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Journal Name

ARTICLE

Facile approach to prepare quasi-one-dimensional anisotropic wetting surface on copper substrate and its wetting properties

Yiping Tang, Xin Xu, Guangya Hou, Huazhen Cao, Guoqu Zheng*

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In this paper, a facile method was reported to prepare a novel quasi-one-dimensional (Q-1-D) anisotropic wetting surface on copper substrate. The Q-1-D microridges structure of stainless steel twilled Dutch weave mesh (SSDM) was replicated onto the surface of copper film by impression and electroforming techniques, and then the copper film was modified by myristic acid to forming numerous nanoclusters upon the Q-1-D microridges. The copper substrate, having the Q-1-D hierarchical structure of micro-ordered ridges/nano-disordered clusters, exhibited distinctive anisotropic wettability. The effects of modification time on wettability and anti-fouling properties were studied. The results showed that modification time affected the wetting properties greatly by changing topographies. After being modified 132h, the static contact angle (SCA) in parallel and vertical directions were 150.9° and 147.9° respectively. This study proposed a new approach for the fabrication of anisotropic wetting surface on copper substrate, and the anisotropic wetting surface may have potential applications in heat transfer, microfluidic and anti-fouling devices.

Introduction

Superhydrophobic behavior is very common in nature such as the leaves of plants[1-3], the wings of insects[4] and etc, which are non-wettable and water drops can take dust and pollutants rolling off the surface. Inspired by these phenomena, numerous fabrications of superhydrophobic materials were developed intensely for its promising applications in the fields of self-cleaning, fluidic drag reduction and anti-fogging. Anisotropic wettability is a special characteristic of some superhydrophobic surfaces, such as the wetting behavior of water droplet on rice leaf and butterfly wings[5,6]. Artificial surfaces with such properties are intensively pursued in the applications of directional microfluidic devices and self-cleaning coatings.

Surface wettability is depended on the chemical composition and surface geometry[7-10], large numbers of studies reported about changing surface energy and roughness to obtain superhydrophobic surfaces. Enlightened by the Lotus effect, the model of special hierarchical micro/nano structures was widely extend. Up to now, a lot of artificial superhydrophobic surfaces with the micro/nano structures have been fabricated by lithography, plasma etching, vapor deposition and others[11-18]. In terms of the substrates, most of the artificial superhydrophobic coatings were fabricated on the surface of polymer, due to the advantages of low-cost and easy processing. However, polymer substrates can't meet

the demands of high temperature, high strength, and high electrical and thermal conduction, for instance in heat transfer. Superhydrophobic surface on metal substrate was much more difficult to prepare than polymer substrate, as the inherent nature of metal such as high surface energy and hard processing. Recently, some studies about superhydrophobic coatings on metal substrates were reported, such as copper, aluminum and titanium substrates prepared by anodization or chemical etching combined with modification of low energy materials, which exhibited good wettability similar to polymer substrates[11,19-22].

Compared with the great progress of fabricating superhydrophobic surface, the studies on anisotropic wettability were limited by the difficult fabrication of 1-D nanostructures. Several researches prepared anisotropic wetting surfaces by complex methods like chemical vapor deposition and laser interference lithography[23-26]. Hitherto, it still remains a great challenge to develop a simple, efficient, and low cost process to fabricate anisotropic wetting surfaces. To the best of our knowledge, there are few reports about the preparation, wetting behavior and properties of the anisotropic wetting surface on metal substrates.

The authors found SSDM is weaved by microsized wires regularly with Q-1-D microridges, thus we proposed a facile method to prepare anisotropic wetting surface on low density polyethylene (LDPE) surface[27]. This paper, based on the previous work, we put forward a novel route to fabricate anisotropic wetting surface on copper substrate by using the techniques of electroforming and fatty acid modification. The final product of copper sheet with a micro-ordered/nano-disordered structure exhibited excellent anisotropic wettability. The novel fabrication is a very simple, low-

College of Material Science and Engineering, Zhejiang University of Technology, Hangzhou, Zhejiang, 310014, China
Email(G.Q. Zheng):Zhengggq@zjut.edu.cn
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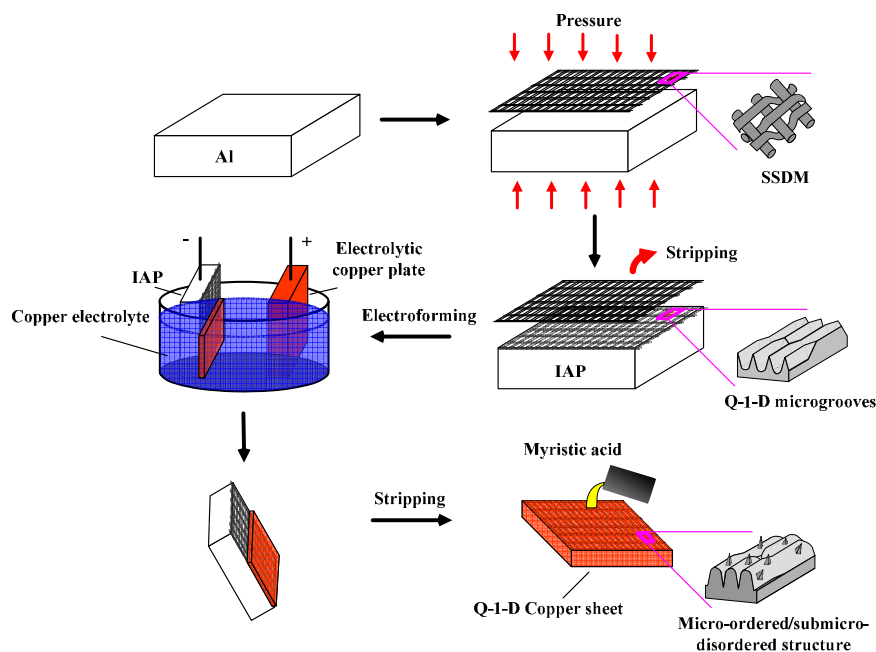


Fig.1. Schematic illustration of the fabrication of the Q-1-D copper sheet with micro-ordered/submicro-disordered structure.

cost, reproducible and large area method. Moreover, it is wide applicable for other metals, if only the metal can be obtained by electroplating and electroforming, such as Ni, Zn, Cr, Sn and etc. And the results indicates that the anisotropic wetting surface on copper substrate may be prospective potential applications in heat transfer, microfluidic and anti-fouling devices.

Experimental

Preparation

Fig.1 shows the fabrication process of the Q-1-D copper sheet. Commercial pure Al plates (99.6%) and SSDMs (1400 mesh) were used and cleaned by the degreaser ($\text{Na}_4\text{P}_2\text{O}_7$: Na_2CO_3 : $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$: OP10 : H_2O = 1.9 : 1.9 : 1.4 : 0.2 : 94.6, weight ratio) at 60~80°C. Then, the Al plates and meshes were washed with distilled water carefully. The SSDMs were laid over the Al plates smoothly and was kept under a constant pressure (about 375 MPa) for 15 min. After the meshes being stripped, specific Q-1-D microgrooves appeared on the impressed Al plates (IAP) surface. The IAPs were immersed in Cu-plating bath for electroforming. The Cu-plating bath was composed of 200 g/L $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, 50 g/L H_2SO_4 , 0.5 g/L sodium lauryl sulfate and 0.5 g/L CuCl_2 . The IAPs with

an exposed surface of 13.4 cm² (3 cm × 4.5 cm), and an electrolytic copper plate was used as anode. The current density is 3 A/dm² and electroforming time is 3.5 h. After electroforming, a thick copper sheet was obtained on the surface of IAP. The copper sheet replicas fully retained the Q-1-D structures of SSDMs. Hence, the copper sheets surface was immersed in the solution of 0.1 M myristic acid in ethanol solution for different time, and then submicro-sized flowers were formed on the Q-1-D structures. Finally, the products of copper sheets with micro-ordered/submicro-disordered structure were obtained. For comparison, some copper sheets were prepared by electroforming and myristic acid modification directly without impression.

Characterizations

The surface morphology of the samples was studied by field emission scanning electron microscopy (FESEM, Hitachi S-4700). The wetting properties were measured by sessile drop method using a surface analyzer (DataPhysics OCA 35). In order to describe the anisotropic wettability exactly, contact angle measured in the directions parallel and vertical to the micro-ordered ridges is defined as shown in Fig. 2. The SCA was measured using a 4μL water droplet. The advancing contact angle (θ_A) was measured

according to the inclination of the surface increases, and the receding contact angle (θ_R) to its reduction. The contact angle hysteresis (CAH) was calculated by the difference between θ_A and θ_R .

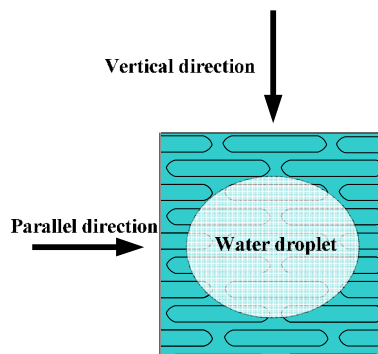


Fig. 2. Schematic for the directional measurement of contact angles on the Q-1-D anisotropic surfaces.

A simple anti-fouling test device was designed as Fig.3 shown. The whole system was fixed to keep the altitude difference constantly. The two water tanks were filled with supersaturated calcium carbonate solution (1 g/L) and the solution was heated up to 80 °C. The as-prepared sample of Q-1-D copper sheet was installed in the container, which was cooled by the flowing water at room temperature. Then the switch and circulating water pump were opened to drive the liquid circular flowing. After 48 h the whole system was closed and the Q-1-D copper sheet was taken out to dry at air environment. The weight change of the sample before and after the anti-fouling test was measured.

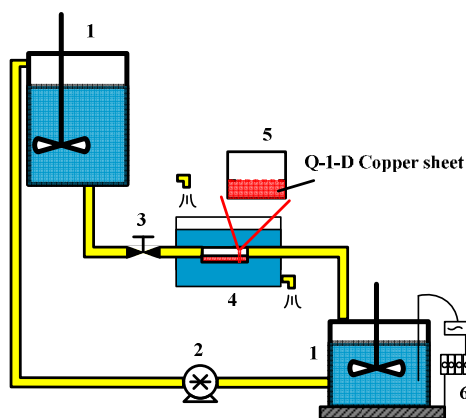


Fig. 3. Schematic for the anti-fouling test device: 1) water tank with a stirrer, 2) circulating water pump, 3) switch, 4) cooling water tank, 5) container with Q-1-D copper sheet and 6) heater.

Results and Discussion

Morphology

The morphology of the replicated samples was observed by FESEM as shown in Fig.4. The SSDM exhibits a regular structure by weaved

steel wires in Q-1-D arrangement, and the diameter of the steel wire is about 38 μm as Fig.4 (a) shown. The hardness of SSDM is higher than that of aluminum, so the ordered ridges of mesh were easily impressed on the Al plate, and thus resulted in the formation of Q-1-D microgrooves on the IAP surface. Electroforming is a traditional replicating technique for the imitation of antiques and crafts, and it is very easy to obtain the replica of Q-1-D copper sheet from IAP, as Fig.4(b) shown. Compared with SSDM, the IAP and the final replica has similar topographical structure. The diameter of the ridges of Q-1-D copper sheet is the same to SSDM 38 μm as Fig.4 (c) shown.

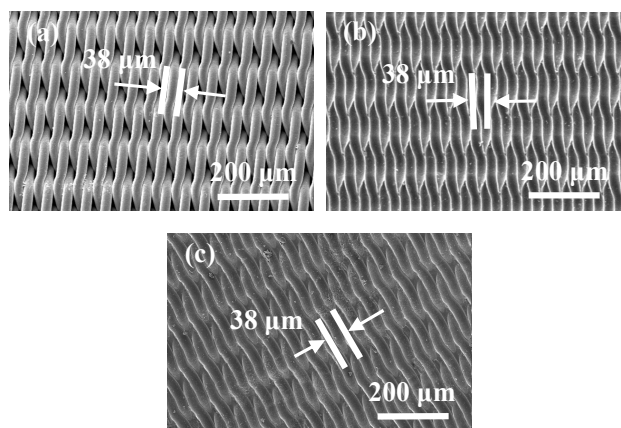


Fig. 4. FESEM images of SSDM (a), IAP (b) and Q-1-D copper sheet (c), showing all of them have similar topographical structure, and the diameter of the ridges and grooves are the same size 38 μm .

The surface topography of the Q-1-D copper sheets modified by myristic acid for different hours were observed as shown in Fig.5. It shows clearly that all the surfaces covered by submicro-sized flower-like materials, and the modification time affects the morphology of flowers greatly. After being modified 33h, several small and short flower clumps distributed on the surface of Q-1-D copper sheet, and the petal diameter was about 1.5 μm , as Fig.5(a-c) shown. The size and amount of the flower clumps was increased gradually with time. When modified 66 h, more petals appeared in each blossom, and the finer petals stood up straight, as Fig.5(d-f) shown, which benefit the improvement of wettability. At 99h, the ridges of the Q-1-D copper sheet were covered by flower clumps, as Fig.5(g-i) shown. As the modification time, the petals became smaller evidently, the diameter was reduced to about 500 nm when immersed for 132h. More flower clumps appeared on the surface even the grooves, which resulting the nearly completed cover, as Fig.5(j-l) shown.

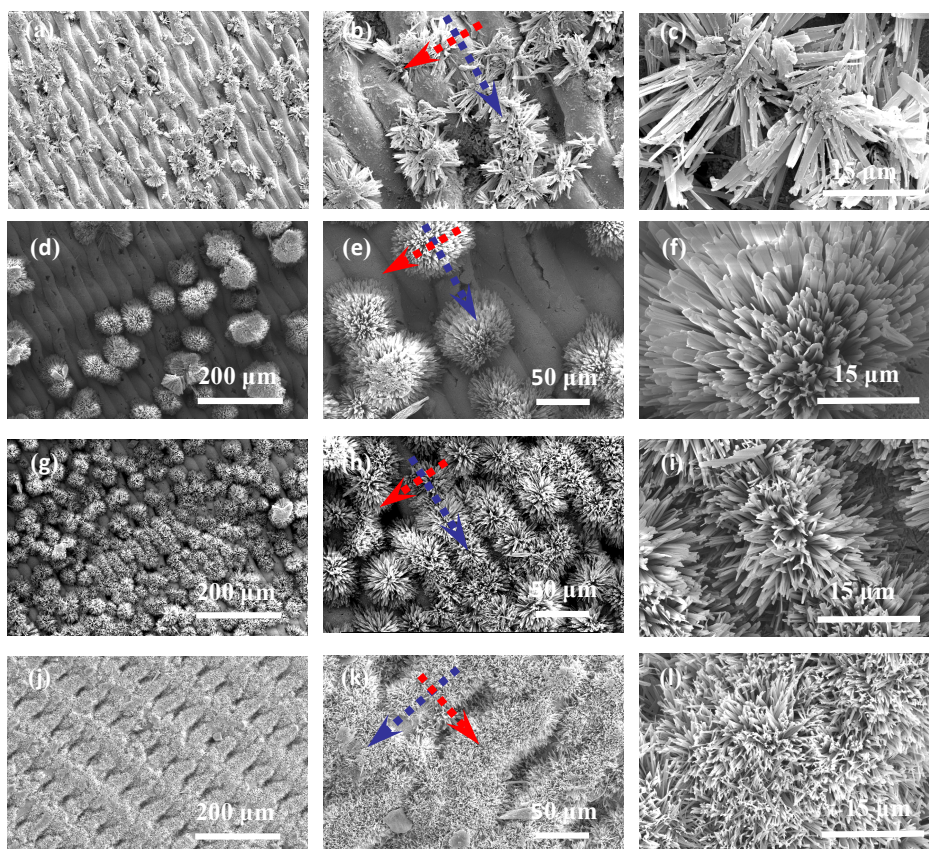


Fig. 5. FESEM images reveal the effects of modification time of myristic acid on the surface topography of Q-1-D copper sheets: (a), (b) and (c) 33 h; (d), (e) and (f) 66 h; (g), (h) and (i) 99 h; (j), (k) and (l) 132 h. The red and blue arrows represent parallel and vertical directions, respectively. After 33 h, several small and short flower clumps distributed on the surface, and the petal diameter was about 1.5 μm . As time went on, at 66h and 99h, the size and amount of the flower clumps was increased gradually. At 132h, the petals became smaller, the diameter was reduced to about 500 nm, more flower clumps appeared on the surface even the grooves, which resulting the nearly completed cover. And it shows obviously that the flowers are arranged regularly along the parallel direction, and the difference of parallel and vertical directions is decreased gradually with the modification time increase.

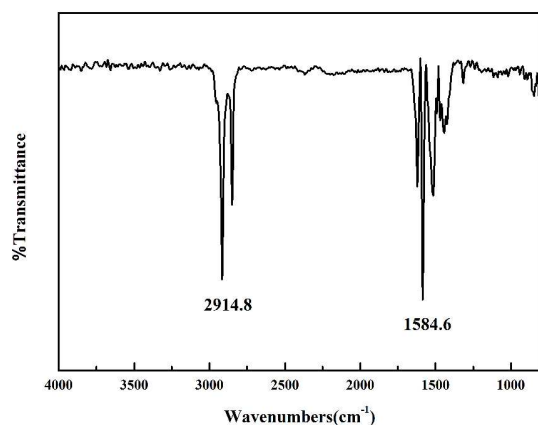


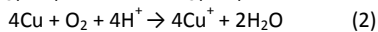
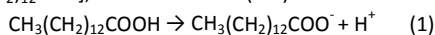
Fig. 6. FTIR spectrum of Q-1-D copper sheet modified by myristic acid for 132 h.

The Q-1-D structure appeared in the surface of copper sheet after modification. Following the parallel and vertical directions, as the red and blue arrows in the Fig.5(b, e, h and k), the flowers are arranged regularly along the parallel direction, the Q-1-D structure

is similar as SSDM. These figures show the flowers almost stand in a line in the parallel direction, and there are some gaps between the near flowers in the vertical direction. And the gaps were reduced gradually with the modification time pass due to the growth of flower clumps on the surface of Q-1-D copper sheet. That means, after the modification of myristic acid, the Q-1-D structure of copper sheet was retained, the difference of the two directions was merely decreased with the modification time. Therefore, for the submicro-sized flowers arising on the Q-1-D surface, the modified copper sheet possesses the hierarchical micro-ordered/submicro-disordered structure, which will result in the novel anisotropic wettability.

The film of Q-1-D copper sheet modified by myristic acid was measured by FTIR as shown in Fig.6. In the FTIR spectrum, the peaks at 1584.6 cm^{-1} and 2914.8 cm^{-1} correspond to the stretching vibrations of COO^- and C-H respectively, which indicates the final product is $\text{Cu}[\text{CH}_3(\text{CH}_2)_{12}\text{COO}]$ with the methyl and carboxyl groups. The possible self-assemble process was deduced as follows[19,21,22]: Myristic acid decomposed to release H^+ and it reacted with Cu resulting in the appearance of Cu^+ , and then Cu^+

reacted with myristic acid to form the final product $\text{Cu}[\text{CH}_3(\text{CH}_2)_{12}\text{COO}]$, as the reactions (1-3) shown.



Wettability

These samples were measured for wettability, which are two direction Q-1-D copper sheets (vertical and parallel) and modified copper sheets without impression, noted as vertical direction, parallel direction and without impression, respectively. The values of SCA and CAH are averaged by measuring ten different positions. The SCAs are shown in Figure 7.

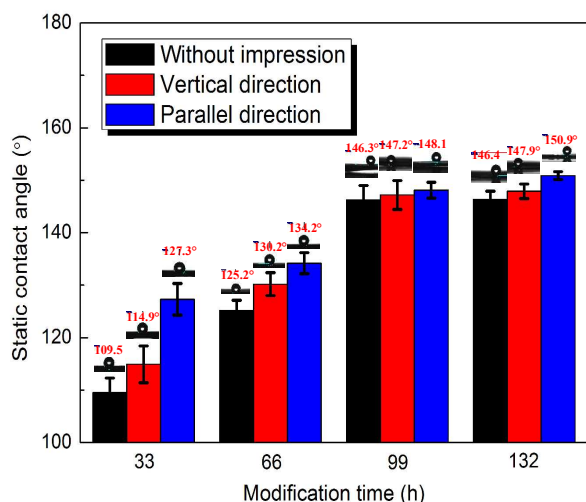


Fig. 7. Variation of SCA of the three samples at different modification time, showing SCA increase with the time, and the vertical direction sample has the highest SCA at the same modification time.

From Fig.7, the SCA of all samples increase with the modification time, which indicates that the film with submicro-sized flowers contributed to the improvement of SCA due to the low surface energy and special nanostructure. There is the same rule that the sequence of SCA is vertical direction (highest), parallel direction, and without impression at all the time. And, with the modification time increase, the SCA gaps among them are gradually narrowing. From 33h to 99h, the SCAs of parallel/vertical direction are $114.9^\circ/127.3^\circ$, $130.2^\circ/134.2^\circ$ and $147.2^\circ/148.1^\circ$ respectively. At 132h, the SCAs of parallel/vertical direction are about $150.9^\circ/147.9^\circ$, it exhibits good wettability as a superhydrophobic and anisotropic Q-1-D copper sheet surface.

The classic models of Wenzel and Cassie-Baxter are widely accepted for explaining some wettability phenomena, especially for some artificial superhydrophobic surface[28-30]. As our pre-research[27], the trend of SCA values (vertical direction > parallel direction > without impression), as Fig.7 shown, is obeyed the both models too, and it transfers from Wenzel to Cassie-Baxter with the modification time increase. The different surface topography results in the different behavior. After 33 h and 66 h modification, some flower clumps were appeared on the surface, and every

clump was composed of numerous long small petals, which increased the roughness of the surface greatly. The water droplet contacted the solid surface completely. According to Wenzel model, the roughness can enhance the wetting property. The roughness of the samples is depended on the Q-1-D micro-ordered/submicro-disordered structure (vertical direction > parallel direction > without impression), and roughness increases with the modification time. Therefore, the roughness rule is consistent with the SCA rule. However, there are enormous changes in the surface topography of the longer modification time, as Fig.5 shown. Flower clumps covered the entire surface even the grooves, there are tiny difference in roughness for different directions, but the hierarchical micro-ordered/submicro-disordered structure is still in the surface. And the smaller petals of the flower clumps trapped a large quantity of air, which accords with the Cassie-Baxter model.

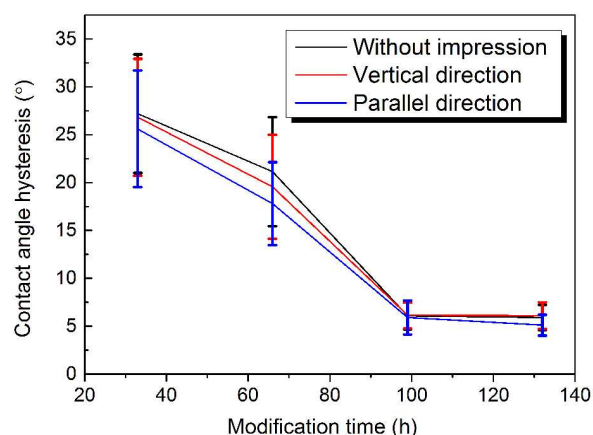


Fig. 8. Variation of CAH of the three samples at different modification time, indicating CAH dropped sharply with the time.

The CAH at different modification time was shown in Fig.8, which was calculated by the difference between θ_A and θ_R . Three curves were dropped sharply from 33h to 99h. At 66h, the CAH in parallel and vertical directions reached $19.6^\circ/17.8^\circ$, which were lower than that of without impression sample 21.1° . And the CAH of all samples approached to nearly the same value 6.0° after 99h modification due to the less and less difference of Q-1-D hierarchical structure in different directions.

For explaining the relationship between wettability and topography, a schematic illustration of water droplet sliding on the surface of Q-1-D copper sheet in two directions was sketched in Fig.9. As we know from Fig.5, the flowers grew on the surface of copper sheet retaining the Q-1-D structure, so the water droplet will be supported by the flowers on the ridges. If it slides in the vertical direction, there are two kinds of gaps should be strided, as the two black circles in Fig.9(a) shown, which means there must be some gaps in each sliding route and it was uncontinuous. However, the sliding route is continuous at the parallel direction, it can detour to near ridges easily if meet the gap, as the two black circles in Fig.9(b) shown. According the three-phase line theory[27,31], the three-phase line in the parallel direction was continuous and short, but in the vertical direction it was discontinuous and long. And, for

the sample without impression, it had continuous and longest three-phase line. Therefore, the CAH order was parallel direction < vertical direction < without impression. But the difference of the two directions tend to decrease with the modification time. As the modification is processed, the amount and size of flowers increase gradually, the gaps (the black circle in Fig.9) will be narrowed and even faded, as Fig.5(b, e, h and k) shown. The less and less gap distance leads to the reduction of difference wettability in the two directions and without impression samples, that is the reason for the small difference of SCA and CAH for all the samples after long timemodification (99h and 132h).

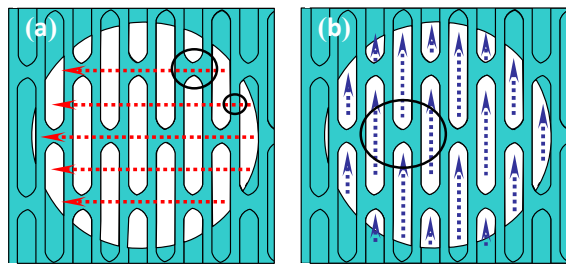


Fig.9. Schematic illustration of water droplet (the white area) sliding on the surface of Q-1-D copper sheet in vertical direction (a) and parallel direction (b). There must be some gaps in each sliding route along the vertical direction, as the black circles shown. However, the sliding route is continuous at the parallel direction, it can detour to near ridges easily if meet the gap, as the black circles shown.

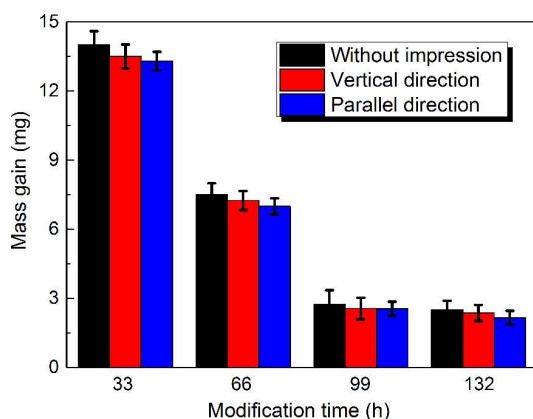


Fig. 10. Comparison anti-fouling properties of the three samples at different modification time. The parallel direction sample always has lower mass gain, indicating the good anti-fouling performance.

The three samples with different modification time were used for anti-fouling test, the results were shown in Fig.10. As the modification time increase, the mass gain of all samples was decreased sharply, and reduced to the lowest at 132h. And it is obvious that the mass gain of parallel direction samples is less than that of without impression and vertical direction samples at different modification time. It implies that the anisotropic wettability of parallel samples with the Q-1-D hierarchical structure results in the better performance of anti-fouling, which means the

Q-1-D anisotropic wetting copper surface has a potential application in anti-fouling devices.

Conclusions

A novel Q-1-D anisotropic wetting copper surface was prepared by a facile method. Q-1-D microridges structure of SSDM was replicated onto the surface of copper by impression and electroforming techniques, and the copper surface was modified by myristic acid to forming the Q-1-D hierarchical structure of micro-ordered ridges/nano-disordered clusters. Modification time affected the wetting properties greatly, after 33h the SCA in parallel and vertical directions were $114.9^\circ/127.3^\circ$, it increased to $150.9^\circ/147.9^\circ$ at 132h. And the parallel direction samples exhibited good performance at anti-fouling test. Hence, the anisotropic wetting copper has promise applications in heat transfer and anti-fouling devices, and the novel method can be applied to prepare other metal materials with anisotropic wetting surface.

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References

1. C. Sanchez, H. Arribart, M. M. G.Guille, *Nature Mater.*, 2005, **4**, (4), 277-288.
2. W.Barthlott, C. Neinhuis, *Planta*, 1997, **202**, (1), 1-8.
3. K.Koch, B. Bhushan, Y. C.Jung, W.Barthlott, *Soft Matter*, 2009, **5**, (7), 1386-1393.
4. F.Xia, L.Jiang, *Advanced Materials*, 2008, **20**, (15), 2842-2858.
5. L.Feng, S. H.Li, Y. S.Li, H. J.Li, L. J.Zhang, J. Zhai, Y. L.Song, B.Q.Liu, L. Jiang, D. B.Zhu, *Advanced Materials*, 2002, **14**, (24), 1857-1860.
6. Y. M.Zheng, X. F.Gao, L. Jiang, *Soft Matter*, 2007, **3**, (2), 178-182.
7. L.Jiang, R. Wang, B.Yang, T. J. Li, D. A.Tryk, A.Fujishima, K.Hashimoto, D. B.Zhu, *Pure and Applied Chemistry*, 2000, **72**, (1-2), 73-81.
8. Q.Cheng, L. Jiang, and Z. Tang, *Acc. Chem. Res.*, 2014, **47**, 1256-1266.
9. Q. Cheng, M. Li, Y.Zheng, B.Su, S. Wang and L. Jiang, *Soft Matter*, 2011, **7**, 5948-5951.
10. Q.Cheng, M.Li, F. Yang, M. Liu, L. Li, S. Wang and L. Jiang, *Soft Matter*, 2012, **8**, 6740-6743.
11. B.T.Qian, Z.Q. Shen, *Langmuir*, 2005, **21**, (20), 9007-9009.
12. J.Fresnais, J. P.Chapel, F. Poncin-Epaillard, *Surface & Coatings Technology* 2006, **200**, (18-19), 5296-5305.
13. K. K. S.Lau, J.Bico, K. B. K.Teo, M.Chhowalla, G. A. J.Amaratunga, W. I.Milne, G. H.McKinley, K. K. Gleason, *Nano Letters*, 2003, **3**, (12), 1701-1705.
14. N.Zhao, F.Shi, Z. Q.Wang, X.Zhang, *Langmuir*, 2005, **21**, (10), 4713-4716.
15. X. J.Feng, L. Feng, M. H.Jin, J. Zhai, L. Jiang, D. B.Zhu, *Journal of the American Chemical Society*, 2004, **126**, (1), 62-63.
16. Q. Cheng, M.Wu, M. Li, L.Jiang, and Z. Tang, *Angew. Chem. Int. Ed.*, 2013, **52**, 3750-3755.
17. Q.Cheng, M. Li, L. Jiang, and Z. Tang, *Adv. Mater.*, 2012, **24**, 1838-1843.

Journal Name ARTICLE

18. J.Wang, L. Lin, Q. Cheng, and L. Jiang, *Angew. Chem. Int. Ed.*, 2012, **51**, 4676-4680.
19. T. Liu, S. Chen, S.Cheng, J. Tian, X. Chang, Y. Yin, *Electrochimica Acta*, 2007,**52**, 8003-8007.
20. S. Chen, Y. Chen, Y. Lei, Y. Yin, *Electrochemistry Communications*, 2009, **11**, 1675-1679.
21. S. Wang, L. Feng, H. Liu, T. Sun, X. Zhang, L.Jiang, and D.Zhu, *ChemPhysChem*, 2005, **6**, 1475-1478.
22. S. Wang, L. Feng, and L.Jiang, *Adv. Mater.*, 2006, **18**, 767-770.
23. S. Wang, T.Wang, P. Ge, P. Xue, S. Ye, H. Chen, Z. Li, J.Zhang, and B.Yang, *Langmuir*, 2015, **31** (13), 4032-4039.
24. P Li, J Xie, J Cheng and K K Wu, *J. Micromech. Microeng.*, **24** (2014) 075004, 1-14.
25. J.Yong, Q. Yang, F. Chen, D. Zhang, U. Farooq, G. Dua and X. Hou, *J. Mater. Chem. A*, 2014,**2**, 5499-5507.
26. P. Goel, S.Kumar, J. Sarkar, and J. P. Singh, *ACS Appl. Mater. Interfaces*, 2015, **7** (16), 8419-8426.
27. Y.P.Tang, X. Xu,H.Z. Cao, G.Y. Hou, G.Q. Zheng, *Surface & Coatings Technology*,2012, **208**, 32-38.
28. A.K. Kota, Y.Li, J. M. Mabry, A. Tuteja, *Advanced Materials*, 2012,**24** (43) 14, 5838-5843.
29. A. Giacomello, S. Meloni, M. Chinappi, C. M. Casciola, *Langmuir*, 2012, **28** (29), 10764-10772.
30. D. Murakami, H. Jinnai, A. Takahara, *Langmuir*, 2014, **30** (8), 2061-2067.
31. Y.Zhao, Q. Lu, M.Li, and X.Li, *Langmuir*, 2007, 23, 6212-6217.