

Electronic Supplementary Information for

Plasmene Nanosheets as Optical Strain

Sensors

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Experimental section

Materials. Gold (III) chloride trihydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$, $\geq 99.9\%$), hexadecyltrimethylammonium bromide (CTAB), sodium borohydride (NaBH_4), L-ascorbic acid (AA), silver nitrate (AgNO_3), cetyltrimethylammonium chloride solution (CTAC, 25 wt % in H_2O), polyvinylpyrrolidone (PVP, average $M_w \sim 55\,000$), indium tin oxide-coated glass slides (ITO glass, 30-60 Ω/sq) were obtained from Sigma-Aldrich. Ammonium hydroxide ($\text{NH}_3 \cdot \text{H}_2\text{O}$, 25 wt %), hydrogen peroxide (H_2O_2 , 30 wt %) and chloroform were purchased from Merck Millipore. Tetrahydrofuran (THF) and hydrochloric acid (HCl, 32 wt %) were purchased from Thermal fisher scientific (Ajax Finechem). Thiol-functionalized polystyrene (PS, $M_n = 50\,000$ and 12 000 g/mol) was obtained from Polymer Source. Polydimethylsiloxane (PDMS, Sylgard 184) was from Dow corning. Milli-Q water was obtained from Milli-Q Advantage A 10 water purification System. All chemicals were used without any further purification.

Synthesis of gold nanocubes (AuNCs). AuNCs were synthesized by the seed-mediated method described in literature.¹ In detail, Au seeds were firstly synthesized by adding 0.1 mL of 25 mM HAuCl_4 and 0.6 mL of freshly prepared ice-cold 0.01 M NaBH_4 into 7.65 mL of 0.1 M CTAB in a 20 mL glass vial. The mixed solution was then put in water bath at temperature of 30 °C and stirred at 500 rpm for 30 s. After that, the solution was kept undisturbed for 1 hour. Then, the obtained Au seed solution was 10-time diluted for the following growth of Au NCs. Different amounts of diluted seed solution (15 μL for small-size AuNCs, 7.5 μL for medium-sized AuNCs, 3 μL for large-sized AuNCs) was added to a mixture of 12 mL of Milli-Q water, 2.4 mL of 0.1 M CTAB, 0.3 mL 10 mM HAuCl_4 and 1.8 mL 10 mM AA to obtain the Au NCs with different sizes. The above solution was then incubated in water bath at

temperature of 30 °C overnight. Finally, AuNCs aqueous suspension was obtained by re-dispersing in 15 mL of Milli-Q water after centrifuging at 7800 rpm for 10 min.

Synthesis of silver (Ag)-coated AuNCs. The above synthesized AuNCs (small-sized) aqueous suspension was used as seed solution to grow Ag-coated AuNCs by the method described in literature² with minor modifications. Firstly, 15 mL of AuNCs aqueous suspension was centrifuged at 7800 rpm for 10 min and then re-dispersed in 10 mL of 80 mM CTAC aqueous solution. Ag-coated AuNCs were then synthesized by adding 1 mL of 10 mM Ag NO₃ and 1 mL of 50 mM AA at injection rate of 0.2 mL/min into the AuNCs in CTAC solution. The growth reaction was kept at 60 °C under stirring for 4 hours. The final Ag-coated AuNCs were collected by centrifuging at 5500 rpm for 10 min and then re-dispersed in 10 mL Milli-Q water for further use.

Fabrication of plasmonic strain sensor. The plasmenes were prepared by a two-step drying-mediated method reported in our previous work.³ Firstly, the NPs including AuNCs and Ag-coated AuNCs were modified by PS or PVP through a ligand exchange process. Briefly, 15 mL of AuNCs aqueous suspension was centrifuged at 7800 rpm for 10 min and then re-dispersed in 5 mL of 4 mg/mL THF-PS solution. For PVP-capped AuNCs, the AuNCs were re-dispersed in 5 mL of 4 mg/mL ethanol-PVP solution. For Ag-coated AuNCs, the aqueous suspension was centrifuged at 5500 rpm for 10 min and then re-dispersed in 5 mL of 4 mg/mL THF-PS solution. PVP (Mn=55 000 g/mol) and PS (Mn= 12 000 g/mol) were used for small-sized AuNCs. PS with Mn= 50 000 g/mol was used for both Ag-coated AuNCs and AuNCs with small-sized, medium-sized and large-sized AuNCs. The Au NPs solutions were then kept undisturbed overnight followed by washing with ethanol for PVP-capped AuNCs and THF for

PS-capped NPs twice and chloroform once. After that, the suspension of Au NPs in chloroform was concentrated by centrifuge. For the preparation of stretchable matrix, the PDMS was mixed with curing agent at weight ratio of 10:1 and then was spin-coated at 400 rpm for 30 s on a plastic petri dish followed by curing at 70 °C in an oven for 30 min. The plasmonic strain sensor was prepared by dropping the above concentrated Au NPs suspension on a sessile water droplet (10 μ L) that sitting on PDMS substrate.

For Ag-coated Au NCs plasmenes, etching process was used to remove Ag shell. $\text{NH}_3 \cdot \text{H}_2\text{O}$ was firstly dropped on the surface of plasmene nanosheets and then H_2O_2 was added. The etching was allowed to proceed for about 4 hours followed by washing with Milli-Q water to remove remaining etching agents. The plasmene nanosheets was finally dried at room temperature for further use.

Numerical simulation of discrete AuNCs in air. All of the simulations were performed on COMSOL Multiphysics. The frequency domain FEM solver was utilised to obtain the optical response of various setups as a function of incident radiation wavelength.

In all our simulations, we used the gold refractive indices as reported in reference⁴ and PDMS refractive indices made publicly available through Vaibhav Gupta's work⁵. For intermediate values, a cubic spline interpolation was used. The first simulations were performed to measure the absorption, scattering and extinction cross sections of AuNCs surrounded by a thin layer of PS with a refractive index of roughly 1.3.⁶ This composite was then surrounded by an air medium and a Perfectly Matched Layer (PML) on all sides. The domain was discretized using a tetrahedral mesh. The size of the air layer and PML was increased until convergence was reached. For Au NCs with size of 40 nm, a PS layer of refractive index 1.3 and thickness 7.1 nm on all sides, the peak of the absorption cross section occurred at 560 nm (Figure S14). We note that the absorption cross section is considered here rather than the extinction cross section,

since the quantity measured by UV-vis spectrophotometry is an inverse transmittance measure that can be considered equivalent to an absorbance measure.

Numerical simulation of stretchable plasmene nanosheets. For the stretchable plasmene nanosheet, we utilised a periodic structure with a unit cell consisting of an AuNC, surrounded by a thin PS layer with thickness equal to the measured un-strained thickness of the PS layer. The top of the unit cell consisted of an infinite air medium and the bottom, an infinite PDMS substrate. The infiniteness of the two media were realised by increasing the extent of the two media in the simulations until convergence was reached. For most setups, saturation was reached by 1000 nm extent in both air and PDMS domains. The incident radiation was directed from the bottom through the PDMS layer and the transmitted radiation was collected from within the air domain at the top. The four sides of the unit cell were surrounded by periodic Floquet boundary conditions. The extent of the PS layers on the four sides were changed based on the calculated separations between adjacent NCs under various strain levels.

The separations between adjacent NCs were determined from the measured initial separations of NCs from SEM images and using the fact that the Poisson ratio for PDMS substrate is 0.5.⁷ This means that when the PDMS substrate is strained in a certain direction, the substrate is compressed in the transverse directions by half that strain value (Figure 4a). The edge-to-edge spacing between NCs in the direction of strain (L_x) was calculated by,

$$L_x = (1 + \varepsilon) (a + s) - a \quad (1)$$

and the edge-to-edge spacing in the transverse direction (L_y) was calculated using,

$$L_y = (1 - 0.5\varepsilon) (a + s) - a \quad (2)$$

Where ε is the applied strain, a is the size of AuNC and s is the initial edge-to-edge spacing between AuNCs.

The -0.5 factor here accounts for the compression of PDMS in the transverse direction by a factor of 0.5. We set the minimum value of L_y to 2 nm to reflect the fact that the NCs cannot get too close due to the PS layer in between. The edge-to-edge spacing values calculated at various strain levels for a 32 nm NC setup with initial NC-NC spacing of 8.3 nm is shown in Figure S14. Note that the separation in the y-direction saturates at 2 nm due to our prescription.

The simulations were run in 2 steps analogous to the UV-vis spectrophotometer experimental procedure. In the first step, the plasmene sheet was removed and the transmittance through the pure PDMS substrate was calculated (T_0). In the next step, the plasmene sheet was activated and the transmittance (T) calculated. The extinction was calculated as $-\log (T/T_0)$. In the simulations, we studied extinction for incident radiation polarized longitudinal to the strain direction (x direction) as well as transverse (y direction) to it. We find that the peak for the transverse polarization shifts rapidly towards the red end of the spectrum for increasing strain. On the other hand, the peak for incident radiation polarized along the strain direction exhibits a blue shift from 643 nm to 558 nm within the visible region at strains from 0% to 100%. (Figure 4b), which shows similar trend as recorded by experiments (Figure 4c). Since the extinction peak of light polarized transverse to the strain axis shifts beyond the spectral region of interest, in simulations, we only focus on light polarized longitudinal to strain.

For the simulations of the size and edge-to-edge spacing effect on the plasmonic coupling peak shift, we tuned the PS refractive index from 1.0 to 1.6. Refractive index of 1.6 is for small-spaced (ss-) plasmene, 1.3 is for medium-spaced (ms-) plasmene and 1.0 for the large-spaced (ls-) plasmenes. For all other plasmenes including small-sized AuNCs (S-AuNCs) plasmene, medium-sized AuNCs (M-AuNCs) plasmene and large-sized AuNCs (L-AuNCs) plasmene, refractive index of 1.3 are applied.

Numerical simulation of rod-like structure. In the experiments, we noticed the plasmonic resonance energy of highly-strained (e.g. 50%) plasmene was even higher than coupling-free resonance energy for discrete AuNCs (e.g. ~ 511 nm v.s. ~ 530 nm in one of our experimental studies shown in Figure S9, blue line). We also observed a heterogenous plasmonic behaviour of plasmene under low strains (e.g. 10%), especially for ss-plasmene (Figure 3a and Figure S11a). To study the reasons for these interesting experimental observations, we simulated the spectrum of an infinite rod-like structure with cubic cross section commensurate with the NC cross section and surrounded by a thin PS layer. The rod-like structure with cubic cross section of side length 40 nm was stimulated with radiation transverse to its axis (Figure S13a), showing a higher resonance energy (~ 530 nm, Figure S13b) than that of discrete AuNC (560 nm, Figure S12b). This result is consistent with our experimental observation, suggesting that at high strain levels, the individual NCs separate significantly along the strain direction and draw extremely close in the transverse direction, effectively forming an array of infinite nanorods. To investigate the heterogeneity, we calculated the spectrum of three rod-like structures assembled by 2, 4 and 10 of closely packed 40 nm-AuNCs with an edge-to-edge separation of 2 nm (Figure S12a). The radiation was longitudinal to the axis of the rod-like structure (Figure S12a). The calculated result shows that the longitudinal resonance peak is varied with different numbers of AuNCs (Figure S12c). This result indicates that the heterogeneous plasmon resonance behaviour of low-strained plasmene is probably due to the formation of heterogeneous rod-like structures with varied lengths (Figure 3b-g).

Characterizations. The morphology of Au NPs and plasmene nanosheets was characterized by scanning electron microscope (SEM, FEI Helios Nanolab 600 focused ion beam (FIB)-SEM operating at a voltage of 5 kV and a current of 86 pA) and transmission electron microscope (TEM, FEI Tecnai G2 T20 TWIN LaB6 TEM operating at a voltage of 200 kV). The extinction

spectra of NPs suspensions were recorded by using an Agilent 8453 UV–vis spectrophotometer. The stretching and releasing cycling test was carried on motorized moving stages (THORLABS Model LTS150/M) which were connected to a computer-based user interface (Thorlabs APT user). For characterization of strain plasmonic strain sensor, one side of the sensor was fixed on a transparent substrate and another side was stretched to a certain strain at which the extinction spectra was recorded by using a J&M MSP210 microscope spectrometry system under a 20× objective. The acquired area for extinction spectra is 6 μm ×6 μm . 10 random locations within each plasmene were checked. The size and edge-to-edge spacing of Au NPs were analyzed by Image J software.

Supplementary Figures

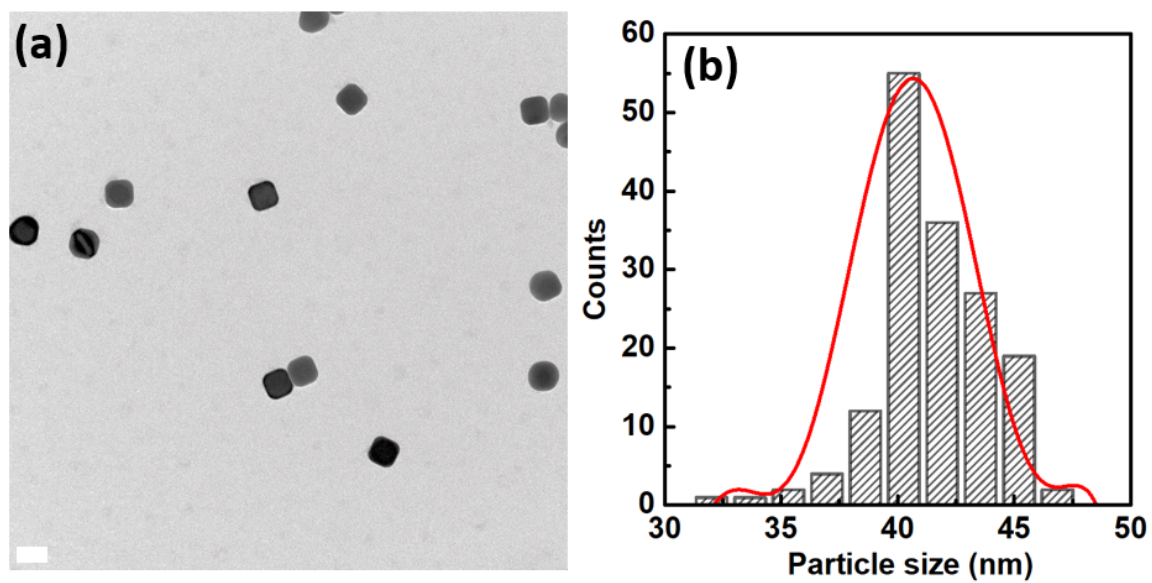


Figure S1 (a) A typical TEM image of AuNCs (Scale bar: 50 nm). (b) Corresponding histogram of AuNC size from TEM image analysis. The average size of AuNC is 41.0 ± 2.4 nm.

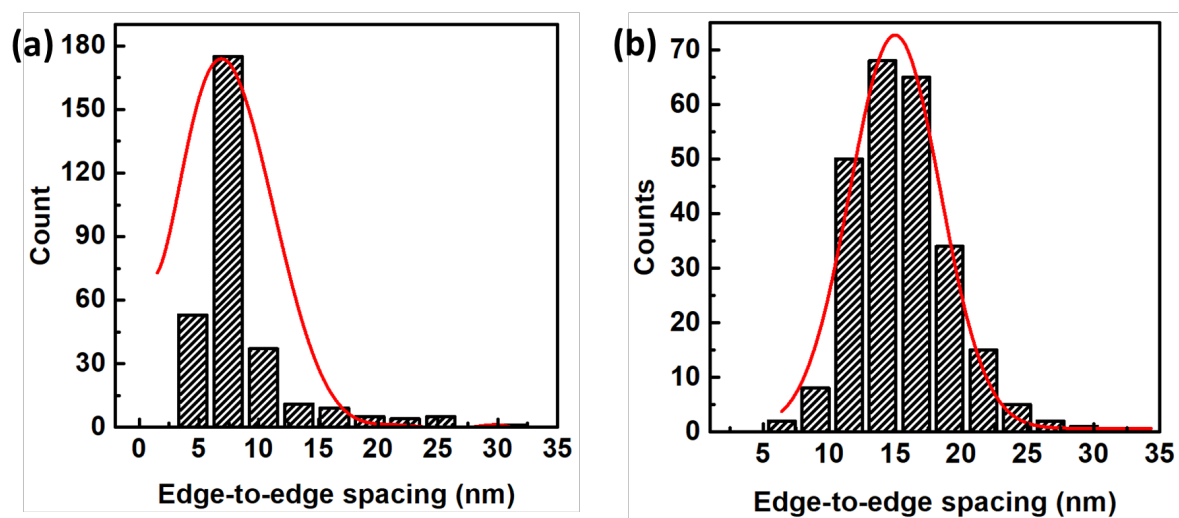


Figure S2 Histogram of edge-to-edge spacing of (a) PVP-capped and (b) PS-capped AuNCs measured from SEM image of AuNC plasmenes on Silicon wafer.

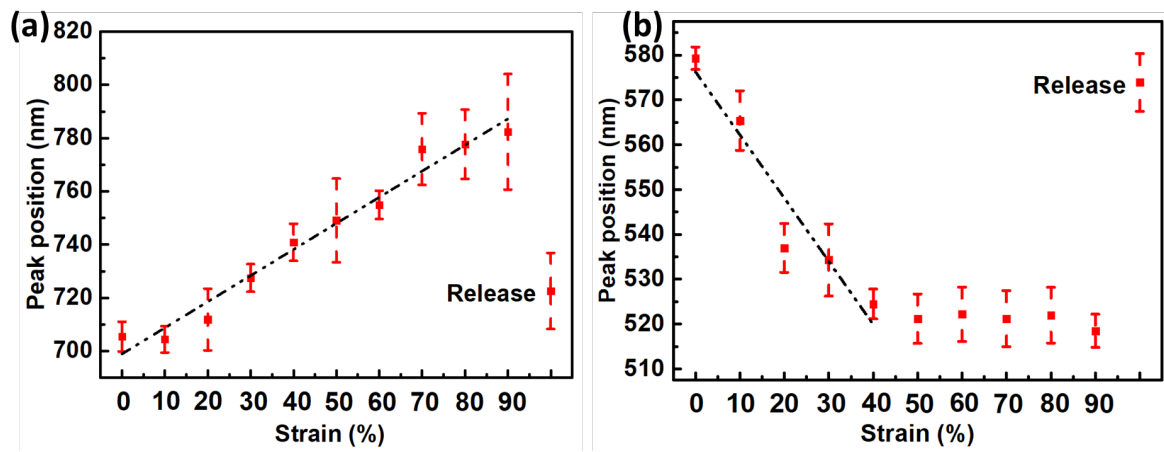


Figure S3 Plasmonic peak shifts of (a) PVP-based and (b) PS-based plasmene under strain from 0% to 90%.

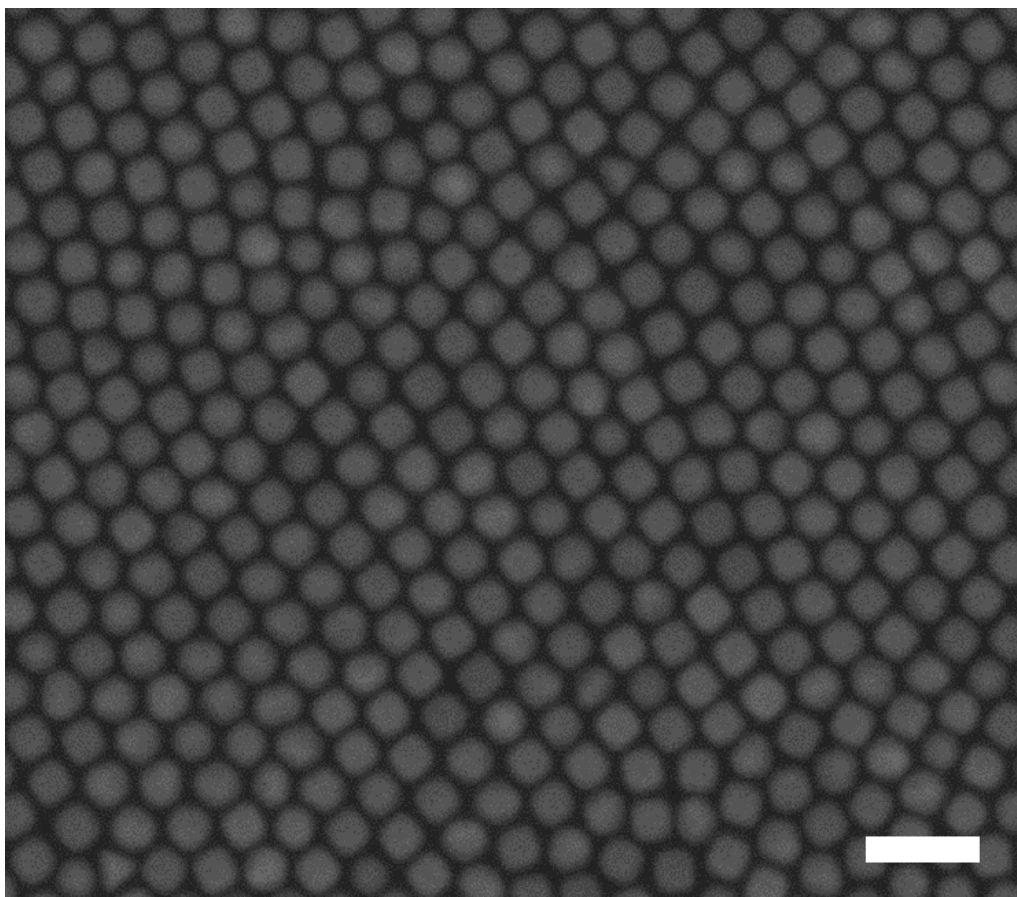


Figure S4 SEM image of small-spaced plasmene (ss-plasmene) on Silicon wafer. The PS with molecular weight of $M_n = 12\,000$ g/mol (12 k) was used for ss-plasmene. Scale bar: 100 nm.

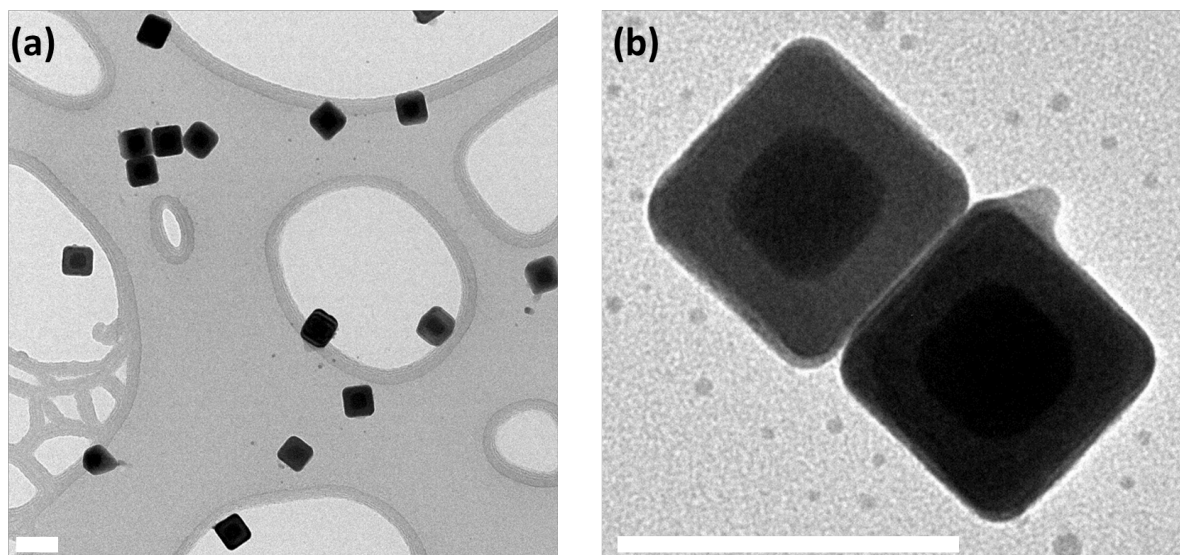


Figure S5 TEM images of Ag-coated AuNCs in (a) small and (b) large magnification. Scale bar: 100 nm

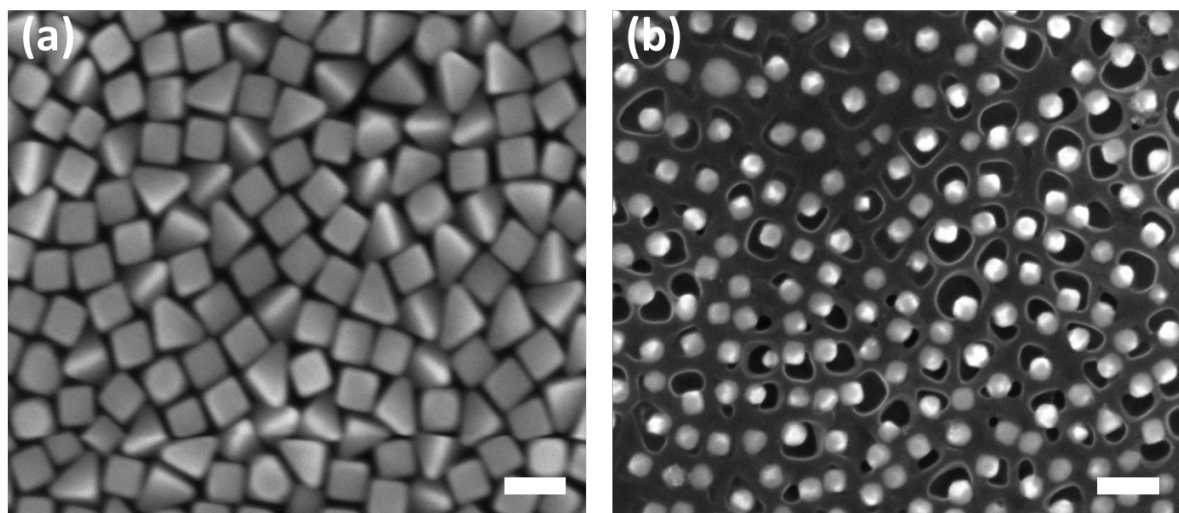


Figure S6 SEM images of (a) Ag-coated AuNC-based plasmene and (b) etched Ag-coated Au NC plasmene on Si wafer. (Scale bar: 100 nm)

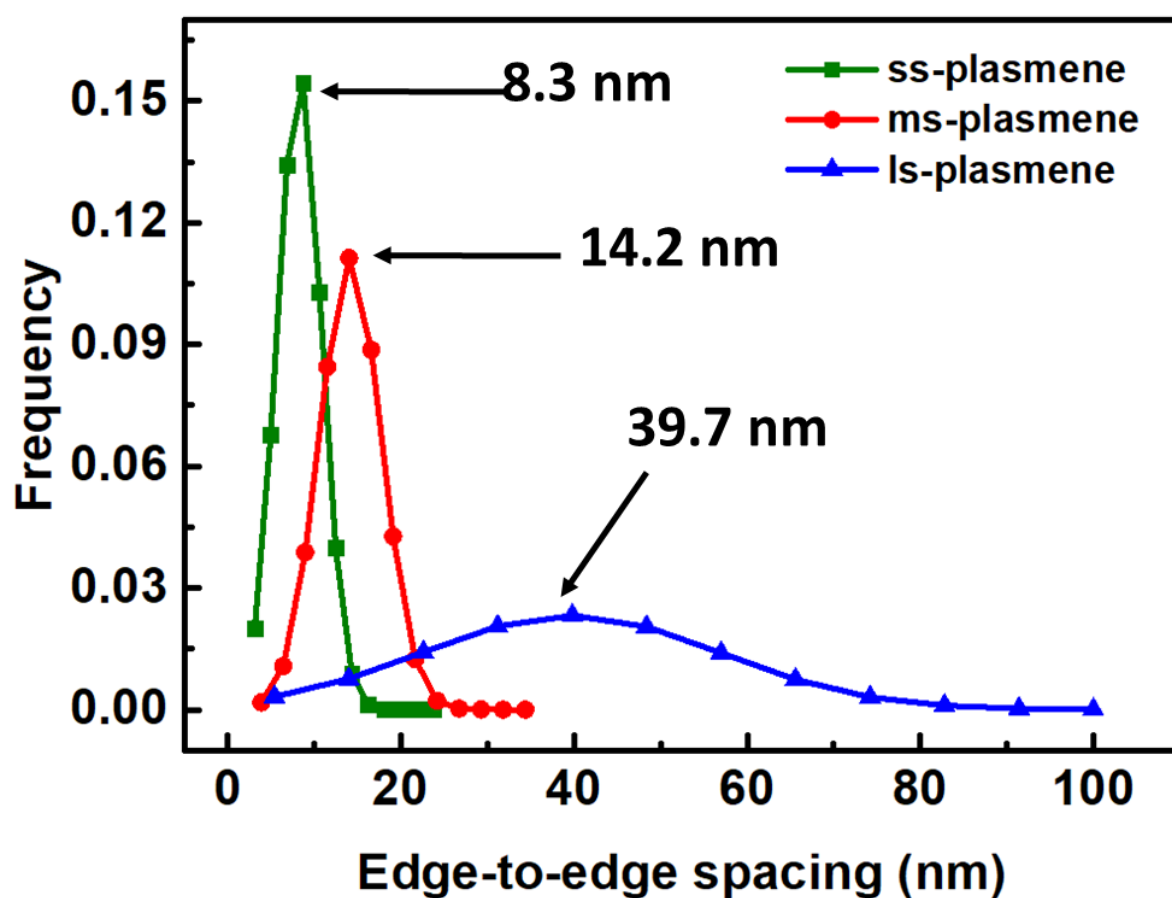


Figure S7 Statistic analysis of edge-to-edge spacing of small-spaced plasmene (ss-plasmene), medium-spaced plasmene (ms-plasmene) and large-spaced plasmene (ls-plasmene). The spacing was all measured from the SEM images on Si wafer.

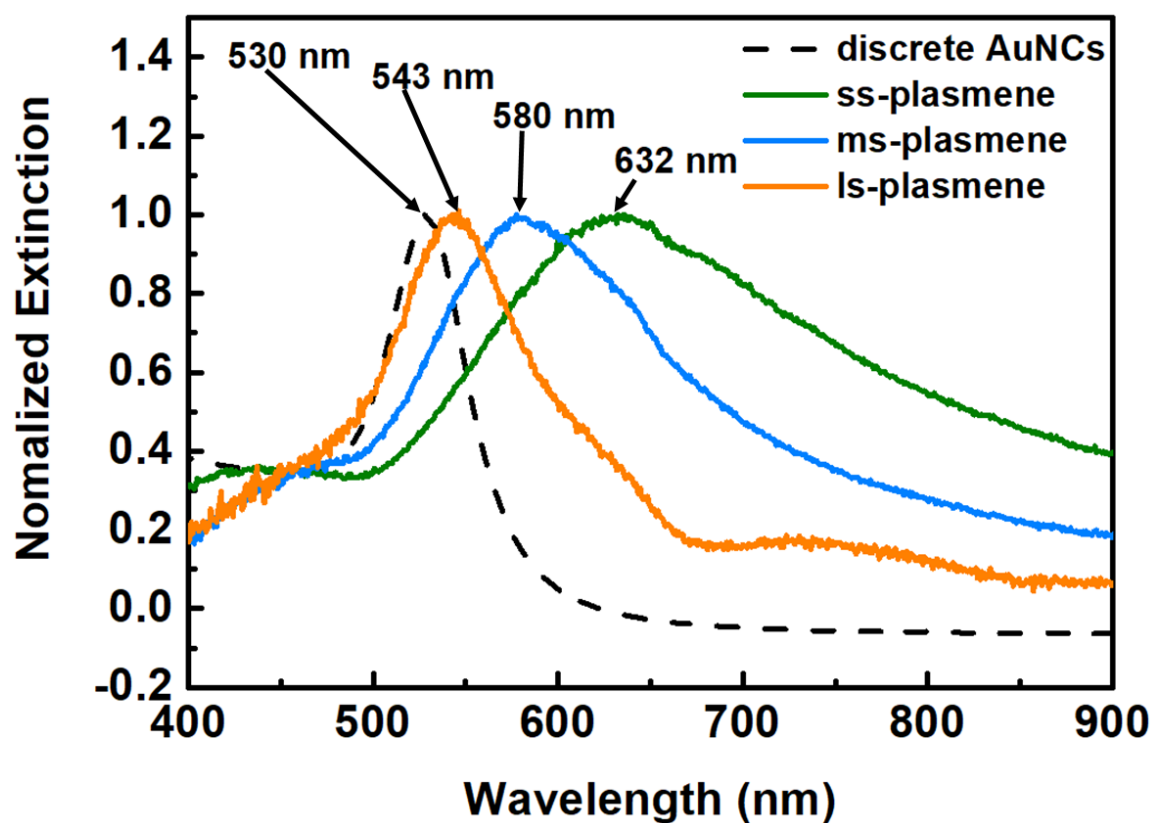


Figure S8 Representative extinction spectra of small-spaced plasmene (ss-plasmene), medium-spaced plasmene (ms-plasmene) and large-spaced plasmene (ls-plasmene) without any strains applied.

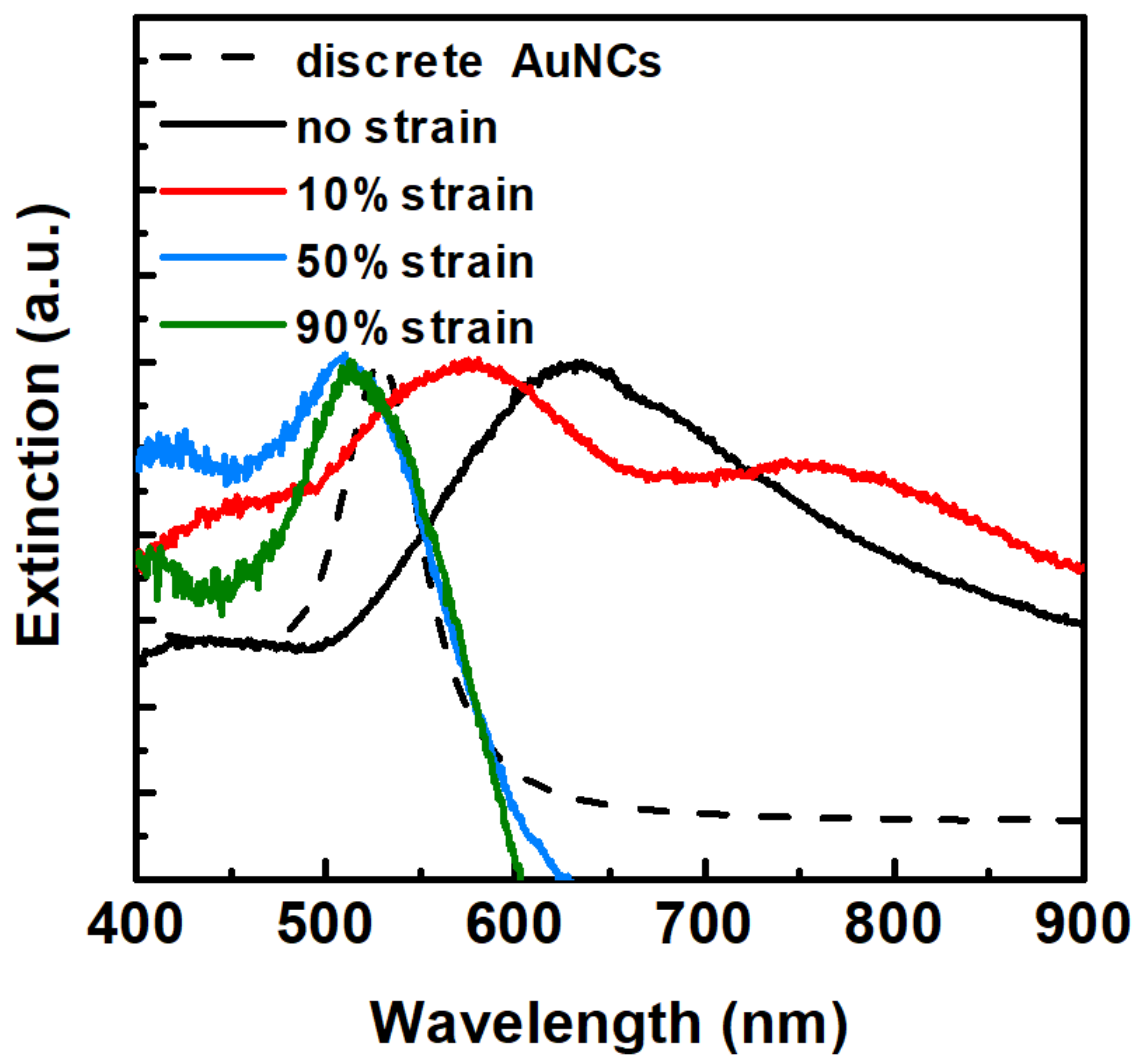


Figure S9 Representative extinction spectra of ss-plasmene under no strain, 10% strain, 50% strain and 90% strain.

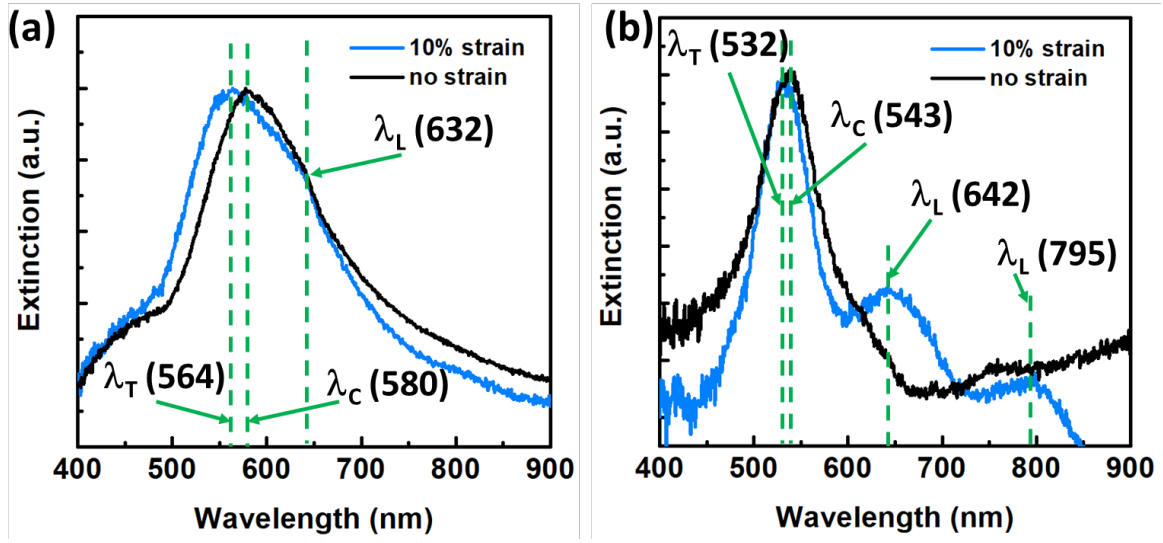


Figure S10 Typical extinction spectra of (a) ms-plasmene and (b) ls-plasmene under no strain and 10% strain.

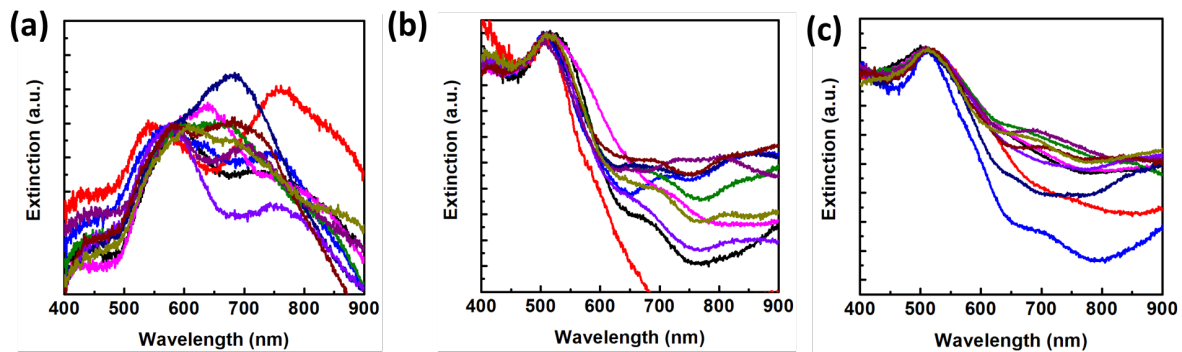


Figure S11 Extinction spectra acquired from 10 different locations in a particular ss-plasmene nanosheets under (a)10% strain, (b)50% strain, (c)90% strain. All spectra were normalized to high-energy peak λ_T . The microscope UV-VIS spectrophotometer with spot size of 6 μm x 6 μm was used to collected the spectra.

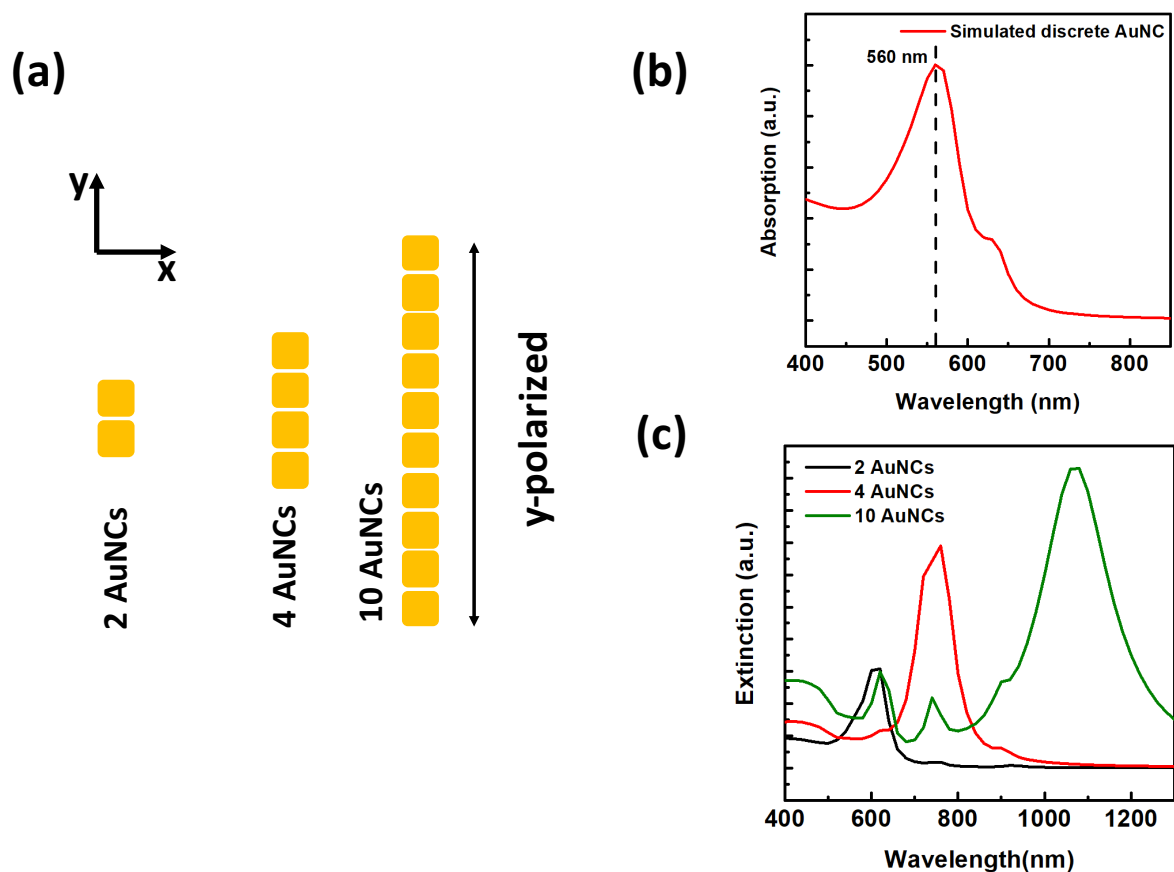


Figure S12 Modelling of AuNC oligomers with y-polarized light. (a) schematic of three chain-like 1D assemblies with 2, 4, 10 AuNCs. (b) Simulated absorption spectra of a single PS-capped AuNC with size of 40 nm in air. (c) Simulated extinction spectra of a rod-like structure formed by 2, 4 and 10 AuNCs with y-direction illumination. The edge-to-edge interparticle spacing in y-direction is 2 nm used for calculation.

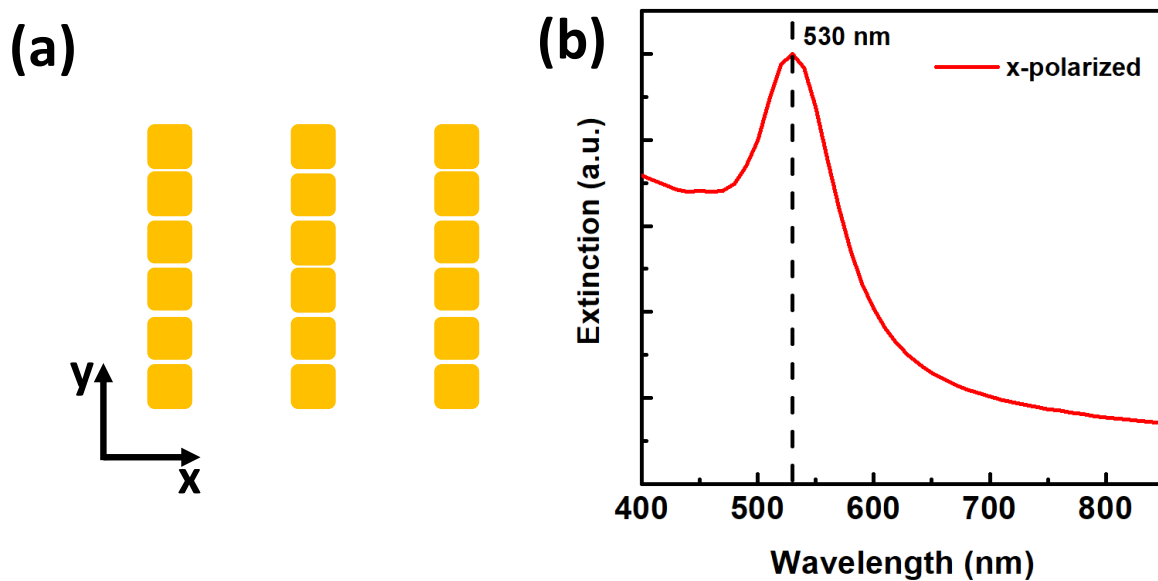


Figure S13 (a) Schematic illustration of strain-induced alignment of AuNCs leading to the formation of a rod-like structure in a stretched plasmene nanosheet. (b) Simulated extinction spectra of a 40nm-AuNC-based rod-like structure excited along x-direction. The edge-to-edge spacing in y-direction is 2nm, and the edge-to-edge spacing in x-direction is 70 nm. Infinite number of AuNCs are considered in the modelling.

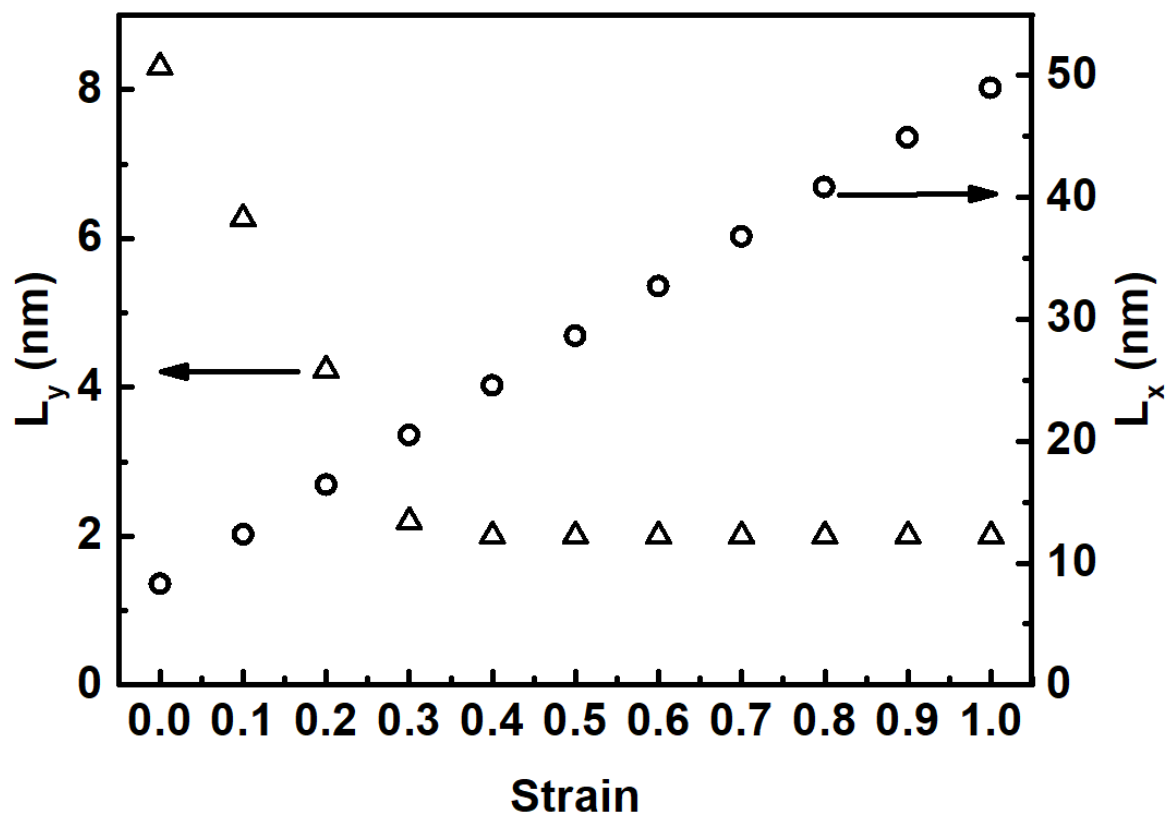


Figure S14 Calculated edge-to-edge spacing evolution with increasing strains (L_x : spacing in the stretching direction; L_y : spacing in the perpendicular direction).

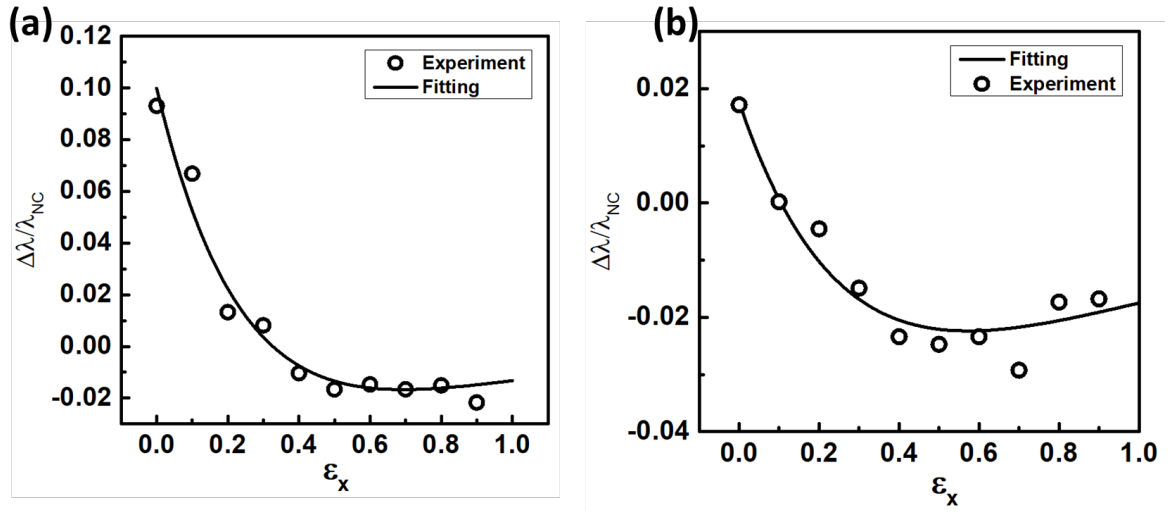


Figure S15 Dependence of fractional plasmonic shift ($\Delta\lambda/\lambda_{NC}$) as a function of strain for (a) medium-spaced plasmene (ms-plasmene) and (b) large-spaced plasmene (ls-plasmene). $\Delta\lambda$ is the plasmonic shift relative to the non-coupling peak of discrete AuNCs in solution, λ_{NC} . Solid line is the two-term plasmonic ruler model fitting by the equation (1) in the main body.

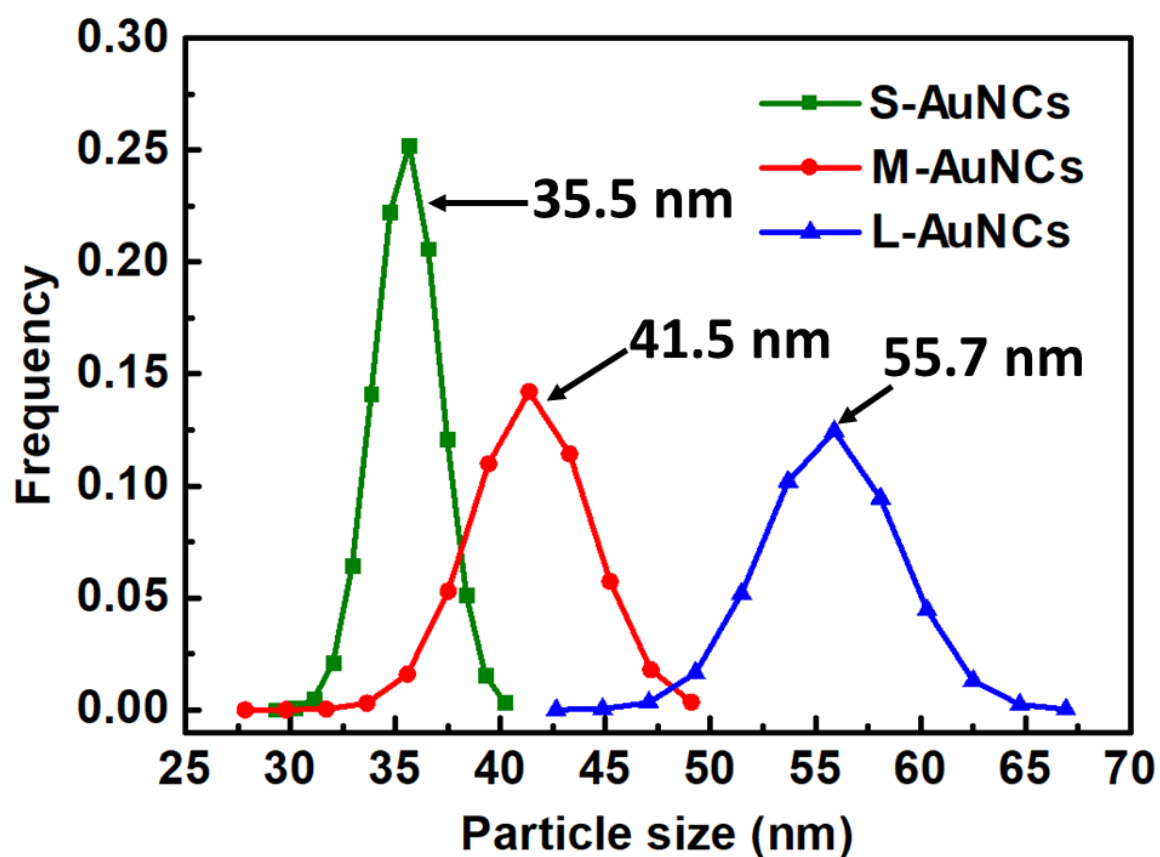


Figure S16 Statistic analysis of AuNCs sizes that were measured from SEM images of plasmene on Si wafer, which shows an averaged sizes of 35.5 nm for small-sized AuNCs (S-AuNCs), 41.5 nm for medium-sized AuNCs (M-AuNCs) and 55.7 nm for large-sized AuNCs (L-AuNCs).

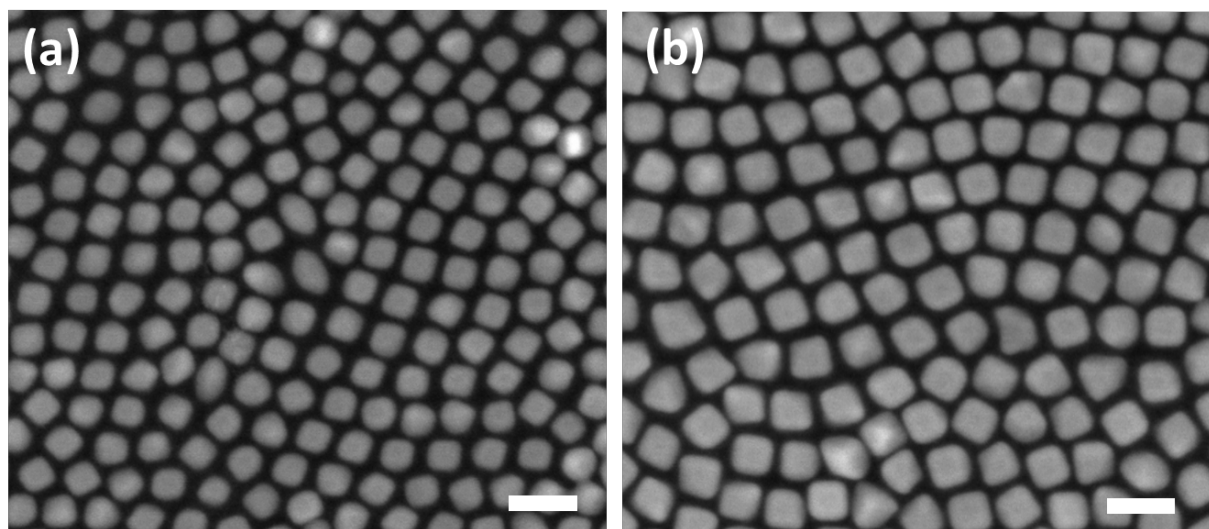


Figure S17 SEM images of (a) medium-sized AuNCs (M-AuNCs) and (b) large-sized AuNCs (L-AuNCs) plasmene on Si wafer. (Scale bar: 100 nm)

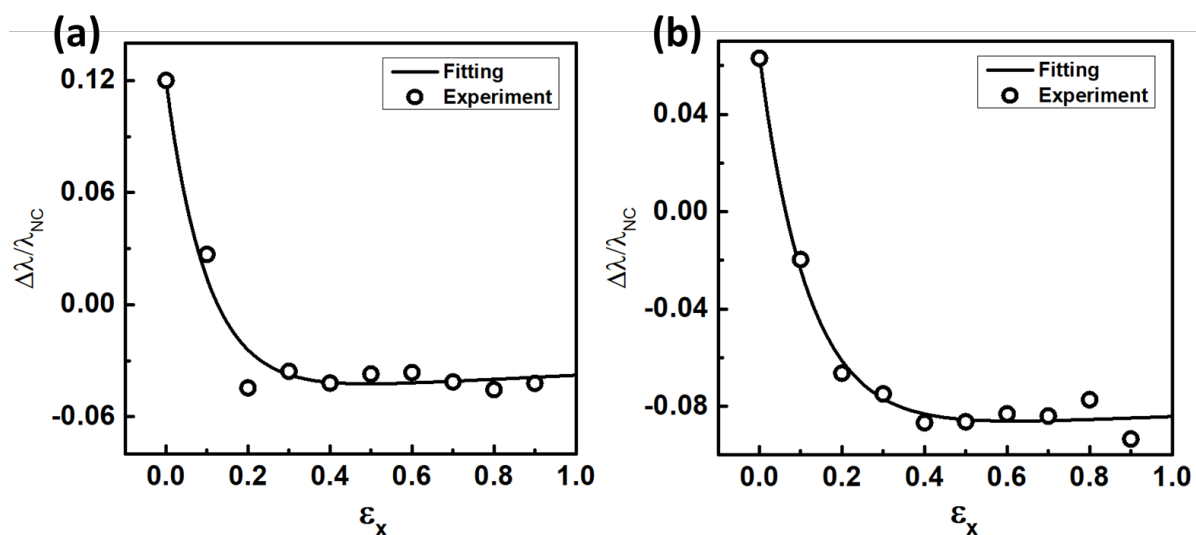


Figure S18 Dependence of fractional plasmonic shift ($\Delta\lambda/\lambda_{NC}$) as a function of strain for different plasmene nanosheets: (a) medium-sized AuNCs (M-AuNCs) plasmene, (b) large-sized AuNCs (L-AuNCs) plasmene. $\Delta\lambda$ is the plasmonic shift relative to the non-coupling peak of discrete AuNCs in solution, λ_{NC} . Solid line is the two-term plasmonic ruler model fitting by the equation (1) in the main body.

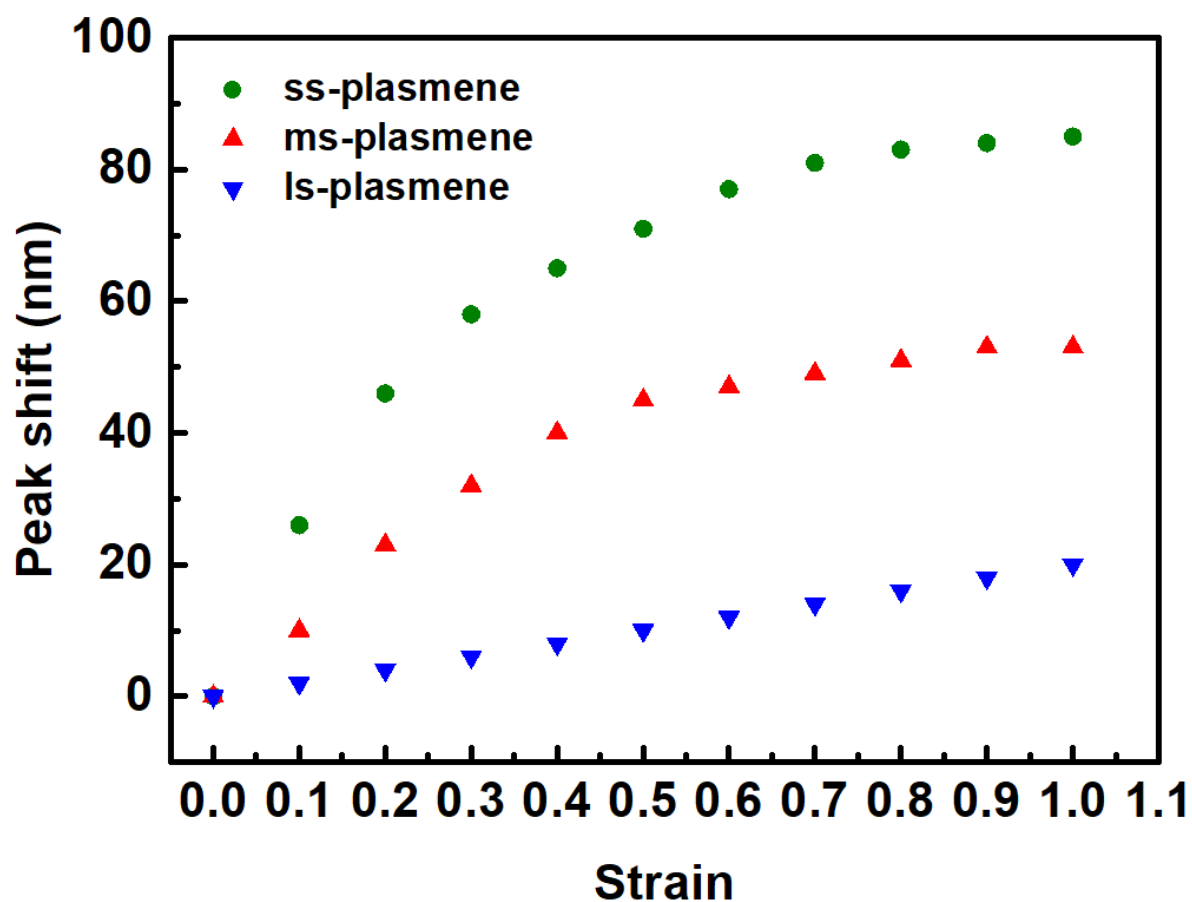


Figure S19 Theoretically calculated plasmonic peak shift relative to the calculated plasmon coupling peak at non-strained states for small-spaced plasmene (ss-plasmene), medium-spaced plasmene (ms-plasmene) and large-spaced plasmene (ls-plasmene). The refractive index used was 1.6 for ss-plasmene, 1.3 for ms-plasmene and 1.0 for ls-plasmene.

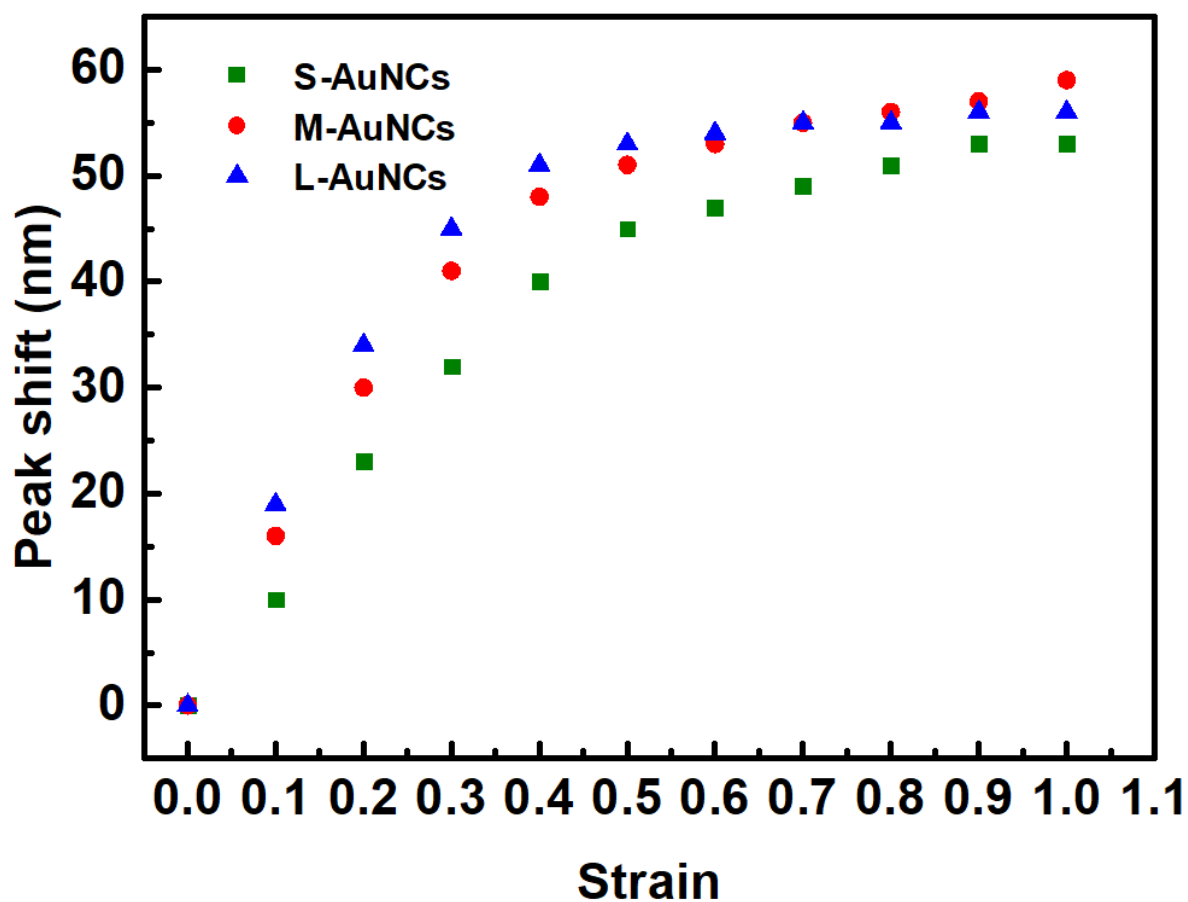


Figure S20 Theoretically calculated plasmonic peak shift relative to the calculated plasmon coupling peak at non-strained states for small-sized AuNCs (S-AuNCs) plasmene, medium-sized AuNCs (M-AuNCs) plasmene and large-sized AuNCs (L-AuNCs) plasmene. The refractive index of 1.3 was used for all plasmenes.

Table S1 Results for fitting parameters for various plasmene nanosheets by using the two-term plasmonic ruler equation as shown in the Equation 1 in the main body.

	a	τ_x	b	τ_y
ss-plasmene	1.33	0.35	1.25	0.41
ms-plasmene	0.77	0.33	0.70	0.41
ls-plasmene	0.33	0.33	0.31	0.70
S-AuNCs	0.77	0.33	0.70	0.41
M-AuNCs	0.41	0.10	0.22	3.54
L-AuNCs	0.39	0.12	0.30	12.29

References

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