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Fabrication of Functionalized Copper Compound Hierarchical Structure with Bionic Superhydrophobic Properties

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Hierarchical structure of flower-like CuO standing on Cu(OH)$_2$ nanorod arrays, similar to that of a lotus leaf, was directly fabricated on the surface of copper foils by a simple one-step solution-immersion process. It was found that the diameter of the nanorods ranges from 100 to 500 nm, and the length of the rods is about tens of micrometers. Synchronously, flower-like CuO with a diameter of about 3−5 μm was also deposited from the bulk solution during the growth of nanorod arrays. The wettability of the surface with hierarchical structure was changed from surperhydrophilicity to superhydrophobicity by chemical modification with stearic acid (STA) or 1*H*,1*H*,2*H*,2*H*-perfluorodecyltriethoxysilane (PDES). The static contact angles (CAs) for water on both of the modified surfaces were larger than 160°, which was closely related to the chemical modification and hierarchical structure. Compared with the STA-modified surface, the PDES-modified surface had a lower CA hysteresis (CAH) and adhesion for water droplets. Furthermore, the surfaces retained good superhydrophobic stability in long-term storage as well, which should be critical to the application of Cu materials in engineering.

Introduction

Wettability of a solid surface is one of the most important properties of materials, which depends on both chemical composition and geometrical microstructures.[1] In recent years, much research on superhydrophobic materials has been inspired by the water-repellent lotus leaf which shows a hierarchically rough structure (nanohairs on microprotrusions) along with a waxy coating.[2−6] A water droplet beads off completely and removes dirt and debris as it rolls off the surface. This kind of self-cleaning property is known as the "lotus effect".[7]

Up to now, many significant techniques have been developed to produce superhydrophobic surfaces by mimicking the lotus leaf. Some examples of this approach include replication of plant leaves,[8] the sol−gel process,[9] the self-assembly technique,[10−12] electrodeposition,[13,14] electrospin,[15,16] hydrothermal synthesis,[17,18] thermal evaporation,[19] the phase separation process,[20] and so forth. Most of these techniques, however, are costly and time-consuming, and often involve complicated multistage processes, and it still remains a great challenge to develop a facile and time-saving method for the fabrication of superhydrophobic surfaces.

As a kind of important engineering material, copper is widely used in many industrial applications. Up to now, various methods such as the electrochemical technique,[21,22] replacement reaction,[23,24] and so forth, have been employed to fabricate artificial superhydrophobic surfaces on copper substrates. To name a few, J. P. Liu et al.[25] fabricated cabbage-like CuO

hierarchical microstructures on copper foil by the self-assembly process, Z. G. Guo et al.[26] prepared CuO microflower-like protrusions by means of surface oxidation, and Q. M. Pan. et al.[27] prepared interconnected Cu(OH)$_2$ nanowires on a copper surface by immersing copper plates in an aqueous solution of sodium hydroxide and potassium persulphate. W. X. Zhang et al.[28−30] constructed nanostructures such as nanotubes and nanorods on copper substrates via a simple solution-immersion method which has rarely been used to fabricate superhydrophobic surfaces. To our excitement, we preliminarily found in our experiments that flower-like CuO can be deposited synchronously from the bulk solution of NaOH and (NH$_4$)$_2$S$_2$O$_8$ during the growth of nanorods. However, Hou et al.[31] found microdeposition of CuO from an aqueous solution of KOH (2.5 mol·L^{-1}) and K$_2$S$_2$O$_8$ (1 mol·L^{-1}) and believed them to be epitaxial scrolls on CuO ribbons, while Zhang et al.[30] reported that CuO sheets prepared from the system of NaOH and (NH$_4$)$_2$S$_2$O$_8$ were transformed from Cu(OH)$_2$. Thus, the reaction process of NaOH and (NH$_4$)$_2$S$_2$O$_8$ was carefully clarified, and the hierarchical structure of flower-like CuO standing on a Cu(OH)$_2$ nanorod was directly fabricated on copper foils by a simple one-step solution-immersion process. Furthermore, the wettability and adhesion of the CuO and Cu(OH)$_2$ hierarchical structures for water droplets were also investigated.

Experimental Section

Flower-like CuO and Cu(OH)$_2$ nanorod arrays were prepared on copper foils by alkali assistant surface oxidation under ambient conditions. The details of the technique have been described elsewhere.[28,30] Briefly, the copper foils with a size of 10 mm × 20 mm × 0.1 mm (Sinopharm Chemical Reagent Co. Ltd., Shanghai, P. R. China; purity 99.8%) were ultrasoni-

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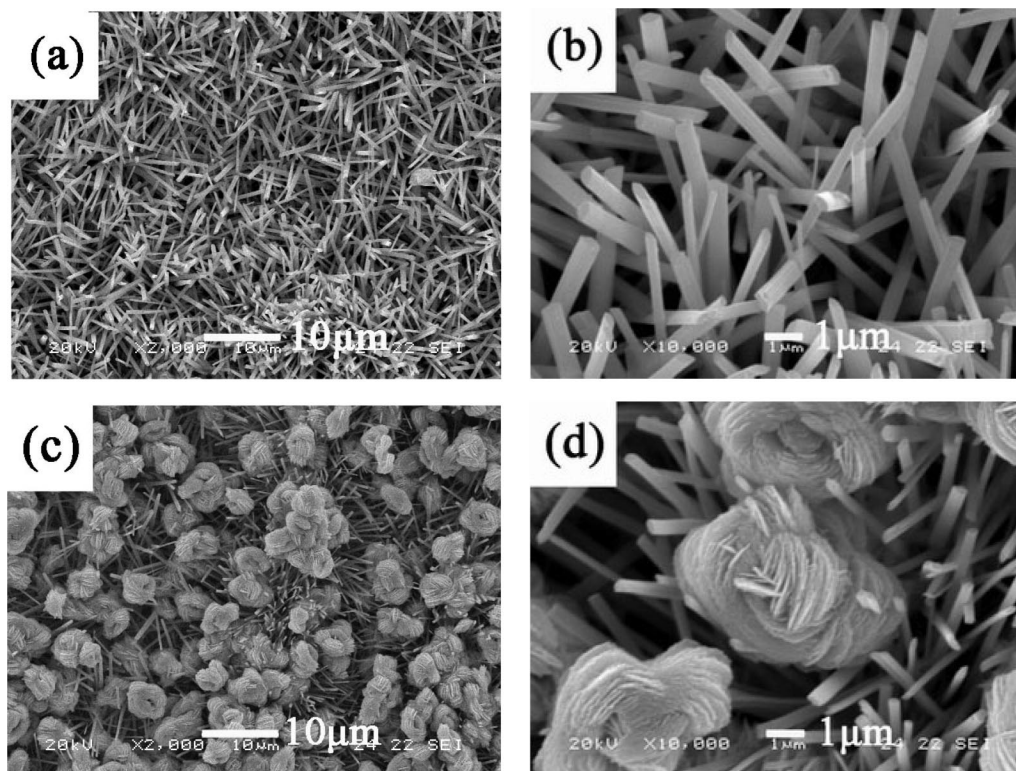
Figure 1. SEM images of Cu(OH)$_2$ nanorod arrays: (a) low magnification (2000×); (b) high magnification (10000×). SEM images of CuO and Cu(OH)$_2$ hierarchical structure on a copper substrate (copper foil immersed in an aqueous solution of 2.5 mol·L^{-1} sodium hydroxide and 0.1 mol·L^{-1} ammonium peroxysulfate for about 30 min at room temperature): (c) low magnification (2000×); (d) high magnification (10000×).

cally cleaned in ethanol and deionized water for about 5 min, respectively, followed by immersion in an aqueous solution of 2.5 mol·L^{-1} sodium hydroxide and 0.1 mol·L^{-1} ammonium persulphate at room temperature for about 10−30 min. During the immersion process, the color of the copper foil surface turned gradually to faint blue, light blue, faint black, and light black. The copper foils were then taken out of the solution and fully rinsed with deionized water, followed by drying in a nitrogen stream. The PDES-modified surface was obtained by immersing one of the pretreated copper foils in ethanol solution of 1*H*,1*H*,2*H*,2*H*-perfluorodecyltriethoxysilane (Chisso Corporation, Japan; molecular formula: *n*-CF$_3$(CF$_2$)$_7$CH$_2$CH$_2$Si(OC$_2$H$_5$)$_3$, serial No. PDES; volume ratio to ethanol: 1/100) for 48 h, followed by washing with ethanol and drying in an oven at 120 °C for about 1 h. The modification of STA was carried out by immersing another pretreated copper foil in a 0.002 mol·L^{-1} ethanol solution of STA for about 24 h. The resulting copper substrates were rinsed with ethanol and dried in a nitrogen stream.

The morphologies of the samples were observed using a scanning electron microscope (SEM, JSM-5600LV, JEOL Ltd., Japan). X-ray diffraction (XRD) patterns were obtained using a multipurpose X-ray diffractometer (X'Pert Pro MPD, Philips, Netherlands; copper target tube, incident beam monochromator, $\lambda = 1.54056$ Å). The chemical compositions and states of the hierarchical structure on copper foil and STA- and PDES-modified surfaces were analyzed on an Axis Ultra X-ray photoelectron spectroscope (XPS, Kratos Analytical Ltd., U.K.) equipped with a standard monochromator Al Kα source ($hv = 1486.6$ eV). The binding energy data were calibrated with respect to the C1s signal of ambient hydrocarbons (C−H and C−C) at 284.8 eV. The static water contact angle (CA), CA hysteresis (CAH), and adhesion for the water droplet were measured with an optical contact angle meter (Dropmaster 300,

Kyowa Interface Science, Japan) at room temperature. The volume of the individual water droplet used for the static CA measurements is 4 μL. CA values were obtained by averaging five measurement results on different areas of the sample surface.

Results and Discussion

The surface morphologies of Cu(OH)$_2$ nanorod arrays synthesized using a method in ref 30 were investigated by SEM (Figure 1a and b). The low magnification SEM image (Figure 1a) shows that Cu(OH)$_2$ nanorods cover a large area of the copper substrate uniformly and compactly, while the higher magnification SEM image (Figure 1b) reveals that the nanorods have a length of over 10 μm and a diameter of 100−800 nm. However, the tips of the rods are uneven, and so are the surfaces of the rods. It seems that the nanorods are composed of several nanowires with a diameter of about tens of nanometers (see Supporting Information Figure S1). The details about the microstructure and controllable morphologies of the nanorods will be reported elsewhere. The hierarchical structures of CuO and Cu(OH)$_2$ on a copper substrate are shown in Figure 1c and d. It is seen that flower-like microspheres with a diameter of 3−5 μm are formed uniformly (Figure 1c). The magnified image of a single microflower (Figure 1d) reveals that the thickness of the flower petals is about 50−100 nm. Interestingly, the nanorod arrays are formed under the microflowers, and the diameter of the rods is about 100−500 nm. In other words, the microflowers are standing on the nanorod arrays. Furthermore, some of the microflowers are transfixed by several nanorods (as seen in Figure 1d). Thus, the microflowers/nanorod arrays with a hierarchical structure similar to that of a lotus leaf were synthesized by a simple one-step solution-immersion process. Compared with the unitary scale, although the
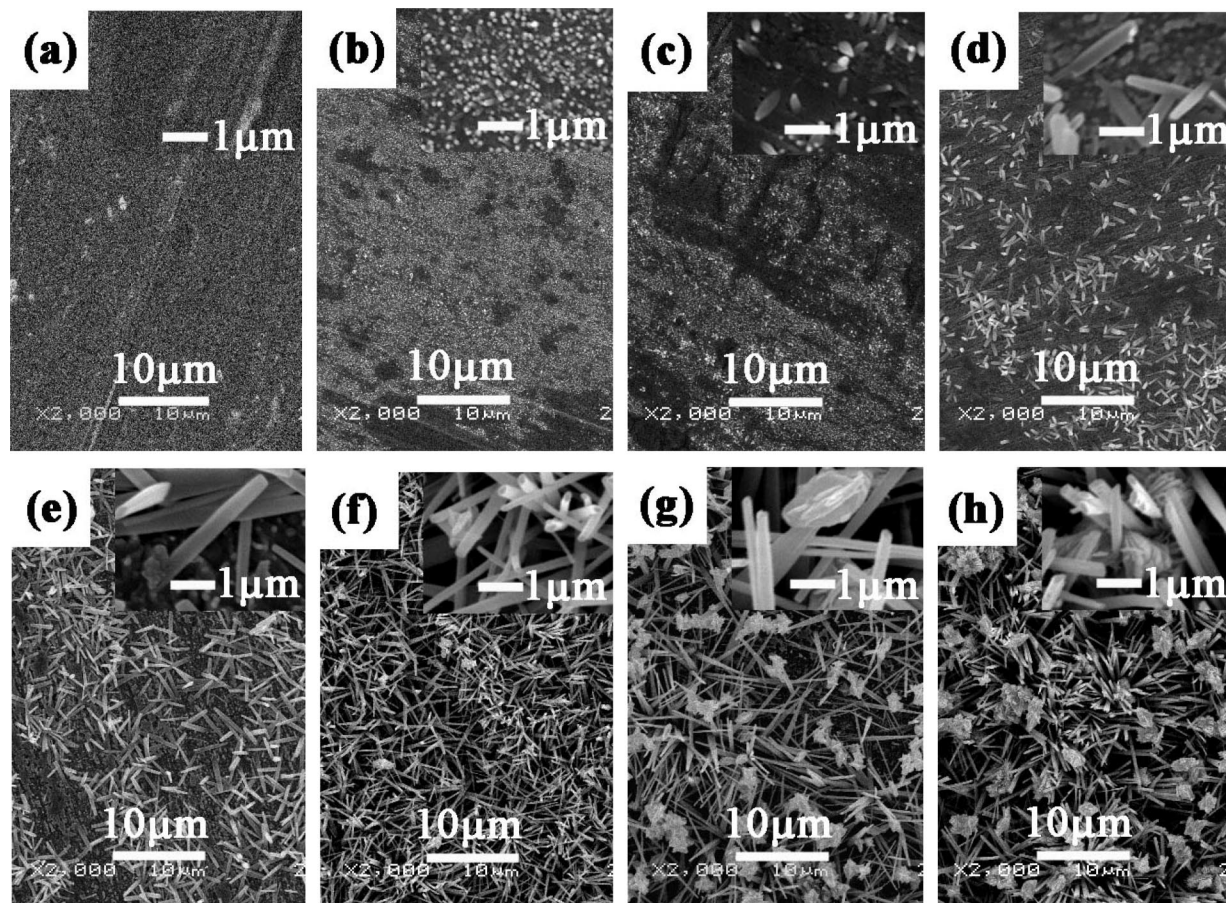
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Figure 2. SEM images at low and high magnification (insets) of copper foils after being immersed in an aqueous solution of sodium hydroxide (2.5 mol·L^{-1}) and ammonium peroxysulfate (0.1 mol·L^{-1}) for different durations: (a) 0 s; (b) 10 s; (c) 20 s; (d) 1 min; (e) 2 min; (f) 3 min; (g) 7 min; (h) 10 min. The scale bars in parts a−f are all 50 μm, and those in the insets are all 1 μm.

hierarchical structure is not indispensable for superhydrophobic surfaces with large CA and small sliding angle (SA),[6] it can help establish stable and robust superhydrophobicity,[32] owing to the kinetics of droplet movement and the themodynamics of wetting.[33]

The formation of Cu(OH)$_2$ nanorod arrays depends mainly on the concentration of NaOH and (NH$_4$)$_2$S$_2$O$_8$,[31] and the growth rate can be controlled by adjusting reaction time and temperature. Taking the solution of 2.5 mol·L^{-1} NaOH and 0.1 mol·L^{-1} (NH$_4$)$_2$S$_2$O$_8$ as a model system, the SEM images of the as-received copper foils are shown in Figure 2. In the initial 10 s (the heterogeneous nucleation stage), nanoparticles with a size of about 100 nm and some nanorods with a diameter of about 100 nm and height of about 300−500 nm were formed. In the next 10 s, some bamboo-shoot-like rods with a diameter of about 200−300 nm, height of about 1 μm, and tip size of less than 100 nm emerged. During the third stage (reaction time of more than 1 min), nanorod arrays were formed, and the length of the rods increased up to tens of micrometers with increasing reaction time, but the diameter of the rods stayed almost unchanged. When the reaction time rose to 3 min and above, some microflowers were synchronously deposited from the bulk solution, due to the reaction of Cu^{2+} ions resulting from copper oxidation and OH$^-$ during the growth of nanorods, and the size of the microflowers increased with extending reaction time. At the same time, some of the microflowers were transfixed by several nanorods as mentioned above (as seen in Figures 1d and 2h). Obviously, the microflowers cannot be removed by ultrasonic cleaning, indicating a good adhesion. When the

reaction time was further prolonged to 1 h, Cu(OH)$_2$ nanorods turned gradually to nanotubes and finally to CuO nanoslices (see Supporting Information Figure S2). The formation of Cu(OH)$_2$ nanostructures on copper surfaces involves inorganic polymerization (polycondensation) reactions under alkaline and oxidative conditions. The assembly of Cu(OH)$_2$ proceeds through the condensation of Cu^{2+} and OH$^-$ (olation reaction), forming μ_4-OH bridges. The OH$^-$ ligand acts as a nucleophile and undergoes a change in coordination only when it switches from a terminal ligand in a monomer to a bridging ligand in a condensed species.[30] At first, a corrugated sheet is formed by edge sharing of the distorted Cu(OH)$_6$ octahedron which is formed by Cu^{2+} and OH$^-$, and then, the sheets stacking together through hydrogen bonds to form Cu(OH)$_2$ particles and rods (Figure 2b). However, under highly basic conditions, the interlayer H-bond linkage at the sheet edges can be weakened, causing stresses in the layers. Therefore, the sheets are rolled so as to relieve the stresses, resulting in the formation of tubular structure (see Supporting Information Figure S2a and c). In fact, the corrugated layer structure of Cu(OH)$_2$ is unstable against oxolation because oxygen atoms are either pentacoordinated or tricoordinated.[30] At a reaction time of more than 3 h, the Cu(OH)$_2$ tubes are transformed to CuO slices, owing to the cleavage of the interplanar hydrogen bonds (see Supporting Information Figure S2b and d), which is in good agreement with the literature.[30] It should be mentioned here that (NH$_4$)$_2$S$_2$O$_8$ is not indispensable for the formation of such hierarchical structures. Namely, copper foil immersed in a concentrated solution of NaOH alone can also be oxidized by dissolved
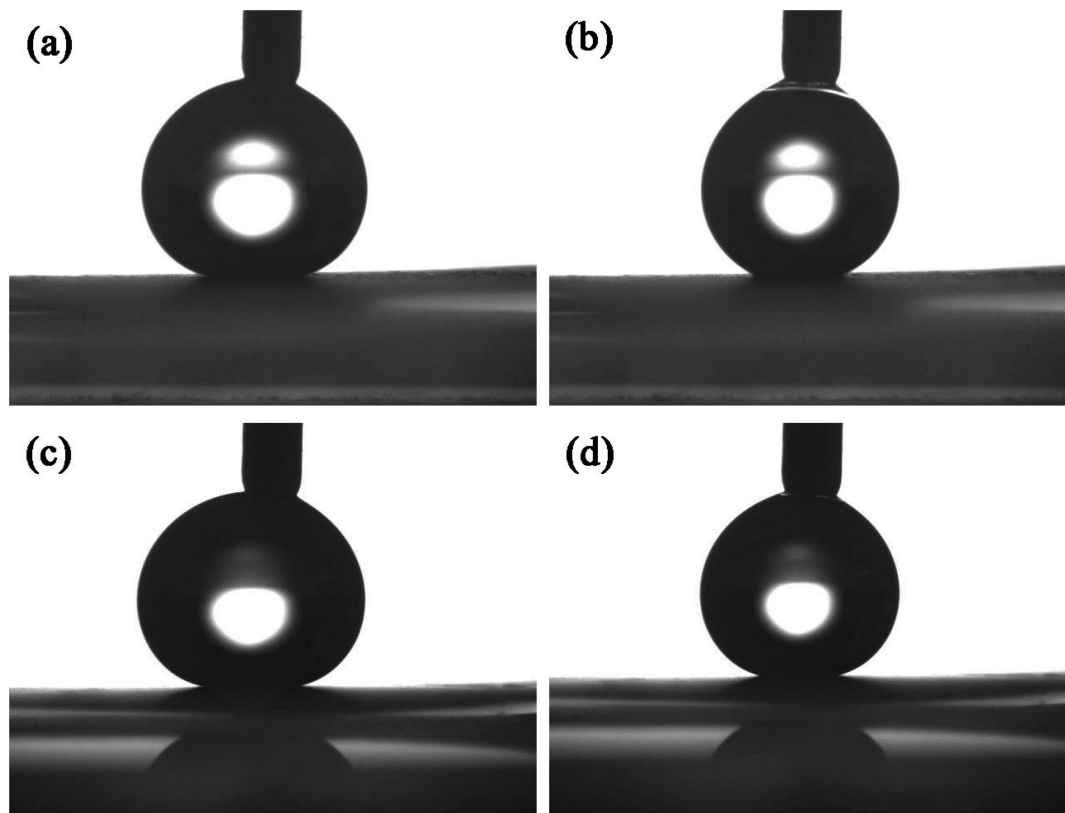
Figure 3. XRD patterns of (a) Cu(OH)$_2$ nanorod arrays and (b) CuO and Cu(OH)$_2$ hierarchical structure on a copper substrate.

Figure 4. XPS survey scan of (a) unmodified, (b) STA-modified, and (c) PDES-modified CuO and Cu(OH)$_2$ hierarchical structure.

Figure 5. C1s core-level XPS spectra of as-prepared CuO and Cu(OH)$_2$ hierarchical structure modified with PDES.

Figure 6. Photographs of water droplets on (a) unmodified, (b) STA-modified, and (c) PDES-modified CuO and Cu(OH)$_2$ hierarchical structure.

oxygen, although it takes a long time (see Supporting Information Figure S3; the details about the microstructure and controllable morphologies of the Cu$_2$O microcrystals and CuO crystals will be discussed later).

XRD analysis was performed to study the crystal structure of the blue film of nanorod arrays and microflowers/nanorod arrays hierarchical structure on a copper substrate (Figure 3). It can be seen from Figure 3a (nanorod arrays; corresponding SEM images are shown in Figure 1a and b) that all of the peaks marked with triangles can be readily indexed to orthorhombic-phase Cu(OH)$_2$ (JCPDS card No. 72-0140), except those marked with an asterisk of the copper substrate. As for the microflowers/nanorod arrays hierarchical structure (Figure 3b, the diffraction peaks marked with black dots indexed to monoclinic-phase CuO (JCPDS card No. 80-0076) appear along with those marked with an asterisk of the copper substrate and orthorhombic-phase Cu(OH)$_2$ marked with triangles (corresponding SEM images are shown in Figure 1c and d), indicating that the hierarchical structure on the copper substrate is mainly composed of CuO and Cu(OH)$_2$ crystals.

Since surface chemical composition has a remarkable effect on the hydrophobicity, the hierarchical structure of CuO and Cu(OH)$_2$ was chemically modified with STA or PDES, aiming at improving the hydrophobicity. Figure 4 shows the typical XPS survey spectra of the CuO/Cu(OH)$_2$ hierarchical structure before and after chemical modification with STA or PDES. C 1s, O 1s, and Cu 2p peaks were detected for both the CuO/Cu(OH)$_2$ hierarchical structure surface and the surface modified with STA (Figure 4a and b). After being treated with PDES, the peak for F 1s was detected at 689.0 eV (Figure 4c, see Supporting Information Figure S4), confirming that PDES had been successfully self-assembled or adsorbed onto the surface of the hierarchical structure.

To get more information on the surface composition of the PDES-modified surface, high resolution XPS data were collected for C 1s. Figure 5 shows the curve-fitted C1s XPS spectra of

CuO and Cu(OH)$_2$ hierarchical structure modified with PDES, where five major peaks of C 1s are identified. Namely, the peaks at 284.8, 291.8, and 294.2 eV can be assigned to CH$_2$, CF$_2$, and CF$_3$ groups, respectively, while the peaks centered at 286.1 and 288.3 eV may be assigned to unhydrolyzed ethoxy groups (O−CH$_2$CH$_3$) and coordinated −COO groups, respectively,[34] which is in good agreement with the literature.[35,36]

To evaluate the wettability of the CuO and Cu(OH)$_2$ hierarchical structure surface, contact angle measurements were conducted by using a water droplet of 4−5 μL. The water droplet spread immediately when it was placed on the resulting copper plates (Figure 6a). However, the wettability of the surface changed from superhydrophilicity to superhydrophobicity after chemical modification with STA or PDES. As illustrated in Figure 6b and c, the water droplet is hardly able to stick on the modified surfaces and rolls off easily. The CA of the STA-modified surface is about 159.3 ± 1.3°, and that of the PDES-modified surface is about 161.2 ± 2.9°; the two surfaces have a sliding angle of lower than 5°. The surface-modified CuO and Cu(OH)$_2$ hierarchical structure still maintain contact angles of about 160° after being stored in air for about a year, indicating that the as-prepared copper has stable long-term superhydrophobicity.

The advancing CAs (θ_A) and receding CAs (θ_R) of the two types of modified surfaces, measured using the method reported by X. D. Wu et al.,[37] are higher than 150°, but the variation between θ_A and θ_R (so-called hysteresis of CAs, $\Delta\theta$) is different (Figure 7). Namely, STA- and PDES-modified surfaces have a CAH of 6.9 and 2.9°, respectively, which could be attributed to the difference in the surface energy and conforms to the difference in adhesion for a water droplet.

The method reported by Gao et al.[38] was used to test the adhesion of a water droplet on STA- and PDES-modified surfaces. Figure 8 shows the approach, contact, deformation, and departure processes of a 4 μL water droplet suspending on a syringe with respect to the chemically modified surfaces. It can be seen that the water droplet may easily and completely depart from the PDES-modified surface, even though severe

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Figure 7. Pictures captured from the goniometer for a water droplet on a CuO−Cu(OH)$_2$ hierarchical structure surface: (a) advancing and (b) receding on a STA-modified surface; (c) advancing and (d) receding on a PDES-modified surface.
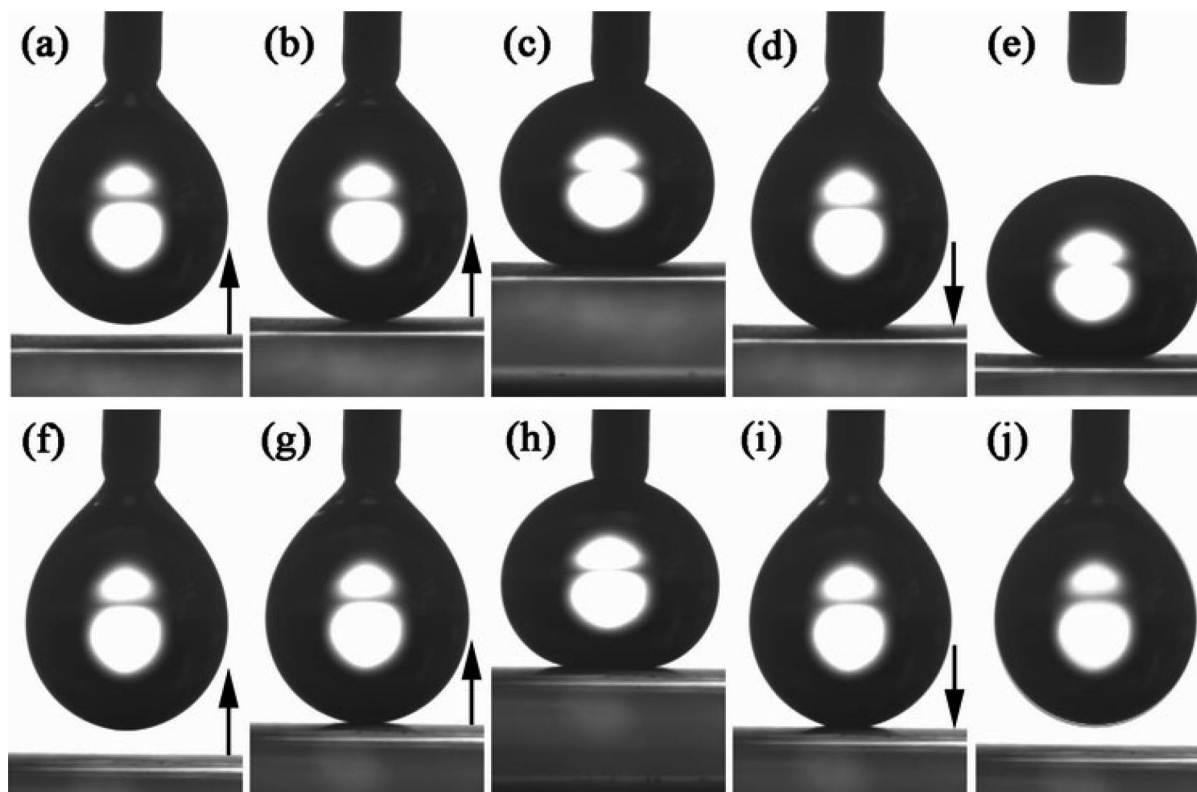

Figure 8. Approach, contact, deformation, and departure processes of a 4 μL water droplet suspending on a syringe with respect to the chemically modified surfaces: (a−e) modified with STA; (f−j) modified with PDES. The arrows represent the moving direction of the substrate.

deformation occurs in this case. Contrary to the above, the water droplet can stay steady on the STA-modified surface. This is because PDES has a much lower surface free energy than STA, although the chain length of STA is longer than that of PDES.

Thus, surfaces of different adhesion can be fabricated through this strategy.

The Cassie and Baxter equation can be cited for full understanding of the superhydrophilicity of the roughened

surface, which is generally valid for very rough heterogeneous surfaces composed of air and a solid:[39]

$$\cos \theta_r = f_1 \cos \theta - f_2$$

where θ_r (159° for the STA-modified surface and 161° for the PDES-modified surface) and θ (86.7° for the STA-modified surface and 113° for the PDES-modified surface) are the CAs of the chemically modified rough and smooth surfaces, respectively; f_1 and f_2 are the fractions of solid surfaces and air in contact with water (i.e., $f_1 + f_2 = 1$), respectively. It is seen from the above equation that increasing fraction of air (f_2) leads to increase of the contact angle on a rough surface (θ_r). According to the equation, the f_2 value of the STA- and PDES-modified surfaces with lotus-like hierarchical structure is estimated to be 0.94 and 0.91, respectively, implying that the larger fraction of air among the interspaces of the chemically modified hierarchical structure might account for the superhydrophobicity of the surface.

Conclusions

A facile alkali assistant surface oxidation technique was developed to fabricate flower-like CuO and Cu(OH)$_2$ nanorod arrays with hierarchical structure similar to that of a lotus leaf by a simple one-step solution-immersion process. Compared with the STA-modified surface, the PDES-modified surface has a lower CA hysteresis and adhesion for water droplets, and the surfaces retained good superhydrophobicity in long-term storage as well. The present approach could provide a new strategy to prepare novel multifunctional materials with potential industrial applications such as corrosion prevention, drag reduction, self-cleaning, and so forth.

Supporting Information Available: SEM images of Cu(OH)$_2$ nanotubes, CuO nanoslices, Cu$_2$O microcrystals, and CuO microflowers; TEM images of a Cu(OH)$_2$ nanorod, a Cu(OH)$_2$ nanotube, and a CuO nanoslice; XPS spectra of F 1s. This material is available free of charge via the Internet at http://pubs.acs.org.

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