Intrinsic Effects of Materials on Superhydrophobicity of Polymer Replicas from Nature

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ABSTRACT

The present work suggests a mass-producible and large scale fabrication method of superhydrophobic polymeric surfaces by means of material processing equipments which can maximize productivity and cost effectiveness. We fabricated two types of polymeric lotus leaf replicas using the nickel mould, i.e. ***R1*** from intrinsically hydrophobic PDMS by means of polymer casting (PC) and ***R2*** from intrinsically hydrophilic UV-curable photopolymer by means of UV-nanoimprint lithography (UV-NIL). In the case of ***R1*** from ***PC***, although the nano-scaled structures were not well reproduced, the contact angle (CA) was remarkably high and the sliding angle (SA) was also close to the original lotus leaf, resulting in superhydrophobic surface. In contrast to ***R1***, in the case of ***R2*** from UV-NIL, the nano-scaled structures as well as micro-scaled structures also relatively well reproduced and the CA was increased noticeably in comparison to flat photopolymer, by around 99°. However, unexpectedly, the SA of ***R2*** was much higher than ***R1***. This work provides useful tips of polymeric material selection, for the industrial mass production of superhydrophobic polymer surface.

Keywords: Superhydrophobic, Lotus effects, UV-nanoimprint lithography, Replication

1 INTRODUCTION

With the advent of micro/nano technologies and their remarkable development, one has revealed the secret of micro- and nano- structures found in natural tissues and has attempted to mimic these natural tissues. The lotus leaf, which can be regarded as one of such typical tissues in nature, motivates researchers to explore the mysteries of nature caused by micro- and nano scaled structures from the chemical and physical viewpoint. Chemically, the wetting property of the flat surface is governed by surface free energy of material itself. However, some tissues such as a lotus leaf show extremely high contact angle (CA), around 160° or above [1, 2] and furthermore, water drops on those surfaces does not stick to them and behave very extraordinarily, e.g., rolling and bouncing [3]. More importantly, when water drops roll off those surfaces, they remove dust on those surfaces (self-cleaning effect) [1, 2]. It is generally well-accepted that this superhydrophobicity is enhanced by the micro and nano combined structures on those surfaces. These superhydrophobic surfaces have attracted many researchers' attention due to their importance in fundamental study and industrial applications [3, 4]. There have been theoretical reports in the literature to elucidate the secrets of the superhydrophobic surfaces [3, 5-9]. Meanwhile, various methods have been introduced to produce such surfaces: for instance, surfaces from chemical processing [10, 11], surfaces replicated from templates [12–14] and so on. From the view point of the industrial production and commercial use of the superhydrophobic surfaces, simplicity of manufacturing, mass-producibility and cost efficiency are of great concern. In this respect, most of the reported methods in literature are not appropriate since they generally require cleanroom-based job or tedious fabrication processes and have some limitations with regard to mass-production capability, material selectivity, cost effectiveness etc.

If one could fabricate a mold which has patterns of micro- and nano- combined structures of interest, the mass-production of superhydrophobic surfaces could be efficiently achieved by employing it as a mold insert in manufacturing methods such as injection molding, hot embossing, polymer casting (PC), UV-nanoimprint lithography (UV-NIL) and so on for the repetitive replication of the patterns. With this in mind, we have introduced a mass-producible fabrication method of superhydrophobic surface by directly replicating natural leaves; the method is composed of two steps: the first one of nickel-mold making via electroforming upon plant leaves and the second step of replication using available manufacturing methods [13]. In this study, among those manufacturing methods mentioned above, we carry out two kinds of replication methods, namely, PC using PDMS (polydimethylsiloxane) and UV-NIL using photopolymer to produce superhydrophobic surfaces making use of nickel-mold directly patterned upon lotus leaf. The replicas from PC and UV-NIL show close similarity in terms of topographic feature and CA with the original lotus leaf. However, astonishingly, it was found that the sliding behavior of each replica is remarkably different according to the intrinsic hydrophobicity of the used polymer.

2 FABRICATION PROCESSES

Nickel Mold. As shown in Fig. 1a, for making a nickel-mold patterned upon lotus leaf, chromium (20 nm) to promote adhesion of the gold layer and gold (80 nm) serving as a nickel seed layer are deposited on the 4 inch-silicon wafer by an ion sputtering system [BJD 1800, TEMESCAL, USA]. Next, lotus leaf (around 6×4 cm^2) is bonded on it by adhesive bonding (LOCTITE, PRISM 401). Since the lotus leaf is not electrically conductive, a gold coating (Paraone, PS-1200, KOREA) is performed on the

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leaf including the previous gold layer. Nickel electroforming is then carried out under appropriate processing conditions (Temperature of electrolyte solution which is composed of $Ni(SO_3NH_2)_2$, $NiCl_2 \cdot 6H_2O$ and H_3BO_3: 55 °C, Current density: 0.3 – 1.3 mA/dm^2, pH: 4.1). Finally unnecessary layers (silicon, chromium, gold and lotus leaf) are stripped, resulting in a pure nickel mold: silicon layer is removed by dipping the nickel-mold into 70°C potassium hydroxide (KOH) solution; the chromium layer and the gold layer are subsequently removed in the solution of CR-7SK and a stripper solution, respectively.

PDMS Replica. For making PDMS replica from PC (Fig. 1b), a well-cleaned 4 inch Petri-dish is prepared and the nickel mold was placed onto the dish. Then PDMS mixture [30g of PDMS (DC-184A, Dow Corning Corporation) and 3g of thermal curing agent (DC-184B, Dow Corning Corporation)] is poured into the dish and kept there for around 30 min at vacuum desiccator to remove the air bubbles in PDMS mixture and to minimize the air-entrapment in the nickel mold. Then solidification process is carried out in an oven at 65°C for 3 h.

Photopolymer Replica. For making photopolymer replica from UV-NIL (Fig. 1c), UV-NIL equipment designed and constructed by our group is used [13, 14]. The used photopolymer is *RenShape* SL 5180 (Vantico Inc.) and the detailed process of UV-NIL is explained in our previous papers [13, 14].

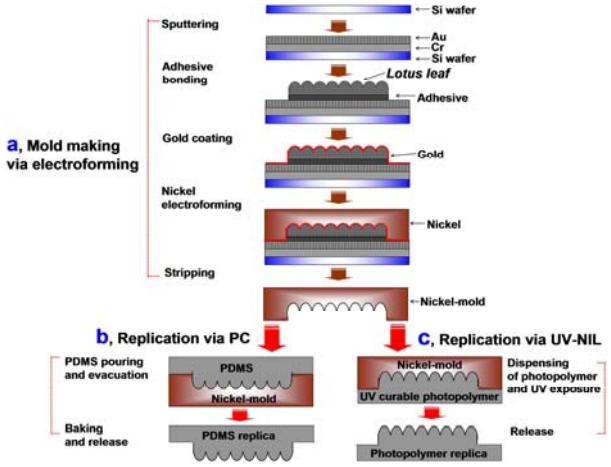

Figure 1: Schematic representation of fabrication process of superhydrophobic surfaces composed of two steps. (a) Nickel mold making step, followed by replication step using (b) PC or (c) UV-NIL. In this wok, using a nickel mold patterned upon lotus leaf, two kinds of polymer replicas (PDMS replica and photopolymer replica) are fabricated by PC and UV-NIL.

3 CHARACTERIZATION

The replication quality and hydrophobic property of the fabricated PDMS replica (***R1***) and photopolymer replica (***R2***) was characterized by scanning electron micrograph, water CA and water sliding angle (SA).

Scanning electron micrographs of the original lotus leaf surface, nickel-mold and its corresponding polymer replicas were taken by a XL 30S (FEI, USA) scanning electron microscope (SEM). The water CA was measured by a sessile drop method using a contact angle measurement system (Krüss GmbH Germany, model: DSA 100) with the distilled water droplet volume of 5 µl. Contact angles were measured at least ten distinct positions and averaged for each case. And with the same equipment the water SA with respect to volume of water drop was measured. Sliding angles were also measured at least ten distinct positions and averaged for each case. In order to establish reference CA values for comparing with ***R1*** and ***R2***, a flat and smooth PDMS surface and photopolymer surface were prepared by using a flat 4-inch silicon wafer as a master [instead of the nickel-mold in figure 1(b) and figure 1(c)]. The reference CA value of the ***R1*** was found to be about 106.1 ± 1.6° and the reference one of R2 was 56.0 ± 1.2°

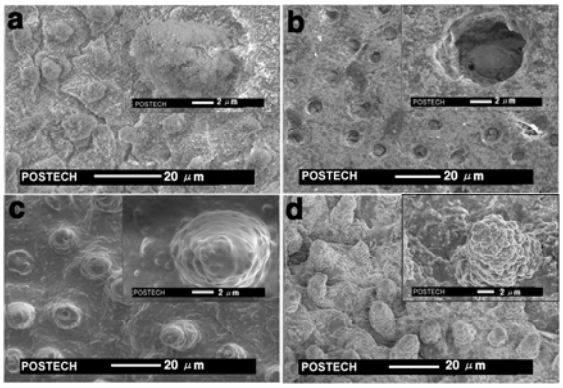

Figure 2: Scanning electron micrographs of diverse surfaces. (a) Original lotus leaf. (b) Nickel mold surface patterned upon lotus leaf (a). (c) PDMS replica (***R***1) from PC (figure 1b). (d) Photopolymer replica (***R2***) from UV-NIL (figure 1(c)). The insets are the magnified images of the large ones, respectively.

4 RESULTS AND DISCUSSION

Replication Quality of the Produced Polymer Replicas. Fig. 2 shows SEM images of (a) a real lotus leaf, (b) a fabricated nickel-mold (Fig. 1a), (c) ***R1***, PDMS replica from PC (Fig. 1b) and (d) ***R2***, photopolymer replica from UV-NIL (Fig. 1c). As shown in Fig. 2a, the lotus leaf has multi-scaled surface structures, that is, micro and nano combined structures. Grass-like nanostructures exist on protruding micro patterns of about 5 µm in size. When compared with the original lotus leaf, Fig. 2b indicates that the nickel mold successfully replicates not only the microstructures of the lotus leaf but also its intricate nanostructures. As shown in Fig. 2c, ***R1*** also shows excellent replication quality in the micro scale structure whereas the nano-scaled structures are relatively poorly replicated. This might be attributed to the air-entrapment between liquid-state PDMS mixture and the fine nickel-mold surface during the evacuation stage and the lack of the

pressing force during the solidification stage of PC, when compared with ***R2*** shown in Fig. 2d. It might be noteworthy that the nanostructures might have been better replicated in ***R2*** than ***R1*** mainly due to the pressure applied onto the photopolymer in the UV-NIL process [13, 14]. There could be another explanation for the poor replication of nano scale features in ***R1*** as follows. The physical properties of the PDMS used in this study, namely low elastic modulus and surface tension could cause deformation of the replica upon releasing from the mold, resulting in poor replication of nano structures in ***R1***. The role of such physical properties of PDMS on the replication quality should be further investigated, in particular, with respect to the effect of nanoscale features on the hydrophobicity in the near future.

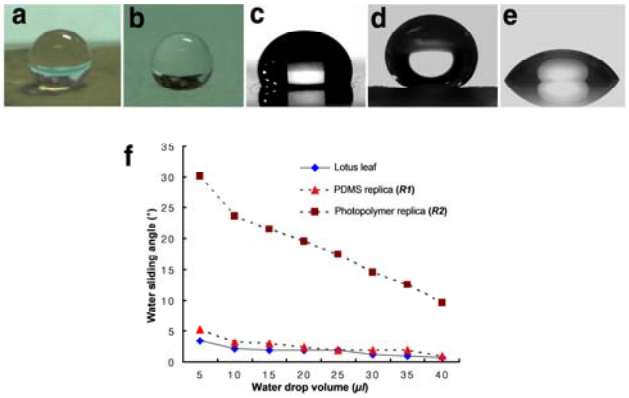

Figure 3: 5 μl water drops on (a) lotus leaf, (b) ***R1***, (c) flat PDMS surface, (d) ***R2*** and (e) flat photopolymer surface. The contact angles (θ=average ± standard deviation): (a) 168.0 ± 1.4°; (b) 163.3 ± 1.8°; (c) 106.1± 1.6°; (d) 155.0 ± 1.8°; (e) 56.0 ± 1.2°. (f) Sliding angles of the three kinds of surfaces (real lotus leaf and its corresponding replicas, i.e. ***R1*** and ***R2***) with respect to various water drop volume. The SA of the lotus leaf is very low and its replica, ***R1*** also has similar level of SA value and sliding behavior. However, in the case of ***R2***, the SA is much higher than lotus leaf and ***R1***, even if the CA value of ***R2*** is also large. The SA might be dependent on intrinsic hydrophobicity. In other words, intrinsically hydrophobic materials might be expected to have low SA like lotus leaf, however intrinsically hydrophilic ones seem to be difficult to have low SA.

Hydrophobic Nature of the Produced Polymer Replicas. The surface wettibility of the two kinds of the produced polymer replicas, ***R1*** and ***R2*** has been evaluated by both the static contact angle (CA) and the sliding angle (SA) measurement. Figures 3(a)-3(e) shows water drops on various surfaces of: (a) lotus leaf; (b) ***R1***; (c) flat PDMS; (d) ***R2***; (e) flat photopolymer surface. CA value of the real lotus leaf is 168° indicating superhydrophobicity. The CA values of the produced replicas from PC and UV-NIL, that is, ***R1*** and ***R2*** are 163° and 155°, respectively. Even if the replication quality of the nano-scaled structures on ***R1*** was not as successful as ***R2***, ***R1*** showed a higher level of superhydrophobic nature. It should be noted that CA values of the flat PDMS and flat photopolymer surfaces are 106° (i.e., intrinsically hydrophobic) and 56°(i.e., intrinsically hydrophilic), respectively. When compared with each flat surface, the CA values of their corresponding replicas are increased by around 57°and 99°, respectively. In the case of ***R2***, although the used photopolymer is intrinsically hydrophilic, the CA increase is quite remarkable when compared with ***R1***. As we infer from the Fig. 2c and 2d, this might be attributed to the difference of the replication quality of ***R1*** and ***R2***. In other words, due to the rough surface feature of ***R2*** (more complicated micro/nano combined structures), ***R2*** has more air pockets than ***R1***, thereby resulting in higher CA increase [8]. Fig. 3f shows SA change against the volume of the used water drops on the lotus leaf, ***R1*** and ***R2***. As indicated in that figure, the SA of the lotus leaf is very low and ***R1*** also shows similar level of SA value. However, ***R2*** has relatively large SA. In summary, ***R1*** has high CA and low SA indicating superhydrophobic nature. In contrast, even if ***R2*** has relatively high CA, the SA value is somehow high. The CA increase and low SA of ***R1*** seems to accord well with the Cassie/Baxter theory [8]: air entrapped in the rough surface could enhance its water-repellency since the water drop can sit partially on air, not on the entire solid surface. Accordingly, the uniformly distributed 5μm order of micro sized protrusions in the replica provides more entrapped air, which can significantly decrease the contact area between the replica surface and the water, resulting in high CA and very low SA. In contrast to ***R1***, both Cassie/Baxter and Wenzel theory [9] is contradictory in the case of ***R2***. It seems that in some cases [12-16] including observed results in this work, Cassie/Baxter and Wenzel state coexist, as described in Fig. 4. Fig. 4c describes the Cassie/Wenzel state that we conjecture from the observed results in this work, which indicates the combined state of both Cassie/Baxter state and Wenzel state. Considering the fact that ***R2*** is made from intrinsically hydrophilic polymer and has high CA and high SA, an intermediate state between Cassie/Baxter state and Wenzel state is likely to exist, sharing both characters. Such an intermediate state could be depicted as Fig. 4c and it looks quite feasible from the physical sense. One may suspect that a water drop on ***R2*** is on pinned state [17], accordingly the CA of the water drops on that surface would decrease as time goes by or the CA would be decreased very easily with even small external disturbance, finally reaching on the Wenzel state. However, during our experiment, we were not able to observe such a decrease of CA of ***R2*** with respect to time. When CA of ***R2*** was measured again around 4 hours later after the first measurement (which was done immediately after the water drop was placed on the surface), the CA was about the same as the initially measured CA and the SA also showed the almost similar level of value with the initially measured SA. And it was found that the CA value was kept up even with external disturbance to some extent. In some literature [15,16,18], similar phenomena related to these kinds of unstable contact state (i.e., sticky water drop

of high CA that does not easily roll off the surface) have been reported and some researchers discussed these phenomena from water drop formation on the surface [15] or energy barrier [16] point of view. However, this problem is still left to be unsolved. One needs to study further with respect to this kind of an intermediate state and investigate behavior of CA and SA on the hydrophilic polymeric materials with rough surface topography.

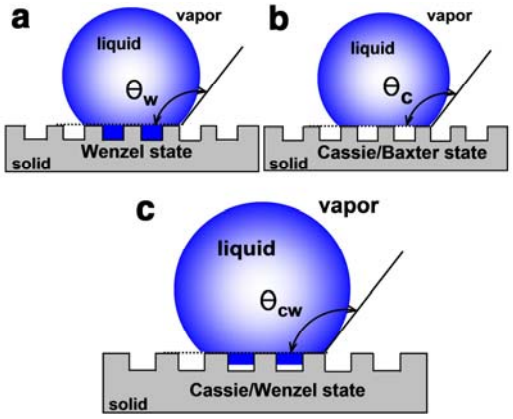

Figure 4: Description of Cassie/Wenzel state that we conjecture from the results observed in replica ***R2***. According to (a) Wenzel's theory [9], the surface roughness enhances both the hydrophilicity of a hydrophilic surface and the hydrophobicity of a hydrophobic surface. In this work, however, the photopolymer is intrinsically hydrophilic ($\theta \approx 56° < 90°$, when θ is the equilibrium CA on the flat surface), and yet its replica, ***R2*** is hydrophobic CA > 90° (CA ≈ 155° Therefore, Wenzel's theory does not correspond to our results. On the other hand, according to (b) Cassie/Baxter theory [8], the CA value of ***R2*** is predicable and agrees well with their theory. However, from the viewpoint of SA, their theory disagrees with our result. Therefore, it seems that there might be an intermediate state to share both Wenzel's theory and Cassie/Baxter's theory as depicted in (c).

5 CONCLUDING REMARKS

In conclusion, two kinds of lotus leaf replicas (***R1*** and ***R2***) were successfully produced by a simple replication method composed of two steps of processing, i.e. mold making via nickel electroforming and replication via PC and UV-NIL. In the case of ***R1*** from PC, although the nano-scaled structures were not well reproduced, the CA was remarkably high and the SA was also close to the original lotus leaf, resulting in superhydrophobic surface. In contrast to ***R1***, in the case of ***R2*** from UV-NIL, the nano-scaled structures as well as micro-scaled structures also relatively well reproduced and the CA was increased noticeably in comparison to flat photo polymer, by around 99°. However, unexpectedly, the SA of ***R2*** was much higher than ***R1***, thereby losing the merits of superhydrophobic nature to some extent. Therefore, as for the mass-production of the superhydrophobic surface using polymeric materials, it is recommended that one had better use intrinsically hydrophobic polymer than intrinsically hydrophilic one, when one uses other manufacturing technologies having superior productivity such as hot embossing, injection molding etc. As far as the electroforming technique suggested in this work is concerned, for the other special purposes, one could apply this technique to other biological surfaces such as insect's wing, fish scale/ skin and flower petal etc, as well as lotus leaf. It may be also mentioned that this promising technique could be widely used in the field of biomimicry using surface replication and conventional electroforming technology.

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