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ARTICLE TYPE

Lotus leaf-like dual-scale silver film applied as superhydrophobic and self-cleaning substrate

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Lotus leaf-like and petal-like substrates were fabricated by chemical deposition, which behave quite different in superhydrophobic property. Excellent non-sticky, self-cleaning and durable properties were obtained based on the
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Lotus leaf-like and petal-like substrates were fabricated by chemical deposition, which exhibit different superhydrophobic properties. Excellent non-sticky, self-cleaning and durable properties were obtained based on the lotus leaf-like substrate.

15 Traditionally, material with a contact angle (CA) higher than 150° is called as the superhydrophobic surface.[1] CA hysteresis is commonly used to evaluate water droplet adhesion to superhydrophobic surfaces.[2] Taking the CA hysteresis into account, superhydrophobic surfaces can be divided into more
20 than 2 states, that are Wenzel's state, Cassie's state, the "Petal" state[3], the so-called "Lotus" state[4] and the transitional state between Wenzel's and Cassie's states.[5]

In nature, there exist some amazing superhydrophobic living organisms, such as lotus leaves[6] and petal.[3, 7] Structures at
25 nanometer and micrometer scale are required to entrap air below water droplets and thus reduce the liquid−solid contact and cause superhydrophobicity. They both composed of micrometric protuberances and nanometric nubs, however, they act completely different in the sliding angle (SA). This indicates that
30 wetting transition will occur when surface structures get small enough at nanometer scale with the water penetrating into the structure.[3, 8] Jiang et al. reported that the surface of the lotus leaf is covered with dual-scale hierarchical structured protuberances.[9] Previous studies have shown that hierarchical structures can
35 effectively reduce the liquid-solid contact area and water droplet adhesion on superhydrophobic surfaces, which can be seen for example in the combination of submicrometer and micrometer scale structures on the lotus leaf.[10] Although the fine structures are generally termed as nanostructures, their actual dimensions
40 are often at the submicrometer scale of tens or hundreds of nanometers. It is reported that small nanometric structures can cause very high adhesive force, which is very different from the large nanometric structures.[8]

Lotus-like superhydrophobic surfaces exhibit self-cleaning[11],
45 anti-corrosive[12], and anti-polluting[13] characteristics, which have promising industrial and biological applications. Recently, it has been found that dual-scale structures can increase surface's mechanical durability and the wetting stability[14]. The preparation

of superhydrophobic lotus-like states is important for the design
50 and construction of superhydrophobic surfaces with self-cleaning properties.[15] Besides the self-cleaning property, increased mechanical durability has been demonstrated by researchers with the formation of hierarchical nanostructures.[16] So far, there are mainly two avenues to fabricate a superhydrophobic surface:
55 either create a rough structure on a hydrophobic material surface or modify the rough surface with a special low surface energy material.[4, 17] Up to now, many efforts have been made to fabricate a lotus-like superhydrophobic surface, such as electrochemical deposition,[18] sol–gel technique[19], soft lithography[20], plasma
60 etching[21] and polymerization,[21] and the combination of any of them.[22] Compared with the methods described above, chemical deposition is an environmentally friendly, efficient, and low-cost method for introducing dual-scale structures on metal substrates.
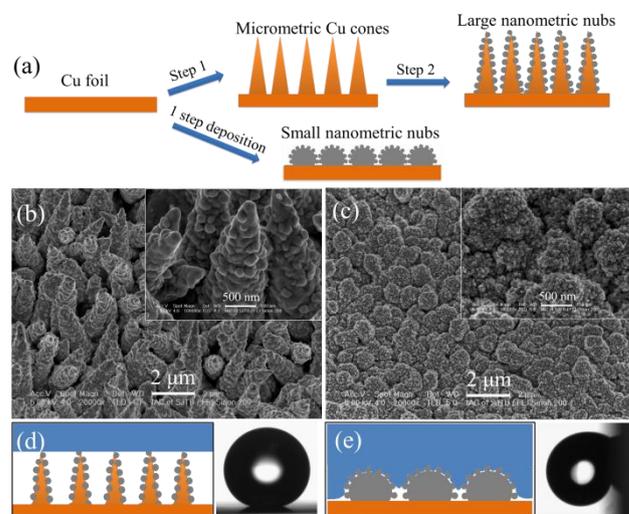

65 **Fig. 1** (a) Schematic image of the preparation process. SEM image of the (b) petal-like silver film, (c) lotus leaf-like silver film, inset is the magnified SEM image. Schematic diagram of the contact state corresponding to (d) Petal state; (e) Lotus leaf state.

70 Herein we reported a two-step chemical deposition method to fabricate lotus leaf-like Cu/Ag dual-scale structure as well as the petal-like dual-scale structure prepared by one-step chemical deposition. Inspired by the lotus leaf, the superhydrophobic surface was prepared by a combination of enhancing the

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micro/nano dual-scale structures and lowering the surface energy through surface modification of n-octadecanethiol (SMO) with the long CH_2 groups.[23] The preparation process is illustrated in Figure 1a. Firstly, Cu microcones were chemically deposited on the copper foil with a diameter about 1μm and a height about 2μm.[24] Then the substrate was immersed into the bath containing 0.02M $AgNO_3$, 0.04M $Na_2S_2O_3$ and 0.02M $K_2S_2O_5$ to form Ag layer on the Cu cone surface. As shown in Fig. 1b, by chemical deposition for 30 min, nanometric nubs with a diameter around 200nm have been formed on the microcones. Just like the lotus leaf surface, this micro/nano dual-scale surface is proved to be non-sticky superhydrophobic with a CA of 166.8° (Fig. 1d) and a SA less than 1° (SI 1) after SMO. In the left of Fig. 1d, the schematic diagram illustrates the liquid-solid-air (LSA) interface between the water drop and the lotus leaf-like surface. It can be seen that the air trapped between the microcones and nanonubs makes contribution to the low CA hysteresis. Superhydrophobic surface with a high CA hysteresis has also been prepared by directly immersing the copper foil into the bath containing 0.02M $C_2H_3AgO_2$ and a certain amount of NH_4OH for 15 min. We can see from Fig. 1c that petal-like structure consisting of micro-scale protuberances and small nanometric nubs with a diameter about 30nm have been deposited on the copper foil. It was tested to be superhydrophobic with a CA of 158.9° (SI 2) and high adhesive with a SA as high as 90° (Fig. 1e). In the left of Fig. 1e, the schematic diagram illustrates that when the size of nanometric nubs getting smaller to tens of nanometers, water will gradually penetrate into the gaps between micro/nano structures.[25] The increasing van der Waal's force between the small nanometric nubs and water will get due to the increasing contact area between water and surface. Consequently, water can adhere tightly to the surface, which is the so-called "Petal effect".
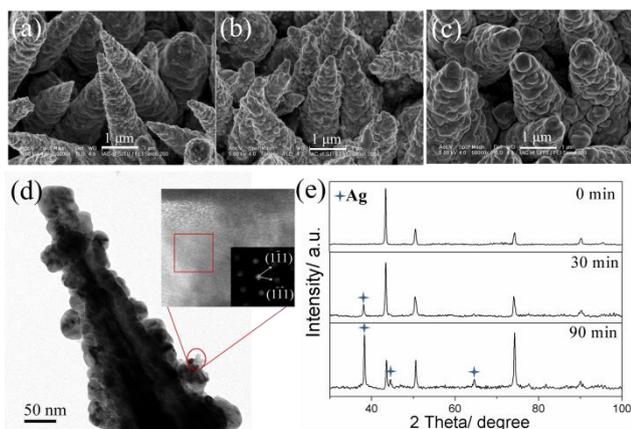

Fig. 2 SEM images of the silver deposited on Cu cones for (a) 10min; (b) 30min; (c) 90min. (d) TEM image of the Cu cone deposited silver for 30s, right-top is the HRTEM image of the red. The inset is the FFT image of the red square part. (e) XRD spectra of the Cu/ Ag dual-scale sample with different deposition time.
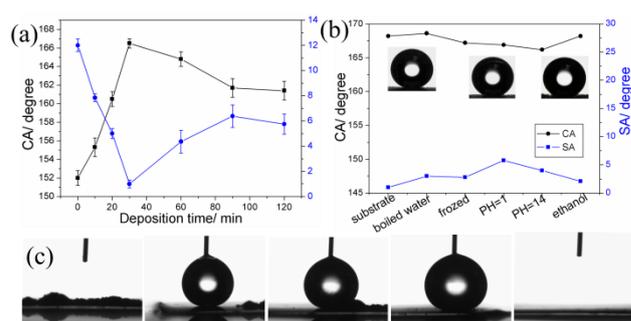

Fig. 3 (a) The change of the CA and SA corresponding to different deposition time. (b) Wettability stability test by immersing the sample into different liquid for 2 hours. (c) Sequential photographs of a self-cleaning test.

From X-ray photoelectron spectroscopy XPS spectra (SI 3), it is notable that the peak of S grew significantly after SMO, which means robust Ag-S bond has formed on the surface with the long alkyl chain pointed outside. Before modification, the CA of lotus leaf-like surface was lower than 10°, while after modification, the CA increased to as high as 166.8°. Unlike the common flat copper surface, wettability changed little after SMO (SI 4), which indicates that the special micro/nano dual-scale structure plays a significant role in superhydrophobicity. Fig.2a-c shows the evolution of surface structure due to different deposition time from 10 min to 90 min of Ag. It is found that at the time of 30 min, distinct nanometric nubs are formed on the Cu cones, which is highly mimicking the lotus leaf structure. When the deposition time comes to 90min, the scale of the nubs increased to submicrometer and thus decreased the air trapped between the microcones. With even longer deposition time, the nubs on the cones will grow into flat, and finally devour the nanogap between microcones (SI 5). These changes in surface nano structure would definitely have an impact on the wettability. Fig. 3a accumulates the CAs and SAs correspond with different deposition time of Ag. It can be seen that as the size of the nanonubs on the Cu cones increased to 20 min, a transition from the Wenzel state to the Cassie state occurs.[26] For 30 min deposition, the lotus leaf-like surface shows the highest CA and the lowest SA. With the disappearance of nanonubs, the transition between the Lotus and Wenzel wetting states will occur as the LAS interface collapses around nanoscale structures.[27]

The crystal growth mechanism of the as-prepared lotus leaf-like substrate has been analysed by X-ray diffraction (XRD) and Transmission electron microscopy (TEM). It is well-known that the free energies associated with the crystallographic planes of an fcc metal decrease in the following order: $\gamma\{110\}>\gamma\{100\}>\gamma\{111\}$.[28] Since {111} crystal face has the lowest free energy in silver crystals, it is reasonable that the deposited Ag are almost contributed by the {111} plane located at 38.1 degrees in the XRD pattern for 30min (Fig. 2e).[29] As the deposition time takes longer, other crystal planes like {220} and {200} will be exposed into a certain amount that can be detected by the XRD equipment. Fig. 2d shows the TEM image of the lotus leaf-like substrate, it is clear to see that a rather thin layer of Ag film was deposited on the Cu cone surface for 1 min deposition. On the border of the Ag layer, HRTEM image exhibits distinct single crystal pattern of Ag. From the Fast

Fourier Transform (FFT) image, we can tell the spots from the {111} and {200} planes, which is coincide with the XRD information.

The purity of lotus leaf is benefited from the self-cleaning property. Our substrate was also tested to behave excellent in self-cleaning. Fig. 3c shows that a 8 μL water droplet cannot stick to the lotus leaf-like substrate though it has to conquer the gravity of the water. By moving the substrate with dust, the water drop can easily sweep the dust away and keep non-sticky to the surface. Durability to different environments and wettability stability are very important for the practical use of the lotus leaf-like substrate. By putting the as-prepared substrate in different extreme environments, such as boiled water, freezing, acid, alkali and organic solutions, after 2 hours, the CA and SA of the substrate slightly changed (Fig. 3b). We also tested the substrate's wettability after exposed in open environment for 2 months, the CA of the lotus leaf-like substrate kept as high as 165° (SI 6). This may be attributed by Ag, which can effectively prevent copper from oxidizing and chemical contaminating from outer environments.[30]

In conclusion, we have successfully fabricated micro/nano dual-scale lotus leaf-like structure by depositing Ag nanonubs on Cu microcones. The Ag layer exhibits perfect single crystal characteristic. Both excellent non-sticky and self-cleaning properties were obtained after SMO. By discussing the different SA performance of two different dual-scale substrates, the mechanism of the transition between Lotus leaf state and Petal state has been somewhat revealed due to the different LSA contact states. Durability to different extreme conditions and stability in wettability property give a promising future for the practical application of the lotus leaf-like substrate.

Notes and references

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1. R. N. Wenzel, *The Journal of Physical Chemistry*, 1949, **53**, 1466-1467.
2. D. Quéré, *Annu. Rev. Mater. Res.*, 2008, **38**, 71-99.
3. L. Feng, Y. Zhang, J. Xi, Y. Zhu, N. Wang, F. Xia and L. Jiang, *Langmuir : the ACS journal of surfaces and colloids*, 2008, **24**, 4114-4119.
4. L. Feng, S. Li, Y. Li, H. Li, L. Zhang, J. Zhai, Y. Song, B. Liu, L. Jiang and D. Zhu, *Advanced materials*, 2002, **14**, 1857-1860.
5. (a) A. Lafuma and D. Quéré, *Nature materials*, 2003, **2**, 457-460; (b) N. A. Patankar, *Langmuir : the ACS journal of surfaces and colloids*, 2004, **20**, 7097-7102.
6. R. N. Wenzel, *Industrial & Engineering Chemistry*, 1936, **28**, 988-994.
7. B. Bhushan and E. K. Her, *Langmuir : the ACS journal of surfaces and colloids*, 2010, **26**, 8207-8217.
8. H. Teisala, M. Tuominen, M. Aromaa, M. Stepien, J. M. Makela, J. J. Saarinen, M. Toivakka and J. Kuusipalo, *Langmuir : the ACS journal of surfaces and colloids*, 2012, **28**, 3138-3145.
9. X. J. Feng and L. Jiang, *Advanced Materials*, 2006, **18**, 3063-3078.
10. X. Zhang, F. Shi, J. Niu, Y. Jiang and Z. Wang, *Journal of Materials Chemistry*, 2008, **18**, 621.
11. (a) K. Koch, B. Bhushan, Y. C. Jung and W. Barthlott, *Soft Matter*, 2009, **5**, 1386; (b) Y. Li, G. Duan, G. Liu and W. Cai, *Chemical Society reviews*, 2013, **42**, 3614-3627.
12. T. da Conceicao, N. Scharnagl, C. Blawert, W. Dietzel and K. Kainer, *Thin Solid Films*, 2010, **518**, 5209-5218.
13. A. Scardino, R. De Nys, O. Ison, W. O'Connor and P. Steinberg, *Biofouling*, 2003, **19**, 221-230.
14. Y. Xue, S. Chu, P. Lv and H. Duan, *Langmuir : the ACS journal of surfaces and colloids*, 2012, **28**, 9440-9450.
15. W. Barthoott and C. Neinhuis, *Planta*, 1997, **202**, 1-8.
16. T. Verho, C. Bower, P. Andrew, S. Franssila, O. Ikkala and R. H. Ras, *Adv Mater*, 2011, **23**, 673-678.
17. G. Jin, H. Jeon and G. Kim, *Soft Matter*, 2011, **7**, 4723-4728.
18. (a)T. Darmanin, E. Taffin de Givenchy, S. Amigoni and F. Guittard, *Adv Mater*, 2013, **25**, 1378-1394;（b）T. Hang, A. Hu, H. Ling, M. Li and D. Mao, *Applied Surface Science*, 2010, **256**, 2400-2404.
19. (a) M. A. Raza, E. S. Kooij, A. van Silfhout, H. J. Zandvliet and B. Poelsema, *Journal of colloid and interface science*, 2012, **385**, 73-80; (b) Y. Li, G. Duan, G. Liu and W. Cai, *Chemical Society reviews*, 2013, **42**, 3614-3627.
20. A. Nakajima, K. Abe, K. Hashimoto and T. Watanabe, *Thin Solid Films*, 2000, **376**, 140-143.
21. B. Balu, V. Breedveld and D. W. Hess, *Langmuir : the ACS journal of surfaces and colloids*, 2008, **24**, 4785-4790.
22. (a) S. Dai, Y. Wang, D. Zhang, X. Han, Q. Shi, S. Wang and Z. Du, *Journal of sol-gel science and technology*, 2011, **60**, 17-22; (b) S.Dai, D. Zhang, Q. Shi, X. Han, S. Wang and Z. Du, *CrystEngComm*, 2013, **15**, 5417.
23. (a) K. Koch, A. Dommisse and W. Barthlott, *Crystal growth & design*, 2006, **6**, 2571-2578; (b) B. Bhushan, Y. C. Jung and K. Koch, *Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences*, 2009, **367**, 1631-1672.
24. W. Zhang, X. Feng, H. Cao, A. Hu and M. Li, *Applied Surface Science*, 2012, **258**, 8814-8818.
25. Y. Wu, T. Hang, N. Wang, Z. Yu and M. Li, *Chemical communications*, 2013, **49**, 10391-10393.
26. M. Gong, Z. Yang, X. Xu, D. Jasion, S. Mou, H. Zhang, Y. Long and S. Ren, *Journal of Materials Chemistry A*, 2014, **2**, 6180.
27. S. Wang and L. Jiang, Advanced Materials, 2007, 19, 3423-3424.
28. (a) B. Nikoobakht, Z. Wang and M. El-Sayed, *The Journal of Physical Chemistry B*, 2000, **104**, 8635-8640; (b) S. Foiles, M. Baskes and M. Daw, *Physical Review B*, 1986, **33**, 7983.
29. (a) J. Brice, *Journal of Crystal Growth*, 1970, **6**, 205-206; (b) J. J. Gilman, *The art and science of growing crystals*, Wiley New York, 1963.
30. P. Li, X. Chen, G. Yang, L. Yu and P. Zhang, *Applied Surface Science*, 2014, **289**, 21-26.