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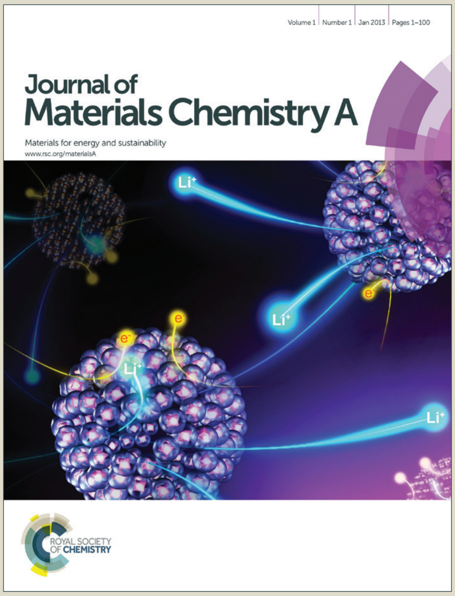

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Water droplet bouncing on superhydrophobic soft porous materials

*Yao Lu, Sanjayan Sathasivam, Jinlong Song, Wenji Xu, Claire J. Carmalt and Ivan P. Parkin**

Yao Lu, Dr. Sanjayan Sathasivam, Prof. Claire J. Carmalt and Prof. Ivan P. Parkin
Department of Chemistry, University College London, 20 Gordon Street, London, WC1H 0AJ, UK
E-mail: i.p.parkin@ucl.ac.uk (Ivan P. Parkin)
Jinlong Song
Department of Mechanical and Industrial Engineering, University of Illinois at Chicago, Chicago, Illinois 60607, USA
Jinlong Song
Key Laboratory for Precision and Non-traditional Machining Technology for Ministry of Education, Dalian University of Technology, Dalian, 116024, People's Republic of China
Prof. Wenji Xu
Key Laboratory for Precision and Non-traditional Machining Technology for Ministry of Education, Dalian University of Technology, Dalian, 116024, People's Republic of China

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Creating superhydrophobic soft porous materials, such as cotton and cloths is an important area of research as these materials have important practical applications such as water repellent clothing. In this paper, a generic method is reported to fabricate superhydrophobic surfaces on soft porous substrates, which were treated with crystalline copper chloride-hydroxide, followed by a fluorinated polymer. Water droplets can be supported as a perfect sphere and even bounce on the prepared surfaces, which demonstrate superior superhydrophobicity. For many soft porous materials, it is difficult to identify superhydrophobicity using water droplet contact angles. This is because water droplets may be trapped in the concave structures, making the necessary contact line to define the contact angle unobtainable. To solve this problem, water bouncing was used as a sufficient and necessary identification for superhydrophobic soft porous materials, a model was also made to discuss how a water droplet can bounce on soft materials.

1. Introduction

Superhydrophobic surfaces are classically defined by means of the solid-liquid-gas contact line between the surface and the droplet - the water contact angle. Surfaces with contact angles greater than 150 ° are typically superhydrophobic - with water droplets forming near spherical shapes. Furthermore it has been found that when a water droplet falls onto a superhydrophobic surface, it tends to bounce- and this bouncing- at least for hard surfaces can be a means to classify the degree of superhydrophobicity [1]. In nature many surfaces, such as the legs of a water strider [2] and the leaves of some plants are superhydrophobic [3, 4]. The Lotus plant in particular is well known for its self-cleaning property due to the Lotus effect that enables dirt particles to be picked up and removed from the surface by the motion of rolling water droplets [3]. Inspired by the Lotus effect, there has been wide interest in fabricating superhydrophobic surfaces on various substrates such as metals [5-8], polymers [9-11], and soft porous materials [12-15]. Recently, superhydrophobic soft porous materials have been studied both for fundamental research and for industrial applications, for example, for use in self-cleaning textiles [16, 17] and oil-water separation [18, 19]. Zhou et al. [20] fabricated superhydrophobic cotton wool via a vapor phase deposition method and tested the oil-water separation property; Wang et al. [21] fabricated a superhydrophobic sponge using carbon nanotube/poly(dimethylsiloxane)-coated polyurethane; Zhang et al. [22] prepared superhydrophobic coatings on filter paper via the synthesis of modified silica particles. Typically, materials like cotton wool, sponge, and filter paper are soft and porous and due to the presence of partially hydroxylated surfaces, the surfaces are hydrophilic and wet very efficiently so that they are used for cleaning purposes. In this paper, we propose a facile and general method to convert intrinsically hydrophilic soft porous materials into superhydrophobic ones. We were guided through this process by design rules that involved the combination of rough micro-nano-scale structures together with low surface energy modifications[23-25]. This was achieved by the use of a facile metathesis reaction to make the micro-nano-scale structures on soft porous materials, followed by the use of fluoroalkylsilane (FAS) to reduce the surface energy.

A second focal point of this work was to establish a method to define superhydrophobicity for a soft porous material where the contact line between the droplet and the surface is not defined. On hard surfaces with a defined contact line between the water droplet and the surface, a superhydrophobic surface typically has a water contact angle above 150^o. However, for most soft porous materials, a contact line is not available as the water droplets may be trapped in the concave structures of the material or supported by threads. Researchers have turned to new methods to quantify the effective properties of superhydrophobic surfaces, for example, to find a physical parameter that follows the scaling and quantifies drag reduction [26]. Jiang et al. [27] reported a method to evaluate the dynamic stability of superhydrophobic copper wires. However, it is difficult to apply those methods on soft porous materials like cotton wool and sponge, as the drag reduction or dynamic stability may be influenced by many parameters such as the material's nature, density, and volume instead of its surface wettability. Elastic water bouncing is also a characteristic property of superhydrophobic surfaces [28]. Bhushan et al. [29] studied the dynamic impact behaviour of water droplets on micro-patterned silicon surfaces and Hong et al. [30] tested superhydrophobic carbon nanotube powders using water droplet bouncing. We have also studied the relationship between water contact angle and the number of water bounces on superhydrophobic polymers [1]. However, virtually all water bouncing experiments have been reported for hard surfaces and there are few reports on soft porous materials. In this paper, we report both a new method of making superhydropobic surfaces and a new protocol to determine the superhydrophobicity of soft porous materials using water bouncing.

2. Results and Discussion

Soft porous surfaces (cotton, paper, sponge) were rendered water repellent in a two-step process as shown in **Scheme 1**; a simple and inexpensive chemical treatment involving formation of crystalline copper chloride- hydroxide, followed by treatment with a fluorinated polymer. The strategy followed was that the first step would introduce micro and nano-scaled roughness on the surface and the second step would render the materials water repellent by introducing a low energy surface for water- one that would encourage beading. It was found that both steps were required to form a superhydophobic surface.

Figure 1 shows the X-ray diffractometer (XRD) patterns of (a) treated scouring pad, (b) untreated scouring pad, (c) treated filter paper, (d) untreated filter paper, (e) treated cotton wool, and (f) untreated cotton wool, respectively. Reflections observed at 7.4°, 14.8° and 18.1° 2θ correspond to paratacamite [$Cu_2Cl(OH)_3$] and were present on the treated scouring pad, filter paper, and cotton wool (PDF NO. 01-070-0821 25-1427, [31]). The XRD pattern for treated cotton wool also shows reflections at 7.4°, 16.2°, 18.1° 2θ matching CuCl(OH) (PDF NO. 01-074-1650 23-1063, [32]). The paratacamite was formed from the action of steel plates on a $CuCl_2$ solution in water. It is formed in a three-step process, initially via a simple metathesis reaction shown in **Equation (1)**; the produced Cu was then oxidized by exposure to air as shown in **Equation (2)**; followed by hydrolysis of the formed copper hydroxide carbonate in the $CuCl_2$ solution [33] as shown in **Equation (3) (4)**. The pH of the solution at the end of the reaction was 4.34 indicating the production of H^+ as shown in **Equation (4)**. It is believed that the micro nano sized structures observed on the treated samples are mainly formed by paratacamite crystallization since CuCl(OH) was not found in all the samples.

$$Fe + CuCl_2 \rightarrow FeCl_2 + Cu \qquad (1)$$

$$2Cu + O_2 + CO_2 + H_2O \rightarrow Cu_2(OH)_2CO_3 \qquad (2)$$

$$CuCl_2 + H_2O \rightarrow CuCl(OH) + HCl \qquad (3)$$

$$Cu_2(OH)_2CO_3 + HCl + H_2O \rightarrow Cu_2Cl(OH)_3 + H^+ + HCO_3^- \qquad (4)$$

Superhydrophobicity of soft porous materials depends on surface micro and nano structures and chemical compositions. **Figure 2** (a-c) shows the scanning electron microscopy (SEM) images of the treated scouring pad with micro scale dome-like features and nano structures on the surface; **Figure 2** (d-f) shows the SEM images of the untreated scouring pad, which was much smoother than the treated superhydrophobic one. A big difference was also observed between the treated and untreated filter paper [**Figure 3**(a-c); **3**(d-f)]. The treated filter paper had more structured morphologies with micro-nano sized features compared to the untreated sample. Treated cotton wool [**Figure 4** (a-c)] also had many micro dome-like features and nano structures on the surface, unlike the untreated cotton wool counterpart [**Figure 4** (d-f)]. In spite of the fact that untreated samples (cotton wool, filter paper and souring pad) had different initial surface morphologies, they all underwent surface roughening through the formation of micro-nano sized structures after the same chemical treatment with paratacamite. This indicates that this method of surface preparation is generic and can be used for almost all types of soft porous material.

FAS ($C_8F_{13}H_4Si(OCH_2CH_3)_3$) was used to reduce the surface energy to encourage beading. **Figure 5** shows the X-ray photoelectron spectroscopy (XPS) spectra of (a) treated scouring pad, (b) untreated scouring pad, (c) treated filter paper, (d) untreated filter paper, (e) treated cotton wool, and (f) untreated cotton wool, respectively. C 1s (between 280 and 290 eV) and O 1s (between 528 and 536 eV) peaks can be found in both treated and untreated samples, illustrating that these soft substrates contain mainly C and O as expected. Cu 2p has two peaks (2p 3/2 and 2p 1/2) between 930 and 960 eV, whereas, the peak Cl 2p is around 200 eV. The Cu and Cl peaks were observed in the XPS of the treated samples due to the presence of paratacamite. No peaks corresponding to Cu and Cl in the region of 930 - 960 eV and 200 eV were found in the untreated samples, therefore showing these soft porous substrates do not contain Cu or Cl. The peak for F 1s between 680 and 690 eV was not observed for the untreated scouring pad, filter paper, or cotton wool. However, the post FAS treated samples show the presence of F revealing FAS was successfully coated on the soft porous materials. Therefore, the analysis (XRD and XPS) show that scouring pad, filter paper and cotton wool could all be treated with paratacamite and FAS.

This method of superhydrophobic surface synthesis can be used generally to treat many soft porous materials such as sponges and various cloths (**Figure S1**). **Figure S2** shows the SEM images of sponge and cloths before and after treatment using this method. The post-treated samples have a more structured morphology.

Figure 6 shows water droplets on treated scouring pad [(a) and (b)], filter paper [(c) and (d)], and cotton wool [(e) and (f)], respectively. The measured water contact angle for the filter paper was 151^{o}, which shows the prepared filter paper was superhydrophobic, however, we required another way to identify that the surfaces of the treated scouring pad and cotton wool were superhydrophobic as there was no easily observable contact line between the liquid and solid interface. Here, water droplets are close to a perfect sphere on the scouring pad and cotton wool surfaces [**Figure 6** (b) and (f)]. Therefore suggesting the contact angles of scouring pad and cotton wool are both 180^{o}. McCarthy et al. [34] have reported a 180 ° superhydrophobic silicon wafer and devised a method to distinguish between surfaces exhibiting contact angles of 180 ° and 179 °. However, their method was based on the contact line between liquid-solid interfaces.

Since there is not a general way to determine superhydrophobicity of soft porous materials, we suggest a new method to characterize superhydrophobicity without the requirement of a contact line by using a water bouncing test. We have previously defined water bouncing on hard superhydrophobic surfaces [35], when droplets break at the point of release from the surface upon bouncing, there will be a small droplet left in contact with the surface, while a larger droplet rises from the surface and then falls as shown in **Figure 7** (a). There are two ways for larger and small droplets to recombine: (I) moving up toward the larger droplet with the whole droplet leaving the surface or (II) the larger droplet gets pulled down and the smaller droplet never leaves the surface. The former case where the whole water droplet is removed from the surface we considered as a bounce.

The case of water droplets impacting on soft porous materials is a slightly different as shown in **Figure 7** (b). When a water droplet impacts on a soft porous material from a certain height [**Figure 7** (b-I)], it will spread out on the surface and the soft substrate tends to form a concave structure (nest) as it absorbs the impact of the water droplet [**Figure 7** (b-II)], however due to the elasticity of the porous material the water droplet has a tendency to reform [**Figure 7** (b-III)]; when the water droplet rebounds, it will either fragment and splash as it may not be forced evenly from soft substrates like on the cotton wool [**Figure 7** (b-IV)], or recoil as an intact droplet from the scouring pad [**Figure 7** (b-V)]; we consider the surface to be superhydrophobic when the whole droplet completely leaves the surface [**Figure 7** (b-VI)], in effect one bounce defines the surface as superhydrohobic.

Generally, the number of times a water droplet bounces on a soft superhydrophobic material will be much smaller than on hard superhydrophobic materials. This is because the water droplet will lose more kinetic energy to the elastic potential energy of the soft porous materials compared to a hard surface. Therefore, once a water droplet bouncing happens on the soft porous substrate, the surface can be determined as superhydrophobic. This new identification on soft porous materials agrees with a definition for superhydrophobic surfaces on hard substrates, where water bouncing only occurred on surfaces with water contact angle over 151 °[1]. That is, at least one bounce can determine superhydrophobicity of a surface. A water bouncing movie on cotton wool and scouring pad can be found in supporting information (**Movie 1**). Based on this new identification, the prepared scouring pad and cotton wool are superhydrophobic.

For soft porous materials, one bounce (the water droplet completely leaves the surface) is enough to show good superhydrophobicity of the surface; however, it does not mean if there is no bounce that the surface is not superhydrophobic. It also depends on factors such as nature and elasticity of materials. Here, the prepared surfaces are in the Cassie-Baxter [36] state as shown in **Scheme 2 (a)**. In the Cassie-Baxter state, air is trapped in micro-nano-scale structures under water droplets, leading to superhydrophobicity of the surface. The Cassie-Baxter equation is written as:

$$\cos \theta^* = -1 + \varphi_s(1 + \cos \theta) \qquad (5)$$

where θ^* is the apparent contact angle on the textured surface, φ_s is the fraction of the solid in contact with the water, θ is the contact angle given by Young's model [37] as shown in **Scheme 2 (b)**. The Young equation is written as:

$$\cos \theta = (\gamma_{sv} - \gamma_{sl})/\gamma_{lv} \qquad (6)$$

where θ is the water contact angle on a smooth surface, γ is the interfacial tension, and the subscripts s, v, and l refer to the solid, vapor, and liquid phases, respectively.

When a water droplet impacts soft porous materials in a Cassie-Baxter state from a certain height h, the impacting velocity V is determined as:

$$V = (2\mathrm{g}h)^{1/2} \qquad (7)$$

where g is the acceleration of gravity. Once the water droplet impacts the surface of soft porous materials, both the droplet and the substrates will deform, meanwhile, the water droplet will still go down until its velocity v decreases from V to 0. The process between the moment of impacting and v becomes 0 can be defined as the impulse process, F is the force that the water droplet presses onto the soft porous substrates, then

$$F = mg + F_a \qquad (8)$$

Where m is the mass of the water droplet, F_a is the force caused by the momentum of the water droplet and can be deduced according to impulse-momentum theorem:

$$F_a = m\Delta v/\Delta t \qquad (9)$$

Where Δt is the unit time in the impulse process, Δv is the variation of v in the unit time. Suppose S is the spread area of the water droplet, the pressure p that the water droplet presses the micro-nano-scale structures (air pockets) of soft porous materials can be written as:

$$p = F/S \qquad (10)$$

Here, the Cassie-Baxter model was taken into soft porous materials to describe the water droplet process. When a water droplet hits a soft porous substrate, some water may hit into the concave structures of the surface as shown in **Scheme 3 (a)**, the pressure p determines the depth L that water droplets hit in the air pockets of structures as shown in **Scheme 3 (b)**, the distance between water and the bottom of the surface is l_0, S_0 is the bottom area of the water in the concave structure. Suppose the structures are sealed, some air will run away along the side of structures. After impacting, the soft porous substrates will push the water up as a result of elasticity as shown in **Scheme 3 (c)**. The water position after rebound is described as the dashed line in **Scheme 4 (d)**, where l is the distance between before and after rebound, and f is the force caused by water surface tension. In the process of rebounding, water will experience a ‘suction’ force, which is from the negative pressure generated in the concave structure. Here, the ‘suction’ force $F\mathbf{s}$ can be written as

$$F\mathbf{s} = p_0S_0 - PS_0 \qquad (11)$$

where p_0 is one standard atmospheric pressure and P is the pressure of the space under water in the concave structure. Base on the Ideal gas law, $PV = nRT$, where V is the volume of air under water in the concave structure, n is the amount of substance of air, T is the temperature of the air and R is the ideal gas constant, **Equation (11)** can also be written as

$$F\mathbf{s} = p_0S_0 - nRT/(l_0+l) \qquad (12)$$

In **Equation (12)**, p_0, S_0, n, R, T and l_0 are all constant, $F\mathbf{s}$ will increase as l gets larger. When $l = L$, the water just leaves the concave structure, if $F\mathbf{s} < f$, water will completely leave the concave structure as shown in **Scheme 3 (e)**; however, when the first time if $F\mathbf{s} > f$, it still happens that $l < L$, this means that the ‘suction’ force is greater than the force from the water surface tension but the water does not get out from the concave structure, in this condition, the water will be split resulting in some water still staying in the concave structure as shown in **Scheme 3 (f)**, that is the reason why some water droplets do not bounce (leaving a fraction on the surface) on superhydrophobic soft porous materials.

Therefore, the mass of water droplet, the dropping height or the impacting velocity will all influence the water bouncing behavior on soft porous materials. However, due to the nature of different soft porous materials, those parameters may have different impacts on the pressure of water to the surface, as well as the depth of water hits into the concave structure, which also help determine whether water droplet would bounce or not. Thus, in our identification, we used one bounce (water droplet completely leave the surface) on soft porous materials as the determination of superhydrophobicity, since one bounce would definitely show a superior water replant property. This is not a necessary condition for superhydrophobicity, but does indicate when a surface is definitely superhydrophobic.

3. Conclusion

In conclusion, we propose a generic way to fabricate superhydrophobic surfaces on soft porous substrates. Water droplets can be supported as a perfect sphere on the prepared surfaces. Micro-nano-scale structures were coated via crystallization of paratacamite, which was prepared by a very simple metathesis reaction using inexpensive reagents. The subsequent immersion of the samples in FAS enabled the formation of a low energy surface. We demonstrate that this is a simple method to obtain superhydrophobic surfaces on many soft porous materials- cotton, paper and sponge. We further showed that water bouncing does occur on soft porous materials and we suggest that observation of a water bounce could be used to define a soft surface as superhydrophobic.

4. Experimental Section

Materials: Soft porous materials such as scouring pad (from a sponge), filter paper, and cotton wool were purchased from Fisher Scientific and used as received. Cupric chloride (98.0%

$CuCl_2 \cdot 2H_2O$) was purchased from BDH Chemicals Ltd. Mild steel was purchased from Goodman. 1H, 1H, 2H, 2H-perfluorooctyltriethoxysilane ($C_8F_{13}H_4Si(OCH_2CH_3)_3$) was purchased from Sigma-Aldrich. Laboratory solvents were purchased from Fisher Scientific and of the highest possible grade. All chemicals were analytical grade reagents and were used as received.

Micro-nano-scale structures fabrication: Mild steel was put into a $CuCl_2$ (0.2 mol/L) solution for 3 hours at 80 ℃ and the produced solvent was exposed to the air for two days. Then scouring pad, filter paper, and cotton wool were placed into the solution and stirred at 300 r/min for 10 min using a magnetic stirrer bar. After stirring, the scouring pad, filter paper, and cotton wool were left immersed in the solution for 2 hours. The samples were then removed and put in a 90 ℃ drying oven for 24 hours.

Low surface energy modification: The aforementioned samples were immersed in a FAS ethanol solvent (1.0 wt % 1H, 1H, 2H, 2H-perfluorooctyltriethoxysilane in absolute ethanol solvent) for 2 hours, and then removed, and dried for 4 hours at 90 ℃.

Characterization: Scanning Electron Microscopy (SEM) was performed to determine surface morphology using a JEOL JSM-6301F Field Emission SEM. The surface was coated with gold to make the samples conductive. The crystal structures of the samples were examined using an X-ray diffractometer (XRD, STOE, SEIFERT analytical X-rays). The X-ray source was a Mo radiation, which was operated within the 2° and 40° 2θ range, at a scanning rate of 0.495 °/step, 30 sec/step. Surface chemical compositions were investigated using an X-ray photoelectron spectroscopy (XPS, Thermo Scientific K-alpha photoelectron spectrometer). The water contact angles were measured at ambient temperature via the sessile-drop method using an optical contact angle meter (FTA 1000, water droplet is 5 µL). Water bouncing videos were taken by a high speed camera (Casio Ex-fh25). pH value was tested using a microprocessor pH mater (HANNA instruments, pH 211, microprocessor pH mater).

Water bouncing test: Water droplets were dropped from a height between 15 and 25 cm using a 1-mL-range syringe fitted with a 21 gauge dispensing tip. The water droplets from this tip were 10 microlitres in size. Methylene blue was added to the water to aid visualisation; this did not change the behaviour of the water droplets on the surface.

Supporting Information

Acknowledgements

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[1] C. R. Crick, I. P. Parkin, *Chem. Commun*. **2011**, *47*, 12059.

[2] X. Gao, L. Jiang, *Nature* **2004**, *432*, 36.

[3] W. Barthlott, C. Neinhuis, *Planta* **1997**, *202*, 1.

[4] Y. Zhang, H. Xia, E. Kim, H. Sun, *Soft Matter*, **2012**, *8*, 11217.

[5] Y. Lu, J. Song, X. Liu, W. Xu, Y. Xing, Z. Wei, *ACS Sustainable Chem. Eng*. **2013**, *1*, 102.

[6] Y. Lu, J. Song, X. Liu, W. Xu, J. Sun, Y. Xing, *Micro Nano Lett*. **2012**, *7*, 786.

[7] Y. Lu, W. Xu, J. Song, X. Liu, Y. Xing, J. Sun, *Appl. Surf. Sci*. **2012**, *263*, 297.

[8] Y. Lu, S. Sathasivam, J. Song, F. Chen, W. Xu, C. J. Carmalt and I. P. Parkin, *J. Mater. Chem. A*, **2014**, Accepted Manuscript, DOI: 10.1039/C4TA02181A.

[9] Y. Zhang, J. Wang, Y. He, Y. He, B. Xu, S. Wei, F. Xiao, *Langmuir*, **2011**, *27*, 12585.

[10] C. R. Crick, I. P. Parkin, *J. Mater. Chem*. **2011**, *21*, 9362.

[11] J. Kong, T. Kim, J. Kim, J. Park, D. Lee, S. Kim and J. Kim, *Nanoscale* **2014**, *6*, 1453.

[12] L. Yang, A. Raza, Y. Si, X. Mao, Y. Shang, B. Ding, J. Yu and S. S. Al-Deyab, *Nanoscale*, **2012**, *4*, 6581.

[13] X. Chen, Y. Wu, B. Su, J. Wang, Y. Song, L. Jiang, *Adv. Mater.* **2012**, *24*, 5884.

[14] N. Nuraje, W. S. Khan, Y. Lei, M. Ceylan and R. Asmatulu, *J. Mater. Chem. A*, **2013**, *1*, 1929.

[15] J. Zimmermann, F. A. Reifler, G. Fortunato, L. Gerhardt, S. Seeger, *Adv. Funct. Mater.* **2008**, *18*, 3662.

[16] Y. Liu, J. Tang, R. Wang, H. Lu, L. Li, Y. Kong, K. Qi, J. H. Xin, *J. Mater. Chem.* **2007**, *17*, 1071.

[17] B. Leng, Z. Shao, G. With, W. Ming, *Langmuir* **2009**, *25*, 2456.

[18] Q. Zhu, Q. Pan, F. Liu, *J. Phys. Chem. C* **2011**, *115*, 17464.

[19] G. Deschamps, H. Caruel, M. Borredon, C. Albasi, J. Riba, C. Bonnin, C. Vignoles, *Environ. Sci. Technol.* **2003**, *37*, 5034.

[20] X. Zhou, Z. Zhang, X. Xu, F. Guo, X. Zhu, X. Men, B. Ge, *ACS Appl. Mater. Interfaces* **2013**, *5*, 7208.

[21] C. Wang, S. Lin, *ACS Appl. Mater. Interfaces* **2013**, *5*, 8861.

[22] M. Zhang, C. Wang, S. Wang, Y. Shi, J. Li, *Appl. Surf. Sci.* **2012**, *261*, 764.

[23] Y. Li, G. Duan, G. Liu, W. Cai, *Chem. Soc. Rev.* **2013**, *42*, 3614.

[24] Y. Li, E. J. Lee, S. O. Cho, *J. Phys. Chem. C* **2007**, *111*, 14813.

[25] Y. Li, W. Cai, B. Cao, G. Duan, F. Sun, C. Li, L. Jia, *Nanotechnology* **2006**, *17*, 238.

[26] L. Bocquet, E. Lauga, *Nature Mater.* **2011**, *10*, 334.

[27] X. Yao, L. Xu, L. Jiang, *Adv. Funct. Mater.* **2010**, *20*, 3343.

[28] D. Richard, C. Clanet, D. Quéré, *Nature* **2002**, *417*, 811.

[29] Y. C. Jung, B. Bhushan, *Langmuir* **2008**, *24*, 6262.

[30] Y. C. Hong, H. S. Uhm, *Appl. Phys. Lett.* **2006**, *88*, 244101.

[31] M. E. Fleet, *Acta Cryst. B* **1975**, *31*, 183.

[32] Y. Iitaka, S. Locchi, H. R. Oswald, *Helvetica Chimica Acta* **1961**, *44*, 2095.

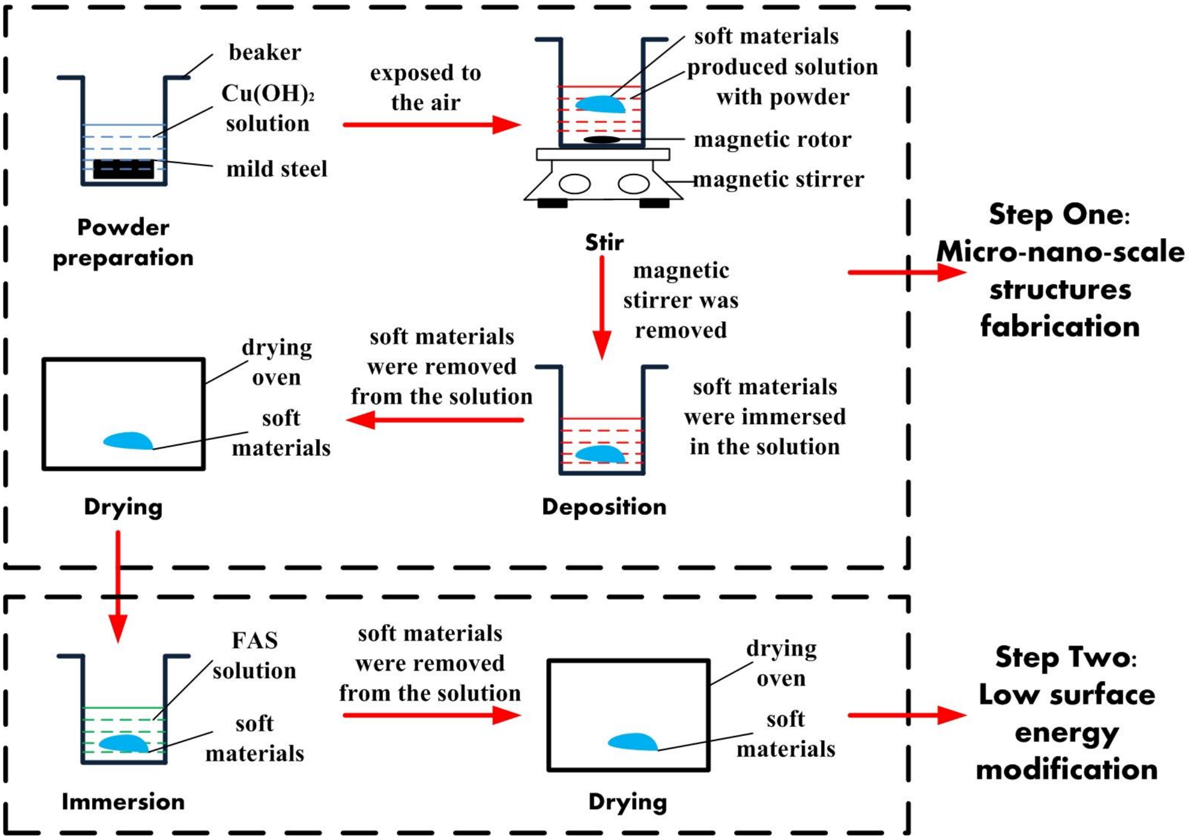
[33] J. B. Sharkey, S. Z. Lewin, *Am. Min.* **1971**, *56*, 179.

[34] L. Gao, T. J. McCarthy, *J. Am. Chem. Soc*. **2006**, *128*, 9052.

[35] C. R. Crick, I. P. Parkin, *J. Mater. Chem. A* **2013**, *1*, 799.

[36] A. B. D. Cassie, S. Baxter, *Trans. Faraday Soc*. **1944**, *40*, 546.

[37] T. Young, *Philos. Trans. R. Soc. London* **1805**, *95*, 65.



Scheme 1. Illustration of the two-step method of superhydrophobic soft porous materials fabrication.

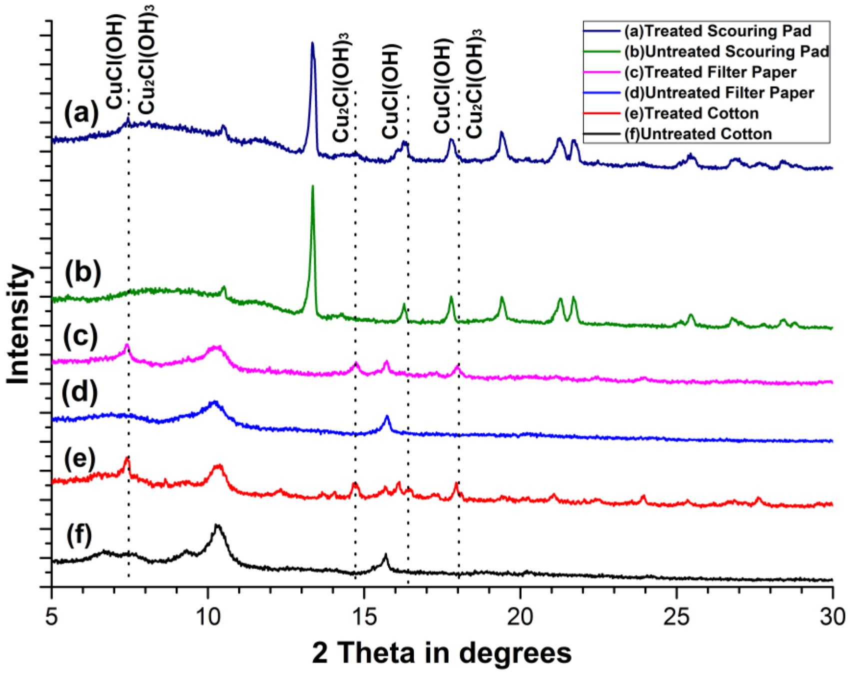


Figure 1. XRD patterns of (a) treated scouring pad, (b) untreated scouring pad, (c) treated filter paper, (d) untreated filter paper, (e) treated cotton wool, and (f) untreated cotton wool, respectively.

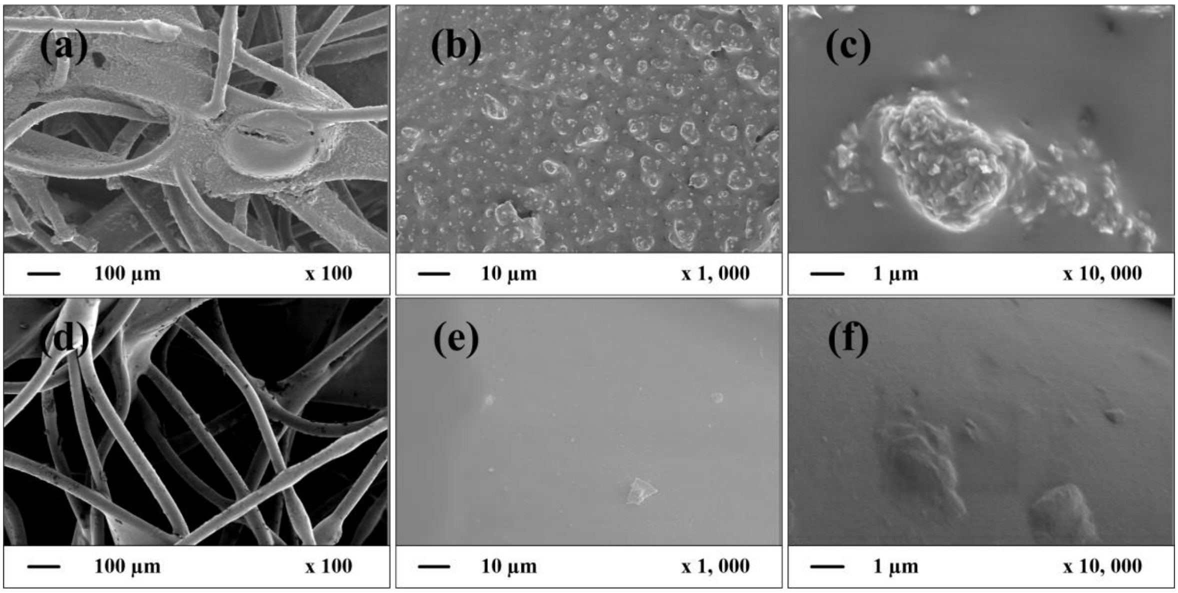


Figure 2. SEM images of (a-c) treated scouring pad, and (d-f) untreated scouring pad in 100 x, 1000 x, and 10000 x magnifications, respectively.

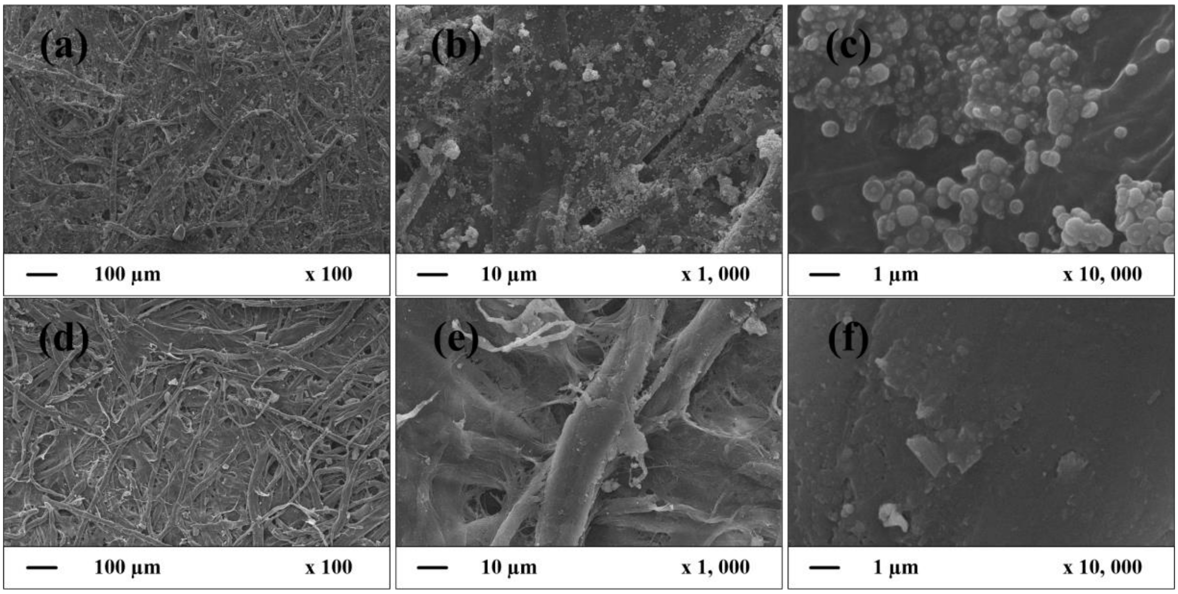


Figure 3. SEM images of (a-c) treated filter paper, and (d-f) untreated filter paper in 100 x, 1000 x, and 10000 x magnifications, respectively.

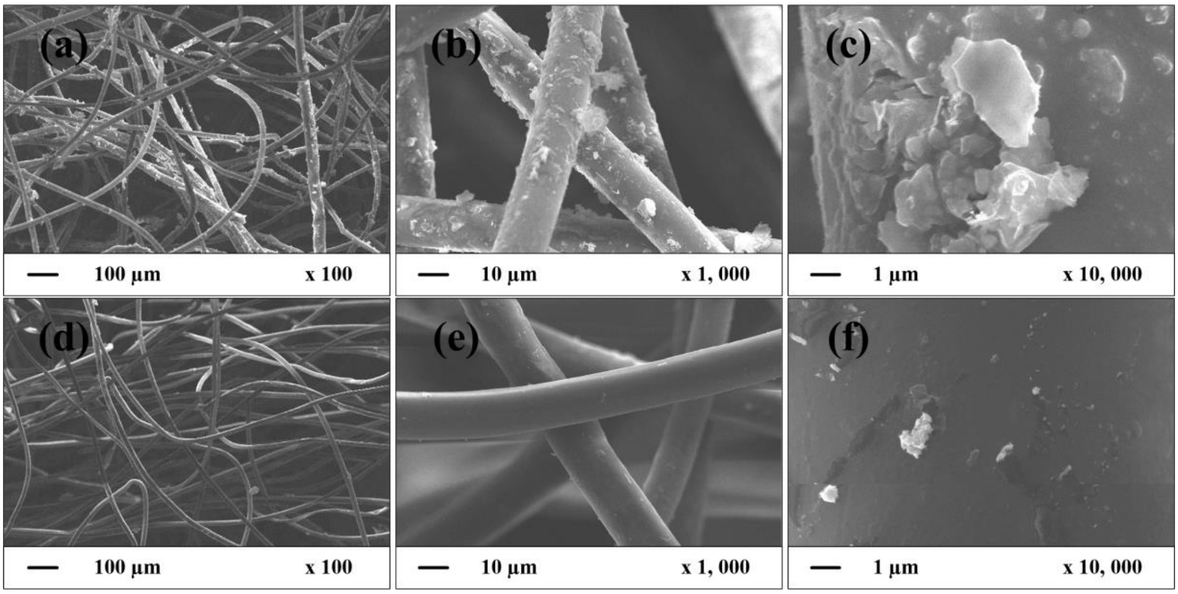


Figure 4. SEM images of (a-c) treated cotton wool, and (d-f) untreated cotton wool in 100 x, 1000 x, and 10000 x magnifications, respectively.

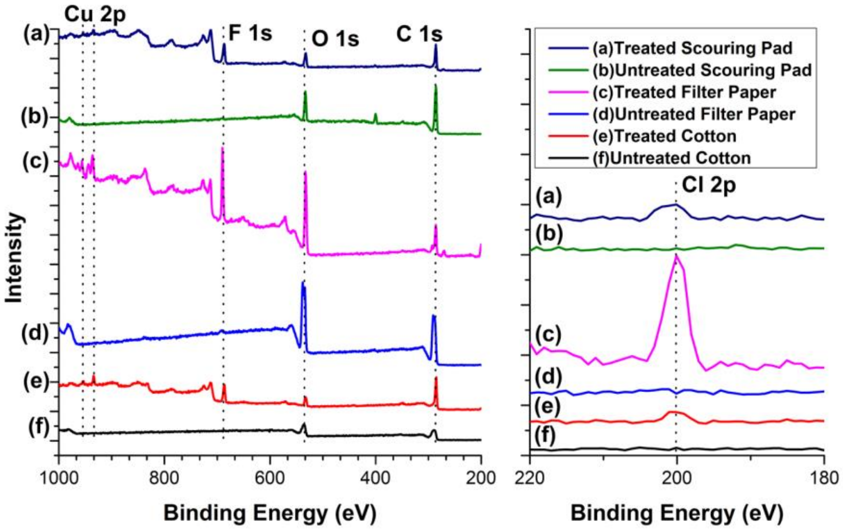


Figure 5. XPS spectra of (a) treated scouring pad, (b) untreated scouring pad, (c) treated filter paper, (d) untreated filter paper, (e) treated cotton wool, and (f) untreated cotton wool, respectively.

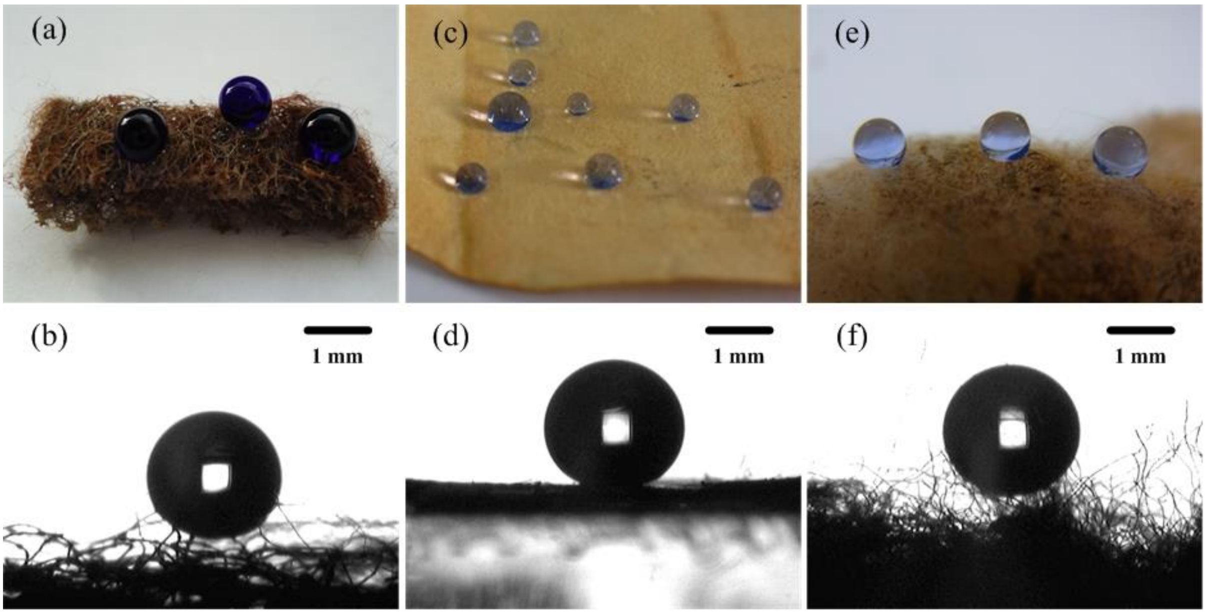


Figure 6. Water droplets on superhydrophobic scouring pad [(a) and (b)], superhydrophobic filter paper [(c) and (d)], and superhydrophobic cotton wool [(e) and (f)], respectively. Here, water droplets were supported by threads of superhydrophobic scouring pad and cotton wool, resulting in no contact line between liquid-solid interfaces.

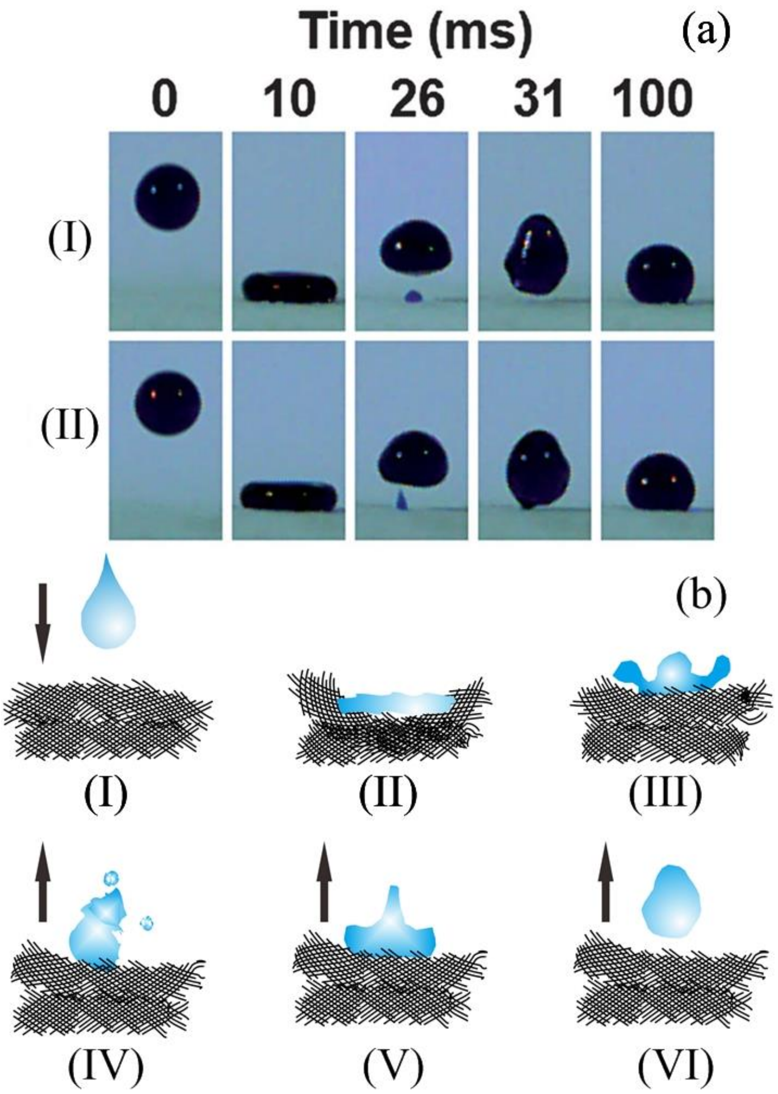
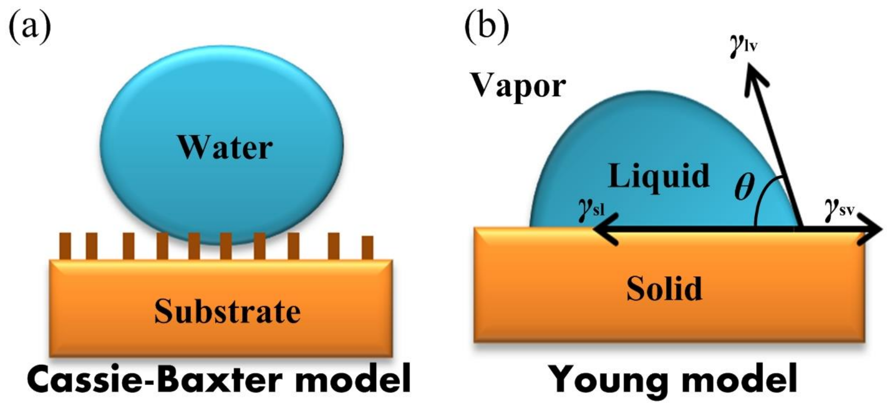
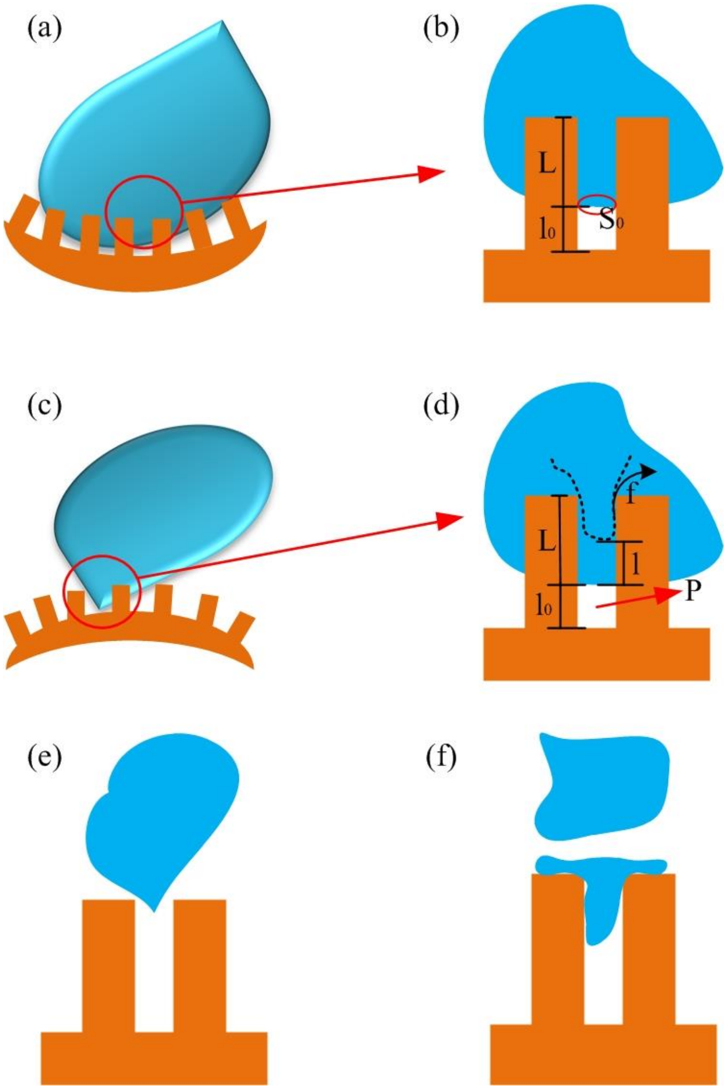


Figure 7. (a) The water droplet recombines with the smaller droplet in two ways – (I) moving up toward the larger droplet with the whole droplet leaving the surface or (II) the larger droplet gets pulled down and the smaller droplet never leaves the surface. Reproduced with permission.[35] Copyright 2013, RSC Publishing. (b) When a water droplet impacts on a soft porous materials from a certain height (I), it will spread out on the surface and the soft substrate will form a concave structure as it absorbs the impact of the water droplet (II), then the water droplet has a tendency to reform (III); when the water droplet gets repelled, it will either splash as it may not be forced evenly from soft substrates like on the cotton wool (IV), or come back with an upward tendency from substrates like on the scouring pad (V); once the whole droplet completely leaves the surface (VI), it is considered as one bounce on soft porous materials.



Scheme 2. (a) Cassie-Baxter model and (b) Young model.



Scheme 3. Cassie-Baxter model to describe water bouncing on soft porous materials.