



Wettability of metal coatings with biomimic micro textures

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ABSTRACT

By combining duplication and electroplating methods, three surface micro textures of rice leaf, lotus leaf and snake skin were duplicated on nickel coatings. Measurements of scanning electron microscopes and optical microscope indicate the micro textures of the replicas are almost in accordance with their biological sources. The nanostructures replicated from snake skin suggest that this technique can achieve features with resolution as low as hundreds of nanometers in width and tens of nanometers in depth on nickel coatings. Contact angle measurements on the replicas surfaces of rice leaf and lotus leaf show the wettability of the metal surfaces was improved with hydrophobicity after duplicated with bio-mimicking micro textures.

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1. Introduction

Functional surfaces with bio-mimicking micro textures have aroused much interest because of their great advantages in applications such as hydrophobic, anti-adhesion etc. For example, some plant leaves and bodies of animals are known to be hydrophobic in nature because of their intrinsic geometric microstructure. In particular, the lotus leaf, on which the water contact angle is larger than 150°, can carry effortlessly the contaminations attached to the leaf when the surface is slightly tilted, which shows self-cleaning function and low hysteresis. The main reason is the presence of micro-bumps and a thin wax film on the surface of the leaf [1–4]. Water striders are remarkable in that they have non-wetting legs, which are composed of numerous needle-shaped setae with diameters on micro scale and that each micro seta is composed of many elaborate nano scale grooves, which enable them to stand effortlessly on water [2]. These unique functions of biological systems are all closely related to their surface textures. Therefore, the research in this field will be useful for manufacturing multifunctional materials.

Inspired by these living organisms in nature, artificial surfaces with some textures are commonly fabricated through many methods such as crystallization control [5], phase separation [6,7], molding [8], anodic oxidization of aluminum [9], immersion of porous alumina gel films in boiling water [10], electrochemical deposition [11–13] and chemical vapor deposition [14,15]. However, all these methods can not fully replicate surfaces with bio-mimicking textures, and also they are with high cost.

In this study, by combining duplication and electroplating methods, surface micro textures of three kinds of biological originals

were fully duplicated on nickel coatings, using original living creatures as templates. The wettability of the metal surfaces was improved with hydrophobicity after duplicated with bio-mimicking micro textures.

2. Experimental

The flowchart for creating metal surface with bio-mimicking textures is shown in Fig. 1. Firstly, a cellulose film is used to replicate the surface micro textures of the biological sample to obtain a negative impression of the bio-mimicking micro textures, which is innovative. A metallic layer is electrodeposited on the top of the cellulose film. Then the positive replicas of the original living creature were obtained after removing the cellulose film.

2.1. Materials

Biological originals (rice leaf, lotus leaf and snake skin), the localities of which and their corresponding habitats are shown in Table 1; cellulose acetate (Sinopharm Chemical Reagent Co. Ltd, China) film (self-made), the viscosity of which is 300–500 Pa s; acetone, octadecanethiol (Aldrich Chemical Company, America), nickel sulfate hexahydrate, nickel chloride hexahydrate, boric acid and sodium dodecyl sulfate are analytically pure, which were used as received; Nickel boards (Kunshan Precision Technology Co. Ltd, China) were cleaned with dilute hydrochloric acid solution and de-ionized water before used.

2.2. Sample preparation

2.2.1. Duplication

First, a kind of cellulose film was cast onto a fresh biological original template to replicate the surface textures of the template.

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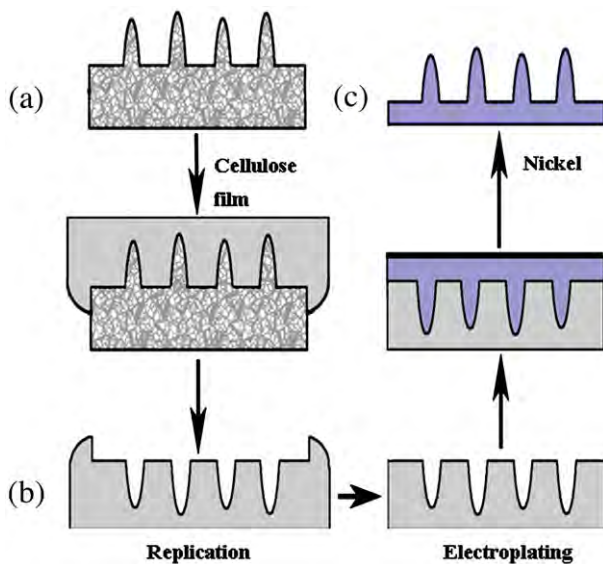


Fig. 1. The schematic diagram of creating metal film with bio-mimicking textures. (a) The original template; (b) Cellulose film with a negative impression of the bio-mimicking textures; (c) Metal film with the bio-mimicking textures.

After the cellulose film solidified, the complement of surface textures of the original template was transferred to the cellulose film [16,17]. Then the textured cellulose films were peeled off directly from the original template and fixed to copper plates with double-sided electrically conductive adhesive sheets. The negative replicas of living creatures were sputtered a gold film, with a thickness of about 100 nm, to enhance their conductivity before electroplating.

2.2.2. Electroplating

The composition of electroplating solution was shown in Table 2. Nickel board was used as anode. The pH value of the solution was 4.5–5.5. Plating time was 2 h and current density was 2 A/dm². Plating experiments were conducted at 39±2 °C.

After the electroplating, the cathode materials were cleaned with acetone to remove the double-sided electrically conductive adhesive sheets and the cellulose film. Then we got the positive replicas of the original living creature on nickel coatings, the thicknesses of which were about 100 μm and the horizontal size can approach to centimeters.

2.2.3. Surface chemical modification

The positive replicas of the original living creature were immersed in 1 mM anhydrous ethanol solutions of octadecanethiol and held for 24 h. Samples were taken from the coating solution and were put in an oven

Table 1
List of the biological originals examined in this study

Species	Locality	Habitat
Rice leaf	Hanzhong city, Shanxi province	Paddy field, hydrophily
Lotus leaf	Hanzhong city, Shanxi province	Pond, hydrophily
Snake skin	Lanzhou city, Gansu province	Terrestrial animal

Table 2
List of the composition of electroplating solution

Chemical	Concentration	Chemical	Concentration
Nickel sulfate hexahydrate	224 g/l	Nickel chloride hexahydrate	45 g/l
Boric acid	30 g/l	Odium dodecyl sulfate	0.11 g/l

maintained at 120 °C for 3 h. Then the samples were ultrasonicated in ethanol to remove the physical adsorbed molecules for 10 min, rinsed with ethanol and dried under a flow of N₂.

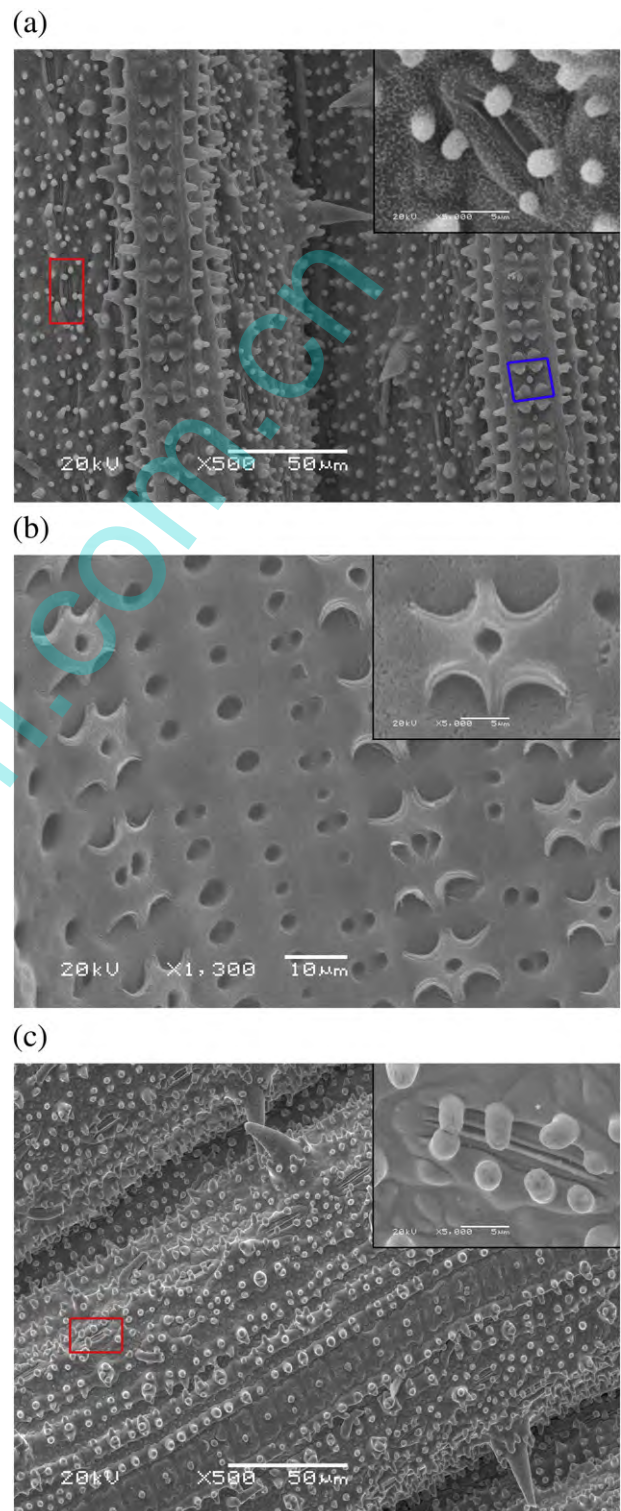


Fig. 2. (a) SEM images of rice leaf and the inset is the high magnification SEM image of the stomata, which is corresponding to the red area; (b) SEM images of negative replica of rice leaf and the inset is corresponding to the blue area as shown in a; (c) SEM images of positive replica of rice leaf and the inset is the high magnification SEM image of the stomata, which is corresponding to the red area. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

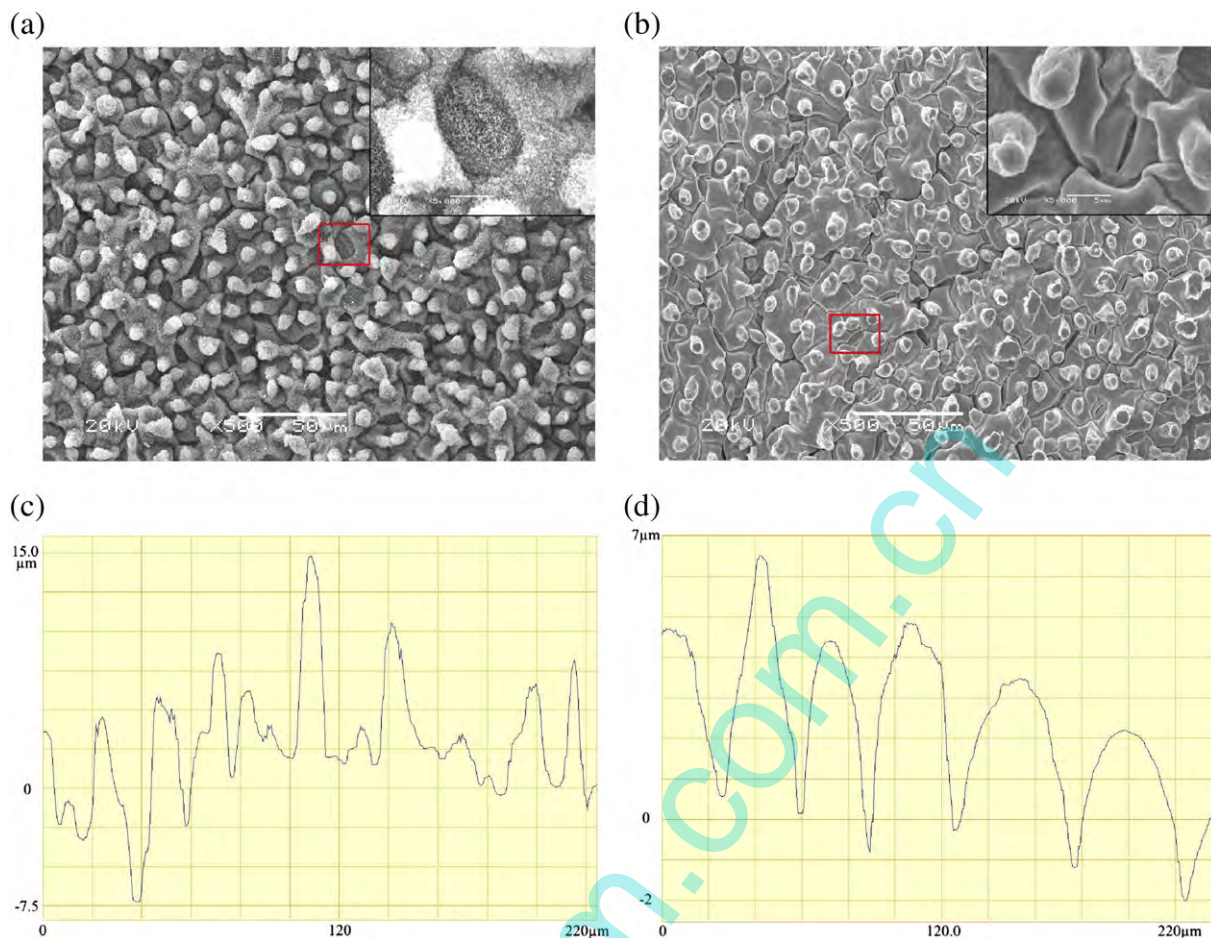


Fig. 3. Images of lotus leaf (left column) and its replicate (right column). (a) SEM images of lotus leaf and the inset is the high magnification SEM image of the stomata, which is corresponding to the red area; b) SEM images of the replica and the inset is corresponding to the red area; (c) 2-D optical profile of lotus leaf; (d) 2-D optical profile of its replica. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

2.3. Surface characterization

The morphologies of these samples of living creature surfaces and their replicas were observed on a JSM-5600LV scanning electron microscope (SEM) at 20 kV and a JSM-6701F field emission scanning electron microscope (FE-SEM) at 50 kV. The 3D morphologies and sizes of these samples were examined with a non-contact interferometric microscope (ADE Phase-Shift) and an atomic force microscope (AFM) (CSPM4000, Being Nano-Instruments Ltd., China), using contact mode. The sessile drop method was used for water contact angle measurements with a CA-A contact angle meter (Kyowa Scientific Company Ltd., Japan). Water droplets (about 4 μl) were dropped carefully onto the surfaces. The average contact angle value was determined by measuring at five different positions of each sample, and the measurement error was below 2°. All the experiments were performed at room temperature.

3. Results and discussion

Fig. 2 shows SEM images of the surface textures of rice leaf and its replica. Fig. 2a indicates a one-dimensional ordered structure on rice leaf surface, on which there are papillae and stomata. On the surface, the papillae with average diameter of about 2–5 μm are arranged and the distance between the adjacent papillae is about 5–10 μm in this dimension. Fig. 2b is the SEM images of textured cellulose film which is the negative replica of rice leaf. Fig. 2c is the SEM images of positive replica of rice leaf. It is inferred that the papillae and stomata are almost duplicated completely and the morphology and the size of the

surface micro textures of nickel coating agree with those of the rice leaf surface very well.

Fig. 3 is the SEM and non-contact interferometric microscope images of lotus leaf and its replica. Clearly, it can be seen that the surface of the lotus leaf is textured with 5–10 μm size protrusions and valleys uniformly, Fig. 3a. Fig. 3b is the SEM image of the replica of lotus leaf, the morphology of which also agrees with that of the lotus leaf surface very well. The distance between the peaks of the adjacent protrusions (P–P distance) of lotus leaf is about 10–20 μm (Fig. 3a) and the height between the peak of the protrusion and the valley (P–V height) is about 3–13 μm (Fig. 3c). Fig. 3b and d indicate that the surface micro textures size of the replica of lotus leaf is in accordance with that of the biological source. The P–P distance is about 10–20 μm (Fig. 3b) and the P–V height is about 3–6 μm (Fig. 3d).

Figs. 4 and 5 are the SEM and AFM images of snake skin and its replica. It can be clearly seen that there are squamose structures on the snake skin, the most obvious features of which are the highly-ordered arrays of micro-protrusions as shown in Fig. 4a. The snake scales are long and parallel between each other and show a periodic interval of about 1 μm , while the periodic intervals along the direction of these micro-protrusions is 2–3 μm . The scales of the replica also show a periodic interval of about 1 μm and the periodic intervals along the direction of these micro-protrusions is 2–3 μm (Fig. 4b). As shown in Figs. 4a and 5a, c and e, it can be clearly seen that the horizontal size of these micro-protrusions on the snake skin is about 300–1400 nm and the vertical size is about 30–300 nm. The horizontal size and the vertical size of these micro-protrusions on the replica are almost consistent with that of their biological originals (Figs. 4b and 5b, d and f).

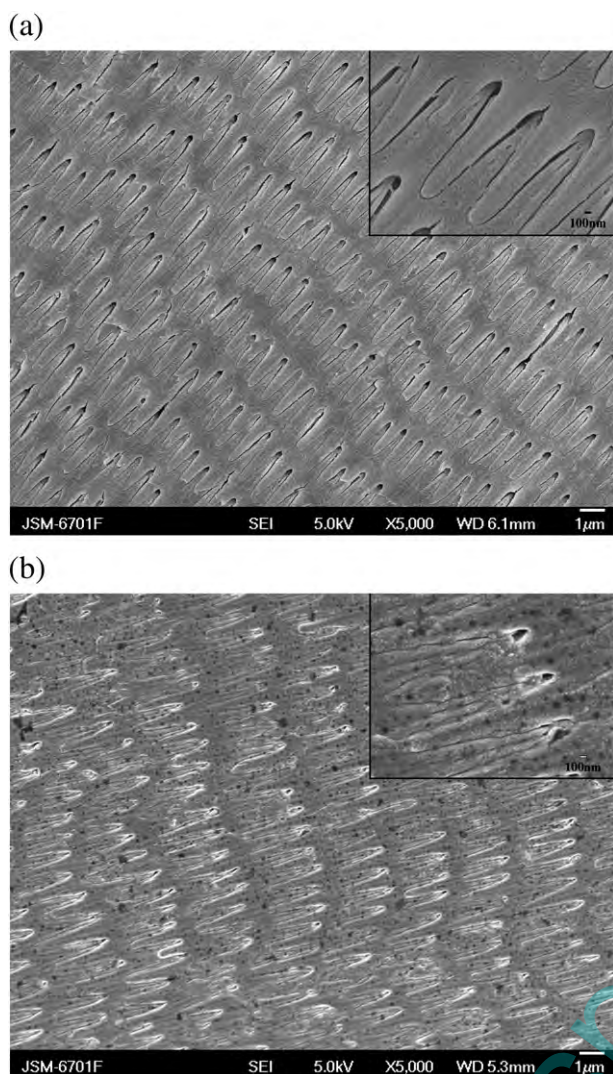


Fig. 4. SEM images of snake (left column) and its replica (right column).

The nickel surfaces with unique textures as duplicated from biological sources are intended to exhibit excellent physical and mechanical properties. The contact angle values of nickel surfaces with bio-mimicking micro textures of rice leaf and lotus leaf and their biological sources are shown in Table 3, and some typical optical microscope images are shown in Fig. 6. The contact angle value of smooth nickel is 65° . So the material itself is hydrophilic. It can be clearly seen that the contact angle values of these replicas are larger. The result is in accordance with the Cassie mode or Cassie and Baxter mode [18].

The wettability of a solid surface depends on both the surface energy and the surface structure. Lowering the surface energy enhances the hydrophobicity [19]. It can be seen that the contact angle values of these nickel samples become larger after coated with octadecanethiol films, all of which are larger than 120° (Table 3).

It can be found that the micro textures sizes of the replicas of lotus leaf, rice leaf and snake skin are in good accordance with that of their biological sources according to the SEM images, non-contact interferometric microscope images and AFM images. It is indicated that the surface microtextures of lotus leaf, rice leaf and snake skin were fully duplicated on nickel surfaces. According to this method, the improvement may be made in step two, changing the current density. One may start with a low value of electric current density at the initial stage and then to increase the value gradually to a constant one at the

end to get fine replication of intricate micro/nano combined structures [20]. However, it is under the thumb of the accuracy of step one. A feature size limitation that can be transferred using poly(dimethylsiloxane) (PDMS) according to a previous report is about 30 nm [16,21]. The nanostructures we have replicated from snake skin suggest that this technique can achieve features with resolution as low as hundreds of nanometers in width and tens of nanometers in depth on nickel coatings. Therefore, according to our knowledge, the surface coating technique does not affect on the duplication of biotexture and there is little we can do to improve the accuracy of the replication about this method. Contact angle measurements on the replicas surfaces of rice leaf and lotus leaf indicate that the wettability of nickel films was improved with hydrophobicity after duplicated with bio-mimicking micro textures, together with the chemical modification.

4. Conclusions

In this study, by combining duplication and electroplating method, we fully duplicated the surface microtextures of the lotus leaf, rice leaf and the snake skin on nickel coatings. The nanostructures replicated from the snake skin suggest that this technique can achieve features with resolution as low as hundreds of nanometers in width and tens of nanometers in depth on metal coatings. Together with the chemical modification, the wettability of the metal surfaces was improved with hydrophobicity after duplicated with bio-mimicking micro textures. It is expected that this method could be extended to duplicate other biological surface micro textures and artificial template surface textures on metal surface. These surfaces with special micro textures are of great importance for both fundamental research and practical applications such as hydrophobic, anti-adhesion.

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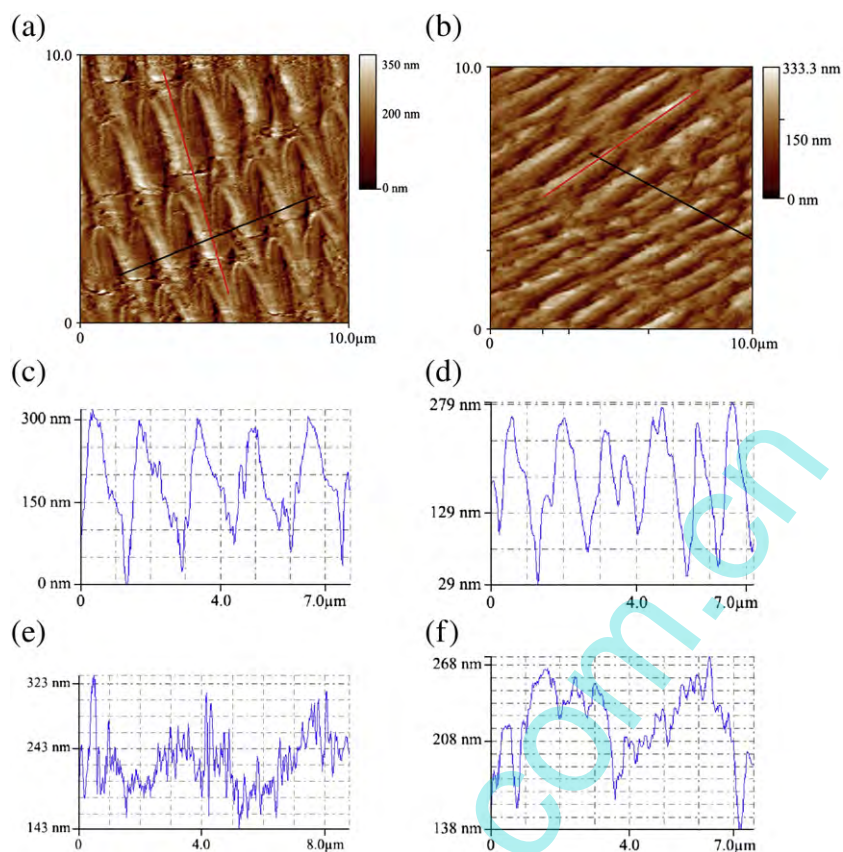


Fig. 5. (a) AFM image of snake skin ($10\ \mu\text{m} \times 10\ \mu\text{m} \times 350\ \text{nm}$); (b) AFM image of the replica ($10\ \mu\text{m} \times 10\ \mu\text{m} \times 333\ \text{nm}$); (c) Cross section map of the snake skin corresponding to the black line as shown in a; (d) Cross section map of the replica corresponding to the black line as shown in b; (e) Cross section map of the snake skin corresponding to the red line as shown in a; (f) Cross section map of the replica corresponding to the red line as shown in b. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 3

List of contact angle values of some samples examined in this study

Sample/contact angle (°)	Replicas	Replicas with thiols film	Original
Rice leaf	89	130	157
Lotus leaf	96	133	161
Smooth nickel coating	\	\	65



Fig. 6. Water droplet on nickel surfaces with octadecanethiol films with different microtextures. a) Replica of rice leaf. b) Replica of lotus leaf. c) Smooth nickel coating without octadecanethiol film.