Replication of Highly-Hydrophobic Surface with Micro/Nano Combined Structures from Nature

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ABSTRACT

Many plant leaves found in nature are known to exhibit a characteristic of superhydrophobicity ("Lotus leaf effect"). In this study, a highly-hydrophobic film has successfully been fabricated by simply replicating plant leaf surface with micro/nano combined structures. A plant leaf was used as a mandrel to make a mold by nickel electroforming (NE). The positive polymer replica was then fabricated by UV-nanoimprint lithography (UV-NIL) using the nickel-mold. This new replication method turns out to be quite promising in view of the replication quality of both micro/nano structures and hydrophobicity.

Keywords: highly-hydrophobic, contact angle (CA), nickel electroforming (NE), UV-nanoimprint lithography (UV-NIL), micro/nano combined structures

1 INTRODUCTION

In these days, the marvelous surface structures of the superhydrophobic plant leaf have attracted many researchers' attention [1]. In particular, the superhydrophobic property induced by those structures has become a quite important issue since there are a variety of practical applications utilizing their self-cleaning, drag reduction, and anti-fogging effects and so on. In this regard, diverse methods have been reported to produce such surfaces: for instance, conventional lithographic techniques [2] and chemistry based processing ones [3]. Besides, theoretical studies to elucidate the secrets of the water-repellent plant leaves' surfaces have also been reported [4-11].

Our previous work reported a successful fabrication method for hydrophobic films in the form of negative replica by directly replicating the micro/nano features using a plant leaf as a master via UV-NIL [12]. This method, however, is not appropriate for mass-production since the plant leaves can be used just once in UV-NIL process.

For the purpose of a mass-production, it is necessary to have a mold on which the same surface structures as the leaf are patterned. In this regard, the present work proposes a new *two-step* replication method for highly-hydrophobic films in the form of positive replica as follows: i) as the first step, a nickel-mold is produced, patterned on a plant leaf surface, by electroforming process; ii) as the second step, UV-NIL is employed to fabricate the positive polymer replica from the nickel-mold. The experimental procedure and basic results are presented first with a bamboo as a typical example, followed by more application examples using three other leaves.

2 FIRST STEP: MOLD MAKING

Fig. 1 schematically shows the nickel-mold making step by electroforming. A silicon wafer is first coated with chromium (20 nm thick) to promote adhesion of the gold layer (80 nm thick) on the silicon wafer. The gold layer is deposited on the chromium layer by an ion sputtering system [BJD 1800, TEMESCAL, USA], serving as a nickel seed layer. Next, a bamboo leaf is bonded on the substrate with the help of an adhesive **(**LOCTITE**,** PRISM 401). Since the leaf is not electrically conductive, a gold ion coating is performed on the leaf surface including the previous gold layer. NE is then carried out under the processing conditions (Temperature of electrolyte solution: 55 ^{o}C, Current density: 0.3 – 1.3 mA/dm^2, pH: 4.1). Finally unnecessary layers (silicon, chromium, gold and bamboo 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.

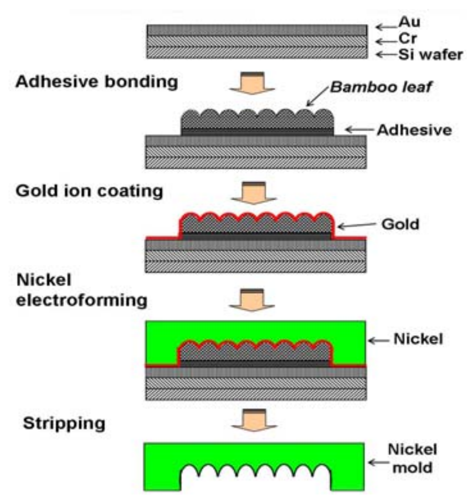

Figure 1: Fabrication process of nickel-mold patterned on the bamboo leaf surface.

3 SECOND STEP: FILM FABRICATION

Fig. 2 schematically shows a UV-NIL equipment together with the fabrication process of polymer replicas using a nickel-mold. The UV-NIL equipment was designed and manufactured by our research group [12].

The procedure of UV-NIL process is as follows: setting up the sequence with specific processing conditions on the PC, fixing the nickel-mold to the vacuum chuck, dispensing UV curable photopolymer on a slide glass, removing air and dust from the vacuum chamber, applying a regulated force to the vacuum chuck system (where the mold is fixed) via a pneumatic cylinder (SMC Korea, model: MB8F40-KRG0474-175-NH), exposing the photopolymer to collimated UV light through the quartz plate using a UV lamp and, finally, detaching the polymer replica from the nickel-mold. The UV curable photopolymer used in this work is *RenShape SL 5180* (Vantico Inc., density: $1.15 \times 10^3 kgm^{-3}$, viscosity: $0.24\ kgm^{-1}s^{-1}$, critical exposure: $13.3 mJcm^{-2}$). The UV light exposure time is controlled by opening time of a lamp shutter. UV lamp adopted in this system is *MRL 1500* (SEN Inc. JAPAN, lamp wave length: 365 nm, lamp effective area: $125 \times 125 mm^2$, lamp power: 1.5KW).

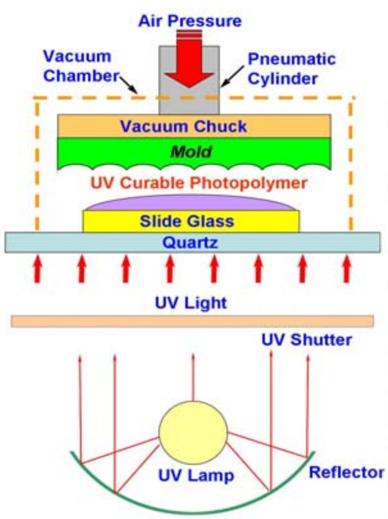

Figure 2: Schematic of UV-NIL process using nickel-mold.

4 CHARACTERIZATION

The replication quality and surface property of the polymer replicas are characterized by scanning electron microscope (SEM) and water contact angle (CA). Scanning electron micrographs of the nickel-mold and their corresponding polymer replicas are taken by a XL 30S (FEI, USA) scanning electron microscope (SEM). Water CA is measured by a sessile drop method using a Krüss Drop Shape Analysis System (Krüss GmbH Germany, model: DSA 10-Mk2) with the distilled water droplet volume of 5μl. A CCD camera captures the shape of droplet on the surface, from which the contact angle is analyzed by commercial software (SCALE 2.0, Paraguay). Contact angles were measured at least ten distinct positions and averaged for each case in this work.

A reference CA value was also measured, to be compared with the produced replicas, from a flat and smooth UV photopolymer (*RenShape SL 5180*) surface. The reference CA is found to be about 56˚.

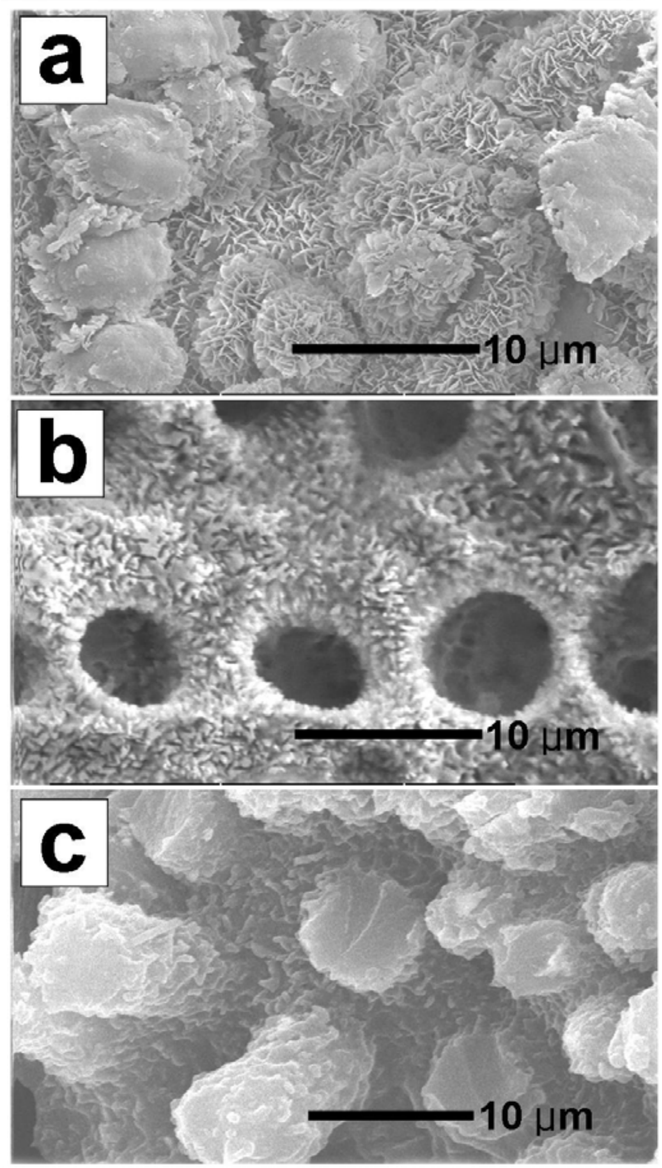

Figure 3: SEM images of (a) real bamboo leaf surface, (b) positive nickel-mold surface patterned upon the bamboo leaf surface (Fig. 3a) and (c) the final product in the form of positive replica from the negative nickel-mold (Fig. 3b).

5 RESULTS AND DISCUSSION

5.1 Replication quality of the surface patterns

Fig. 3a shows SEM images of the real bamboo leaf surface which has multi-scaled structures, that is, a combination of micro- and nano-structures. Rose quartz petal-like nanostructures exist on protruding micro patterns of about 5μm in size. As compared with Fig. 3a, Fig. 3b shows SEM images of the nickel-mold produced by electroforming process. It was found that the microstructures of the leaf were successfully replicated in the mold. As far as the nanostructures are concerned, they look alike in both the bamboo and mold. This well replicated mold enables a quite successful positive polymer replica via UV-NIL. The final product shown in Fig. 3c is a good negative replication of the mold, resulting in a positive replica of the original leaf (Fig. 3a) in a satisfactory level with respect to the similarity from the micro to the nano scale structures.

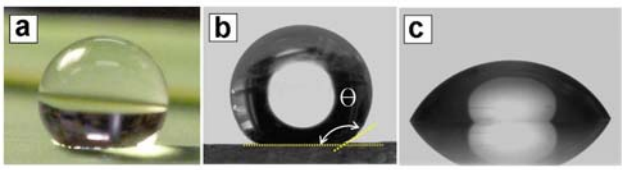

Figure 4: 5μl water drops on the various surfaces. (a) original bamboo leaf (Fig. 3a), (b) positive replica (Fig. 3c) and (c) flat and smooth surface. The contact angles (average ± standard deviation) of these surfaces were (a) 152 ± 2.9˚; (b) 150 ± 2.5˚; (c) 56 ± 1.2˚.

5.2 Contact angle as a measure of hydrophobicity

Water CA is a well accepted measure of hydrophobicity. Since the purpose of the proposed replication method is the mass-production of highly-hydrophobic film of which the main use is associated with water repellency, practicability of the replication method can be best evaluated by the measure water CA. Fig. 4 shows water drops on various surfaces: (a) a real bamboo leaf, (b) a positive replica, and (c) a flat and smooth polymer film. CA value of the real bamboo surface is 152˚ indicating highly-hydrophobicity. The CA values for the flat and smooth surface and the positive replica surface are 56˚ and 150˚, respectively. The positive replica has high CA, just a little smaller than the bamboo leaf itself only by 2˚. It may be noted that CA value of 56˚ in the flat and smooth surface indicates that the polymer with no micro/nano structures is hydrophilic.

According to the experimental results so far, the positive replica becomes hydrophobic, its CA being much higher than the reference flat film even if the film is made of the same material as the flat film. This observation of changing the hydrophilicity to hydrophobicity could be explained by the change of their topographical features, namely the micro/nano combined structures of polymer replica, which is consistent with the observation in [12]. Cassie-Baxter theory [10] might be referred to associate with this observation.

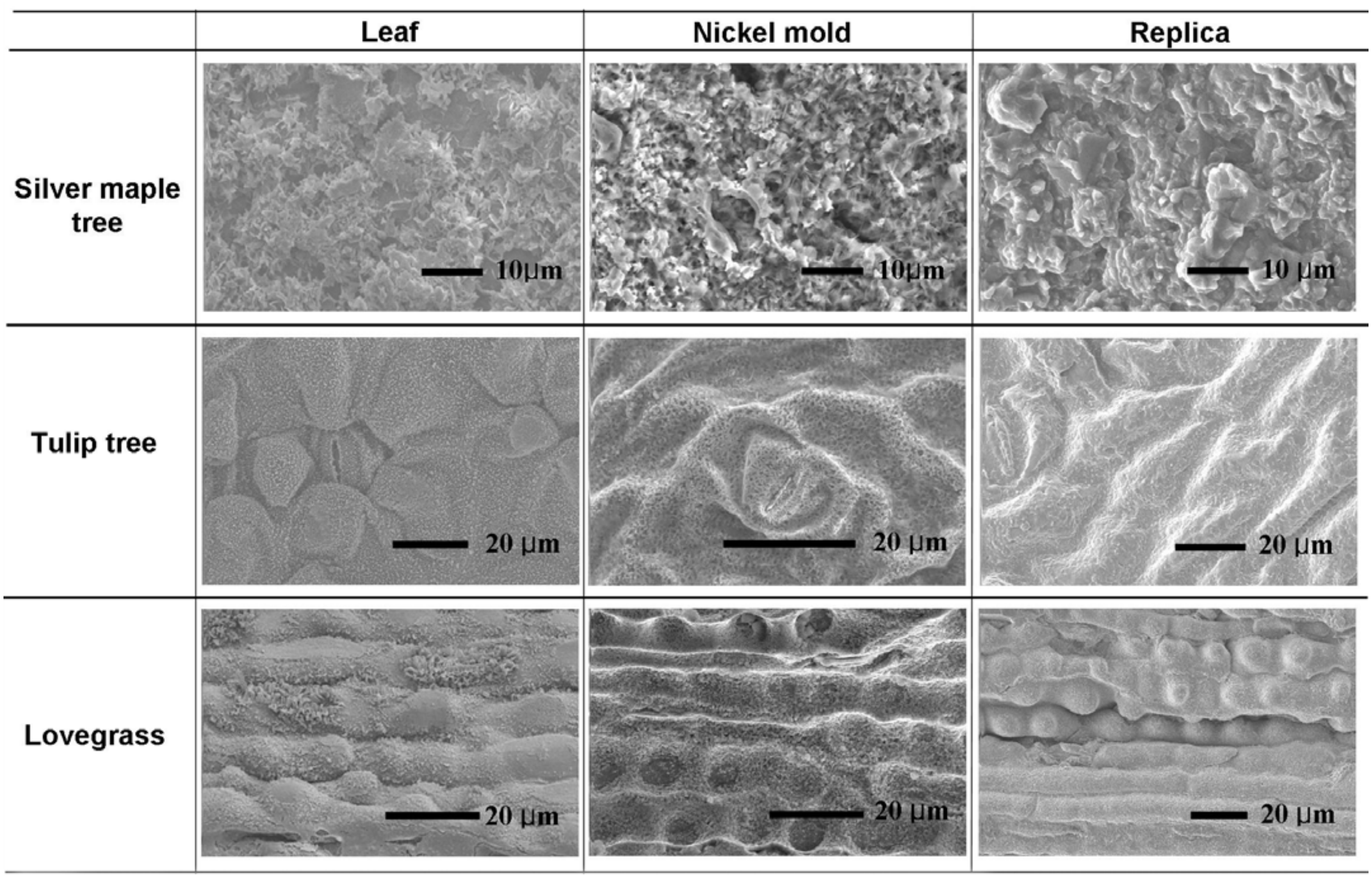

Figure 5: SEM images of the original plant leaves, negative nickel-molds and positive polymer replicas of the original plant leaves.

Table 1. Contact angle values of plant leaves and their corresponding positive polymer replicas.

(average ± standard deviation)

	Silver maple tree	*Tulip tree*	*Lovegrass*
Leaf	149 ± 2.3˚	148 ± 1.7˚	154 ± 3.7˚
Positive replica	145 ± 3.4˚	143 ± 2.3˚	151 ± 2.2˚

So far, the successful replication of the intricate micro/nano combined structures of the bamboo leaf was demonstrated as a typical example. It might be of quite importance to make sure that the same method could be successfully applied to other plant leaves. With this mind, three other plant leaves [*tulip tree* (*Liriodendron tulipifeva L.*)*, silver maple tree* (*Acer saccharinum L.*)*,* and *lovegrass* (*Eragrostis terruginea*)] were selected to validate the general applicability of the proposed replication method of highly-hydrophobic surface. To our satisfaction, negative nickel-molds and subsequently positive replicas were successfully fabricated for the three leaves. Fig. 5 shows SEM images of plant leaves, their negative nickel-molds and corresponding positive polymer replicas for three plant leaves. As indicated in Fig. 5, the replicas are quite similar to the original leaf surfaces in terms of their micro/nano combined structures. The measured CA values in these cases are listed in Table 1. CA values of all the replicas are less than those of the natural surfaces only by 3˚ to 5˚, indicating their highly-hydrophobicity.

6 CONCLUDING REMARKS

The present study proposes a mass-producible fabrication method of highly-hydrophobic polymer films by simply replicating the plant leaf surfaces with micro/nano combined structures in *two steps*: the first step of making a nickel-mold via electroforming and the second step of replication via UV-NIL.

Measured CA values of final products from the bamboo leaf are 150˚, to be compared with CA value of 152˚ for the real bamboo leaf. This level of hydrophobicity is attributed to the surface topographic features, namely micro/nano combined structures, regardless of the hydrophilicity or hydrophobicity of material itself. Furthermore, the proposed replication method has been also found to be successfully applied to many highly-hydrophobic plant leaves from nature.

If UV-NIL for the second step could be replaced with other processing technologies which are more suitable for mass-production, one can enhance the productivity of the replication of highly hydrophobic films. The possible processing one can think of are, for instance, PDMS casting, injection molding or hot embossing processes. Moreover, injection molding or hot embossing processes could enable final replica products of various polymeric materials such as polystyrene (PS), poly(methyl methacrylate) (PMMA), polycarbonate (PC), cyclic olefin copolymer (COC) and so on.

ACKNOWLEDGEMENT

This research was financially funded partially by a grant (2000-N-NL-01-C-148) via the National Research Laboratory Program and a grant (R01-2005-000-10917-0) for Interdisciplinary Research, which are supported by Ministry of Science and Technology, Korea.

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