Supporting Information

Prewetting dichlormethane induced aqueous solution adhered on Cassie superhydrophobic substrates to fabricate efficient fog-harvesting materials inspired by Namib Desert beetles and mussels

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This ESI contains:

Table S1-2, Figures S1-23

Movie S1-4

Table S1. Surface tension (20℃) of different organic solvents and their oil contact angles on the superhydrophobic copper sample

Sample	Tetrachloro-methane	Bromethyl	Dichloro-methane	Petroleum ether	Cyclohexane	n-hexane
Surface tension (mN/m)	35.2	23.1	23.1	19.5	25.9	20.3
OCA	< 5°	< 5°	< 5°	< 5°	< 5°	< 5°

Table S2. Physicochemical parameters affected aquous drops adhered on the Cassie superhydrophobic surfaces

	ST (mN/m)	**Density (g/mL)**	**SVP (Kpa, 20℃)**	**Solublness**	**CA (°)**	**VT (s)**	***Drop adhered on the surface***
n-hexane	20.3	0.69	5.33	—	<5	62.8 ± 4.6	√
Cyclohex-ane	25.9	0.778	12.7	—	<5	44.5 ± 3.4	√
Petroleum-ether	19.5	0.65	53.2	—	<5	7.8 ± 0.9	√
Dichlor-methane	23.1	1.326	46.5	—	<5	25.5 ± 3.2	√
Bromoeth-ane	23.1	1.456	<1.6	—	<5	30.5 ± 1.7	√
Carbon Tetrachlo-ride	35.2	1.595	11.9	—	<5	61.5 ± 7.5	√
Ethanol	22.3	0.79	5.8	MS	<5	152.5 ± 9.6	×
Acetone	18.8	0.758	24	MS	<5	22.1 ± 3.1	×
Silicone oil	20.6	0.95	<0.6	—	<5	∞	×
Propane-diol	38.0	1.04	0.007	MS	62.5	∞	×
Acetic acid	31.9	1.05	1.52	MS	<5	∞	×

Here, **ST** means the surface tension, **SVP** is the saturated vapor pressure, **CA** is the oil contact angle on the surface, **VT** is the volatilized time, **MS** represents the mutual dissolution between aqueous solution and organic solvents.

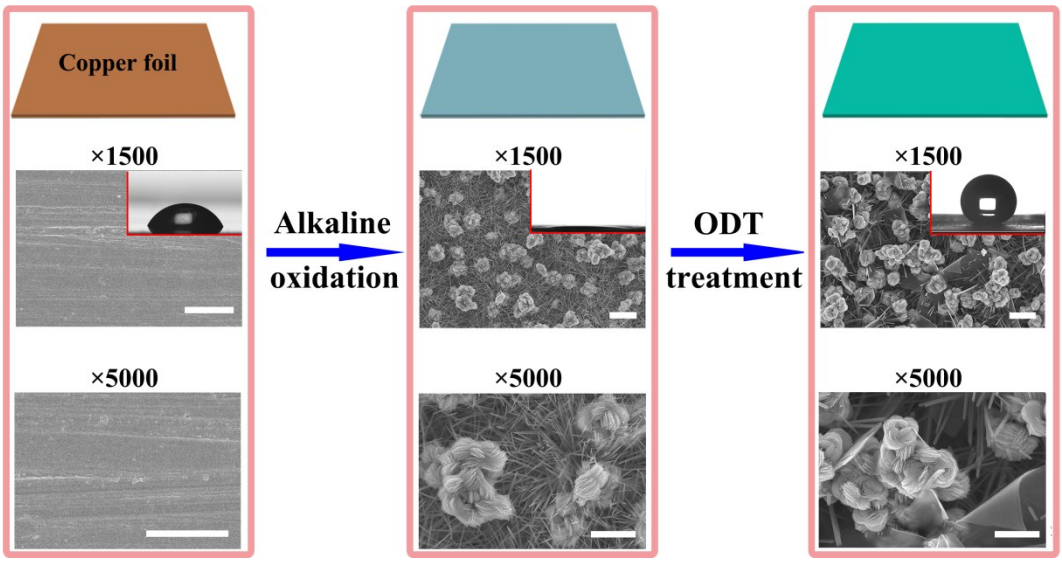


Figure S1: Schematic illustration of the fabrication of the superhydrophobic copper foil. A clean Cu foil showed smooth surface and hydrophilic wetting behavior. After the alkaline oxidation for 15 min, micro-flower and nano-needles formed on the sample, which exhibited the superhydrophilicity. Followed by the ODT treatment, superhydrophobicity was obtained, and the micro-sheets were emerged on the copper surface. Scale bars: left, ×1500, 30μm; ×1500, 10 μm. Middle and right, ×1500, 10 μm; ×5000, 5 μm.

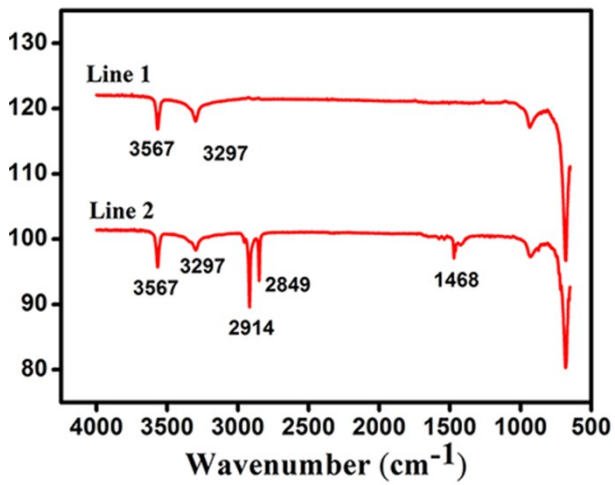


Figure S2. The FTIR measurements of copper foils after alkaline oxidation etching (line 1) and thiols treatments (line 2). In line 1, $Cu(OH)_2$ was confirmed at the the wavenumber of 3567 cm^{-1}. In line 2, after thiols modification, the wavenumbers of 2914 cm^{-1}, 2849 cm^{-1}, 1468 cm^{-1} were proved that the existence of $-CH_3$, $-CH_2-$, and $S-CH_2$ on the sample, indicating the low surface energy composition of ODT was modified on the surface.

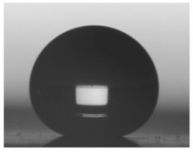
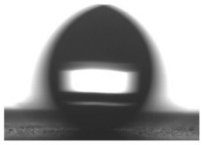
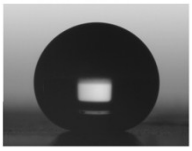
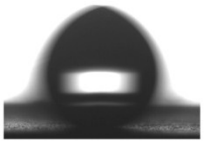
Wetting / Drop	CA	RA
Water	 161.5 ± 1.5°	 3.5 ± 0.9°
Dopamine	 155.7 ± 2.3°	 6.7 ± 1.5°

Figure S3. The wetting behaviors on the Cassie superhydrophobic substrate. The surface possessed the water contact angle (CA) of 161.5 ± 1.5° and rolling-off angle (RA) of 3.5 ± 0.9°. As for the dopamine aqueous drop, the surface showed CA and RA of 155.7 ± 2.3° and 6.7 ± 1.5°, respectively.

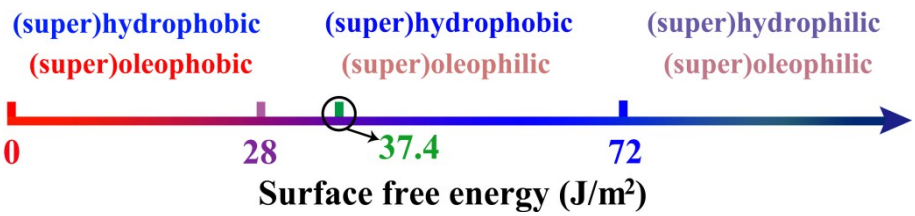
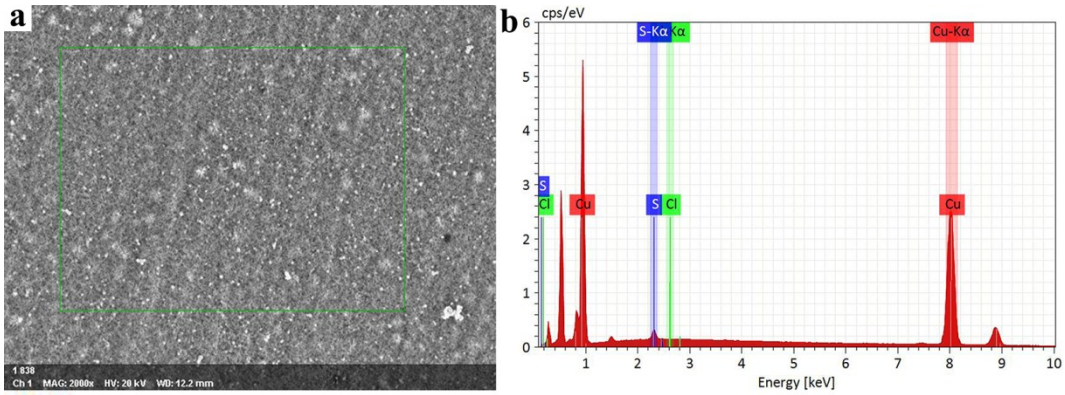


Figure S4. The relations between surface wetting behaviors and surface free energy. Surface tension and surface free energy (SFE) are different in physical quantities, but their values and dimensions are the same. Water possesses the surface tension of about 72 mN/m and all the organic oils show the average surface tension of 28 mN/m. When SFE > 72 J/m^2, the surface manifests the (super)hydrophilicity and (super)oleophilicity. When 28 J/m^2 < SFE < 72 J/m^2, the surface shows the (super)hydrophobicity and (super)oleophilicty. When 0 < SFE < 28 J/m^2, the surface exhibits the (super)hydrophobicity and (super)oleophobicity. As for our sample, it owns the surface free energy of 37.4 J/m^2, which combined the sufficient roughness to endow the surface with superoleophilic ability.

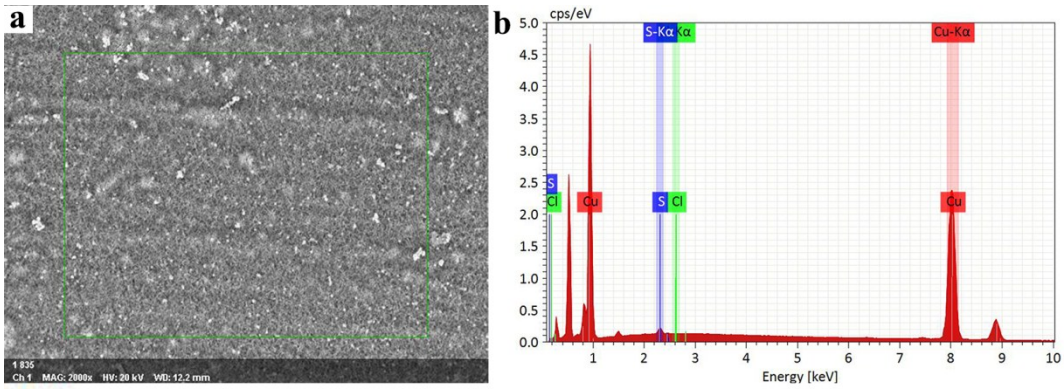


Map

c

Element	At. No.	Netto	Mass [%]	Mass Norm. [%]	Atom [%]	abs. error [%] (1 sigma)	rel. error [%] (1 sigma)
S	16	15691	0.91	1.18	2.31	0.06	6.46
Cl	17	27	0.00	0.00	0.00	0.00	20.59
Cu	29	407409	76.52	98.82	97.69	2.07	2.71
		Sum	**77.43**	**100.00**	**100.00**		

Figure S5, EDS measurements on the Cassie superhydrophobic copper surface, Cu and S was distributed on the sample.



Map

c

Element	At. No.	Netto	Mass [%]	Mass Norm. [%]	Atom [%]	abs. error [%] (1 sigma)	rel. error [%] (1 sigma)
S	16	7577	0.45	0.58	1.14	0.04	9.41
Cl	17	0	0.00	0.00	0.00	0.00	1.34
Cu	29	394821	77.89	99.42	98.86	2.11	2.70
		Sum	**78.34**	**100.00**	**100.00**		

Figure S6. Dichlormethane was dropped on the superhydrophobic surface, after the complete volatilization, EDS measurements was also tested on the superhydrophobic surface before enough ethanol washing and N_2 drying, Cu and S was distributed on the sample while no Cl was found, indicating the volatilized dichlormethane showed no remnant on the surface.

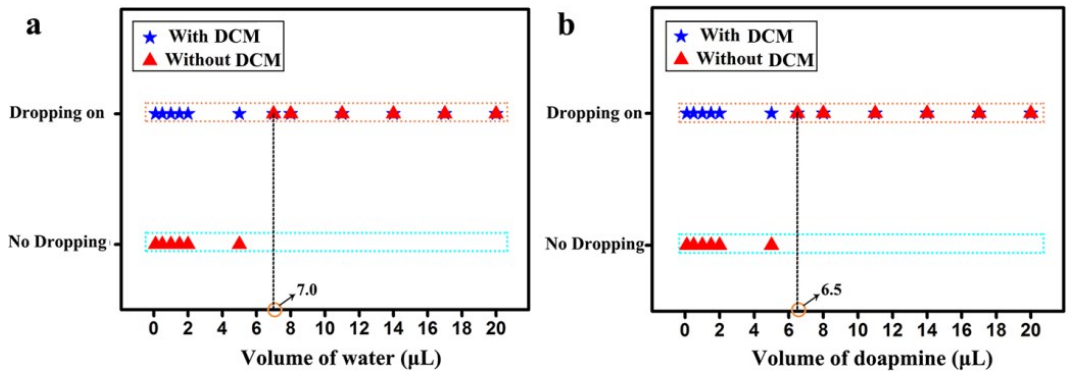


Figure S7. When dichlormethane was used to prewet the Cassie superhydrophobic substrate, the volume of water and dopamine drops could be controlled in as low as 0.1 μL to set on DPCSS. However, on the Cassie superhydrophobic surface, water and dopamine drops could not be settled until its volume increased to 7.0 μL and 6.5 μL, respectively.

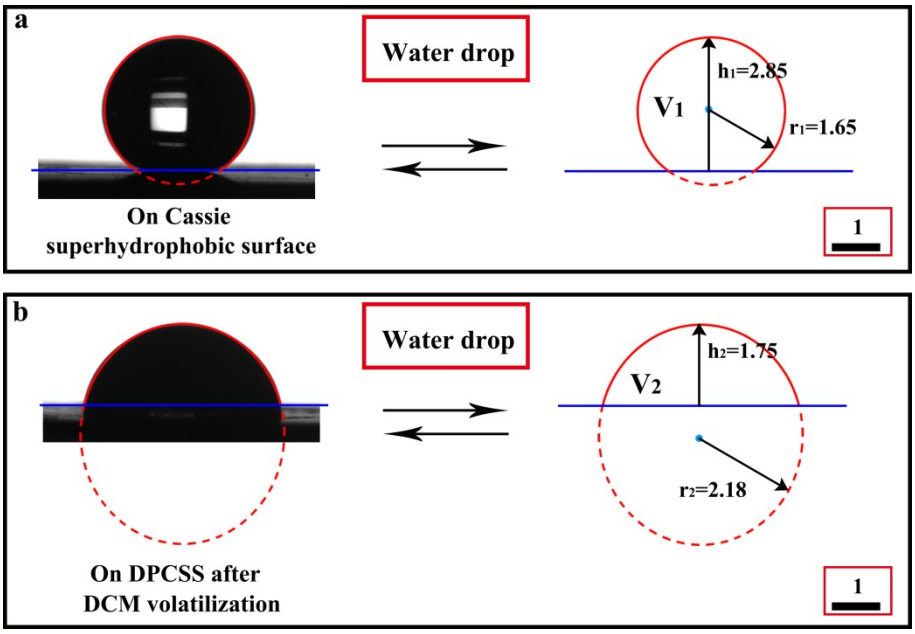


Figure S8. Two water drops (Volume: 8 μL) were set on the Cassie superhydrophobic surface a) and on DPCSS b), which can be nearly treated as spherical crowns. The below full lines represent the front view of two drops. Here, we set a standard length as 1, and further obtained height (h_1, h_2) and radius (r_1, r_2) of the spherical crowns. Thus, the superficial area and volume can be calculated as:

$$S = 2\pi hr \qquad V = \pi h^2(r-h/3)$$

As for the water drop on the Cassie superhydrophobic surface,

$$S_1 = 2*3.14*2.85*1.65 = 29.53 \qquad V_1 = \pi h_1^2(r_1-h_1/3) = 3.14*2.85^2(1.65-2.85/3) = 16.73$$

And, for the water drop on DPCSS after DCM volatilization,

$$S_2 = 2*3.14*1.65*2.3 = 23.83 \qquad V_2 = \pi h_2^2(r_2-h_2/3) = 3.14*1.65^2(2.3-1.65/3) = 14.96$$

Because

$$S_1 = 29.53 > S_2 = 23.83 \qquad V_1 = 16.73 > V_2 = 14.96$$

The water evaporation can be neglected in such short time. Thus, as for the water drop on DPCSS after DCM volatilization, the observed drop volume was less. The loss volume is inferred to fill into the valleys on the surface rough structures.

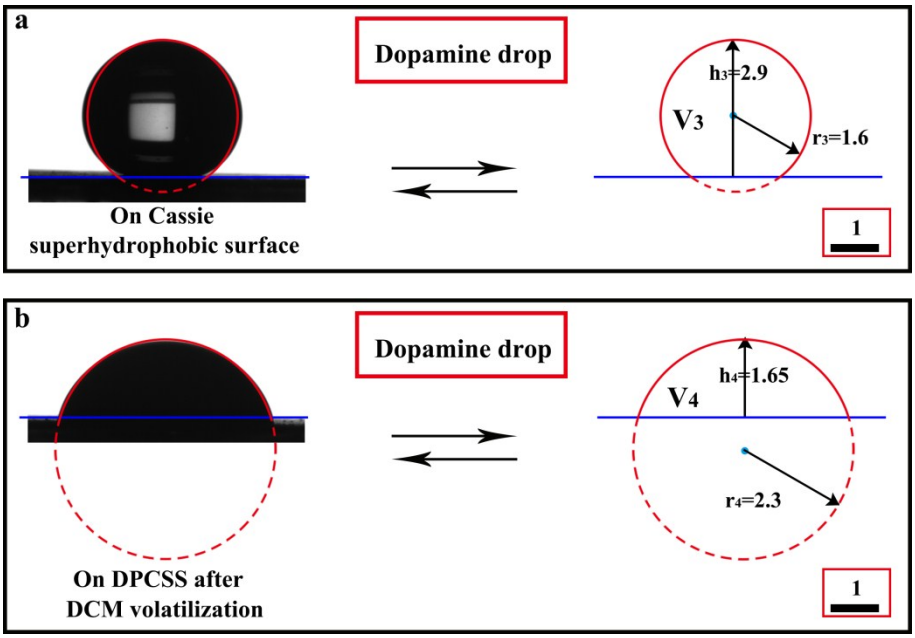


Figure S9. Two dopamine drops (Volume: 8 μL) were set on the Cassie superhydrophobic surface a) and on DPCSS b). The same discussions are shown below:

Superficial area and volume of spherical crowns can be calculated as:

$$S = 2\pi hr \qquad V = \pi h^2(r-h/3)$$

As for the dopamine drop on the Cassie superhydrophobic surface,

$$S_3 = 2*3.14*2.9*1.6 = 29.14 \qquad V_3 = \pi h_3^2(r_3-h_3/3) = 3.14*2.9^2*(1.6-2.9/3) = 17.85$$

And, for the dopamine drop on DPCSS after DCM volatilization,

$$S_4 = 2*3.14*1.65*2.3 = 23.83 \qquad V_4 = \pi h_4^2(r_4-h_4/3) = 3.14*1.65^2(2.3-1.65/3) = 15.35$$

Because

$$S_3 = 29.14 > S_4 = 23.83 \qquad V_3 = 17.85 > V_4 = 15.35$$

So, after DCM volatilization, the dopamine drop on DPCSS also indicated to seep into the rough structures.

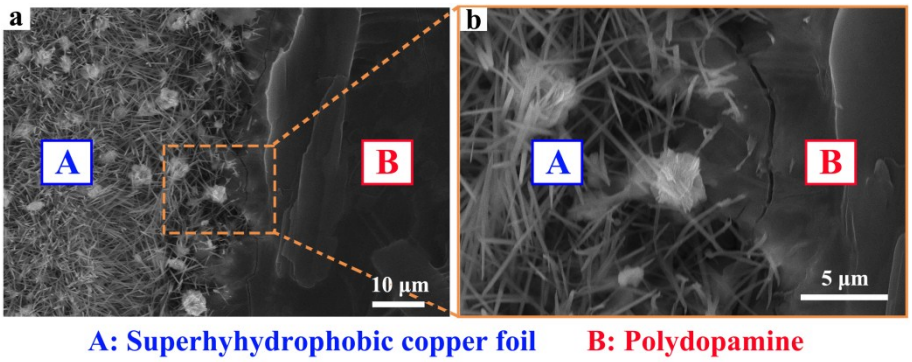


Figure S10. a-b) Top view SEM images of boundary morphology of superhydrophoic copper foil and polydoapmine pattern, b) is the enlarged view of a). The observeations showed polydopamine penetrated the rough structures on the copper surface.

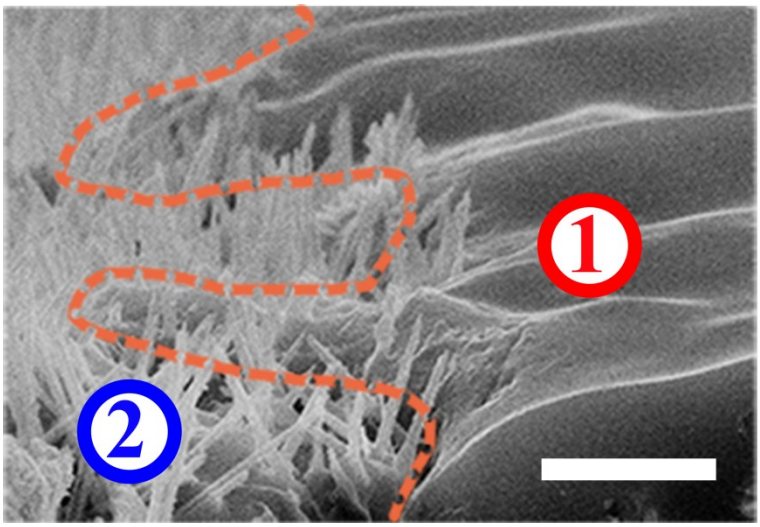


Figure S11. Titled side view SEM image of boundary morphology of polydoapmine pattern and siperhydrophobic surface, the dashed curve shows the edge of polydopamine, which indicated polydopamine permeated into the rough structures on the copper surface. red circle 1 is the polydopamine, blue circle 2 is the rough structures on Cu surface. Scale bar: 5 μm.

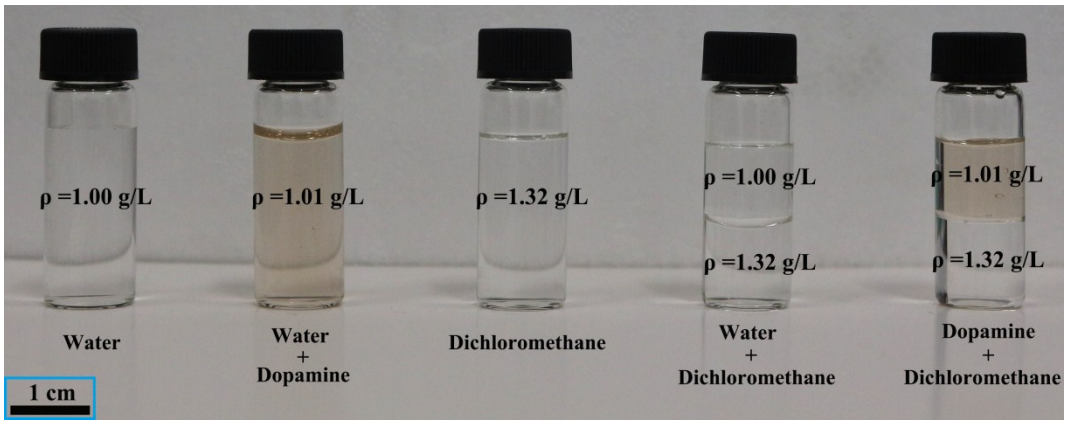


Figure S12. The solubilities among dopamine, water, dichlormethane were showed. Dopamine could dissolve in water (ρ= 1.00 g/L),while water and dopamine aqueous solution (ρ= 1.01 g/L) showed no mutual solubility with dichlormethane (ρ= 1.32 g/L).

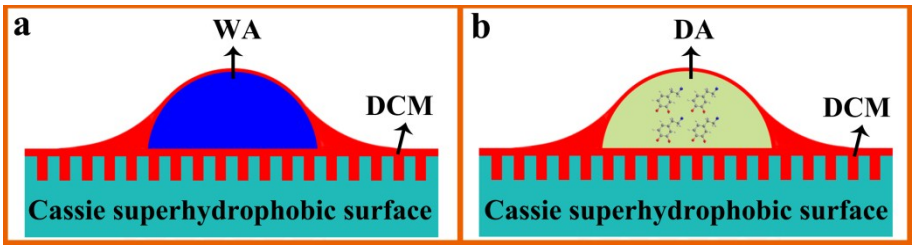


Figure S13. The criterion: $S_{ow(a)} = \gamma_{wa} - \gamma_{wo} - \gamma_{oa}$, was used to judge the cloaking state, where γ is the interfacial tension between the two phases designated by subscripts w (water or dopamine), o (oil), and a (air).

As for water dropped on the dichlormethane surface a), γ_{wa} and γ_{oa} is the respective surface tension of water and dichlormethane in air, γ_{wa} = 72 mN/m, γ_{oa} = 23.1 mN/m, and γ_{wo} means the interfacial tension of water and dichlormethane, γ_{wo} = 27.8 mN/m.

Thus, $S_{ow(a)} = (72 - 27.8 - 23.1)$ mN/m= 21.1 mN/m > 0, **dichlormethane would cloak water drop on the surface.**

As for dopamine drop b), γ_{wa} = 68.5 mN/m, γ_{wo} = 22.2 mN/m,

$S_{ow(a)} = (68.5 - 22.2 - 23.1)$ mN/m= 23.2 mN/m > 0, so **dichlormethane also cloaked dopamine drop on the surface.**

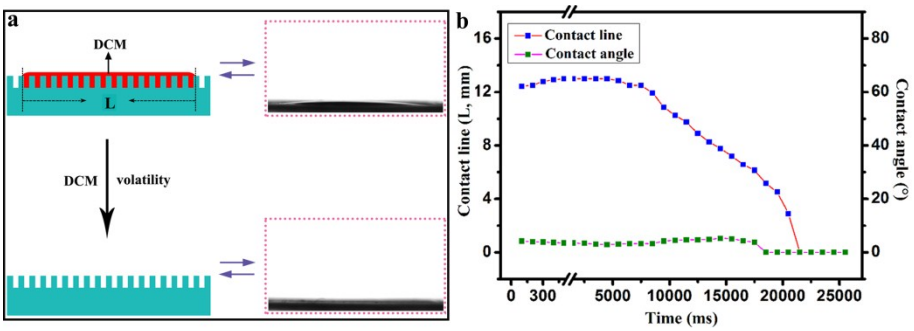


Figure S14. On the Cassie superhydrophobic surface, 20 μL of DCM was dropped on. We observed DCM spread and volatiled on the sample a) with the changing contact line and oil contact angle b).

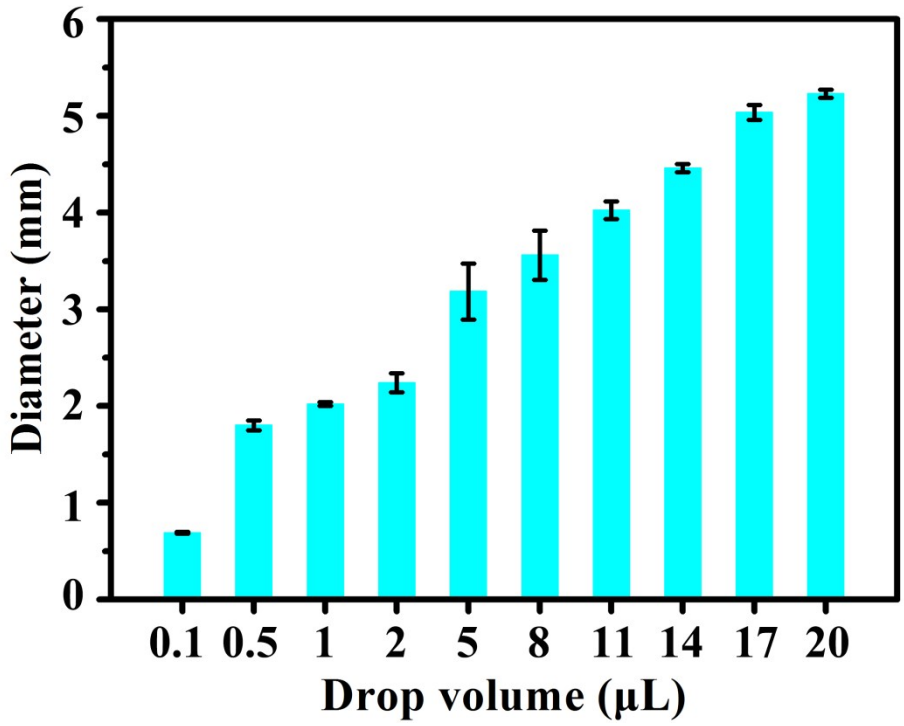


Figure S15. The diameters of the constructed circular patterns was varied depending on different volumes (0.1 μL, 0.5 μL, 1 μL, 2 μL, 5 μL, 8 μL, 11 μL, 14 μL, 17 μL, 20 μL) of dropped dopamine aqueous solution on DPCSS after DCM volatilization.

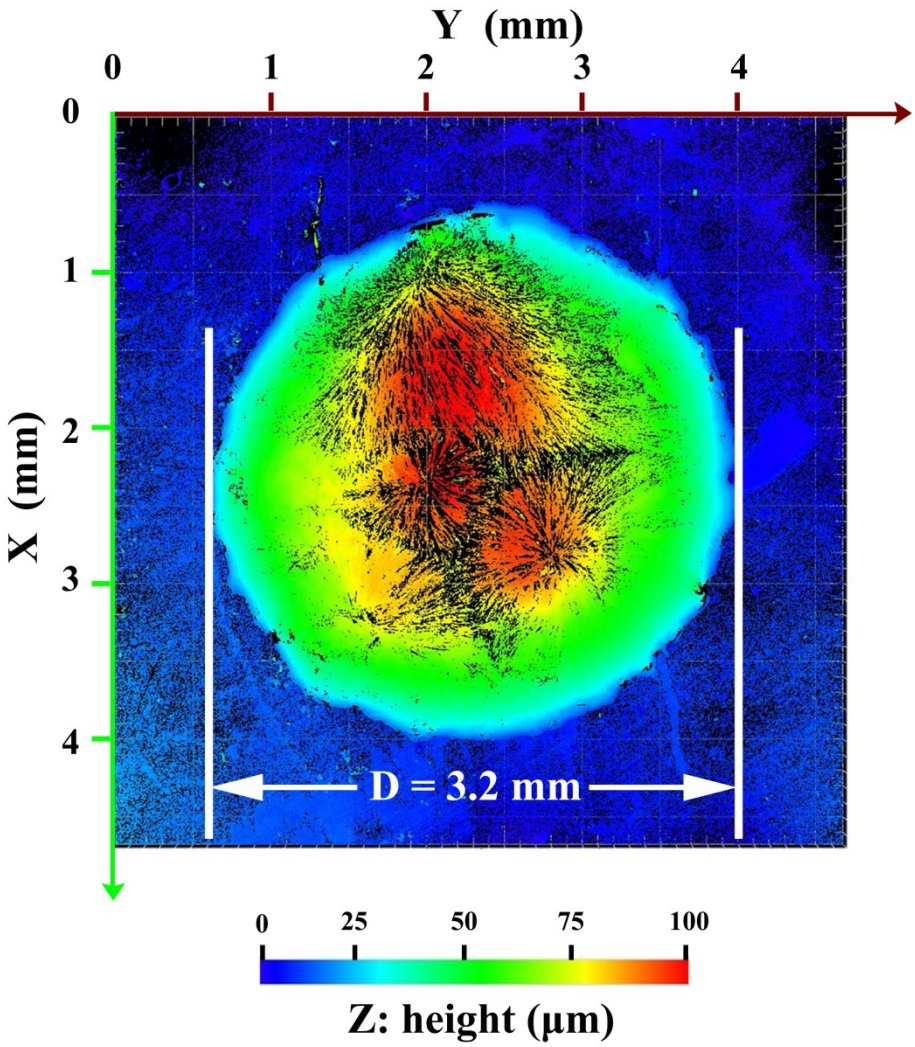


Figure S16. 3D surface view of LCFM images of polydopamine pattern on the Cassie superhydrophobic Cu foil with the bottom diameter of about 3.2 mm, where the colorful circular area represented the polydopamine pattern and the blue area means the superhydrophobic substrate. Z shows the contour line from the superhydrophobic substrate to polydopamine pattern.

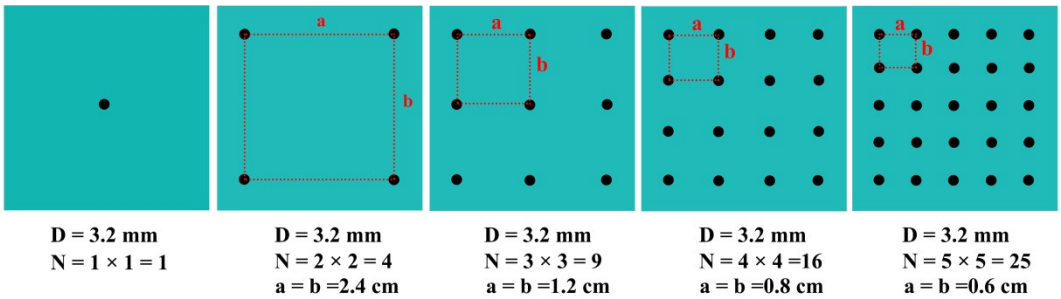


Figure S17. The illustratation of polydopamine patterns prepared on the Casie superhdyrophobic substrates (3×3 cm^2). All the diameters (D) of the polydopamine patterns are about 3.2 mm, the number (N) of arranged patterns are respective 1, 4, 9, 16, 25. a and b means the distance of nearby two patterns, a = b.

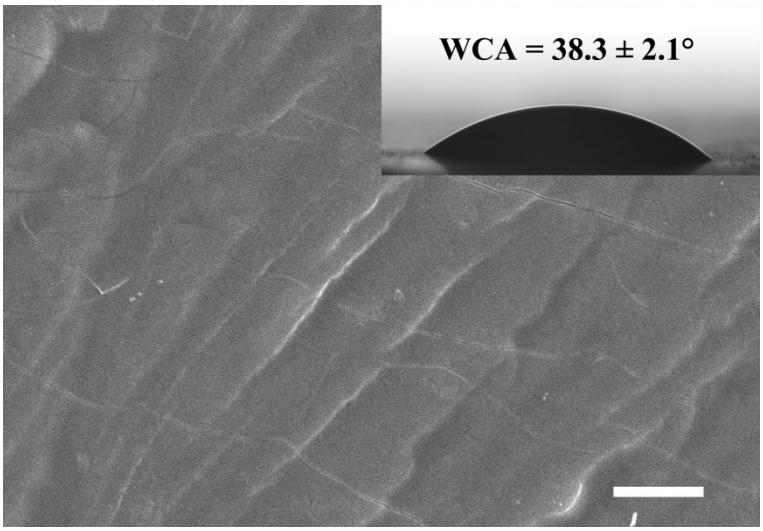


Figure S18. SEM image of polydopamine coated surface, inset shows water contact angle of 38.3 ± 2.1° on the surface. Scale bar: 10 μm.

Sample	Number of patterns (N)	Area of patterns (mm2)	Percentage of SHI areas (%)
Surface I	0	0	0
Surface II	1	7.96	0.9
Surface III	4	31.85	3.5
Surface IV	9	71.67	8.0
Surface V	16	127.41	14.2
Surface VI	25	199.08	22.1
Surface VII	1	900	100

Figure S19. The patterns number, total areas of patterns, percentage of hydrophilic patterns with respect to the total surface area on the seven prepared samples.

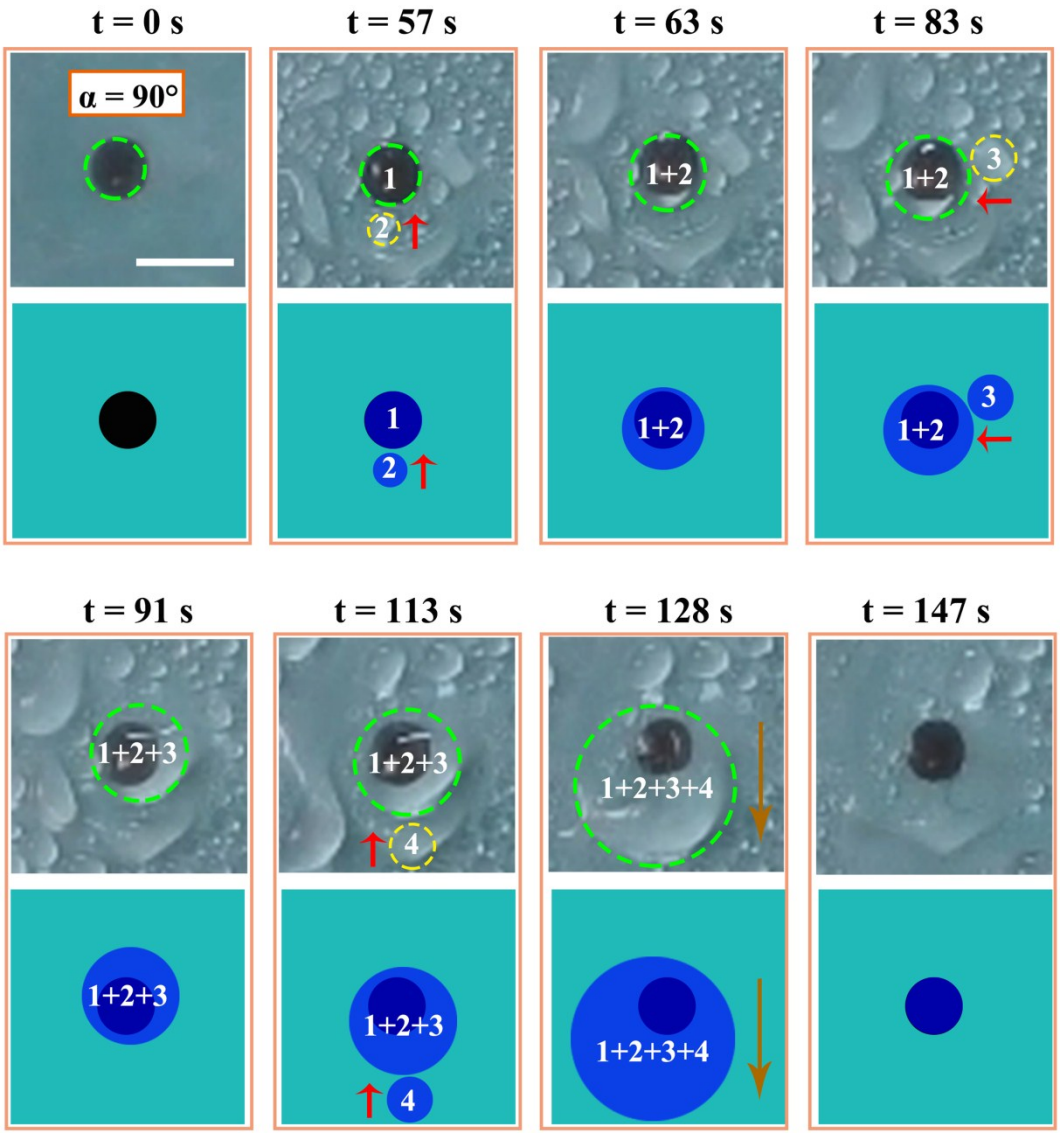


Figure S20. Optical images and schematic images fog harvesting processes on the hydrophilic/superhydrophobic patterned sample at the inclined angle of 90°. Fog was generated from the humidifier at t = 0 s, the hydrophilic pattern capture water from the foggy condition (t = 57 s) (drop 1 in the green dotted line). Then, the nearby drop 2 in yellow dotted line on the superhydrophobic surface would coalesce (red arrow) with drop 1 into a larger drop (drop 1+2), then continue to coalesce with drop 3, drop 4, finally, drop 1+2+3+4 was formed. Once drop 1+2+3+4 grew in a critical size, it would transport from (orange arrow) the sample under gravity. The scale bar is 5 mm.

The phenomenon of water transported to the hydrophilic domain can be explained by the literature of Whiteside and Chaudhury.[1] Because of the imbalance force induced by different wetting behaviors, water would transport to more wettable or high surface energy regions, where the driving force (F_D) can be showed as below:

$$F_D \approx \gamma_W(\cos\theta_I - \cos\theta_O) \quad (1)$$

Here, γ_W is the surface tension of water, θ_I and θ_O means the WCA on the hydrophilic polydopamine pattern and superhydrophobic substrate, respectively. In the above, it was known that $\theta_I < 90°$, $\theta_O > 90°$. So, $F_D > 0$, it produced a force to drive water to hydrophilic area.

However, the large pinning force (F_P) generated by hydrophilic pattern is harmful for water drainage from the surface.[2] F_P can be described as:

$$F_P = \gamma_W L_1(\cos\theta_R - \cos\theta_A) \quad (2)$$

Whereby, L_1 represents the contact line length of the water drop on hydrophilic area, θ_R and θ_A means the receding and advancing contact angles, respectively.

When the pinning water extended to the superhdyrophobic site, the pinning force induced by superhdyrophobic area cannot be neglected anymore: [3]

$$F_P = \gamma_W L_1(\cos\theta_R - \cos\theta_A) + 2\gamma_W L_2 \quad (3)$$

Here, L_1 and L_2 represent the contact line on the hydrophilic pattern and superhydrophobic area.

To ensure water drop fall down from the sample, the drop gravity is of importance to overcome the strong pinning force.[4-5] Then, the result force of water drop can be denoted as F_R, which is simply estimated by:

$$F_R = mg\sin\alpha - F_P = mg\sin\alpha - \gamma_W L_1(\cos\theta_R - \cos\theta_A) - 2\gamma_W L_2 \quad (4)$$

There, m is the water weight captured on the surface, α is the surface inclined angle to horizontal line, here α = 90°. At first, water was captured on the hydrophilic circle, FP is much larger than the gravity of the drop (mg), namely, FR < 0, water was thus pinned on the

surface. With the extension of time, the drop grew larger and larger at a critical size till mg is more than FP, then, FR > 0. So, water can be successfully transported away. Moreover, along the rolling path, many small drops would be taken away and collected in the below container.

Reference

1. (a) M. K. Chaudhury, G. M. Whitesides, *Science* 1992, **256**, 1539; b) X. J. Zeng, L. Qian, X. X. Yuan et al., *ACS Nano* 2017, **11**, 760.
2. C. Antonini, F. J. Carmona, E. Pierce, M. Marengo, A. Amirfazli, *Langmuir* 2009, **25**, 6143.
3. S. J. Hong, C. C. Chang, T. H. Chou, Y. J. Sheng, H. K. Tsao, *J. Phys. Chem. C* 2012, **116**, 26487.
4. C. Dorrer, J. Rühe, *Langmuir* **2008**, **24** , 6154.
5. (a) A. Lee, M. W. Moon, H. Lim, W. D. Kim, H. Y. Kim, *Langmuir* 2012, **28**, 10183. (b) H. Zhu, F. C. Yang, J. Li, Z. G. Guo, *Chem. Commun.* 2016, **52**, 12415.

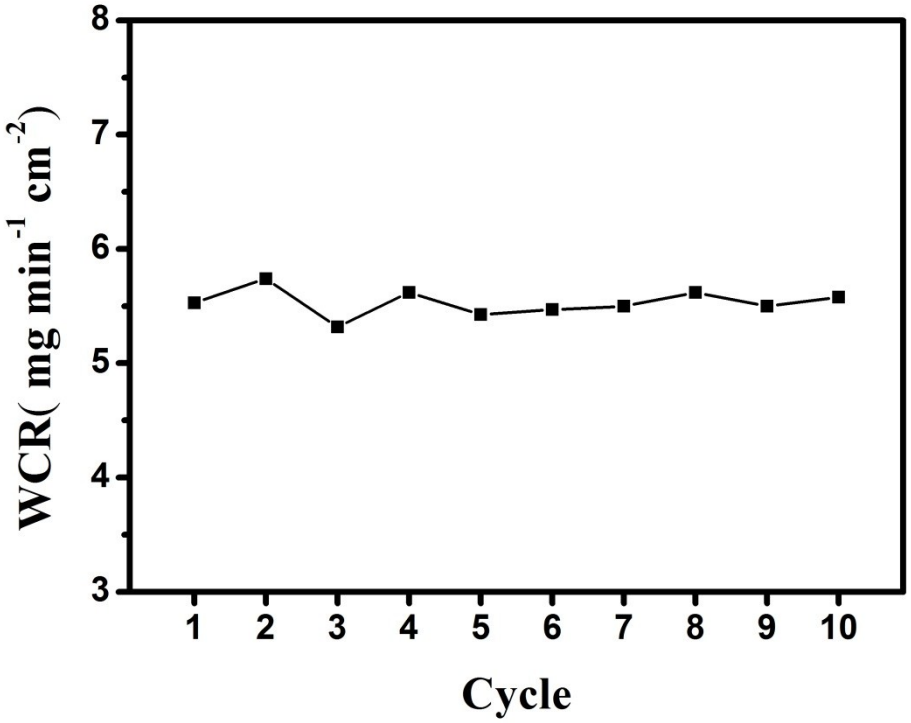


Figure S21. The water collection efficiency cycles were conducted for 10 times on the Cassie superhydrophobic samples with the PHA of 8.0%, which showed excellent efficiency stability.

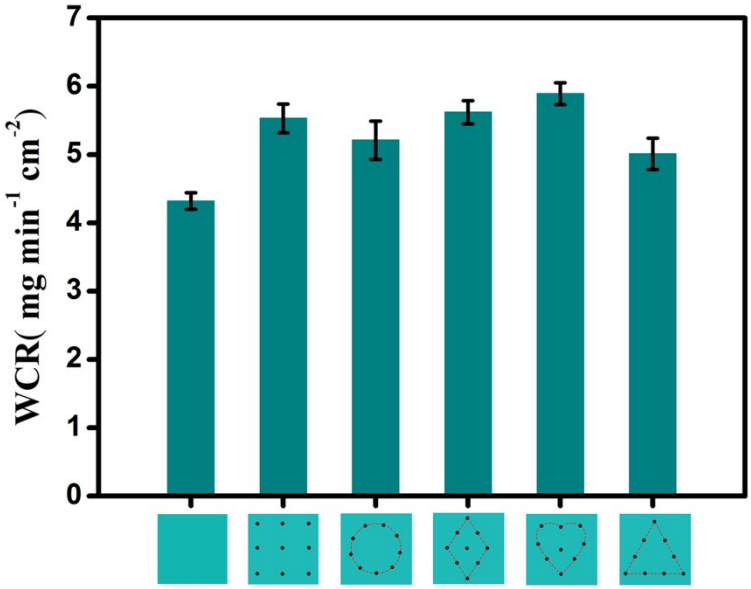


Figure S22. The water collection efficiencies on the Cassie superhydrophobic samples with no pattern, square, circle, diamond, heart, triangle shapes of patterns arrangements. Nine polydopamine patterns on the surface with the PHA of 8.0% showed superior water collection efficiencies.

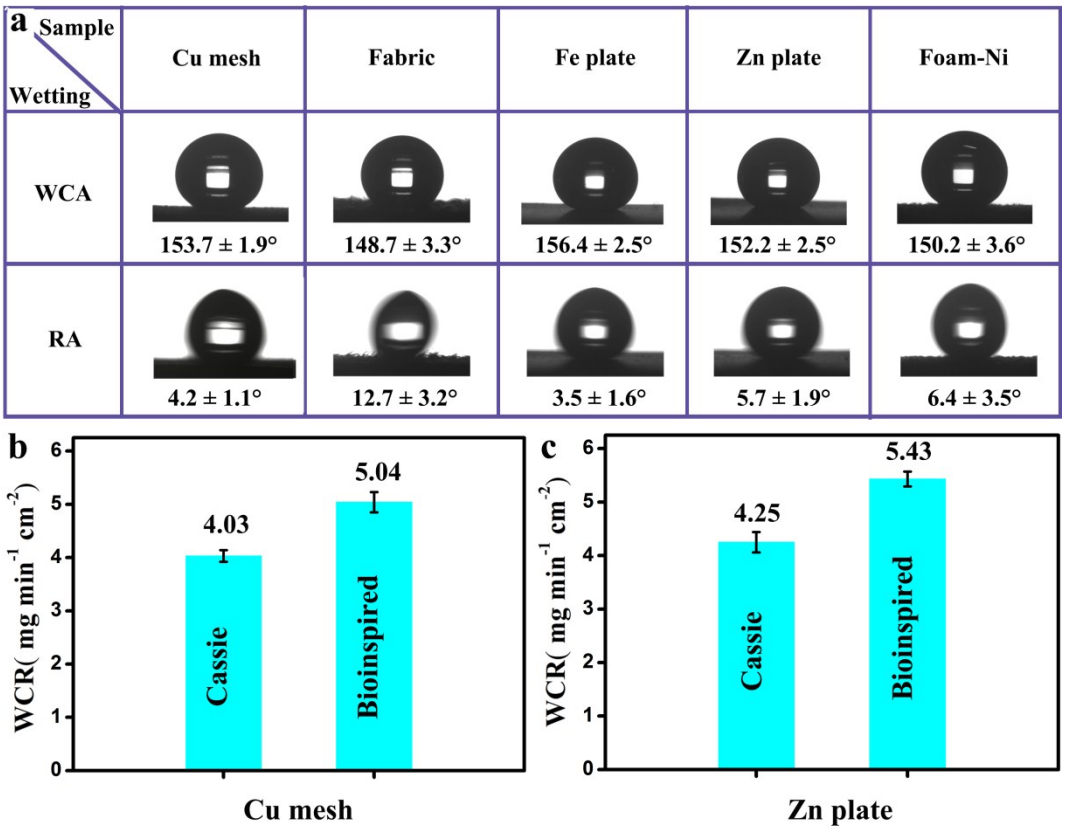


Figure S23. a) Measurements of water contact angles (WCA) and critical rolling-off angles (RA) on the fabricated superhydrophobic materials, i.e., Cu mesh, fabric, Fe plate, Al plate, foam-Ni. Insert images are the optical image of a water drop stably standing on and rolling away from the surfaces. All of the samples exhibit high WCAs and low RAs, indicating the surfaces are superhydrophobic in Cassie state. b-c) Both of the bioinspired beetle-like Cu mesh and Zn plates showed the better WCRs than their Cassie superhydrophobic substrates, As for Cu mesh, $WCR_B = 5.04 \pm 0.19$ mg min^{-1} cm^{-2} > $WCR_C = 4.03 \pm 0.11$ mg min^{-1} cm^{-2}. For Zn surface, $WCR_B = 5.43 \pm 0.14$ mg min^{-1} cm^{-2} > $WCR_C = 4.25 \pm 0.19$ mg min^{-1} cm^{-2}. WCA and RA on the copper wire were not tested because of its extreme shape.

Video S1: Fabrication processes of beetle-like surface. Dopamine aqueous drop (5 μL) was hard to be set on the Cassie superhydrophobic copper foil. Then, dichloromethane (20 μL) was dropped on the sample, which was quickly followed by the dropped dopamine solution (5 μL) on. After dichloromethane volatility, the dopamine drop was firmly pinned to the surface. With enough ethanol washing and N_2 dry to clear the residues, the processes were cycled for more patterns fabrications.

Video S2: Replacing the above dopamine solution by water drop, the similar wetting behaviors in Video S1 can be also observed.

Video S3: In contact angle analyzer, 20 μL of dichloromethane was firstly dropped on the Cassie superhydrophobic copper surface, then 5 μL of dopamine solution was followed to set on the dichloromethane surface, saucer-shaped liquid was formed with varied liquid length and angle along with volatile dichloromethane.

Video S4: In contact angle analyzer, 20 μL of dichloromethane was dropped on the superhydrophobic copper surface and then completely volatilized.