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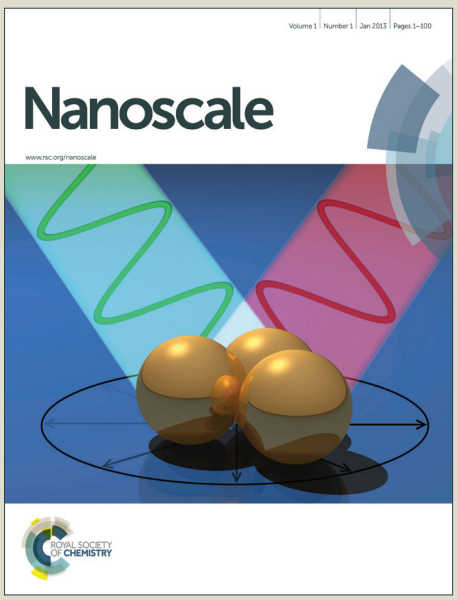

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Adhesion switch on the Gecko-foot inspired smart nanocupule surface

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Abstract

Gecko-foot inspired nanocupule surface was prepared by AAO template covering method that was composed of poly(N-isopropylacrylamide) and polystyrene blend. Both superhydrophobicity and high adhesion force were exhibited on the PNIPAm/PS film at room temperature. Moreover by controlling the temperature, the wettability of the film could be switched between 138.1±5.5^{o} and 150.6±1.5^{o}, and the adhesion force could also be tuned accurately by temperature correspondingly. This reversibility in both wettability and adhesion force would be used to construct smart device for water droplet selection finely. The proof-of-concept was demonstrated on the selected catching of the precise weight controlled water droplet at different temperature. This work could help us to design new type device for blood bioanalysis or lossless drug transportation.

The researches on the adhesion of solid-liquid interface have been developed in decades due to their great theoretical and practical instructional signification in industry and biological science, such as the construction of micro-fluidic devices, new type adhesion tape, coating of auto windshield and ocean ship, artificial vessel, and so on [1-17]. Learning from nature offers us an optimized way to fabricate such surfaces with special adhered property [18-21]. The most famous example is gecko feet that exhibits remarkable adhesion and friction force, and allows it walking on the vertical walls or ceilings randomly [22-25]. This special ability can be attributed to the weak van der Waals forces between solid surface and hundreds of spatulae at the end of each seta on gecko feet [26]. Many research works have been developed to fabricate gecko-foot inspired surfaces with high adhesion force [27-29]. Prof. Geim and his co-workers[30] prepared a flexible plastic pillars array surface using microfabrication technique, which exhibited self-cleaning and re-attachable dry adhered properties. However the durability and mass production of the prepared surface are still needed to be resolved. To improve the practicability and inspired by gecko foot, Prof. Metin Sitti and his co-workers [22] prepared tilted micropillar array surface for pick-and-place micromanipulation. It could be easily attached or detached on a part and exhibited well repeatability. They also found that the pick-to-release adhesion ratio on the micropillar surface with flat tip conformation and shear displacement control was higher than the one with round tip and vertical displacement control, respectively. The prepared polymer micropillars surface could be effective on most materials and in different environments, such as air, vacuum, and liquid. Using Anodic Aluminum Oxide (AAO) template method, Prof. Lei Jiang and his co-workers [31] reported a special superhydrophobic polystyrene (PS) surface with high adhesion force compared to the traditional low adhered superhydrophobic surface. Their results showed that the prepared surface was composed of large amount of arrayed nanotubes. The hydrophobic property of PS and the tubular structures in nano-scale resulted in the superhydrophobicity of the prepared surface; on the other hand, the enhancement of van der Waal forces between the densely packed PS nanotubular surface and water droplet leaded to the

high adhesion force of the prepared surface. This high adhesion force on the superhydrophobic surface is benefit to precise location of the liquid droplet, which is important to construct bioanalyzed device.

Consequently the controlling of surface adhesion becomes more necessary, the strategy for constructing such surfaces is usually considered from two aspects: surface chemistry and rough structures [13-14, 32]. Prof. Jiang and his coworkers [33] fabricated a superhydrophobic substrate with thermally reversible adhesion property using side-chain liquid crystal polymer. The pinned and rolled states of water droplet on the superhydrophobic substrate could be attributed to the precise combination of the rough structures and the interfacial chemical compositions. Other stimuli-responsive materials can also be introduced to broaden the fabrication of such surfaces. Prof. Feng Zhou and his co-workers [34] grafted poly(N-isopropylacrylamide) (PNIPAm) and poly(dimethylamino) ethyl methacrylate on the irregular anodized alumina substrates respectively, the prepared surfaces exhibited well adhesion switch behavior for water droplets with different pH values and salt solution triggered by temperature, pH and electrolyte. However the responsive adhesion researches basing on the gecko-foot structured inspired surfaces are still scarce [35], in this contribution, inspired by the special structures of gecko feet, superhydrophobic PS/PNIPAm surface with nanocupule structures was prepared by AAO template covering method. The high adhesion force was exhibited on the prepared surface; moreover the surface adhesion force could also be controlled accurately by temperature. The reversibility of both wettability and adhesion force were showed on the prepared surface, which could be used to construct smart device for liquid selection.

The typical experimental process could be exhibited in Figure 1. In brief, 33 wt% mixture solution of PS (Mw ~ 200000, BASF Corporation, Germany) and PNIPAm (Sigma-Aldrich Corporation) (99:1, w/w) in THF was added dropwise onto a clean glass slide, and then the AAO template (pore diameter ~ 200nm, thickness ~ 60μm, Watman Int. Ltd, England) was covered on it. The polymer solution would be solidified in air for 12 h. Finally the AAO template was removed by being immersed

in 4 M NaOH solution, the prepared polymer surface was fully washed by deionized water and dried in a nitrogen flow. The structure of the prepared surface was showed in Figure 2 A, numerous circle-liked structures in nano-scale were observed in a density of about 1.6×10^7 cells/mm^2. The micro-scale cracks on the surface could also be found that was supposed to be generated during the solidified process. The magnified SEM image (Figure 2 B) showed each circle-liked structure exhibited a typical cupule conformation that the diameter and wall thickness of each cupule were around 284nm and 31nm. The depth of each one was about 38 nm measured by AFM as showed in Figure 2 E. In Figure 2 C and D the lateral images showed the prepared surface was composed of nanofibrils that were perpendicular on the substrate. Meanwhile blend PNIPAm/PS film with different weight blend rates, such as 1:1, 1:2, 1:10, 1:99, 1:500, 1:800 and 1:1000, were prepared to optimize the film formation. As shown in Figure S1 in supporting information, the surfaces of the prepared films in weight rates of 1:1, 1:2 and 1:10 were almost smooth; and the ones in weight rates of 1:500, 1:800 and 1:1000 exhibited many defects and poor film formation. Therefore it could be concluded that the 1:99 blend rate of PNIPAm and PS in our experiment was the optimized condition for constructing the film.

The wettability was measured by Contact Angle System OCA20 (Dataphysics Inc. Germany) with temperature controlling system (Julabo F25, Germany) and 5μl water droplet was used in the CA measurement. This special structure made the prepared film show high hydrophobic property with contact angle (CA) ~138.1±5.5^o at room temperature. Comparing to CA on the pure PS nanotube (CA~162.0±0.5^o) fabricated in a similar procedure [31], CA on this blend PS/PNIPAm surface was lower than pure one because the hydrophilic -NH2 and -C=O groups in the PNIPAm polymer chains were introduced in the blend polymer system; On the other hand the high hydrophobic property was maintained due to the large content of polystyrene in the blend film. When the temperature was increased to 40^{o}C, the CA on the prepared surface was changed to 150.6±1.5^o. This CA change could be attributed to the hydrogen bonding transition from intermolecular to intramolecular in the PNIPAm chains when the temperature was high than its LCST~32^{o}C [36-39]. Comparing to

the polymer film at room temperature the hydrophilic -NH_2 and -C=O groups in the PNIPAm chains tended to contribute the intramolecular hydrogen bonding that made them difficultly contact water molecule on the surface. Moreover the 5µl water drop could not move even when the substrate was placed vertically or inversely at both room temperature and 40^{o}C. Moreover the contact angle changes of the prepared film with blend rates of 1:500, 1:800 and 1:1000 were also investigated as shown in table 1. Comparing to them, the maximum change was exhibited on the film with blend rate of 1:99, which meant that the maximum adhesion force could be found in this condition. The wettability on the prepared nanocupule film was also exhibited reversible property as showed in Figure 2 B due to the introduction of PNIPAm.

Using the high sensitivity micro-electrodynamic balance system (Data-Physics DCAT 11, Germany) the Adhesion force between water drop and the prepared blend PS/PNIPAm nanocupule film with temperature changes was measured. In detailed a 3µl droplet that kept spherical shape was fixed on the thin metal loop which was hung on the microbalance. The nanocupule film was fixed on the microbalance. When the microbalance was closed to the droplet till contacted, the adhesion force was zero showed by the red dot line in Figure 3 C I; once the nanocupule film contacted to the water droplet, it would start to move away automatically. The adhesion force increased gradually till the droplet leave off the surface as the blue dot line showed in Figure 3 C II. The maximum of the adhesion force (about 85µN) was appeared when the droplet detached from the prepared film, which meant that the water drop weighted less than 8.5mg could be caught up. When the droplet broke away from the nanocupule film, the adhesion force became zero again as showed in Figure 3 C III. The adhesion force at 40^{o}C was measured in the same procedure that was showed by the pink and green dot lines in Figure 3 C. The maximal adhesion force (about 65µN) was less than the one at room temperature which meant the droplet weight caught up should be lower than 6.5mg. The 20µN force difference of the adhesion force between the droplet and the nanocupule film at room temperature and 40^{o}C will allow us to design a new type smart device that

can be used to select liquid droplet subtly on the superhydrophobic substrate with low adhesion force. Example was shown in Figure 4, at room temperature an 8mg water droplet was placed on a superhydrophobic substrate, it would be caught up after the prepared nanocupule film contacted it and left up; when the nanocupule film was heated to 40^{o}C and contacted it and left up, we found that the water droplet could not be caught up (Videos were showed in supporting information).

According to the report by Prof. Lei Jiang [31], the adhesion force between water droplet and arrayed nanotube surface is determined by the amount of the nanotubes and the value of the binding force. On one hand, due to the high hydrophobic property of the PS/PNIPAm nanocupule surface the area of water droplet contacting with it was relative small; on the other hand, the effect of the roughness of the prepared surface in microscale and the nano-structured single cupule enhanced the practical contact area between the water droplet and the nanocupule surface, which would bring the high adhesion force. Typically the adhesion force between water droplet and nanocupule film includes capillary forces, Van der Waals' force and hydrogen bonding force[26, 40-41]. When the water droplet contacted with the nanocupule surface, capillary bridge between the water and surface would generate and increase with the increasing of the surface roughness. The special arrayed nanocupule structures might result in the high adhesion force of the prepared nanocupule surface. Moreover the introduction of PNIPAm endowed the changable adhesion force of the nanocupule surface triggered by temperature. The PNIPAm chains in coiled conformation were loose at room temperature, the hydrophilic -NH_2 and -C=O groups easily contacted with water molecules that intermolecular hydrogen bonding occupied mainly contribution. Comparing to the maximum adhesion force (60 μN) of the pure PS nanotube film[31], the adhesion force increased to 85μN. When the nanocupule film was heated to 40^{o}C, the phase inversion of PNIPAm would occurred and the hydrophilic -NH_2 and -C=O groups on the PNIPAm chains would form intramolecular hydrogen bonding, which made them contact with water molecules difficultly. The hydrogen bonding would become weaker resulted in the decreasing of the adhesion force on the nanocupule film.

In this contribution gecko-foot inspired nanocupule film composed of the blend of PS and PNIPAm was prepared using AAO template covering method. High hydrophobic property and high adhesion force were realized on the prepared film, moreover they could also be controlled by temperature due to the responsive polymer PNIPAm introduction. Adhesion force on the film could be regulated from 85 μN to 65 μN that allowed us to design smart device for water droplet selection. This work could also inspire us to design new type device for blood bioanalysis or lossless drug transportation.

Acknowledgements

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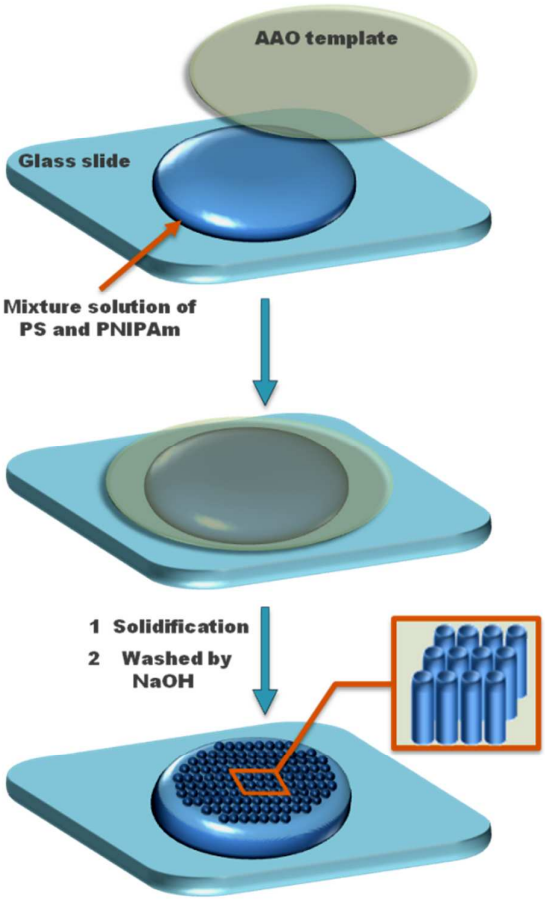

Figure 1 A typical process on preparing the bioinspired responsive nanocupule surface.

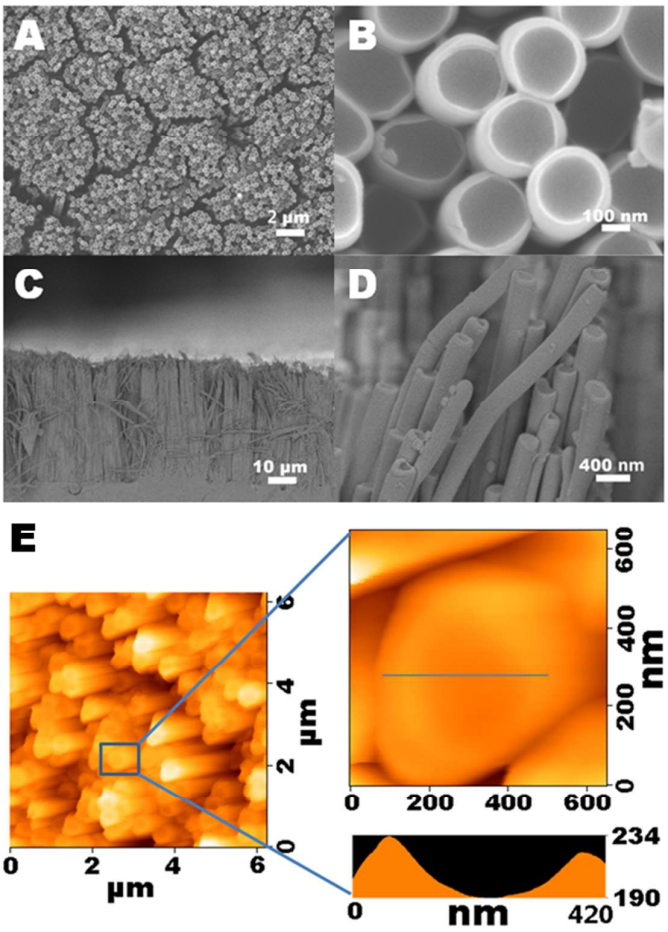

Figure 2 A) and C) the SEM images of the prepared nanocupule surface in top and profile view, respectively; B) and D) the magnified ones correspondingly; E) the AFM image of the prepared surface, which showed the diameter and depth of each cupules were 284nm and 38nm individually.

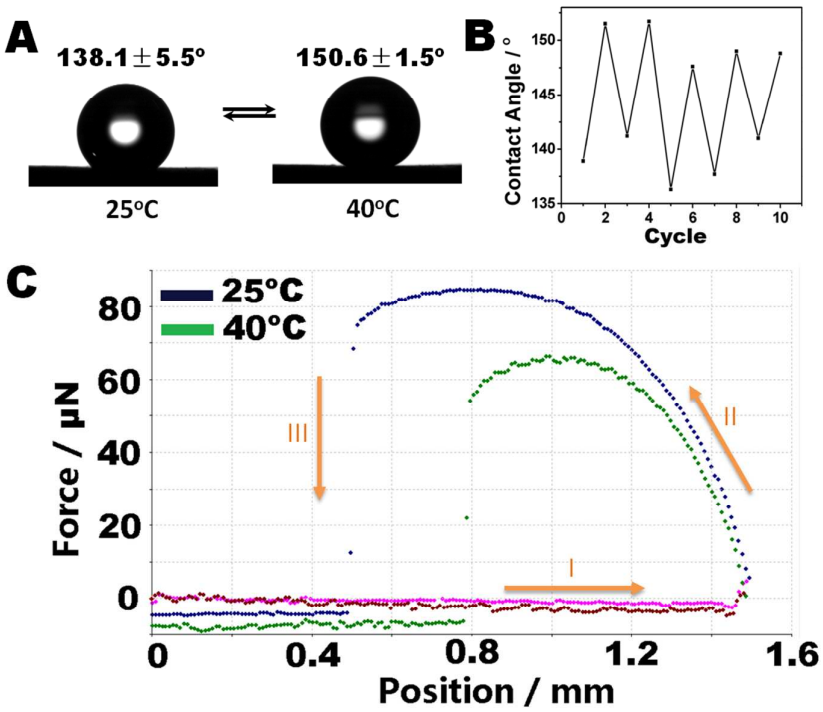

Figure 3 A) contact angle changes of the nanocupule surface at 25°C and 40°C; B) the repeatability of the fabricated film; C) the adhesion force of the prepared film at 25°C and 40°C, on which the maximum values were 85μN and 65μN, correspondingly.

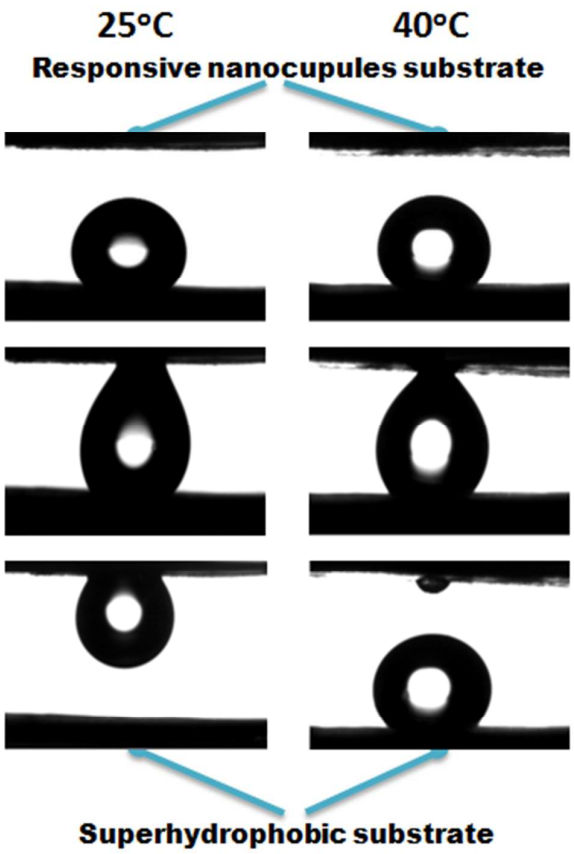

Figure 4 A application of the responsive nanocupule surface on the water selection. 8mg water droplet was placed on a superhydrophobic substrate, the droplet could be caught up at 25 ^{o}C; when the temperature was increased to 40 ^{o}C, it could not be caught up.

PNIPAm:PS(w/w)	1:99	1:500	1:800	1:1000
22.4ºC	138.1±5.5º	131.1±1.8º	142.8±2.6º	141.8±2.4º
40.2ºC	150.6±1.5º	138.1±3.4º	147.0±1.9º	144.6±2.8º

Table 1 The contact angle changes of the prepared PNIPAm/PS film.