Superhydrophobic pure silver surface with flower-like structures by a facile galvanic exchange reaction with $[Ag(NH_3)_2]OH$†

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Superhydrophobic pure silver film composed of flower-like microstructures built by interconnected silver nanoplates on a copper plate without any modification was prepared by a facile galvanic exchange reaction between the aqueous $[Ag(NH_3)_2]OH$ and the copper plate, giving rise to a contact angle as high as 157°.

Superhydrophobic surfaces, inspired by water-repellent surfaces in nature, have attracted a great deal of interest for fundamental research and practical applications.[1,2] The superhydrophobic surfaces are usually fabricated *via* two approaches: creating micro-nanostructures on intrinsically hydrophobic substrates, or chemically modifying the micro-nanostructured surfaces (either hydrophobic or hydrophilic) by materials with low surface free energy.[3] Many elegant methods, such as template synthesis,[4] electrochemical deposition,[5] and so on,[6] have been developed to construct micro-nanostructures on a hydrophilic substrate. To the best of our knowledge, however, it still remains a great challenge to create a superhydrophobic pure metal surface without any modification, as the free metal surface is generally hydrophilic with high surface energy.

Among various metals investigated as the superhydrophobic substrate, copper has attracted intensive interest because it is an important engineering metal with many applications. Several groups have fabricated superhydrophobic surfaces on copper substrates.[7] For example, Jiang and co-workers reported a one-step solution-immersion process for the fabrication of stable bionic superhydrophobic surfaces by oxidizing copper plates with n-tetradecanoic acid.[7a] Safaee *et al.* demonstrated that superhydrophobic silver-coated films on a copper surface can be obtained after passivation by stearic acid.[7d] In both cases, the surfaces were modified without exception by an alkanoic acid that has low surface free energy. However, the existence of such a chemical modification layer on the metal surfaces might affect their intrinsic properties, such as conductivity in the former case, and electrical contacts or surface enhanced Raman spectroscopy of the silver film in the latter case.[8] Therefore, it is both theoretically and practically significant to create silver films of superhydrophobicity on the copper plate without any chemical modification, especially considering the overpotential of the electrodes, corrosion resistance, and so on.

In this communication, we report the preparation of a conducting and superhydrophobic pure silver film on a copper plate without any modification by a facile galvanic exchange reaction, giving rise to a contact angle (CA) as high as 157°. It is suggested that the superhydrophobicity of the as-prepared silver film might result from the formation of micro-nanostructures, *i.e.*, the flower-like microstructures made of interconnected nanoplates. The micro-nanostructure of the film has been readily controlled by adjusting the reaction time and the concentration of precursor, providing different environmentally stable and durable superhydrophobic silver films, even after being exposed to air for several months.

The method started with a surface treatment of the copper substrate, which was firstly immersed in hydrochloric acid to remove oxidants from the surface, and then rinsed with water to eliminate contaminants. Subsequent immersion of this freshly treated copper substrate into an aqueous solution of $[Ag(NH_3)_2]OH$ (0.03 M) led to the formation of a layer of silver film on the copper substrate, through the galvanic exchange reaction,

$$Cu + 2[Ag(NH_3)_2]OH \rightarrow [Cu(NH_3)_4](OH)_2 + 2Ag.$$

Fig. 1a shows a scanning electron microscope (SEM) image of the as-prepared film immersed for 12 h. High magnification SEM indicates that the film is made up of flower-like architectures that are built by interconnected nanoplates (Fig. 1b). The flower-like structures have diameters ranging from 0.5 to 5 μm (Fig. S1†). The building blocks of the flower-like microstructures, *i.e.*, curved nanoplates, have a length of 80 to 300 nm, and a thickness around 8 ± 2 nm. The crystallinity and composition of the nanoplates are characterized by the use of transmission electron microscopy (TEM) and energy-dispersive X-ray spectroscopy (EDX), respectively. The EDX curve (Fig. 1c) of an as-prepared sample exhibits strong peaks of Ag as well as Cu, consistent with the hybrid structure of a silver film coated on a copper substrate. Silver nanoplates removed from the copper plate are characterized by the electron diffraction method. The diffraction spots (Fig. 1f) recorded by directing the electron beam perpendicular to the flat faces of an individual nanoplate are arranged in a six-fold rotational symmetry, implying that the silver nanoplates are

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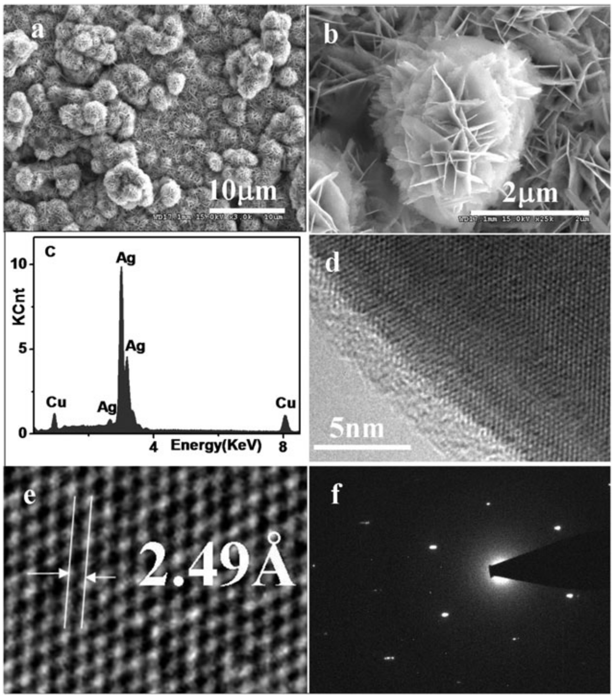

Fig. 1 (a) SEM images of the as-prepared silver surfaces at 12 h. (b) High magnification of (a). (c) EDX of (a). (d) High-resolution TEM of Ag nanoplate. (e) Magnification image of (d). (f) Selected-area electron diffraction pattern obtained by focusing the electron beam perpendicular to the flat surface of the Ag nanoplate.

crystallized in a face-centered cubic (fcc) lattice with the (111) flat surfaces. The set with a lattice spacing of 2.49 Å (Fig. 1e, high-resolution TEM image) is believed to originate from the (1/3){422} reflection that is normally forbidden by an fcc lattice.[9,10*a*,*b*] The uniformity and continuity of the lattice fringes indicate nanoplates are silver crystalline, rather than silver oxide or others. All of these results confirm that pure silver crystalline film on a copper plate is obtained in our experiments by a facile one-step galvanic exchange reaction, without assistant additives as reported by Dai *et al.*[10*c*]

The as-prepared silver film in Fig. 1a resembles the natural lotus-like micro- and nano-hierarchical structures. These structures normally give rise to superhydrophobic surfaces. Indeed, a wetting experiment shows that the water contact angle (CA) of the silver micro-nanostructure film coated on the copper plate is about 156.7 ± 1.6° (Fig. 2c). Moreover, the morphology of the water droplet on the film does not change even after a few minutes, indicating that the film has good chemical and structural stability. The as-prepared pure silver film with superhydrophobicity, which can protect itself from electrochemical corrosion, makes itself very stable and durable.

The wettability of the as-obtained silver film on the copper plate was carefully examined with different immersion times. As shown in Fig. 2a, the freshly treated copper plate itself is hydrophilic with a CA 63 ± 2° (Fig. 2b), consistent with the value reported in the literature.[11] By immersing this copper plate into 0.03 M [Ag(NH$_3$)$_2$]OH solution for 1 h, its wettability switched from hydrophilic to hydrophobic (CA = ∼140°), and became superhydrophobic (CA > 153°) if the immersion time > 6 h. These results reveal that the superhydrophobicity (CA > 150°) of a pure silver surface on a metal substrate can be achieved without any chemical modification.

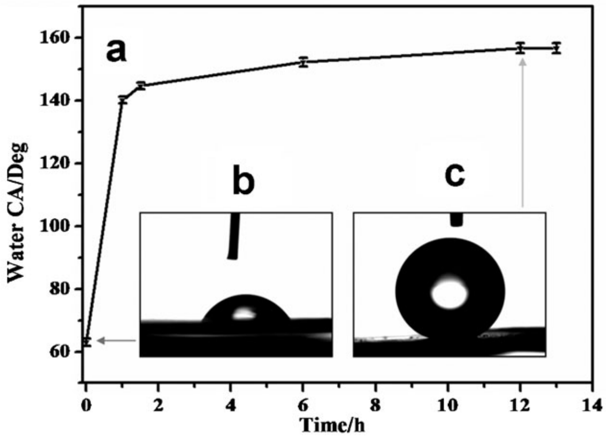

Fig. 2 (a) Water CA measurements on the surfaces of the obtained films as a function of the duration of the solution-immersion time. (b) The shape of a water droplet on a pure plain copper plate. (c) The shape of a water droplet on the film obtained at 12 h.

As the surface morphology and roughness play a very important role in the superhydrophobicity, we studied the surface morphology of the obtained silver films as it evolved as a function of time in different concentrations of [Ag(NH$_3$)$_2$]OH solution. Fig. 3a shows that the silver film is made of interconnected nanoplates with a CA of 140.4 ± 1.0°, obtained by immersing the copper plate into 0.03 M [Ag(NH$_3$)$_2$]OH solution for 1 h. This morphology built by interconnected nanoplates is crucial for turning the silver film to hydrophobic. For example, the silver film obtained by immersing the copper plate into 0.05 M [Ag(NH$_3$)$_2$]OH solution for 1 h is also made of interconnected nanoplates, except that the silver nanoplates are larger (Fig. 4). It is also hydrophobic and the CA is 136.4 ± 1.0°. However, silver films with aligned nanobars are obtained upon decreasing the concentration to 0.01 M;

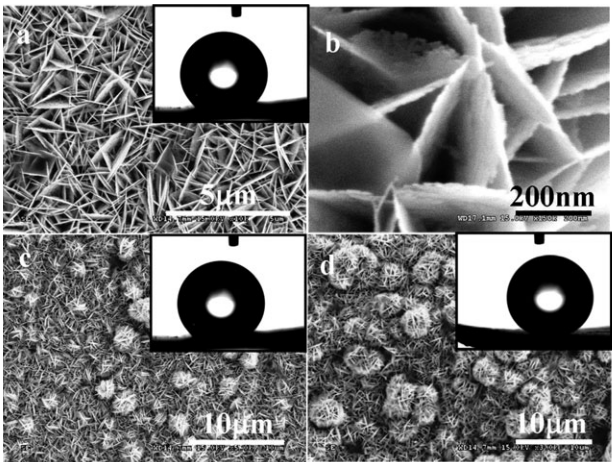

Fig. 3 SEM images of the as-prepared silver surfaces at different time intervals: (a) 1 h, (c) 1.5 h, and (d) 6 h, respectively. (b) is a high magnification image of (a). The inserts in (a), (c) and (d) are the shape of a water droplet on the film obtained at each different immersion time.

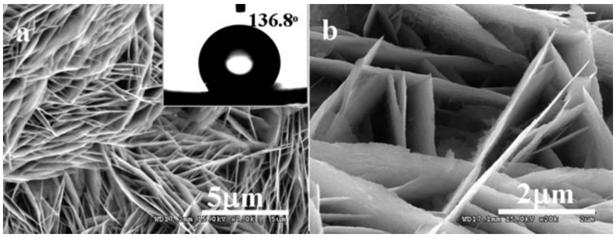

Fig. 4 SEM images of different magnification of the as-prepared silver surfaces (0.05 M, 1 h). The insert image in (a) is the shape of a water droplet on the film.

meanwhile, the CA decreased to 89 ± 1.0° (Fig. S2†), and the films were not hydrophobic. Therefore, it is rational to conclude that this morphology built by interconnected nanoplates is responsible for the hydrophobicity of the film.

When the immersion time in the 0.03 M $[Ag(NH_3)_2]OH$ solution increases to 1.5 h, small flower-like structures organized by nanoplates start to emerge (Fig. 3c). The silver film is hydrophobic and the CA increases. A further increase in the immersion time leads to an increased surface area of the flower-like structures and the flower-like structures grow bigger (Fig. 3d). The obtained film starts to show superhydrophobicity. For immersion times close to 12 h, the flower-like structures grow bigger, become continuous, and almost cover the whole sheet (Fig. 1a). Thus, an interesting continuous coating of flower-like structures is formed on the copper surface and the CA is up to 156.7 ± 1.6°. It is reasonable to deduce that the CA varies according to the surface area of the silver flower-like structures formed at different immersion times, which indicates that the cooperation of lotus-like micro- and nano-hierarchical structures plays an important role in fabricating the superhydrophobic film.

To thoroughly understand the superhydrophobicity of the pure silver film, we describe the CA in terms of the Cassie equation. The CA on a composite surface can be expressed by the equation:[12] $\cos\theta r = f_1\cos\theta - f_2$. Here θr and θ are the CA on the silver film with a rough surface and on the native smooth silver film, respectively; f_1 and f_2 are the fractional interfacial areas of the micro-nanostructures of silver aggregates and of the air in the interspaces among the micro-nanostructured silver, respectively (*i.e.* $f_1 + f_2 = 1$). It is easy to deduce from this equation that increasing the fraction of f_2 increases the CA of the rough surface (θr). Therefore, we ascribe the superhydrophobicity to the contribution of the air trapped in the interspaces of double-scale micro-nanostructures, which means that the surface morphology and roughness are essential in attaining the superhydrophobic film.

In conclusion, although the metal surfaces are generally hydrophilic with high free surface energy, an endurable superhydrophobic pure silver film on a copper substrate without any subsequent chemical modification has been prepared by using a facile galvanic exchange reaction with aqueous $[Ag(NH_3)_2]OH$. The use of $[Ag(NH_3)_2]OH$ here facilitated the formation of unprecedented well-defined silver micrometre flower-like structures composed of nanoplates, which are responsible for the superhydrophobicity of the pure metal surface. In consideration of the special optical and electrical properties of silver nano-materials, the achievement of a superhydrophobic pure silver surface on a pure copper substrate will enable us to find new promising technological applications for them.

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Notes and references

1 (*a*) A. Lafuma and D. Quéré, *Nat. Mater.*, 2003, **2**, 457; (*b*) Z. Gu, D. Wang and H. Möhwald, *Soft Matter*, 2007, **3**, 68; (*c*) T. Sun, L. Feng, X. Gao and L. Jing, *Acc. Chem. Res.*, 2005, **38**, 644; (*d*) N. Takeshita, L. A. Paradis, D. Oner, T. J. McCarthy and W. Chen, *Langmuir*, 2004, **20**, 8131; (*e*) Y. Zheng, X. Gao and L. Jiang, *Soft Matter*, 2007, **2**, 178; (*f*) M. Li, J. Xu and Q. Lu, *J. Mater. Chem.*, 2007, **45**, 4772; (*g*) S. Chen, C. Hu, L. Chen and N. Xu, *Chem. Commun.*, 2007, 1919.

2 (*a*) X. Gao and L. Jiang, *Nature*, 2004, **432**, 36; (*b*) Z. Gu, A. Fujishima and O. Sato, *Angew. Chem., Int. Ed.*, 2002, **41**, 2067; (*c*) Z. Gu, H. Uetsuka, K. Takahashi, R. Nakajima, H. Onishi, A. Fujishima and O. Sato, *Angew. Chem., Int. Ed.*, 2003, **42**, 894; (*d*) L. Gao and T. J. McCarthy, *Langmuir*, 2007, **23**, 9125; (*e*) L. Gao and T. J. McCarthy, *J. Am. Chem. Soc.*, 2006, **128**, 9052; (*f*) T. Wang, X. Hu and S. Dong, *Chem. Commun.*, 2007, 1849; (*g*) X. Zhang, H. Kono, Z. Liu, S. Nishimoto, D. A. Tryk, T. Murakami, H. Sakai, M. Abe and A. Fujishima, *Chem. Commun.*, 2007, 4949.

3 L. Feng, S. Li, Y. Li, H. Li, L. Zhang, J. Zhai, Y. Song, B. Liu, L. Jiang and D. Zhu, *Adv. Mater.*, 2002, **14**, 1857.

4 (*a*) G. Zhang, D. Wang, Z. Gu and H. Möhwald, *Langmuir*, 2005, **21**, 9143; (*b*) J. Y. Shiu, C. W. Kuo, P. Chen and C. Y. Mou, *Chem. Mater.*, 2004, **16**, 561.

5 (*a*) J. L. Zhang, L. J. Xue and Y. C. Han, *Langmuir*, 2005, **21**, 5.

6 (*a*) X. Zhang, F. Shi, X. Yu, H. Liu, Y. Fu, Z. Wang, L. Jiang and X. Li, *J. Am. Chem. Soc.*, 2004, **126**, 3064; (*b*) X. T. Zhang, O. Sato and A. Fujishima, *Langmuir*, 2004, **20**, 6065; (*c*) L. Jiang, Y. Zhao and J. Zhai, *Angew. Chem., Int. Ed.*, 2004, **43**, 4338; (*d*) S. Shibuichi, T. Onda, N. Satoh and K. Tsujii, *J. Phys. Chem.*, 1996, **100**, 19512.

7 (*a*) S. T. Wang, L. Feng and L. Jiang, *Adv. Mater.*, 2006, **18**, 767; (*b*) Z. Guo, J. Fang, J. Hao, Y. Liang and W. Liu, *ChemPhysChem*, 2006, **7**, 1674; (*c*) Y. Zhao, W. Yang, G. Zhang, Y. Ma and J. Yao, *Colloids Surf., A*, 2006, **277**, 111; (*d*) A. Safaee, D. K. Sarkar and M. Farzaneh, *Appl. Surf. Sci.*, 2008, **254**, 2493.

8 B. Wiley, Y. Sun and Y. Xia, *Acc. Chem. Res.*, 2007, **40**, 1067.

9 (*a*) R. C. Jin, Y. W. Cao, C. A. Mirkin, K. L. Kelly, G. C. Schatz and J. G. Zheng, *Science*, 2001, **294**, 1901; (*b*) R. C. Jin, Y. C. Cao, E. Hao, G. S. Metraux, G. C. Schatz and C. A. Mirkin, *Nature*, 2003, **425**, 487.

10 (*a*) Y. Sun, *Chem. Mater.*, 2007, **19**, 5845; (*b*) Y. Sun and P. Wiederrecht, *Small*, 2007, **3**, 1964; (*c*) L. Qu and L. Dai, *J. Phys. Chem. B*, 2005, **109**, 13985.

11 S. T. Wang, L. Feng, H. Liu, T. L. Sun, X. Zhang, L. Jiang and D. B. Zhu, *ChemPhysChem*, 2005, **6**, 1475.

12 A. B. D. Cassie and S. Baxter, *Trans. Faraday Soc.*, 1944, **40**, 546.