Supporting Information

Superhydrophobic, highly adhesive arrays of copper hollow spheres produced by electro-colloidal lithography

Damien Bazin[§]*, Chrystel Faure*[‡]*.

[§]Université de Bordeaux, Centre de Recherche Paul Pascal, Avenue du Dr Schweitzer, 33600 Pessac, France

[‡] Université de Bordeaux, Bordeaux INP, Chimie et Biologie des Membranes et Nano-objets, Allée Geoffroy St Hilaire, 33600 Pessac, France

* E-mail: chrystel.faure@enscbp.fr, Phone number : 0033540006833

Experimental section and methods

Cu^{2+}-loaded spherulites production

Cu^{2+}-loaded multi-lamellar vesicles (MLVs) were prepared by mixing an equal amount of a 0.68 mol.L^{-1} $CuSO_4$, $5H_2O$ (Sigma-Aldrich) solution with GenaminT020 (GT020, Hoechst, Frankfurt, Germany). GT020 is a surfactant that self-organizes into a lamellar phase in the cupric aqueous solution. Under shear, the lamellar phase turns into a dense MLV phase. Cupric ions are trapped inside MLVs by chemical affinity to the GT020 polar headgroup. Here, shearing was produced by a simple mixing of the GT020-$CuSO_4$ mixture using a spatula. After c.a. 5 min. mixing, the paste was centrifuged for 5 min at 3000 rpm and both steps were repeated until the sample color was homogeneously blue. Dispersions of MLVs (500mg/mL) in distilled water were prepared by gentle mixing with a mechanical stirrer (500 rpm).

2D planar electrochemical cell fabrication

ITO electrodes (Delta Technologies Limited, 70-100Ω) were first treated to decrease surface roughness by plunging them into a KOH-saturated isopropanol solution for 24 hrs. Then, electrodes were sonicated in a bath containing a Hellmanex® solution (Sigma, dilution 1:50 v:v) for 1 hr before rinsing with distilled water, ethanol and acetone. After drying, both electrodes were separated by a 250 µm circular silicon spacer (Goodfellow, Lille, France), delimiting a 2 cm² working surface. The silicon joint was cut to let two apertures by which particles dispersions are introduced.

2D assembling of functionalized PS beads under AC field

Sulfate-modified PS beads (Polysciences, Eppelheim, Germany) dispersions were introduced into the cell and let to rest under an AC field (5 kHz, 120V/cm) to allow particle sedimentation (c.a. 30 min). Then, the frequency was continuously decreased down to 2 kHz by 1 kHz step, then down to 800 Hz, every 2 minutes. For this frequency, particles formed distended

aggregates (no contact between particles). Then, frequency was increased to a final frequency of 1200 Hz by 200 Hz step every 2 min. This step led to a separation of the particles that formed "disordered" hexagonal arrays. The organization was drastically improved by a rise in AC field amplitude from 120 V/cm to 290 V/cm by 10 V/cm step every 2 min.

Organized particles were then stuck onto the electrode using a DC generator connected in parallel to the AC power supply (Hewlett Packard, 3324A). The sticking electric field value was set to 90V/cm was applied during 5 min.

PS beads were removed with tetrahydrofuran (THF, Sigma-Aldrich) after opening the cell.

Surface characterization

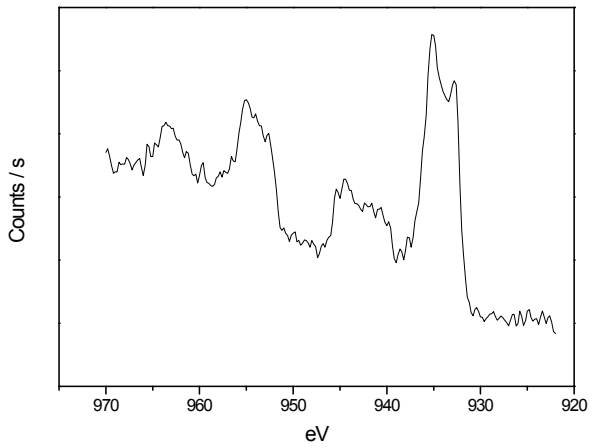
The morphology of the metal deposits was examined by a SEM (HITACHI S4500, V= 15 kV) microscope. For bowls imaging, the patterned surfaces were tilted (30°) in order to visualize ring-shape excrescences. Atomic Force Microscopy (AFM) (Nanoscope III, Digital Experiment) imaging was performed in tapping mode with a silicon tip.

Static contact angle

Static contact angle was measured using a contact-angle meter (Kruss, GmbH). Deionized water was used for experiments. A micropipette is located to approximately 2 cm above the sample, and an 8 μL drop is dispensed onto the sample surface. The measured contact angle was the average of five measurements.

S1: XPS analysis of patterned surfaces

The two peaks located at 935,1 and 932,6 eV correspond to copper oxide Cu(II) and metal copper Cu(0), respectively.

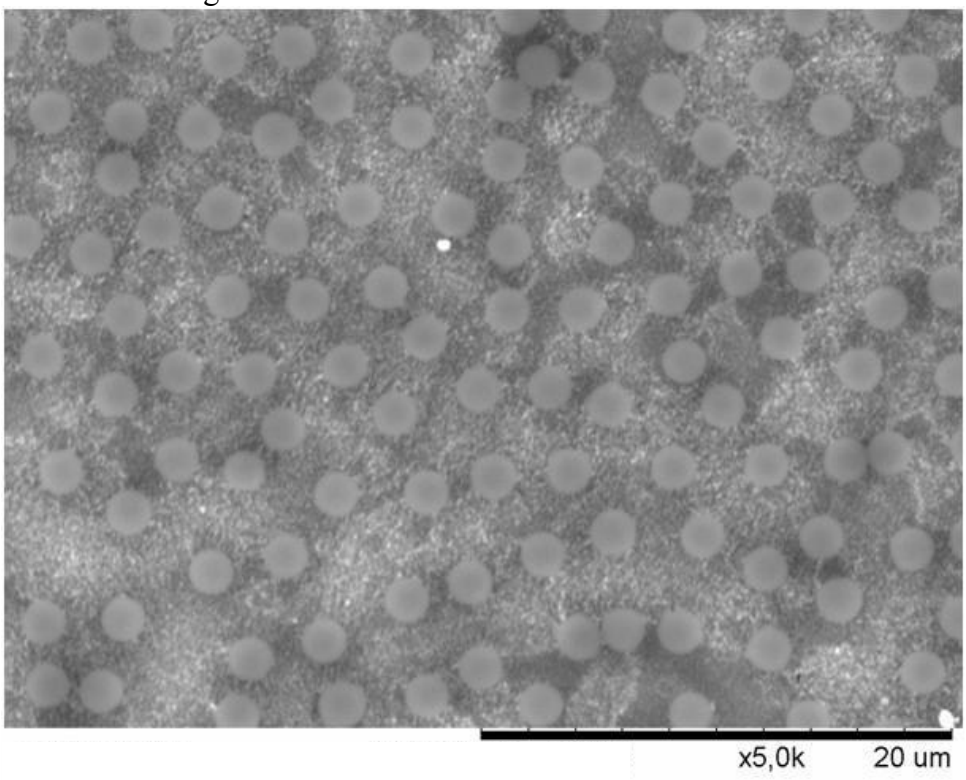


Platzman, I.; Brener, R.; Haick, H.; Tannenbaum, R. *The Journal of Physical Chemistry C* **2008**, *112*, 1101.

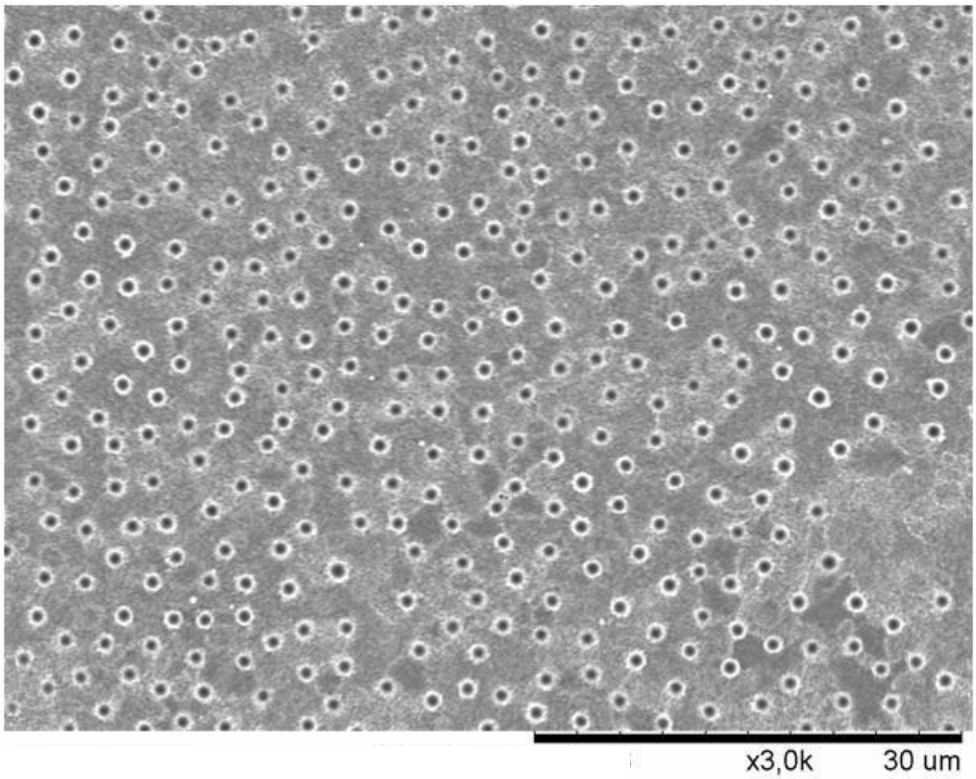
S2: imaging of copper"rings" covered surfaces

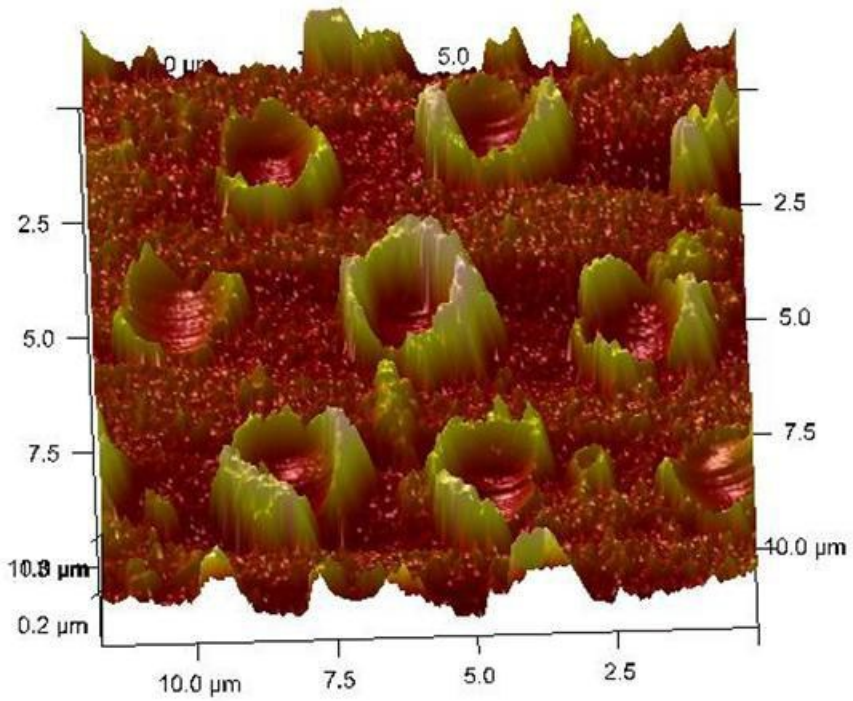
SEM analysis

Before removing PS beads



After removing PS beads using THF:



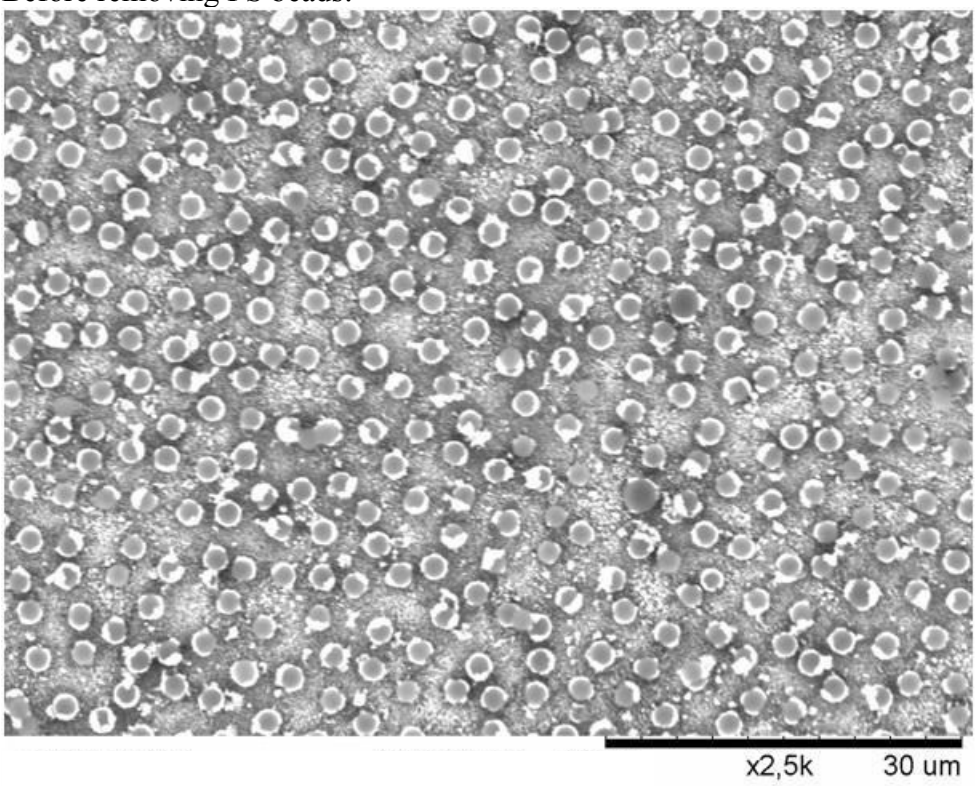


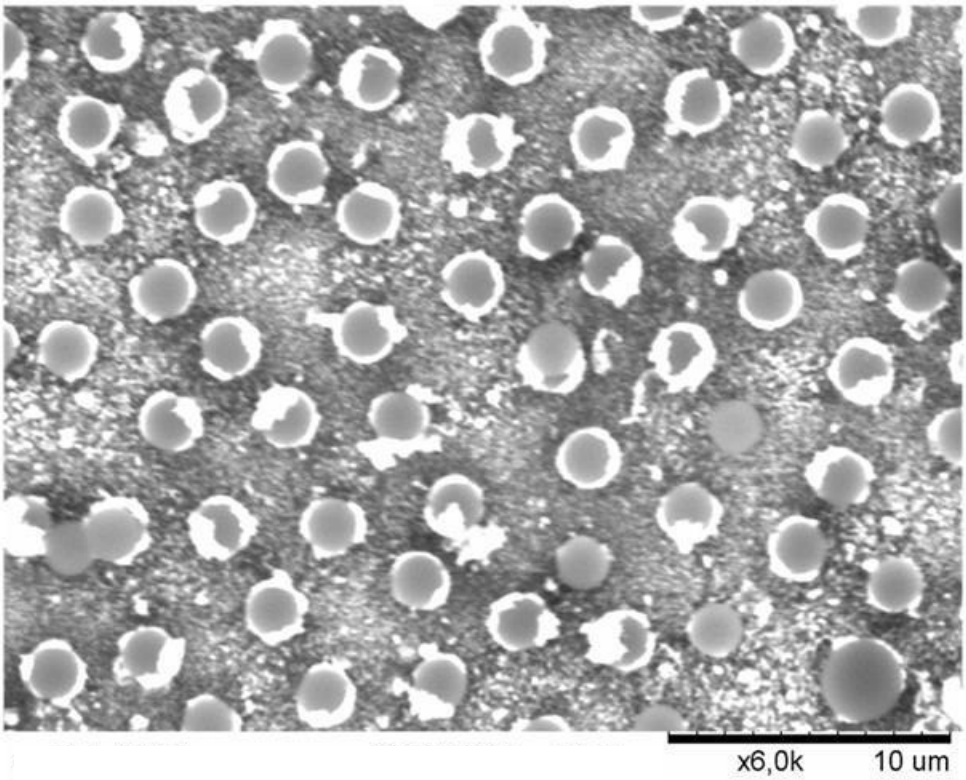
AFM image

S3: imaging of copper hollow spheres covered surfaces

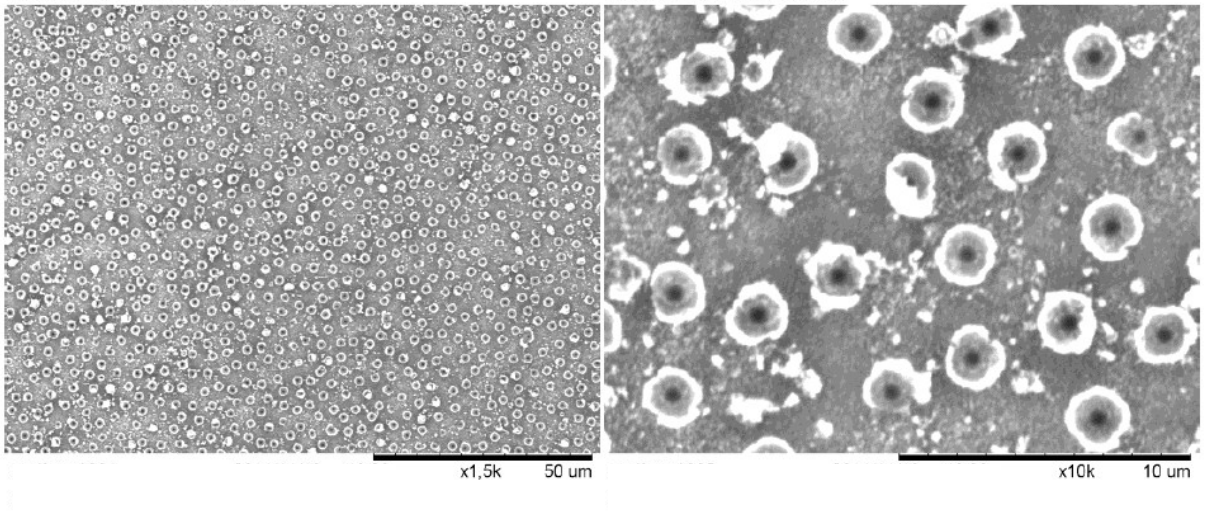
SEM analysis

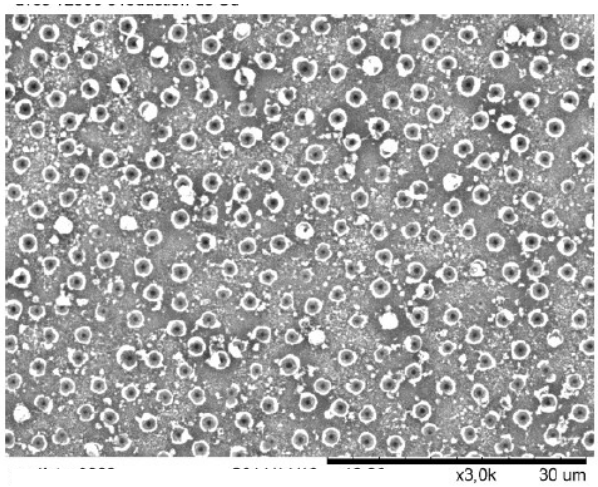
Before removing PS beads:



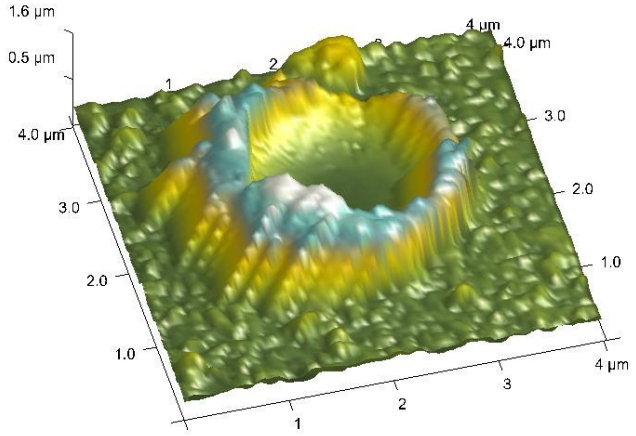


After removing PS beads :





S4: Hollow sphere imaged by AFM



S5 : mathematical model

From Pythagore law, one can express x as a function of R_b, the radius of PS beads, and H, the global height of copper deposit (**Figure 3c**):

$$x = \sqrt{R_b^2 - (R_b - H)^2} \qquad (1')$$

In our experimental conditions:

R_b = 1000 nm, d_{CC}=3700 nm, δ=537 ± 47 nm as measured by AFM.

Moreover, H is directly correlated to h, the height of the excrescence. Indeed $H = h + H_{Cu}$ where H_{Cu} is the thickness of the copper layer in between the copper items (**Figure 3c**). In a previous paper,[39] the following relationships were established:

$$H = 10.7 + 5\ t_{DC} \qquad (2')$$

$$H_{Cu} = -1.07 + 1.28\ t_{DC} \qquad (3')$$

with t_{DC} the duration of DC field application.

Combining Equation 2' and Equation 3' gives:

$$H = -3.81 + 1.26\ h \qquad (4')$$

Then introducing Equation 4' in Equation 1' leads to Equation 3 of the manuscript.