

Tunable Plasmonics by Self-Assembled Stretchable Superlattices on Macroscopic Scale

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Abstract — We present a process to create flexible 2D superlattices of nanoparticles, self-assembled into discrete and long-range ordered clusters. The process is readily scalable and grants access to mechano-responsive nanostructures on square centimeter areas. The elastic properties of the support allow for post-assembly tailoring of the lattice periodicity. The corresponding change in collective lattice coupling results in a gradual shift of the extinction maximum upon mechanical strain. Our results give a proof-of-principle for tunable plasmonics by mechano-responsive nanostructures.

Keywords – lattice plasmons, mechano-plasmonics, self-assembly, gold nanoparticles, enhanced spectroscopy

I. INTRODUCTION

Plasmonic substrates are powerful tools for enhanced spectroscopy, such as Raman spectroscopy or localized surface plasmon resonance (LSPR) sensing [1]. However, high signal intensities demand matching of the plasmon resonance with the excitation wavelength [2]. Periodical arrangements of nanoparticles (NPs), so-called superlattices, feature intensive lattice plasmons because of long-range ordered domains. Such lattice plasmons arise from an interference between the LSPR of the individual domains and an in-plane diffracted wave, the so-called Rayleigh anomaly. As a consequence, the optical response of superlattices shows high sensitivity on the lattice period [3]. Superlattices on flexible supports would grant access to tunable plasmonic. So far, the methods reported focus on the use of bulk gold nanostructures made by electron-beam lithography (EBL) [4]. EBL is inherently a slow and expensive method and not readily compatible with flexible substrates. We present here a fast and scalable process to create superlattices of NPs on a flexible substrate. The optical properties of such substrates upon mechanical strain will be discussed in detail and compared to reference substrates of defined periodicities.

II. RESULTS AND DISCUSSION

A. Fabrication Process

We use a templated self-assembly process to fabricate plasmonic substrates. This process is described in Fig. 1a [5]. A droplet of gold nanosphere dispersion (water, ethanol, surfactant, NPs@polyethyleneglycol) is cast on a glass slide or PDMS (polydimethylsiloxane) slab. This droplet is then confined between a nanostructured template, made of PDMS and the target substrate (Fig. 1a). The template is composed of an array of squared wells (Fig. 1b). Capillary forces guide the NPs into the holes of the template, yielding a superlattice of NPs after drying. The size of the domains can be controlled by the size/volume ratio of the template structure and the NP size [2,5,6]. Here, we use PDMS both as template mold as well as a soft flexible target substrate. For that purpose, the PDMS target surface needs to be functionalized with a thin layer of a

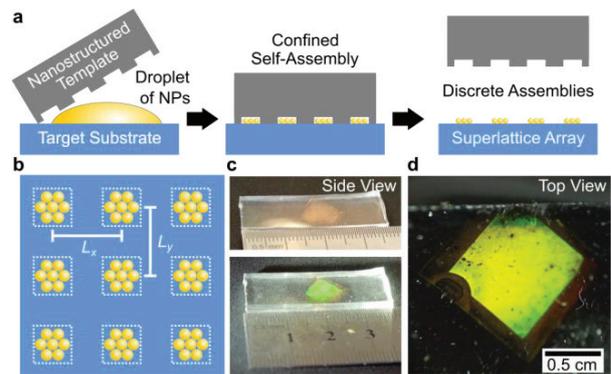


Fig. 1. Superlattice fabrication by template-assisted colloidal self-assembly: (a) Schematic depiction of the nanoscale confinement of NPs guided by capillary forces between a nanostructured template (top) and a flat target substrate (bottom); (b) Top-view schematic of the nanostructure design; (c,d) Photographs of a sample of an 8x8 mm² superlattice of periodically arranged clusters of gold NPs (diameter 65 nm) supported on a flexible substrate under different illumination angles with white light.

few nanometers of polyethyleneimine (PEI, branched, 25 kg/mol). PEI inhibits a cohesive contact between template and substrate and promotes the transfer of NPs from the mold to the substrate [6]. Fig. 1c shows the angle-dependent reflection of a superlattice illuminated with white light. The green color is caused by interaction of the white light with the periodical arrangements of NPs (Fig. 1d). Using EBL for nanostructuring of such an area of around 8x8 mm² would take several tens of hours.

B. Macroscopic Strain-Induced Lattice Deformations

Upon stretching, a gradual color shift from green (100%) to red (128% elongation) can be observed (Fig. 2a). This optical change in reflection can be explained by the change in periodicity of the nanosphere clusters. Fig. 2b depicts the deformation of the lattice induced by macroscopic strain. The effect of lattice variation was investigated by SEM imaging for a superlattice of 65 nm NPs of 500 nm period fabricated by the templated self-assembly process described in Part A (Fig. 2c). Elongated to 148%, the distances between the clusters are considerably augmented from 500 to 900 nm (Fig. 2d), however, after elongation, the clusters by themselves were found to remain close-packed. This robustness is an important point for keeping the plasmonic properties of the sample unperturbed. The robustness of assemblies is controlled by the balance of cohesive and adhesive interactions at the interface. Assemblies of similar NP sizes and surface chemistry were found to experience structural changes upon elongation to 130% [6].

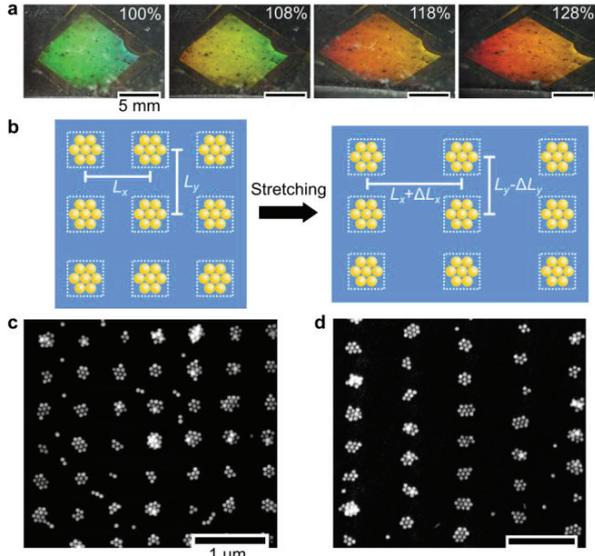


Fig. 2. Macroscopic strain-induced lattice deformations: (a) Gradual color change from green to red upon elongation under white light illumination. (b) Schematic depiction of the lattice deformation and SEM images in (c) unstretched and (d) stretched state.

As a reference experiment, we used nanostructured PDMS molds of 500 and 600 nm periods to fabricate superlattices of the corresponding periodicities. The extinction spectra of superlattices of 500 and 600 nm spacings are plotted in Fig. 3a. The main resonances are located at 750 and 900 nm, respectively. This redshift can be attributed to changes in far-field coupling because of the increased lattice spacing [2,3]. The main advantage of having a flexible substrate is that the lattice parameter of a substrate could be adjusted simply and reversibly by stretching, thus, allowing tuning of the plasmonic response. Consequently, the lattice plasmon of choice could be tailored without the need to fabricate the corresponding mold geometries.

C. Tunable Plasmonics

Fig. 3a shows the optical response of a superlattice of 500 nm in an unstretched state and at 108%, 118%, and 128% of elongation. Initially, the unstretched sample shows a plasmon resonance at around 790 nm, as expected for a sample of 500 nm period. Upon further elongation at approx. 115%, a redshift of the plasmon resonance starts to become apparent. The resonance continues to shift linearly toward the red (Fig. 3c). Precisely, the extinction maximum may be tuned from 795 (100%) to 971 nm (at 160%). At the same time, the high-energy signature below 700 nm seems to remain almost completely unperturbed. This spectral range is expected to be dominated by the ensemble-averaged optical properties of the individual clusters. If so, this would give further proof for the high structural robustness of the particle assembly - even upon high strain values.

In a next step, we correlate the lattice plasmon shift obtained by stretching with reference substrates fabricated using molds of corresponding lattice periodicities. Superlattices of 600 nm period support a lattice plasmon at 900 nm (Fig. 3a). To yield the same lattice plasmon, the flexible superlattice of initially 500 nm periodicity need to be stretched to approx. 120%, which is equivalent to a horizontal periodicity of 600 nm. This is in excellent agreement with the uniaxial deformation of a square lattice to a rectangular lattice. The overall optical change upon uniaxial deformation was

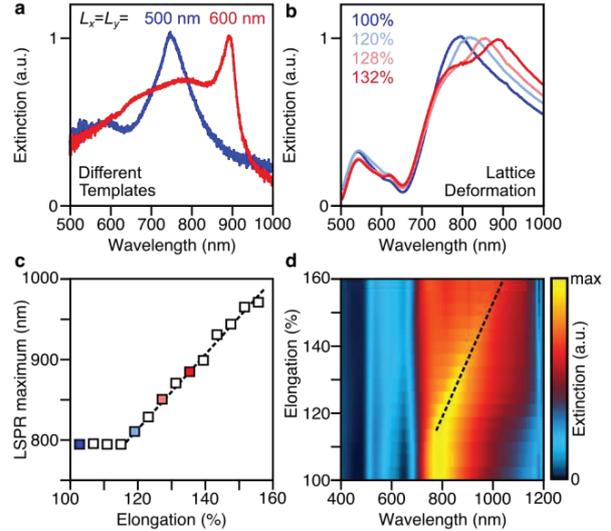


Fig. 3. Tunable plasmonics: (a) Normalized vis/NIR extinction spectra of samples made with molds of 500 and 600 nm. (b) Spectral evolution of the normalized extinction upon elongation. (c) Maximum extinction and (d) 2D map of the optical response of a 65 nm nanosphere cluster in a 500 nm lattice at different elongations.

monitored by a series of vis/NIR spectra (Fig. 3d). The non-normalized 2D map highlights the mechanoresponsive shift of the lattice plasmon (yellow) for the increasing periodicity.

III. CONCLUSION

We have presented a templated self-assembly process that allows the formation of plasmonic superlattices on a flexible support. These superlattices show increased robustness against stretching and the optical properties of the periodic substructure is maintained. Thanks to this robustness, the plasmonic response can be fine-tuned to the excitation wavelength of choice.

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