'Flower-like' micropillars of copper with porous nanowalls as effective hydrophobic surface

C. F. Tian[1], F. L. Zhang[1], H. H. Cai[2], J. X. Fang*[1] and B. J. Ding[1]

The wetting properties of porous Cu nanowall arrays prepared by a facile replacement reaction are reported. The influences of various experimental parameters including the concentrations of Cu ions and reaction time on final products were investigated. It was found that a hierarchical structure containing micro- and nanoscale structure can be formed on zinc substrate. The measurements of water contact angle indicated that the hydrophobic nature of the hierarchical nanostructures can be tuned by reaction times. When reaction time reached 5 min, its wettability switched from hydrophilic to hydrophobic with a contact angle of $>120°$. By using modified Cassie–Baxter models, we investigated the relation between hierarchical structure and hydrophobic property. Moreover, Cu flower-like hierarchical nanostructures exhibits good hydrophobic properties.

Keywords: Hydrophobic surface, Contact angle, Nanostructures, Roughness, Chemical synthesis

Introduction

In the past several years, copper metal nanomaterials have been investigated widely due to their significant promising applications.[1,2] It was well known that the shapes and textures of nanomaterials determine their electronic,[3] catalytic[4–6] and hydrophobic properties.[7] Hydrophobic surfaces inspired by some plants' leaves and insects' shells hold two common features that one is made of (or covered by) hydrophobic materials, and the other is hierarchical structure at the micro-/nanometre scales.[8–12] Thus, the hydrophobic surfaces are usually fabricated through two approaches: creating micro-/nanostructures on intrinsically hydrophobic substrates or chemically modifying the surfaces (either hydrophobic or hydrophilic) by materials with low surface free energy.[13] Although artificial synthetic hydrophobic surfaces have been fabricated through various approaches, including template method,[7] colloidal assembly,[14,15] nanosphere lithography,[16,17] polyelectrolyte multilayer as matrix,[18,19] electrochemical deposition,[20,21] electrohydrodynamic technique[22] and lithographic patterning,[23] there is still a big challenge to create a hydrophobic pure metal surface without any modification, as the free metal surface is generally hydrophilic with high surface energy.[24]

Among various metals investigated as the hydrophobic substrate, copper and copper alloys have attracted intensive interests to be used as superhydrophobic substrates because it is an important engineering metal with many applications.[24–30] It is noted that Cao *et al.*[24] had successfully built the superhydrophobic pure silver film composed of flower-like microstructures on a Cu plate. However, an economic and facile synthetic route remains quite few. Recently, He's group[21] fabricated porous cobalt nanowall arrays on copper substrate using an electrochemical deposition with polyvinyl pyrrolidone as the protectant, which shows a good ferromagnetic behaviour. However, simple methods, without protectant and surfactant, energy saving and prominent property, are still quite rare for the large scale production and application.

Here, we present a cost effective and facile route through a simple replacement reaction to fabricate copper nanowall arrays on zinc foil. It is noted that the unique self-cleaning property of lotus leaves was due to the interaction of micro- and nanostructures on these surfaces.[31,32] In the present study, by altering and controlling the concentrations of solution and the reaction times, we observe that a hierarchical structure, consisting of flower-like Cu micropillars with nanowalls, was gradually formed. By using modified Cassie–Baxter models, we investigated the relation between the hierarchical structure of the copper nanowall arrays and the hydrophobic property, especially when the rough surfaces change from hydrophilic to hydrophobic to hydrophobic with increasing times.

Experimental

All experiments were carried out at room temperature, and all chemical reagents in the present work were of analytical grade purity without special interpretation.

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[1]School of Science, MOE Key Laboratory for Nonequilibrium Synthesis and Modulation of Condensed Matter, Xi'an Jiaotong University, Xi'an 710049, China
[2]Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou 350002, China

*Corresponding author, email jxfang@mail.xjtu.edu.cn

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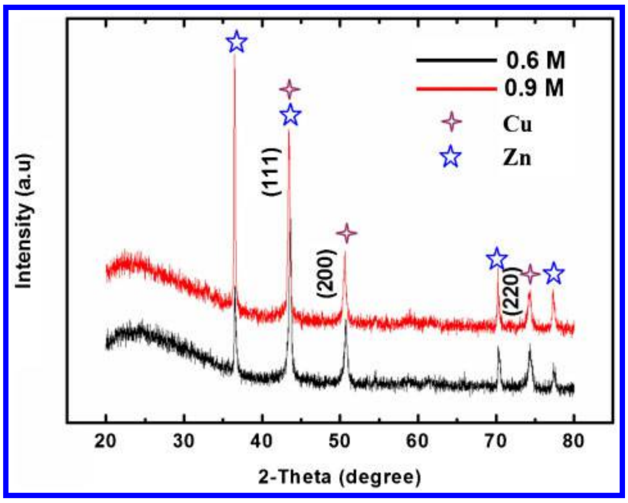


1 **XRD patterns of porous copper nanowall arrays obtained at 0·6 and 0·9M $CuSO_4$ solution for reaction time of 5 min**

To fabricate nanostructures on zinc foil, typically, the zinc foil was first immersed in hydrochloric acid to remove oxidants from the surface and then cleaned by sonication in analytical acetone for 5 min. After rinsing with water to eliminate contaminants, this freshly treated zinc substrate was immersed into 4 mL $CuSO_4$ solution. Different experimental parameters including various concentrations of cupric sulphate solution and the time of replacement reaction were used to study their influences on the hydrophobic properties of the Cu surface. Thus, porous copper nanowall arrays on the zinc substrate were formed through the replacement reaction.

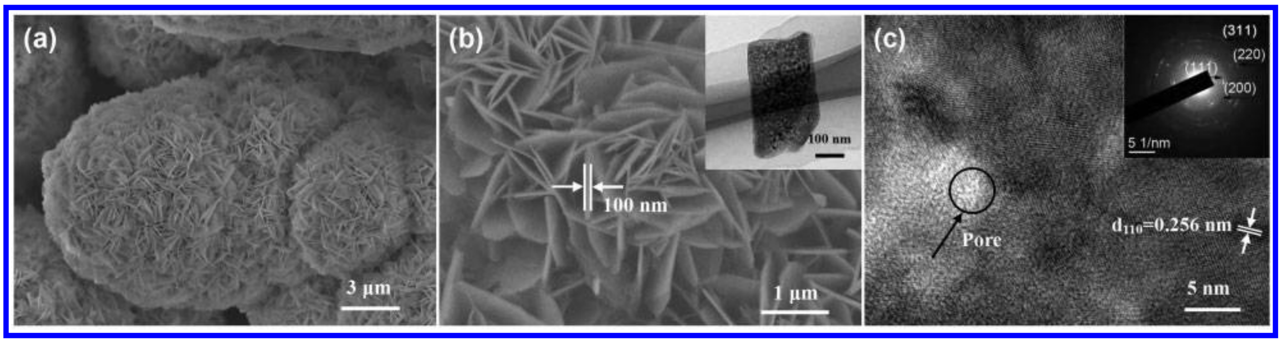
X-ray diffraction (XRD) analysis was carried out using a Bruker D8 ADVANCE X-ray diffractometer with graphite monochromatised Cu K_α radiation (λ=1·5406 Å). A scan rate of 0·028° min^{-1} was used to record the patterns in a 2θ range of 20–80°. The surface structure of the copper was characterised by scanning electron microscopy (SEM, JSM-7000F) and transmission electron microscopy (TEM, JEM-2100). The samples used for TEM observations were prepared by diluting the Cu dispersed solution with ethanol and then placing a drop of the diluted solution onto a copper grid and evaporated in air at room temperature. The sessile drop method was used for contact angle measurements on a commercial contact angle metre (JC2000A, Shanghai). The weight of water droplets used for the measurements was approximately 1 mg. Contact angles were measured at five different points for each sample, and average values were calculated.

Results and discussion

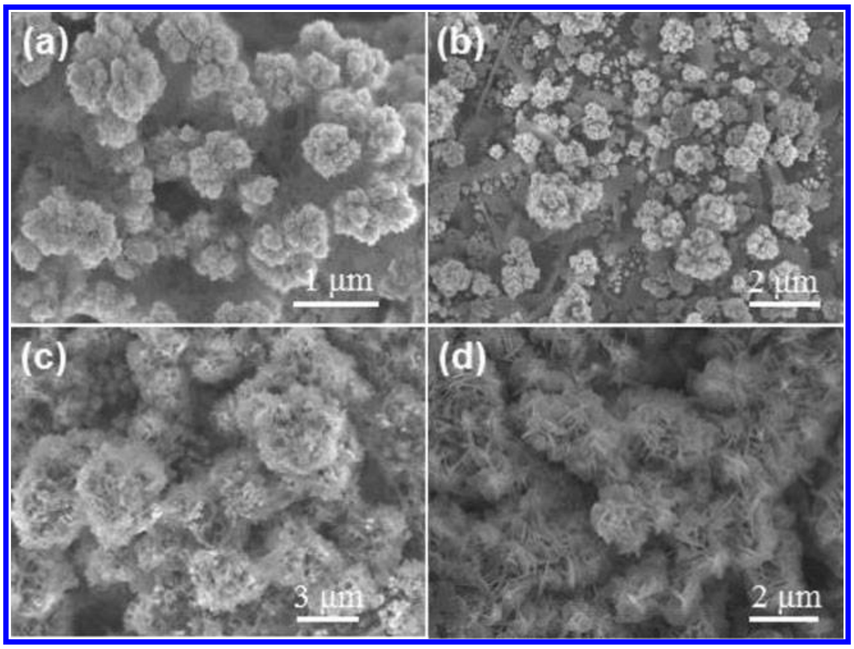
Structural analysis and morphology characterisation

A hierarchical structure of flower-like micropillars with porous nanowalls is formed on zinc substrate at high concentration of Cu ions. The phase structure and purity of the copper nanowall arrays were examined by XRD characterisation. Figure 1 displays the XRD patterns of the as prepared copper nanowalls arrays at 0·6 and 0·9M Cu ion solution respectively. Two sets of Bragg peaks at 2θ of about 43·5, 50·8 and 74·4° are in agreement with the diffraction angles value reported by Song *et al.*[33] and can be assigned to the (111), (200) and (220) planes of copper. This could readily be indexed to the face centred cubic (fcc) structure of metal copper with lattice parameter $a=b=c=3{\cdot}615$ Å, which is consistent with the standard fcc copper (JCPDF no. 85–1326). In addition, the peaks from zinc substrate were marked in Fig. 1. No impurity peaks from copper oxide or hydrate were found in the experiment range, indicating that the copper array was pure metallic copper.

The typical morphologies and structural characters of copper nanowall arrays formed at 0·9 mol L^{-1} Cu ion concentration after 5 min were observed by SEM and TEM in Fig. 2. Figure 2*a* shows an SEM image of as prepared Cu nanowall arrays with most of them perpendicular to the substrate of zinc foil, which reveals that the product consists of a high yield and large amount of flower-like micropillars. In order to gain an insight into the details of the morphology clearly, the magnified SEM image (Fig. 2*b*) is demonstrated, indicating that the thickness of nanowalls are around100 nm and widths are on the scale of hundreds nanometres to several micrometres. A single wall obtained from the broken Cu nanopillars by the ultrasonic treatment in water was further closely observed under TEM (inset in Fig. 2*b*), which indicated that the porous structure had successfully been obtained using the above strategy. To determine the fine microstructure of the obtained products, the high resolution TEM image of a single wall was taken as shown in Fig. 2*c*. It shows that there are several nanopores and numerous small grains having



2 ***a* low magnification SEM image of as deposited flower-like Cu micropillar arrays on zinc foil synthesised at 0·9M $CuSO_4$ solution for 5 min, *b* high magnification SEM image showing porous Cu nanowalls (inset is TEM image of single nanowall broken from copper arrays) and *c* magnified high resolution TEM images of copper nanowall (inset is SAED pattern)**



a 1 mmol L^{-1} 60 min; *b* 50 mmol L^{-1} 10 min; *c* 0·1 mol L^{-1} 5 min; *d* 0·6 mol L^{-1} 5 min

3 Typical SEM images of Cu nanostructures synthesised under various concentrations of CuSO$_4$ solution and different reaction times

crystallite size of approximately 4–10 nm. The corresponding selective area electron diffraction of a collection of nanocrystals is shown in the inset of Fig. 2*c*, which confirms its polycrystalline nature. The diffraction patterns show the rings corresponding to the (111), (200), (220) and (311) reflections. These distances are characteristic of the fcc structure of copper. It should be noted that the rings are constituted of a collection of spots typical of polycrystal. Hence, the formation of copper nanocrystals without any detectable traces of copper oxide can be determined.

Influence of ion concentration and reaction time

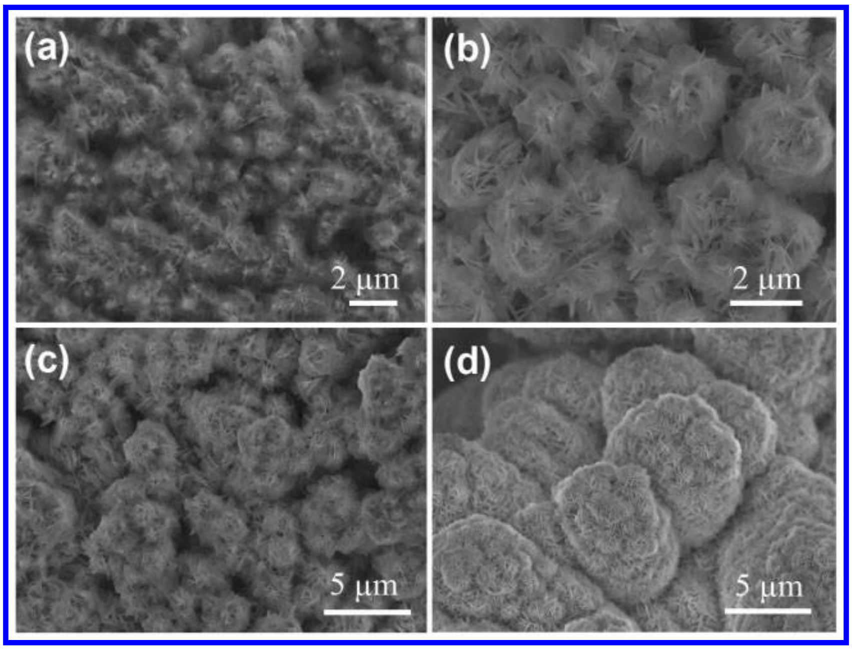
The concentrations of reaction solution were a crucial prerequisite for the formation of the hierarchical structure. Figure 3 shows SEM images of Cu obtained at different concentrations of Cu ions. When the Cu ion concentration was 1 mmol L^{-1} as shown in Fig. 3*a*, even with a relatively long reaction time reaching 60 min, the product displays a morphology consisting of some primary nanoparticle aggregation, combining with a few Cu nanowalls. As the concentration of Cu ions increases up to 50 mmol L^{-1} (Fig. 3*b*), the morphology of sample is quite similar to the one of 1 mmol L^{-1} with more detectable small nanoplates appearing and filling up the aggregated nanoparticles. When the Cu ion concentration reaches 0·1 mol L^{-1}, the morphology of Cu nanostructures converts to the micropillars of 3–5 μm dominated by a great amount of thin nanowalls combining with a few small nanoparticles as shown in Fig. 3*c*. While Zn foil is immersed into a higher concentration of CuSO$_4$ aqueous solution, such as 0·6 mol L^{-1} for 5 min (Fig. 3*d*), the product displays nanowall aggregated Cu micropillars, with the thickness of the wall approximately 20–50 nm.

According to the previous observation, one can find that the growth of Cu nanostructures under various concentrations of Cu ions demonstrates a transition from nanoparticles to nanoplate aggregated micropillars. When Cu nanostructures were synthesised at low reactant concentrations, the growth speed was relatively slow, and the product was dominated by nanoparticle aggregated morphology,[34] combining with a few plate-like Cu nanowalls. On the contrary, with a higher concentration of Cu ions, the reaction is dominated by the kinetic factor,[35] the morphology converts from micro-'hillocks' to micropillars and the process of nanowall growth gradually takes place. Hence, the copper hierarchical structure made up of flower-like micropillars and dense nanowall arrays can be synthesised by means of changing the reaction conditions. The materials with such structural features named 'double roughness',[36] which was inspired by the water repellent nature of lotus leaves, are ideally suited to the hydrophobic surface.[31,37]

The morphological evolution of porous copper nanowalls at different growth stages was carefully monitored by SEM as shown in Fig. 4, displaying the copper arrays obtained by immersing the zinc substrate into a solution of 0·9M CuSO$_4$. When the immersion time is 0·5 min, one can see that nanohillocks with fine nanowalls and microinterspaces grow up on the zinc surface (Fig. 4*a*). Increasing the immersion time, it was clearly shown that the substrate was densely covered by many flower-like micropillars with an average diameter of about 1·5–3 μm (Fig. 4*b* and *c*). The micropillars became bigger with time increasing, e.g. after 5 min, the zinc foil was covered by plenty of flower-like micropillars with nanowalls (about 100 nm thickness shown in Fig. 2*b*, having an average diameter of close to 4–6 μm) (Fig. 4*d*). Thus, a hierarchical structure, containing micro- and nanoscale structure, was formed on zinc substrate.

Hydrophobic property

The wetting property of the as prepared copper arrays on zinc foil with different immersed times was carefully examined as shown in Fig. 5. We performed static contact angle measurements by placing a droplet



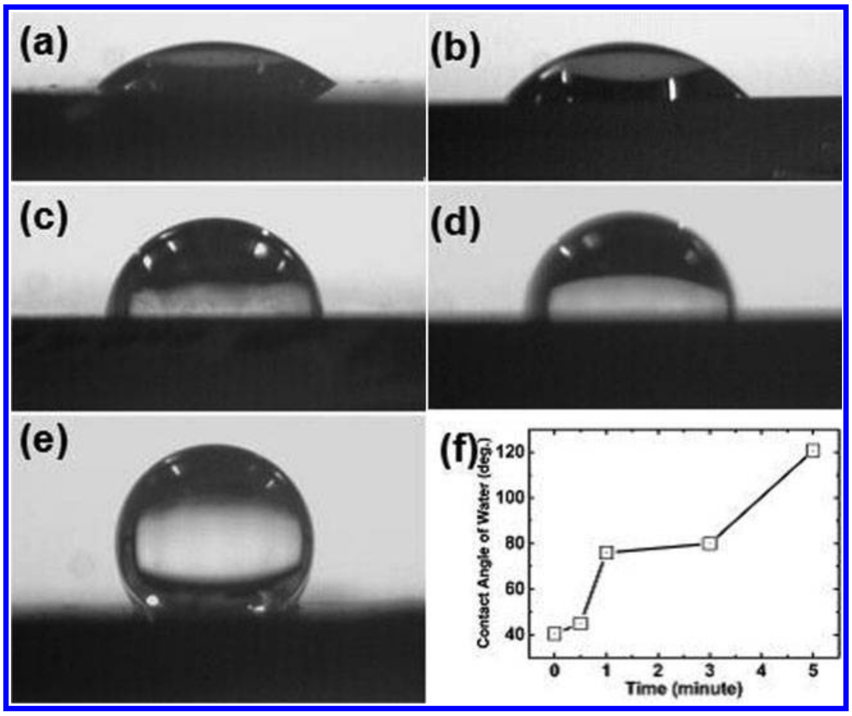
a **0·5 min;** ***b*** **1 min;** ***c*** **3 min;** ***d*** **5 min**

4 Typical SEM images of flower-like Cu micropillar arrays fabricated in 0·9M $CuSO_4$ solution for different growth times

of deionised water (~1 μL) on the surface of bare zinc substrate (image of Fig. 5*a*) and the copper arrays respectively (images of Fig. 5*b–e* for 0·5, 1, 3 and 5 min of immersion time respectively). The contact angle was 41, 45, 76, 80 and 121° for different surfaces, observing from Fig. 5. The measured contact angle for zinc foil (41°) and copper array before 5 min were hydrophilic. By immersing the zinc foil into 0·9M $CuSO_4$ solution for 5 min, its wettability switched from hydrophilic to hydrophobic (contact angle=121°), which can be distinctly seen in Fig. 5*f*. To thoroughly understand the hydrophobic property of the porous copper arrays, we describe the contact angle in terms of the modified Cassie–Baster model.[38] On the assumption that a water contact angle is 180° for air and θ for flat surface of solid, the contact angle θ^c is derived as follows

$$\cos\theta^c = f\cos\theta + (1-f)\cos\pi = f(\cos\theta + 1) - 1$$

where f is the area fraction of solid/liquid interface and $(1-f)$ is the solid/air interface. It is easy to deduce



5 ***a*** **profile of water drop on zinc surface that has contact angle of 41°; profiles of water drop on as prepared flower-like Cu micropillar arrays on zinc surface displaying contact angle after various reaction times of** ***b*** **45°, 0·5 min;** ***c*** **76°, 1 min;** ***d*** **80°, 3 min and** ***e*** **121°, 5 min with 0·9M $CuSO_4$ solution; and** ***f*** **contact angles of water droplet on different surfaces as function of reaction time**

from this equation that the contact angle θ^c increases with decreasing the fraction of f. That is to say, θ^c increases with the increasing part of air trapped in the film surface. Therefore, we ascribe the hydrophobic property to the contribution of the air trapped in the liquid/solid interspaces, which means that the surface morphology and roughness play dominant roles in controlling the wetting properties of the solid surfaces.

Conclusions

In summary, a facile method has been employed to synthesise microflower-like copper micropillars by reducing Cu ions with zinc plate in aqueous solution. It was shown that the reaction time and the concentration of $CuSO_4$ aqueous solution have a great influence on the density and sizes of flower-like micropillars of the porous copper. The measurements of contact angle for zinc foil (41°) and copper array growth from 0·9 mol L^{-1} concentration with a short immersion time (e.g. <1 min) demonstrate the hydrophilic feature. Furthermore, a hydrophobic surface composed of flower-like Cu micropillars synthesised from 0·9M $CuSO_4$ solution for 5 min reaction time was finally obtained with a contact angle of >120°. The analysis using modified Cassie–Baxter models implied that the surface roughness and microstructure played an important role on the wetting property of porous copper nanowalls.

References

1. L. Lu, M. L. Sui and K. Lu: *Science*, 2000, **287**, 1463.
2. J. A. Eastman, S. U. S. Choi, S. Li, W. Yu and L. J. Thompson: *Appl. Phys. Lett.*, 2001, **78**, 718–720.
3. Y. S. Hu, Y. G. Guo, W. Sigle, S. Hore, P. Balaya and J. Maier: *Nat. Mater.*, 2006, **5**, 713–717.
4. R. L. V. Wal: *Chem. Phys. Lett.*, 2000, **324**, 217–223.
5. Y. Li, J. Liu, Y. Wang and Z. L. Wang: *Chem. Mater.*, 2001, **13**, 1008–1014.
6. J. S. Lee, G. H. Gu, H. Kim, W. S. Jeong, J. Bae and J. S. Suh: *Chem. Mater.*, 2001, **13**, 2387–2391.
7. Y. Li, W. Z. Jia, Y. Y. Song and X. H. Xia: *Chem. Mater.*, 2007, **19**, 5758–5764.
8. T. Sun, L. Feng, X. Gao and L. Jiang: *Acc. Chem. Res.*, 2005, **38**, 644–652.
9. F. Shi, Y. Y. Song, H. Niu, X. H. Xia, Z. Q. Wang and X. Zhang: *Chem. Mater.*, 2006, **18**, 1365–1368.
10. V. A. Lifton, J. A. Taylor, B. Vyas, P. Kolodner, R. Cirelli, N. Basavanhally, A. Papazian, R. Frahm, S. Simon and T. Krupenkin: *Appl. Phys. Lett.*, 2008, **93**, 043112-1–043112-3.
11. C. D. Gu and T. Y. Zhang: *Langmuir*, 2008, **24**, 12010–12016.
12. X. J. Feng and L. Jiang: *Adv. Mater.*, 2006, **18**, 3063–3078.
13. 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**, 1857–1860.
14. G. Zhang, D. Wang, Z. Gu and H. Möhwald: *Langmuir*, 2005, **21**. 9143–9148.
15. S. Shibuichi, T. Onda, N. Satoh and K. Tsujii: *J. Phys. Chem.*, 1996, **100**, 19512–19517.
16. J. Y. C. Shiu, W. Kuo, P. Chen and C. Y. Mou: *Chem. Mater.*, 2004, **16**, 561–564.
17. J. L. Zhang, L. J. Xue and Y. C. Han: *Langmuir*, 2005, **21**, 5–8.
18. L. Zhai, F. C. Cebeci, R. E. Cohen and M. F. Rubner: *Nano Lett.*, 2004, **4**, 1349–1353.
19. X. Zhang, F. Shi, X. Yu, H. Liu, Y. Fu, Z. Wang, L. Jiang and X. Li: *J. Am. Chem. Soc.*, 2004, **126**, 3064–3065.
20. X. T. Zhang, O. Sato and A. Fujishima: *Langmuir*, 2004, **20**, 6065–6067.
21. W. He, P. Gao, L. Chu, L. G. Yin, Z. Li and Y. Xie: *Nanotechnology*, 2006, **17**, 3512–3517.
22. L. Jiang, Y. Zhao and J. Zhai: *Angew. Chem. Int. Ed.*, 2004, **43**, 4338–4341.
23. D. Öner and T. J. McCarthy: *Langmuir*, 2000, **16**, 7777–7782.
24. Z. W. Cao, D. B. Xiao, L. T. Kang, Z. L. Wang, S. X. Zhang, Y. Ma, H. B. Fu and J. N. Yao: *Chem. Commun.*, 2008, **23**, 2692–2694.
25. S. T. Wang, L. Feng and L. Jiang: *Adv. Mater.*, 2006, **18**, 767–770.
26. Z. Guo, J. Fang, J. Hao, Y. Liang and W. Liu: *Chem. Phys. Chem.*, 2006, **7**, 1674–1677.
27. Y. S. Zhao, W. S. Yang, G. J. Zhang, Y. Ma and J. N. Yao: *Colloids Surf. A*, 2006, **277A**, 111–118.
28. A. Safaee, D. K. Sarkar and M. Farzaneh: *Appl. Surf. Sci.*, 2008, **254**, 2493–2498.
29. C. D. Gu, H. Ren, J. P. Tu and T. Y. Zhang: *Langmuir*, 2009, **25**, 12299–12307.
30. C. D. Gu, X. J. Xu and J. P. Tu: *J. Phys. Chem. C*, 2010, **114C**, 13614–13619.
31. X. F. Gao and L. Jiang: *Nature*, 2004, **432**, 36.
32. S. T. Wang, L. Feng, H. Liu, T. L. Sun, X. Zhang L. Jiang and D. B. Zhu: *Chem. Phys. Chem.*, 2005, **6**, 1475–1478.
33. W. Song, J. J. Zhang, Y. F. Xie, Q. Cong and B. Zhao: *J. Colloid Interface Sci.*, 2009, **329**, 208–211.
34. X. L. Ren, D. Chen and F. Q. Tang: *J. Phys. Chem. B*, 2005, **109B**, 15803–15807.
35. J. X. Fang, H. J. You, P. Kong, Y. Yi, X. P. Song and B. J. Ding: *Cryst. Growth Des.*, 2007, **7**, 864–867.
36. I. A. Larmour, S. E. J. Bell and G. C. Saunders: *Angew. Chem.*, 2007, **119**, 1740–1742.
37. Y. T. Cheng and D. E. Rodak: *Appl. Phys. Lett.*, 2005, **86**, 144101-1–144101-3.
38. A. B. D. Cassie and S. Baxter: *Trans. Faraday Soc.*, 1944, **40**, 546–551.