

DROPLET MANIPULATION ON HIGH ADHESION SUPERHYDROPHOBIC SURFACES

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Abstract: Micro droplet handling is very important for micro and nano fluidic devices and an intelligent bio interface. Micro droplet transfer via high adhesion superhydrophobic surfaces has been reported in recent years. We demonstrated water droplet adhesion controllable superhydrophobic metal-polymer surfaces. Moreover we achieved micro droplet transfer between superhydrophobic surfaces by using different droplet adhesion properties. Water micro droplets were transferred from a low-adhesive superhydrophobic surface to a middle-adhesive superhydrophobic surface via a high-adhesive superhydrophobic surface without any mass loss. After transferred droplet possessed high water contact angle over 150 degrees. These moving processes were performed repeatedly. Droplet handlings on the adhesion superhydrophobic surfaces will be expected for fluidic bio devices with energy saving.

1 INTRODUCTION

Droplet manipulations mimicking behaviours on plant or insect surfaces such as lotus leaf effect are now interesting because simple surface structures provide amazing functionalities. Superhydrophobic surfaces which have the water contact angle larger than or near 150° are much paid attention, since its good water repellent property is used various applications in coating and electronic technologies (Zhang, 2008). Many researchers have been reported to obtain strong water repellent surface such as a hydrophobic fractal surface (Onda, 1996) and a nanopin array surface (Hosono, 2005). Recently several reports were published about water droplet adhesive superhydrophobic surfaces in mimicry of gecko's feet (Cho, 2008) and rose's petals (Feng, 2008). These adhesion properties were caused by van der Waals' force on large real surface area against small apparent surface area. It was difficult to control the adhesion forces because the adhesion was caused by the surface structures.

Herein we demonstrated that a superhydrophobic

metal-polymer (MP) surface with different droplet adhesion properties. The adhesive superhydrophobic surfaces were composed of hexagonally ordered polymer pillar arrays made from a self-organized honeycomb-patterned polystyrene film (Yabu, 2005) and metal micro domes deposited by nickel electroless plating (Ishii, 2008). The dome density was changed by catalyzation process for electroless plating.

Droplet manipulations such as a transfer were achieved by using the MP surface possessing different water adhesion force. Micro droplet handling by control of wettability is important for further understanding of superhydrophobic surfaces and application in microfluidic bio devices.

2 EXPERIMENTAL

2.1 Preparation Method

The superhydrophobic metal-polymer surface (MP surface) composed of hydrophobic polymer pillar

arrays and metal micro domes was fabricated by electroless plating for honeycomb-patterned polymer films and peeling process (See Figure 2).

According to our previous report (Karthaus, 2000), the honeycomb films were prepared by casting a chloroform solution of 10:1 mixture of polystyrene (PS; $M_w = 280\,000\text{ g mol}^{-1}$) and synthesized amphiphilic copolymer (CAP; $M_w = 270\,000\text{ g mol}^{-1}$) on a glass substrate with hexagonally condensed water droplet arrays. The honeycomb film cut to $1 \times 1\text{ cm}^2$ was soaked in a catalytic mixture solution of 6.0 ml containing 0.010 mol dm^{-3} poly(allylamine hydrochloride) (PAH; $M_w = 14\,000\text{ g mol}^{-1}$) and 0.010 mol dm^{-3} PdCl_2 at 25°C . The catalytic solution was gradually heated to 30°C , 45°C , and 60°C , respectively, and kept for 10 min under horizontal shaking at 10 rpm. Treated honeycomb films were immersed in a nickel plating bath (Ishii, 2006) at 25°C containing 0.10 mol dm^{-3} $\text{Ni}(\text{H}_2\text{PO}_2)_2 \cdot 6\text{H}_2\text{O}$, 0.19 mol dm^{-3} H_3BO_3 , 0.030 mol dm^{-3} CH_3COONa and $0.0098\text{ mol dm}^{-3}$ $(\text{NH}_4)_2\text{SO}_4$ without any rinse and drying. Then the plating bath including the treated honeycomb film was heated to 70°C and kept for 2h with no stirring. After rinsing and drying, a nickel layer was covered on the honeycomb film. After electroless plating, metallic faces of the nickel-covered honeycomb films were adhered on an acryl substrate by an epoxy resin. After heating at 70°C for 2h, a lower half layer of the nickel-covered honeycomb film was peeled off from the acryl substrate.

2.2 Physical Measurements

Surface structures of the MP surfaces were observed by a scanning electron microscope (SEM; Hitachi S-5200, Japan). A water contact angle (WCA) to 3 mg water droplet on a surface was measured by contact angle meter (Kyowa Interface Science DW-300, Japan). A sliding angle (SA) was measured to tilt the surfaces with a micro-droplet of 5 mg. Density of the metal dome which is defined by division of the

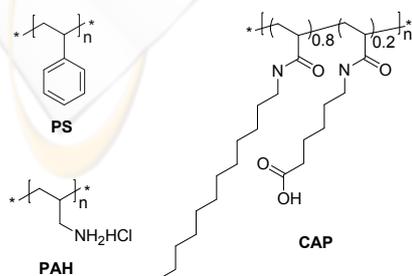


Figure 1: Chemical structures used in this report.

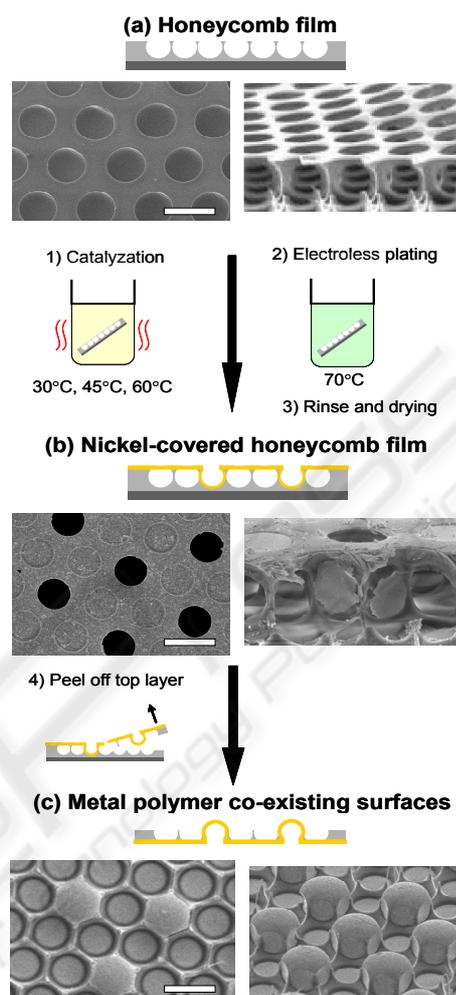


Figure 2: Schematic illustrations of a preparation method of MP surfaces. SEM images of top (left) and tilt (right) views of (a) a honeycomb film, (b) a nickel-covered honeycomb film fabricated by immersion in the catalytic mixture solution at 45°C , and (c) a MP surface fabricated by peeling off a top layer of the nickel-covered honeycomb film shown in Figure 2b. (Scale bar: $10\ \mu\text{m}$).

number of metal domes by the number of honeycomb holes was calculated by means of low-magnified SEM images.

2.3 Droplet Manipulations

Droplet manipulations such as droplet transfer were demonstrated by using the MP surfaces with different adhesion properties. Figure 3 shows a schematic illustration of water droplet transfer. The 5-mg water droplet was prepared on the MP surface fabricated by using the catalytic mixture solution at 30°C . Then the MP surface fabricated by using the catalytic mixture solution at 60°C was closed to the

water droplet from above and touched a little bit. The upper MP surface was pulled up slowly from the lower MP surface. Then the upper MP surface catching the water droplet was closed and touched to the other MP surface fabricated by using the catalytic mixture solution at 45°C. Finally the upper MP surface was pulled up again.

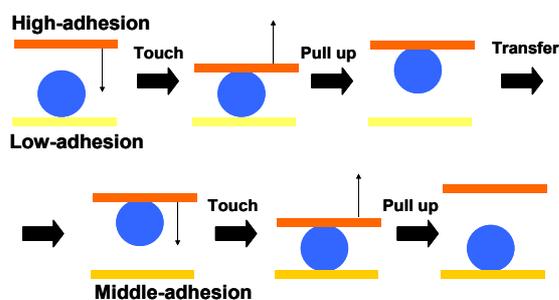


Figure 3: Schematic model of a micro-droplet transfer by using the MP surfaces with different adhesion properties.

3 RESULTS AND DISCUSSION

3.1 Superhydrophobic Metal–polymer Surface

SEM images of a honeycomb film, a nickel covered honeycomb film fabricated by immersion in the catalytic solution at 45°C, and a MP surface fabricated by immersion in the catalytic solution at 45°C are inserted in Figure 2. An average diameter of a honeycomb hole was about 7 μm . A nickel-covered honeycomb film possessing some pores, which were distributed in the honeycomb holes, were obtained after electroless plating including immersion in the catalytic mixture solution. A tilted SEM image shown in a right column of Figure 2b clears that the pores were openings of micro mono vessels. When the temperature of the catalytic mixture solution was changed low (30°C) and high (60°C), the number of the vessels was decreasing and increasing, respectively. In general, wettability of all surfaces including the PS honeycomb film is influenced by a solution temperature, because the surface tension of all solutions is represented by function of the solution temperature. This result indicates that the number of the vessels was dependent on wettability of the catalytic mixture solution to the honeycomb film. In the case of immersion in the catalytic solution at low temperature, wettability of the honeycomb film was low, so that the number of the vessels in the nickel-covered honeycomb film was a few. On the other

hand, in the case of immersion in the one at high temperature, the number of the vessels was much because of good wettability to the honeycomb film. The number of the vessels of the nickel-covered honeycomb film was easily changed by the catalytic mixture solution temperature.

The MP surfaces after peeling off the top half of the nickel-covered honeycomb film were composed of superhydrophobic PS pillar arrays and hydrophilic nickel micro-domes as shown in Figure 2c. The nickel micro-dome was reverse side of the micro mono vessel in the nickel-covered honeycomb film. This result anticipates that density of the nickel dome to the honeycomb hole is controlled indirectly by temperature of the catalytic mixture solution. Figure 4 shows SEM images of the MP surfaces having different nickel dome density. The nickel dome density of the MP surface prepared by immersion in the catalytic mixture solution at 30°C, 45°C, and 60°C was about 3%, 15%, and 25%, respectively. The surface properties such as surface wettability and droplet adhesion properties were controlled easily, because hydrophilic-hydrophobic balance was varied by difference of the nickel dome density (See Table 1).

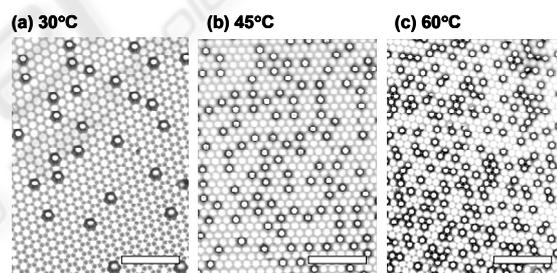


Figure 4: SEM images of the superhydrophobic metal–polymer surfaces fabricated by using the catalytic mixture solution at (a) 30°C, (b) 45°C, and (c) 60°C. The black dots indicate the nickel domes. (Scale bar: 100 μm).

Table 1: Surface properties of the MP surfaces.

Sample	Density	WCA	SA	Adhesion
30°C	3%	155°	<5°	Low
45°C	15%	150°	30°	Middle
60°C	25%	145°	N/A	High

3.2 Micro-droplet Transfer

The water droplet adhesion properties were measured by water contact angles (WCAs) and sliding angles (SAs). The MP surface with nickel dome density of 3% possessed a WCA of 155° and a SA of less than 5°, and was abbreviated as a low-adhesion MP surface. The MP surface with dome

density of 15% possessed a WCA of 150° and a SA of 30° (a middle-adhesion MP surface). The MP surface with dome density of 25% possessed a WCA of 145° and a not measured SA because the droplet adhered the surface when turned upside down (a high-adhesion MP surface). As the dome density was increasing, the WCA was decreasing and the SA was increasing, which means that the hydrophilic nickel domes gave the adhesion behaviors. This result made clear that the adhesion property was controlled by the quantity of the nickel dome easily changed by the catalytic mixture solution temperature for electroless plating.

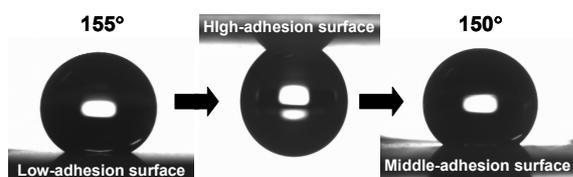


Figure 5: Droplet transfer of 5.0-mg water droplet from the low-adhesion MP surface to the middle-adhesion MP surface via the high-adhesion MP surface.

Water micro droplet transfer was attempted by using the MP surfaces with different adhesion properties as shown in Figure 5. A water droplet of 5 mg on the low-adhesion MP surface was carried with the high-adhesion MP surface by means of pulling off after slight contact from above. However, in the case of the middle-adhesion MP surface, a water droplet did not remove from the low-adhesion MP surface. On the other hand, the high-adhesion MP surface was not caught a water droplet on the middle-adhesion MP surface from above. These results suggest that the adhesion force of the high-adhesion MP surface was stronger than that of the low-adhesion MP surface plus gravity on the water droplet, and weaker than that of the middle-adhesion MP surface plus gravity on the water droplet. By using this difference, the water droplet was transferred from the low-adhesion MP surface to the middle-adhesion MP surface via the high-adhesion MP surface. After transfer, the water droplet on the middle-adhesion MP surface was sliding when the surface was tilted at about 30° . A droplet transfer reported in the past is from a superhydrophobic surface to a hydrophilic surface via an adhesion superhydrophobic surface (Cho, 2008). Therefore, after transfer, the water droplet is spreading, and is unable to be handled. The novel transfer method in this report remains a droplet shape after transfer, so that the droplet was handily manipulated again. These behaviors were useful to microfluidic devices,

bio interfaces, and micro-reactors.

4 CONCLUSIONS

We could fabricate water repellency and adhesion properties of superhydrophobic metal-polymer surfaces by electroless plating for self-organized honeycomb films including immersion in a catalytic Pd salt and a cationic polymer mixture solution. It was found that a water contact angle and a water droplet adhesion property were changed by metal dome density which was easily controlled by the temperature of the catalytic mixture solution. Droplet transfer between superhydrophobic surfaces was demonstrated by means of using the metal-polymer surfaces with different adhesion properties.

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