Controlled Wetting Properties through Heterogeneous Surfaces Containing Two-level Nanofeatures

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Supporting Information

1. SEM Images of Nanoflower Morphologies with Varying Immersion time

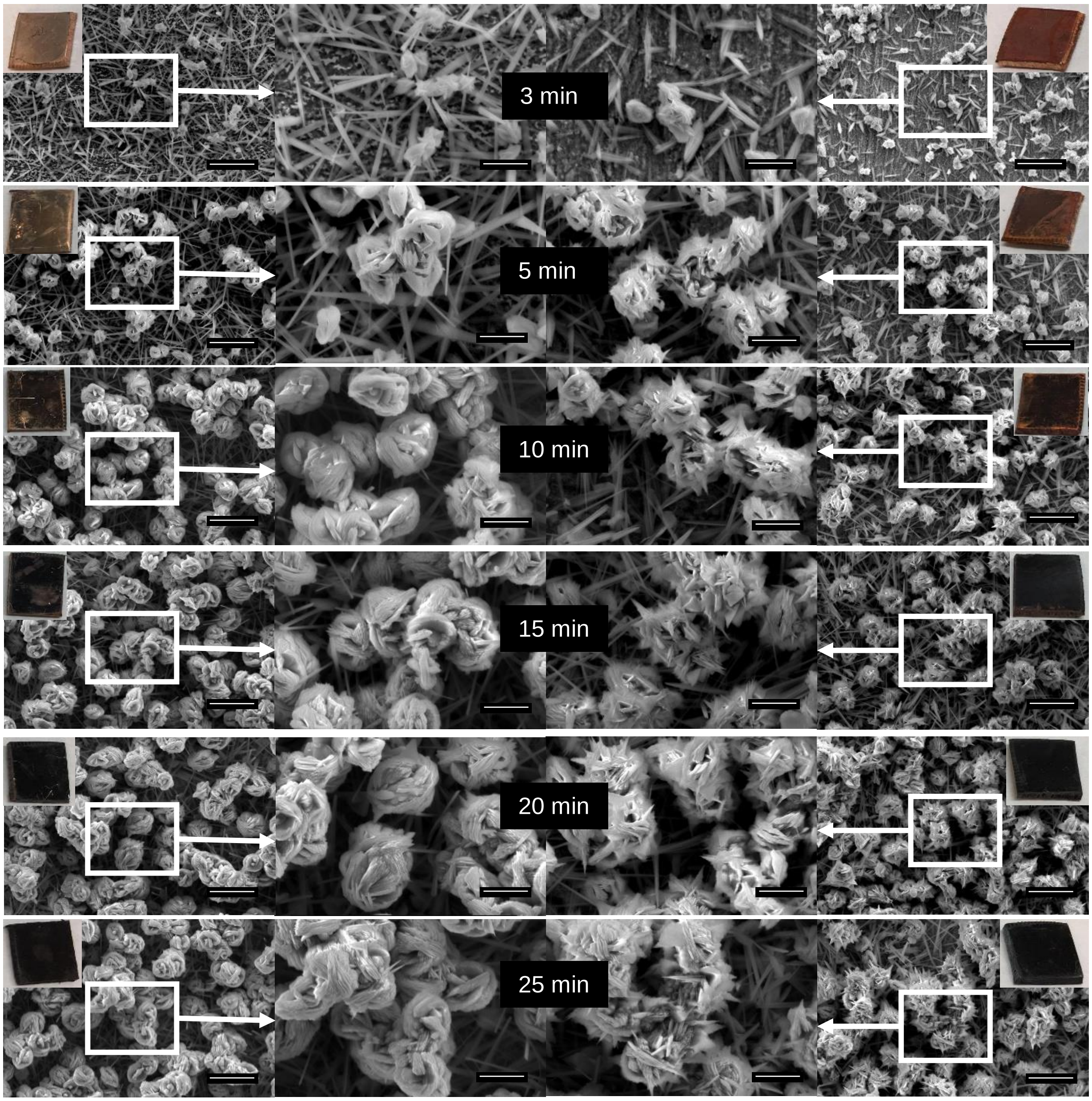

Figure S1. SEM images of round (left two columns) and spiky (right two columns) nanoflowers. It shows a clear trend of increasing the density and size of nanoflowers with increasing immersion time. Inset figures show macroscopic images. Scale bars are 5μm (for first and last columns) and 2μm (for middle columns).

Morphological effects of nanostructures are investigated using scanning electron microscope (SEM) images (Philips XL30 Scanning Electron Microscopy). As the immersion time increases up to 25 minutes (top to bottom), the color of samples turns from brown to black (Figure S1 insets). The images also show a clear trend of nanoflowers' nucleation, resulting in an increase in diameter and average of nanoflowers (as the values from the image analysis are shown in Figure 2). This shows the growth of nanograss and nanoflowers with through the oxidation method. A close observation of the nanoflower petals (middle two columns) shows the round-shaped petals and sharp-shaped petals of round and spiky nanoflowers, respectively. Each sample is scanned for images at 5 random locations.

2. 3D reconstruction and relative roughness analysis of single SEM images

As a next step, three-dimensional (3D) topography of nanostructures is reconstructed by combining top-view SEM images with cross-sectional images using FIB-SEM (FEI Quanta 3D FEG Dual Beam, Figure S2a and b) using a commercial software (MountainsMaps®). The apparent maximum height is calculated from the lowest point to the highest point on the milled surface based the titled angle of the sample of 52^{o} (Figure S2c). The cross-sectional images clearly confirm the dendritic growth of nanofeatures. Round nanoflowers at t = 15 minutes (Figure S2a) show a comparatively smoother surface profile with thicker and rounder nanograsses fabricated comparing to spike nanoflowers at t = 15 minutes (Figure S2b). This post-image processing method enables the quick and low-cost reconstruction of 3D topography with an accuracy while atomic force microscopy (AFM) might be limited because of the "tip convolution effect"[1]. In order to improve the accuracy of 3D topographies, SEM images should be carefully taken with a larger contrast without losing a good depth of focus.

Representative 3D reconstructed images of round (Figure S3) and spike (Figure S4) nanoflowers fabricated at t=15 minutes are shown. Table 1 lists the average of the roughness parameters evaluated using the ISO 25178 standard. The skewness and kurtosis for both nanoflowers do not differ much, proving the distribution is equally skewed. This may be taken as a quantitative indicator that the images are collected at equal contrast and brightness values for a fair comparison. Note that the roughness r is the ratio of actual surface area to projected surface area where developed interfacial area Sdr is the ratio of liquid-solid interfacial area to projected surface area. Thus, the correlation between r and Sdr is expressed as $Sdr = 100(r\text{-}1)$ (%). In the grass-dominated regime at $t < t_c$, round nanograsses show larger roughness than spike nanograsses while spike nanoflowers show larger roughness in the flower-dominated regime at $t > t_c$.

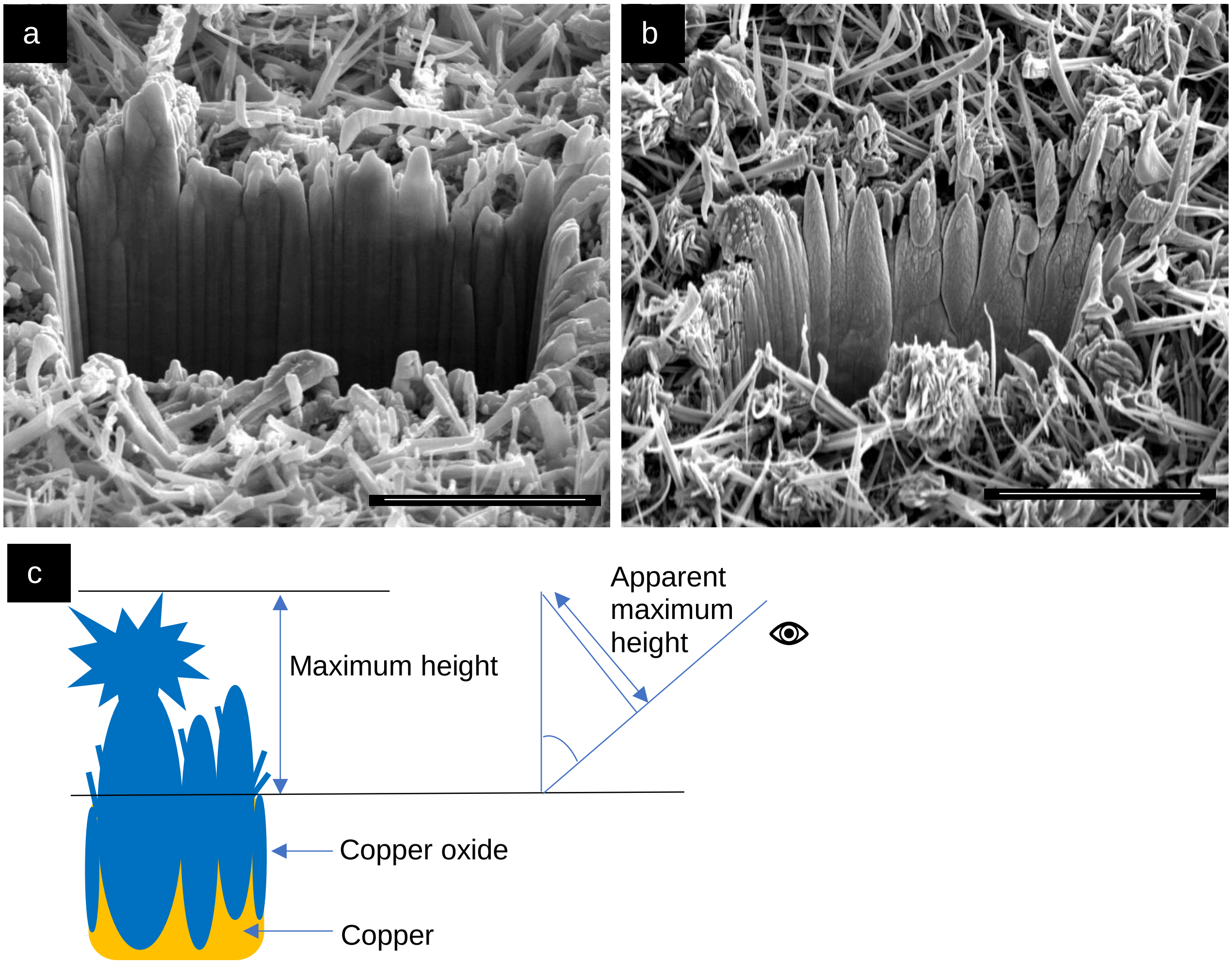

Figure S2. FIB-SEM images of round (a) and spiky (b) naonflowers fabricated at t=15 minutes are used to quantify maximum height data to reconstruct the3D image. Scale bar is 5μm. (c) For the height calculations, the apparent maximum height is modified based on the titled angle of the sample.

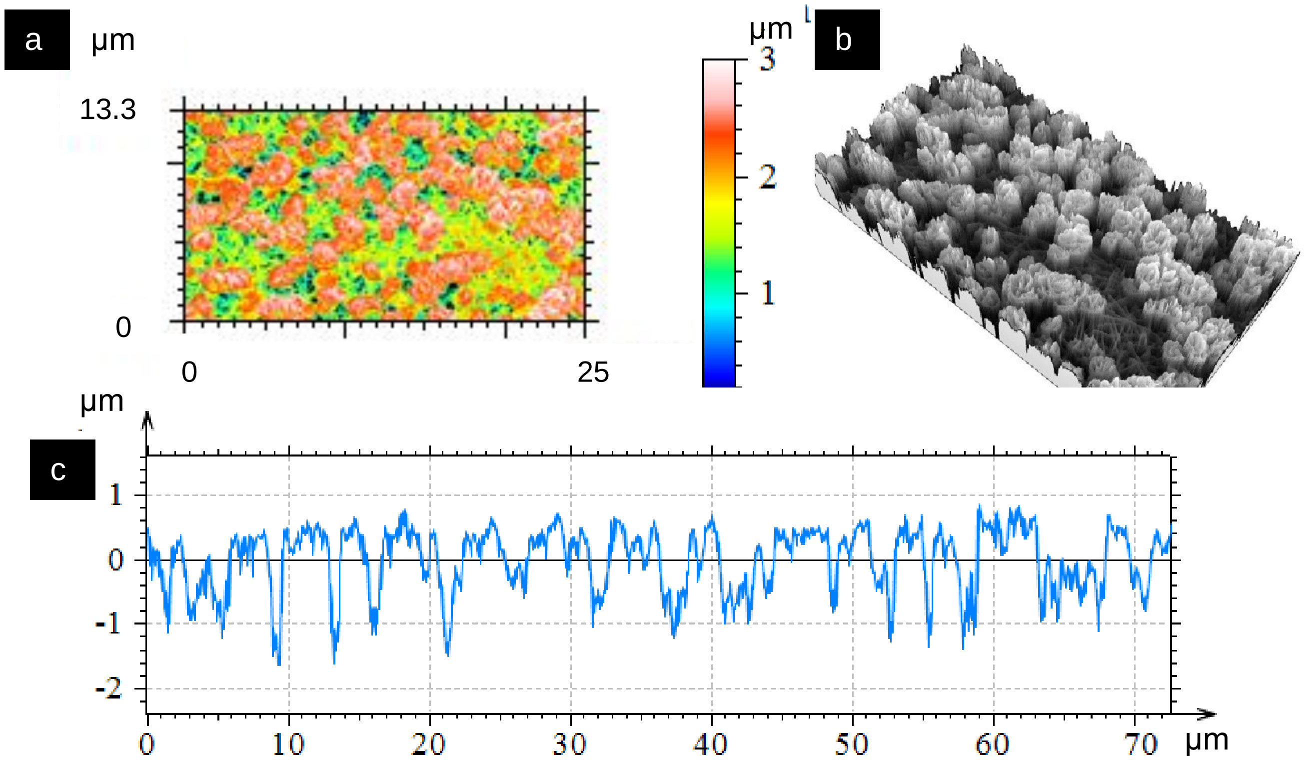

Figure S3. 3D reconstruction process of round nanoflowers fabricated at t = 15 minutes. (a) Topological plot, (b) 3D visualization, and (c) roughness profile.

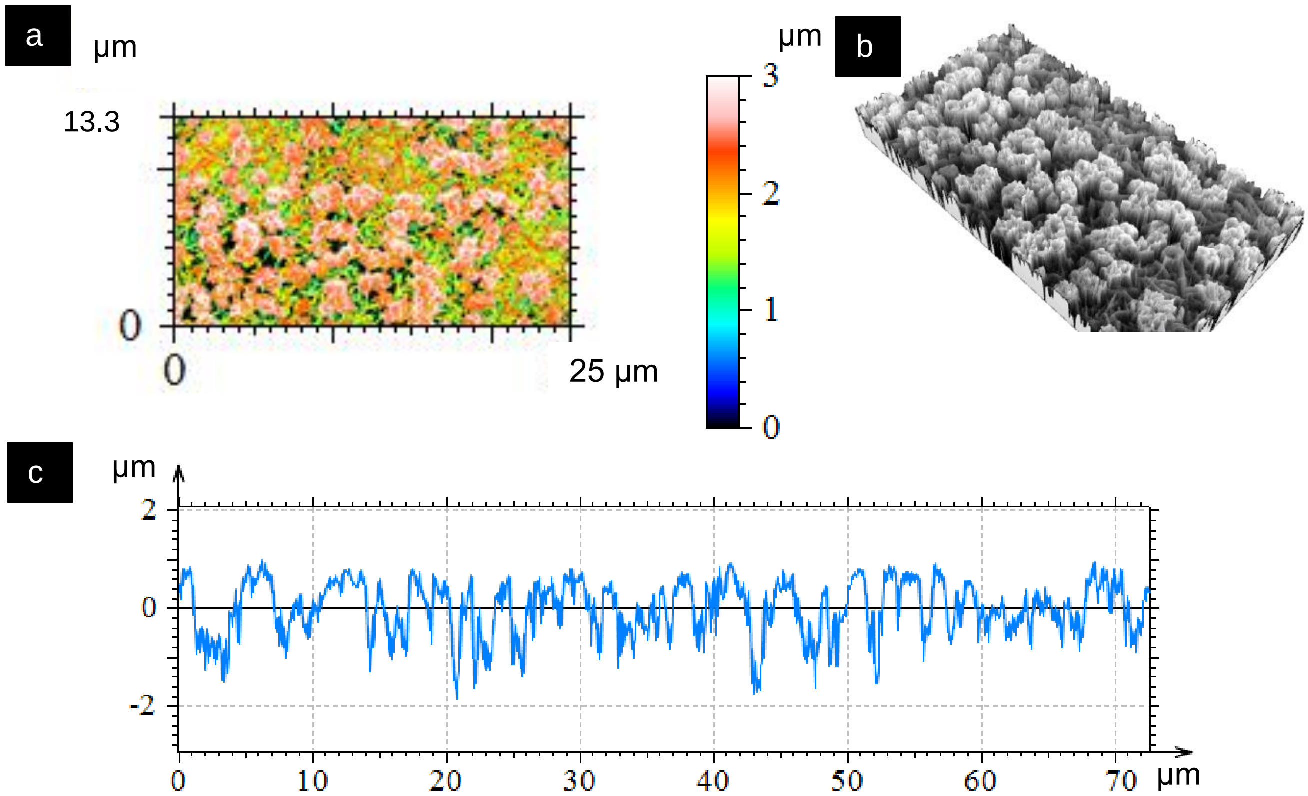

Figure S4. 3D reconstruction process of spiky nanoflowers fabricated at t = 15 minutes. (a) Topological plot, (b) 3D visualization, and (c) roughness profile.

Table S1. Parameters evaluated from the 3D reconstructed images.

Parameters	Round nanoflower	Spike nanoflower
Immersion time (t)	15 minutes	15 minutes
Root-mean-square height (Sq)	0.682 μm	0.832 μm
Maximum peak height (Sp)	1.07 μm	1.09 μm
Maximum pit height (Sv)	1.93 μm	1.91 μm
Skewness (Ssk)	-0.978	-1.04
Kurtosis (Sku)	3.66	3.29
Arithmetic mean height (Sa)	0.551 μm	0.656 μm
Developed interfacial area ratio (Sdr)	625 %	985 %

3. Nanostructure Surface Chemistry

Nanostructure surface chemistry is investigated using Relative Intensity Ratio (RIR) of Grazing Incidence X-ray Diffraction (GI-XRD) patterns. GI-XRD pattern (figure S5) shows that the intensity of both CuO and $Cu(OH)_2$ increases (circle a) while Cu decreases (circle b) with increasing immersion time. Relative-Intensity-Ratio (RIR) method for GI-XRD obtains surface phase weight percentage (figure S6) clearly shows a drastic increase in weight percent of CuO with a simultaneous decrease in weight percent of Cu with immersion time. The increase in the surface $Cu(OH)_2$ content is relatively small compared to that of CuO on account of the transformation of the metastable $Cu(OH)_2$ to CuO. This is because the formation of CuO nanoflowers may also be accompanied with the breaking of interlayer H-bonds at the sheet edges of $Cu(OH)_2$ causing them to roll up [2,3]. This analysis also observes that spiky nanoflowers show higher weight percent of Cu on the surface than round nanoflowers. This might be attributed to a lower concentration of NaOH used during solution immersion. At lower immersion time (t = 5 minutes), the weight percent of CuO and $Cu(OH)_2$ is approximately equal. However, at t = 25 minutes, Cu and $Cu(OH)_2$ transform to CuO indicating the formation of nanoflowers originating from nanograsses.

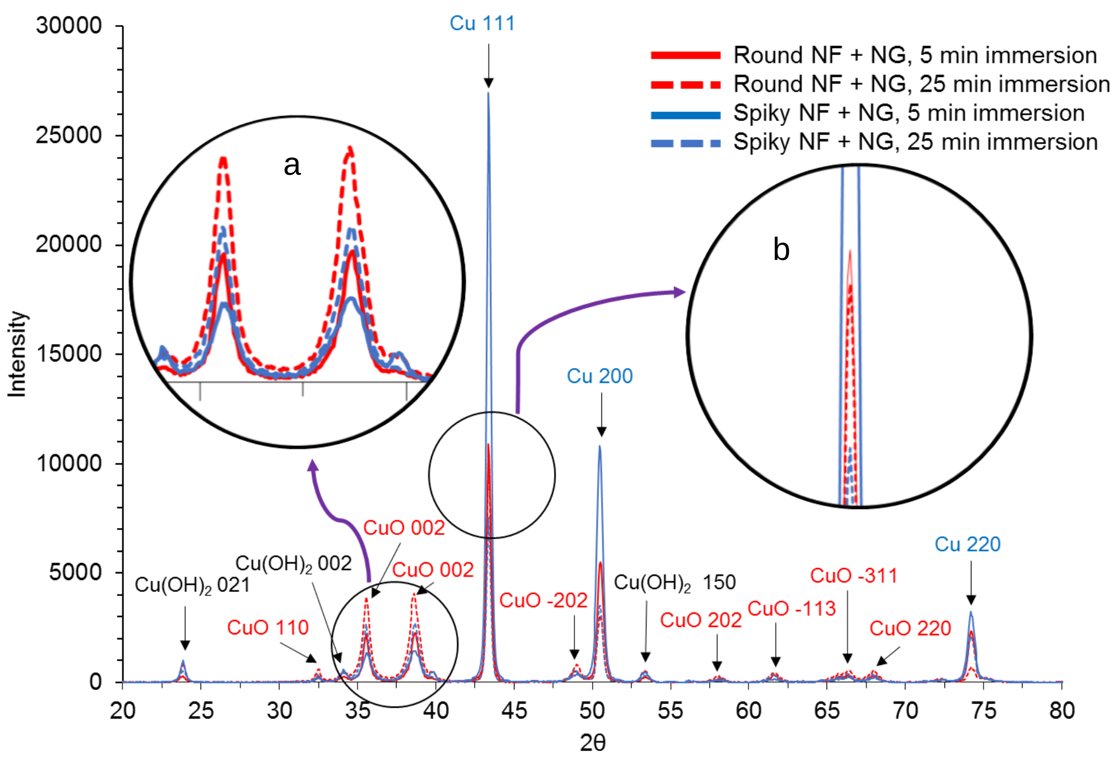

Figure S5. GI-XRD patterns of round and spiky nanostructures at t = 5 min and 25 min immersion time.

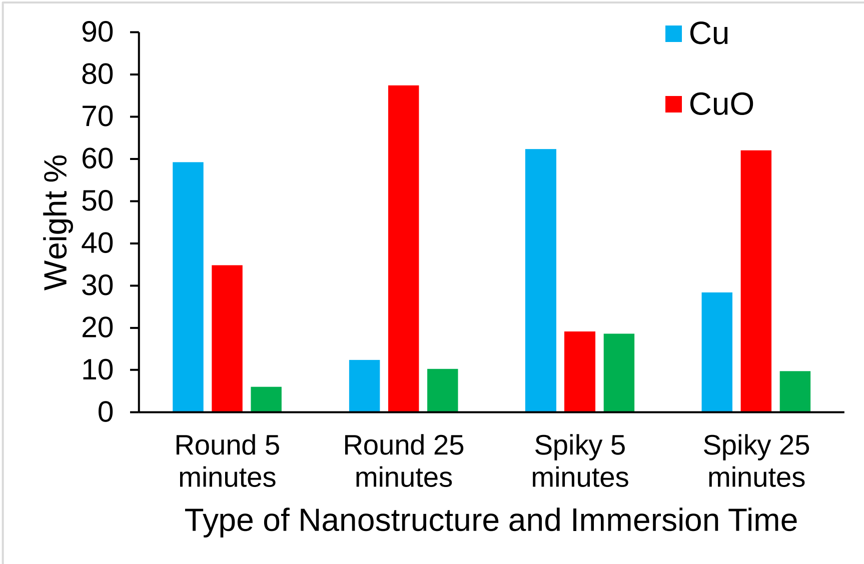

Figure S6. RIR quantitative analysis of round and spiky nanoflowers at 5 minutes' and 25 minutes' oxidation

REFERENCES

(1) Tabet, M. F.; Urban, F. K. Comparison of Atomic Force Microscope and Rutherford Backscattering Spectrometry Data of Nanometre Size Zinc Islands. *Thin Solid Films* **1996**, *290–291*, 312–316 DOI: 10.1016/S0040-6090(96)08968-7.

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