# Plasmonic coupling induced by growing processes of metal nanoparticles in wrinkled structures and driven by mechanical strain applied to a polydimethylsiloxane template

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**Abstract**—We report the mechanical control of plasmonic coupling between gold nanoparticles (GNPs) coated onto a large area wrinkled surface of an elastomeric template. Self-assembly and bottom-up procedures, were used to fabricate the sample and to increase the size of GNPs by exploiting the reduction of $HAuCl_4$ with hydroxylamine. The elastic properties of the template, the increase of the nanostructure size joined with a particular grating configuration of the surface have been exploited to trigger and handle the coupling processes between the nanoparticles.

The property of noble metal nanostructures to generate local electric fields, local surface plasmon resonance (LSPR), produced by the coherent oscillation of the conduction electrons plasma driven by an external electrical field [1-3], is one of the most powerful tools in nanophotonic applications. Surface-enhanced Raman spectroscopy (SERS) [4-6], thermoplasmonics [7-9] as a new method to combat cancer disease [10], optical metamaterials [11-13] and sensing devices [14-16] are some of the fields of research where the plasmonic properties of nanoparticles are used. In these applications the coupling between the plasmonic fields, plays an important role [17-20]. The process is closely related to the separation between the nanostructures, which must be smaller than the diameter of a single particle of the system [17]. To decrease this distance, top-down [22-23] and bottom-up [13, 19, 24] techniques have been applied.

In our work, we used a self-assembly procedure to coat spherical gold-nanoparticles onto an elastomeric wrinkled surface of Polydimethylsiloxane (PDMS) [25]. The wrinkle period can be tuned by the exposure time, by the power and by the pressure selected during the air plasma treatment applied to the pre-strained template [25-27]. The wrinkle structure, which is orthogonal to the stretching direction, insures a higher density of coated nanoparticles in the concave zone of the grating with respect to the convex one, which is due to a higher charge density in the former region. Moreover, we submitted gold nanoparticles to a nanochemistry procedure of growing [28] to increase their size and, consequently, to reduce their separation. Then, by exploiting the properties of the elastic template that is contracted transversally to the direction of stretching, it was possible to further decrease the separation between GNPs, as already shown in our previous work [19]. Therefore, by increasing the size of GNPs with several cycles of growth and by applying mechanical strain, we were able to reduce the separation between nanoparticles and to realize a controlled coupling. The sample at rest and under stretching was characterized with UV-VIS spectroscopy. The extinction spectra have been acquired with the beam probe polarized longitudinally (p-pol) and transversally (s-pol) with respect to the direction of stretching. In Figs. 1a-b we show the spectra acquired from the sample before the growing processes (Fig. 1a), and after the 5$^{th}$ cycle of growth (Fig. 1 b) with the s-polarized beam probe.

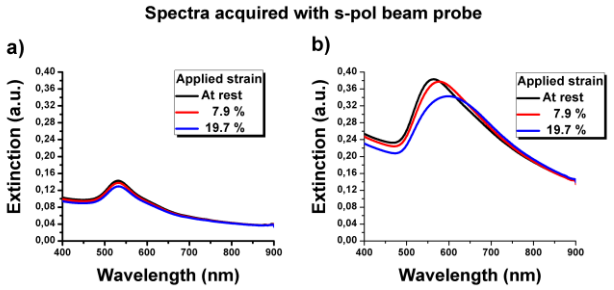


Fig. 1. a) UV-VIS spectra acquired with a sample at rest and under stretching: the GNPs are not grown, the plasmon resonance is peaked at 532nm, and there is no shift between spectra acquired at rest (black curve) and under the maximum applied strain (blue curve). b) UV-VIS spectra acquired with sample at rest and under stretching: the GNPs are submitted to 5 cycles of growth, the plasmon resonance at rest is peaked at 564nm (black curve), while at 19.7% of stretching (blue curve), the peak is at 598nm with a red-shift of 34nm.

In Figures 2a-b we show the spectra acquired with the p-polarized configuration. The two series of spectra (Figures 1b and 2b), for the sample after the 5$^{th}$ cycle of growth, acquired with the beam probe polarized

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transversally and longitudinally with respect the stretching direction, respectively, show a different red-shift related to different degree of plasmonic coupling. This is due to close packing arrangement of GNPs in the concave zone of the wrinkled structures of the PDMS template. When we increase the stretching, the period of this grating begins to enlarge in the direction of applied strain while transversally there is a shrinking. This latter behaviour of the template enhances the close packing between the nanoparticles, while in the longitudinal direction the process is less pronounced.

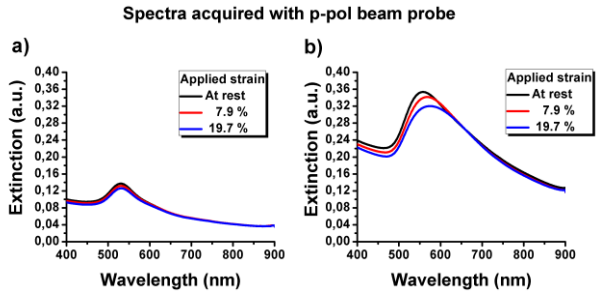


Fig. 2. a) UV-VIS spectra acquired with a sample at rest and under stretching: the GNPs are not grown, the plasmon resonance is peaked at 530nm, there is no shift between spectra acquired at rest (black curve) and under the maximum applied strain (blue curve); b) UV-VIS spectra acquired with a sample at rest and under stretching: the GNPs are submitted to 5 cycles of growth, the plasmon resonance at rest is peaked at 558.5nm (black curve), while at 19.7% of stretching (blue curve), the peak is at 575nm with a red-shift of 16.5nm.

In Figure 3 we show the morphology of the surface as measured by AFM. Figures 4 and 5 reveal a line profile and a tri-dimensional view of the surface, as extracted from Figure 3. As seen in Figure 4, the period of the wrinkled structures is around 200nm. The morphological analysis shows that the random coating of GNPs follows the wrinkled morphology of the surface.

In this work we showed that by using bottom-up and self-assembling procedures, we could fabricate samples with a random distribution and high concentration of GNPs that follow the wrinkled configuration of the surface of an elastomeric template. By the synergy between nanochemistry, i.e. reduction processes that increase the size of GNPs, and the elastic properties of a template, we can control and manage the coupling processes between the plasmonic fields around the nanoparticles. Moreover, by applying mechanical strain to an amorphous elastomeric plasmonic device, it is possible to handle the plasmonic fields at the nanoscale.

PDMS was acquired from DownCorning®. The elastomeric and curing agent components were mixed in a ratio 10:1. The liquid mixture was first degassed and then cured at 80°C for 45 min. Afterwards, a stripe of PDMS, stretched by 29.76%, was submitted to air plasma treatment under a pressure of 165 mTorr and a power of 7.2 Watt, for an exposure time of 8 min. Then the stripe was relaxed and a shorter piece (24mm × 16.6mm × 1.2mm) was cut. This template was then dipped in a mixture of Milli-Q water and 3% of 3-aminopropyltriethoxysilane (from Sigma Aldrich) for 30 min. After removing, the functionalized template was well rinsed and dried, and then dipped in a colloidal solution of GNPS for 2h 20 min. The GNPs were synthesized with the Turkevich method as described in our previous paper [19]. The nanochemistry growing process, utilized to increase the size of nanoparticles, is described in the Ref. [19, 28].

The UV-VIS characterization procedure with a custom homemade experimental apparatus is also described in our previous work [19].

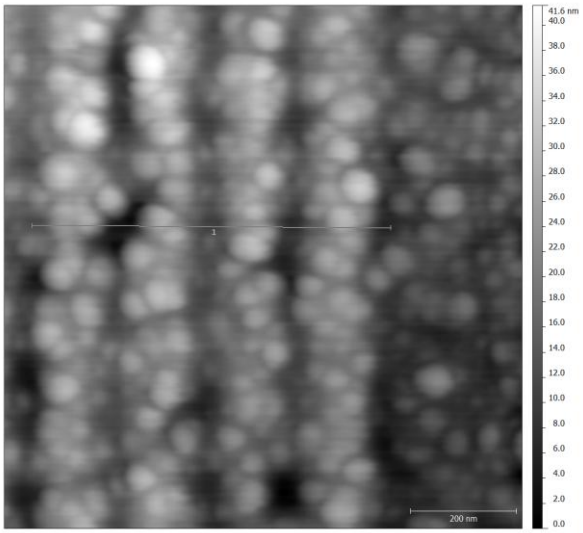

Fig. 3. AFM image of the surface of a sample acquired in tapping mode with an Asylum microscope. The tip has a radius of 9nm.

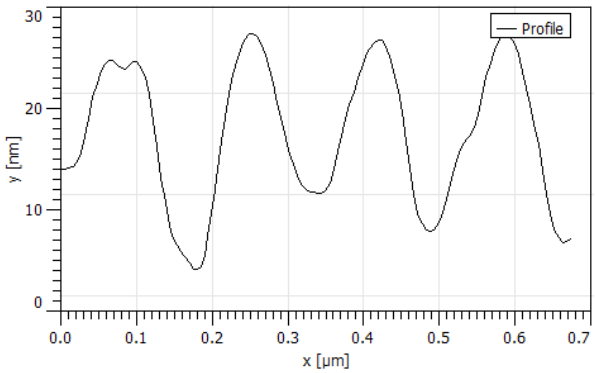


Fig. 4. The graph shows the profile extracted from Figure 3.

 

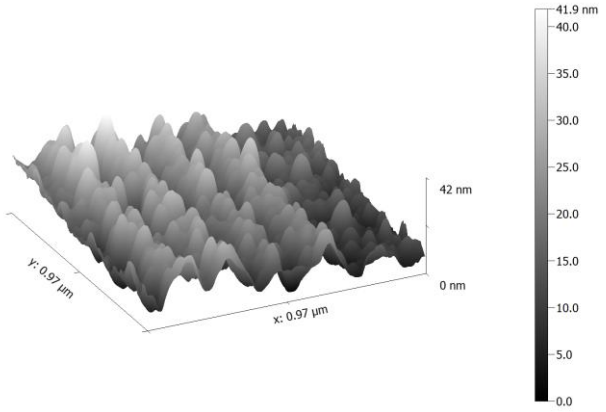


Fig. 5. Tri-dimensional view of the image shown in Figure 3.

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