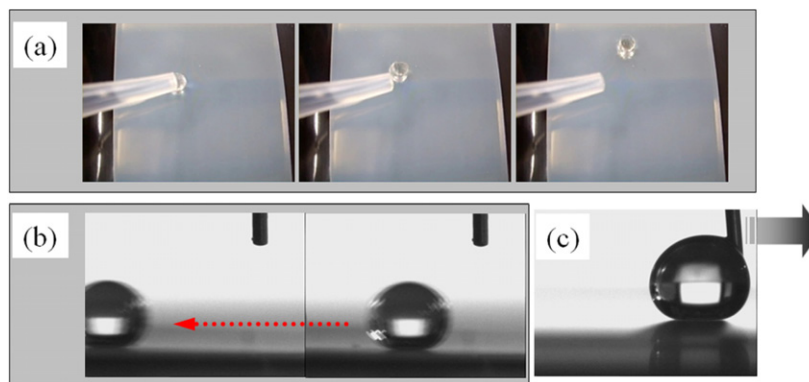


Figure 4. Sliding behavior of a water droplet on prepared film: (a) water droplet weighing 30 mg on the film (4 cm by 6 cm) with dual-scale roughness when placed horizontally; (b) water droplet weighing 10 μ g on the film with dual-scale roughness when placed horizontally; (c) anti-adhesion behavior of 20 μ g water droplet: no degradation of droplet shape when moved by syringe from left to right after sitting on the surface for a couple of minutes.

for a few minutes, as shown in figure 4(c). When the syringe was moved parallel along the film surface on an optical bench after the droplet had been in contact with the surface for a couple of minutes, the droplet still moved freely with the syringe without any degradation of the droplet shape. These results indicate that the surface possesses uniform and robust multiscale roughness over the entire surface.

It is well known that the wetting state of a water droplet can be described by two distinct modes of the Wenzel and the Cassie states, depending on the degree of surface roughness.

When governed by the Wenzel state, the water droplet becomes pinned to the surface and remains motionless even when the film is tilted to a significant angle, whereas it slides off easily even when the film is tilted only a few degrees when governed by the Cassie state. According to the quantitative relationship between the CA hysteresis and the sliding angle, a , a lower CA hysteresis results in a smaller sliding angle as given by equation (1) [15]:

$$mg(\sin a)/w = \gamma_{lv}(\cos \theta_R - \cos \theta_A) \quad (1)$$

where θ_A and θ_R are the advancing and receding CAs, respectively, g is the gravity, and m and w are the mass and width of the droplet, respectively. The simulations by Johnson and Dettre [14] have shown that the contact mode can make a transition from the Wenzel to the Cassie regime with increasing surface roughness. Since surface roughening ensures an increase in the amount of trapped air and thus a water droplet sits partially on air pockets, the Cassie regime offers a lower sliding angle.

Based on the fact [16] that the force required to move a water droplet over a solid surface is $F \sim mg(\sin a)$ and even a 30 mg water droplet slid quickly off without any external force, it can be concluded that the hierarchical surface structure has excellent superhydrophobic properties, both satisfying a higher contact angle ($>150^\circ$) and a near-zero sliding angle.

4. Conclusion

We have presented a controllable approach for creating micro-/nano-dual-scale hierarchical structures by combining a top-down micromolding method and a bottom-up assembly with a hydrophobic self-assembled monolayer. The fabricated surface exhibits a CA as high as 160° and a sliding angle as low as 1° , similar to the characteristics of the self-cleaning lotus leaf. For the dimension control of the hierarchical structure, the base micro-scale topography can easily be altered by changing the engraved pattern of the rigiflex mold while the nanoscale roughness can be adjusted by using nanoparticles of different size. It is envisioned that several useful features of the method presented here, including exclusion of any solvent in materials, use of various substrates, extremely high stability at ambient

conditions and high reproducibility, would be suitable for cheap, large-area fabrication of a superhydrophobic surface.

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