

## Supporting Online Material

### **Manipulating the Optical Properties of Pyramidal Nanoparticle Arrays**

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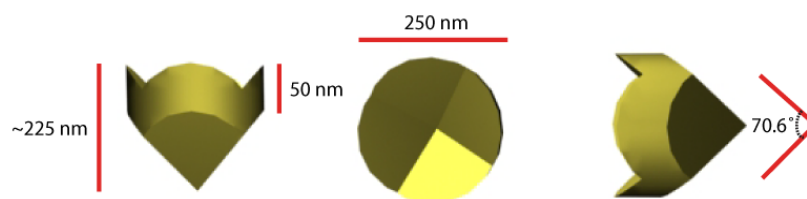
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## METHODS AND MATERIALS

### 1. Fabrication of Arrays of Au Pyramidal Particles

Phase-shifting photolithography was used to generate arrays of 250-nm diameter posts in positive-tone photoresist (Shipley 1805) on Si(100) wafers. Cr (10 nm) was evaporated on the posts (Kurt J. Lesker, PVD-75 E-beam Evaporation System), and the resist was removed by sonicating the pattern in acetone to reveal round holes in the Cr film. Pyramidal pits were formed beneath the holes by etching the exposed Si with an anisotropic etchant (23 g KOH, 33 mL isopropyl alcohol, in 100 mL H<sub>2</sub>O at 72°C). 50-nm of Au was evaporated on this pattern, and then the Cr film was removed using commercial etchant (Transene Corp., Danvers, MA) to reveal the Au pyramids within the Si pits.

In these experiments, the pyramidal shells with 250-nm circular bases have dimensions as shown in the image below.



### 2. Encapsulation of Au Pyramidal Particle Arrays in PDMS

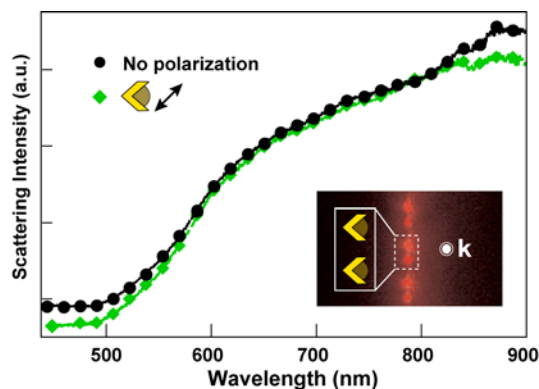
Substrates with arrays of Au pyramids within Si pits were exposed to an anisotropic Si etch such that Au pyramids could be supported on Si pedestals. Then, the Si was passivated with tridecafluoro-1,1,2,2-tetrahydrooctyl-1-trichlorosilane (Gelest, Inc.) for ~90 min. The Au pyramids were functionalized by immersing the pattern in a 3 mM solution of (3-Mercaptopropyl)trimethoxysilane (MPTMS, Aldrich) for 30 sec and washing with de-ionized water and ethanol. This pattern was placed in a solution of 1 mM HCl for 15 min and rinsed again with deionized water and ethanol.<sup>S1</sup> Next, the pattern was pressed into a thin layer of unpolymerized *h*-PDMS<sup>S2</sup> that was supported by a 0.5 mm-layer of Sylgard 184-PDMS. Before curing in an oven at 70°C for 30 min, the sample was placed into a dessicator (10 min) to remove air bubbles. Removal of the Si pedestal

substrate revealed Au pyramid arrays partially encapsulated in *h*-PDMS. The exposed Au tips were functionalized with MPTMS prior to encapsulation with *h*-PDMS.

### 3. Optical Characterization

Scattering spectra were collected with an inverted microscope (Eclipse TE-200, Nikon) using a standard transmission dark field (DF) setup. Collimated white light (Halogen) was passed through a DF condenser (NA = 0.8-0.95) equipped with a rotatable polarizer so that the incident light could be polarized at certain angles with respect to the particle array. Some of the light passing through the condenser acquires a component perpendicular to the sample.<sup>S3</sup> We found that blocking this component did not affect the spectral response; therefore, we omitted this step and assumed that most of the deflected light incident on the particle arrays maintained a polarization similar to the one as before the condenser. The light scattered from the sample was collected with a 20X objective (NA = 0.75) and focused onto a Czerny-Turner spectrometer (Triax 552/LN<sub>2</sub>-Cooled CCD, Horiba Jobin Yvon, Inc.). The scattering data was corrected by subtracting the PDMS background and then dividing by the spectrum of the white light source.

Comparison of spectra with pyramids in **orientation II** revealed that the spectra acquired when the polarization vector was 45° was very similar to the spectra produced from unpolarized white light and was roughly the average of spectra from parallel and perpendicular polarization directions (Fig. 4B).



#### 4. Numerical Calculations

All calculations on the pyramidal shell structures have been performed using the Discrete Dipole Approximation (DDA).<sup>S4-S6</sup> DDA discretizes the polarization using point dipoles to represent small volumes that collectively describe the response of the entire particle. Each dipole oscillates in response to the total electromagnetic field at that spatial location, obtaining a polarization written as

$$\mathbf{P}_j = \alpha_j \left[ \mathbf{E}_j^{\text{inc}} - \sum_{k \neq j}^N \mathbf{A}_{jk} \mathbf{P}_k \right] \quad (1)$$

where  $\alpha$  is the polarizability,  $\mathbf{E}^{\text{inc}}$  is the incident field, and  $\mathbf{A}$  is an interaction matrix. The polarizability is determined from experimental values for the dielectric constant of gold<sup>S7</sup> using a lattice dispersion relation.<sup>S8</sup> The total field is the superposition of an incident plane wave, and the fields radiating from all of the other dipoles in the array given by

$$\mathbf{A}_{jk} \mathbf{P}_k = \frac{\exp(ikr_{jk})}{r_{jk}^3} \left\{ k^2 \mathbf{r}_{jk} \times (\mathbf{r}_{jk} \times \mathbf{P}_k) + \frac{(1 - ikr_{jk})}{r_{jk}^2} \left[ r_{jk}^2 \mathbf{P}_k - 3\mathbf{r}_{jk} (\mathbf{r}_{jk} \cdot \mathbf{P}_k) \right] \right\} \quad (2)$$

Assigning the diagonal elements of matrix  $\mathbf{A}$  to be  $\alpha^{-1}$  allows the system of  $N$  complex, linear equations to be written as the matrix equation

$$\tilde{\mathbf{A}} \tilde{\mathbf{P}} = \tilde{\mathbf{E}}^{\text{inc}} \quad (3)$$

where  $\tilde{\mathbf{P}}$  and  $\tilde{\mathbf{E}}^{\text{inc}}$  are  $3N$ -dimensional vectors and  $\tilde{\mathbf{A}}$  is a  $3N \times 3N$  matrix. Sizeable particles such as these require a large number of dipoles to accurately represent the true response, so a matrix inversion to obtain the polarization is not feasible. Alternatively, an iterative solution can be used to find the polarization of each dipole. The extinction and absorption cross sections are calculated by

$$C_{\text{ext}} = \frac{4\pi k}{|\mathbf{E}^{\text{inc}}|^2} \sum_{j=1}^N \text{Im} \{ \mathbf{E}_j^{\text{inc},*} \cdot \mathbf{P}_j \} \quad (4)$$

and

$$C_{\text{abs}} = \frac{4\pi k}{|\mathbf{E}^{\text{inc}}|^2} \sum_{j=1}^N \left[ \text{Im} \left\{ \mathbf{P}_j \cdot (\alpha_j^{-1})^* \mathbf{P}_j^* \right\} - \frac{2}{3} k^3 \mathbf{P}_j \cdot \mathbf{P}_j^* \right]. \quad (5)$$

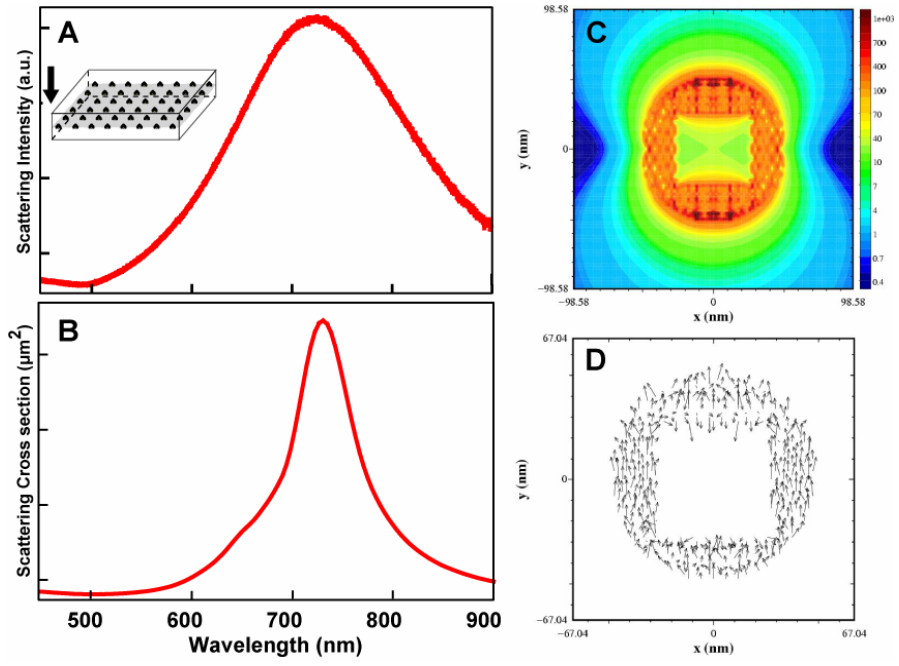
The scattering cross section (6) is then just the difference between (4) and (5):

$$C_{\text{scat}} = C_{\text{ext}} - C_{\text{abs}} \quad (6)$$

We have represented each face of the pyramidal shell as an equilateral triangle. The shell thickness is assumed to be constant from the base to tip. The sharp tips in the base of the pyramid have been rounded off, so as to better represent the true shape of the particles fabricated experimentally. This makes the base of the shell structure circular not square. The effects on the optical spectrum are to blue shift the dominant spectral features, as well as decrease the peak intensities.

### 5. A Test Case: 100-nm Au Pyramidal Particles

To provide a calibration for the DDA calculation for a particle structure that is not as difficult to study as 250-nm particles, we present results for 100-nm particles. Square arrays of 100-nm diameter Au pyramidal particles with a 400-nm pitch (center-to-center) were fabricated and optically characterized using the procedures described above. The plane of the nanoparticle array was oriented perpendicular to the optical axis of the microscope with tips pointed toward the light source (**A**, inset). The scattering spectrum obtained with unpolarized white light exhibited a very strong peak at 725 nm (**A**). The calculated scattering spectrum for a 100 nm particle with a 22-nm shell agrees well with experiment when the polarization vector is parallel to the base (**B**). This resonance corresponds to a well-defined dipole excitation localized in the base of the pyramidal shell as can be seen by the field intensity (**C**) and polarization plot (**D**). The vectors indicate a nanoparticle polarization is consistent with dipolar excitation, where there is one positively charged region and one negatively charged region.



## REFERENCES

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