SUPPORTING INFORMATION

METHODS:

2D planar electrochemical cell fabrication: The fabrication of the electrochemical cell (Fig. 1) was detailed elsewhere. [31] ITO electrodes were treated to decrease surface roughness by plunging them into a KOH saturated isopropanol solution for 24 hrs. Then, electrode were sonicated in a bath containing an 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 the dispersion of particles (either P1 or P2 population) is introduced.

2D assembling of 2µm-sized sulfate-functionalized PS beads under AC field: PS beads (Polysciences, Eppelheim, Germany) dispersions was introduced into the cell and let to rest under an AC field (5 kHz, 12V.cm^{-1}) to allow particle sedimentation (c.a. 10 min). Nadal et al. [22] showed that at low frequency, electrohydrodynamic attraction forces dominate which leads to the formation of aggregates of organized particles with hexagonal structure. On the other hand, at high frequency the electrostatic dipolar repulsion forces are more important and particles go away from each other. Then, the frequency was continuously decreased down to 2 kHz by 1 kHz step and down to 0.8 kHz by 0.2 kHz step every 2 min to get hexagonal close packed arrays before being increased up to 1.2 kHz or 400 Hz depending on the desired final frequency by 0.2 kHz step every 2 min. The rise in frequency allows the separation of the beads without affecting hexagonal organization. Then, the electric field was increased up to 29 V.cm^{-1} by 0.8 V/cm step every 2 min. to improve the long-range order (personal results). Organized particles were fixed onto the electrode using a DC generator connected in parallel to the AC power supply (Hewlett Packard, 3324A).

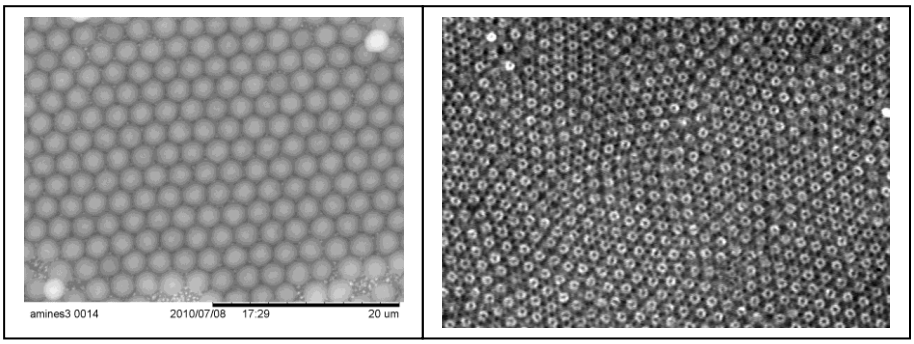
Cu^{2+}-loaded MLVs production: Cu^{2+}-loaded MLVs preparation was detailed elsewhere [31]. Briefly, it consists in mixing an equal amount of a 0.68 mol.L^{-1} $CuSO_4$, $5H_2O$ solution with GenaminT020

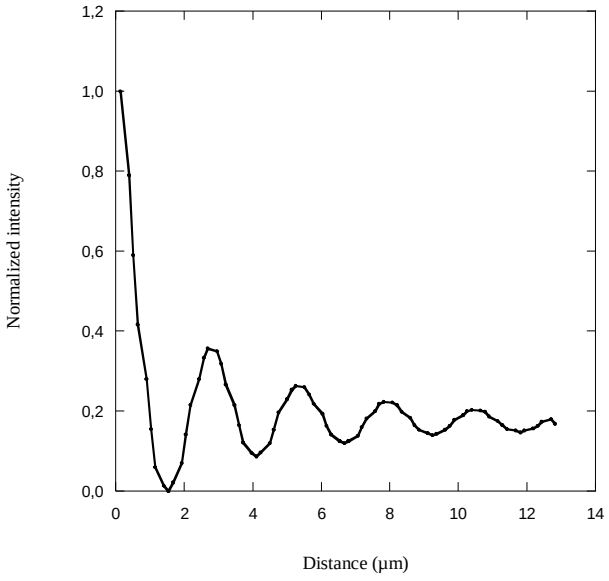
(GT020). GT020 is a surfactant that self-organizes into a lamellar phase in the Cu ion aqueous solution. Under shear, the lamellar phase turns into a dense multilamellar vesicle phase. Cu ions are trapped inside MLVs by chemical affinity to the GT020 polar headgroup. Here, shearing was produced by a 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 blue color of the sample was homogeneous. A dispersion of MLVs in distilled water (500 mg/mL) was then prepared by gentle mixing with a mechanical stirrer (500 rpm).

HAD-functionalization of polymer particles: 10 µl of commercial micro-beads dispersion was dispersed in 1 ml of hexamethylenediamine (Aldrich) at 10^{-1} M. The solution was stirred for 12 hrs.

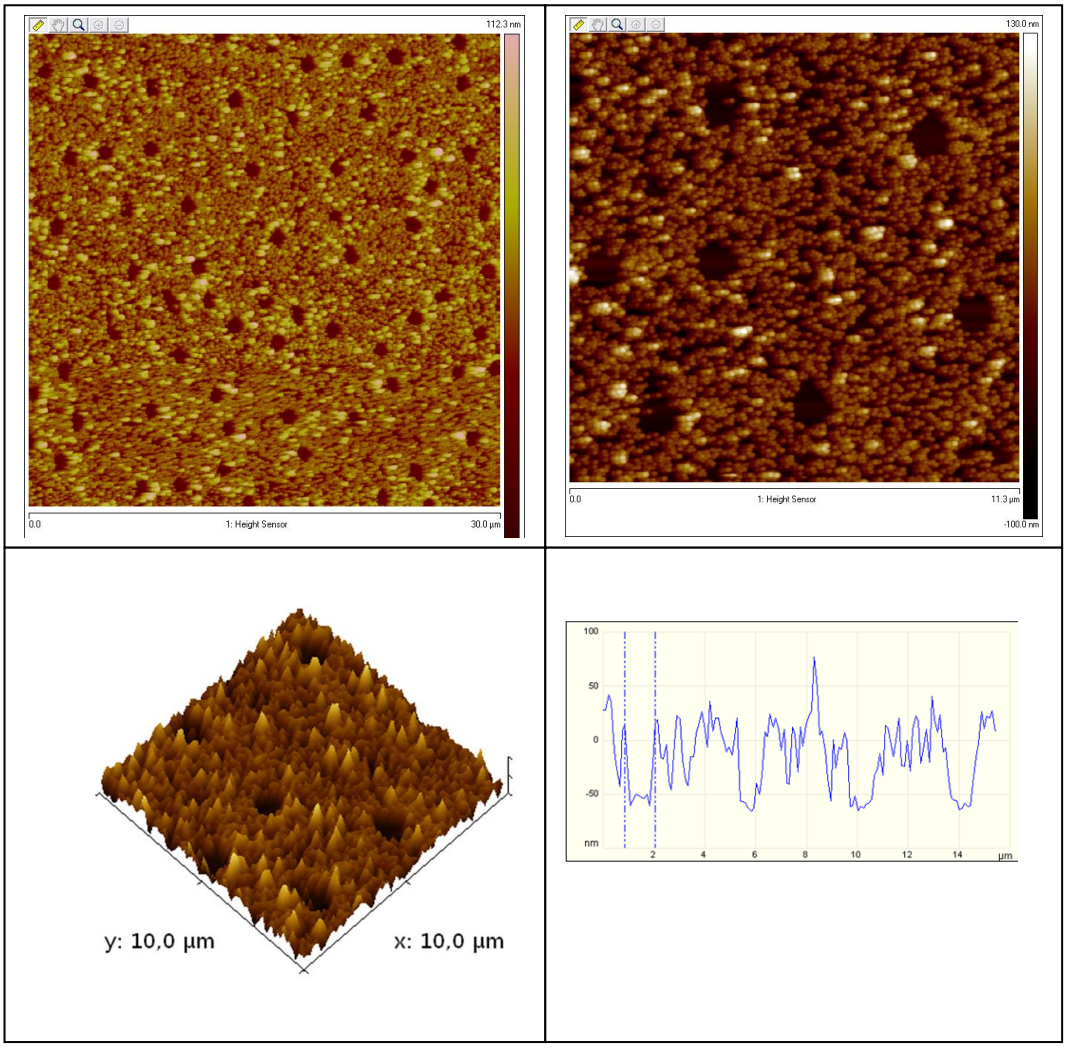
Surface characterization: The morphology of the metal deposits was examined by a (HITACHI S4500, V= 15 kV) microscope. AFM (Nanoscope III, Digital Experiment) imaging was performed in tapping mode with a silicon tip.

S.I.1: Organization of PS micro-beads in hexagonal arrays by application of an A.C. field. (left) 3µm amine-modified PS microbeads under (1600Hz, 12V/cm) AC field, a close packed hexagonal array is produced, the equilibrium distance is 3µm (right) 2 µm carboxylate-modified PS microbeads under (500Hz, 29V/cm) AC field, the equilibrium distance is 2.7 µm as measured from the radial profile of the image correlation shown below images.



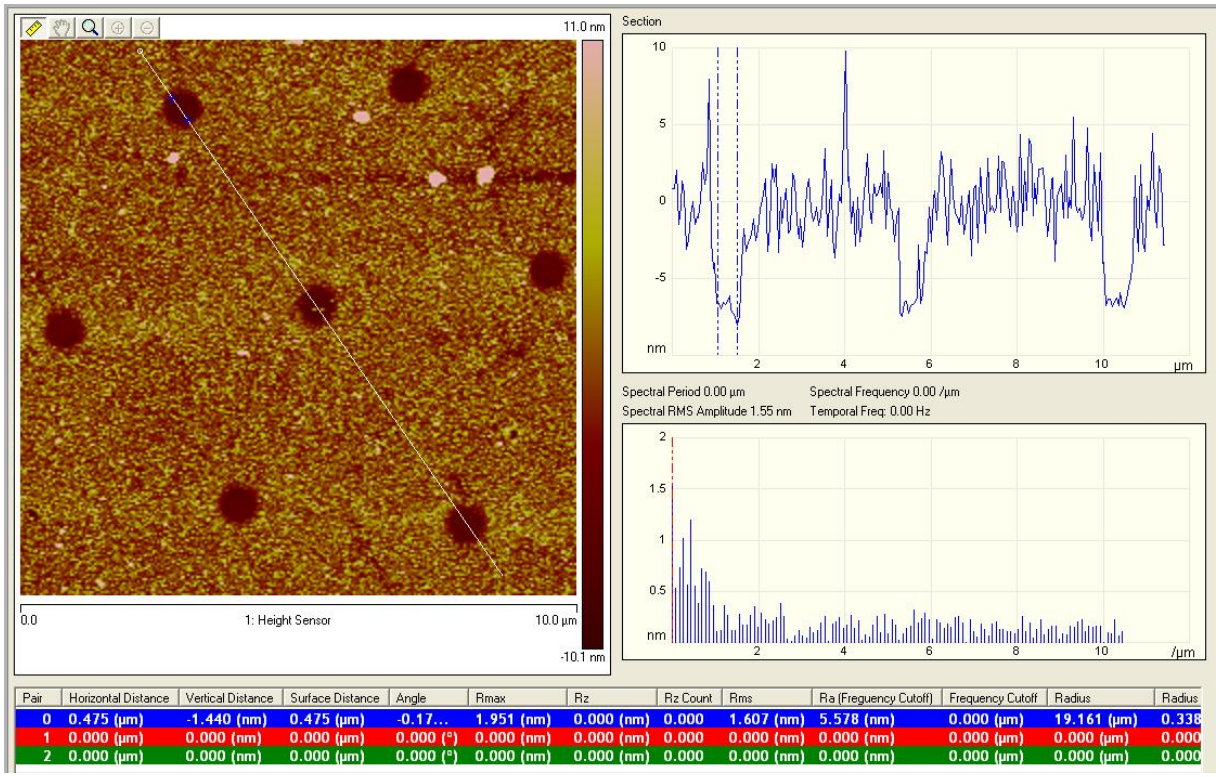


S.I.2: AFM images of hexagonal arrays of conductive holes using 2 µm-sized sulfate functionalized PS beads for the P1 population, and HAD-modified 100 nm-sized sulfate functionalized PS beads for the P2 population. The holes diameter is c.a. 1.5 µm, the height of polymer matrix is c.a. 60 nm.



S.I.3: Hexagonal arrays of conductive holes in a matrix of polymer nano-beads (18 nm cyclam-functionalized nanoparticles) obtained from (a) 2 µm-sized sulfate-functionalized PS beads (P1) under 1200 Hz, 29 V/cm; distance between holes: 4 µm, hole size: 475 nm, (b) from 1 µm-sized amine-functionalized PS beads (P1) under 800 Hz, 22 V/cm; distance between holes 2 µm, hole size: 370 nm. The height of the polymer matrix is c.a. 8 nm in both cases.

(a)



Pair	Horizontal Distance	Vertical Distance	Surface Distance	Angle	Rmax	Rz	Rz Count	Rms	Ra (Frequency Cutoff)	Frequency Cutoff	Radius	Radius
0	0.475 (µm)	-1.440 (nm)	0.475 (µm)	-0.17...	1.951 (nm)	0.000 (nm)	0.000	1.607 (nm)	5.578 (nm)	0.000 (µm)	19.161 (µm)	0.338
1	0.000 (µm)	0.000 (nm)	0.000 (µm)	0.000 (°)	0.000 (nm)	0.000 (nm)	0.000	0.000 (nm)	0.000 (nm)	0.000 (µm)	0.000 (µm)	0.000
2	0.000 (µm)	0.000 (nm)	0.000 (µm)	0.000 (°)	0.000 (nm)	0.000 (nm)	0.000	0.000 (nm)	0.000 (nm)	0.000 (µm)	0.000 (µm)	0.000

(b)