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Supplementary Information

Growing gold nanoparticles on a flexible substrate to enable simple mechanical control of their plasmonic coupling

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List of figures cited in the text of the paper

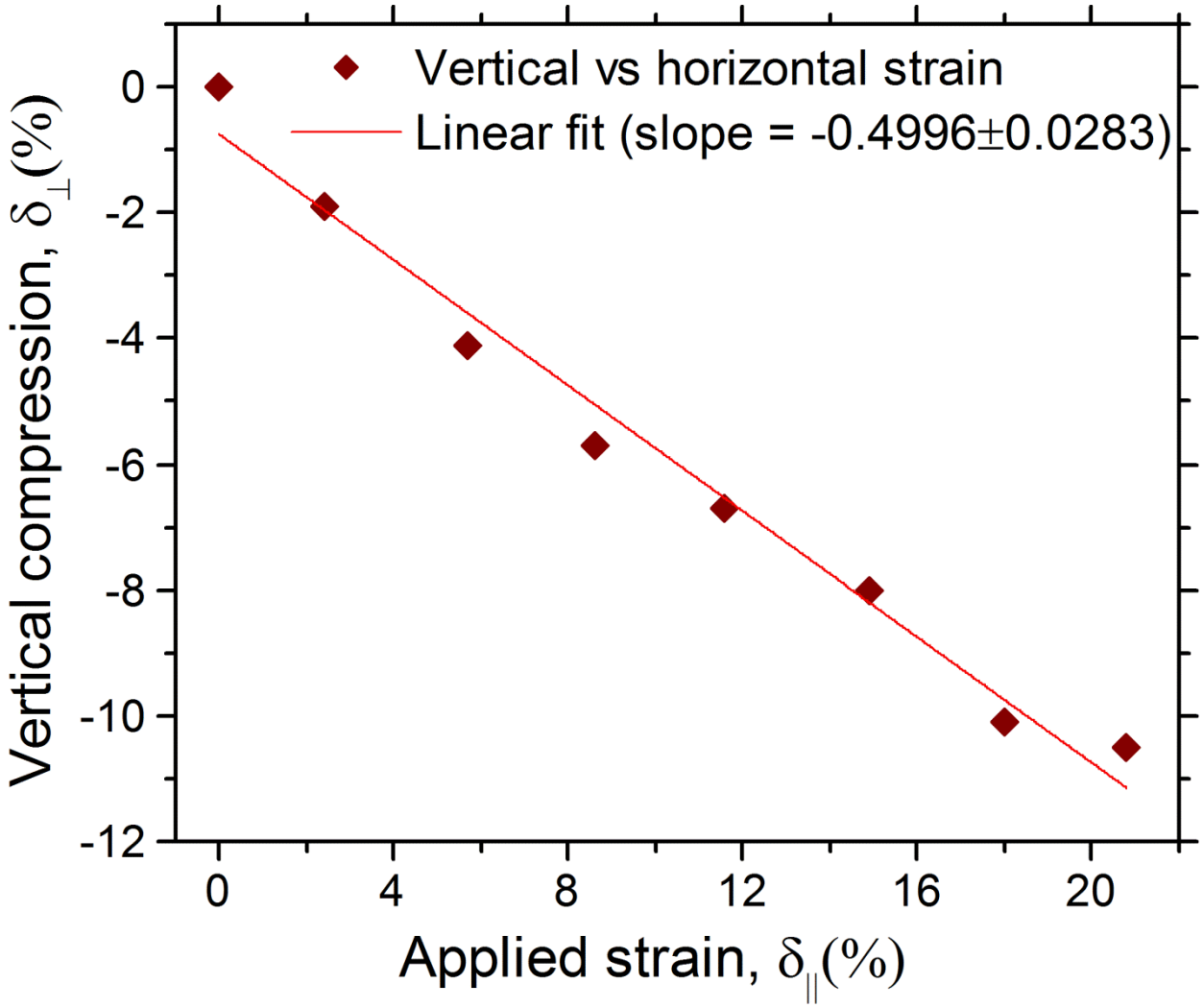

Fig. S1 Measurement of the percentage compression that the sample undergoes in the direction perpendicular to the applied strain. The linear fit (red line) confirms a Poisson coefficient of about 0.5 for the PDMS substrate.

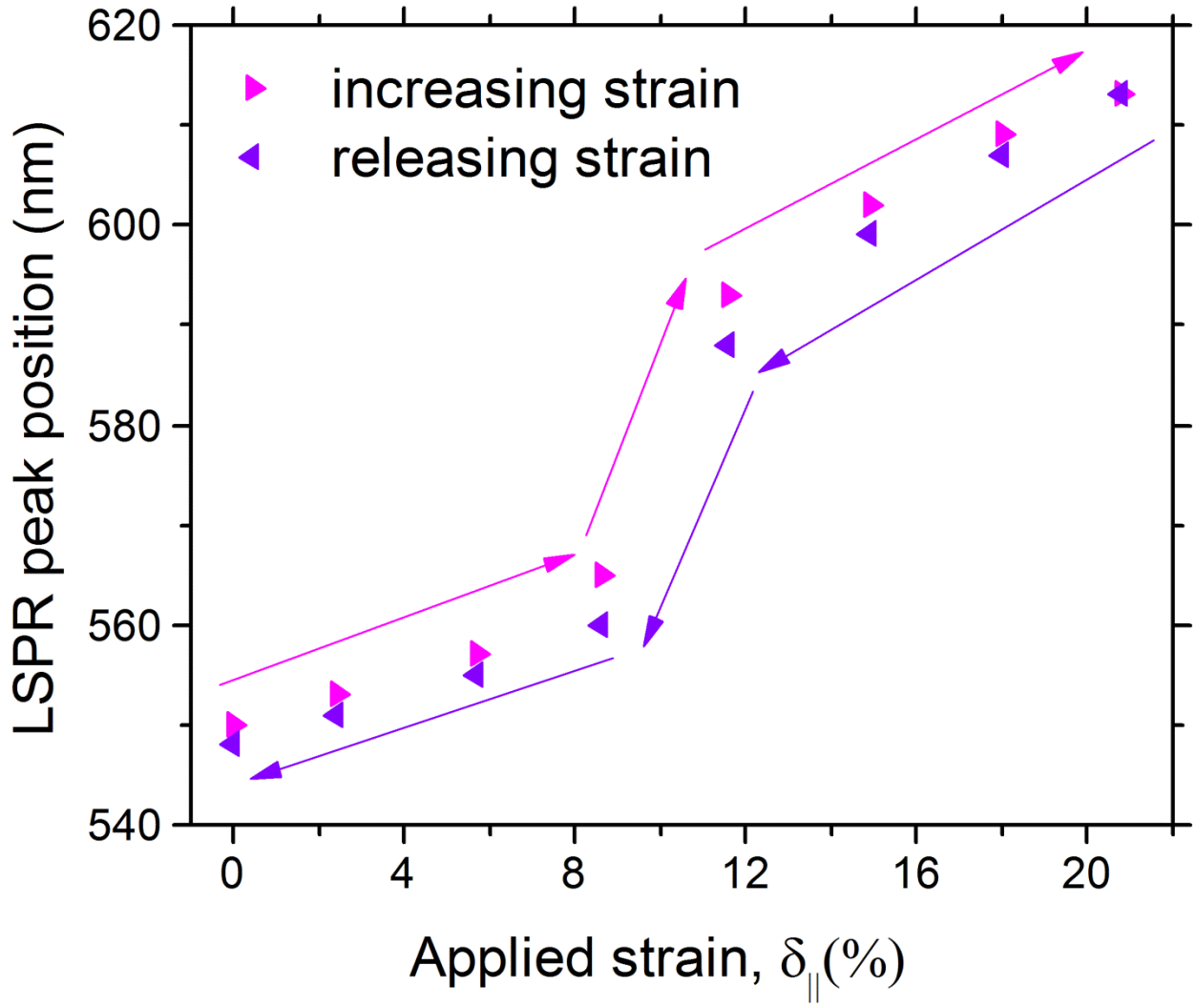

Fig. S2 Measurement of the spectral position of the resonance peak maxima as a function of the applied strain, during a straining-releasing cycle. The optical properties are reversible.

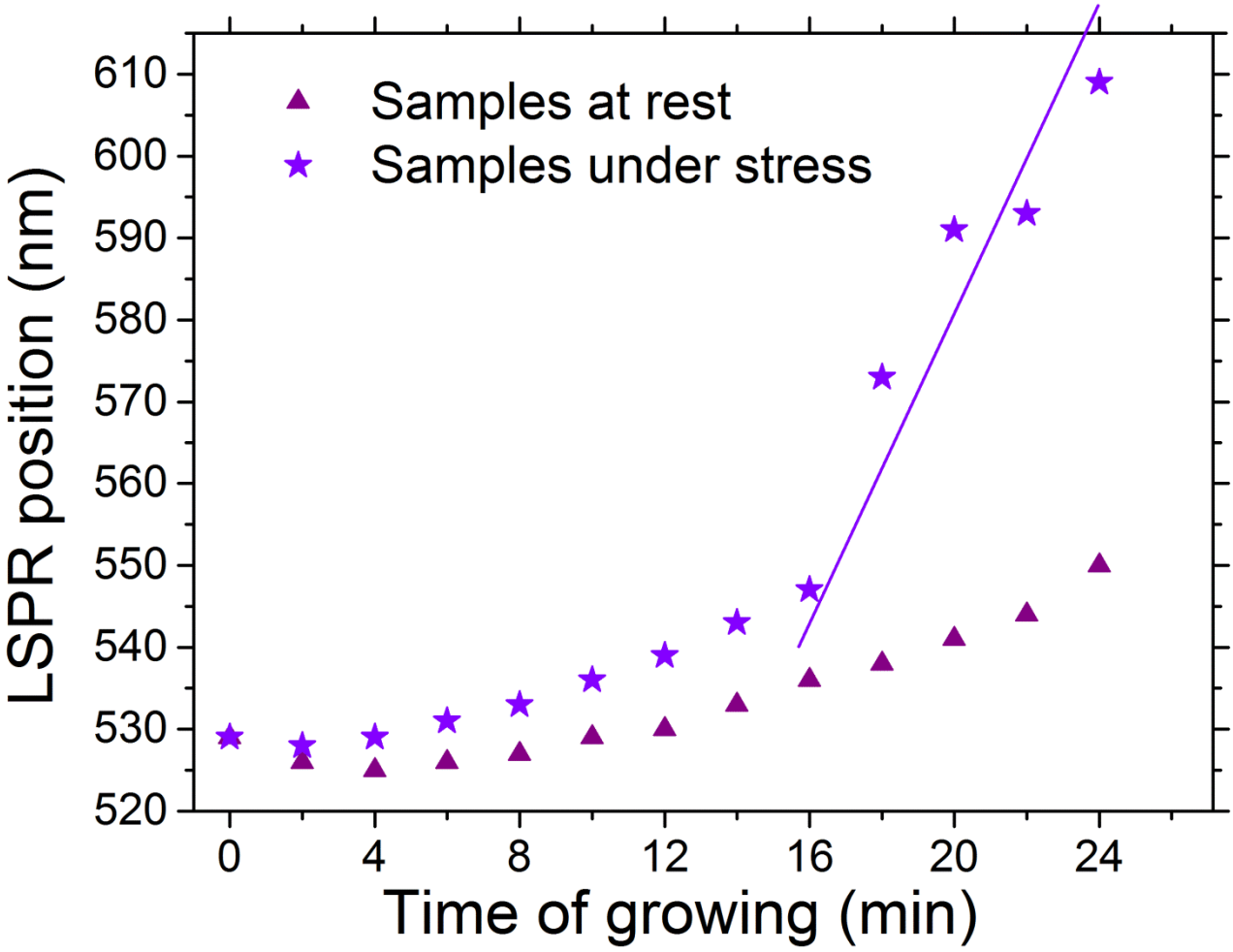

Fig. S3 Plot of the localized surface plasmon resonance peak position as a function of the number of growth cycles (2 minutes each), both for samples at rest (triangles) and under applied strain (stars).

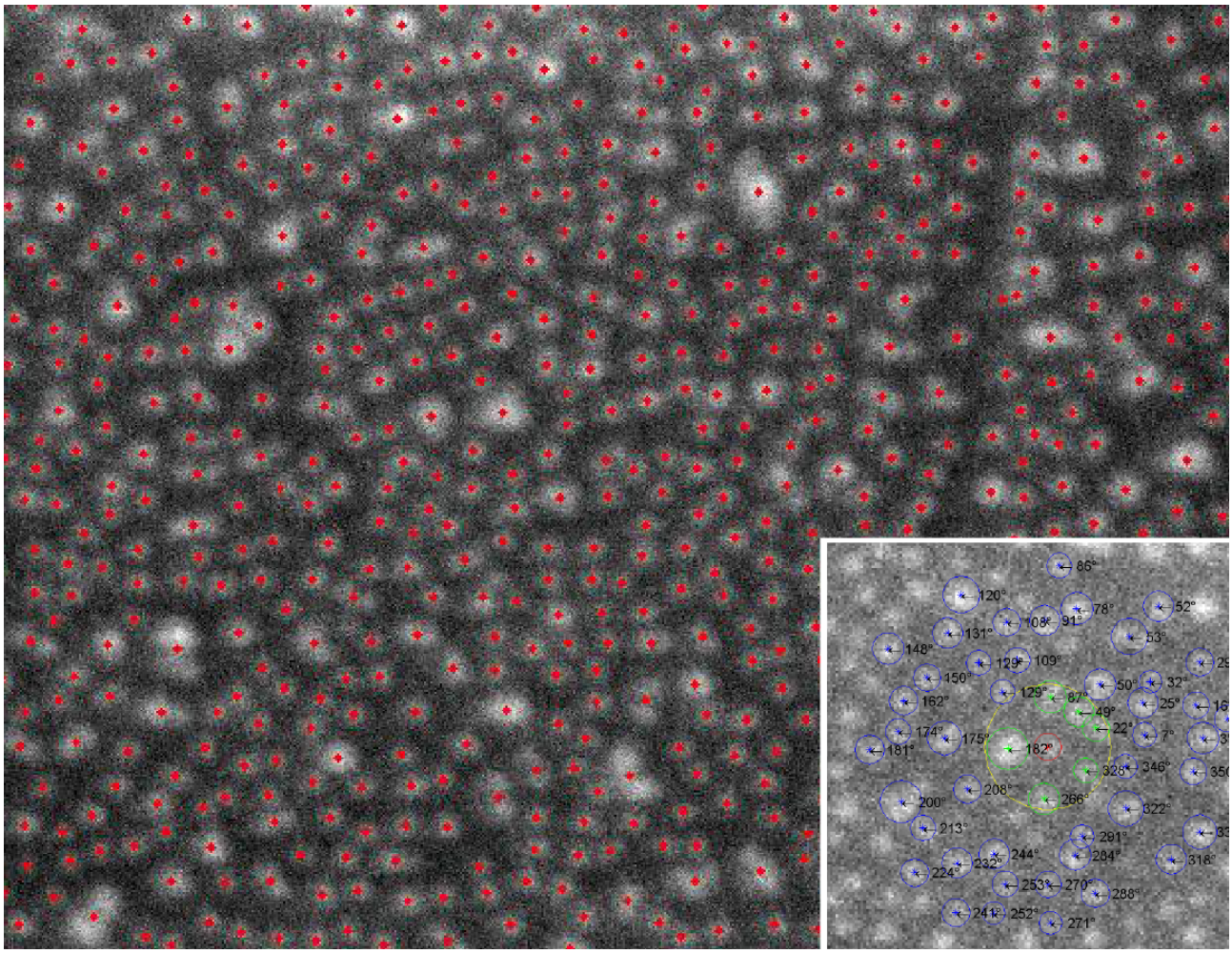

Fig. S4 Result of the image analysis performed on the SEM micrograph of Fig. 2a. In red, the centres of particles are depicted as identified by a MatLab code implemented to the scope. In the inset of the figure, the nearest neighbours (circled in green) and all other neighbours (circled in blue) of a single particle are marked.

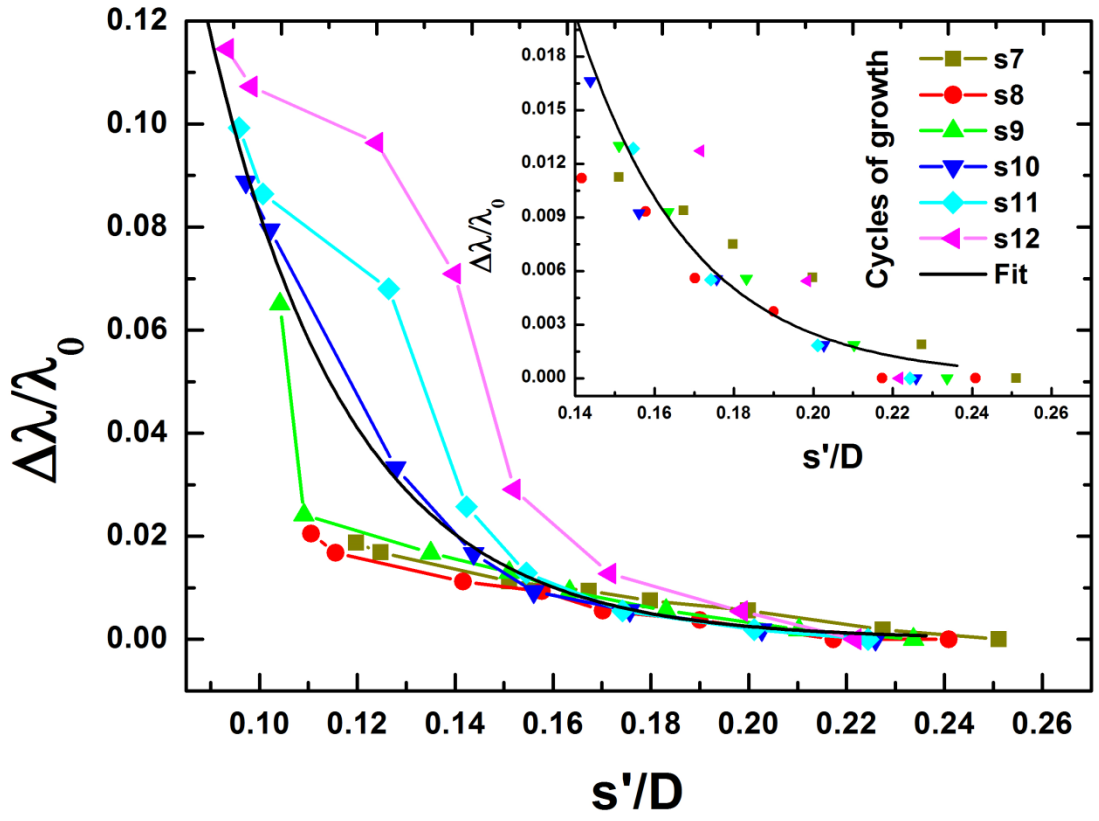

Fig. S5 Experimental dependence of $\Delta\lambda/\lambda_0$ on s'/D (normalized shift and normalized interparticle gap respectively of the samples under stretching, see experimental section) is plotted for samples with a different number of cycles of growth (from seven to twelve cycles). Each absorption spectrum has been acquired while increasing the applied stretching δ (0%; 2.4%; 5.6%; 8.6%; 11.6%; 14.9%; 18.0%; 20.8%). The sizes of nanoparticles here have been obtained by exploiting the linear fit (Fig. S6) between the 7^{th} and the 12^{th} cycle of growth. The comparison of this graph with the one in Fig. 4 shows that the deviation between the two analyses is negligible.

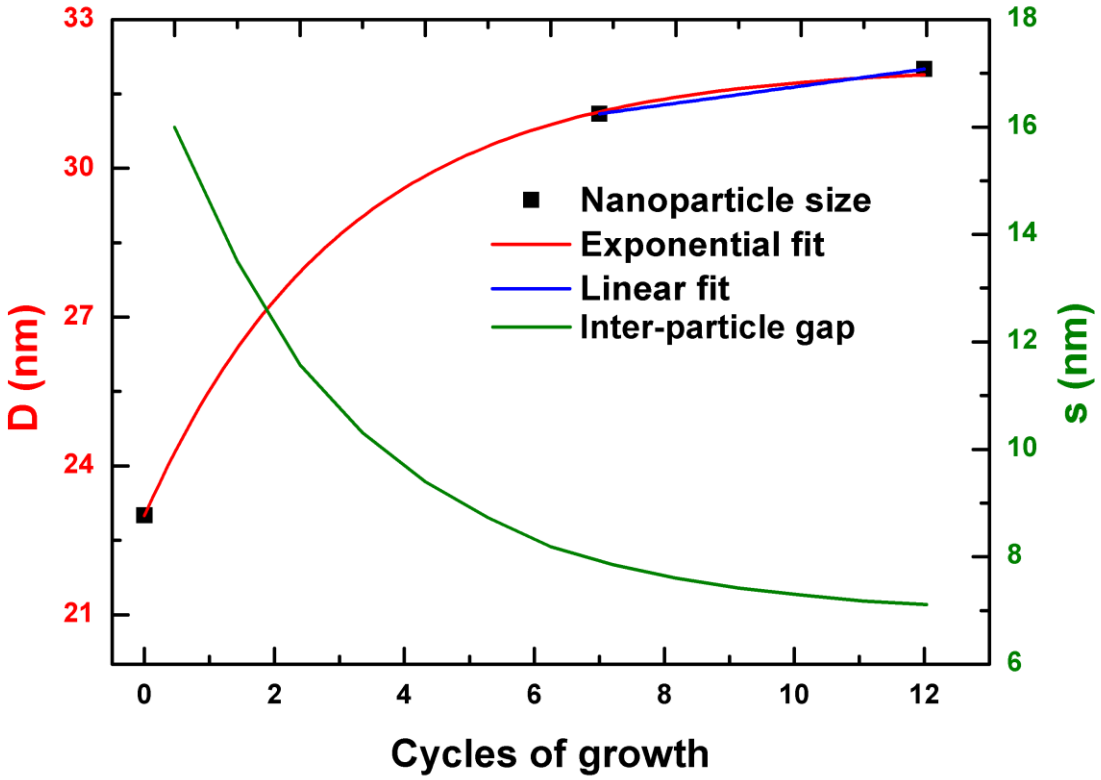

Fig. S6 Increase of size that nanoparticles undergo during the growth process. An exponential fit of nanoparticles sizes is reported (red line). When considering the 7th to 12th cycles, the deviation between linear and exponential fit is negligible. In the same graph, the curve (green line) is reported showing how the inter-particle gap varies by growing the particles.

Potential energy variation of a dimer during the application of a mechanical strain

The potential energy between two interacting dipoles put at distance **r** can be written as:

$$U = -\frac{\xi|\mu|^2}{4\pi\varepsilon_0 r^3} \qquad \text{(S1)}$$

where the factor $\xi=3\cos\theta_1\cos\theta_2-\cos\theta_{12}$ takes into account the relative orientation of the interacting dipoles between each other and with respect to the exciting field **E**, as sketched in Fig. S7.

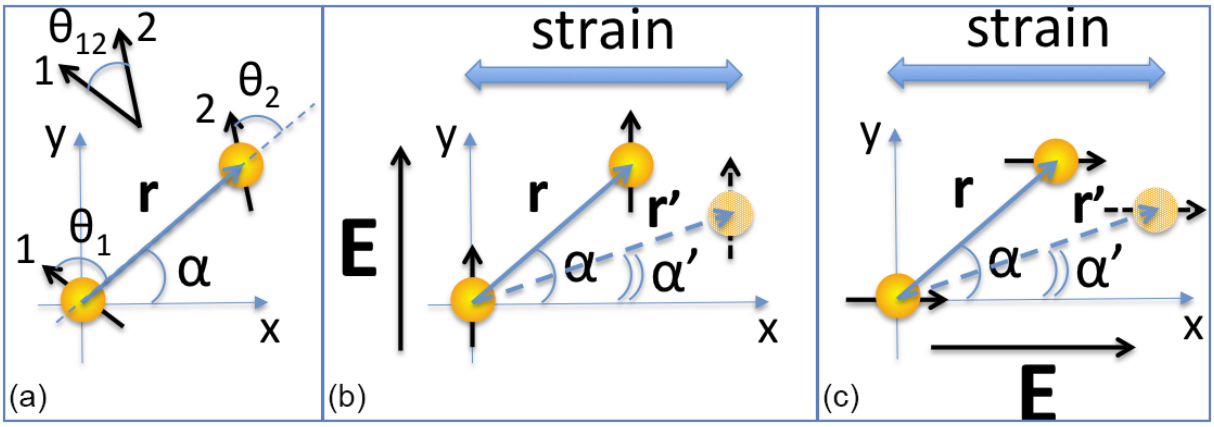

Fig. S7 Sketch of coupled nanoparticles considered as interacting dipoles; (a) general situation of two interacting dipoles; (b) Excitation of a dimer with ⊥-polarized light and geometrical configuration with and without applied strain; (c) Excitation of a dimer with //-polarized light and geometrical configuration with and without applied strain.

In more detail, θ_1 and θ_2 are the angles respectively formed by dipole 1 and dipole 2 with **r** while θ_{12} is the angle they form with each other. If the relative position of the two interacting plasmonic particles is modified by the macroscopic strain applied to the PDMS substrate where they are immobilized, the energy variation ΔU related to the new configuration can be written as:

$$\Delta U = U'_{\perp,//} - U_{\perp,//} = -\left(\frac{\xi'_{\perp,//} |\mu|^2}{4\pi\varepsilon_0 r'^3} - \frac{\xi_{\perp,//} |\mu|^2}{4\pi\varepsilon_0 r^3} \right) \qquad \text{(S2)}$$

where $r'=r[(1+\delta)^2\cos^2\alpha+(1-0.5\delta)^2\sin^2\alpha]^{1/2}$ is the distance, after strain, between considered particles and α is the initial angle made by **r** with the x-axis (Figs. S7b,c). In the expression for r', it has been also considered that, for all applied strains (δ=0%÷20.8%), the PDMS sample is in elastic regime (PDMS Poisson's ratio ≈ 0.5). As far as ξ values are considered, since dipoles 1 and 2 are induced by the exciting field **E**, they are oriented parallel to it, hence $\theta_1=\theta_2=\theta_{\perp,//}$ and $\theta_{12}=0$ while $\theta_\perp=\pi/2-\alpha$

for ⊥-polarized field (**E//y)** and $\theta_{//}=\alpha$ for //-polarized field (**E⊥y)**. As such, in our specific case, the polarization-dependent expressions for ξ are:

$$\xi_{\perp}=3\cos^2\left(\pi/2-\alpha\right)-1 \quad ; \quad \xi_{//}=3\cos^2(\alpha)-1 \qquad (3)$$

In Fig. S8a,b, Eq. S2 is plotted as a function of the angle α and for several values of the strain parameter δ. For a given polarization of the exciting light, the energy variation strongly depends on the angular interval that α belongs to. In particular, Fig. S8a indicates that, for ⊥-polarized light (**E** field perpendicular to the stretching direction) $\Delta U_{\perp}<0$ for $0°<\alpha<25°$ and $70°<\alpha<90°$, while $\Delta U_{\perp}>0$ for $25°<\alpha<70°$. For $\Delta U_{\perp}<0$ ($\Delta U_{\perp}>0$) a red-shift (blue-shift) of the plasmon band is expected. Since in the relaxed state the particles are (almost) not interacting, above considerations on $\Delta U_{\perp}$ and related shifts can apply only to those dimers whose inter-distance r decreases upon stretching. As shown in Fig. S8c, this holds only for large angles ($60°<\alpha<90°$).

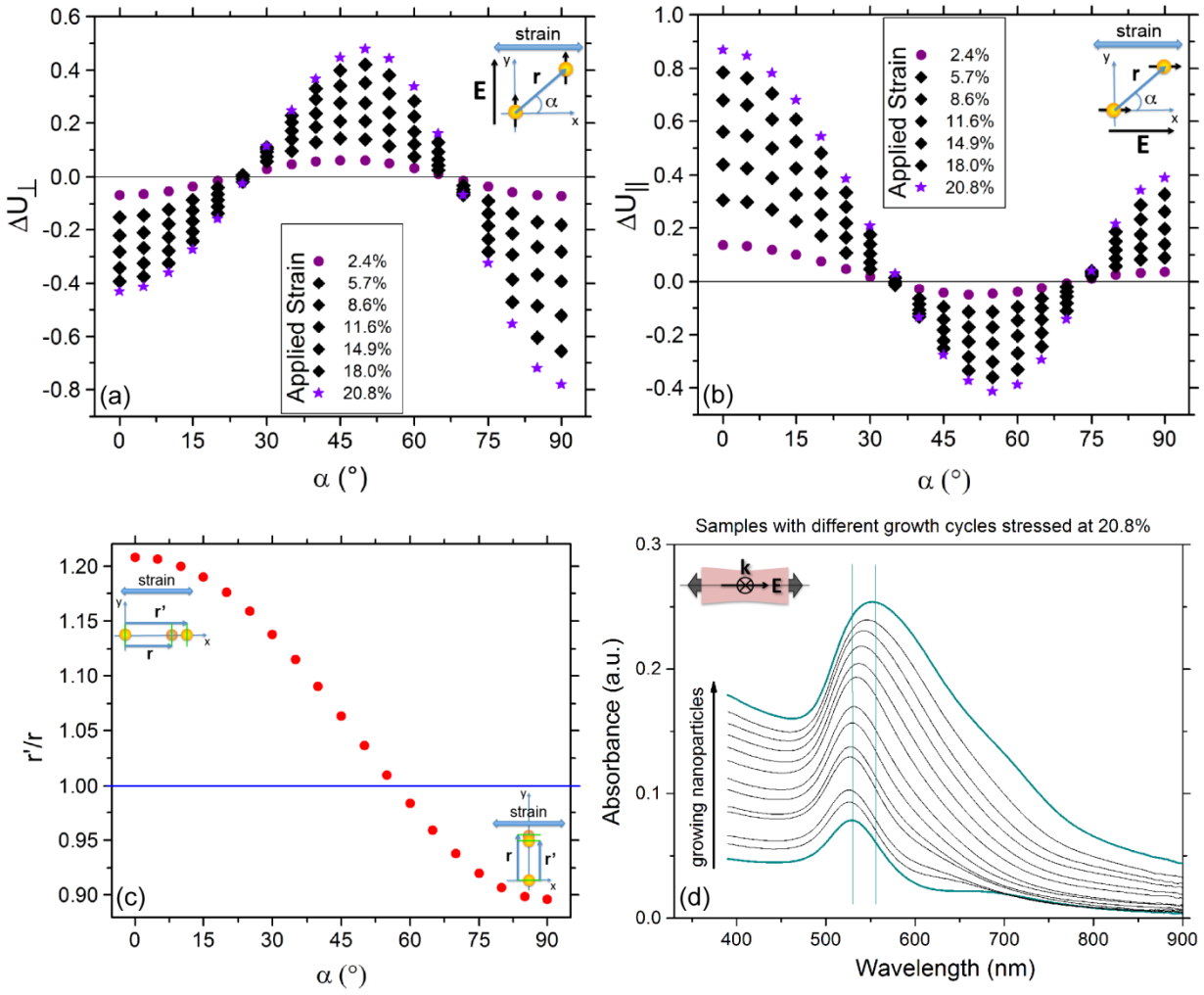

Fig. S8 Stretched-unstretched interaction energy variation (related to the initial value of the interaction energy) plotted as a function of the angle made by the inter-dipole axis with the x-axis, both for (a) ⊥- and (b) //-polarized exciting light. (c) Plot of the ratio between the inter-particle distance (center-to-center) with applied (r') and non-applied stretching (r). The upper left and lower right insets show the condition of two gold nanoparticles that, upon stretching, respectively undergo an increase and a decrease of their inter-distance; (d) Extinction spectra of gold nanoparticle coated PDMS samples that underwent different growth cycles of particles, with an applied strain of 20.8%. Samples have been excited with //-polarized light.

In other words, only a limited number of dipoles undergo plasmon coupling during the stretching experiment. When considering a given dipole and its nearest neighbours, this dipole potentially interacts only with the ones laying in a well-defined double angular cone with an aperture of 60° (Fig. S9).

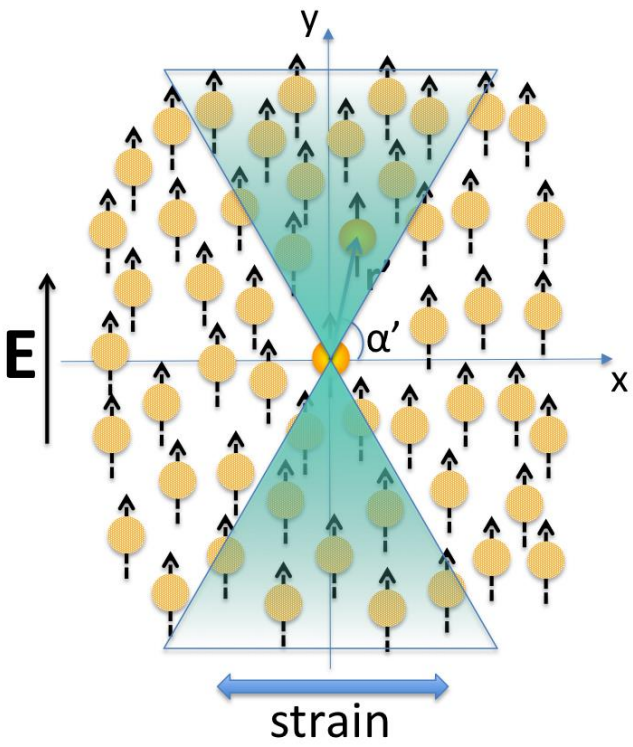

Fig. S9 A given dipole and its neighbours are considered. Upon stretching and starting from an uncoupled condition, this dipole potentially only interacts with the ones laying in a well-defined double angular cone with an aperture of 60° because only for the dipoles in this angular region the r'/r<1 (Fig. S8 c).

Due to the effect of the angle α both on distance and interaction energy, a pronounced dependence of the plasmon shift on the polarization of the impinging light is, in fact, expected. In case of an exciting //-polarized light (**E** field parallel to the stretching direction), the situation is reversed. Indeed, for small and large α angles ($0°<\alpha<35°$ and $75°<\alpha<90°$), the applied strain yields a blue-shift of the plasmon while, for intermediate angles ($35°<\alpha<75°$), a red-shift is expected. Again, we only consider the interval $60°<\alpha<90°$, since only in this case r decreases upon stretching. In this angular region, Fig. S8b indicates a comparable red- and blue-shift. Indeed, this conclusion is experimentally verified in Fig. S8d, where the overall plasmonic red-shift is very limited for the sample excited with //-polarized light and the main result is a mere broadening of the plasmon band. Above considerations qualitatively explain the strong polarization dependent behaviour of the amorphous and initially isotropic samples when stretched by about 20% or even less. Key to this behaviour is the growth of the particle size, such that the gap *s* between them (more precisely *s/D*)

allows weak coupling. Upon stretching, this coupling is weakened in one direction (parallel to the stretching) and enhanced in the orthogonal one.