# Supporting Information for "Pre- and Post-Assembly Modifications of Colloidal Plasmonic Arrays: The Effect of Size Distribution, Composition and Annealing"

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## EXPERIMENTAL SECTION:

### 1. Materials:

Hexadecyltrimethylammonium chloride (CTAC, 25 wt% in water, CAS: 112-02-7, Lot #STBJ9502), hydrogen tetrachloroaurate trihydrate ($HAuCl_4 \cdot 3H_2O$, ≥ 99.9%, CAS: 16961-25-4, Lot #MKCP1782), silver nitrate ($AgNO_3$, ≥ 99.8%, CAS: 7761-88-8, Lot #STBH0727), L-ascorbic acid (AA, ≥ 99%, CAS: 50-81-7, Lot #MKBW7789V), tannic acid (TA, ≥ 99.9%, CAS: 1401-55-4, Lot #MKCH9318), sodium bromide (NaBr, ≥ 99.0%, CAS: 7647-15-6, Lot#MKCH6907), sodium borohydride ($NaBH_4$, 99%, CAS: 16940-56-2, Lot #STBB0401L9), sodium citrate (≥ 99%, CAS: 6132-04-3, Lot #BCBX6867), poly(ethylene glycol methyl ether thiol (PEG-SH, MW 2000 g/mol, Lot#MKCK7227), 1H,1H,2H,2H- perfluorooctyl-trichlorosilane (97%), Hellmanex III solution. were purchased from Sigma-Aldrich. Acetone (≥ 99.6%, CAS: 67-64-1, Lot#21H33250), 2-propanol (IPA, ≥ 99.8%, CAS: 67-63-0, Lot#21D32468GC), sodium hydroxide (2.0 ± 0.002 M, CAS: 1310-73-2, Lot#20F30250) ethanol (≥ 96%, CAS: 64-17-5, Lot#21C32223AV) were purchased from Labbox. Polydimethylsiloxane (PDMS, Sylgard 184) was purchased from Dow Corning (Michigan, USA). Coverslip glass (LABBOX Spain, COVN-020-1K0, 20x20 mm) or silicon wafers were used as substrates.
All chemicals were used as received. Milli-Q water (resistivity 18.2 MΩ · cm at 25 ºC) was used in all experiments. All glassware was washed with *aqua regia* (3:1 HCl:$HNO_3$), rinsed with Milli-Q water, sonicated three times for 3 min, and dried before use. (**Warning:** *aqua regia* is an extremely corrosive liquid and strong oxidizer, and require proper personal protective equipment to be handled safely).

### 2. Instrumentation:

Transmission electron microscopy (TEM) images were collected with a JEOL 1210 TEM instrument (Tokyo, Japan) operating at 120 kV using carbon-coated 400 square mesh copper grids. Scanning electron microscopy (SEM) images were collected with a FEI QUANTA 200 Field Emission Gun, and a FEI Magellan 400L, operating between 5 and 30 kV. Energy Dispersive X-ray Spectroscopy maps were collected using a FEI Magellan 400L equipped with a X-Max Ultim Extreme EDX (Oxford Instruments) detector. Thermal annealing was performed in a AS-Micro Rapid Thermal Annealing Furnace by Annealsys. Extinction spectra of the colloids were recorded using a Hitachi U-3000 spectrophotometer. Far-field transmission measurements in the 400 to 1100 nm range were collected using a custom-built setup. Briefly, a Tungsten Halogen Lamp (Ocean Optics, HL-2000-HP, Florida, USA) was used as light source; samples were mounted on a rotational stage (Thorlabs, RP03/M, New Jersey, USA) that allows to vary the illumination angle

θ, while a custom-made sample holder allows for a precise adjustment of the azimuthal angle φ (± 3 º); the transmitted light was then collected using a fiber coupled spectrophotometer (Ocean Optics, QEPro-FL). Air was used as reference. All spectra were collected with a 4× objective (Olympus, RMS4X, NA: 0.10).

## 3. Preparation of the colloids

### *3.1 Synthesis of gold nanoparticles*

All gold nanospheres used were synthetized *via* a seed-mediated method, based on CTAC/AA reduction of $HAuCl_4$, as previously reported.[1,2] Size control is achieved by a combination of thermodynamic and kinetic effects, exploiting both the reduction of new precursor and Ostwald ripening.

#### *3.1.1. Seed preparation*

50 µL of a 50 mM $HAuCl_4$ solution was added to 5 mL of 0.1 M CTAC solution, afterwards 200 µL of a freshly prepared 20 mM $NaBH_4$ solution was injected under vigorous stirring. After 3 min, the mixture was diluted 10 times using a CTAC 100 mM solution.

#### *3.1.2. 10 nm Au nanoparticles preparation*

10 nm Au nanoparticles. 7.2 mL of the previously diluted seeds@CTAC was added to 80 mL of 25 mM CTAC solution, followed by 320 µL of a 0.1 M AA solution. The growth is initiated by the addition of 400 µL of a 50 mM $HAuCl_4$ solution under vigorous stirring. The mixture is left undisturbed at room temperature for at least 10 min.

#### *3.1.3. 20-100 nm Au nanoparticles preparation*

This is a three step process. The proceeding of each step was monitored using the absorbance at 400 nm via UV-visible spectroscopy; once the absorbance does not increase (decrease) the growth (etching) process is terminated.[3] The amounts given here are for 100 mL of product.

- Step 1: a certain volume (depending on the desired final size, see table S1) of 10 nm nanoparicles suspension was added to 100 mL of 25 mM CTAC solution, followed by the addition of 250 µL of 0.1 M AA and 250 µL of 0.05 M $HAuCl_4$ under vigorous stirring. The mixture was left undisturbed at room temperature for 30 min.

- Step 2: The growth solution is heated to 40 ºC and another aliquot of 250 µL of the 0.05 M $HAuCl_4$ is added, partially oxidizing the nanoparticles through comproportion reaction initialized by $Au^{3+}$. Once the etching is completed (30-40 min), the solution is heated to 75 ºC and kept at that temperature for 20-30 min, favoring the solvothermal growth of the particles into more isotropic products.

- Step 3: The colloidal solution is cooled down to 40 ºC, and a final oxidative etching is performed to further improve the spherical shape of the particles. Specifically, 100 mg of NaBr and 250 µL 0.05 M $HAuCl_4$ solution are added to the growth mixture.

Finally, the synthetized particles were centrifuged (see table S1) to eliminate unreacted reagents, reduced the surfactant concentration to [CTAC] = 1mM, and reduce the volume to $1/20^{th}$ of the original growth solution (~ 5mL for 100mL synthesis). It is important to complete at least the first centrifugation step immediately after the end of Step 3, as the $Au^{+1}$ left in solution would proceed to reshape the particles and increase size/shape inhomogeneity. The size of the final product was tuned by changing the volume of 10 nm gold nanoparticles@CTAC added in step 1 (see Table S1).

### *3.2. Synthesis of silver nanoparticles*

All silver nanoparticles were synthesized *via* a sequential overgrowth procedure using silver nitrate reduction by TA/Citrate, as described by N. Bastús *et al.*[4] Size control is achieved exploiting both the reduction of new precursor and Ostwald ripening.

#### *3.2.1. Seed preparation*

200 mL of Citrate 5 mM was added on a three-neck round bottom flask, and the solution was heated up using a silicon oil bath and a Liebig condenser. Once the solution reaches a vigorous boiling, 8 mL of TA 2.5 mM are added to the mixture. After 1 min, nucleation was triggered by adding 2 mL of $AgNO_3$ 25 mM under stirring.

#### *3.2.2. Particle growth*

The seeds are grown in repetitive reduction steps until the desired size is reached. Specifically, 40 mL of the growing batch were withdrawn and analyzed to verify nanoparticle size *via* UV-vis characterization. Following the characterization, in order to proceed to the next growing step, 33 mL of $H_2O$ are added, and the mixture is brought back to 90ºC. Once the desired temperature is reached, 1 mL of Citrate 25 mM and 3 mL of TA 2.5 mM were added, and after 1 min the growth is imitated by the addition of 2 mL of $AgNO_3$ 25 mM. Once the desired size is achieved the solution is centrifuged three times (see table S1) to eliminate any excess of unreacted reagents and to concentrate the colloid to $1/20^{th}$ of the original volume. Particles were resuspended in water in preparation to the ligand exchange step.

**Table S1: Reagents volumes and centrifugation details for each gold colloid.**

| Material | Diameter (nm) | 10 nm particles (mL) | Centrifuge velocity (rpm; min) |
|---|---|---|---|
| **Au** | 24 ± 3 | 4 | 15000 ; 40 |
| | 49 ± 3 | 0.7 | 4000; 15 |
| | 96 ± 9 | 0.150 | 2500; 10 |
| **Ag** | 45 ± 4 | Does not apply | 5000; 15 |

### *3.3. PEG-SH functionalization*.

Ligand exchange reaction was initiated by the dropwise addition of a concentrated PEG-SH aqueous solution under vigorous stirring to achieve a final concentration of 1 mg/mL. The mixture was left to react overnight. The next day, the colloidal suspension was centrifuged 3 more times to clean the leftover PEG-SH. After the last centrifugation step the precipitated nanoparticles were resuspended, into a 60:40 $H_2O$:EtOH mixture containing [CTAC] = 50 μM

### *3.4. Particle concentration adjustment.*

Templated self-assembly relies on the preparation of highly concentrated colloidal suspension in order to control the organization of the particle with a minimum amount of solvent.

#### *3.4.1 Concentration of gold colloids*

Exploiting gold interband transition, it is possible to estimate [$Au^0$] evaluating the $Abs_{400nm}$ by UV-vis-NIR spectroscopy. Specifically, $Abs_{400nm}$ = 1.2 equal to a [$Au^0$] of 0.5 mM.[3] In order to prepare the colloids for self-assembly, we brought all suspensions to a [$Au^0$] = 50 mM.

*3.4.2. Concentration of silver colloids*

The interband transition of silver falls too deep in the UV portion of the spectra to be easily measured by standard UV-vis spectroscopy. Consequently, the concentration of the silver colloids was estimated by measuring the extinction maxima of their LSPR, and adjusting the concentration trough trial and error. For the used colloid (45 ± 4 nm) optimal self-assembly was achieved at an extinction maxima equal to 487.0 (all colloids were diluted 1000 times before spectroscopic analysis).

## 4. Preparation of the patterned stamps

### *4.1. Preparation of the original master structures*

The original silicon masters were purchased from EULITHA (Switzerland), consisting of arrays of holes in silicon substrates with lattices of 500 nanometers in 0.7×0.7 $cm^2$ areas, a hole diameter of 277 nm and a hole depth of 390 nm. The masters were silanized with an anti-sticking layer of 1H,1H,2H,2H- perfluorooctyl-trichlorosilane to prevent the adhesion of silicones and photoresists during replication. The silanization took place through chemical vapor deposition, leaving the masters for 20 minutes under vacuum in a desiccator together with 2µl of the perfluorooctyl-trichlorosilane. The substrates were rinsed with acetone and heated to 120 ºC for 20 min to remove unreacted silane.

### *4.2. Preparation of the working masters*

Intermediate masters are negative replicas of the original masters, used to obtain a final replica in PDMS of the original hole arrays. These negative hard molds were prepared using UV-nanoimprinting. Specifically, a drop of Ormostamp, a photosensitive resist, is placed directly on top of the silanized silicon master. Then, a cleaned glass slide is treated with 10 min of UV-ozone and then gently pressed on top making sure no bubbles remained trapped between the slide and the Ormostamp. The photoresist is then cross-linked and harden by UV lamp for 10 minutes. To demold the Ormostamp working master, we place the substrates on a hot plate, performing a temperature ramp of 60, 120, and 180°C, maintaining the temperature for 10 min at each step. The difference in thermal expansion between photoresist and silicon induces the detachment of the Ormostamp mold. Finally, the working masters are silanized as explained before for the original masters. However, isopropanol is used instead of acetone, to avoid the detachment of the photoresist layer from the glass slide.

### *4.3. Preparation of the PDMS Molds*

Soft PDMS molds were used for all patterns. They were prepared by standard PDMS protocols. A 10:1 mixture of the monomer and curing agent are mixed vigorously and then centrifuged at 3200 rpm for 5 min to eliminate bubbles (alternatively the mixture is degassed for 1 hour). The mixture is then gently poured onto the Ormostamp master and left degassing under vacuum for 20-30 minutes. Next, the polymer is cured at 100°C for another hour. Once the PDMS is cured, it is manually demolded from the master.

## 5. Preparation of the plasmonic arrays

### *5.1. Preparation of the substrates for the assembly*

Borosilicate microscope coverslips were cut into pieces of roughly 10×10 $mm^2$ to be used as substrates. Before proceeding with the assembly the glasses were cleaned by a sonication in acetone, Hellmanex III 2% solution and isopropanol for 5 min each, and lastly a hydrophilization with NaOH 10% for 10 min, with Milli-Q water rinsing in between.

***5.2. Preparation of the colloidal mixtures (pre-assembly modifications)***

All the prepared colloids were prepared at the correct concentration for the assembly and with the same PEG-SH coating.

*5.2.1. Co-Assembly of different size colloids*

The different gold colloids were simply mixed using the desired volume ratio. Specifically, the final mixtures yielded a 1:1 and a 1:3 volume ratio between 25 and 100 nm colloids. It is important to keep in mind that due to the significant volume difference between 25 and 100 nm colloids (64 times), a volume ratio of 1:3 still implies a higher number of 25 nm colloids.

*5.2.2. Co-Assembly of gold and silver colloids*

Since silver and gold particle concentrations were optimised through different methods, the two colloids couldn't simply be mixed using the desired volume ratio. To overcome this problem, and to have control over particles proportion, we first analysed the gold to silver ratio of a 1:1 mixture through EDX, that was used as a base to find the correct volume ratio. After optimisation, the mixtures yielded a 1:8.5 and a 1.7:1 volume ratio between Au and Ag colloids, which corresponded to a fraction of gold nanoparticles ($\chi_{Au}$) of 0.75, and 0.35, respectively (see Figure S2).

*5.3. Template-assisted colloidal assembly*

1 μL drop of the desired nanoparticle suspension is deposited on top of the cleaned coverslips. Immediately, the drop is covered with the PDMS mold, and the solvent is left to evaporate overnight. The next day the mold is removed, leaving the assembly on the coverslip substrates. The PDMS molds can be reused after cleaning with adhesive tape, followed by rinsing with ethanol and water.

*5.4. RTA temperature treatment*

Right after demolding, the samples were annealed using a rapid thermal annealing system, under a nitrogen atmosphere and a mild vacuum ($10^{-2}$ torr). A heating ramp of 20 ºC/s, and a dwelling time of 60 min were applied to all samples, with a final annealing temperature of either 300 or 450 ºC.

*5.5. Index matching*

In order to exchange the air superstrate with PDMS (n ~1.45), a soft PDMS 10:1 mixture is prepared as explain above (see section 4.3.). After centrifugation, 1 drop of the mixture is placed on top of the plasmonic array. Immediately, a clean glass coverslip (20 × 20 mm2) is gently placed face down on top of the drop, evenly spreading the PDMS over the entire surface. The sample is left undisturbed at room temperature until the PDMS is completely cured.

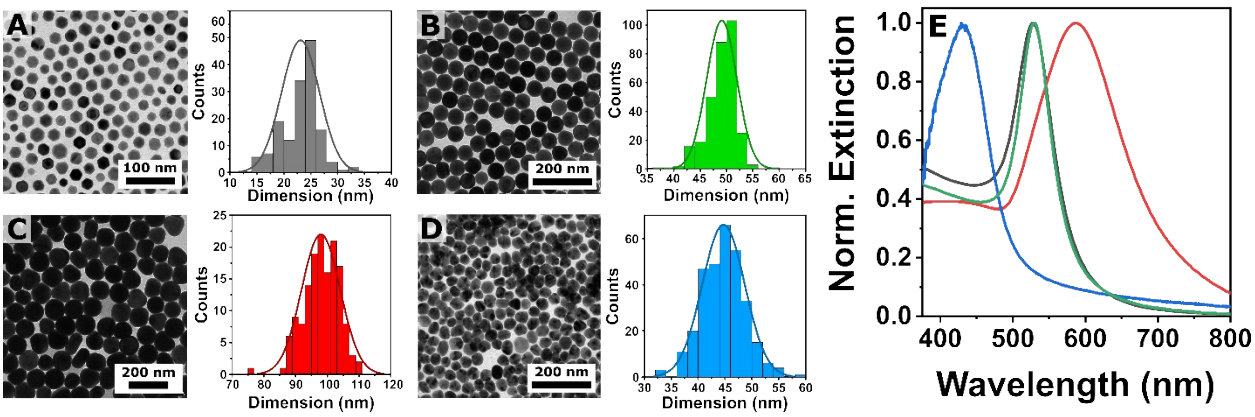


**Figure S1:** Transmission electron microscopy (**left, A-D**), and relative size distribution histograms (**right, A-D**) and UV-vis (**E**) characterization of the colloids used: 24 ± 3 (**A, black line**), 49 ± 3 (**B, gren line**), and 96 ± 9 nm gold nanoparticles (**C, blue line**), and 45 ± 4 nm silver nanoparticles (**D, red line**).

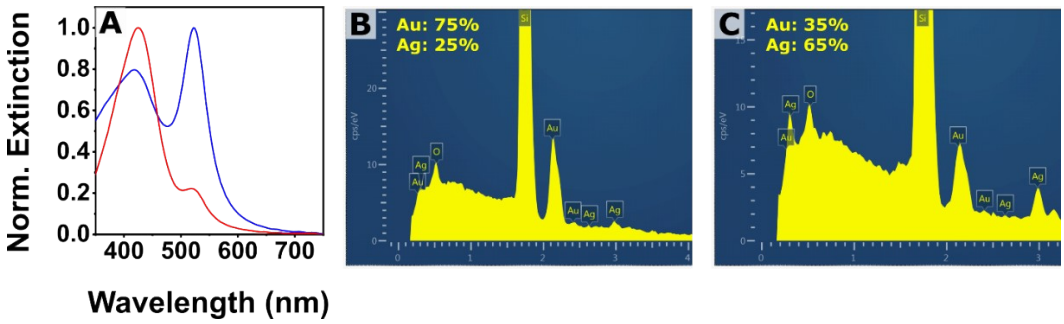


**Figure S2:** UV-vis (A) and energy dispersive X-ray spectroscopy (B, C) of the mixtures of gold and silver colloids: $\chi_{Au}$ = 0.75 (**B, blue line**), and $\chi_{Au}$ = 0.35(**C, red line**).

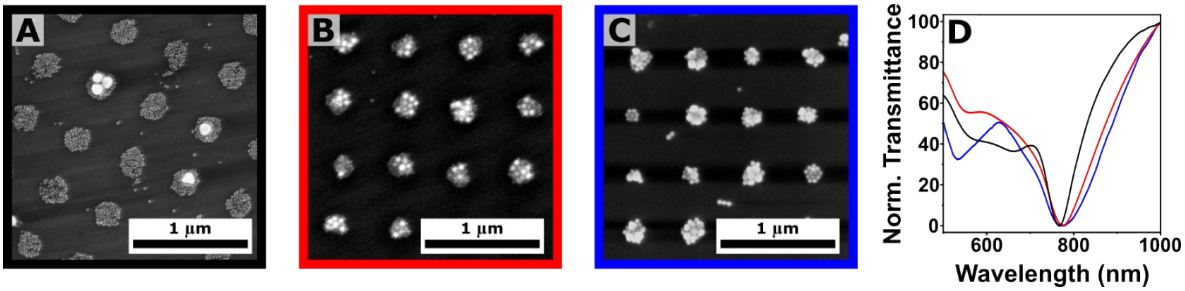


**Figure S3: A-C:** Scanning electron microscopy analysis of plasmonic arrays (Λ = 500 nm) fabricated by co-assembling of an equal ratio of gold nanoparticles of: 25:100 (**A**), 25:50 (**B**), and 50:100 nm (**C**). **D:** corresponding normalized transmittance spectra with the same color code: 25:100 (**black**), 25:50 (**red**), and 50:100 nm (**blue**).

**Sequential deposition approach.**

In this approach a low-diffusivity bigger colloid is pre-loaded into a PDMS stamp. This is obtained by treating the PDMS mold by a light UV-Ozone treatment (25 min) to make the surface hydrophilic, increasing its affinity for the colloid that are prepared in aqueous environment. The affinity contrast of the colloid is amplified by performing the templated self-assembly over a highly hydrophobic surface (in our case a silanized glass). Upon demolding, the colloid will remain inside the mold, choosing the most hydrophilic surface (**Figure S3A, B**). In the following step, the pre-loaded mold is used for the standard templated self-assembly procedure of a high-diffusivity smaller colloid, yielding a mixed plasmonic array of the two components. The sequential method contrasts the formation of clusters consisting solely of the smaller colloid. This was teste using 96 ± 9 and 24 ± 3 nm gold nanoparticles.

The SEM analysis (**Figure S3C, D**) confirms that a higher percentage of the clusters are occupied by at least one large nanoparticle. However, the formation of empty rings composed of smaller colloids is also observed, suggesting that some of the 100 nm nanoparticles do not transfer from the PDMS template during the second assembly. This can potentially be improved by a weaker activation of the PDMS mold, or the use of a chemical modification instead of an UV-Ozone treatment. The transmittance profile of the samples fabricated by sequential deposition confirms the formation of a lattice response, with a relatively sharp signal at 780 nm (**Figure S3E**).

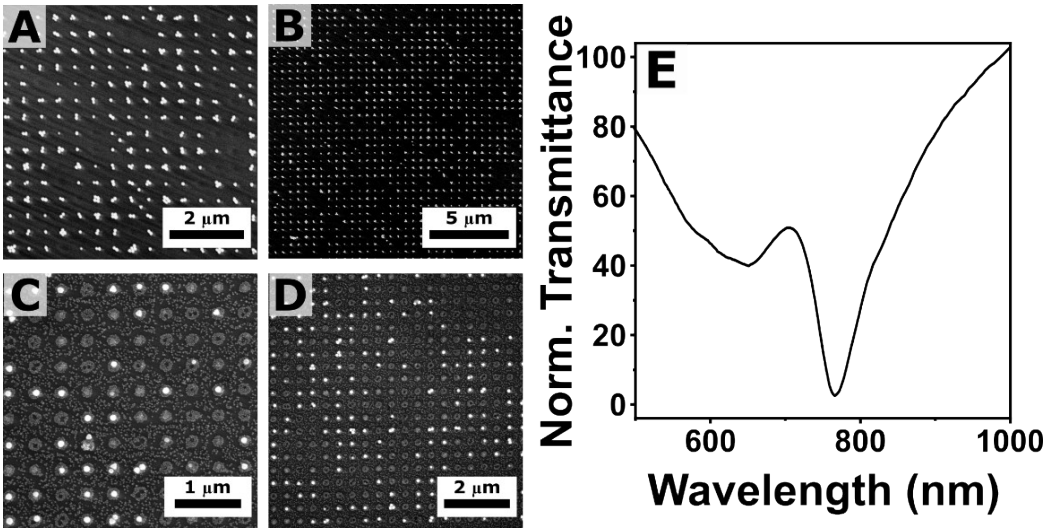


**Figure S4. A-D:** Scanning electron microscopy images of the PDMS mold pre-loaded with 96 ± 9 nm gold nanoparticles (**A, B**), and the final assembly obtained after sequential deposition with 24 ± 3 nm nanoparticles (**C, D**). **E:** Normalized transmission spectra of the final product.

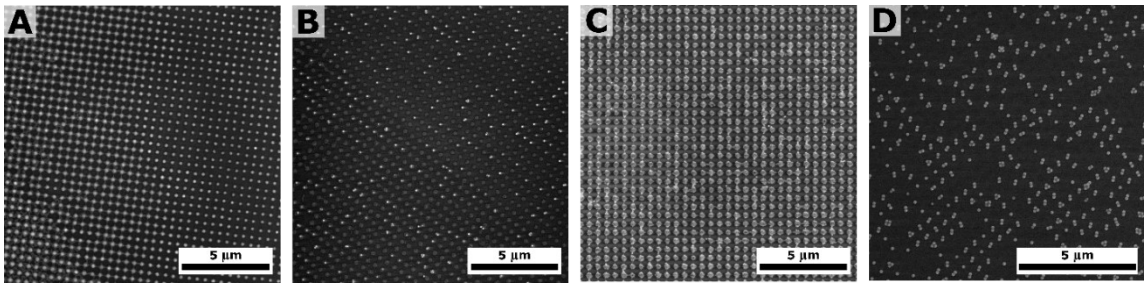


**Figure S5. A-D:** Scanning electron microscopy images of plasmonic arrays (pitch = 500 nm) prepared using 24 ± 3 and 96 ± 9 nm gold nanoparticles with different proportions: 1:0 (only small colloid, **A**),1:1 (**B**), 1:3 (**C**), and 0:1 (only big colloid, **D**).

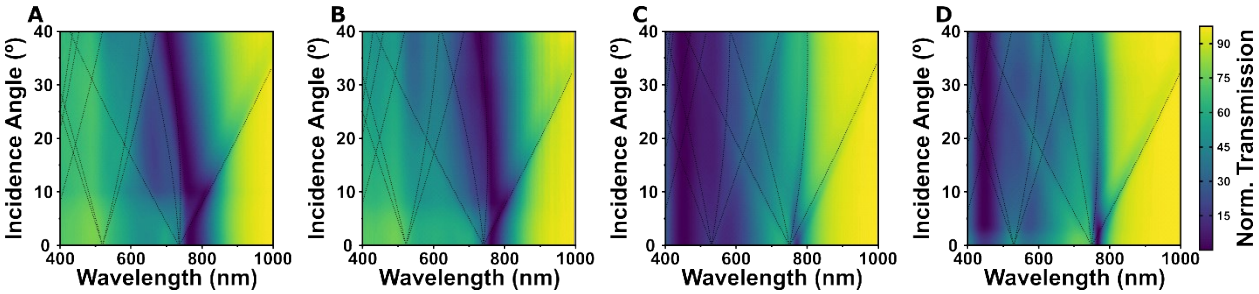


**Figure S6.** **A-E**: Normalized extinction contour plots as a function of the illumination angle of plasmonic arrays prepared with a pitch of 500 nm using a mixture of gold and silver nanoparticles with fraction of the gold colloid of: $\chi_{Au}$ = 1 (**A**), 0.75 (**B**), 0.35 (**C**), and 0 (**D**). The black dashed lines are analytical calculations of the Wood´s anomalies angular dependence taking into consideration the polarization of the incident field respect to the azimuthal angle of the sample that was used for the measurements.[1]

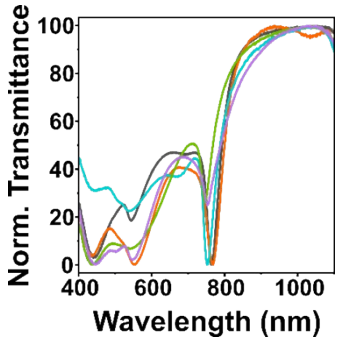


**Figure S7:** Sample-to-sample variation in the position of the lattice plasmon resonance of a plasmonic arrays prepared using silver nanoparticles. All the other samples show a similar variation.

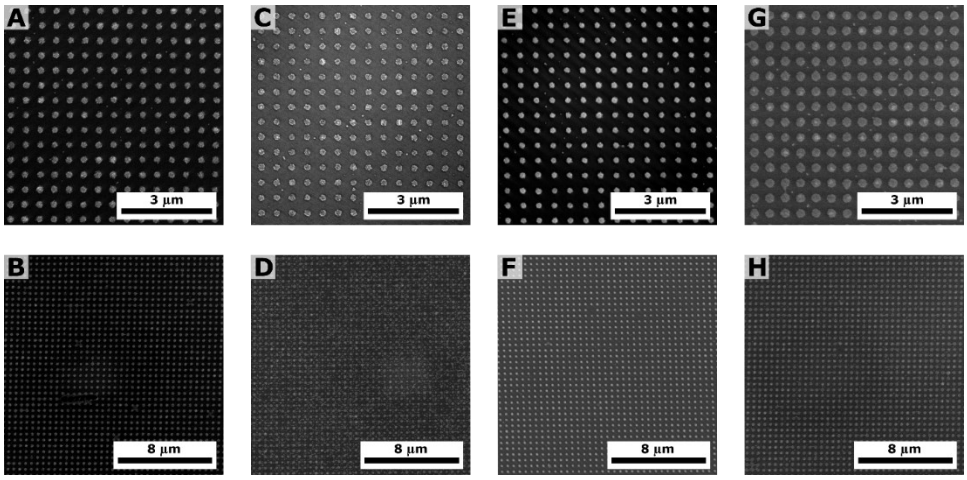


**Figure S8.** Scanning electron microscopy images of plasmonic arrays with a pitch of 500 nm, prepared using a mixture of gold and silver nanoparticles with fraction of the gold colloid of: $\chi_{Au}$ = 1 (**A, B**), 0.75 (**C, D**), 0.35 (**E, F**), and 0 (**G, H**).

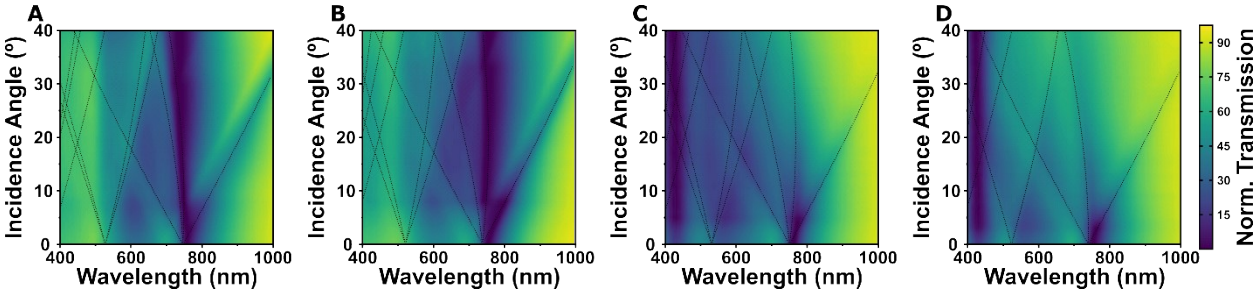


**Figure S9. A-E**: Normalized extinction contour plots as a function of the illumination angle of plasmonic arrays with a pitch of 500 nm after thermal annealing at 300 °C, prepared using a mixture of gold and silver nanoparticles with fraction of the gold colloid of: $\chi_{Au}$ = 1 (**A**), 0.75 (**B**), 0.35 (**C**), and 0 (**D**). The black dashed lines are analytical calculations of the Wood´s anomalies angular dependence taking into consideration the polarization of the incident field respect to the azimuthal angle of the sample that was used for the measurements.

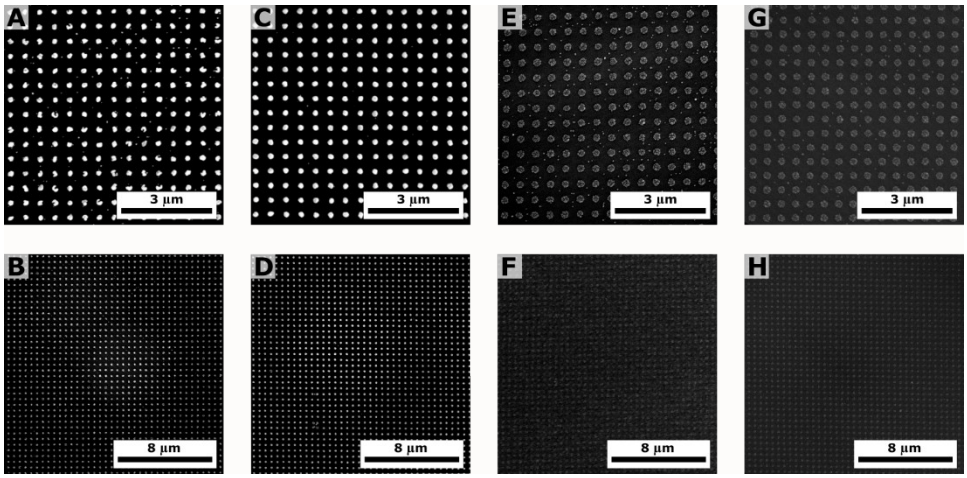


**Figure S10.** Scanning electron microscopy images of plasmonic arrays with a pitch of 500 nm after thermal annealing at 300 °C, prepared using a mixture of gold and silver nanoparticles with fraction of the gold colloid of: $\chi_{Au}$ = 1 (**A, B**), 0.75 (**C, D**), 0.35 (**E, F**), and 0 (**G, H**).

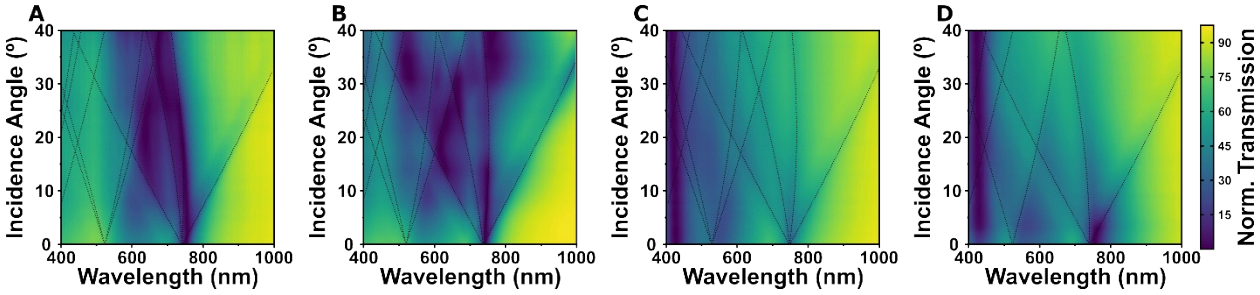


**Figure S11. A-E**: Normalized extinction contour plots as a function of the illumination angle of plasmonic arrays with a pitch of 500 nm after thermal annealing at 450 °C, prepared using a mixture of gold and silver nanoparticles with fraction of the gold colloid of: $\chi_{Au}$ = 1 (**A**), 0.75 (**B**), 0.35 (**C**), and 0 (**D**). The black dashed lines are analytical calculations of the Wood´s anomalies angular dependence taking into consideration the polarization of the incident field respect to the azimuthal angle of the sample that was used for the measurements.

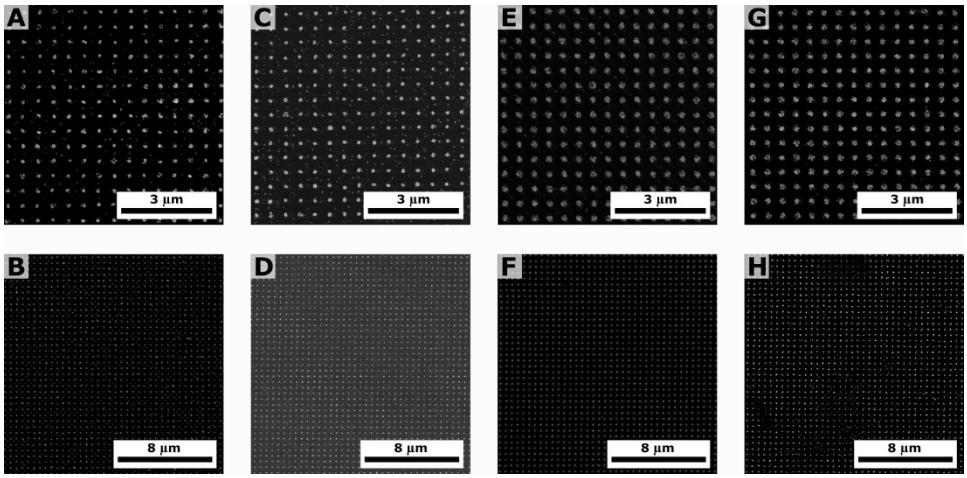


**Figure S12.** Scanning electron microscopy images of plasmonic arrays with a pitch of 500 nm after thermal annealing at 450 °C, prepared using a mixture of gold and silver nanoparticles with fraction of the gold colloid of: $\chi_{Au}$ = 1 (**A, B**), 0.75 (**C, D**), 0.35 (**E, F**), and 0 (**G, H**).

**Quantitative analysis of volume reduction during thermal annealing.**

Table S2 reports the average diameters of the clusters composing the plasmonic arrays at room temperature and after thermal annealing at 300 and 400 °C.

**Table S2. Average clusters diameter for different compositions and annealing temperature.**

| Annealing Temperature | φAu = 1 | φAu = 0.75 | φAu = 0.35 | φAu = 0 |
|---|---|---|---|---|
| **Room Temperature** | 250 ± 20 | 200 ± 20 | 200 ± 20 | 240 ± 20 |
| **300 °C** | 160 ± 20 | 150 ± 20 | 170 ± 20 | 220 ± 20 |
| **450 °C** | 170 ± 10 | 130 ± 10 | 140 ± 20 | 170 ± 20 |

The percentage by which the cluster size is reduced is plotted in Figure S13. Increasing the fraction of silver decreases the contraction of the clusters after annealing at 300 °C, indicating a lower degree of coalescence between neighbor particles composing the clusters. Nonetheless, this separation is drastically reduced when the annealing temperature is increased to 450°C.

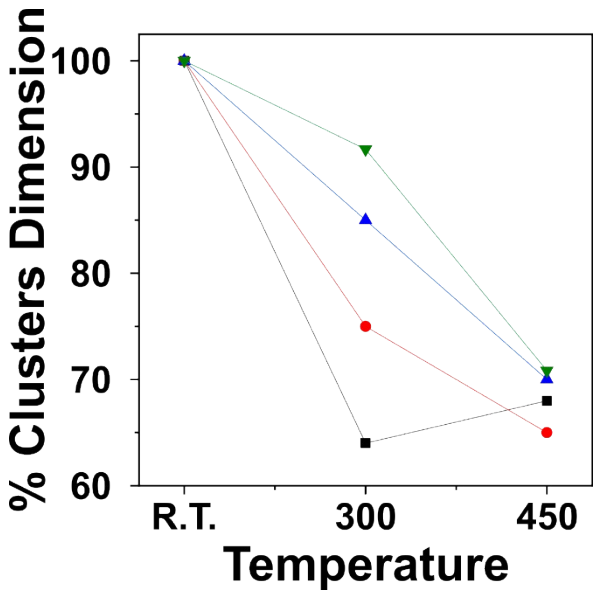


**Figure S13.** Relative cluster size reduction measure by scanning electron microscopy as a function of annealing temperature (R.T.: room temperature). The composition of the samples is ϕAu = 1 (**black circles**), 0.75 (**red squares**), 0.35 (**blue triangles**), 0 (**green triangles**).