Supporting Information

Synthesis of polydopamine at the femtoliter scale and confined fabrication of Ag nanoparticles on surfaces

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S1. Materials and Methods

Polydopamine synthesis and coating. Polydopamine was obtained following a previously described and widely used procedure[1]. Dopamine hydrochloride (2 mg/mL) was dissolved in 10 mM Tris·HCl (pH 8.59) solution. Prior to coating, substrates were cleaned by sonication during 15 min in Acetone, EtOH and Milli-Q water and dried in a N_2 stream. Substrates were placed in vertical orientation into the mixture solution for 1h or overnight (≈15h) while stirring to minimize non-specific deposition. Afterwards, substrates were rinsed with Milli-Q water and dried under a nitrogen stream. For AFM-assisted lithography experiments, the freshly prepared basic solution of dopamine was used as ink without further modification.

Direct-write AFM lithography experiments. PDA lithographies were performed using a commercial dip-pen writer DPN 5000 System (Nanoink Inc.). Commercial silicon nitride Type A tips and Type M probe arrays (Nanoink Inc.) with a spring constant of 0.05 $N\cdot m^{-1}$ or tip arrays from Nanosensors™ (0.3 $N\cdot m^{-1}$) were used for patterning. The tips were coated with the ink solution described before using a microfluidic ink delivery chip-based system (Inkwell, Nanoink Inc.) that had been placed in an O_3/UV cleaner (UV Ozone Cleaner-ProCleaner™ from BioForce Nanosciences) for 10 min before the experiments were performed, in order to facilitate the flow of the ink solution through the channels. The reservoirs were filled with fresh ink and tips were loaded by dipping them into the microwells for a given time (typically 2-5 min). Afterwards, the tips were carefully brought into contact with the surface to fabricate the desired patterns by traversing the tip over the surface. Noteworthy, the unavoidable increase of the viscosity of the ink solution, associated with polymerization of dopamine and solvent evaporation should be avoided by performing the experiments within a short period of time (≈ 2 h per ink solution) and at high relative humidity levels (≈70%). An integrated environmental chamber as part of the DPN 5000 controlled the environmental conditions (humidity and temperature) during all the lithographic processes.

On-surface Ag(I) reduction by PDA. The substrates coated with PDA were immersed in a 50 mM $AgNO_3$ solution in Milli-Q water and kept in the darkness for 24 hours. Afterwards, they were thoroughly rinsed with copious amounts of water and dried under a nitrogen stream.

For the patterned substrates, they were immersed in a 10 mM solution of $AgNO_3$ and placed it in the oven at 60ºC for an hour. After that time, the sample was removed from the oven and carefully rinsed with ultrapure water.

AFM imaging and force-distance measurements. AFM imaging and adhesion force measurements were performed using an Agilent 5500 AFM/SPM microscope combined with PicoScan software from Agilent Technologies. Intermittent contact mode AFM was used for topographical characterization using beam shaped silicon cantilevers (Nanosensors) with nominal force constants of 42 $N \cdot m^{-1}$ and ≈7 nm tip radius.

Contact mode imaging and force-distance measurements were carried out using aluminum-coated silicon cantilevers with nominal force constant of 0.2 $N \cdot m^{-1}$ and ≈7 nm tip radius. Adhesion data were extracted from deflection-separation data by measuring the jump-out of the tip during the retraction movement. After the adhesion experiments, all the cantilevers were calibrated (in sensitivity and spring constant). On PDA coatings, F-d curves were recorded all along the surface. On PDA lithographies, the exact location of the dot-like features was first found by scanning the patterned areas in contact mode while keeping the deflection to a minimum. Then, the FlexGrid tool present in PicoScan was used to obtain the F-d curves in the desired specific locations. This feature allows selection of up to 25 points of an image and a F-d curve is performed in each selected location. After each series of measurements we obtained F-d curves on clean areas of the same substrate in order to check if the tip had been damaged or contaminated. Using this methodology, a maximum of three lithographies could be examined using the same tip.

X-ray photoelectron spectroscopy. XPS was carried out in a Phoibos 150 analyzer (SPECS GmbH, Berlin,Germany)) in ultra-high vacuum conditions (base pressure $1 \cdot 10^{-10}$ mbar) equipped with a monochromatic Kα X-ray source (1486.6eV) was used. Spectra were based on photoelectrons with a takeoff angle of 0º (takeoff angle considered with respect to the surface normal).

Scanning electron microscopy. The in-situ generation of silver nanoparticles was confirmed by SEM (Magellan 400L, Quanta 650 FEG, FEI) operating at 5 kV for secondary electrons imaging and 10 kV for backscattered electrons. EDS analysis was performed using an Inca 250 SSD XMax20 detector.

Optical microscopy. Optical microscopy images were obtained using a Zeiss Axio Observer Z-1 inverted optical/fluorescence microscope with motorized XY stage, halogen lamp excitation source, AxioCam HRc digital camera and standard filters.

Electrical resistivity. The electrical resistivity of the samples was measured with a two-point contact resistance method. Conventional electron beam lithography and lift-off methods were used to deposit two small titanium/gold electrodes on top of the silver/PDA structures. The gap between these two small electrodes was about 10 µm. These were connected to big gold pads on which the two point contact methodology was performed. The electrical characteristics of the silver islands were measured with a Karl Suss probe station and a semiconductor parameter analyzer HP4155. The I–V curves were acquired by applying a bias voltage ranging between –100 mV and 100 mV while recording the current.

1. H. Lee, S. M. Dellatore, W. M. Miller, and P. B. Messersmith, *Science*, 2007, **318**, 426–30.

S2. PDA patterns (AFM characterization)

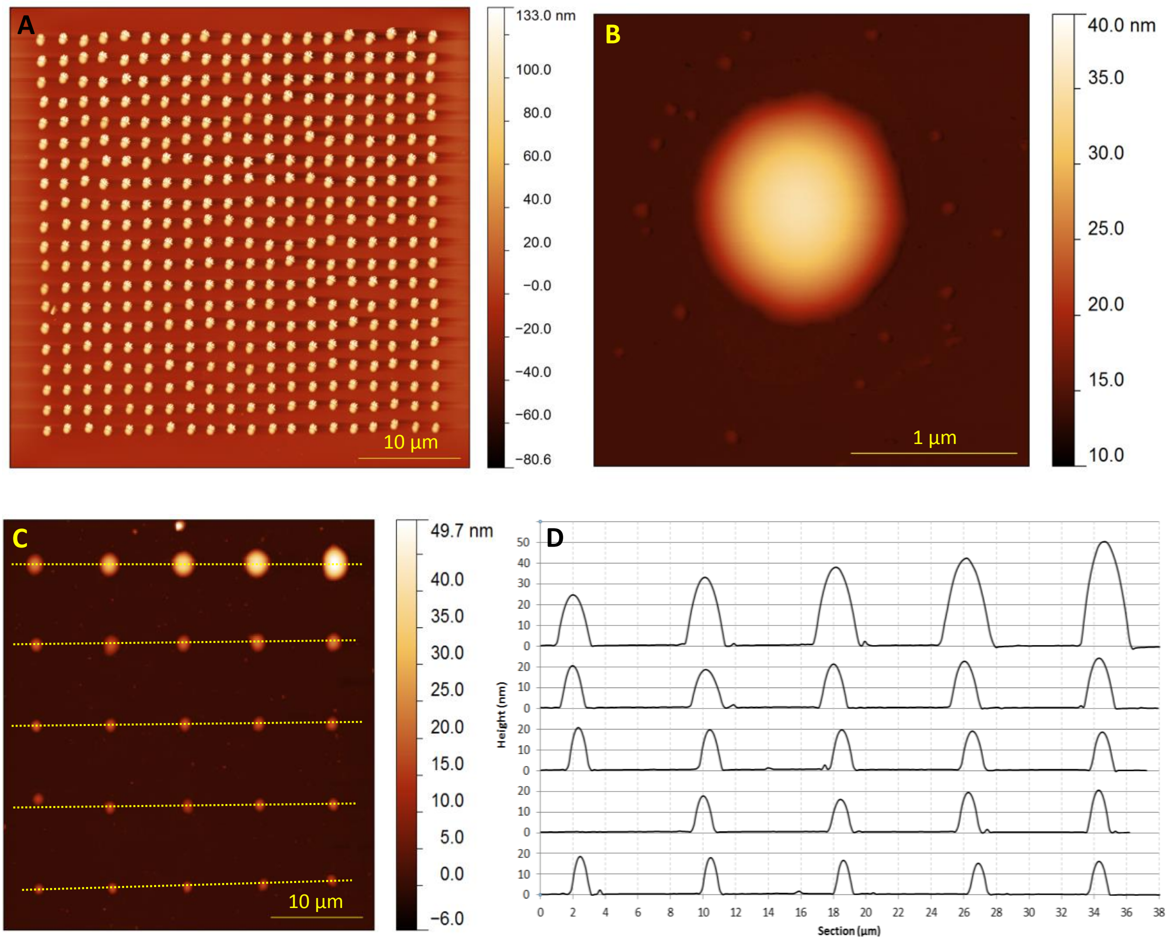

Figure S2.Tapping mode AFM images of (A) a 20x20@2 µm dot array, (B) a single dot. (C) Tapping mode AFM image of a 5x5 dot array and (D) topographical profiles. It can be observed how the ink depletion caused the gradual reduction in size (height and diameter) of the dots in panel (C). Differences are much more noticeable in the first dots of the array (two top rows). However, in the array displayed in panel (A) the writing was stable and a total number of 400 dots of similar dimensions are obtained.

S3. Control on the dimensions of the nanostructured materials (AFM characterization)

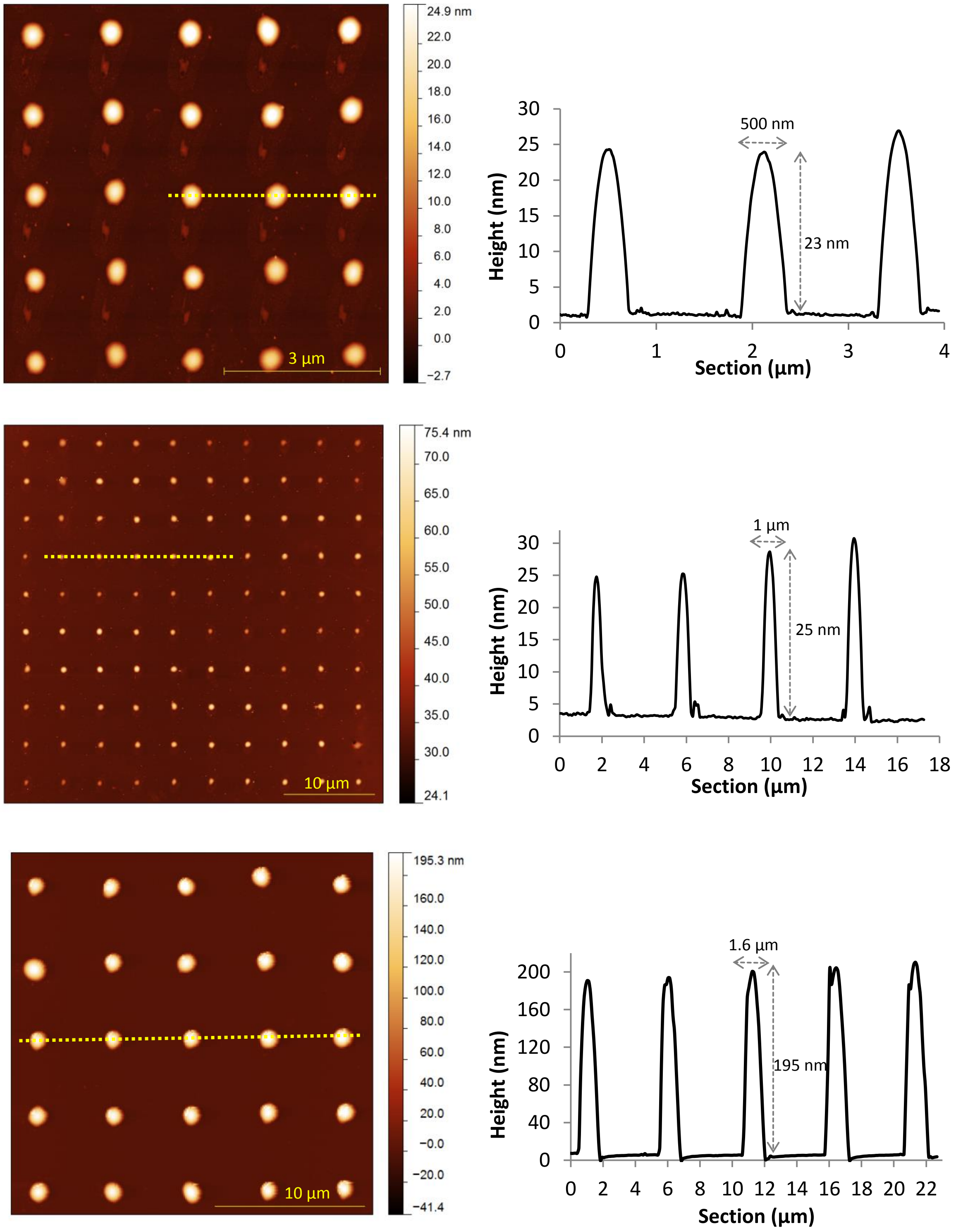

Figure S3. Tapping mode AFM images of several PDA lithographies and their corresponding profiles. The dimensions of the drops were varied by controlling the contact time, pressure of the tip on the surface and depletion of the ink.

S4. Dynamic writing and patterning of extended areas

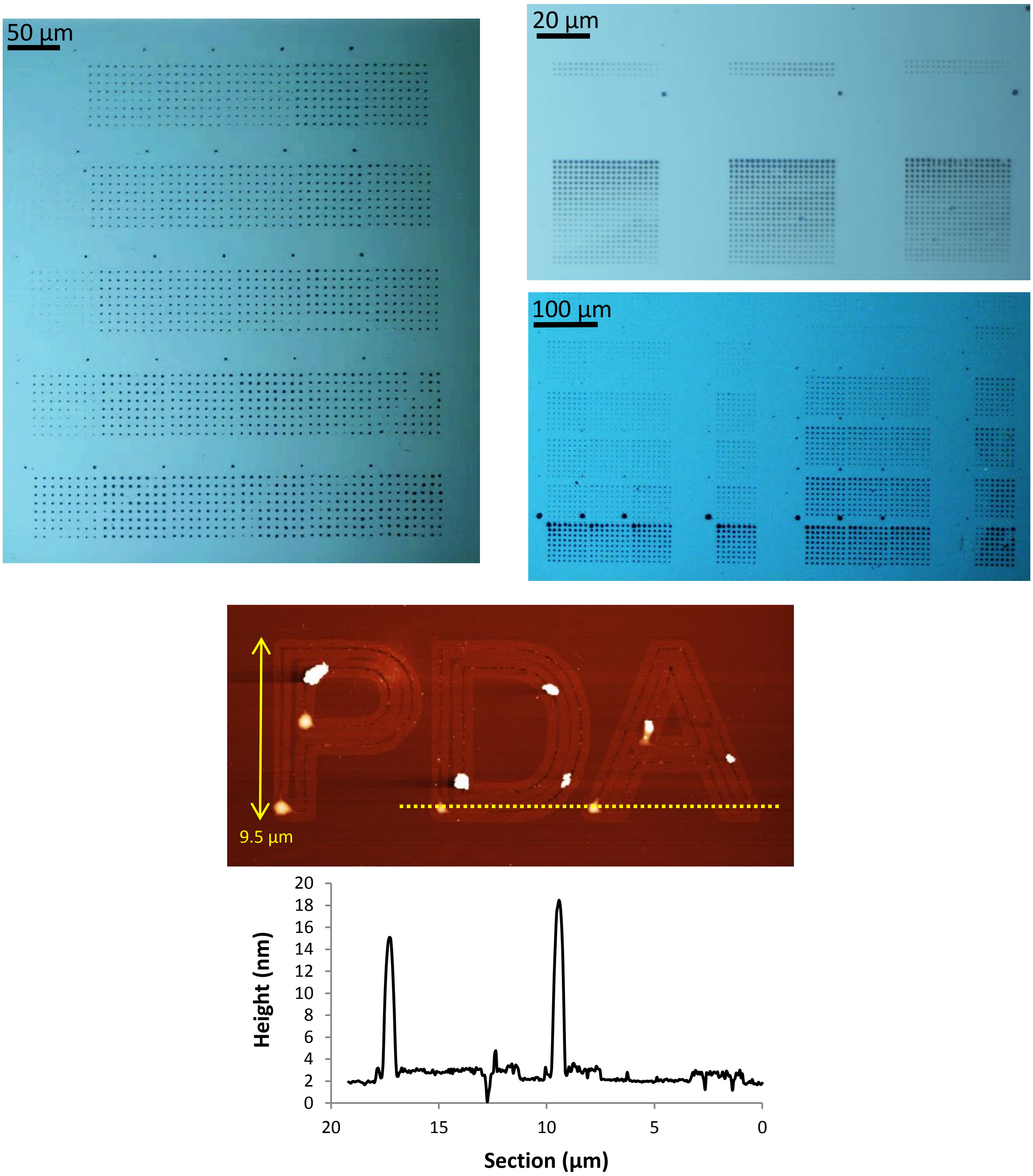

Figure S4. Optical microscopy images of PDA patterns on Si substrates. Patterns were obtained over areas up to 0.5 mm^2 in size (top). AFM topography image of microscale letters written with polydopamine forming the contraction *PDA* and the corresponding height profile.

S5. In-situ synthesis of Ag nanoparticles from a silver salt on PDA coatings

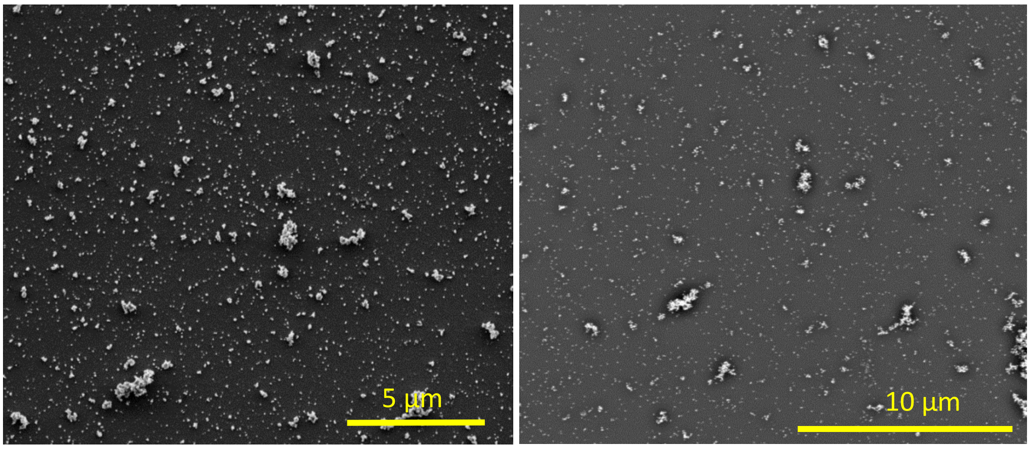

Figure S5a. SEM images of a Si wafer coated with PDA overnight and then immersed in a $AgNO_3$ 50 mM solution for 24h showing the formation of Ag particles on the surface. Secondary electrons image (left). The backscattered electrons image (right) shows that the particles are composed of an element (Ag) that is much heavier than the background (Si, O, C, N).

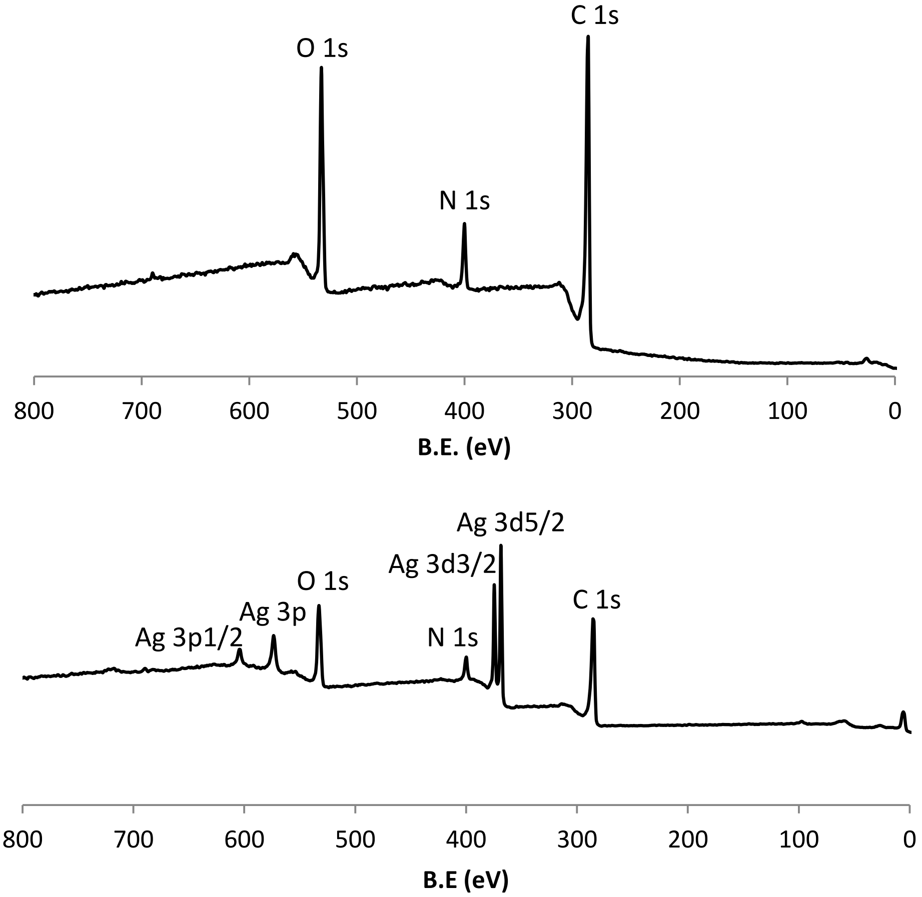

Figure S5b. XPS spectra of a Si wafer coated with PDA overnight (top) and Si wafer coated with PDA and immersed in a $AgNO_3$ solution (10 mM in water) for 24 hours (bottom). The formation of Ag particles is showed by the appearance of characteristic Ag^0 bands.

S6. Unsuccessful attempts to fabricate Ag on the PDA nanoarrays

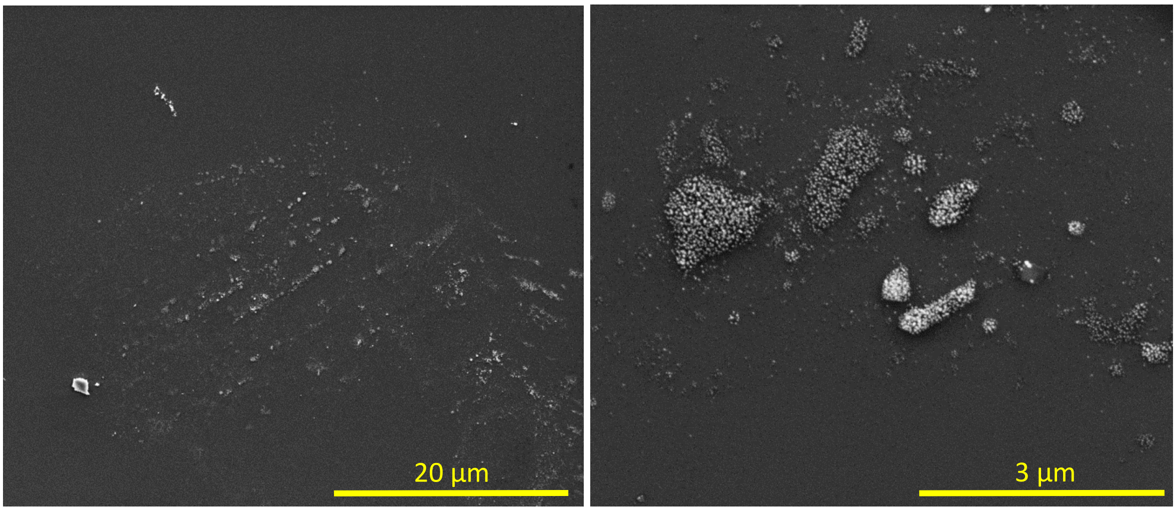

Figure S6a. SEM images of PDA patterns immersed overnight in a $AgNO_3$ 50mM solution from where the disappearance of the nanoarrays can be clearly inferred.

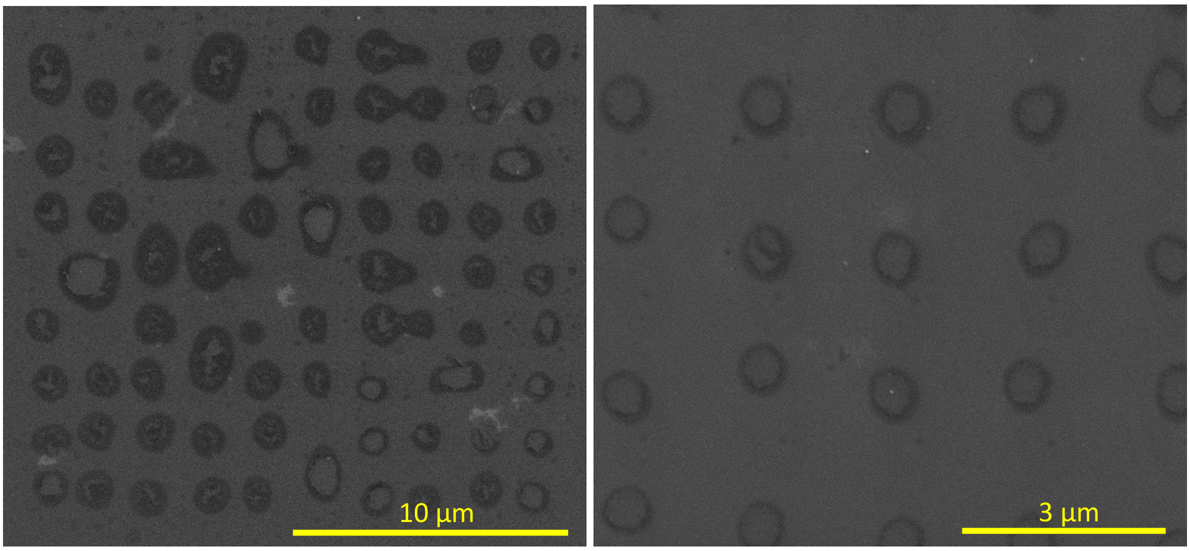

Figure S6b. SEM images of PDA arrays treated at 90ºC for 24h and immersed in a 50 mM $AgNO_3$ solution for 1h. PDA features were partially erased and do not show the formation of Ag nanoparticles.

S7. Obtention of Ag nanoparticles on the PDA nanoarrays

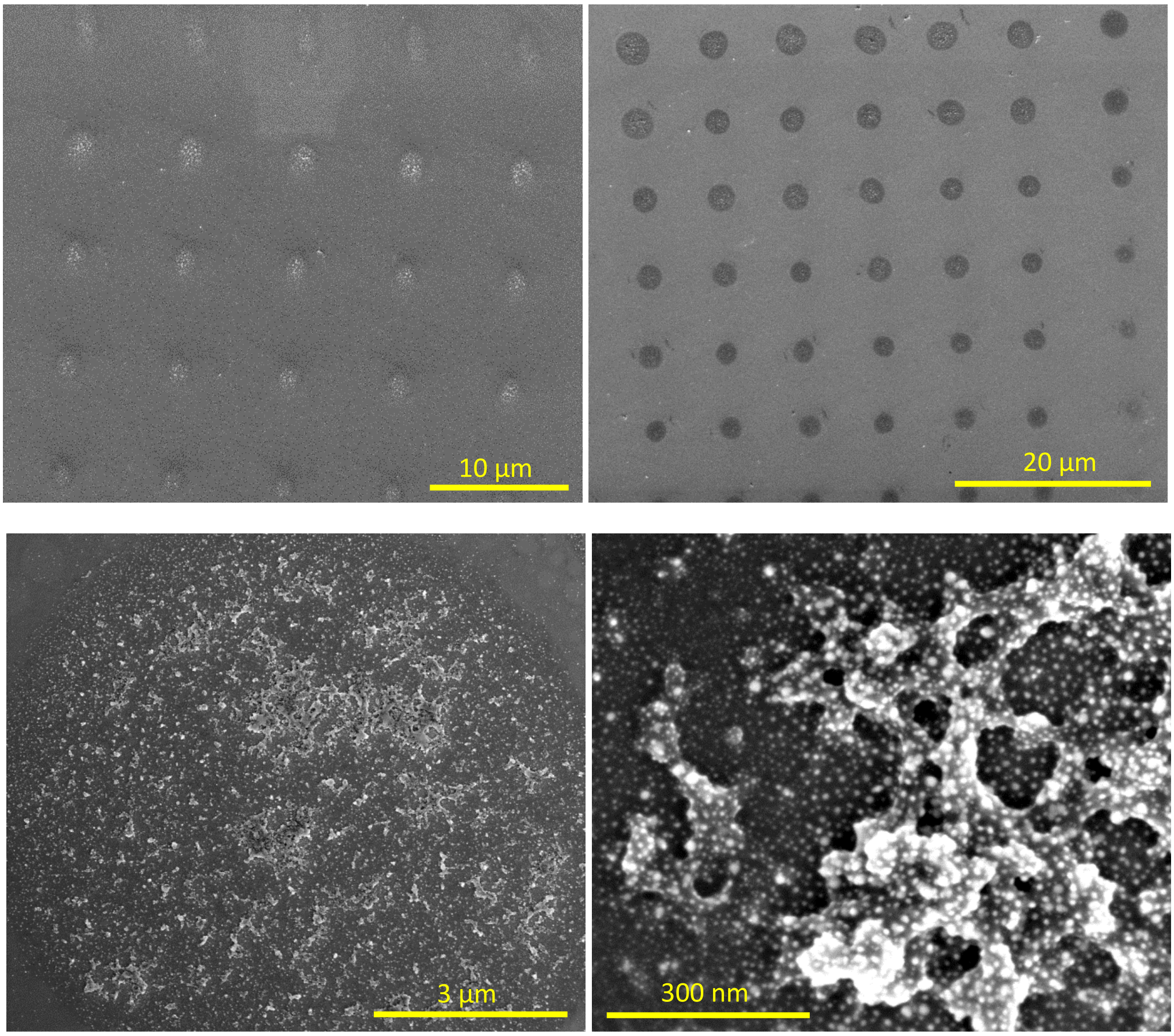

Figure S7a. SEM images of Ag nanoparticle patterns obtained by in-situ reduction of Ag(I) over PDA motifs (by immersion in a 10 mM $AgNO_3$ solution for 1h while heating at 60ºC). (Top right) PDA dot-like features with differing sizes (due to ink depletion) translate into Ag patterns of corresponding size and shape.

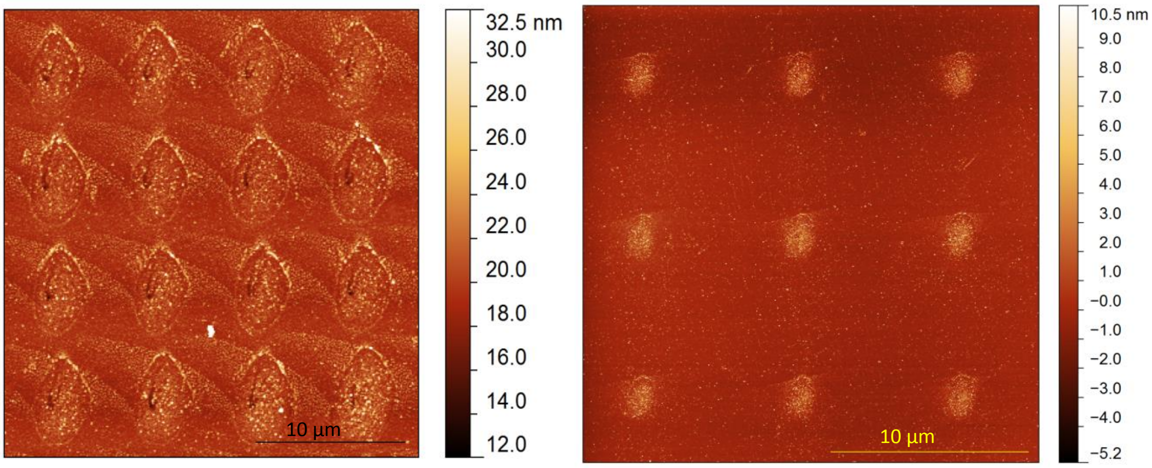

Figure S7b. Tapping mode AFM image of silver nanoparticles obtained by in-situ reduction of Ag^+ on a PDA pattern.

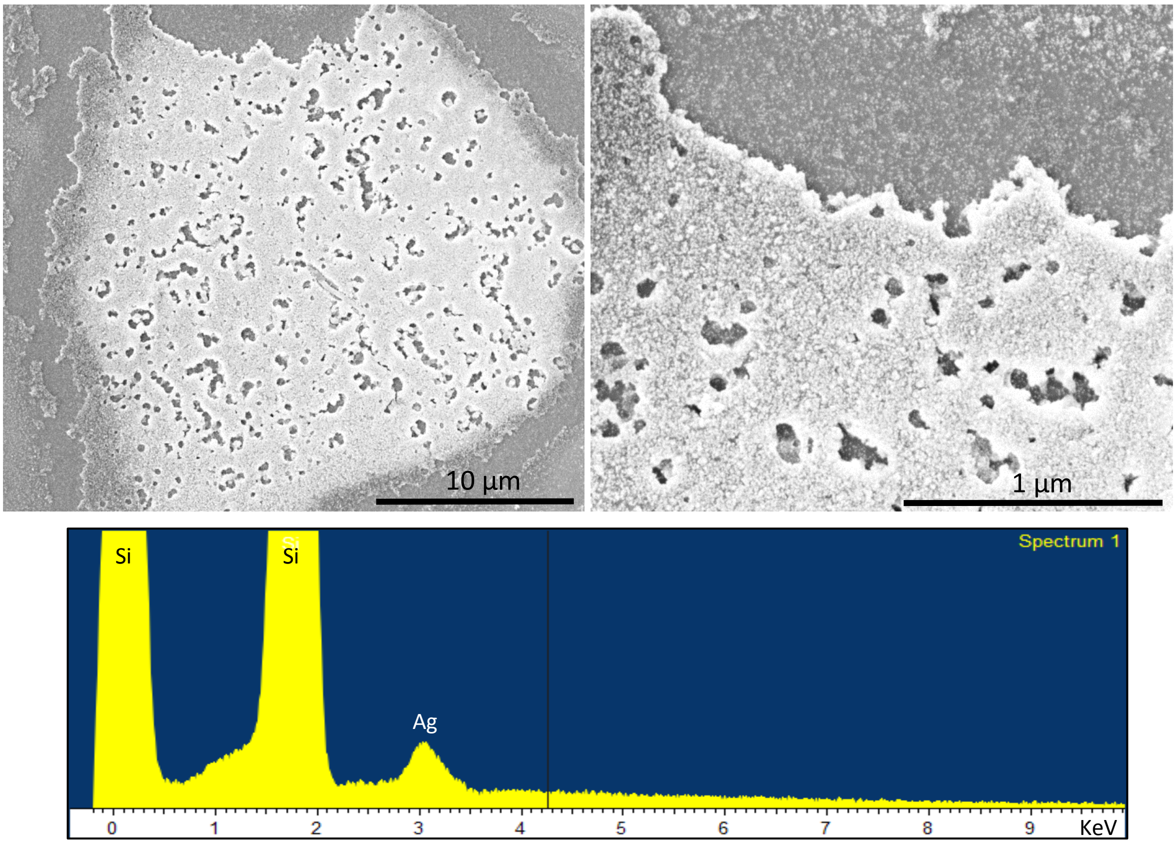

Figure S7c. EDS was performed on thicker Ag coatings obtained on big PDA deposits. In dot array patterns, where the silver coating was thinner, the Si signal was too high to allow the detection of Ag.

S8. Electrical Resistivity

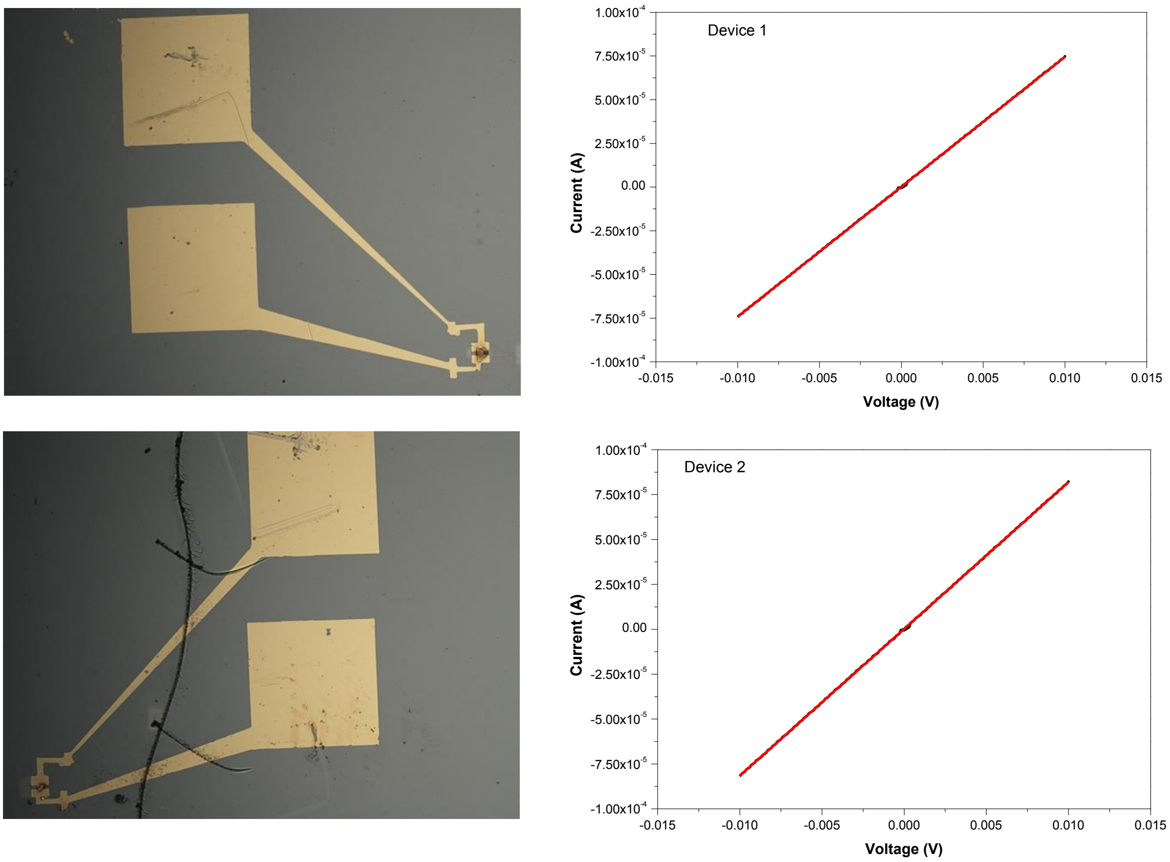

Figure S8. Optical images of two Ag/PDA islands contacted with gold electrodes fabricated by electron beam lithography (right). Ohmic I-V profiles for the two silver/PDA islands (left). Resistances of 134 and 122 Ω were calculated for the two structures. Taking into consideration the gap length of the electrodes (L) and an averaged contact area (A) of $1.7\cdot10^{-10}$ m^2, a Ag/PDA structure resistivity (ρ) of2.2 10^{-3} Ω·m was estimated (ρ = RA/L).