View Article Online / Journal Homepage / Table of Contents for this issue
Dynamic Article Links

ChemComm

Cite this: *Chem. Commun.*, 2011, **47**, 11285–11287

www.rsc.org/chemcomm

COMMUNICATION

Direct synthesis of a macroscopic array of naked Ag nanoparticles†

Omar Ayyad,[abc] **David Muñoz-Rojas‡**[a] **and Pedro Gómez-Romero***[ac]

Received 6th June 2011, Accepted 5th September 2011
DOI: 10.1039/c1cc13353e

A 2-D array of naked Ag nanoparticles has been synthesized through interfacial reduction of Ag^+ under hydrothermal conditions. The process bestows the synthesis, nucleation, growth and self-assembly of the nanoparticles in a simple one-pot reaction and makes use of no additive or capping agent. The resulting macroscopic liquid silver mirror is highly stable and composed of tightly packed naked Ag nanoparticles (17 (3) nm diameter, with interparticle gaps of 1.3 (1.0) nm) which can be easily transferred to a given substrate for application.

To build and how to build self-assembled arrays of nanoparticulate matter are questions engaging a growing number of labs around the world. We all know by now that nanoparticles present chemical and physical properties radically different from their bulk counterparts.[1] But assemblies of these very same nanoparticles show, in turn, collective properties which set them apart from their disordered dispersions.[2] Thus, research emphasis is quickly shifting to the understanding and control of self-assembly processes. This constitutes a hot topic with a double target. On the one hand, the fundamental understanding of those emerging collective properties and on the other hand the integration of assembled arrays on substrates amenable to practical use.[3]

Conventional self-assembly research involves multi-step methods;[4] namely synthesis, purification and assembly. Indeed, the common starting point is a pre-synthesized sample of monodisperse colloidal nanoparticles with a given size and shape, followed by a purification process, achieved through a variety of size-selection techniques.[5] Finally, the assembly process is typically carried out by means of various liquid–liquid[6] or air–liquid[7] interfacial techniques, such as Langmuir–Blodgett (LB) films,[8] solvent evaporation,[9] or DNA-templated method.[10] In many cases self-assembly is attained at the very same C-coated copper TEM grid.[11]

The need remains though to be able to fabricate this type of complex assemblies on a macroscopic length scale through cheap, fast and simple methods.

Yet, the present state of the art makes use of all sorts of organic additives to stabilize and order nanoparticles into arrays,[2d,12] either used as surfactants,[13] as surface functionalizing ligands,[14] or as charge stabilizing agents for colloidal nanocrystals.[15]

Herein we report for the first time an utterly simple approach for the simultaneous synthesis and self-assembly of naked silver nanoparticles leading to the formation of macroscopic 2-D arrays in nanometric order. This is a swift one-step method, which conforms to the criteria to be considered as green chemistry,[16] and makes use of hydrothermal conditions involving no organic additive neither to protect/stabilize nor to direct the assembly of the nanoparticles. As far as we know, this is the first example of such an "all-in-one" synthesis and self-assembled growth process and could have important implications for the understanding and design of this type of systems.

The synthesis reactions were carried out under hydrothermal autogenous pressure (*ca.* 2.0 bars) in a two-compartment thermostated setup as shown in Fig. S1 (inset) (ESI†). Thus, a 5 ml beaker containing solution I (inner solution) was introduced into a screw-cap Pyrex bottle which contained solution O (outer solution). In a typical reaction, a silver nitrate solution was contained in the inner beaker and a polyvinylpyrrolidone (PVP) solution in water was the outer solution. Silver nanoparticulate layers were formed at the surface of the inner solution after 45 minutes at 145 °C in the absence of any physical contact between the two solutions.

Fig. 1a shows photographs of the resulting superficial silver layer. Photographs were taken both by reflection (top) and transmission (bottom inset). It should be stressed that these layers were formed in the absence of any contact between I ($AgNO_3$) and O (PVP) solutions. Fig. 1b displays a TEM micrograph of this sample adhered onto a C-coated copper grid by a careful single contact with the mirror surface. This TEM image shows a remarkable close-packed monolayered array of reasonably monodisperse silver nanoparticles. Fig. 1c presents the corresponding particle-size distribution histogram with an average size of 17 nm and a standard deviation of 3 nm (size polydispersity 18%). We also carried out statistical analyses of interparticle separation in these arrays and found average values of 1.3 (1.0) nm. Fig. 1d shows a SAED pattern of the sample confirming an fcc metallic silver phase.

---

[a] *Centro de Investigación en Nanociencia y Nanotecnologia, CIN2 (CSIC-ICN), UAB, Bellaterra 08193, Spain. E-mail: pedro.gomez@cin2.es, omar.ayyad@cin2.es; Fax: +34 935868020; Tel: +34 935868010*
[b] *Department of Materials Science and Metallurgical Engineering, University of Barcelona, Martí i Franqués, 1, 08028 Barcelona, Spain*
[c] *MATGAS Research Center, Campus UAB, 08193, Barcelona, Spain*

† Electronic supplementary information (ESI) available: Experimental details and Fig. S1 and S2. See DOI: 10.1039/c1cc13353e

‡ Present address: Department of Materials Science and Metallurgy, University of Cambridge, Pembroke St., Cambridge CB2 3QZ, UK.

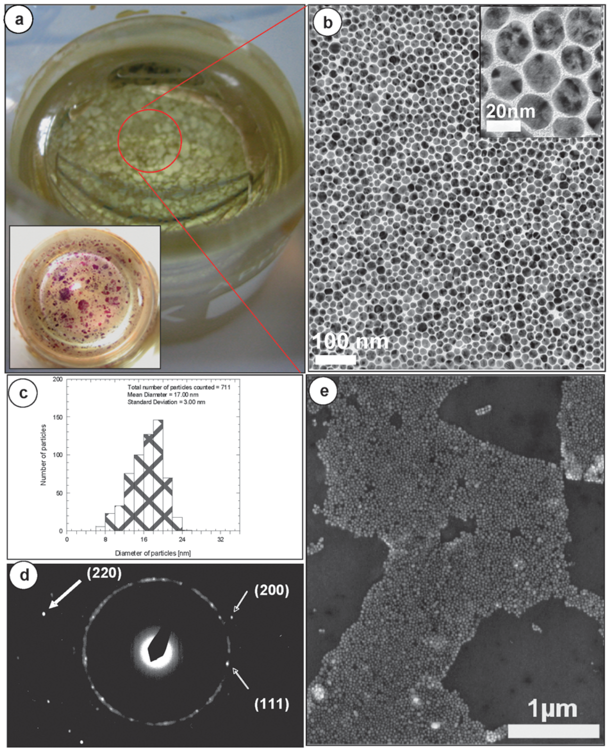

Fig. 1 (a) Photographs of a silver mirror of self-assembled nanoparticles grown at the vapour–water interface, main (reflection) and inset (transmission). (b) TEM image of the monolayer array of silver nanoparticles. Inset: HRTEM image showing the very tight close-packing arrangement. (c) Particle-size distribution histogram for 711 nanoparticles in (b). (d) Selected area electron diffraction (SAED) pattern of the sample confirming a fcc metallic silver phase. (e) SEM image of nanoparticle array sheets, ripped-up while being transferred from the water surface onto a glass slide.

Fig. 1e shows a SEM image of the arrays (partly ripped-up) on a glass slide, showing the same two-dimensional structure of homogeneous spherical nanoparticles as seen in TEM but at a larger scale. This demonstrates the extended nature of the self-assembled mirror as well as the feasibility of transferring a monolayer onto a given substrate by mere contact. This transportability is remarkable in itself when compared with the difficulties normally reported in the literature to assemble nanoparticle arrays on similar substrates.[17]

The first question coming to mind after these experiments and observations concerns the process of reduction of silver ions. The reproducible formation of silver nanoparticulate films in the two-compartment hydrothermal setup described, with no physical contact between I and O solutions, rules out the possibility of a direct reduction of silver ions by PVP. Our hypothesis was that certain decomposition products of PVP at high temperature could be responsible for the reaction. In order to answer this question we carried out Gas Chromatography/Mass Spectrometry experiments which could detect those decomposition products. Fig. S1 (ESI†) shows the GC/MS trace of an aqueous PVP solution treated at 140 °C under autogenous pressure for 60 minutes, *i.e.* under conditions as close to the experimental synthesis as possible. Interestingly, acetaldehyde, ethanol, isopropanol and traces of furan were detected. Acetaldehyde and alcohol vapors can readily reduce silver ions and therefore they would suffice to induce the nucleation and growth of metallic silver at the water–air interface, which would explain why reduction is limited to the water surface.

In order to detect any possible organic compound present in the nanoparticle array we recorded FTIR-ATR spectra of the silver mirror layer. Although no contact between PVP and silver ions was allowed, we could not rule out the possibility that some ethanol, isopropanol or even acetic acid from the oxidation of acetaldehyde could be present in the mirror. The nanoparticulate mirror array presents no sign of organic matter as evidenced by the lack of any peak in the FTIR (Fig. S2, ESI†). Of course, we cannot rule out the presence of traces of organic matter. What these data show is the absence of any organic compound in a concentration sizeable enough to provide stabilization of the whole silver array.

Our present results question the notion that surface modification with organics is necessary for effective nanoparticle self-assembly. This "all-in-one" process takes place on the surface due to the heterogenous reaction with organic vapors and the nanoparticles formed stay there due to surface tension forces, while remaining homogeneously separated by the effect of their electrical double layer.

We measured UV-Visible spectra (Fig. 2) for (i) the self-assembled nanoparticle array (a1) and (ii) a bulk dispersion of silver nanoparticles of similar size and shape (b1) (prepared as described in experimental details). The latter presents a typical absorption peak at 417 nm,[18] whereas the absorption spectrum of the nanoparticulate array presents a much broader feature with a maximum at 495 nm, and with a long tail extending into the near IR region, beyond 1000 nm (hence the purple-red colour).

Normally a shift in the plasmon absorption of nanoparticles is attributed to changes in size or shape. This is not the case here. Instead, we must conclude that the nanoparticulate array presents a very significant red-shift and broadening derived not from polydispersity but from a collective optical behavior of the array itself. This is in good agreement with previous observations.[2e,13]

In conclusion, we have shown here, for the first time, the possibility to integrate the reduction, nucleation, growth and self-assembly of silver nanoparticles, all in a single step. Thus, the two-compartment hydrothermal method described has

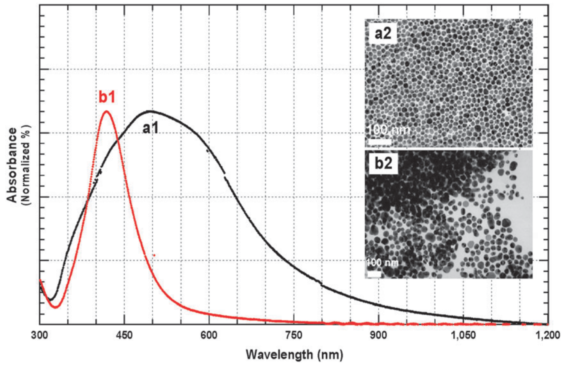

Fig. 2 Absorption spectra of an array of self-assembled silver nanoparticles on a glass slide (a1) and of silver nanoparticles in PVP aqueous solution (b1). a2 and b2 show TEM images of the corresponding samples.

This journal is © The Royal Society of Chemistry 2011

allowed the reproducible direct synthesis of a self-assembled array of monodisperse silver nanoparticles forming a macroscopic interfacial mirror with long term stability. No organic structure-directing compound has been needed to make this self-assembly possible, which challenges conventional wisdom concerning the use of surfactants or other surface-modifying ligands as necessary elements for self-assembly. Despite the greater simplicity of our method, the resulting nanoparticles present size polydispersity of 18%, which are narrow and comparable to those resulting from the leading conventional methods in the field.[19] This is remarkable, specially taking into account that no treatments such as size selection techniques were applied in our additive-free method.

Furthermore, the resulting extended array of truly naked nanoparticles constitutes an optimal system for the tailor-made modification of the nanoparticulate surface with organic compounds or biomolecules for a great variety of specific applications. In particular, the tightly closed naked Ag nanoparticles forming this system allow us to predict a high number of very active hot-spots and therefore these arrays seem particularly well-suited as substrates for Surface-Enhanced Raman Spectroscopy.[20] Further research with very promising preliminary results is presently being pursued along this line.

This research was supported partially by the Ministry of Science and Innovation (CTQ2008-06779-C02-01 and MAT2011-28931) and MATGAS. The authors thank CSIC and the European Social Fund for financing D.M.-R. through the I3P program. O.A. gratefully acknowledges a loan from Al-Quds University.

Notes and references

1 M. Sastry, in *Colloids And Colloid Assemblies: Synthesis, Modification, Organization and Utilization of Colloid Particles*, ed. F. Caruso, Wiley-VCH, Weinheim, 2004, pp. 369–397.

2 (*a*) C. B. Murray, C. R. Kagan and M. G. Bawendi, *Annu. Rev. Mater. Sci.*, 2000, **30**, 545; (*b*) H. W. Duan, D. A. Wang, D. G. Kurth and H. Mohwald, *Angew. Chem., Int. Ed.*, 2004, **43**, 5639; (*c*) A. Courty, *J. Phys. Chem. C*, 2010, **114**, 3719; (*d*) Z. Nie, A. Petukhova and E. Kumacheva, *Nat. Nanotechnol.*, 2010, **5**, 15; (*e*) L. M. Liz-Marzán, *Langmuir*, 2006, **22**, 32.

3 (*a*) C. Burda, X. B. Chen, R. Narayanan and M. A. El-Sayed, *Chem. Rev.*, 2005, **105**, 1025; (*b*) A. R. Tao, J. X. Huang and P. D. Yang, *Acc. Chem. Res.*, 2008, **41**, 1662.

4 (*a*) Y. Yang, S. M. Liu and K. Kimura, *Angew. Chem., Int. Ed.*, 2006, **45**, 5662.

5 (*a*) A. Courty, A. Mermet, P. A. Albouy, E. Duval and M. P. Pileni, *Nat. Mater.*, 2005, **4**, 395; (*b*) N. Zheng, J. Fan and G. D. Stucky, *J. Am. Chem. Soc.*, 2006, **128**, 6550.

6 (*a*) Y. Lin, H. Skaff, T. Emrick, A. D. Dinsmore and T. P. Russell, *Science*, 2003, **299**, 226; (*b*) C. N. R. Rao and K. P. Kalyanikutty, *Acc. Chem. Res.*, 2008, **41**, 489.

7 (*a*) K. M. Gattas-Asfura, C. A. Constantine, M. J. Lynn, D. A. Thimann, X. J. Ji and R. M. Leblanc, *J. Am. Chem. Soc.*, 2005, **127**, 14640.

8 (*a*) S. Acharya, J. P. Hill and K. Ariga, *Adv. Mater.*, 2009, **21**, 2959; (*b*) H. J. Tsai and Y. L. Lee, *Soft Matter*, 2009, **5**, 2962.

9 (*a*) I. Lisiecki, P. A. Albouy and M. P. Pileni, *J. Phys. Chem. B*, 2004, **108**, 20050; (*b*) T. P. Bigioni, X. M. Lin, T. T. Nguyen, E. I. Corwin, T. A. Witten and H. M. Jaeger, *Nat. Mater.*, 2006, **5**, 265.

10 F. McKenzie, K. Faulds and D. Graham, *Nanoscale*, 2010, **2**, 78.

11 A. Courty, A. I. Henry, N. Goubet and M. P. Pileni, *Nat. Mater.*, 2007, **6**, 900.

12 M. P. Pileni, *J. Phys. Chem. B*, 2001, **105**, 3358.

13 A. Guerrero-Martínez, J. Pérez-Juste, E. Carbó-Argibay, G. Tardajos and L. M. Liz-Marzán, *Angew. Chem., Int. Ed.*, 2009, **48**, 9484.

14 M. Schulz-Dobrick, K. V. Sarathy and M. Jansen, *J. Am. Chem. Soc.*, 2005, **127**, 12816.

15 F. Reincke, S. G. Hickey, W. K. Kegel and D. Vanmaekelbergh, *Angew. Chem., Int. Ed.*, 2004, **43**, 458.

16 P. Raveendran, J. Fu and S. L. Wallen, *J. Am. Chem. Soc.*, 2003, **125**, 13940.

17 A. N. Shipway, E. Katz and I. Willner, *ChemPhysChem*, 2000, **1**, 18.

18 O. Ayyad, D. Muñoz-Rojas, J. Oró-Solé and P. Gómez-Romero, *J. Nanopart. Res.*, 2010, **12**, 337.

19 M. P. Pileni, *Pure Appl. Chem.*, 2000, **72**, 53.

20 A. Sánchez-Iglesias, P. Aldeanueva-Potel, W. Ni, J. Pérez-Juste, I. Pastoriza-Santos, R. A. Alvarez-Puebla, B. N. Mbenkum and L. M. Liz-Marzán, *Nano Today*, 2010, **5**, 21.

Supplementary Information

Direct Synthesis of a Macroscopic Array of Naked Ag Nanoparticles

Omar Ayyad,*[a,b,c] David Muñoz-Rojas,[a] Pedro Gómez-Romero*[a,c]

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).

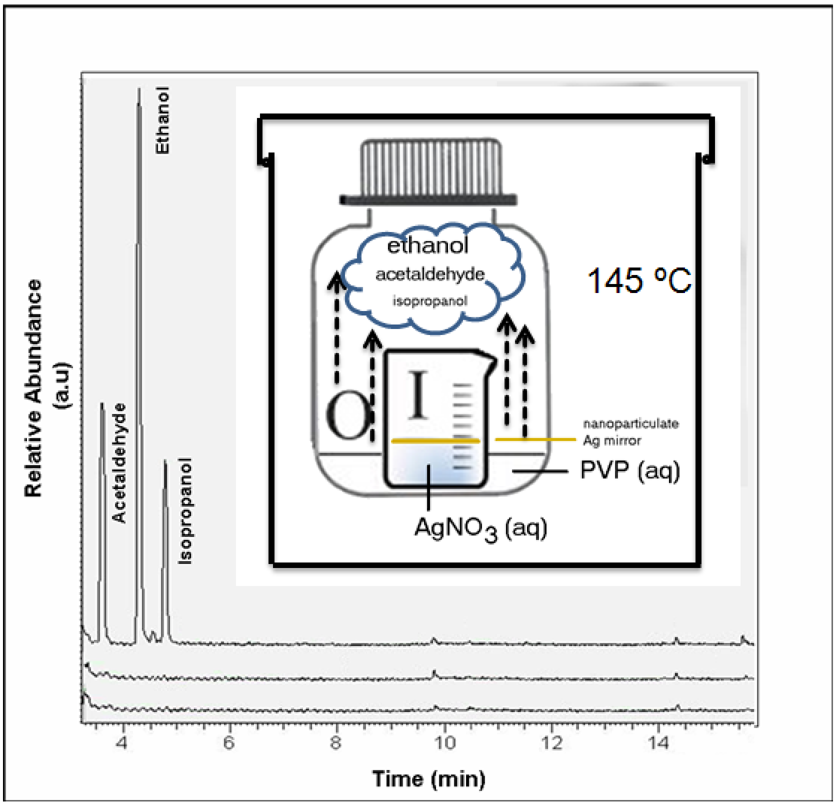

Figure S1. GC-MS spectra for samples of deionized water (bottom), 1M $AgNO_3$ solution (middle) and 2M PVP solution (top) all treated at 140 ºC for 60 minutes. The small peak at 4.6 min. corresponds to furane. Inset: Schematic diagram of the two-compartment hydrothermal setup. PVP decomposition products 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.

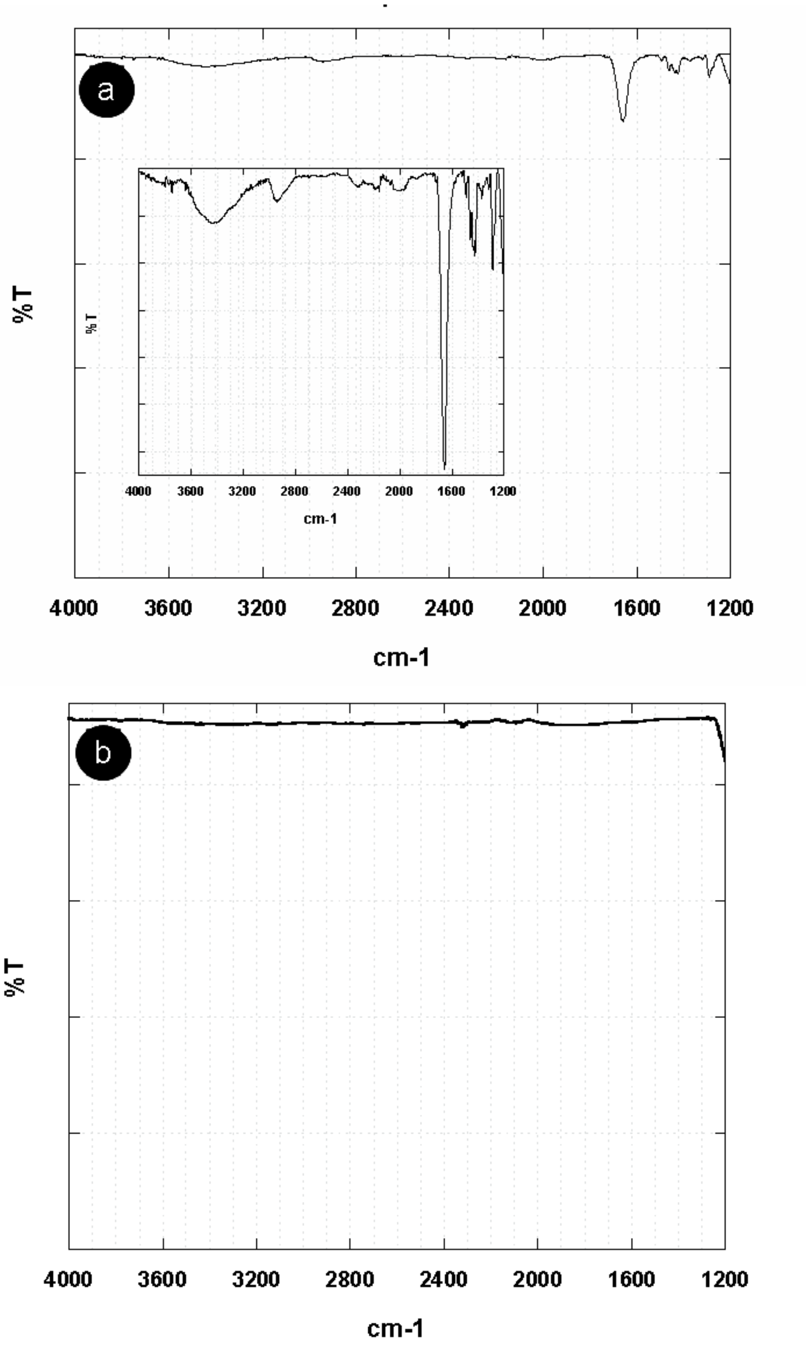

Figure S2. (a) FTIR-ATR spectra of a self-assembled silver nanoparticles array after mixing it with the PVP solution; inset: magnification of the FTIR spectra, showing the adsorption of PVP onto silver nanoparticles (b) FTIR-ATR spectra of the pristine self-assembled silver nanoparticles array.

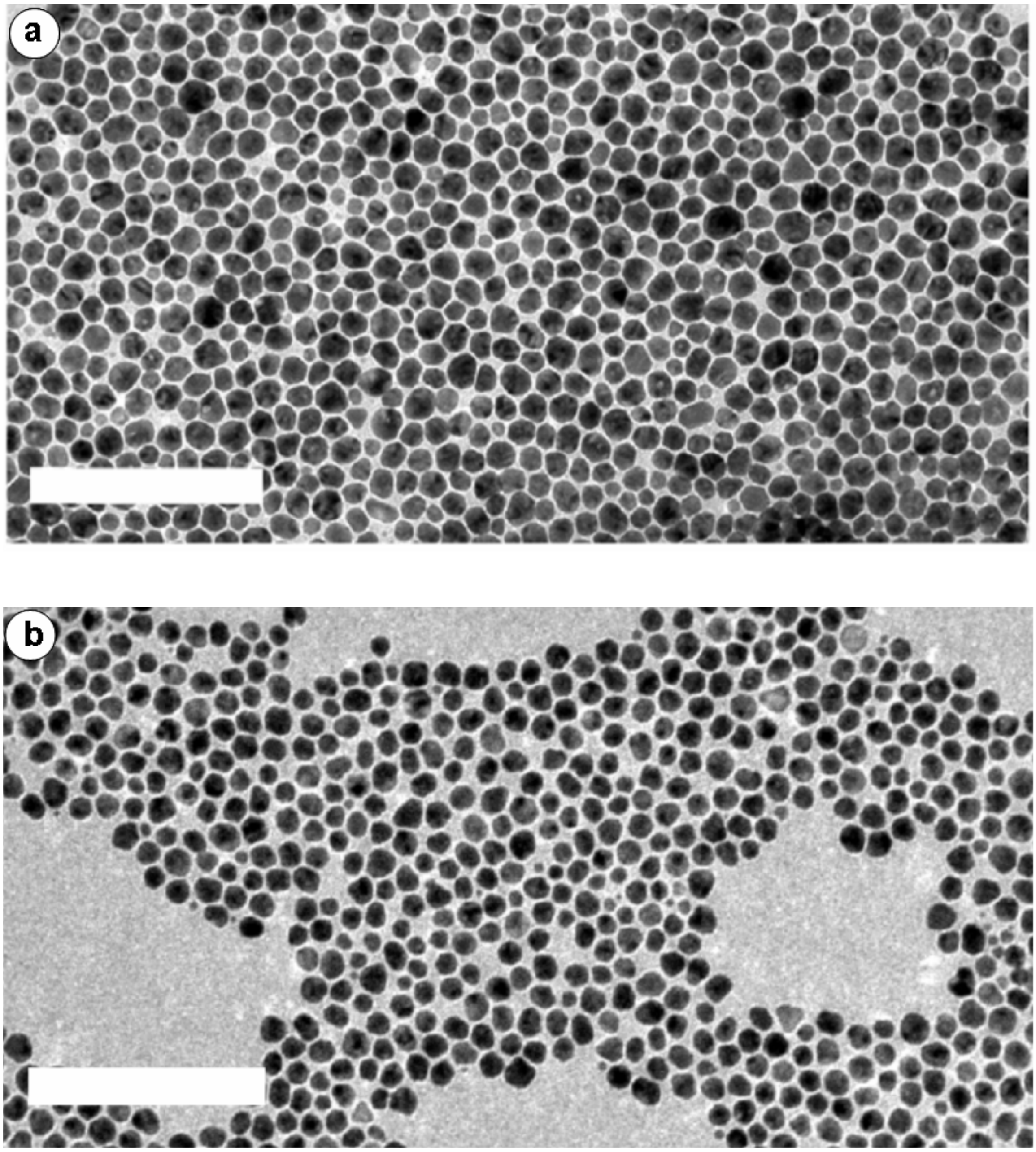

Figure S3. (a) TEM image of the pristine self-assembled silver nanoparticle mirror (without mixing with PVP solution after its formation). This array formed at the vapor-water interface with an average interparticle separation of 1.3(1.0) nm. (b) TEM image of the preformed interfacial silver nanoparticle 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.