APPLIED PHYSICS LETTERS **100**, 073101 (2012)

Stretch-induced plasmonic anisotropy of self-assembled gold nanoparticle mats

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(Received 30 November 2011; accepted 20 January 2012; published online 13 February 2012)

Close-packed monolayers of 20 nm Au nanoparticles are self-assembled at hexane/water interfaces and transferred to elastic substrates. Stretching the resulting nanoparticle mats provides active and reversible tuning of their plasmonic properties, with a clear polarization dependance. Both uniaxial and biaxial strains induce strong blue shifts in the plasmonic resonances. This matches theoretical simulations and indicates that plasmonic coupling at nanometer scale distances is responsible for the observed spectral tuning. Such stretch-tunable metal nanoparticle mats can be exploited for the development of optical devices, such as flexible colour filters and molecular sensors. © *2012 American Institute of Physics*. [doi:10.1063/1.3683535]

Noble metal nanoparticles possess different optical properties to the bulk materials. Gold nanoparticles can exhibit vivid colours ranging from red to green according to their different shapes and sizes. This arises when light incident on a metal nanoparticle induces oscillations of the electrons, resulting in resonances known as localized surface plasmons.[1] Surface plasmons explicitly depend on nanostructure geometries, which can be significantly influenced by the proximity of other nanoparticles. Coupled nanoparticles at close distances show intense optical fields concentrated in the interparticle gaps and broad spectral tunability is achieved by simply varying interparticle spacing.[2] These aspects are crucial for many applications, such as molecular sensing and optical filtering.

Among a wide variety of coupled plasmonic nanosystems, self-assembled metal nanoparticle arrays[3–7] are able to provide a cheap and effective bottom-up approach for the mass fabrication of large-area plasmonic devices. Previous work indicates that plasmonic resonances on 2D nanoparticle arrays are indeed sensitively dependent on interparticle separation. However, the demonstrations reported to date have concentrated on measurements of floating nanoparticle arrays in a Langmuir-Blodgett trough[3,8] or have measured the isotropic optical response of nanoparticle (NP) arrays on elastomeric substrates.[6,7] For practical applications, reversible modulation of the optical properties of such nanoparticle arrays atop solid substrates as well as a thorough understanding of the modified array geometry and its associated plasmonic response are required.

Here we report self-assembly of 20 nm Au nanoparticle monolayers and the dynamic investigation of their opto-elastic properties. Monolayers of close-packed Au nanoparticles are first self-assembled at a hexane/water interface and then transferred to elastomeric substrates. Stretching the underlying elastic films tunes the interparticle spacing, thereby providing a tunable and reversible optical response. The films are stretched both uniaxially and biaxially (in both in-plane directions) and their induced spectral response found to be strongly polarization dependent on the strain orientation.

We employ a method similar to that reported by Park *et al.*[9] to synthesize and self-assemble Au nanoparticles. Large densities of aqueous near-spherical Au colloids (20 ± 3 nm) in solution are produced and used to form self-assembled Au nanoparticle monolayers by placing 500 μl Au nanoparticle solution in a teflon beaker with 330 μl of acetone. Adding 380 μl of 15 mM 1-dodecanethiol (DDT) in hexane to the top provides an immiscible organic/water interface. The beaker is covered and shaken vigorously for 1 min, then left to settle until the hexane evaporates.

During the process, the DDT molecules bind to the surface of Au nanoparticles, partially tuning the hydrophobicity (Fig. 1(a), top). For small nanoparticles ($<$10 nm), tuning the hydrophobicity results in nanoparticles moving into the hexane solution,[10] while larger nanoparticles ($\geq$20 nm, as used here) are trapped at the hexane/water interface,[9] decreasing the interfacial tension between the two liquids. This trapping leads to the formation of close-packed monolayers of Au nanoparticles (Fig. 1(a), middle; SEM in Fig. 1(b)) dependant on the amount of DDT used.[9] After the hexane evaporates, the self-assembled nanoparticle mat can then be picked up from the water and transferred to other substrates via horizontal lifting (Fig. 1(a), bottom). Elastomeric substrates of polydimethylsiloxane (PDMS) are used for stretchable optical measurement and conductive substrates (Si) used for SEM imaging (Fig. 1(b)).

The optical properties of close-packed nanoparticles are significantly different from those of either individual nanoparticles or continuous films. After forming monolayers, the nanoparticle mats have a shiny mirror-like metallic sheen (inset, Fig. 1(b)), which is very different from the red nanoparticle colloids. The measured reflectivity (red line, Fig. 1(c)) of a monolayer of 20 nm Au nanoparticles confirms this difference from either a 20 nm thick layer of continuous Au

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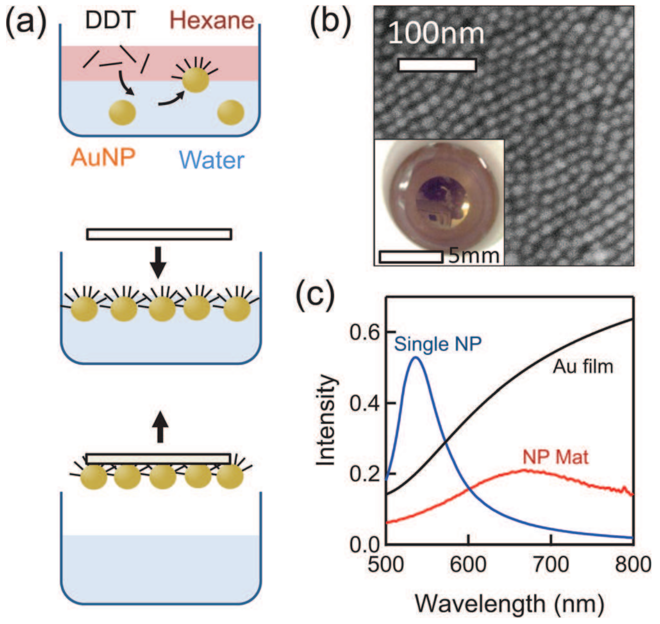

FIG. 1. (Color online) (a) Schematic of Au nanoparticle self-assembly and transfer. (b) SEM image of nanoparticle mat. Inset: optical image of nanoparticle mat in a teflon beaker. (c) Measured optical reflectivity of Au nanoparticle mat, with calculated spectra of a 20 nm continuous Au film and scattering spectrum of a single 20 nm Au sphere (scaled), both embedded in a medium of refractive index $n = 1.4$.

film (black line, Fig. 1(c)) or the scattering spectrum of a single Au nanoparticle (blue line, peak wavelength 536 nm, Fig. 1(c)). The reflectivity of the Au nanoparticle mat exhibits a resonant peak around 665 nm. This 130 nm red shift of the resonant peak from individual nanoparticles indicates the significant coupling between the closely-spaced nanoparticles. We thus exploit this known sensitivity to interparticle spacing and nanostructure geometry for spectral tuning.[2,11]

To dynamically investigate the optical properties of the Au nanoparticle mats, they are transferred to stretchable PDMS films through horizontal lifting (Fig. 1(a)). To protect the nanoparticle mat, another layer of PDMS film is applied and cured on top of the PDMS film supporting the nanoparticle mat. The film is elastically manipulated in two different ways. First, the film is *uniaxially* stretched along one axis. The measured reflection spectra at increasing strains (Fig. 2(a)) show a blue shift when the polarization of light is along the stretching direction. This is expected since along the stretch axis the nanoparticles move further apart from each other with increasing strain.[2] The nanoparticle mat can also be uniformly *biaxially* stretched along both lateral directions, using a specifically designed rig (inset, Fig. 2(b)). The PDMS film is clamped between two metal plates containing apertures to allow optical measurement. The film is lowered onto a hemispherical lens covered with index matching fluid which allows for free lateral movement of the PDMS. As the film is lowered, the hemispherical lens stretches it evenly in all directions. Optical reflection spectra taken as the stage is lowered reveal an even larger blue shift as the film stretches (Fig. 2(b)).

The spectral shifts of the resonances in the reflection spectra with strain (Fig. 3(a)) show different induced blue-shifts. At low strains blue-shifting rates of 40 nm/unit strain are seen for 1D (uniaxial strain) while 70 nm/unit strain is found for 2D (biaxial) strains. The shift of peak wavelength is nonlinear with strain, saturating at lower strains (30%) for 1D compared to 2D and showing a power law dependence (dashed lines, Fig. 3(a)). This is consistent with recently reported spectral shifts with interparticle spacing for dimers[2] and 1D chains.[11] This tuning process is completely reversible: when the stretched PDMS is relaxed, the spectrum red-shifts back as a result of decreasing interparticle spacing (Fig. 3(a) ▽).

Omnidirectional stretching is found to be independent of incident light polarization, as expected when the nanoparticles are equally separated in all directions and the nanoparticle mat order has no directionality. However, uniaxial stretching exhibits significant anisotropy for different polarizations. For polarizations parallel to the stretch direction, the spectrum blue shifts monotonically with increasing strain (Fig. 3(a) ▼). However when the polarization is perpendicular to the stretch direction, the measured reflection spectra show a more complicated behaviour, first blue-shifting (strain <10%) then red-shifting above 10% strains (Fig. 3(a) ▲). To quantitatively explain this phenomenon, full three-dimensional elastic and electromagnetic simulations of large numbers of Au nanoparticles are required (to be reported elsewhere). However, qualitative understanding is possible from considering nanoparticle chains. Unlike 1D nanoparticle chains where there is only one gap orientation, a hexagonal nanoparticle array contains multiple nanoparticle chains of various orientations, each particle having 6 nearest neighbors with three types of interparticle separation, d_1, d_2, and d_3, each representing different nanoparticle chains (Fig. 3(b)). When the nanoparticle mat is stretched these distances change depending on the angle of the chain to the

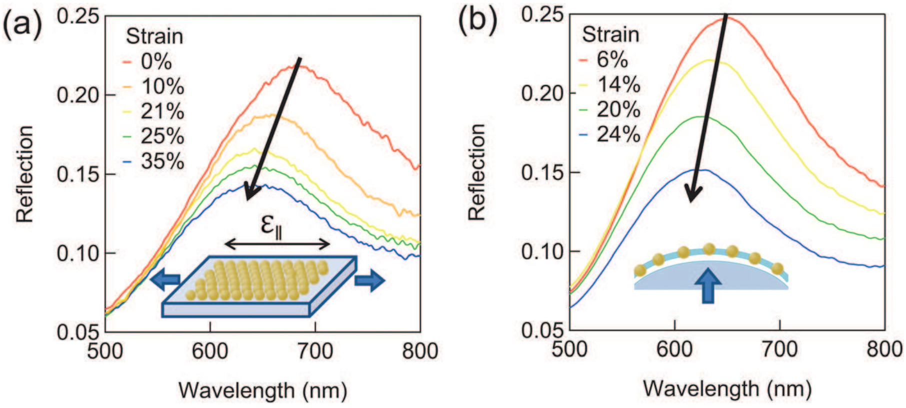

FIG. 2. (Color online) Reflection spectra of Au nanoparticle mats under increasing strain. (a) Uniaxial stretch parallel to optical polarization and (b) biaxial uniform stretch with unpolarized light. The discrepancy in intensity if due to the curved film on the lens surface.

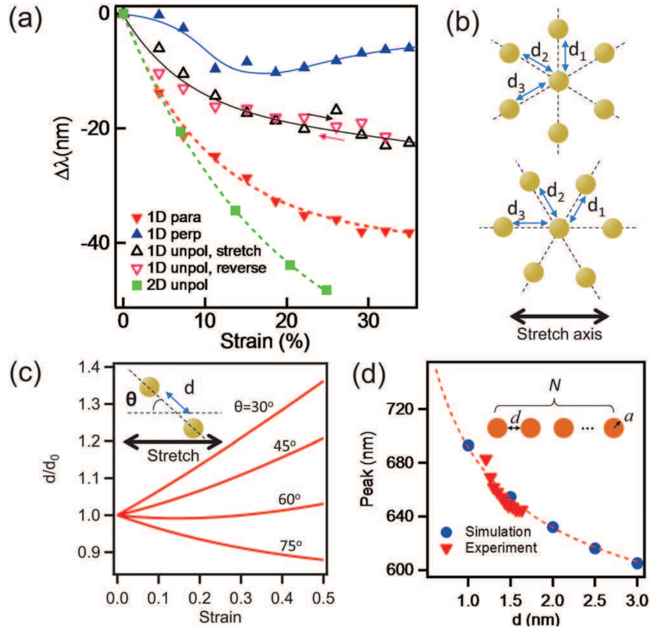

FIG. 3. (Color online) (a) Resonant shifts of Au nanoparticle mats *vs* strain, for 1D stretch (▼, polarization parallel to stretch axis), 1D stretch (▲, polarization perpendicular to stretch axis), 2D stretch (■, unpolarized light), 1D stretch (▽ extension and △ contraction, unpolarized light) with power-law fits (dotted lines). (b) Hexagonal array with equal interparticle separations can be aligned at different angles relative to the stretch axis. With increasing strain the distances d_1, d_2, and d_3 will change depending on their angle to the stretch axis. (c) Change in interparticle separation in a dimer depending on angle θ to the stretch axis. (d) 1D parallel polarized data fitted with simulations of resonant scattering peaks for 1D Au nanoparticle chain shown in inset. $N = 19$, $a = 10$ nm, polarization along chain axis, embedded in medium with $n_{\mathrm{PDMS}} = 1.4$.

stretch axis. Chains along (or with chains orientated <60° to) the stretch axis move further apart, hence the spectra blue shift. Chains perpendicular (or with chains at >60° to) the stretch direction move closer, therefore the spectra should red shift. This behaviour can be illustrated using a simple dimer model (Fig. 3(c)). The competition between these two effects gives rise to the complicated behaviour. Initially the blue shift effect is more significant, as PDMS stretches twice as much along the stretch direction as contracts in the perpendicular directions (for Poisson ratio = 0.5).[12] At higher strains, plasmonic coupling along the stretch direction drops significantly (interparticle spacings > diameter), while perpendicular to the stretch direction it increases dramatically given the smaller interparticle spacing. This nonlinear power law for plasmonic coupling thus strongly accentuates the anisotropy of 2D plasmonic mats. Blue shifts are larger for biaxial stretching since the spacing of nanoparticles in chains of *all orientations* increases.

To provide a simple quantitative estimate, we simulate a 1D linear chain of Au nanoparticles which confirms the plasmonic coupling is indeed sensitively dependent on interparticle spacing (Fig. 3(d)). The simulations use chains of $N = 19$ spheres, because the scattering spectra saturate beyond $N \geq 18$ spheres. As the spacing increases, the peak positions of scattering spectra blue shift considerably (Fig. 3(d) ●), while minimal shifts are seen in the orthogonal polarization. Such a saturation phenomenon has also been similarly observed elsewhere.[11,13] The peak position of 1D nanoparticle chains follows a power-law dependency on the interparticle spacing, $\lambda_{pk} \propto d^{-0.6}$ (Fig. 3(d), red dotted line). When the polarization of light is parallel to the uniaxial stretch direction, nanoparticle mats may be approximated as 1D nanoparticle chains, since plasmonic coupling of chains orientated along the stretch direction contributes most to the observed spectra. Experimental results of 1D parallel stretching are compared with the simulations by matching the strain (Fig. 3(d)), indicating that the initial interparticle separation of the nanoparticle mat is 1.2 ± 0.1 nm, which is the same scale as the full stretched length of a 1-dodecanethiol molecule (1.7 nm).[14]

While the 2D mat supports a more complex plasmonic response, it can be well accounted for by such a simple linear chain model. We thus induce an elastic phase transition in the originally isotropic 2D plasmonic mat, producing an anisotropic plasmonic response that mirrors the nanoscale architecture. Such a symmetry-breaking response has been seen in stretching elastic photonic crystals,[15] but this is now observed here in a plasmonic system sensitive to sub-nm deformations.

In conclusion, we report reversible and actively tunable plasmonic properties of self-assembled two-dimensional Au nanoparticle mats on elastic substrates. Stretching such opto-elastic films changes their interparticle separation, thereby modifying the optical properties and inducing a nano-geometrical polarization anisotropy. The blue shifts observed in the reflection depend on the strain geometry, due to plasmonic coupling effects at nanometer scale distances. Such metal nanoparticle mats can potentially be exploited for the development of stretchable optical colour filters and molecular sensors. By achieving interparticle separations small enough to allow quantum tunnelling, stretch-induced reversible metal-insulator transitions are in prospect in this system.[16]

This work is supported by EPSRC Grants EP/G060649/1, EP/F059396/1 and the Nokia Research Center.

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