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A facile method for the fabrication of super-hydrophobic surfaces and their resulting wettability

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Stable, flower-like super-hydrophobic surfaces on copper substrate were fabricated by means of a facile method using one-step solution immersion. The contact angles (CAs) of the surfaces with test liquids were >150°, and scanning electron microscopy showed hierarchical micro- and nanostructures. X-ray diffraction pattern revealed that the as-fabricated surface was crystallized and was of sheet structure, which can be observed in a layer structure.

Keywords: Layered structures; Scanning electron microscopy (SEM); Surface energy; Ageing; Hierarchical structure

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The wettability of solid materials is one of the most important properties related to many fields ranging from biology [1], chemistry [2], physics [3,4], to materials science and engineering. In particular, super-hydrophobic surfaces with a water contact angle (CA) greater than 150° or super-amphiphobic surfaces with CAs greater than 150° for both water and oil have aroused much interest. Super-hydrophobicity was first observed on lotus leaves [5] where a high water CA and low hysteresis cause water that falls on the surface to bead and roll off the surface, thereby leading to water repellency and self-cleaning characteristics. Such surface properties are also critical in industrial applications including the fabrication of microfluidic devices, the prevention of the adhesion of snow to antennas, and the self-cleaning of traffic signals [6–8], as well as microelectromechanical systems (MEMS) antistiction, friction reduction and anticorrosion [9–11].

Artificial super-hydrophobic surfaces have been achieved by either creating a rough topography on a hydrophobic surface or by modifying a rough surface by chemical compositions with a low surface free energy [7,12]. A number of methods have been proposed to fabricate super-hydrophobic surfaces, including plasma etching [13], lithographic patterning [14], electrochemical deposition [15], sol–gel [16], layer-by-layer assembly [2] and chemical vapor deposition [17]. However, these methods are subject to certain limitations, such as severe conditions, multistep, expensive materials, poor durability, etc. Therefore, a facile, inexpensive and convenient strategy is highly needed. Herein, we report a facile method based on solution immersion to fabricate stable super-hydrophobic surfaces with a hierarchical structure similar to that of the lotus flower.

The flower-like surfaces were fabricated by using one-step solution immersion method. The fabrication process was adopted from Zhang et al. [18] with the following modifications. (i) Copper plates as substrates were polished with very fine sandpaper and etched in 0.3 M HNO_3 for 30 min to remove surface oxides and organic compounds and to provide fresh and active surfaces. The polished and etched substrates were promptly rinsed with pure ethanol followed by deionized water. (ii) They were subsequently immersed in ethanolic (C_2H_5OH, J.T. Baker) solutions of myristic acid ($CH_3(CH_2)_{12}COOH$, SigmarAldrich) at room temperature for given periods of time. (iii) The immersed substrates were taken from the solution after a given

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period of immersion and rinsed with deionized water and ethanol. Finally, the substrates were dried in air thoroughly.

Figure 1a–c shows scanning electron microscopy (SEM) images of the as-fabricated super-hydrophobic surfaces on copper plate, corresponding to the reaction times of 6, 18 and 36 h in an ethanolic solution of myristic acid (0.03 M), respectively. The formation process of flower-like clusters can be observed. When the immersion time is as short as 6 h, a few flowers and nano-sheets are observed, sparsely covering the substrate. When the reaction time is increased to 18 h, however, the flowers become bigger and the nano-sheets in Figure 1a grow to flowers. When the reaction time is further increased to 36 h, flower-like clusters composed of micro- and nano-sheets cover the copper substrate densely. The substrate in Figure 1c has a rough surface 20–30 μm long, 3 μm wide and about 200 nm thick, which resembles the shape of petals. Therefore, this morphology with a flower-like structure is expected to reveal super-hydrophobicity without chemical modifications. In general, it is known that the super-hydrophobic properties of chemically treated surfaces deteriorate over time, bringing about significant problems to the practical application of super-hydrophobic surfaces.

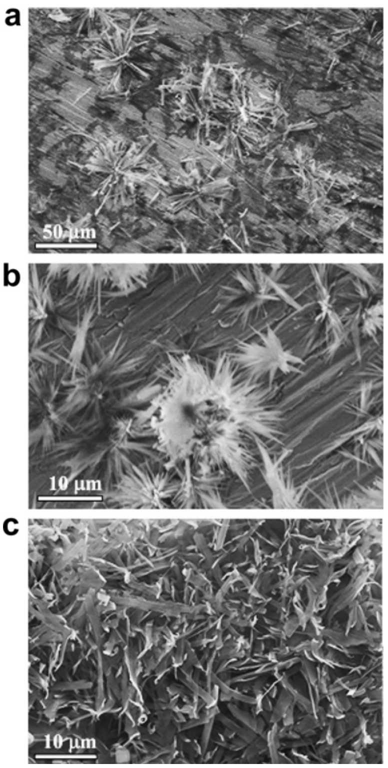

Figure 1. SEM images of the as-fabricated super-hydrophobic surfaces on copper plate, corresponding to the reaction times of (a) 6, (b) 18 and (c) 36 h in an ethanolic solution of myristic acid (0.03 M).

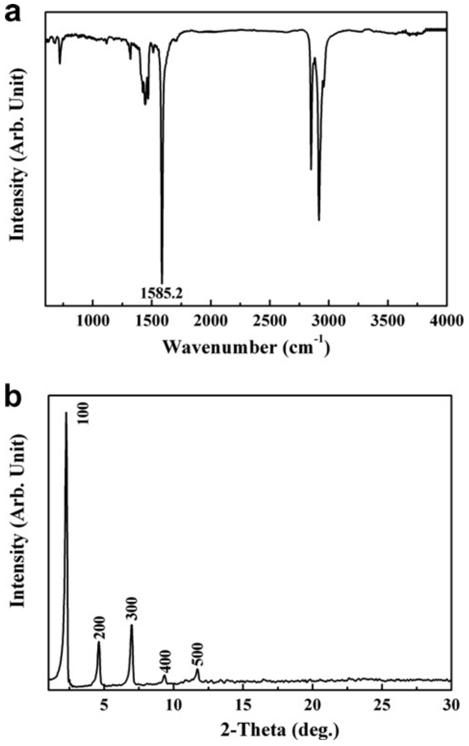

Figure 2. FTIR spectrum of $Cu[CH_3(CH_2)_{12}COO]_2$on copper substrate. (b) XRD pattern of $Cu[CH_3(CH_2)_{12}COO]_2$obtained from the as-fabricated surface.

The Fourier transform infrared (FTIR) spectrum in Figure 2a exhibits the chemical groups of the as-fabricated surface. Typically, the carboxyl group (COO) from myristic acid appears at 1702 cm^{-1}, resulting from free COO band. However, the free COO band is not present in Figure 2a. Instead of the free COO band, a new band appears at 1585.2 cm^{-1}, which stems from coordinated COO functional groups. In general, natural oxidation of copper metal by naturally dissolved oxygen in water is very slow owing to surface oxide layer. However, this spontaneous oxidation reaction can be accelerated not only in the presence of formamide [18] but also in the presence of myristic acid in ethanolic solution. Cu^{2+} ions are released from copper substrate into myristic acid solution while oxygen is reduced ($O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$). The released copper ions are then immediately combined through coordination with myristic molecules to form copper carboxylate ($Cu^{2+} + 2CH_3(CH_2)_{12}COOH \rightarrow Cu[CH_3\ (CH_2)_{12}COO]_2 + 2H^+$), showing coordinated COO functional groups in Figure 2a. Figure 2b displays the XRD pattern of as-fabricated surface. As revealed in Figure 2b, the flower-like clusters on the copper substrate are crystallized and have a layer structure, which is reported in previous articles [19,20], revealing five sharp peaks that can be assigned to the $l00$ (l is integer) peaks of a layered solid with a preferred orientation. Thus, the flower-like clusters grown on the copper substrate in Figure 1 have a composition of $Cu[CH_3(CH_2)_{12}COO]_2$and are crystalline.

Figure 3a–f shows photographic images of liquid droplets on copper substrates. The CAs with liquids were measured using a CA analysis system with a computer-controlled liquid dispensing system. Liquid droplets with a volume of about 20 μl were allowed to fall on substrates to measure the static CAs. The CA measurements were repeated five times on each sample. Figure 3a–c are photographs of polyethylene glycol (CA ~ 42°), glycerol (CA ~ 45°) and water (CA ~ 52°)