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Article

Chemical Instability Induced Wettability Patterns on Superhydrophobic Surfaces

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Abstract: Chemical instability of liquid-repellent surfaces is one of the nontrivial hurdles that hinders their real-world applications. Although much efforts have been made to prepare chemically durable liquid-repellent surfaces, few attentions have been paid to exploit the instability for versatile use. Herein, we propose to create hydrophilic patterns on superhydrophobic surface by taking advantage of its chemical instability induced by acid solution treatment. Superhydrophobic $\text{Cu}(\text{OH})_2$ nanoneedles covered Cu plate that shows poor stability towards HCl solution (1.0 M) is taken as an example. Results show that 2.5 min of HCl solution exposure leads to the etching of $\text{Cu}(\text{OH})_2$ nanoneedles and partial removal of self-assembled fluoroalkyl silane molecular layer, resulting in the wettability transition from superhydrophobicity to hydrophilicity, and the water contact angle decreases from $\sim 160^\circ$ to $\sim 30^\circ$. Hydrophilic dimples with different diameters are then created on the superhydrophobic surfaces by depositing HCl droplets with different volumes. Afterwards, the hydrophilic dimple patterned superhydrophobic surfaces are used for water droplet manipulations, including controlled transfer, merging and nanoliter droplets deposition. The results thereby verify the feasibility of creating wettability patterns on superhydrophobic surfaces by using their chemical instability towards corrosive solutions, which broadens the fabrication methods and applications of functional liquid-repellent surfaces.

Keywords: superhydrophobic surface; chemical instability; wettability pattern; droplet manipulation

1. Introduction

Bio-mimic superhydrophobic surfaces have drawn rapidly increasing research interests because of their great significance for versatile applications such as self-cleaning [1-3], chemical detection and sensors [4-7], liquid droplet manipulation [8, 9], icephobicity [10-14], immiscible liquids separation [15-17], enhanced heat transfer [18-20], and anti-corrosion [21-23]. However, most superhydrophobic surfaces suffer from chemical instability in harsh conditions like highly concentrated acid/alkaline/salty solution immersion, organic solvent invasion, thermal treatment, UV irradiation and active species exposure [24-26]. The chemical instability usually results in the loss of superhydrophobicity with varying degrees due to interfacial chemical processes induced surface chemistry and/or morphology change, which could obviously shorten the lifespan of superhydrophobic surfaces and thus be commonly considered as one of the major limitations for their real-world applications. As a result, great efforts have been made to fabricate chemically durable superhydrophobic surface, and much progress has been achieved in recent years [25, 26].

Although chemically stable superhydrophobic surfaces are crucial in some cases, such as chemical shielding and anti-corrosion [27-29], external stimuluses triggered chemical instabilities are sometimes more desired [26, 30, 31]. For example, Ghosh et al. [32] took the advantage of chemical instability of superhydrophobic TiO_2 coatings upon UV exposure to prepare superhydrophobic/superhydrophilic patterns which could be employed to realize high-rate, pumpless liquids transport on open substrates. Xu et al. [33] reported a selective UV irradiation induced superhydrophilic patterns on octadecyltrichlorosilane-modified superhydrophobic silica coating, and demonstrated its potential application towards microgravity biosensing. Plasma contains amount of active species, such as high-energy electrons, metastable particles, etc., so it can

always initiate surface chemistry and/or texture changes and thus causes instability (hydrophilization) of superhydrophobic surfaces [30, 31, 34]. Huang et al. [35] used the chemical instability of superhydrophobic surface towards plasma treatment to fabricate superhydrophilic patterns on superhydrophobic surface, which was further used for underwater spontaneous pumpless transportation of organic liquids. Liu et al. [36] fabricated hydrophilic patterns on superhydrophobic surface by micro-plasma jet treatment and reported its versatile ability in water adhesion controlling. Additionally, Liu et al. [37] showed that a superhydrophobic Cu mesh could be completely converted to be superhydrophilic after being immersed in tetrahydrofuran for 5 min, which facilitated the subsequent reversible oil/water separation. Therefore, chemical instability of superhydrophobic surfaces towards external stimuluses is not always a drawback for their applications, making ingenious use of the instability can provide additional possibilities for constructing special functional surfaces [26].

Immersion in acid/alkaline/salty solution triggered chemical corrosion could sometimes change the surface morphology and/or surface chemistry of superhydrophobic surfaces, thereby changing their surface wettability (i.e., chemical instability) [38-41]. Although some works involving pH-responsive switchable super-wettability have been reported [39-41], they were limited to smart surface fabrication or reversible oil/water separation, indicating that the full exploitation of their chemical instability for beneficial usage was largely insufficient. In this paper, we took superhydrophobic $\text{Cu}(\text{OH})_2$ nanorods covered Cu surface, which was unstable towards HCl solution exposure, as an example to demonstrate the feasibility of creating wettability patterns by using this chemical instability. HCl etching (1.0 M, 2.5 min) turned the superhydrophobic surface into hydrophilic one, and the related mechanism was studied. Hydrophilic-dimples patterned superhydrophobic surfaces were then prepared and employed to realize water droplet manipulation, such as transfer, merging, and deposition.

2. Materials and Methods

Copper plates ($3 \times 4 \times 0.1 \text{ cm}^3$) were bought from Huaru copper co. LTD (Guangzhou, China). Analytical-grade HCl, NaOH and $(\text{NH}_4)_2\text{S}_2\text{O}_8$ were supplied by Tianjin Kemiou Chemical Reagent Co., Ltd (China). 1H,1H,2H,2H-Perfluorodecyltriethoxysilane (fluoroalkyl silane, FAS) with 97% purity was purchased from Alfa Aesar.

Superhydrophobic surface on copper substrate was fabricated according to a previously reported method [42]. Briefly, copper plate was firstly polished mechanically using 1000# and 2000# abrasive paper and then ultrasonically cleaned in sequence in HCl (0.1 M), alcohol and deionized water. Then, the cleaned copper plate was placed into the aqueous solution containing NaOH (2.5 M) and $(\text{NH}_4)_2\text{S}_2\text{O}_8$ (0.1 M) for 5 min to construct micro/nano structures. Then the substrate was taken out and washed with abundant ultrapure water. After drying with blowing air, the sample was immersed into 1wt% ethanol solution of FAS for 1 hour to lower the surface energy. Then the plate was washed with ethanol and dried at 90°C . Finally, the copper surface was imparted with superhydrophobicity.

The instability of the obtained superhydrophobic Cu surface was triggered by HCl (1.0 M) solution, and the chemical instability was characterized by water contact angles (WCAs) of the surface after being exposed to HCl solution for different times (0–5 min). Hydrophilic dimple patterns were fabricated by exposing the as-prepared superhydrophobic Cu surfaces to HCl (1.0 M) droplets with different volumes for 2.5 min.

WCA of the sample surfaces were measured by an optical contact angle meter (AST-VCN Optima, USA) at room temperature. The 3D morphology and corresponding cross-sectional profile were recorded by a confocal laser scanning microscope (CLSM, Carl Zeiss LSM 700, Germany). The surface morphologies and corresponding chemical compositions of the samples were observed by scanning electron microscope (SEM, SUPRA 55 SAPHIRE, Germany) equipped with an energy dispersive spectroscopy (EDS) at an accelerating voltage of 15 kV. The surface chemistries were also characterized by X-ray photoelectron spectroscopy (XPS, Thermo ESCALAB 250Xi, American) with a monochromatic $\text{Al K}\alpha$ (1486.6 eV) X-ray beam, and the C 1s peak at 284.8 eV was used as reference.

The spot size was 400 μm , and the pass energy and energy step size of the full spectrum scan were respectively 100 eV and 1.0 eV, while those of the C 1s high-resolution spectrum were 50.0 eV and 0.1 eV, respectively. X-ray diffractometer (XRD, Bruker AXS D8 Discover, Germany) with an X-ray source of Cu K α ($\lambda = 1.5418 \text{ \AA}$) was used to observe the crystal phase structure of the samples, the scanning rate was 2 $^\circ/\text{min}$.

3. Results and discussion

The as-prepared superhydrophobic Cu surface possessed excellent water repellence with a water contact angle (WCA) of 160 $^\circ$, and the solid-liquid interfacial adhesion was negligible when it was pressed to make contact with a water droplet (5.0 μL), as shown in Figure 1(a). By contrast, as illustrated in Figure 1(b), if the superhydrophobic substrate was moved up and contacted with a HCl droplet (1.0 M, 5.0 μL), obvious interfacial adhesion could be observed when the substrate was moved down, and the HCl droplet was even dragged down from the liquid feeding outlet and then tightly adhered on the surface, demonstrating locally damaged water repellence of the surface upon HCl droplet exposure. The HCl solution induced chemical instability of the superhydrophobic surface was further studied by measuring the WCA of samples that were immersed in HCl for different durations. Figure 1(c) shows the influence of immersion time on the WCA of the superhydrophobic surface. It could be seen that the WCA decreased with the immersing time in HCl, and the surface lost its superhydrophobicity within several seconds chemical etching. Finally, the WCA stabilized at $\sim 30^\circ$ after immersing for 150 s, and the surface turned its color to be bronze, and the deposited water droplet spread rather than beaded up on the etched surface, as depicted in Figure 1(d), indicating complete loss of the water repellence by exposing the surface to corrosive HCl solution.

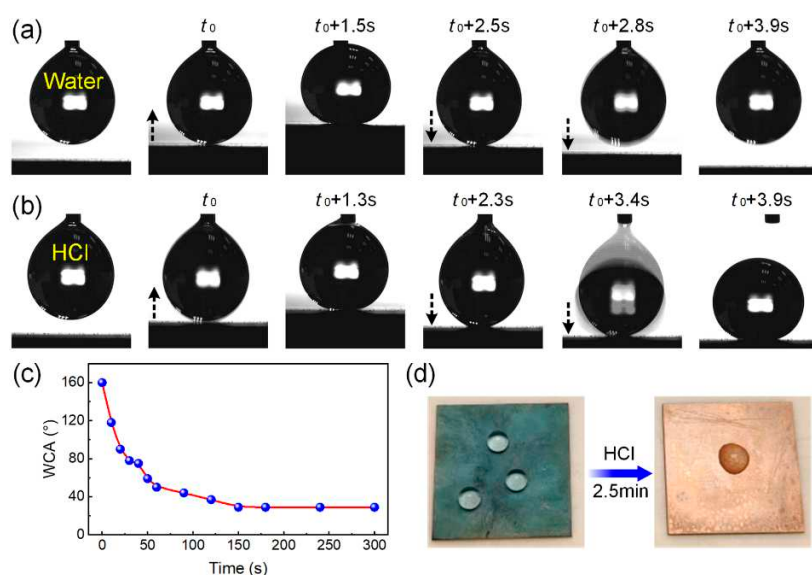


Figure 1. Chemical instability of the superhydrophobic Cu substrate towards HCl solution: image sequences showing the dynamic processes of (a) a water droplet (5.0 μL) and (b) a HCl droplet (1.0 M, 5.0 μL) contacts with and detaches from the superhydrophobic surfaces; (c) the influence of immersion time in HCl solution on the WCA of the superhydrophobic surface; (d) digital image of water droplets on the original and HCl etched (for 2.5 min) superhydrophobic surface.

Taking advantage of the HCl-induced chemical instability of the superhydrophobic surfaces, hydrophilic patterns can be constructed on the surfaces. Here, we propose to create hydrophilic dimple patterns on superhydrophobic Cu surfaces by depositing HCl droplets on the surface to trigger localized chemical etching, as illustrated in Figure 2(a). Figures 2(b)-(f) show the surface morphology characterizations of the dimple pattern prepared by using a HCl droplet with volume of 0.2 μL . As depicted in Figures 2(b) and (c), the CSLM image and the corresponding cross-sectional profile clearly showed that a circular dimple with diameter of $\sim 390 \mu\text{m}$ and depth of $\sim 3 \mu\text{m}$ was

obtained on the superhydrophobic surface. It is widely known that when a water droplet is deposited on a superhydrophobic surface, a circular liquid-solid-vapor composite contacting interface can be built. Here the placed HCl droplet triggered chemical corrosion occurred at the HCl-Cu(OH)₂ contact area, and finally created a dimple pattern with round shape. Figures 2(d)-(f) show the SEM images of the hydrophilic dimple-patterned superhydrophobic surface with different magnifications. It could be clearly seen that the as-prepared superhydrophobic Cu surface (i.e., the unetched area in Figure 2(d)) was covered with numerous nanorods and some flower-like microstructures, as could be observed in Figure 2(e). By contrast, after being etched by HCl droplet, the nanorods and flower-like microstructures were obviously destroyed and replaced by closely packed irregular particles with size in a range from hundreds of nanometers to several micrometers (Figure 2(f)). Zooming into these irregular particles revealed that they were decorated with nano-scale granules.

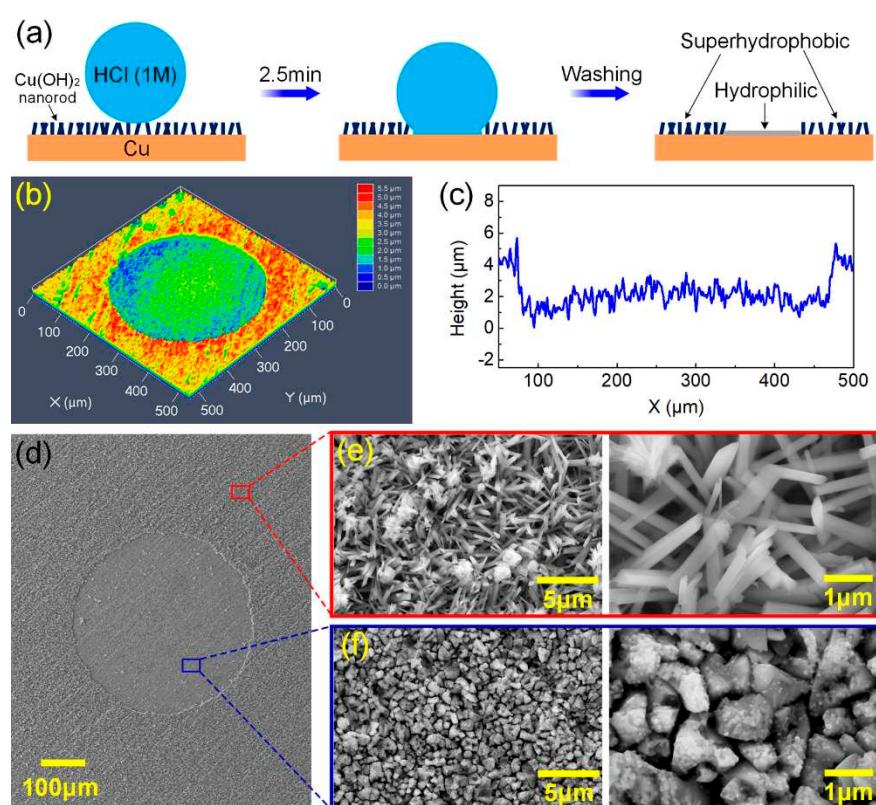


Figure 2. Surface morphologies of the HCl droplet (0.2 μ L) etched superhydrophobic surface: (a) the CLSM image and (b) the corresponding cross-sectional profile; (c)-(e) SEM images with different magnifications.

Figure 3. shows the surface chemistries of the original and HCl etched areas on superhydrophobic Cu surface. Figures 3(a) and (b) respectively depicted the EDS and XPS spectra of the two areas. The relative atomic percent of element F was measured to be 20.8% at the original superhydrophobic area, which originates from FAS molecules and contributes to the formation of superhydrophobicity. After HCl etching, the surface F decreased to 4.17%, Cu reduced from 14.74% to 7.61% and O decreased from 26.74% to 15.78%. Notably, Cl with a content of 4.97% was detected on the HCl etched area. According to the high-resolution C 1s spectra shown in Figure 3(c), peaks assigned to -CF₂ and -CF₃ groups of the FAS molecules were markedly detected on the superhydrophobic area [31], while the corresponding peaks for the HCl etched area could hardly be observed, that was, the peak intensities were greatly weakened after HCl-induced corrosion. Figure 3(d) shows the XRD patterns of original superhydrophobic area and HCl etched area. It could be seen that besides the diffraction peaks at $2\theta = 43.3, 50.4, 74.1$ and 89.9° respectively attributed to face-centered cubic Cu planes of (111), (200), (220) and (311) (JCPDS card No. 04-0836) that originated from the Cu substrate, new orthorhombic-phase Cu(OH)₂ planes of (021) at 23.7° , (002) at 34.0° , (111) at 35.8° , (041, 022) at 38.0° , (130) 39.7° and (150,

132) at 53.2° (JCPDS card No. 80-0656) were detected, confirming the well-known alkali assisted oxidation of Cu to generate Cu(OH)₂ [42, 43].



In comparison, these diffraction peaks of Cu(OH)₂ disappeared after HCl etching, while three new characteristic peaks corresponding to CuCl planes of (111) at 28.6°, (220) at 47.5° and (311) at 56.3° (JCPDS card No. 06-0344) were observed. It is commonly known that neutralization happens when Cu(OH)₂ contacts with HCl as described in the following equation:



Then the generated CuCl₂ could partly etch the exposed Cu substrate with the assistance of HCl, which was finally reduced to CuCl and precipitated on the Cu substrate [44, 45]:

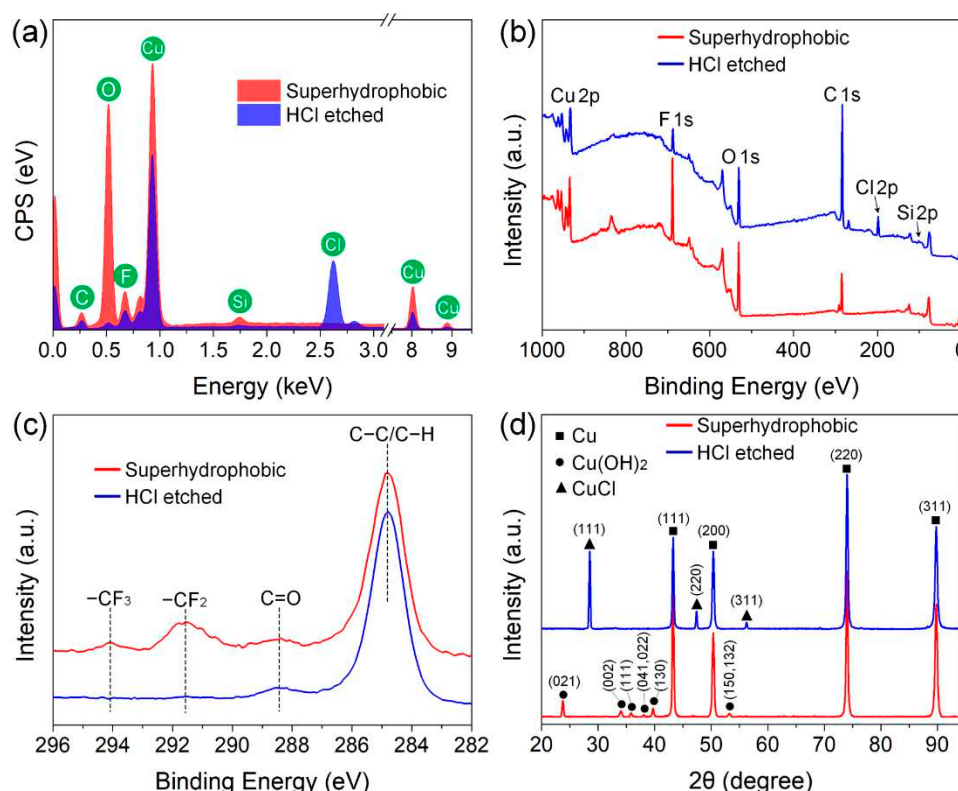


Figure 3. Surface chemistries of the original and HCl etched areas on superhydrophobic Cu surface: (a) EDS spectra; (b) XPS spectra; (c) high-resolution C 1s spectra; (d) XRD patterns.

According to the above results, we could conclude that NaOH assisted surface oxidation generated Cu(OH)₂ micro/nano rough structures on Cu substrate, and the subsequent immersion in FAS successfully triggered the formation of F-containing monolayer with low surface tension, the obtained surface thereafter possessed superhydrophobicity [42, 46-49]. However, when HCl solution invaded, the Cu(OH)₂ nanorods were chemically etched and partially washed away as well as the self-assembled FAS layer, which resulted in the content decrease of surface Cu, O and F. Therefore, the HCl etched area lost its superhydrophobicity and showed hydrophobicity, which enabled us to construct hydrophobic patterns on the superhydrophobic Cu surface by using its chemical instability towards HCl.

We then examined the influence of the volume of deposited HCl droplet (V_{HCl}) on the diameter of the obtained dimple (D), the results were depicted and fitted in Figure 4. It could be seen that the diameter of the obtained dimple grew almost linearly with the increase of V_{HCl} . For example, when $V_{\text{HCl}} = 1.0 \mu\text{L}$, the dimple diameter was about $0.47 \pm 0.01 \text{ mm}$, and it increased to $0.91 \pm 0.03 \text{ mm}$ when V_{HCl} was $5.0 \mu\text{L}$. According to the linear fitting of the experimental data (the correlation coefficient $R^2 = 0.99$), the dimple diameter, D , could be estimated as follows,

$$D = 0.375 + 0.111V_{\text{HCl}} \quad (4)$$

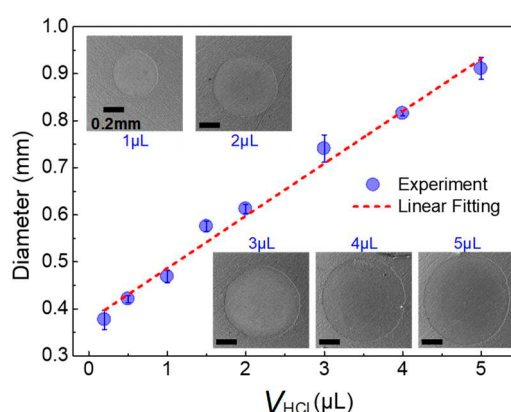


Figure 4. Relationship between the volume of deposited HCl droplet (V_{HCl}) and the diameter of the obtained dimple, spot is the experimental value, while the dotted line is their linear fitting ($R^2 = 0.99$), and the inserted SEM images show the prepared dimples with different V_{HCl} .

Programmable liquid droplet manipulations, including controllable transfer and deposition, have been widely explored on wettability-patterned surfaces [50-53]. Here we tested water droplets manipulations on the HCl etching patterned hydrophilic/superhydrophobic surface. Figure 5 shows water droplet transfer by hydrophilic dimple-patterned superhydrophobic substrates. Figure 5(a) illustrates the schematic diagram of the pre-designed patterned surfaces, consisting of one hydrophilic dimple on each superhydrophobic substrate. As shown in the image in Figure 5 (b), a water droplet ($5 \mu\text{L}$) was initially pre-deposited on position A of the superhydrophobic surface, position B and C were created hydrophilic dimples with diameter of 0.62 mm and 0.81 mm , respectively. Figures 5(c) and (d) depicted that an upward move of the lower substrate enabled the contact between the droplet and dimple B, and then the droplet adhered to the upper substrate via dimple B when the lower plate was moved down. As could be seen in Figures 5(e)-(h), when the hung droplet came in contact with dimple C on the lower plate, it was grabbed by the dimple and then re-deposited onto the lower substrate, i.e., the droplet was transferred from position A to C. Therefore, the as-prepared patterned surface herein could be used for water droplet transfer.

Figure 6 shows water droplets merging by using the as-prepared hydrophilic dimples patterned superhydrophobic surfaces. As can be seen from Figure 6(a), water droplets #1 ($7.0 \mu\text{L}$) and #2 ($4.0 \mu\text{L}$) were respectively deposited at position A (superhydrophobic area), and position B (a hydrophilic dimple with diameter of 0.81 mm); position C and D on the upper plate were a hydrophilic dimple (diameter 0.62 mm) and superhydrophobic area, respectively. Figures 6(b)-(d) shows that after the two droplets came in contact with the upper plate at position C and D, the subsequent downward movement of the lower plate enabled the capture of droplet #1 by the upper plate due to high adhesion of dimple C, while droplet #2 remained at dimple B because the adhesion of position D, original superhydrophobic surface, was extremely low. Then horizontal and subsequently perpendicular movement of the lower substrate enabled the merging of droplets #1 and #2, resulting in the formation of a new droplet #(1+2) at dimple B, as depicted in Figures 6(d)-(f). Consequently, we could envision that the proposed chemical instability induced patterned superhydrophobic surfaces could be potentially used for droplet-based micro-reactors [54].

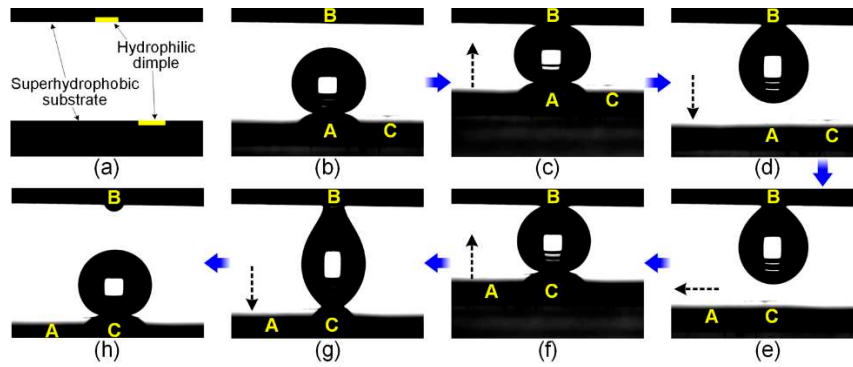


Figure 5. Water droplet transfer by hydrophilic dimple-patterned superhydrophobic substrates: (a) the schematic diagram of the employed substrates; (b)-(h) the image sequences showing the water droplet (5 μ L) transfer from position A to C via dimple B, the black dotted arrows indicate the moving directions of the lower substrate.

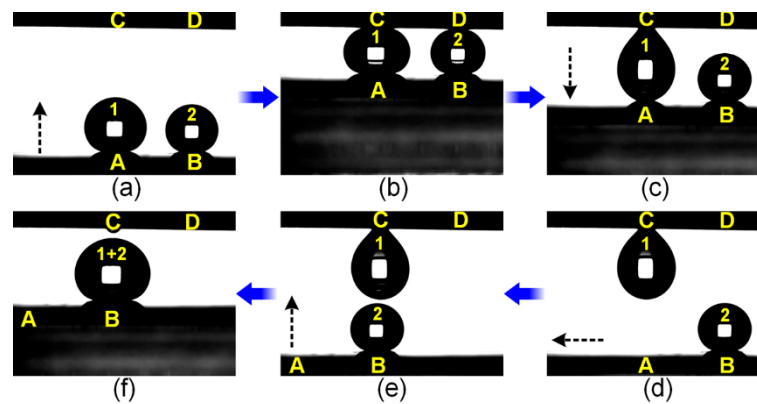


Figure 6. Water droplets merging by hydrophilic dimple-patterned superhydrophobic substrates, the black dotted arrows indicate the moving directions of the lower substrate.

Deposition of nanoliter sized droplet is important in many chemical and biomedical droplet-based microfluidic applications, such as fluorescence detection [50] and high-throughput cell screening [55]. We show here the nanoliter water deposition by the as-prepared hydrophilic dimple-patterned superhydrophobic surface, which was schematically illustrated in Figure 7(a). As could be seen in Figure 7(b), a water droplet (1.5 μ L) attached on a needle was initially positioned on the superhydrophobic area of the patterned surface. When the substrate was horizontally moved with a velocity of ~ 0.6 mm/s, the droplet remained quasi-spherical shape until it adhered to the dimple. Afterwards, the droplet gradually deformed and broke, leaving a tiny droplet deposited on the dimple. According to the schematic diagram in Figure 7(c), the deposited water could be roughly considered as a spherical crown intercepted from a sphere with radius of R to estimate its volume. The intercepted area's diameter (d) and height (h) of the spherical crown could be experimentally measured from the recorded images. According to the Pythagorean theorem, we could know that:

$$x^2 + y^2 = R^2 \quad (5)$$

$$(R - h)^2 + (d / 2)^2 = R^2 \quad (6)$$

The volume of the deposited water, V_d , could be described as:

$$V_d = \int_{R-h}^R \pi x^2 dy \quad (7)$$

According to Equations (5) to (7), the volume of the deposited water could be expressed as:

$$V_d = \frac{\pi h(3d^2 + 4h^2)}{24} \quad (8)$$

According to Equation (8), the deposited water droplet in Figure 7(b) was calculated to be ~ 20 nL. Then we prepared hydrophilic dimples with different diameters by using HCl droplets with varying volume (Figure 4), and studied the influence of the dimple diameter on the volume of

deposited droplet. As shown in Figure 7(d), the volume of deposited droplet increased with the growing of dimple diameter within the examined regime, and the volume of as low as 10.5 ± 1.1 nL could be deposited on dimple with diameter of 0.37 ± 0.02 mm.

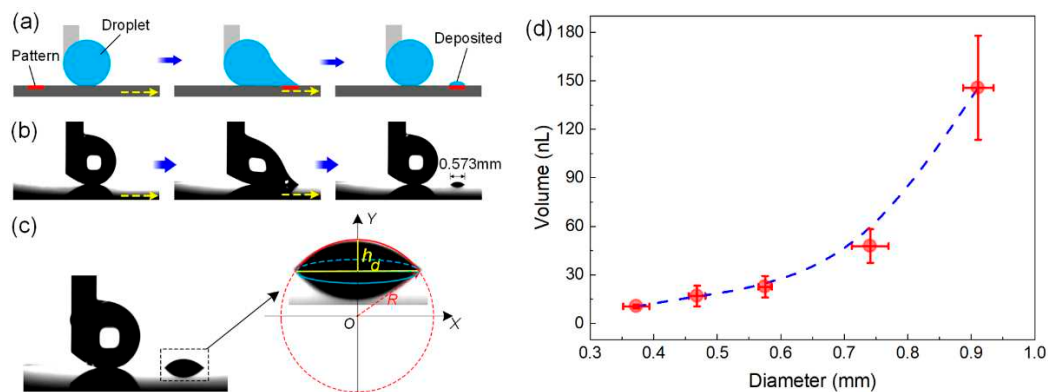


Figure 7. Nanoliter water deposition on hydrophilic dimple-patterned superhydrophobic substrates: (a) the schematic diagram and (b) image sequences showing a nanoliter water deposition process, the yellow arrows indicate the moving directions of the substrate; (c) the schematic diagram of volume estimation for the deposited water; (d) the relationship between the diameter of hydrophilic dimple and the volume of deposited water droplet.

4. Conclusions

In summary, we reported a simple method to create hydrophilic patterns on superhydrophobic Cu surface by using HCl solution triggered chemical instability. 2.5 min of HCl exposure led to the etching of surface micaro/nanostructures and partial removal of the FAS molecular layers, enabling the treated superhydrophobic area to be hydrophilic. Based on this HCl-induced chemical instability, we prepared hydrophilic dimples with diameters of 0.38–0.91 mm by depositing HCl droplets with volumes of 0.2–5.0 μL on the superhydrophobic surfaces. Typical applications, such as controlled droplet transfer, merging and nanoliter droplets deposition, have been demonstrated on the hydrophilic dimple patterned superhydrophobic surface. These results demonstrated the feasibility of creating wettability patterns on superhydrophobic surfaces by using their chemical instability towards corrosive solutions, which could enrich the fabrication methods of liquid-repellent surfaces with patterned wettability, and promote their applications in droplet manipulation.

Author Contributions: Conceptualization, T.C. and F.C.; methodology, T.C. and F.C.; validation, T.C. and F.C.; formal analysis, T.C.; investigation, T.C.; resources, F.C.; data curation, F.C.; writing—original draft preparation, T.C.; writing—review and editing, F.C.; visualization, T.C. and F.C.; supervision, F.C.; project administration, F.C.; funding acquisition, F.C. All authors have read and agreed to the published version of the manuscript

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Data Availability Statement: The data presented in this study are available on request from the corresponding author. The data are not publicly available due to confidentiality request.

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Conflicts of Interest: The authors declare no conflict of interest.

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