

Phonon Modulation of Strongly Coupled Gold Tetrahedral Plasmonic Nanoparticles and a Carbocyanine J-Aggregate

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Supporting Information

Synthesis of gold tetrahedra

Chemicals. Hydrogen tetrachloroaurate trihydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$, $\geq 99.9\%$ trace metals basis), sodium borohydride (NaBH_4 , 99%), L-ascorbic acid (BioXtra, $\geq 99.0\%$), hydrochloric acid (HCl , 37%) and nitric acid (HNO_3 , 70%) were purchased from Sigma Aldrich. Hexadecyltrimethylammonium bromide (CTAB, $\geq 98.0\%$) and hexadecyltrimethyl ammonium chloride (CTAC, $\geq 95.0\%$) were purchased from TCI America. All chemicals were used as received without further purification. Ultrapure water (resistivity= $18.2 \text{ M}\Omega \cdot \text{cm}$ at 25°C) obtained from a Barnstead® GenPure® (Thermo Scientific) water purification system was used in all experiments. All glassware was cleaned with aqua regia (a mixture of HCl and HNO_3 in 3:1 volume ratio), rinsed thoroughly with water and dried before use.

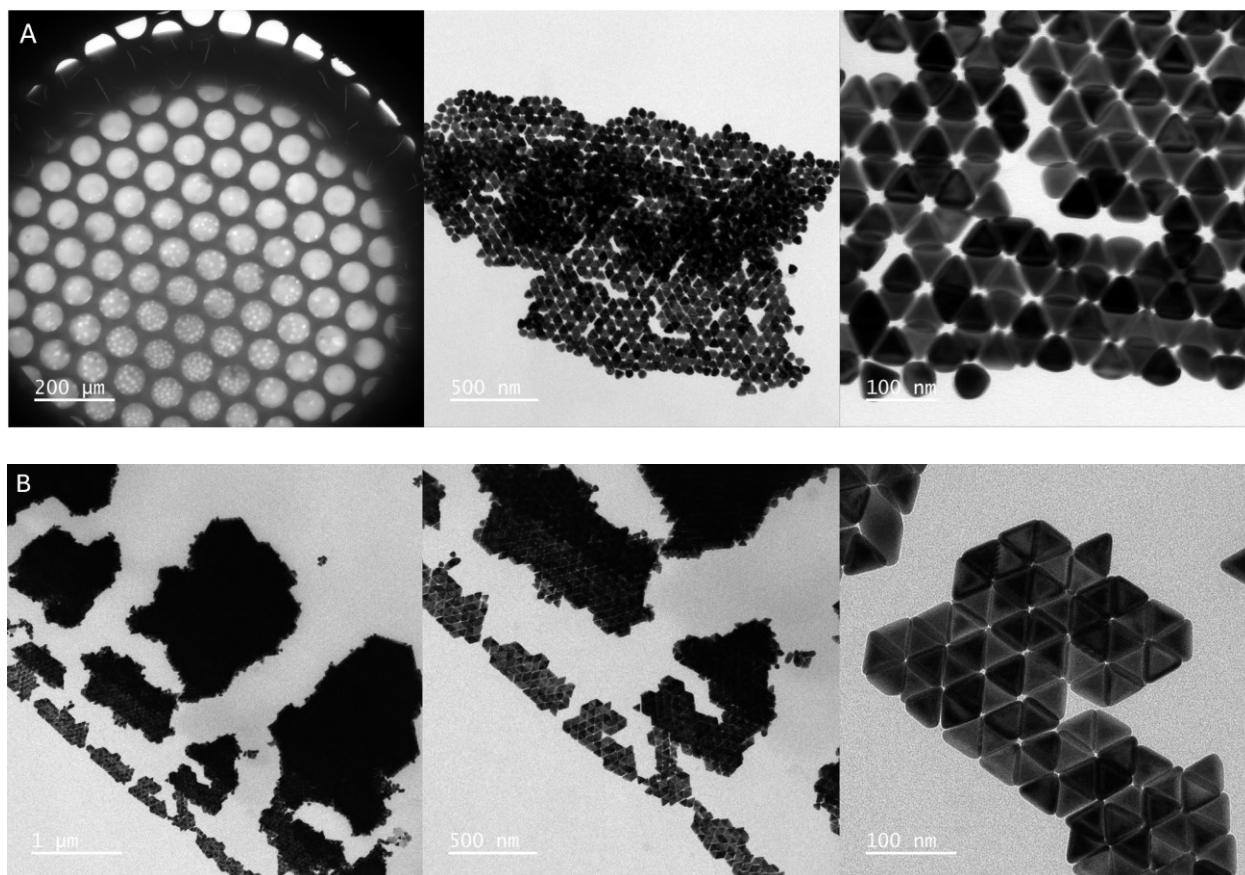
Synthesis of gold tetrahedra. Gold tetrahedra were synthesized based on a previously reported method.¹ The following section parallels the methods reported in Chandler et al.²

First, ~ 10 nm gold spheres were synthesized. Typically, 5 mL of 0.5 mM HAuCl_4 was mixed with 5 mL of 200 mM CTAB in a 20 mL scintillation vial at 28°C . Then, 0.6 mL of freshly prepared 10 mM NaBH_4 was quickly injected under rapid stirring. After stirring for 30 s, the mixture was left undisturbed at 28°C for 4.5 h to form the seed solution. Separately, a growth solution was prepared by mixing 80 mL of 200 mM CTAC, 80 mL of 0.5 mM HAuCl_4 and 60 mL of 100 mM L-ascorbic acid solutions. Upon the growth solution turning colorless, 4 mL of the seed solution was added and the resulting solution was gently stirred for 1 h at 28°C to grow ~ 10 nm nanospheres. Gold spheres were purified via two rounds of centrifugation at 8000 rpm for 90 min, each time re-dispersed into 20 mM CTAC (aq). The gold sphere solution was finally brought to an optical density (O.D.) of 2.0 at the extinction peak wavelength of ~ 521 nm using 20 mM CTAC (aq).

The gold tetrahedra were then prepared using gold spheres as seeds. Typically, 3 mmol (0.96 g) of CTAC, 1 mmol (0.364 g) of CTAB and 40 mL of H_2O were mixed under stirring at 30°C . Once CTAC and CTAB were fully dissolved, 20 mL of 200 mM L-ascorbic acid (aq) and 2 mL of the above gold sphere solution were added consecutively. Then, 20 mL of 2.5 mM HAuCl_4 solution was added dropwise via a syringe pump (4.8 mL/h) under gentle stirring at 29°C . The reaction mixture was left undisturbed at 29°C for 10 min. Gold tetrahedra were purified via three rounds of centrifugation at 7000 rpm for 15 min, each time re-dispersed into 20 mM CTAC (aq). Finally, gold tetrahedra were dispersed into ~ 1 mL of 20 mM CTAC. The size of gold tetrahedra was tuned by changing the volume of HAuCl_4 solution.

Purification of gold tetrahedra by using depletion attraction. Typically, 0.5 mL of the tetrahedron solution was added to a 15 mL centrifugation tube, then 4.5 mL of CTAC was added. Different concentrations of CTAC were employed to purify gold tetrahedra of different sizes.¹ This mixture was left undisturbed overnight to allow the flocculation and sedimentation of tetrahedra. The supernatant was then removed with a pipette, and the pellets at the bottom of the tube were further rinsed with 100 μ L CTAC twice to remove any weakly adsorbed impurity particles. The pellets were dispersed in 1 mL of 20 mM CTAC, purified via one round of centrifugation, and re-dispersed in 0.5 mL of 20 mM CTAC for later use.

TEM Images



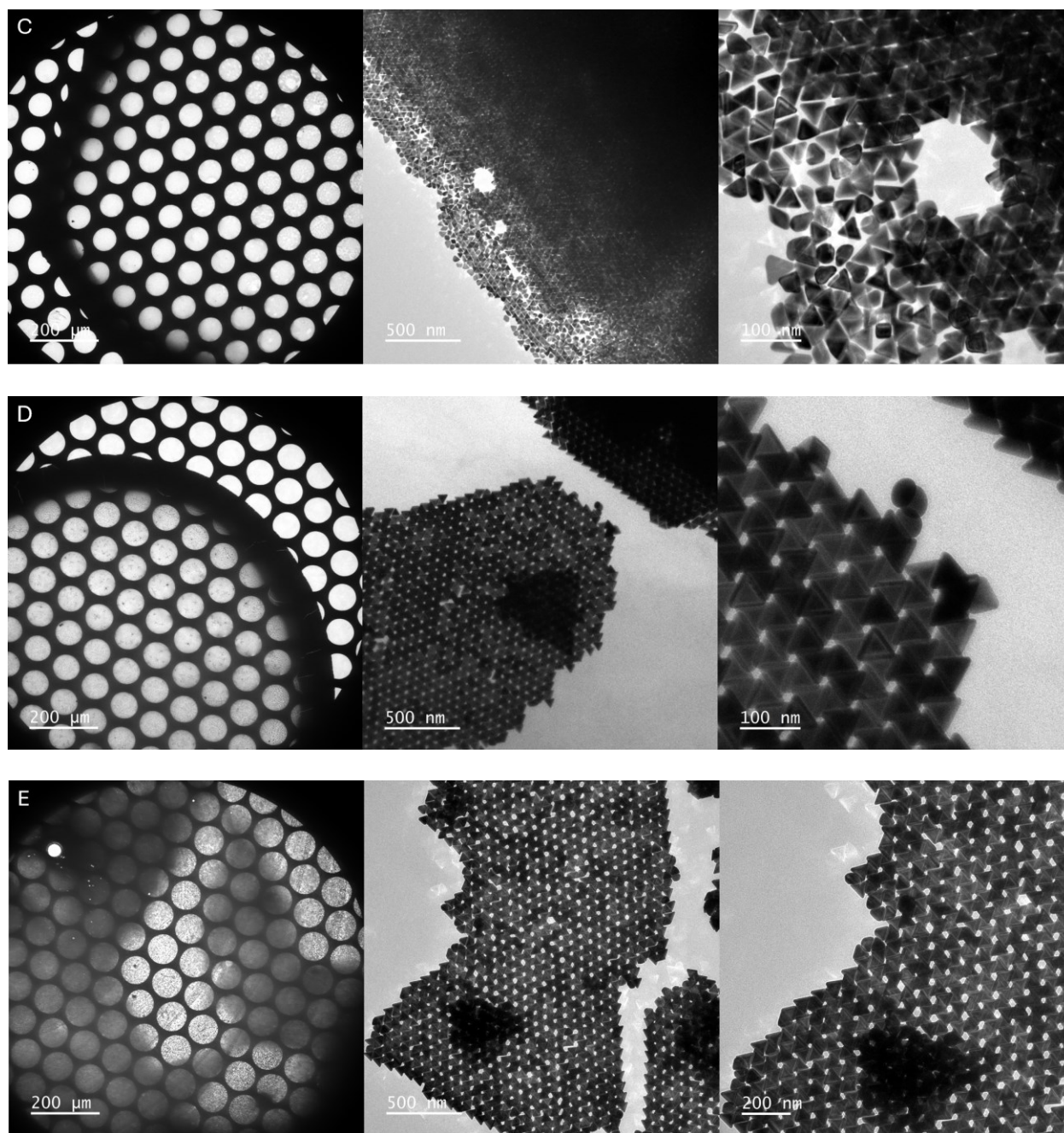


Figure S1: TEM images of samples A-E with LSPR ranging from 564- 622 nm at 3 levels of magnification.

Transient Absorption Power Dependent Studies

Additional studies at varying pump powers were performed on the LSPR=584 nm hybrid sample, excited at 530 nm. As the pump power increased, the upper and lower bleach features begin to converge until they resemble a single plasmon bleach.

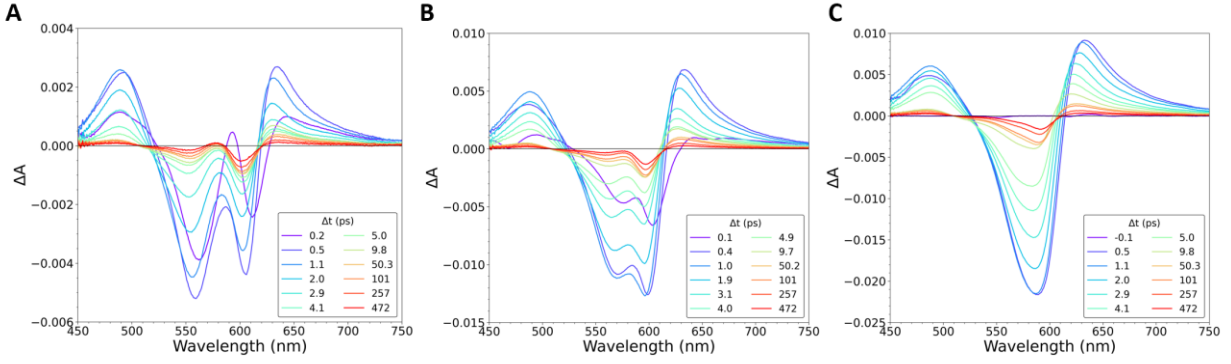


Figure S2: LSPR=584 nm hybrid polariton sample photoexcited at 530nm using A) $33 \mu\text{J}/\text{cm}^2$, B) $85 \mu\text{J}/\text{cm}^2$, and $151 \mu\text{J}/\text{cm}^2$.

Additional 2D OAS Analysis

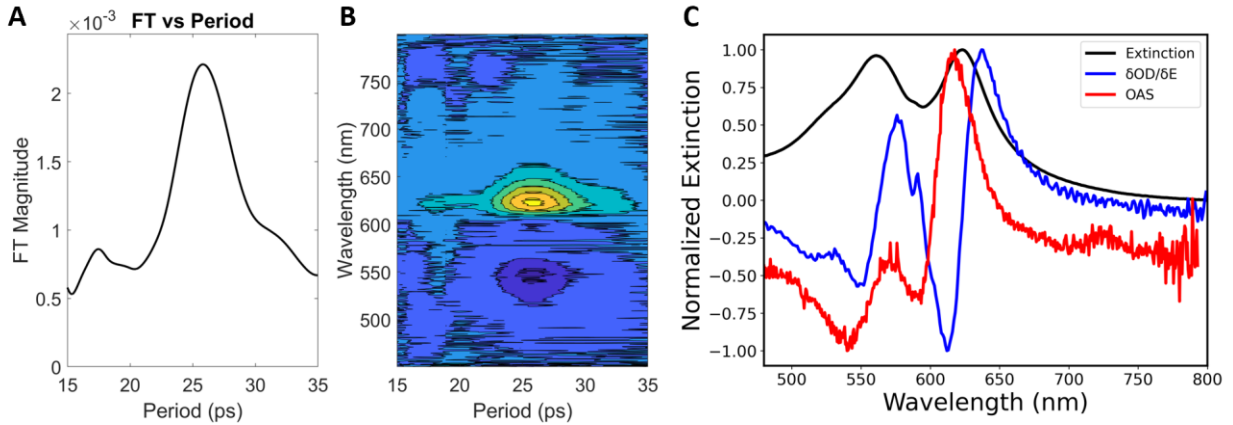


Figure S3: A) Averaged Fourier transform as a function of period of oscillation for LSPR= 584 nm polariton hybrids pumped at a power of $33 \mu\text{J}/\text{cm}^2$. B) 2D oscillation associated spectra for polariton hybrid. C) Static extinction spectrum and first derivative of static extinction for polariton hybrid. OAS slice taken at 25.78 ps.

Additional OAS analysis for the lowest power study of LSPR=594 nm were performed. While the lower polariton is still convoluted with the plasmon signal, the OAS signal shows the presence of two nodes where oscillations shift 180 degrees in phase, suggesting the presence of both polariton features. However, as noted in the main text, these oscillatory features do not appear to impact coupling strength of the two polaritons, and instead only result in oscillations of the amplitude.

Polariton Extinction Spectral Fits

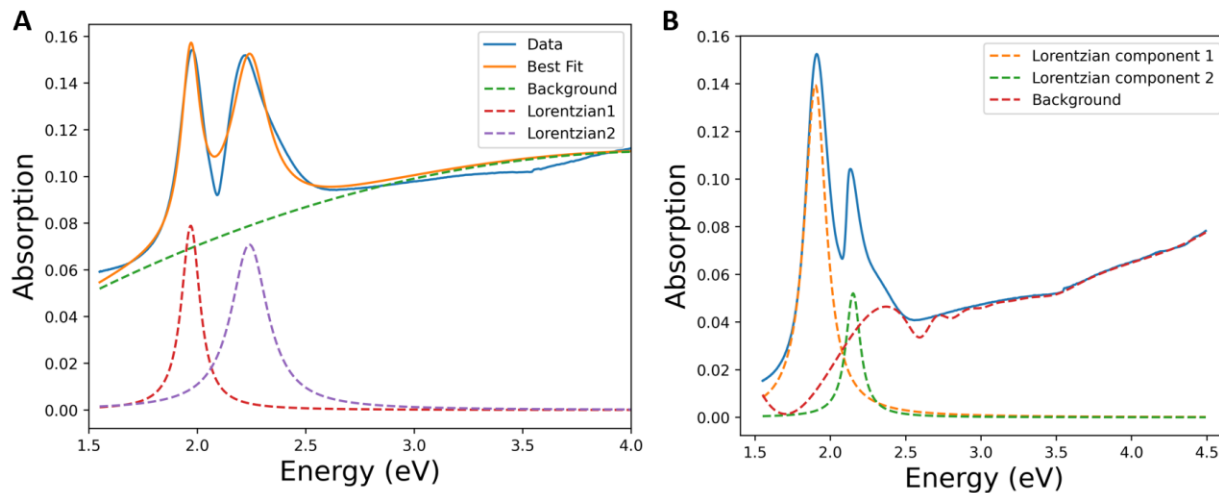


Figure S4: A) Static absorption of LSPR=584 hybrid polariton sample fit to sum of Lorentzian functions with background. B) Static absorption of LSPR=622 hybrid polariton sample fit to sum of Lorentzian functions with background.

References

1. Wang, Y.; Chen, J.; Zhong, Y.; Jeong, S.; Li, R.; Ye, X. Structural Diversity in Dimension-Controlled Assemblies of Tetrahedral Gold Nanocrystals. *J. Am. Chem. Soc.* **2022**, *144* (30), 13538-13546. DOI: 10.1021/jacs.2c03196.
2. Chandler, B. M.; Dey, D.; Wang, Y.; Ye, X.; Schatz, G. C.; Chen, L. X.; Schaller, R. D. Coherent Phonon Dynamics in Plasmonic Gold Tetrahedral Nanoparticle Ensembles. *J. Phys. Chem. Lett.* **2024**, *15* (38), 9686-9691. DOI: 10.1021/acs.jpcllett.4c02146.