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Selective growth of metallic nanostructures on microstructured copper substrate in solution

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Supporting information

Experimental Section

Materials. The 25-μm thick copper foils (Alfa Aesar, item No.13382) were used as the substrate. Ethanol, acetone, isopropanol, n-hexane, sodium hydroxide, ammonium persulphate and silver nitrate were purchased from Sigma Aldrich, and 1H,1H,2H,2H-Perfluorodecyltrichlorosilane (FDTS) and carbon black was purchased from Alfa Aesar. All these chemicals were used as received. The deionized (DI) water with a resistivity of 18.2 MΩ·cm^{-1} was used for the contact angle measurements.

Fabrication of microstructures. The copper foil was cut into small pieces and washed by ethanol, acetone and isopropanol, respectively, followed by drying using a nitrogen spray gun. During a photolithography process, a Karl Suss MA6 mask aligner with a soft exposure mode was used to prepare ma N-440 negative photoresist micropillars and cross-shaped micropatterns. Afterwards, the chemically assisted ion beam etching (CAIBE) was used to fabricate micropillars on copper foil substrates. The neutralizer current and beam current were 600 mA and 500 mA, and the beam voltage and accelerator were 500 V and 300 V, respectively. The etching time was chosen from 10 to 30 min with argon and oxygen as the etching gases. Finally, the copper foils were washed by ethanol, acetone and isopropanol again.

Fabrication of nanostructures. The above microstructured copper foils were immersed in a mixed aqueous solution of 2.5 mol L^{-1} sodium hydroxide and 0.1 mol L^{-1} ammonium persulphate at room temperature for a certain time (10 to 45 min).[1] Then, these copper foils were taken out from the solution, fully rinsed with deionized water, and dried with a nitrogen gun. The obtained substrates were dried at 120 ^{o}C for 2 h to make Cu(OH)2 become stable CuO by completing dehydration reaction.

Chemical modification. These copper foils were incubated in a 0.5 wt% n-hexane solution of 1H,1H,2H,2H-Perfluorodecyltrichlorosilane (FDTS) at room temperature for 1 h, followed by drying at 120 ^{o}C for 1 h.[2]

Characterization. The morphologies of the resulting copper surfaces were observed by using a Hitachi S5500 field emission scanning electron microscope (FESEM). The element composition was characterized by using a TM3000 X-ray energy-dispersive (EDX) spectrometer. X-ray diffraction (XRD) was utilized to characterize the copper substrates on an Ultima III X-ray diffractometer with an incident angle of 3^{o} and a scan angle range of 10-60^{o}.[3] The purpose of this low angle XRD was to determine surface crystal structures of different CuO micro/nanostructures to avoid the possible influence of the copper substrate. TEM images of nanoneedles of MN2 were studied by a 200 kV field-emission JEOL 2010F microscope. Besides, the TEM specimen was prepared by crushing nanoneedles from micropillars and dispersing them in ethanol, and subsequently dripping the dispersion onto a TEM gold grid covered by an amorphous electron transparent holey carbon foil. Moreover, the water contact angles (CAs) of different copper substrates were measured by using a CAM 200 contact-angle system at room temperature with a water droplet volume of 10 μL. The water adhesion force was investigated by Dynamic Contact Angle Tensiometer (dataphysics DCAT11®) at room temperature and each substrate was tested for five times.

References

1. A. Chaudhary and H. C. Barshilia, *J. Phys. Chem. C*, 2011, **115**, 18213-18220.
2. J. Feng, Y. Pang, Z. Qin, R. Ma and S. Yao, *ACS Appl. Mater. Interfaces*, 2012, **4**, 6618-6625.
3. E. D. Eanes, *J. Roy. Micros. Soc.*, 1964, **83**, 197-206.

Photoresist micropillars with different views are shown in Figure S1a-d, and they will be dissolved after immersing them in alkaline solution for 30 min. Compared with the growth of CuO nanoneedles on copper substrate in Figure S5, there are no flower-like CuO microstructures over nanoneedles in Figure S1e-h. Therefore, the role of photoresist micropillars is only to delay the growth of CuO.

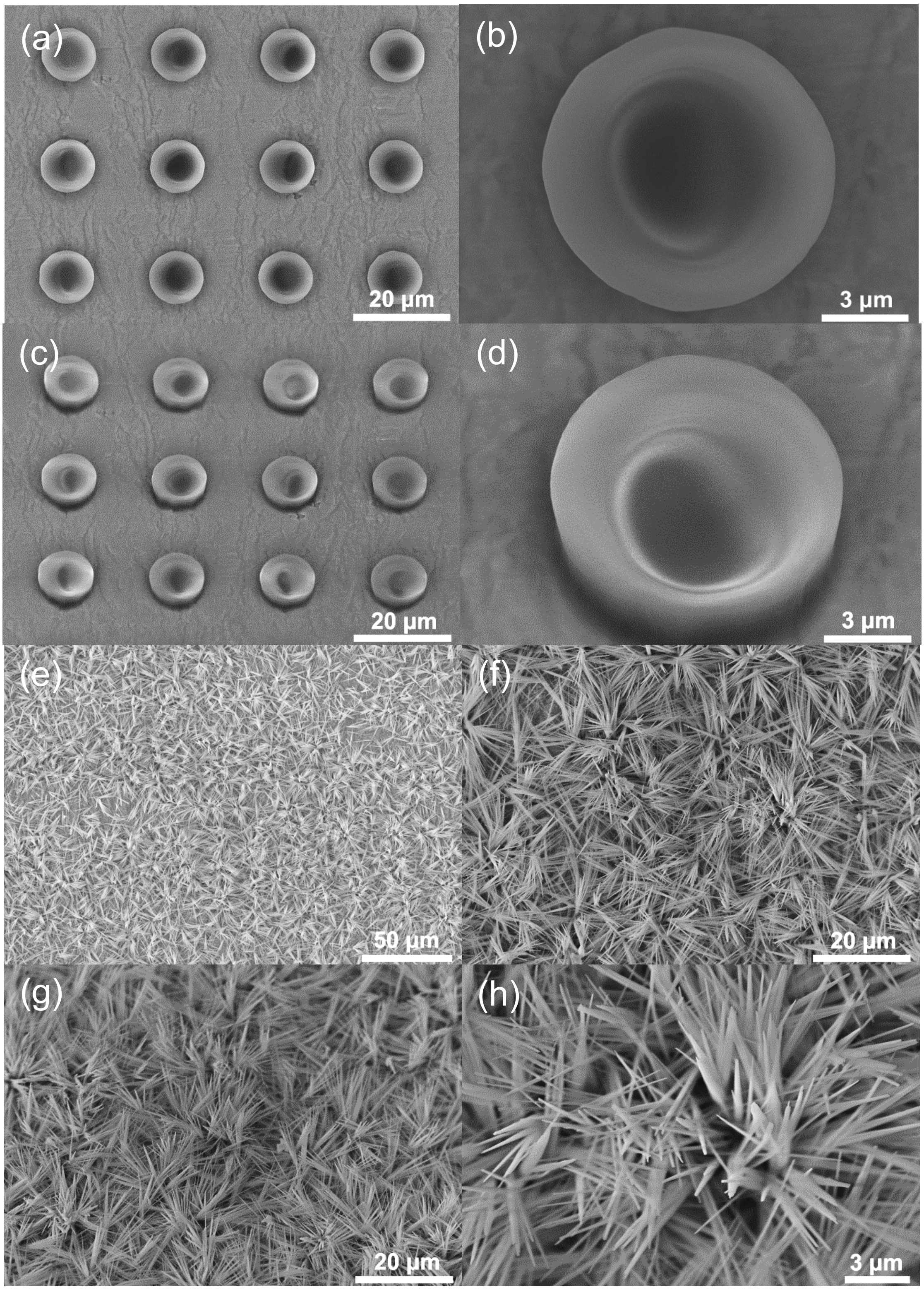


Figure S1. (a-d) Photoresist micropillars and (e-h) CuO nanoneedles were obtained by immersing the photoresist micropillars in alkaline solution for 30 min.

After the Ar etching, the redeposition of Cu around photoresist micropillars can be found in Figure S2a&b. Then, the carbon layers and residual photoresist will be removed completely during O_2 etching for 10 min.

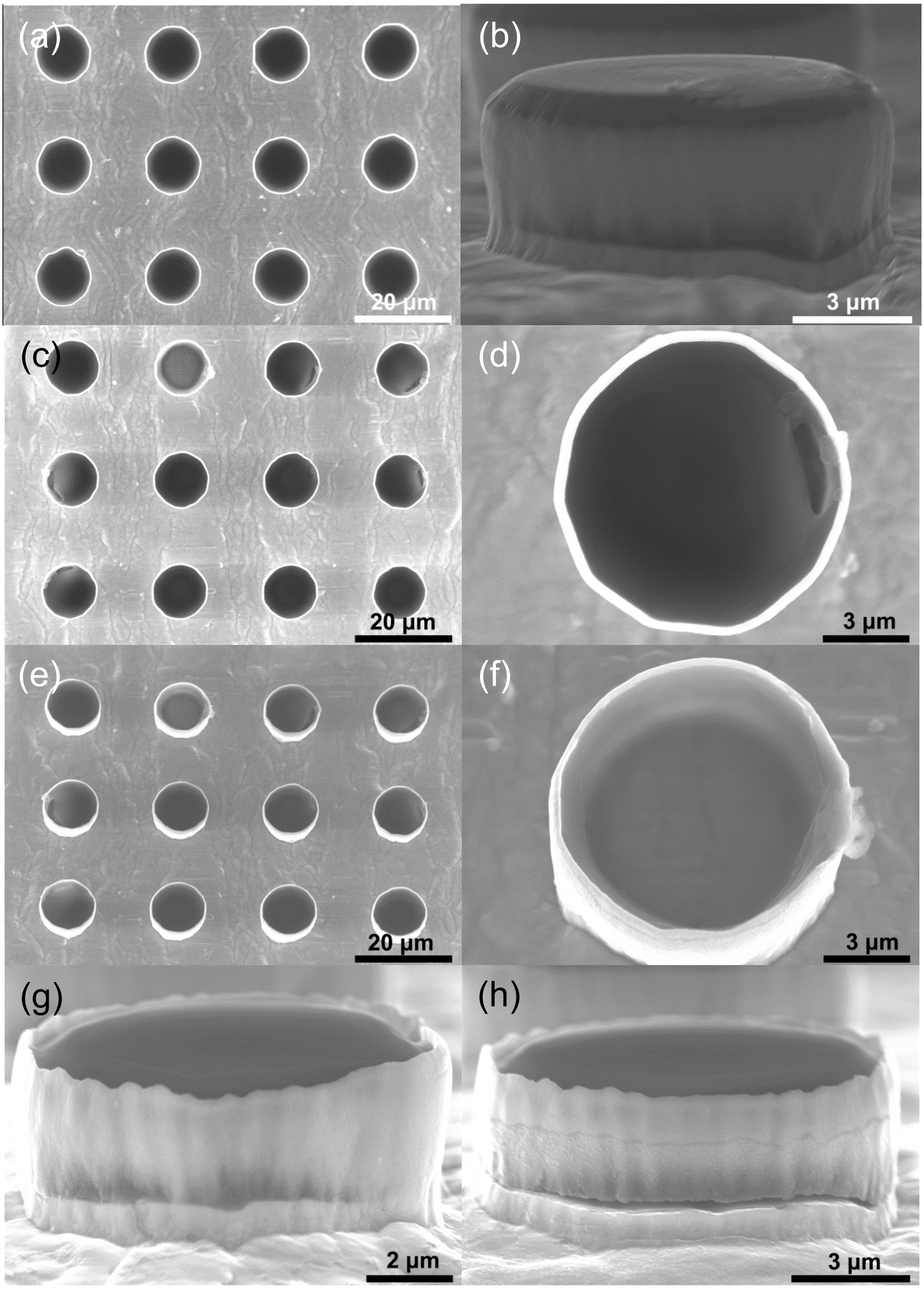
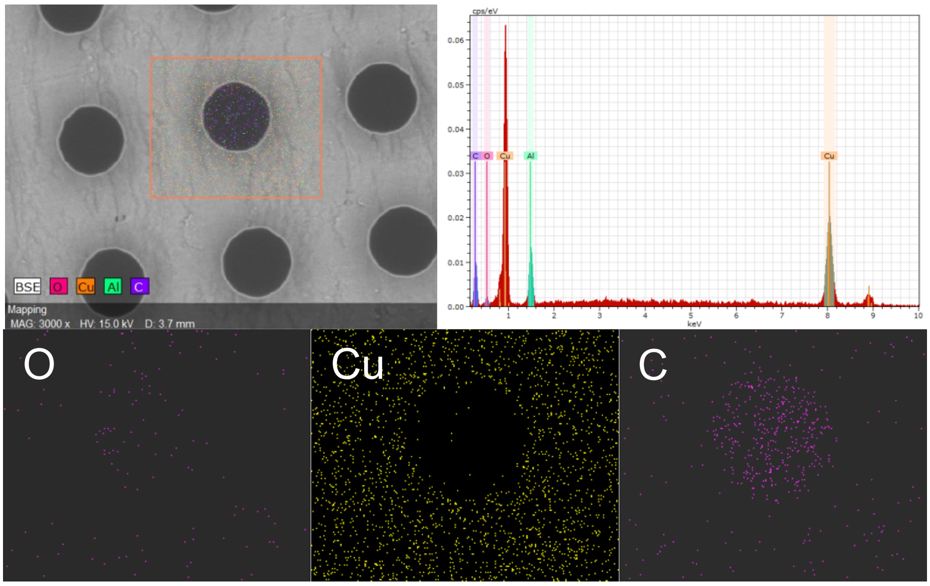


Figure S2. (a, b) Copper micropillars were etched by Ar for 30 min; (c-h) the copper micropillars were etched by O_2 for 5 min after the Ar etching.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Cu
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C
Mapping
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cps/eV
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0.05
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0.03
0.02
0.01
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C
O
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1
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keV
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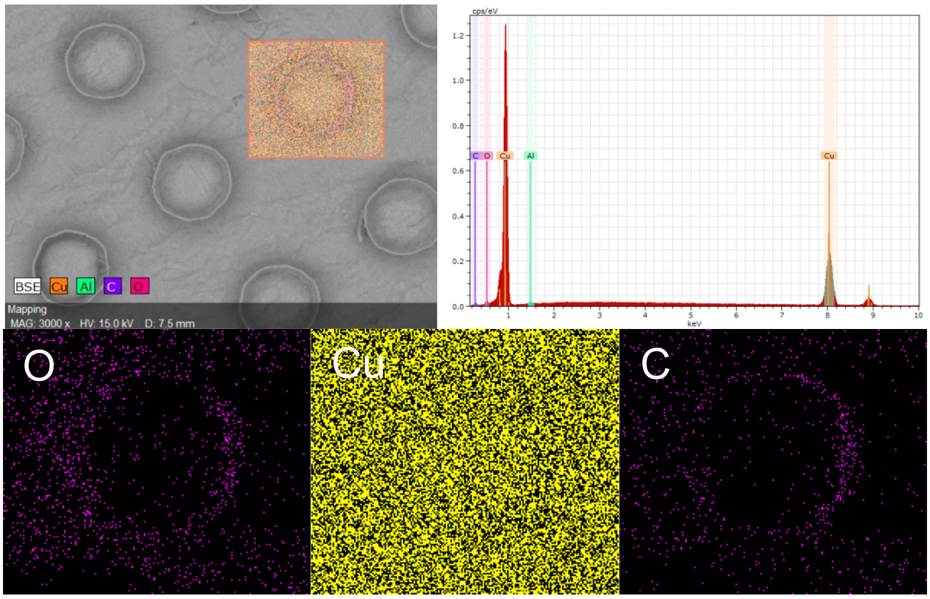
(a)


BSE
Cu
Al
C
O
Mapping
MAG: 3000 x HV: 15.0 kV D: 7.5 mm
cps/eV
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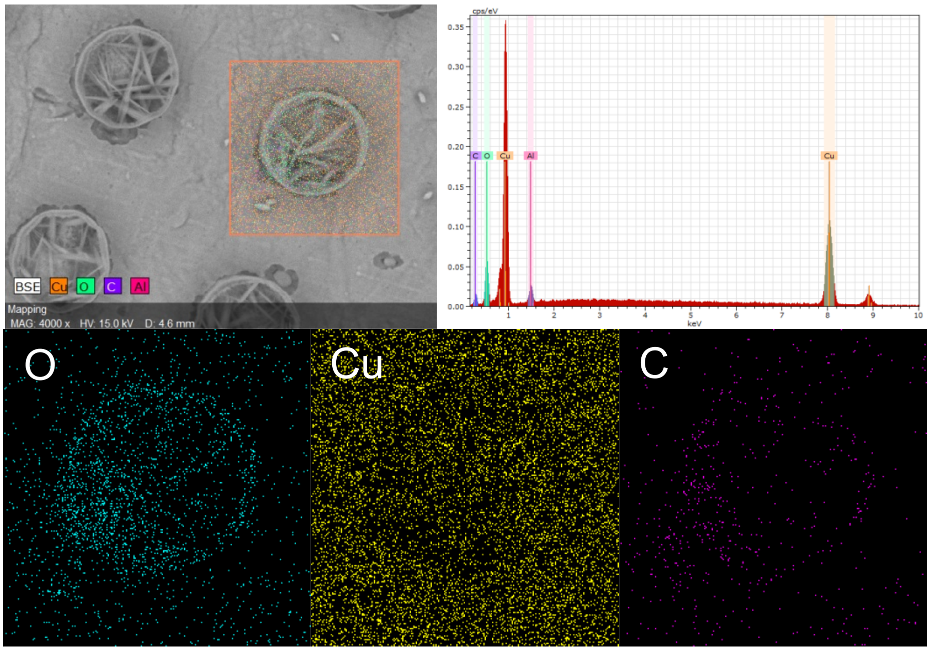
1.0
0.8
0.6
0.4
0.2
0.0
C
O
Cu
Al
Cu
1
2
3
4
5
6
7
8
9
10
keV
O
Cu
C

(b)



(c)

Figure S3. EDS images of MN1 in the process A: (a) after Ar etching; (b) after O_2 etching; (c) MN1

In Figure S4, thin-wall hollow CuO micropillars are obtained by both Ar and O2 etching for only 10 min. CuO nanoneedles (Figure S4b) and flower-like CuO nanostructures (Figure S4c&d) can be found after the immersion reation. Interestingly, the growth of flower-like CuO nanostructures is over CuO nanoneedles as the immersion time increased,[1] which can also be seen from Figure S4a.

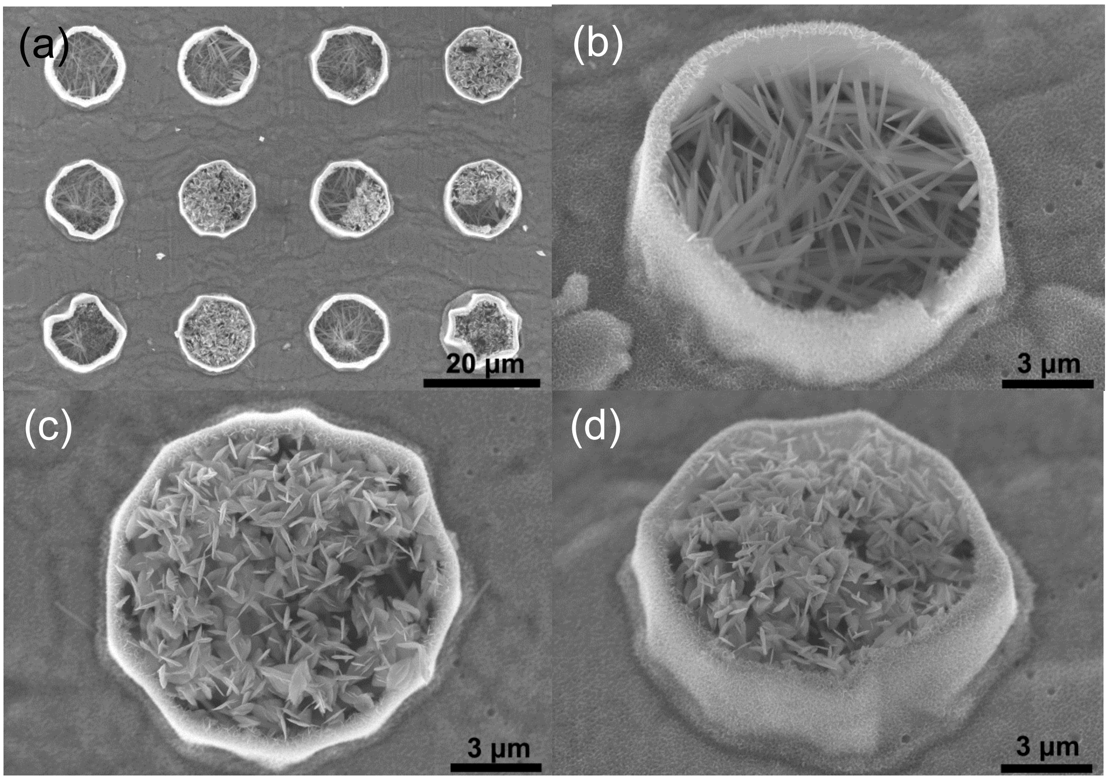


Figure S4. CuO nanoneedles and CuO nanoflakes only grew inside thin-wall and hollow copper micropillars with the immersion reaction of 30 min. As for these thin-wall and hollow copper micropillars, both the Ar and O_2 etching time is only 10 min. (a) Micro/nanostructures containing both nanoneedles and nanoflakes; (b) nanoneedles; and (c&d) nanoflakes.

In Figure S5b-d, flower-like CuO microstructures grow over CuO nanoneedles and the size of these microflowers increased as the immersion time ranges from 10 min to 30 min.

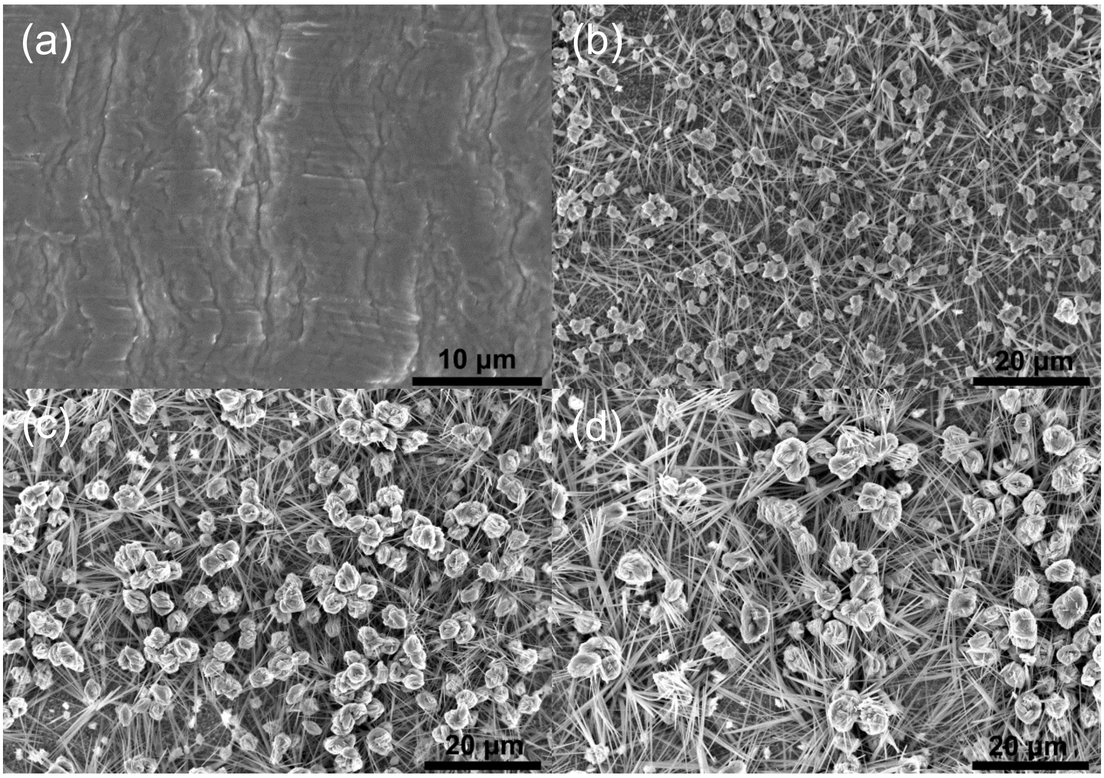


Figure S5. The morphology of (a) the bare copper foil; and flower-like CuO microstructures after the immersion reaction for (b) 10 min, (c) 20 min, and (d) 30 min.

Similar to Figure S4&5, flower-like CuO grows over CuO nanoneedles inside hollow Cu micropillars after the immersion reaction for 45 min as shown in Figure S6d-f. The difference between Figure S6a-c and Figure S6d-f is that flower-like CuO grew over hollow micropillars and CuO nanoflakes grow over the ends of CuO nanoneedles.

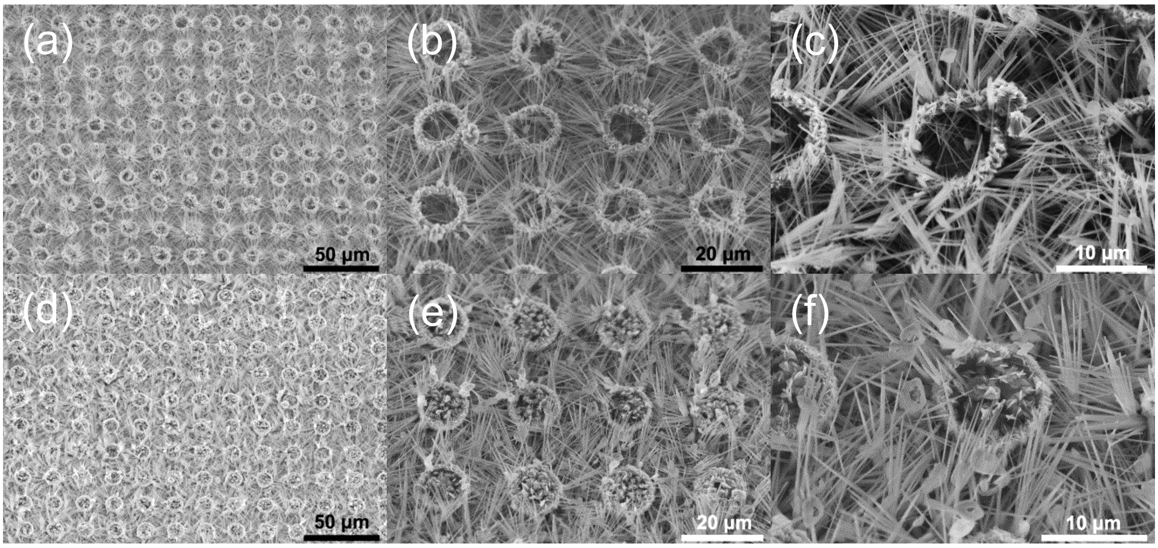


Figure S6. The micro/nanostructures prepared by process B. The micropillars were etched by Ar for 30 min. The immersion reaction time: (a-c) 30 min; (d-f) 45 min.

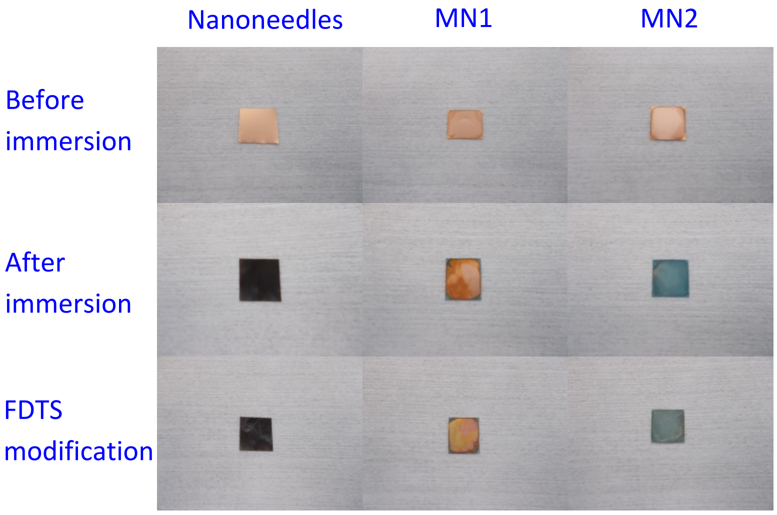


Figure S7. Photographs of nanoneedles (NN), MN1 and MN2 before and after the immersion reaction, and after the modification of FDTS.

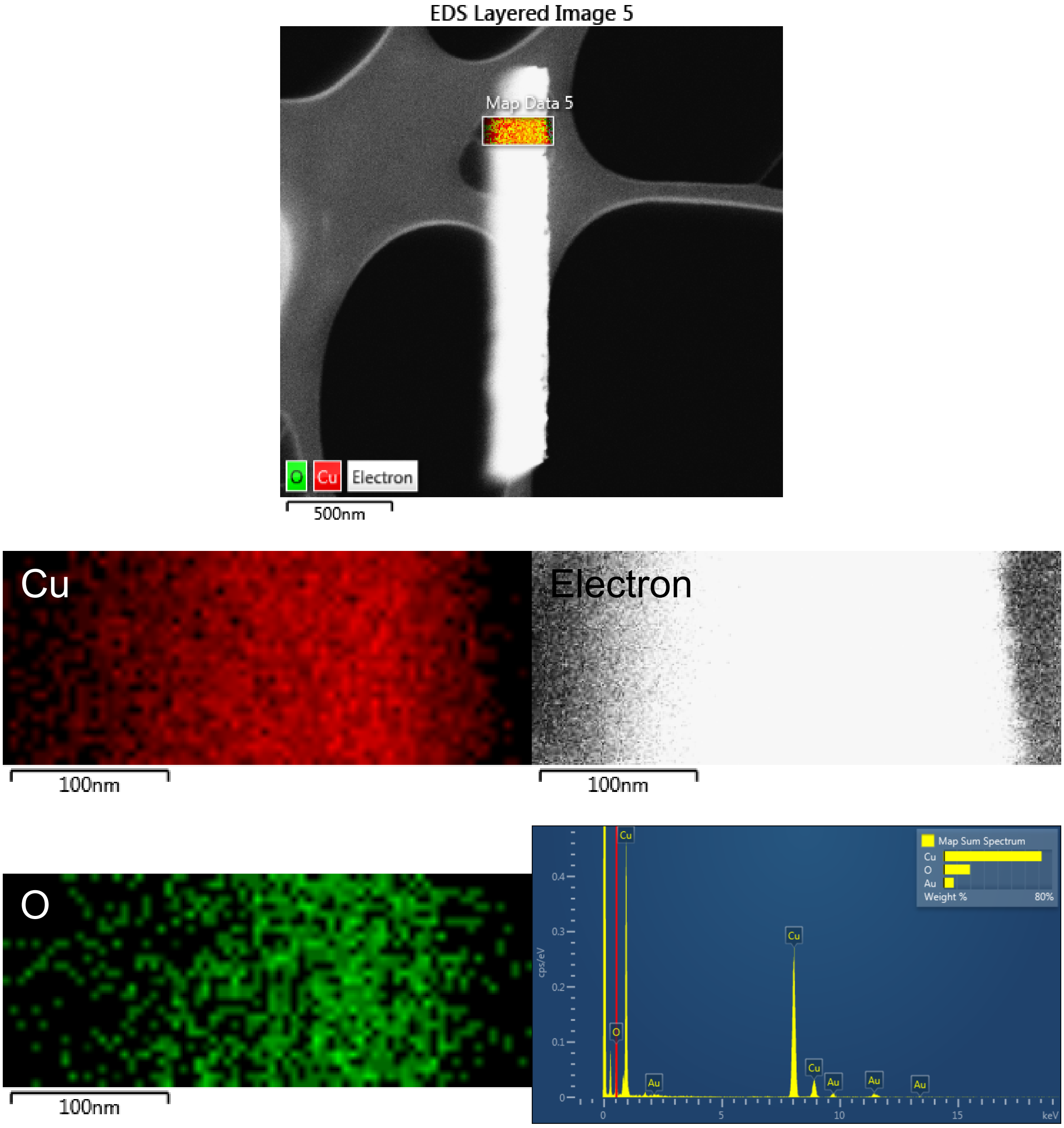


Figure S8. EDS images of nanoneedles of MN2, including the distribution and relative proportion (intensity) of defined elements (oxygen and copper) and electrons over the scanned area.

An abundant amount of carbon black powder or chalk dust is dispersed to make contaminated surfaces (MN1 and MN2). Then, water droplets are slowly dripped to clean these contaminated surfaces. Figure S9 clearly shows good self-cleaning properties of MN1 and MN2 if enough water drops are provided. Moreover, a high speed water jet impact is used to study the stability of superhydrophobicity, and MN2 displays an excellent repelling property.

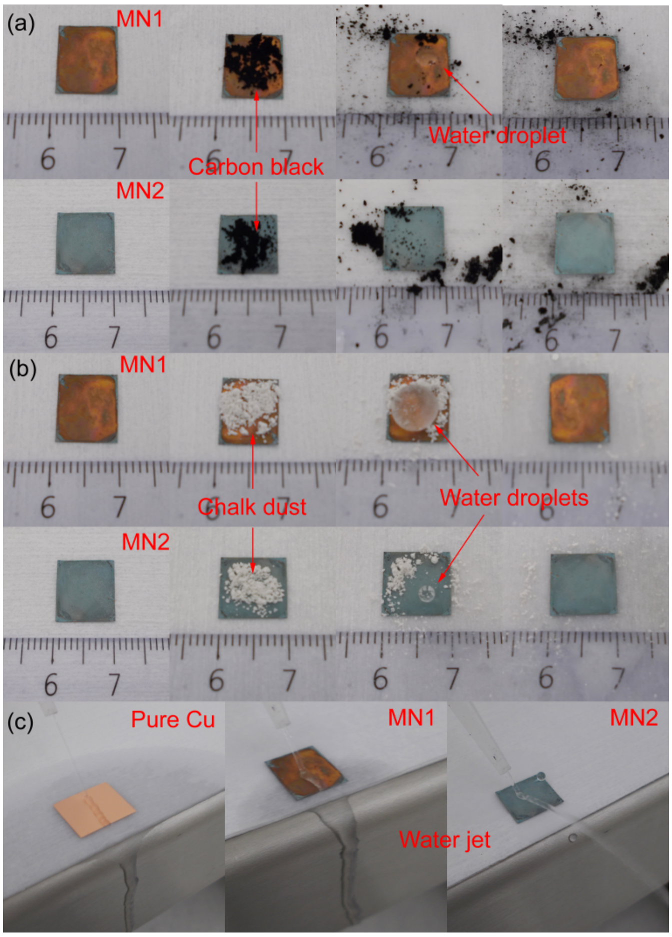


Figure S9. Self-cleaning performance on MN1 and MN2, (a) carbon black powder and (b) chalk dust; (c) water jet impact on pure Cu, MN1 and MN2.