Supplementary Information

Direct Synthesis of a Macroscopic Array of Naked Ag Nanoparticles

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Experimental details

Polyvinylpyrrolidone (PVP40T-500G, Average Mol. wt. 40,000 g/mol) was purchased from Aldrich; silver nitrate ($AgNO_3$, ≥99.0%) was purchased from Sigma-Aldrich. Both chemicals were used as received without further purification. De-ionized water was used in all the experiments. All glassware used in our experiments was cleaned with soap, aqua regia, and then rinsed thoroughly with de-ionized water before use. Synthesis of self-assembled silver nanoparticle arrays at air/water interface were carried out under hydrothermal conditions, namely under autogenous pressure at different temperatures in a reactor as that shown in Figure S1 enclosed in a safety container and heated in the oven. Thus, a 5 ml Pyrex (or Teflon) beaker containing solution I (Inner solution, 0.5 M $AgNO_3$) was carefully introduced in a 100 ml red screw-cap Pyrex bottle (standing temperatures up to 180 ºC) which contained solution O (Outer solution, 20 ml of a 0.5 M solution of polyvinylpyrrolidone (PVP) in deionized water). The closed setup was introduced in a home-made safety container and heated in a thermostated oven at 145 ºC for 45 minutes The formation of a metallic luster (mirror) on the surface of the Inner solution took place in the absence of any physical contact between I and O solutions.

It should be stressed that the reaction between $AgNO_3$ and PVP solutions, mixed together and subject to the same hydrothermal conditions, does not lead to the formation of a silver mirror on the solution surface, but to a bulk reduction instead. Thus, a synthesis with 0.2 ml of 0.5 M PVP added from the beginning to the $AgNO_3$ solution in the inner beaker and heated hydrothermally at 145 ºC, led to the formation of dispersed silver nanoparticles, as indicated by the colored solution, but no interfacial mirror was formed at all.

We propose that the nanoarray is formed by reaction of Ag+ ions (I solution) with gas-phase decomposition products of PVP (O solution). Related to this hipothesis, we carried out a series of synthesis experiments substituting the outer 20ml PVP(0.5M aq) solution by 20ml solutions of its decomposition products, namely i) acetaldehyde (0.5M aq) or ii) ethanol (0.5M aq) or iii) isopropanol (0.5M aq) solutions or iv) a mixture of the three above solutions. The results are most interesting, and add to the uniqueness of our method to prepare well-ordered arrays. Indeed, all three reagents reduce silver ions but they do so yielding final results quite different from the title nanoparticulate array. The following are the results obtained which are now included and briefly described in the Suplementary Material section:

i) Acetaldehyde solutions reduced silver ions in the inner solution but lead to a white solid formed by large microcrystals very far from the nanoparticulate array.

ii) Ethanol solutions were the only ones leading to some interfacial solid but covering only a minimal part of the surface of the Inner solution

iii) Isopropanol led to the formation of conventional silver mirrors on the bottom and walls of the beaker.

iv) A mixture of all the above solutions led to a white solid similar to that described in i)

Thus, despite the fact that all three products are able to reduce Ag+ ions (as expected), the kinetic conditions are only optimal when these products are slowly released from the decomposition of PVP solutions under the reported experimental conditions.

The solution of silver nanoparticles used for comparison (i.e. Figure 2b2) was prepared as follows: 10 ml of 0.8 M PVP solution in deionized water was heated up to 130 ºC for 60 min in a screw-cap 100 ml Pyrex bottle. After cooling the PVP solution down to around 90 ºC, 10 ml of 0.2 M $AgNO_3$ solution was added, the bottle was closed and then the mixture heated up to 140 ºC for 60 min.

Scanning Electron Microscopy (SEM) was performed with a FEI Quanta 200 FEG ESEM instrument. For SEM characterization, the mirror formed at the air-water interface was transferred onto pre-cleaned 1x1 cm glass-slide substrates by simple contact at room temperature. UV-Visible spectra were recorded using a Cary 5 (Varian) UV-Vis-NIR high resolution optical spectrophotometer. The spectrum for the silver nanoparticles in PVP aqueous solution (b1 in figure 2) was obtained using 1 cm path length quartz cuvette. A portion of the self-assembled nanoparticles layer formed at the air-water interface was transferred onto pre-cleaned 1 mm thick, 1x1 cm glass-slide substrates by simple contact at room temperature for optical characterization. The absorption spectrum was obtained using a slide sample holder. TEM images and selected-area electron diffraction (SAED) patterns were recorded using two different microscopes, a JEOL JEM-1210 microscope operating at 120 keV and a JEOL JEM-1400 operating at 80 keV. High-resolution TEM images were obtained with a JEOL JEM 2011 electron microscope operating at 200 keV and equipped with energy dispersive X-ray spectrometer (EDX) for elemental analysis. For TEM characterization, the different samples were prepared as follows: For the silver nanoparticles in solution, one single drop was placed on carbon-coated copper grid. In the case of the self-assembled nanoparticles arrays at the air-water interface, a portion of the mirror was adhered onto a carbon-coated copper grid by a careful single contact with the mirror surface. FTIR spectra were recorded from 4000 to 650 cm−1 using a PerkinElmer Spectrum One spectrophotometer equipped with a universal Attenuated Total Reflectance (ATR) sampling accessory supplied with a top plate diamond crystal. For FTIR-ATR analysis, a fraction of the mirror (self-assembled nanoparticles) formed at the air-water interface was transferred onto pre-cleaned 1x1 cm glass-slide substrates by simple contact at room temperature. Then, the sample slide was placed onto the crystal and its spectrum was recorded. All spectra are the average of two independent measurements with 10 scans each at a resolution of 4 cm-1. For GC-MS experiments a DSQII equipment (ThermoFisher Scientific) equipped with a headspace module was used. Samples were treated in air-tight 10 ml headspace vials and heated at 140 ºC for 60 minutes. Then 1ml of the vapor phase was injected into the GC-MS using a syringe kept at a temperature 5 ºC higher than the treatment temperature. (Scan: 29-300 amu, 1.8 ml/min Helium).

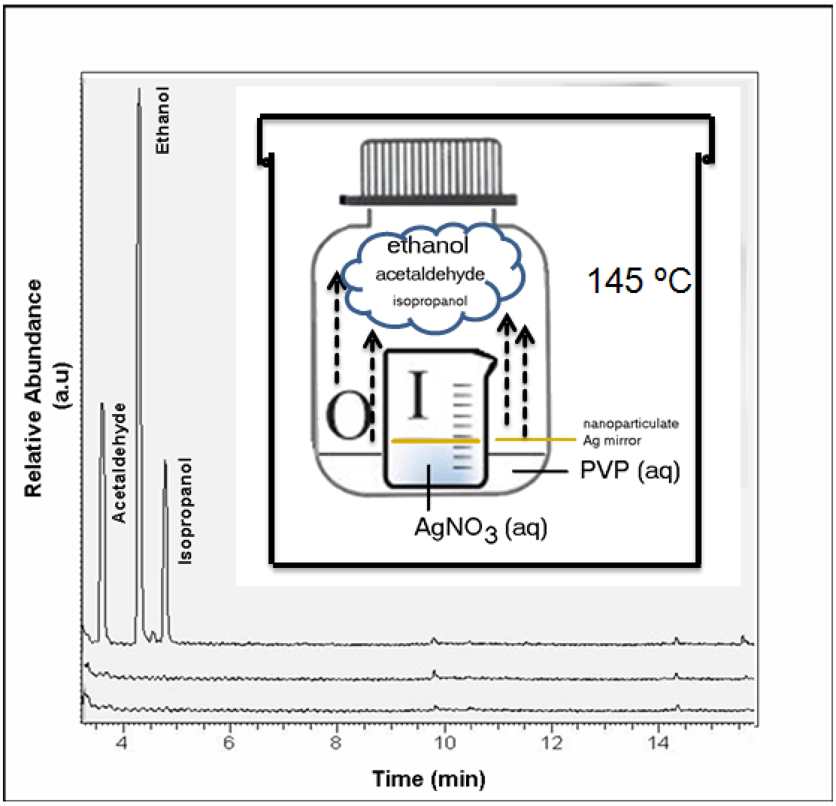

Figure S1. GC-MS spectra for samples of deionized water (bottom), 1M $AgNO_3$ solution (middle) and 2M PVP solution (top) all treated at 140 ºC for 60 minutes. The small peak at 4.6 min. corresponds to furane. Inset: Schematic diagram of the two-compartment hydrothermal setup. PVP decomposition products act as reducing vapors for the formation and self-assembly of Ag nanoparticles. The two-compartment hydrothermal reaction is necessary for the preparation of the nanoparticulate silver interfacial mirrors described. An outer solution of PVP in deionized water (O) and an inner solution of $AgNO_3$ (I) were used as described in the experimental section. Although in our hands there was no problem, it should be noted that autogenous pressure is generated by heating at 145 ºC. The red screw-caps are able to stand up to 180 ºC. Yet, in order to avoid any possible risks, these flasks should be enclosed in safe containers. In our case a home-made stainless steel container.

Finally, we carried out a series of experiments involving the mixing of the nanoparticulate arrays with PVP in order to ascertain the effect of organic matter present in the arrays on their spectroscopic and microstructural features.

Thus, after preparation of a nanoparticulate interfacial array, as described in the manuscript, we did stir the solution so as to mix the inner (Ag-mirror containing) and Outer (PVP) solutions. Interestingly, after stirring the mixture for 60 minutes at 90ºC, the mirror was not destroyed and stayed on the surface. We carried out several analyses on this mirror "after-mixing" including TEM and, of course, FTIR-ATR. The results are shown below (Figures S2 and S3). It should be noted that FTIR-ATR detects quite clearly the presence of PVP on this mirror (fished onto a glass slide) (Figure S2a). Furthermore, TEM images and their statistical analyses show that the incorporation of PVP after mixing, leads to significantly larger inter-particle gaps.

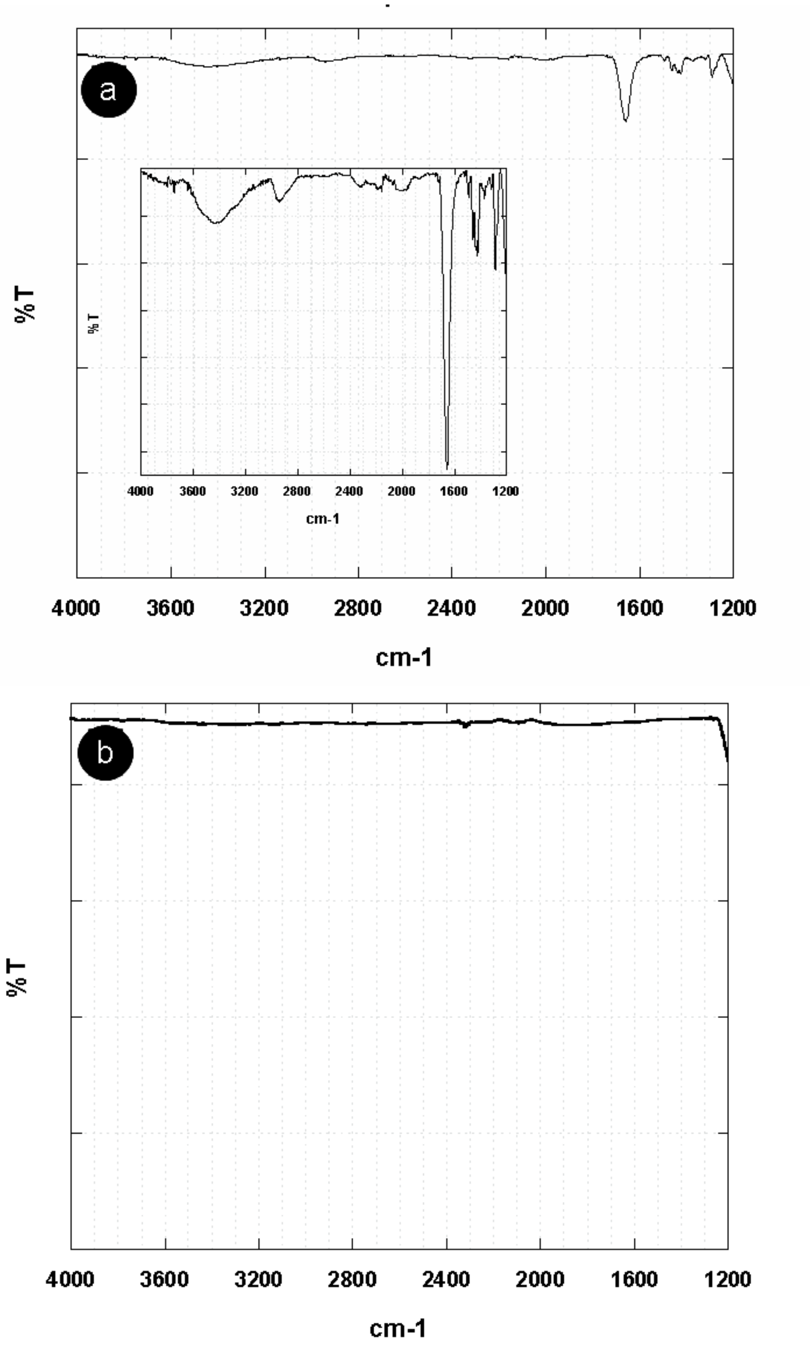

Figure S2. (a) FTIR-ATR spectra of a self-assembled silver nanoparticles array after mixing it with the PVP solution; inset: magnification of the FTIR spectra, showing the adsorption of PVP onto silver nanoparticles (b) FTIR-ATR spectra of the pristine self-assembled silver nanoparticles array.

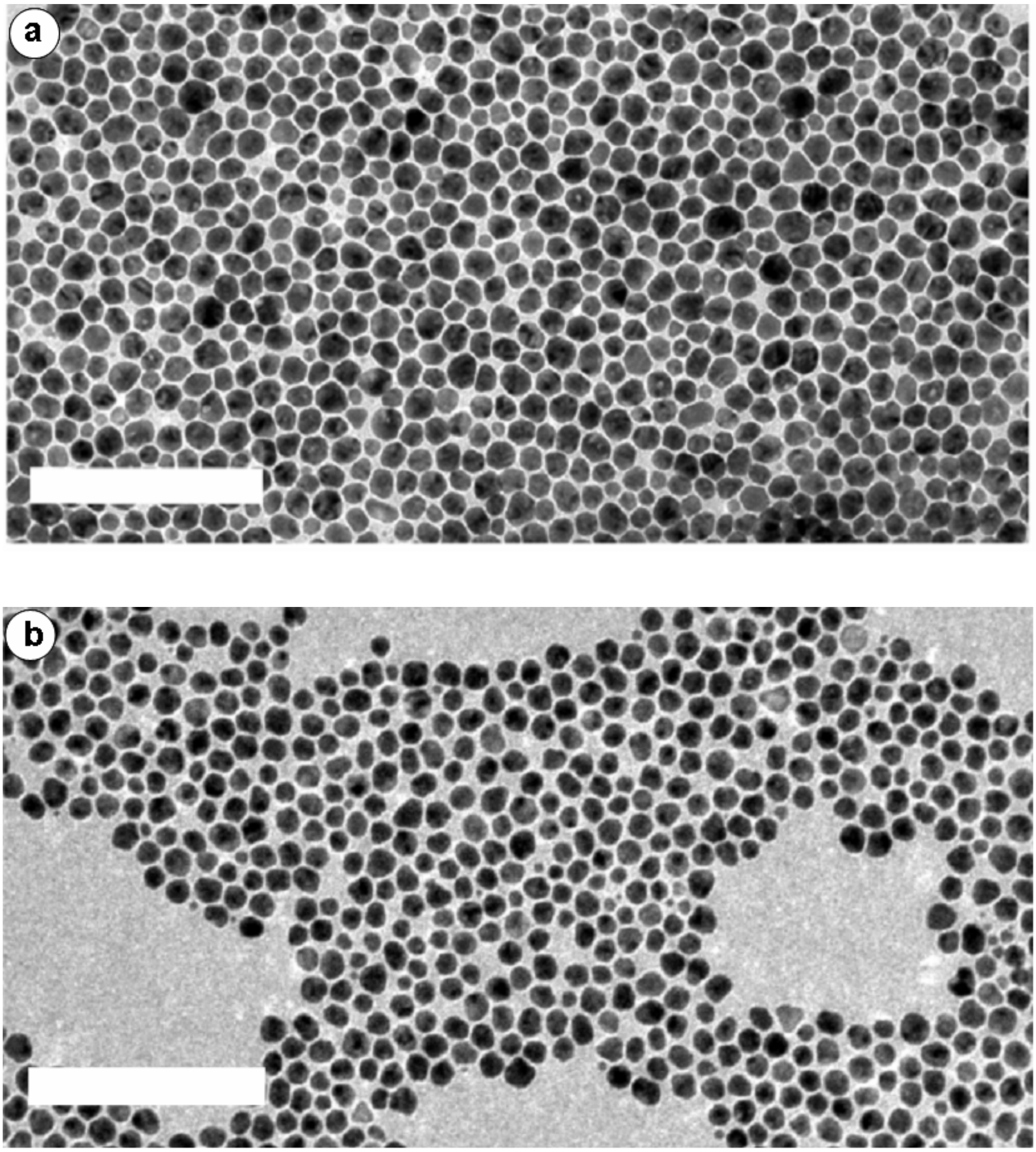

Figure S3. (a) TEM image of the pristine self-assembled silver nanoparticle mirror (without mixing with PVP solution after its formation). This array formed at the vapor-water interface with an average interparticle separation of 1.3(1.0) nm. (b) TEM image of the preformed interfacial silver nanoparticle mirror mixed with PVP solution. The average interparticle separation of this array is 2.4(0.7) nm. The scale bar in both images is 100 nm.