Plasmonic Macroscopic Structures: from linear assemblies to 3D structured super-crystals

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Abstract. Confinement controlled drying in combination with spin coating is presented as a novel fast and inexpensive approach to produce organized arrays of plasmonic nanoparticles. The presented method is quite versatile allowing the production of many different structures, from simple linear assemblies with a defined periodicity, width, and high to complex 3D microstructured super-crystals with defined morphology and dimensions which, can be produced either as continuous or as isolated assemblies. Moreover, this methodology is completely up-scalable allowing micro-structuration over large areas in the macro scale. Furthermore, their plasmonic collective behavior can be tuned by controlling the size and shape of the nanoparticles and the structures independently. Obtained organized structures have been proved to be very effective for SERS sensing showing very good reproducibility among big areas.

1. Introduction

Great control over the chemical synthesis of plasmonic nanoparticles and thus, their optical response has been achieved during the last decade. However, for many technological applications,1-8 their controlled organization over extended areas and the control of their collective behavior is crucial. Long-ranged ordered macroscale materials using metal nanoparticles (NPs) as building blocks5, 9 are very attractive because they preserve their nanoscale properties, meanwhile new properties arise due to the interaction between their individual constituents.10-12 Unfortunately, the fabrication of such structures is not trivial due to the small size of the building blocks, and was mostly restricted to expensive and time-consuming lithographic techniques.13-14 Therefore, bottom-up approaches based on the self-assembly of colloidal particles12, 15-16 known as super crystals are in the focus of many researches as a promising alternative.6, 8, 17-18

In this work, we report novel methods to produce arrays of nanoparticles, either as continuous or as isolated super-crystals. These structures are made of plasmonic nanoparticles in a new fast and inexpensive approach based on the drying confinement of colloidal particles combined with spin coating. Allowing the production of periodical arrays (linear assemblies and super-crystals) of organized nanoparticles over extended areas. Furthermore, this technic allows the production of 3D complex morphologies that can be either connected between them or discontinuous. Additionally, the plasmonic properties of these structures were exploited for the generation of ultrasensitive and ultrafast sensors based on surface-enhanced Raman scattering (SERS) spectroscopy.12
2. Results and discussion

One of the crucial points for the successful generation of densely packed and well-ordered three-dimensional super-crystals is the quality of the nanoparticles. They have to be highly pure and monodisperse. Moreover, since a high quantity of NPs are required to form the crystals, they must be stable at very high concentrations meanwhile having low surfactant concentrations which will disturb the crystal structure.

2.1. Assembly process steps

The assembly process can be divided in two main steps: 1) Template production; 2) Nanoparticles confinement [5, 9, 12].

2.1.1. Template production. Two types of templates were produced either to make linear arrays or super crystals. In both cases, the elastomer polydimethylsiloxane (PDMS) was chosen because their surface properties can be easily changed from hydrophobic to hydrophilic by plasma treatment. Wrinkled templates: The cross-linked PDMS elastomer was cut into stripes. These stripes were stretched uniaxially in a custom-made apparatus to a strain of 125% of their initial length. The stretched substrate was oxidized a concrete time in an oxygen plasma. After that, the sample was relaxed and wrinkles with a wanted spacing were obtained (controlling the plasma exposure time, the period of the wrinkles can be tuned). The hydrophilic wrinkled substrates were used directly after plasma treatment (Figure 1 shows a schematic representation of the process). Templates with complex morphologies: Replica molding was used to topographically duplicate Si-masters with various topographies. Two replica molding steps were performed to obtain the negative and positive replicas of the Si-masters. The 1st replicas (negative), were prepared by casting PDMS on the Si-masters and curing them. To produce the exact same morphologies of the masters (positive replicas), a 2nd replica molding step was performed using the negative replicas as templates. However, to avoid that the 1st PDMS replica cross-link and merge irreversibly with the new PDMS casted, the 1st PDMS replica needs to be silanized before use.

![Figure 1. Schematic representation of the wrinkling template process and the NPs assembly (A). Two representative SEM images of Au NPs assembled into periodic lines (B).](image-url)

2.1.2. Nanoparticles confinement and assembly. Two different but similar approaches were used to organize the NPs. I) On wrinkled PDMS: To assemble the NPs into lines, first a highly concentrated drop of the NPs solution was spin coated onto the wrinkled PDMS to confine the particles on the groves. After that, to transfer the particles to a substrate, a drop of water was placed on a glass slide and the wrinkled PDMS was placed on top of the wet surface and left undisturbed until water evaporates. Next, the PDMS was removed leaving the particles organized on the substrate. Remarkably, this method leads to a highly homogeneous patterning over cm². Figure 1 shows a schematic representation of the wrinkling process and particle assembly together with some representative SEM images. II) On PDMS replicas with complex morphologies: In order to confine the NPs wetting contrast in a defined region was used. To do that, a PDMS piece with a hole in the middle was placed on the structured surface of the PDMS replica and treated with O₂ plasma. After removing the PDMS on top a hydrophilic region on the hydrophobic PDMS surface was created. Because of the wetting contrast, the NPs droplet remains
confined in the hydrophilic region without spreading. After that, the NPs are allowed to sediment. A humidity chamber was used to avoid solvent evaporation. After sedimentation, continuous super crystals can be obtained removing the system from the humidity chamber and letting it dry. If discrete crystals are desired, the solvent containing surfactant is removed via spin-coating and two additional cleaning steps are performed using water to remove the excess of NPs on top. The crystals were then peeled out with adhesive tape and transfer to the desired surface (see Figure 2).

![Figure 2](image)

**Figure 2.** Schematic representation of the NPs assembly process using PDMS replicas with complex morphologies (A). Two representative SEM images of continuous (up) and discrete (down) crystals made of Au NPs (B).

### 2.2. SERS enhancing properties

The colloidal crystals were cleaned with O₂ plasma to remove all residual organics from the metallic surfaces. A Raman active molecule as Benzenethiol (BT) was selected as the Raman probe and deposited on the crystals through gas phase. After characterizing crystals with different morphologies, two major features were found: I) All 3D microstructured crystals exhibit larger intensities than the non-structured ones. II) The absolute intensity increases as the wide of the structures increase independently of the crystal geometry, and the enhancements are similar for similar crystal wide (see Figure 3).

![Figure 3](image)

**Figure 3.** Benzenethiol SERS spectra (left). Comparison of the absolute SERS intensity of 3D super crystals with different morphologies. Showing an increase as the wide (x) of the structures increases for all crystal geometries. Similar enhancements were found for similar wide (x) for different morphologies.

### 3. Conclusions

In summary, we have developed an innovative cheap, easy, and fast process to produce homogeneous macroscale assemblies of NPs. This technique allows the production of linear assemblies and microstructured super crystals with complex geometries and 3D features over very large areas using plasmonic nanoparticles as building blocks. Permitting also the production of either continuous or discrete structures. The proposed process, the plasma drop confinement is very convenient and innovative, because of its simplicity and versatility for macroscopic areas. The obtained plasmonic super crystals also show a very high and uniform SERS enhancement.
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