Self-Organized Silver Nanoparticles for Three-Dimensional Plasmonic Crystals

Methods

Nanocrystal Synthesis: Octahedra-shaped nanocrystals were prepared using a polyol reduction of silver ions. Silver nitrate ($AgNO_3$), cupric chloride ($CuCl_2$), poly(vinyl pyrrolidone) (PVP, Mw=55,000), and 1,5-pentanediol used as obtained from Sigma Aldrich. A 0.043 M solution of $CuCl_2$ was prepared prior to the nanocrystal synthesis and stored at room temperature. The $AgNO_3$ precursor solution was prepared by sonicating 0.20 g $AgNO_3$ and 40 μL of the $CuCl_2$ solution in 5 mL of 1,5-pentanediol until all the salt crystals were dissolved, around 30 min to a few hours. The solution turned a bright-yellow orange color. The PVP precursor solution was prepared by dissolving 0.10 g PVP in 5 mL pentanediol. The reaction solution was prepared by heating 20 mL pentanediol in a 100 mL glass round bottom flask under continuous stirring in an oil bath heated to 193°C. It should be noted that the actual temperature of the reaction solution inside the flask was measured to be 175°C. The $AgNO_3$ and PVP precursor solutions were alternately injected into the hot pentanediol at a rate of 500 μL/min and 320 μL/min respectively. The injections were continued until the solution turned an opaque yellow color (after approximately 6 minutes), at which point the solution was characterized by UV-Vis spectroscopy. If spectrum indicated the formation of silver cubes, the reaction was continued until the UV-Vis spectrum indicated the formation of silver octahedra (approximately 100 minutes). If the spectrum did not show the presence of nanocubes, the reaction resulted in a heterogeneous mixture of shapes and sizes and precursor injections were not continued. Upon reaction completion, the hot flask was immediately removed from the oil bath and allowed to cool to room temperature under constant stirring.

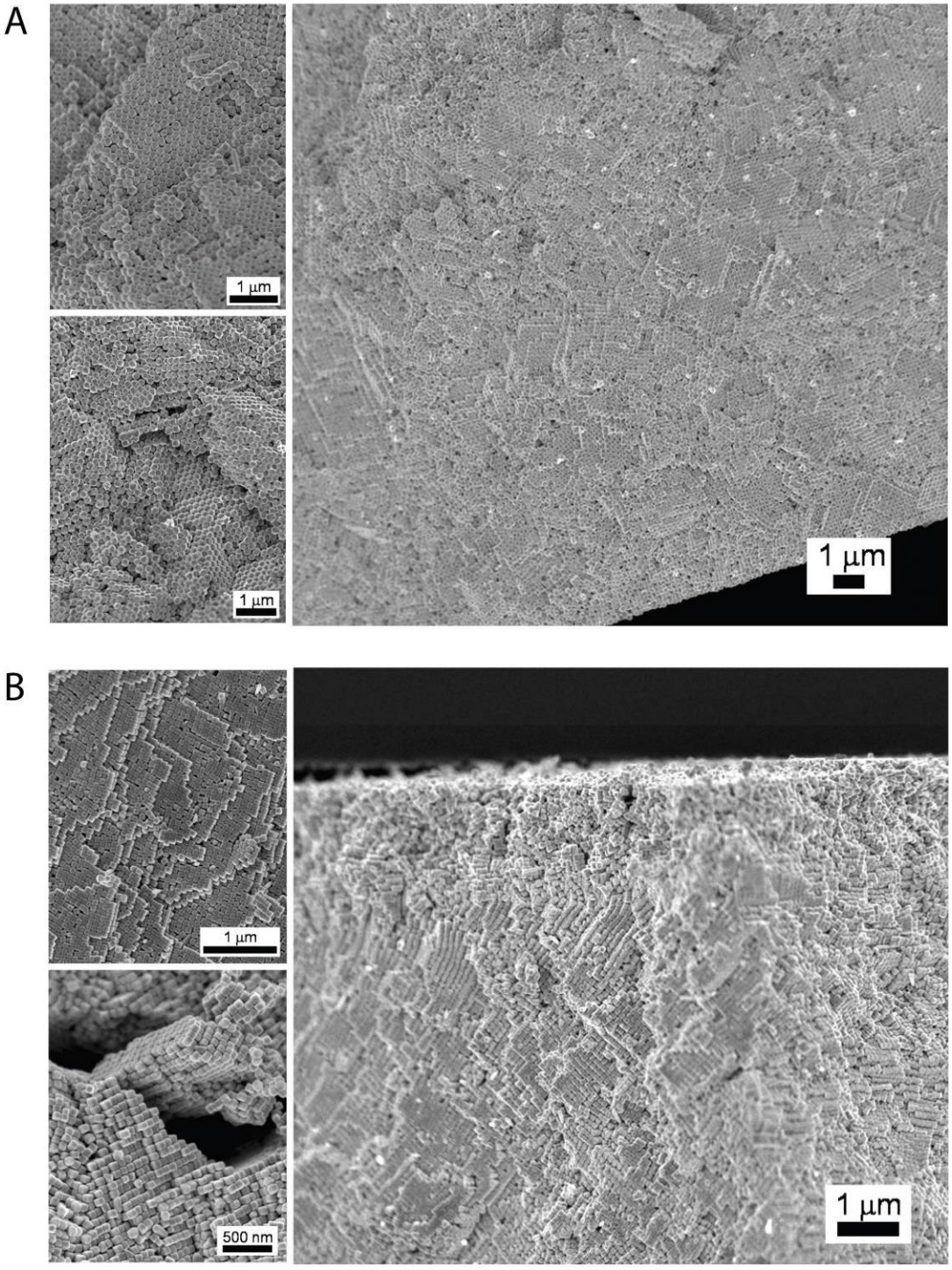
Nanocrystal purification: The as-made nanocrystal dispersions were diluted to a total volume of 300 mL using absolute ethanol and then centrifuged at 5000 rpm for 30 minutes. After removing the supernatant, the pellet was redispersed in a 1:1: mixture of deionized water and ethanol to obtain a total dispersion volume of approximately 100 mL. This solution was then filtered through a 5 μm membrane filter to remove nanowires, which are a common by-product of the synthesis. The solution was then subsequently filtered through membranes with decreasing pores sizes (0.65, 0.45, and 0.22 μm PVDF hydrophilic Durapore filters, Millipore). The final solution was then centrifuged and redispersed at the desired concentration in either water or ethanol.

Nanocrystal assembly: The purified nanocrystal dispersion was brought to a final concentration of ~10^{13} particles/cm^3 in ethanol water. For dried assemblies, a 30 μL drop of the suspension was placed on a hydrophobic silicon substrate treated with HMDS. The drop was left uncovered and allowed to evaporate at room temperature.

TEMPEST Simulations: TEMPEST uses the staggered grid developed by Yee. The background medium, water, was modeled as loss-less with a frequency independent refractive index of 1.2. The dielectric function of silver was simulated as a Drude model and implemented with an auxiliary differential equation formulation reported by Kupka et al. Periodic boundary conditions were used in the plane of the supercrystal to model an infinitely periodic array. Complex frequency shifted perfectly matched layers were used to terminate the computational grid without reflection in the third dimension. The cell size was chosen as 2 nm to achieve the appropriate spatial resolution and the time step was chosen as 1.93×10^{-4} fs to avoid numerical instabilities at sharp corners.

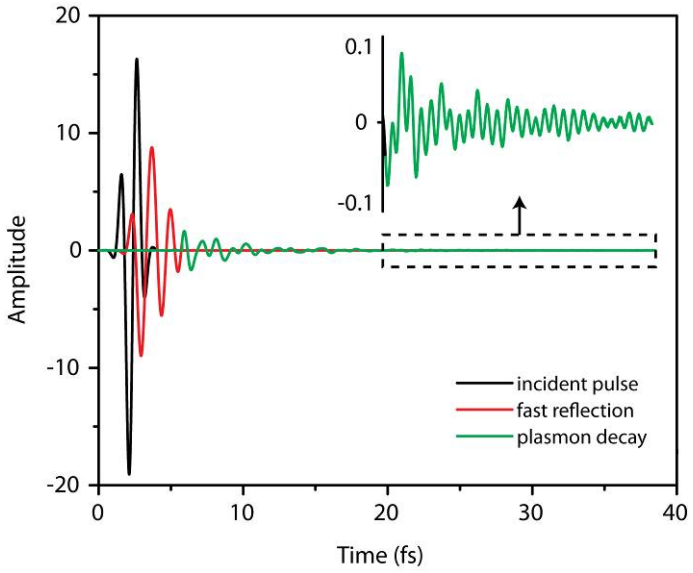
Plane-wave illumination was used to compute reflections and steady-state field patterns within the super-crystal. Reflection and transmission efficiencies were computed by illuminating the crystal with a pulse and Fourier transforming the reflected and transmitted pulses. The pulse had a modulated Gaussian temporal profile with a center frequency of 8.3×10^{14} Hz (361 nm wavelength) and a full-width half-max (in field amplitude) bandwidth of 89% of the center frequency. Losses due to resistive heating were computed through conservation of power. Sinusoidal temporal profiles were used to compute steady-state field patterns within the super-crystal.

S1



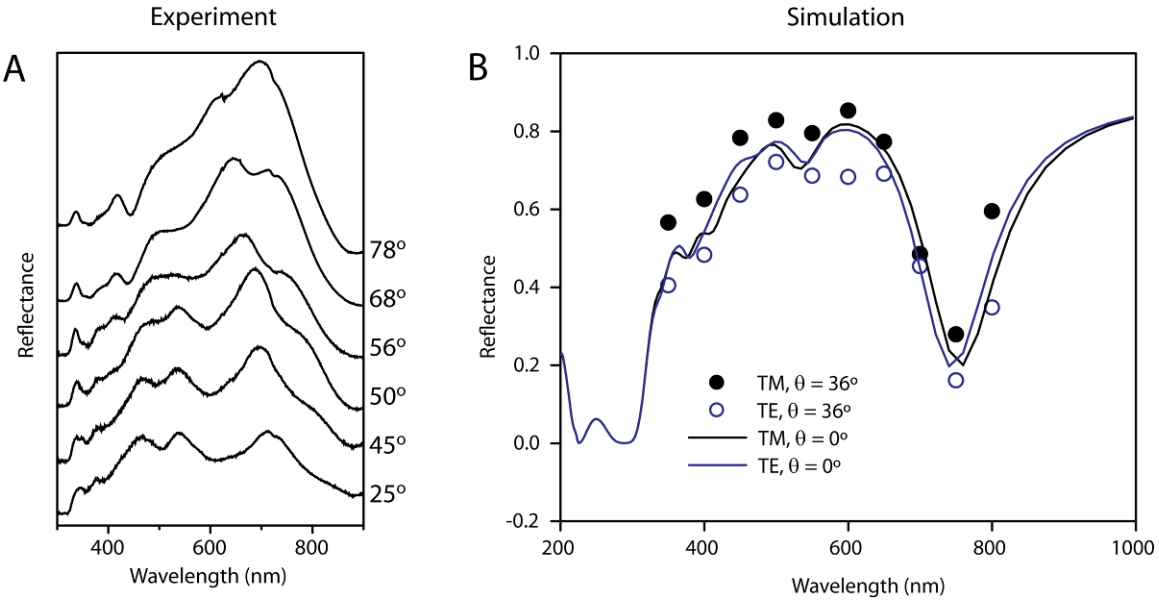
S1. Nanocrystal superlattices composed of different polyhedral building blocks. Assemblies of (A) cuboctahedra and (B) cubes were fabricated by drying a droplet of the appropriate colloidal suspension on a solid substrate. SEM images were obtained after cleaving the evaporated droplet.

S2



S2. Simulated electromagnetic response of a nanocrystal slab with 6-nm spacing. After subjecting the slab to an incident light pulse (black), light is either immediately reflected (red) or coupled into a slowly decaying plasmon resonance (green). Inset: The tail-end amplitude displayed for clarity.

S3



S3. Angular and polarization dependence of optical reflectance. (A) Reflectance spectra of a closest-packed supercrystal assembly taken at different angles of incidence. Spectra were obtained using fiber optic couplers for excitation and collection. (B) Simulated reflectance curves for an off-axis angle of incidence and rotated polarization.