Surface Chemistry

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Remarkably Simple Fabrication of Superhydrophobic Surfaces Using Electroless Galvanic Deposition**

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Much of the recent research on hydrophobic materials has been inspired by the water-repellent nature of lotus leaves (*Nelumbo nucifera* and *N. lutea*), which show a double roughness on their surfaces (nanohairs on microbumps) along with a waxy coating.[1–5] Numerous synthetic hydrophobic surfaces based on polymers,[6–9] glasses,[10] metals,[11] carbon nanotubes,[12,13] and waxes[14,15] have mimicked the lotus's double roughness, and many display superhydrophobicity (usually arbitrarily defined as contact angle, θ, $>150°$). However, very few have achieved the extremely high (170–180°) contact angles that are the most interesting, and those that have are either difficult to prepare[8,12,16–18] or very fragile.[14,15] Here we report a remarkably straightforward method for treating metals which yields robust double-roughness metal surface coatings that pass McCarthy's test for 180° contact angles[19] and which is carried out under ambient conditions using readily available starting materials and laboratory equipment.

The method uses electroless galvanic deposition to coat a metal substrate with a textured layer of a second metal, for example immersion of zinc foil in $AgNO_3$(aq) gives a matt black textured silver surface coating. Subsequent immersion of the metal-coated sample in a solution of a conventional surface modifier such as 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluoro-1-decanethiol (HDFT) covers the textured coating with a low-surface-energy self-assembled monolayer and renders the composite material hydrophobic. Despite the simplicity of this preparation method, it reliably gives materials whose surfaces have the properties associated with the best quality superhydrophobic surfaces. The roll-off angle of 20-mm^3 stationary water droplets on Ag/HDFT-treated Zn plates was found to be $0.64° \pm 0.04°$, and the contact angle, determined by curve fitting of high-resolution images of deposited drops, was approximately $173° \pm 1°$ (Figure 1). Owing to the well-known problems associated with the measurement of very high contact angles,[20,21] we have also used the water-affinity test suggested by Gao and McCarthy which involves searching for any indication of adhesion when a surface is pulled away from a drop of liquid.[19] Our surfaces passed this test for "180°" contact-angle materials. There is clearly a need for detailed investigation of the methods used to characterize these extreme contact angles (the photographic method appears to underestimate the value suggested by the adhesion method), but here we wish to concentrate on this new surface-treatment method and some of the phenomena that it has allowed us to explore, rather than on detailed arguments about contact-angle measurements.

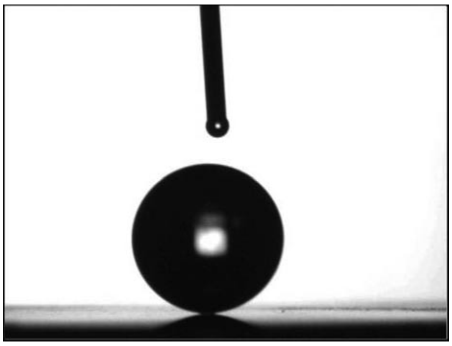

Figure 1. A water drop (8 mm^3) on a silver/HDFT superhydrophobic surface deposited on a copper substrate. Images recorded on similarly coated zinc substrates were identical.

One striking effect of the surface modification is the change in appearance of the treated samples on immersion in water. When a matt black treated metal sheet is immersed in water and viewed at a glancing angle, it appears as a silver mirror (Figure 2). To our knowledge this is the first time that this optical property has been reported for a synthetic material. The critical angle was determined as $48.6° \pm 0.9°$,

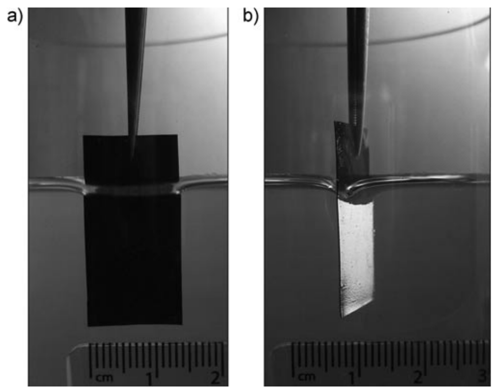

Figure 2. A superhydrophobic copper plate in water viewed a) perpendicular to the surface and b) past the critical angle.

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identical to that for reflection at a normal water/air boundary (48.626°). The absolute reflectivity at 514 nm was found to be $96 \pm 4\%$ at 27.5°. The high absolute reflectivity and the critical-angle measurements both suggest that these are Cassie–Baxter surfaces[22] where the mirrorlike appearance is due to an air layer between the water and superhydrophobic surface. A theoretical discussion of the possibility of such surfaces displaying underwater superhydrophobicity has recently been published.[23] If we assume that the Cassie equation can be applied to these surfaces, then we calculate that less than 1% of the water surface is in contact with the thiolated metal.

This surface-treatment method is extremely flexible: the main requirement for selection of the pair of metals for the substrate and coating layers is that their redox potentials allow the spontaneous reduction of an aqueous solution of the coating metal. For example, we have also prepared superhydrophobic surfaces from gold deposited on zinc, silver on copper foil, and gold on copper foil. Changing the bulk metal has no significant effect on the photographically measured contact angle ($173° \pm 2°$ for silver on copper), and the surfaces also pass Gao and McCarthy's 180° test.

Scanning electron microscopy of all four combinations of silver and gold coatings on copper and zinc substrates revealed the textured metal surfaces that give Cassie–Baxter behavior. It is evident that the deposition of the coating metal naturally generates sufficient roughness to give superhydrophobicity. Figure 3a shows that the gold structures

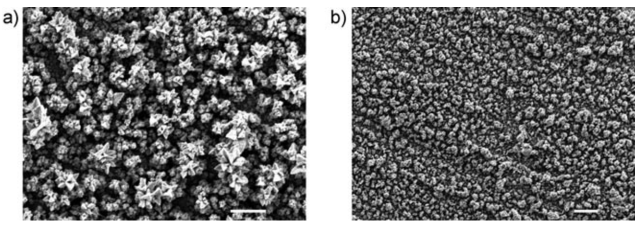

Figure 3. SEM images of a) gold on etched zinc and b) silver on copper. The scale bar in each case is 1 μm.

deposited on zinc are made up of "flowers" each 0.20 to 1 μm and composed of smaller (ca. 60 to 200 nm) faceted crystallites, so there is an obvious "double roughness". The double roughness is less obvious in the silver structures deposited on copper (Figure 3b), but close examination does show that the coating is composed of 150–300-nm clusters of 50–100-nm particles. The exact nature of the surface morphology is clearly not critical because the photographically measured contact angles of both the surfaces shown in Figure 3 (after treatment with HDFT) were identical within the $\pm 2°$ experimental uncertainty. Although there is no significant difference in contact angle between similarly treated copper and zinc objects, we prefer to work with copper since it gives very stable surfaces that show no deterioration even after immersion in water for a week. In contrast, the Zn surfaces degraded over days of immersion with formation of non-hydrophobic areas of $Zn(OH)_2$ (Zn/O atomic ratio 1:2.04, determined by energy-dispersive X-ray spectroscopy (EDX)).

It is known that appropriate surface roughness can enhance hydrophilicity as well as hydrophobicity.[24,25] We have found that treatment of the deposited metal surfaces with 1-mercaptohexanol, which would be expected to form less hydrophobic self-assembled monolayers, leads to a complete reversal of the wettability; the contact angle decreases from the 173° value found for HDFT to $2.8° \pm 0.9°$.

The simplicity of the coating method makes it possible for us to take Cu or Zn objects of any reasonable size or shape and to make their surfaces extremely hydrophobic. The entire process is performed under ambient conditions and takes less than 15 min. This has given us the opportunity to study metal objects more complex than simple foil sheets. For example, the deformed meniscus in Figure 2b prompted us to take further inspiration from nature and construct a model pond skater. Pond skaters (*Gerridae*) are supported on water by superhydrophobic legs, which have a hierarchical structure based on oriented microsetae with nanogrooves.[26] In our model (Figure 4), which has a mass of 0.13 g (10 times more than pond skaters of the same size), the copper legs have been treated with silver and HDFT.

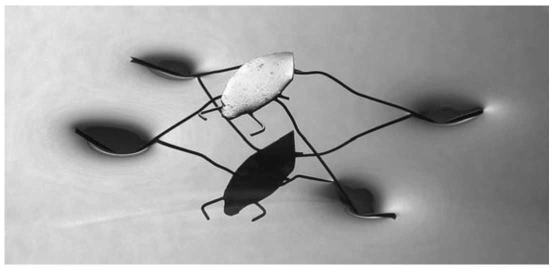

Figure 4. A metallic model "pond skater" (body length 28 mm) standing on a water surface. Note the deformation of the surface around the legs.

On a more practical level these surfaces appear to be ideal for the fabrication of planar microfluidic devices since they can be patterned by mechanical removal of the surface coating, to provide areas or channels of different wettability. Moreover, if fully enclosed conduits or pipes are treated, the flowing water will have minimal contact with the container walls due to the air layer, reducing friction in turbulent flows. It is relevant in these contexts that the surfaces are also simple to repair/regenerate if they are physically damaged, for example, if they are accidentally scraped by a sharp metal object. Immersing the damaged sample into the aqueous metal ion solution results in redeposition of the textured metal, which can then be rethiolated.

Finally, despite the wealth of potential practical applications, we believe the main significance of these materials will be that researchers in many different fields will be able to investigate and exploit superhydrophobic materials with contact angles at or near the 180° limit without being confined to particular substrate geometries or investing in complex fabrication tools.

Experimental Section

Zinc or copper were cleaned with acetone and absolute ethanol, and coated in silver or gold by immersion in aqueous $AgNO_3$ (0.010 mol dm^{-3}) for 20 s or aqueous $HAuCl_4$ (0.004 mol dm^{-3}) for 60 s, washed with water, and blown dry with compressed air. The superhydrophobic surfaces were prepared by immersing the coated metal substrate in $CF_3(CF_2)_7CH_2CH_2SH$ in CH_2Cl_2 (1 mmol dm^{-3}) for 5 min, washing with CH_2Cl_2, and blowing dry. The superhydrophilic surface was prepared by immersing silver-coated copper foil in $HO(CH_2)_6SH$ in water (1 mmol dm^{-3}) for 5 min, washing with CH_2Cl_2, and blowing dry.

Contact-angle measurements were performed by First Ten Angstroms Europe, Cambridge (UK), using a FTA200. Roll-off angles were determined from the tilt angles required to roll initially stationary droplets off the surface in opposite directions and were measured on apparatus designed and built in-house. Adhesion was measured with an FTA200 contact-angle instrument with a frame rate of greater than 40 frames mm^{-1} (frame rate [frames s^{-1}]/speed of surface withdrawal [mm s^{-1}]). SEM images were recorded on a JEOL 6500 FEGSEM operating at 2.5 kV with EDX and WDS chemical analysis systems.

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[1] Y. T. Cheng, D. E. Rodak, *Appl. Phys. Lett.* **2005**, *86*, 144101.
[2] Y. T. Cheng, D. E. Rodak, A. Angelopoulos, T. Gacek, *Appl. Phys. Lett.* **2005**, *87*, 194112.
[3] Y. T. Cheng, D. E. Rodak, C. A. Wong, C. A. Hayden, *Nanotechnology* **2006**, *17*, 1359.
[4] L. C. Gao, T. J. McCarthy, *Langmuir* **2006**, *22*, 2966.
[5] W. Barthlott, C. Neinhuis, *Planta* **1997**, *202*, 1.
[6] J. Y. Shiu, C. W. Kuo, P. L. Chen, C. Y. Mou, *Chem. Mater.* **2004**, *16*, 561.
[7] W. Ming, D. Wu, R. van Benthem, G. de With, *Nano Lett.* **2005**, *5*, 2298.
[8] D. H. Jung, I. J. Park, Y. K. Choi, S. B. Lee, H. S. Park, J. Ruhe, *Langmuir* **2002**, *18*, 6133.
[9] Y. Li, W. P. Cai, B. Q. Cao, G. T. Duan, F. Q. Sun, C. C. Li, L. C. Jia, *Nanotechnology* **2006**, *17*, 238.
[10] K. Ogawa, M. Soga, Y. Takada, I. Nakayama, *Jpn. J. Appl. Phys. Part 2* **1993**, *32*, L614.
[11] B. T. Qian, Z. Q. Shen, *Langmuir* **2005**, *21*, 9007.
[12] 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 Lett.* **2003**, *3*, 1701.
[13] H. J. Li, X. B. Wang, Y. L. Song, Y. Q. Liu, Q. S. Li, L. Jiang, D. B. Zhu, *Angew. Chem.* **2001**, *113*, 1793; *Angew. Chem. Int. Ed.* **2001**, *40*, 1743.
[14] T. Onda, S. Shibuichi, N. Satoh, K. Tsujii, *Langmuir* **1996**, *12*, 2125.
[15] S. Shibuichi, T. Yamamoto, T. Onda, K. Tsujii, *J. Colloid Interface Sci.* **1998**, *208*, 287.
[16] L. L. Yan, K. Wang, J. S. Wu, L. Ye, *J. Phys. Chem. B* **2006**, *110*, 11241.
[17] J. T. Han, Y. Zheng, J. H. Cho, X. Xu, K. Cho, *J. Phys. Chem. B* **2005**, *109*, 20773.
[18] T. Baldacchini, J. E. Carey, M. Zhou, E. Mazur, *Langmuir* **2006**, *22*, 4917.
[19] L. C. Gao, T. J. McCarthy, *J. Am. Chem. Soc.* **2006**, *128*, 9052.
[20] A. Marmur, *Soft Matter* **2006**, *2*, 12.
[21] D. Q. Li, *Colloids Surf. A* **1996**, *116*, 1.
[22] A. B. D. Cassie, S. Baxter, *Trans. Faraday Soc.* **1944**, *40*, 546.
[23] A. Marmur, *Langmuir* **2006**, *22*, 1400.
[24] F. Shi, X. X. Chen, L. Y. Wang, J. Niu, J. H. Yu, Z. Q. Wang, X. Zhang, *Chem. Mater.* **2005**, *17*, 6177.
[25] X. Yu, Z. Q. Wang, Y. G. Jiang, F. Shi, X. Zhang, *Adv. Mater.* **2005**, *17*, 1289.
[26] X. F. Gao, L. Jiang, *Nature* **2004**, *432*, 36.

