

## Supplementary Information

Electrostatic-Guided Positioning of Gold Colloids using Periodic Nanopatterns

Produced by Block Copolymer Lithography

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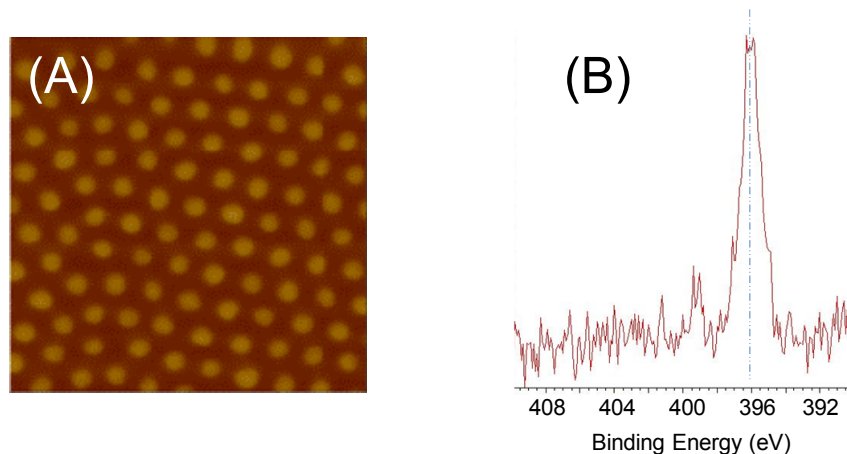
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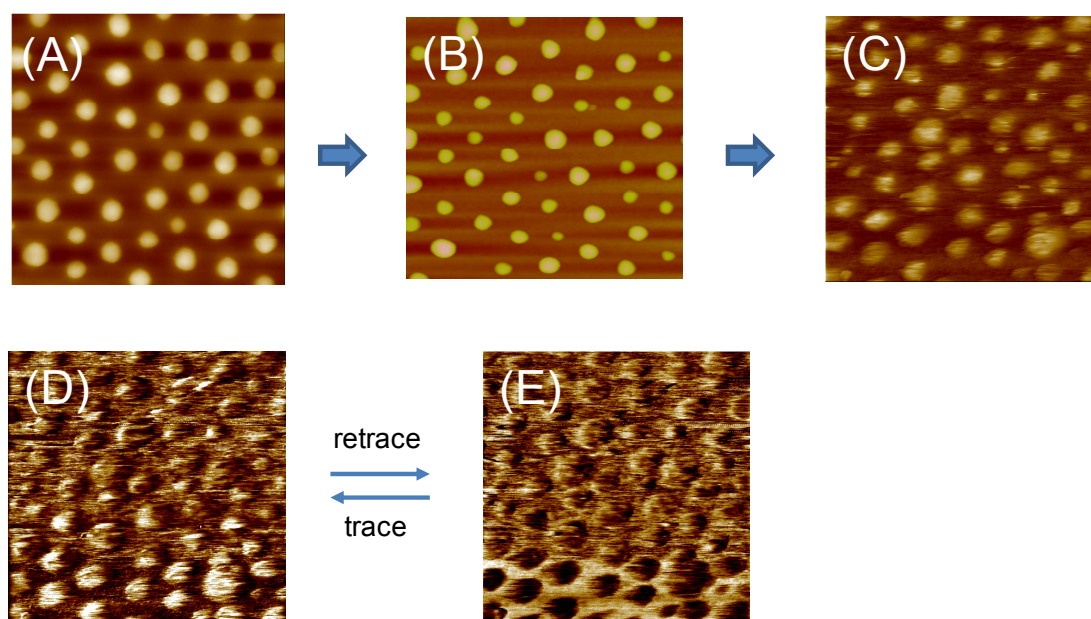
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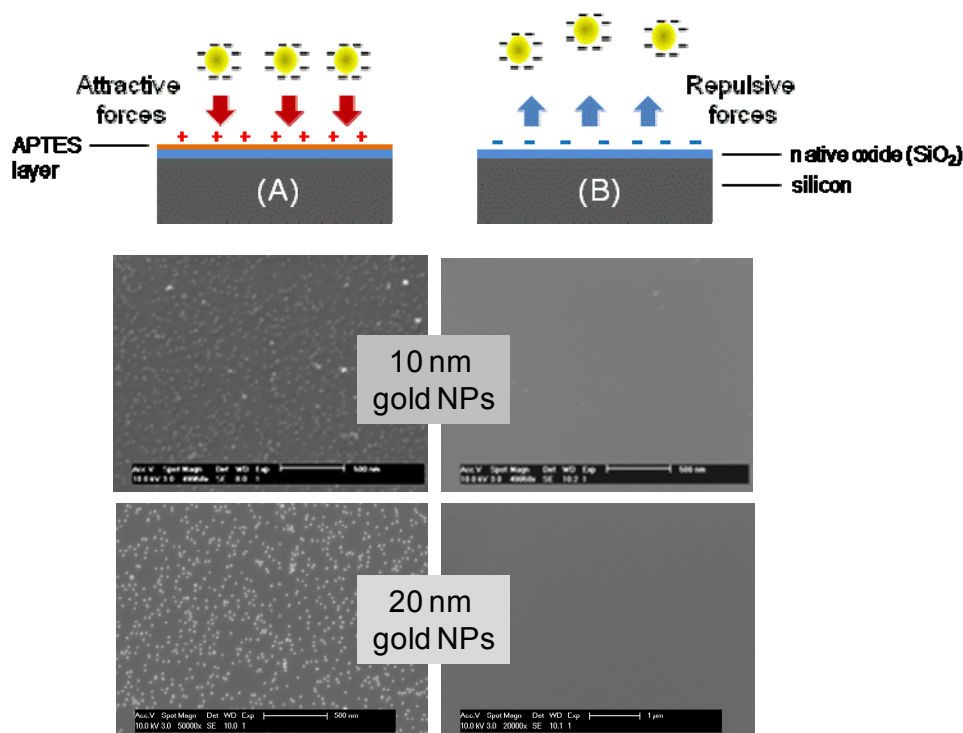
Gold colloids: The gold colloidal solutions with mean NP size of 10, 20, 30 and 40 nm were purchased from Ted Pella Inc. and used as received. The concentrations were  $5.7 \times 10^{12}$ ,  $7.0 \times 10^{11}$ ,  $2.0 \times 10^{11}$ ,  $9.0 \times 10^{10}$  and  $4.5 \times 10^{10}$  NPs/ml, respectively. According to the manufacturer the gold NPs were prepared by reduction of  $[\text{AuCl}_4]^-$  with sodium citrate. The colloidal stability was thus insured by surrounding the NPs by an electrical double layer constituted of citrate and chloride ions. Values of pKa for citric ( $\text{C}_6\text{H}_8\text{O}_7$ )/citrate ( $\text{C}_6\text{H}_5\text{O}_7^{3-}$ ) acid-base couple can be found in the literature at pKa1 = 3.13, pKa2 = 4.76 and pKa3 = 6.4. Given the dissociation constants of the citrate groups at pH~6 of the colloidal solutions, the predominant species are  $\text{C}_6\text{H}_6\text{O}_7^{2-}$  and  $\text{C}_6\text{H}_5\text{O}_7^{3-}$ , meaning that the gold NPs are stabilized in aqueous solution by negative carboxylate ( $\text{COO}^-$ ) surface charges.



**Fig. S1.** (A) Topography AFM image of reverse PS-*b*-P2VP ( $102\text{-}97\text{ kg.mol}^{-1}$ , BCP-a) micelles deposited on bare silicon substrate (scan size:  $1\times 1\text{ }\mu\text{m}$ , z scale: 100 nm). The micelles have a similar size and spacing to the ones deposited on APTES layer (Fig. 1). (B) N1s XPS spectrum showing the typical signal of the pyridine groups recorded at 396 eV.

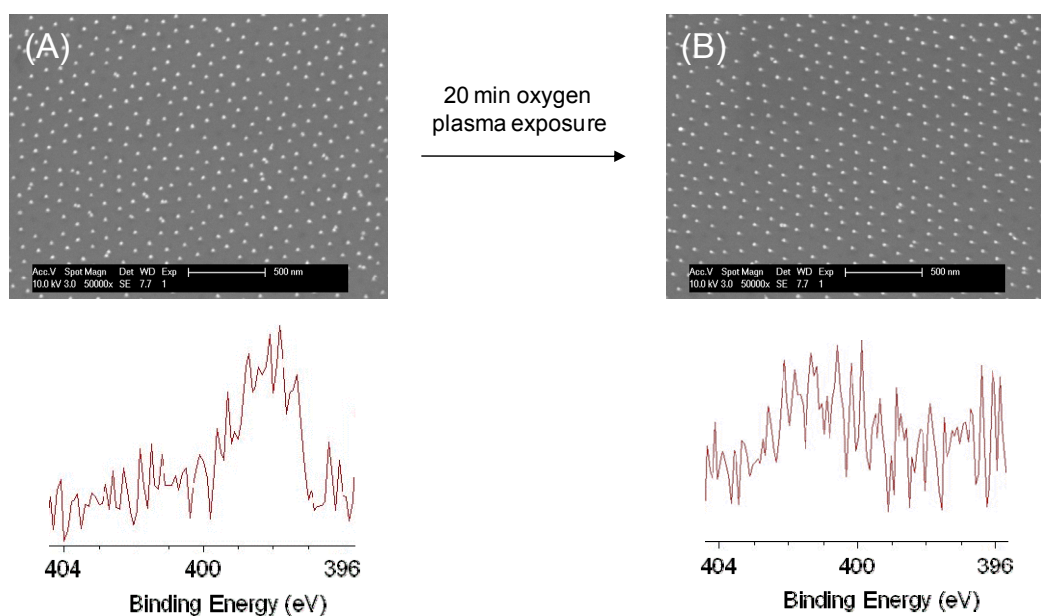


**Fig. S2.** Formation of APTES nanopatterns using BCP-b micellar mask. Topography AFM images of (A) reverse BCP-b micelles deposited on APTES-modified silicon substrate (tapping mode, z scale: 100 nm), (B) surface after oxygen plasma exposure for 50 s (tapping mode, z scale: 50 nm), and (C) APTES nanodomains after removal of the residual micelles in DMF (contact mode, z scale: 5 nm). AFM images (D) and (E) show APTES nanodomains analyzed in trace and retrace friction mode, respectively. For all AFM images the scan size is  $1 \times 1 \mu\text{m}$ .



**Fig. S3.** SEM images showing surface morphologies resulting from the adsorption of 10 and 20 nm gold NPs onto (A) APTES-modified silicon and (B) bare Si/SiO<sub>2</sub> surfaces. The surfaces were immersed in gold colloidal solutions for 1h, followed by rinsing in methanol and drying under nitrogen. Gold NPs are attracted by the positively charged APTES layer (NH<sub>3</sub><sup>+</sup>), whereas the repulsive electrostatic forces prevent their adsorption on negatively charged Si-O<sup>-</sup> surface.

Removal of the APTES patterns: The underlying APTES nanopatterns which serve for the positioning process may prevent the use of metal NPs for applications where a direct contact with the substrate is required (e.g. for catalysis and nanofabrication). Below, we show that APTES layer can be completely removed by exposing the surface to oxygen, without alteration of the periodical NP arrangement.



**Fig. S4.** SEM pictures of 20 nm gold NP arrays (A) after the positioning on APTES nanopatterns and (B) after 20 min of oxygen plasma treatment. XPS spectra recorded in the N1s region are given below their respective SEM images. The disappearance of the N1s signal corresponding to the terminal amino groups of APTES indicates a complete degradation of the APTES nanopatterns.