Controlled Wetting Properties through Heterogeneous Surfaces Containing Two-level Nanofeatures

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ABSTRACT: Addressing the direct control of surface wettability has been a significant challenge for a variety of applications from self-cleaning surfaces to phase-change applications. Surface wettability has been traditionally modulated by installing surface nanostructures or changing their chemistry. Among numerous nanofabrication efforts, the chemical oxidation method is considered a promising approach because it allows cost-effective, quick, and direct control of the morphologies and chemical compositions of the grown nanostructures. Despite the wide applicability of the surface oxidation method, the precise control of wetting behaviors through the growth of nanostructures has yet to be addressed. Here, we investigate the wetting characteristics of heterogeneous surfaces that contain two-level features (i.e., nanograsses and nanoflowers) with different petal shapes and structural chemistry. The difference in growth rates between nanograsses and nanoflowers creates a time-evolving morphology that can be classified by grass-dominated or flower-dominated regimes, which induces a wide range of water contact angles from 120 to 20°. The following study systematically quantifies the structural details and chemistry of nanostructures associated with their wetting characteristics. This investigation of heterogeneous surfaces will pave the way for selective growth of copper nanostructures and thus a direct control of surface wetting properties for use in future copper-based thermal applications.

INTRODUCTION

In recent years, controlling the wettability of solid surfaces has drawn significant attention for a variety of emerging interfacial physics applications ranging from phase-change applications to self-cleaning surfaces and membrane surfaces. A rational design of the wetting behavior will provide the unique interfacial physics control for performance breakthroughs in the presented applications. In particular, the design of copper surfaces’ wetting properties will be promising in phase-change applications as copper is widely used in the industry. Various efforts to control the wettability of copper-based surfaces have been pursued through structural engineering methods, chemical modification techniques, or a combination of the two methods. Of the listed nanostructuring techniques, chemical oxidation through solution immersion proves to be an effective and low-cost method to install nanostructures on two-dimensional (2D) and three-dimensional (3D) surfaces over a large area. By modulating the processing parameters of chemical oxidation methods, such as process temperature, solution immersion time, and chemical composition, different morphologies of nanoscale copper oxide (CuO) can be created on copper surfaces. Examples of CuO-based features in previous studies include different forms of spheres, cylinders, flowers, and crystals. Despite the significant interest in the surface engineering to modify surface properties, the majority of others work has been limited to the manufacturing process itself. A comprehensive understanding of wetting properties related to surface morphology and chemistry is not well understood. Although the creation of heterogeneous nanostructures has a potential to possess a wide range of wetting properties because of multilevel hierarchy, the control of their wetting behaviors has yet to be addressed. Although typical chemical solutions yield a single level of random nanostructures, the combination of chemical solutions used in our process can be designed to create two-level features containing nanograsses and nanoflowers. In such heterogeneous surfaces containing two-level features, the different growth rates between nanograss and nanoflower exhibit time-evolving morphologies that can be categorized by grass- and flower-dominated regimes with immersion time. The presented chemical oxidation method in this study enables a direct control of nanostructure morphologies by modifying process parameters, including chemical composition and immersion time, to modulate their surface wettability.

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In this study, we investigate the wetting properties of CuO nanofeatures through (1) identifying two-level features such as nanograsses and nanoflowers, (2) modifying the petal shapes (i.e., round or spiky shapes) of nanograsses and nanoflowers by changing chemical concentrations, and (3) defining time-evolving regimes from grass- to flower-dominated regimes. For this, we fabricate various heterogeneous nanostructured surfaces through the use of the chemical oxidation method to study their surface morphology and chemistry. In brief, the fabricated CuO nanograsses show water contact angles (WCAs) of 70°–120°, whereas CuO nanoflowers consistently show lower WCAs of 20°–50°. This study suggests the selective nanostructuring through a combination of nanograsses and nanoflowers will enable a wide range of wettability for use in various applications involving copper surface modification.

## RESULTS AND DISCUSSION

We systematically modulate copper oxide nanostructures’ morphologies by using different combinations of chemical solution composition as well as immersion time (see the Method section for the details). The combination of chemical solutions of NaOH and K$_2$S$_2$O$_8$ creates heterogeneous surfaces possessing two-level features, such as nanograsses and nanoflowers. During the oxidation process, nanograsses and nanoflowers exhibit different nucleation densities and rates, creating time-dependent nanostructure morphologies. In detail, nanograsses initially start growing on the substrate within the “grass-dominated regime” until the critical time $t_c$, whereas the transition between morphological regimes occurs at the flower area ratio $\phi_{NF} = 0.5$. After $t > t_c$, the nanoflowers keep increasing their sizes with immersion time by the Ostwald ripening mechanism $^{24}$ and occasionally agglomerate to form short chains and piles in the “flower-dominated regime”.

The different chemical compositions in the oxidation process affect the morphology of nanograsses and nanoflowers due to their level of alkalinity in the solutions. $^{27}$ Solution 1 produces round-shaped features and thin, long nanowires, defined as “round nanoflower” and “round nanograss”, as indicated in the scanning electron microscope (SEM) images in Figures 1a–d and 2i. The lower NaOH concentration in solution 2 yields spike-shaped features and wide, short nanowires, defined as “spiky nanoflower” and “spiky nanograss” (see SEM images in Figure 1e–h and analysis in Figure 2i). The preferential growth of nanoflowers occurs at surface defects (i.e., impurities, scratches, and grain boundaries) that determine the number of nanoflowers, quickly leading to saturation. The tightly packed nanograsses on such limited spaces of surface defects are prone to depart from the surface and begin to agglomerate, forming clusterlike nanoflowers to reduce their surface energy $^{28}$. The differences in the nanoflowers’ petal shapes are expected to be contributed by the amount of nanograss agglomeration that occurs. That is because a highly basic solution (solution 1) causes a more active nanograss agglomeration, rounding the nanofeatures to produce round nanoflowers, whereas the low agglomeration level of spiky nanograsses causes rough-edged petals to form.

The image quantification of nanofeatures is conducted by investigating both top and side view SEM images (Figure 2a,b). The top view SEM images are used to quantify the morphological details of nanograsses and nanoflowers (i.e., the area ratio $\phi$, diameter $d$, number density $n$, length $l$, and width $w$), where the subscripts NG and NF denote nanograss and nanoflower, respectively. The side view images are obtained using the focus ion beam (FIB) technique, which mills the structure to enable a top-angled view. The side view images through the FIB SEM technique allow us to calculate nanoflower heights $h_{NF}$ and maximum peak height $h_{NF,\text{max}}$. On the basis of those top and side view 2D images, 3D topographical images can be reconstructed to allow us to compute the roughness $r$ by using a commercial software (MountainsMap, see Supporting Information). This postimage processing analyzes the difference in contrast and brightness of an image of interest to construct a relative topographical map.

Figure 1. Scanning electron microscope (SEM) images of time-evolving nanostructures using different combinations of chemical solutions. Round nanograsses and nanoflowers are prepared at immersion time of (a) $t = 3$, (b) $t = 10$, and (c–d) $t = 15$ min. Using different chemical concentrations, spiky nanograsses and nanoflowers at (e) $t = 3$, (f) $t = 10$, and (g–h) $t = 15$ min are observed. Close-up views show (d) round- and (h) spiky-shaped flower petals, respectively. Insets illustrate the evolution of nanograsses and nanoflowers with immersion time. All scale bars are 5 μm.
with the estimation of $h_{\text{NF, max}}$. As a result, a representative 3D topography image of round nanoflowers is shown in Figure 2c.

The plot in Figure 2h showing the nanoflower area ratio $\phi_{\text{NF}}$ confirms that the nanofeature growth can be classified into two distinguishable regimes: nanograsses-dominated ($t < t_c$) and nanoflowers-dominated ($t > t_c$) regimes, where $\phi_{\text{NF}}$ is the ratio of the sum of individual flower area to the total area. The transition between two-level morphologies occurs due to the different growth rates of nanograss and nanoflowers and is shown to approximately occur at $t_c = 7$ min in this study. In addition to the area fraction calculation, the nanoflowers’ (d) diameters $d_{\text{NF}}$, (e) maximum height $h_{\text{NF}}$, (f) number density $n_{\text{NF}}$, (g) roughness $r$, and (h) the area ratio $\phi_{\text{NF}}$. (i) Structural information including length $l_{\text{NG}}$, width $w_{\text{NG}}$, and area ratio $\phi_{\text{NG}}$ of nanograss is plotted.

Another important structural parameter that affects surface wettability is the roughness $r$, defined as the ratio of the interfacial surface to projected surface; thus, a flat surface will have $r = 1$. The $r$ values with varying morphologies are computed using 3D images, as shown in Figure 2g. The $r$ of the round nanostructure is 75% larger than that of the spiky nanostructure in the grass-dominated regime ($t < t_c$) due to its larger nucleation density. In the flower-dominated regime ($t > t_c$), the $r$ of round nanoflowers is 25–50% smaller than that of spiky nanoflowers. Such a noticeable increase in the $r$ of spiky nanoflowers is contributed by the spiky nanoflowers’ sharp-edged petals as well as larger number density $n$ in the flower-dominated regime.

We perform a point-by-point energy-dispersive spectroscopy (EDS) analysis to understand how the chemical composition of individual nanofeatures affects their wetting properties. The ratio of the surface copper to oxygen Cu/O for both round and spiky nanofeatures is plotted as a function of immersion time in

Figure 2. Effects of chemical immersion time on nanostructure morphologies. Representative SEM images of round nanoflowers from (a) top and (b) side-angled view at $t = 15$ min. (c) The top and side views enable the reconstruction of the three-dimensional topography to calculate the nanostructures’ roughness. Image analysis is followed to investigate the morphological details of nanoflowers, including nanoflowers’ (d) diameters $d_{\text{NF}}$, (e) maximum height $h_{\text{NF}}$, (f) number density $n_{\text{NF}}$, (g) roughness $r$, and (h) the area ratio $\phi_{\text{NF}}$. (i) Structural information including length $l_{\text{NG}}$, width $w_{\text{NG}}$, and area ratio $\phi_{\text{NG}}$ of nanograss is plotted.
Figure 3a,b. In Figure 3a, round nanograsses in the grass-dominated regime show a larger ratio of surface content (Cu/O = 0.3−0.4 at \( t < t_c \)) than round nanoflowers (Cu/O = 0.1−0.2), where the surface is mostly covered by grasses instead of flower. Thereby, the resulting wetting properties of round nanostructures (\( t < t_c \)) will be determined by the greater presence of copper, as indicated in Figure 4a. In Figure 3b, spiky nanograsses in the grass-dominated regime show a much larger ratio of surface content (Cu/O = 0.6 at \( t < t_c \)), whereas spiky nanoflowers show a lower ratio of surface content (Cu/O = 0.1−0.2). However, the nucleation density of spiky nanograss is smaller than that of round nanograss. The resulting nanograss area ratio \( \phi_{NG} = \sim 0.2 \) (Figure 2i) at \( t = 3 \) min minimizes the impact of copper-containing spiky nanograsses on the wetting properties (Figure 4a). As time evolves in the flower-dominated regime, the ratio of surface content for all four entities gradually reduces (i.e., the level of oxide increases) to generate hydrophilic surfaces. On the basis of the morphologies and

Figure 4. (a) Phase diagram shows the dependency of surface chemistry (copper regime vs oxide regime) on morphology (grass-dominated regime vs flower-dominated regime). (b) Wettability measured for both round and spiky nanofeatures with varying immersion times shows decreasing water contact angles with immersion time. (c) Variation in \( \cos \theta^* \) as a function of \( \cos \theta \) for round and spiky nanostructures demonstrates that surface roughness governs the wetting behavior in the flower-dominated regime, whereas surface chemistry dominates the grass-dominated regime. (d) Temperature-dependent water contact angles for round and spiky nanostructures (\( t = 25 \) min).
chemistry of nanofeatures, the phase diagram in Figure 4a shows the governing surface chemistry (copper vs oxide) depending on the structural evolving stages (grass-dominated regime vs flower-dominated regime) for both morphologies (round and spiky features). In this phase diagram, round and spiky nanograsses ($t < t_e$) possessing more copper suggest relative hydrophobicity, whereas nanoflowers show more oxide components. In addition to the EDS analysis about the surface oxide, we conduct grazing incidence X-ray diffraction (GI-XRD, Rigaku Smartlab X-ray Diffractometer) to confirm the average surface composition of nanostructures up to 0.6 μm in depth. The relative-intensity-ratio (RIR) method quantifies the surface phase percentage (Figure S6) from the XRD pattern (Figure S5), which shows a drastic increase in the weight percent of CuO, whereas a decrease in the weight percent of Cu with increasing immersion time for all the nanofeatures is observed. This indicates that the formation of nanoflowers is accompanied by the breaking of H-bonds at the edges of Cu(OH)$_2$ layers (see the Supporting Information for details). Despite the changes in morphologies and chemical content ratios in different features, all XRD patterns show the peaks at Cu, CuO, and Cu(OH)$_2$, validating our structures studied in this work are all polymorphs.

After observing the changes in surface morphology and chemistry, we evaluate the wetting characteristics of the fabricated surfaces by measuring their contact angles. For this, we use a contact angle meter (MCA-3, Kyowa Interface Science) that dispenses nanoliter-sized droplets. A high-speed camera at 100 000 fps captures transient and temperature-dependent liquid films on structured surfaces. The contact angle measurements are taken at 10 different locations on each sample to account for spatial variation. The measured WCAs are plotted as a function of the immersion time in Figure 4b. In the grass-dominated regime, round nanograsses exhibit relatively hydrophobic wettability, showing the WCAs of $110^\circ$–$70^\circ$. This might be attributed to the dominance of surface copper in nanograsses, as illustrated by the phase diagram in Figure 4a. Because the regimes are predominantly covered by nanoflowers as $t$ increases, both round and spiky nanoflowers contain more surface oxide and show hydrophilicity. Spiky nanoflowers consistently show lower WCAs because of the combination of surface chemistry and sharp morphology. The role of structural information and chemistry related to surface wettability can be explained by Wenzel’s$^{31}$ or Cassie’s model. In Wenzel’s model, a liquid is assumed to completely fill the grooves of a rough surface, whereas vapor pockets are assumed to be trapped underneath a liquid drop, creating a composite surface in Cassie’s model. Because most surfaces reported in this study are hydrophilic, we employ the Wenzel’s analysis to explain the correlation between surface chemistry and its wettability. The Wenzel’s model is expressed as $\cos \theta^* = r \cos \theta$ where $\theta^*$ is the apparent contact angle on a rough surface, $\theta$ is the contact angle on a flat surface with identical chemical composition, $31$ and $r$ is the roughness. In this analysis, $\theta$ ($\sim 75^\circ$–$90^\circ$) is calculated using $\theta^*$ (WCAs on nanostructured surfaces) and $r$ from image analysis on the basis of Wenzel’s equation. The data sets are placed in the Wenzel quadrant, as plotted in Figure 4c. Both round and spiky nanofeatures show a relatively noticeable difference ($d\theta \sim 15^\circ$) between the regimes, confirming the difference in structural chemistry from grasses to flowers. Again, both round and spiky nanostructures show a small deviation ($d\theta \sim 5^\circ$ at $t > t_e$), revealing that $r$ governs the wettability. The use of Wenzel’s equation is valid in this study because the droplet diameter (300–400 μm) is 2 orders of magnitude larger than the characteristic length of the nanostructures ($\sim 5–8 \mu$m), whereas the gravity effect is negligible.

In addition to the modulation of WCAs via tuning the nanofeature morphology, it is important to investigate the temperature-dependent wetting properties of such nanofeatures because of their potential use in heat transfer devices. In particular, it is of interest to investigate our most hydrophilic samples (i.e., fabricated at $t = 25$ min) for the use in heat pipe applications at elevated temperature. Here, we vary the substrate temperatures ranging from 25 to 90 °C using a thermal stage attached to the substrate to measure the temperature-dependent WCAs, as plotted in Figure 4d. In this process, temperatures are confirmed with a thermocouple taped to the thermoelectric modules and the sample surface. Spiky nanoflowers show a gradual increase in WCAs with increasing temperatures, whereas round nanoflowers show constant WCAs. This phenomenon might be attributed to the formation of local vapor blankets below the highly rough spiky nanoflowers. In general, this measurement confirms the creation of stable and hydrophilic nanostructured surfaces at higher temperatures.

### CONCLUSIONS

In this work, we report the wetting behaviors of heterogeneous surfaces containing two-level features of nanograsses and nanoflowers that are fabricated using a chemical oxidation method. The variation in chemical solutions creates round- or spiky-shaped flower petals, providing different structural roughness over the nanostructures. The difference in nucleation rates of grass and flower related to the immersion time dictates the presence of a grass-dominated regime ($t < t_e$) and flower-dominated regime ($t > t_e$), which is separated by a transition time ($t_e = 7$ min). With these structures, grass-dominated regimes show larger water contact angles due to the presence of surface copper, whereas flower-dominated regimes consistently show smaller water contact angles. In the flower-dominated regime, the surface roughness is a dominating factor in determining the surface wettability, as demonstrated with the Wenzel equation. In addition to this, the temperature-dependent wettability of hydrophilic nanostructured surfaces is reported for their potential use in thermofluidic applications. The new knowledge gained in this study will help us to understand the design parameters of heterogeneous surfaces containing multilevel nanofeatures to directly control their wetting characteristics.

### METHOD

The copper substrate samples with a size of 1 cm x 1 cm and thickness of 0.15 cm (McMaster-Carr, purity 99.9%) are polished with grits of 220, 320, 400, 600, 800, 1000, and 1200 and rinsed with acetone, methanol, and isopropanol for 30 s, followed by additional deionized water. The samples are cleaned using 2 M HCl (Sigma-Aldrich) to remove the nascent copper oxide film and then immersed in either (1) solution 1: 2 M NaOH and 0.1 M K$_2$S$_2$O$_8$ (Sigma-Aldrich) or (2) solution 2: 1 M NaOH and 0.1 M K$_2$S$_2$O$_8$ at room temperature. The solution immersion techniques have been very useful, as most allow scalable, simple, and direct control of engineered features’ morphologies and chemical compositions over a large area.
The characterization was performed at the Irvine Materials Outreach Program and the School of Engineering at the University of California at Irvine.

Notes
The authors declare no competing financial interest.

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REFERENCES

(1) Im, Y.; Dietz, C.; Lee, S. S.; Joshi, Y. Flower-Like CuO Nanostructures for Enhanced Boiling. Nanoscale Microscale Thermophys. Eng. 2012, 16, 145–153.

(2) Seo, J.; Lee, S.-K.; Lee, J.; Seung Lee, J.; Kwon, H.; Cho, S.-W.; Ahn, J.-H.; Lee, T. Path-Programmed Water Droplet Manipulations on an Adhesion Controlled Superhydrophobic Surface. Sci. Rep. 2015, 5, No. 12326.

(3) Liu, J.; Huang, X.; Li, Y.; Suleiman, K. M.; He, X.; Sun, F. Hierarchical Nanostructures of Cupric Oxide on a Copper Substrate: Controllable Morphology and Wettability. J. Mater. Chem. 2006, 16, 4427.

(4) Kulminich, S. A.; Farhadi, S.; Nose, K.; Du, X. W. Superhydrophobic Surfaces: Are They Really Ice-Repellent? Langmuir 2011, 27, 25–29.

(5) Drelich, J.; Chibowski, E.; Meng, D. D.; Terpiłowski, K. Hydrophilic and Superhydrophilic Surfaces and Materials. Soft Matter 2011, 7, 9804.

(6) Kong, L.-H.; Chen, X.-H.; Yu, L.-G.; Wu, Z.-S.; Zhang, P.-Y. Superhydrophobic Cuprous Oxide Nanostructures on Phosphor-Copper Meshes and Their Oil-Water Separation and Oil Spill Cleanup. ACS Appl. Mater. Interfaces 2015, 7, 2616–2625.

(7) Kim, P.; Kreder, M. J.; Alvarenga, J.; Aizenberg, J. Hierarchical or Not? Effect of the Length Scale and Hierarchy of the Surface Roughness on Omniphobicity of Lubricant-Infused Substrates. Nano Lett. 2013, 13, 1793–1799.

(8) Eskandari, A.; Sangpour, P.; Vaezi, M. R. Hydrophilic Cu2O Nanostructured Thin Films Prepared by Facile Spin Coating Method: Investigation of Surface Energy and Roughness. Mater. Chem. Phys. 2014, 147, 1204–1209.

(9) Sung, W.; Kim, W.; Lee, S.; Lee, H.; Kim, Y.; Park, K.; Lee, S. Field Emission Characteristics of CuO Nanowires by Hydrogen Plasma Treatment. Vacuum 2007, 81, 851–856.

(10) Zou, Y.; Li, Y.; Zhang, N.; Liu, X. Flower-like CuO Synthesized by CTAB-Assisted Hydrothermal Method. Bull. Mater. Sci. 2011, 34, 967–971.

(11) Nam, Y.; Ju, Y. S. Fabrication and Characterization of Superhydrophobic Microposts for Micro Heat Pipes. Proc. PowerMEMS 2009, 2009, 123–126.

(12) Xu, X.; Yang, H.; Liu, Y. Self-Assembled Structures of CuO Primary Crystals Synthesized from Cu(2CH3COO)2NaOH Aqueous Systems. CrystEngComm 2012, 14, 5289.

(13) Mäjkovic, N.; Enright, R.; Nam, Y.; Lopez, K.; Dou, N.; Sack, J.; Wang, E. N. Jumping-Droplet-Enhanced Condensation on Scalable Superhydrophobic Nanostructured Surfaces. Nano Lett. 2013, 13, 179–187.

(14) Wang, S.; Feng, L.; Jiang, L. One-Step Solution-Immersion Process for the Fabrication of Stable Bionic Superhydrophobic Surfaces. Adv. Mater. 2006, 18, 767–770.

(15) He, Z.; He, J.; Zhang, Z. Selective Growth of Metallic Nanostructures on Microstructured Copper Substrate in Solution. CrystEngComm 2015, 17, 7262–7269.

(16) Huang, D.; Leu, T. Applied Surface Science Fabrication of High Wettability Gradient on Copper Substrate. Appl. Surf. Sci. 2013, 280, 25–32.

(17) Zhang, N.; Lu, S.; Xu, W.; Zhang, Y. Controlled Growth of CuO-Cu/Pt/Cu Micro-Nano Binary Architectures on Copper Substrate and Its Superhydrophobic Behavior. New J. Chem. 2014, 38, 4534–4540.

(18) Zeng, O.; Wang, X.; Yuan, Z.; Wang, M.; Huang, J. Fabrication of a Superhydrophobic Surface on Copper Foil Based on Ammonium Bicarbonate and Paraffin Wax Coating. Surf. Topogr.: Metrol. Prop. 2015, 3, No. 035001.

(19) Chen, X.; Kong, L.; Dong, D.; Yang, G.; Yu, L.; Chenand, J.; Zhang, P. Fabrication of Functionalized Copper Compound Hierarchical Structure with Bionic Superhydrophobic Properties. J. Phys. Chem. C 2009, 113, 5396–5401.

(20) Nam, Y.; Ju, Y. S. Comparative Study of Copper Oxidation Schemes and Their Effects on Surface Wettability. Heat Transfer, Fluid Flows, and Thermal Systems, Parts A, B, and C; ASME, 2008; Vol. 10, pp 1833–1838.

(21) Huang, D. J.; Leu, T. S. Fabrication of High Wettability Gradient on Copper Substrate. Appl. Surf. Sci. 2013, 280, 25–32.

(22) Liu, J.; Huang, X.; Li, Y.; Li, Z.; Chi, Q.; Li, G. Formation of Hierarchical CuO Microcabbages as Stable Bionic Superhydrophobic Materials via a Room-Temperature Solution-Immersion Process. Solid State Sci. 2008, 10, 1568–1576.

(23) Guo, Z.-G.; Fang, J.; Hao, J.; Liang, Y.; Liu, W. A Novel Approach to Stable Superhydrophobic Surfaces. ChemPhysChem 2006, 7, 1674–1677.

(24) Pei, M.-D.; Wang, B.; Li, E.; Zhang, X.; Song, X.; Yan, H. The Fabrication of Superhydrophobic Copper Films by a Low-Pressure-Oxidation Method. Appl. Surf. Sci. 2010, 256, 5824–5827.

(25) Wang, G.; Zhang, T.-Y. Easy Route to the Wettability Cycling of Copper Surface between Superhydrophobicity and Superhydrophilicity. ACS Appl. Mater. Interfaces 2012, 4, 273–279.

(26) Chaudhary, A.; Barshilia, H. C. Nanometric Multiscale Rough CuO/Cu(OH)2 Superhydrophobic Surfaces Prepared by a Facile One-Step Solution-Immersion Process: Transition to Superhydrophilicity with Oxygen Plasma Treatment. J. Phys. Chem. C 2011, 115, 18213–18220.

(27) Zhang, W.; Wen, X.; Yang, S. Controlled Reactions on a Copper Surface: Synthesis and Characterization of Nanostructured Copper Compound Films. Inorg. Chem. 2003, 42, 5005–5014.

(28) Jung, H. S.; Kim, K.; Kim, M. S. Raman Spectroscopic Investigation of the Adsorption of 4-Mercaptopyridine on a Silver-Sol Surface. J. Mol. Struct. 1997, 407, 139–147.
(29) Mitsunaga, T. X-Ray Thin-Film Measurement Techniques II. Out-of-Plane Diffraction Measurements. *Rigaku J.* 2009, 25, 7–12.
(30) Cooper, M. J. X-Ray Absorption Coefficients for Certain Metals. *Acta Crystallogr.* 1965, 18, 813.
(31) Wenzel, R. N. Resistance of Solid Surfaces. *Ind. Eng. Chem.* 1936, 28, 988—994.
(32) Cassie, A. B. D.; Baxter, S. Wettability of Porous Surfaces. *Trans. Faraday Soc.* 1944, 40, 546—551.
(33) Marmur, A.; Bittoun, E. When Wenzel and Cassie Are Right: Reconciling Local and Global Considerations. *Langmuir* 2009, 25, 1277–1281.
(34) Meiron, T. S.; Marmur, A.; Saguy, I. S. Contact Angle Measurement on Rough Surfaces. *J. Colloid Interface Sci.* 2004, 274, 637–644.