

Supporting Information for

Extended Seed-Mediated Silver Nanorods: Co-solvent Mediated Synthesis and Plasmon Mode Reassignment

Jun Zhu,^{a,†} Ruixue Chen,^{a,†} Alexander Al-Feghali,^a Amy Szuchmache Blum,^a R. Bruce Lennox^{a,*}

a. Department of Chemistry and Quebec Center for Advanced Materials (QCAM), McGill

University, 801 Sherbrooke St. West, Montreal, QC H3A 0B8, Canada

Experimental Section

Commercial reagents and general instrumentation: The compounds cetyltrimethylammonium bromide (CTAB, >99%), silver nitrate (>99%), trisodium citrate (>99%), L-ascorbic acid (ACS grade), and sodium borohydride were purchased from Aldrich and used as received. All reagent solutions were prepared using MilliQ water (>18.2 M Ω). Freshly prepared silver nitrate and ascorbic acid solutions were wrapped in aluminum foil and stored in the fridge before use. To avoid degradation, these solutions were freshly prepared every week. UV-Vis spectra were measured with a Cary 5000 UV-Vis-NIR spectrometer (Agilent Technologies). Transmission electron microscopy (TEM) images were collected using a Thermo Scientific Talos F200X G2 (S)TEM. Size distribution was calculated after measuring 100 AgNRs for each sample. FDTD simulations were performed using Ansys' Lumerical FDTD.

General procedure for the seed mediated synthesis of silver nanorod.

Preparation of silver nanoparticle seed. Adding 10 μ L of 50 mM AgNO₃ and 6.7 μ L of 75 mM trisodium citrate into 1.923 mL of Milli-Q water. 60 μ L of fresh prepared ice-cold 10 mM NaBH₄ was added under mild stir. Continue stir for 1 min, the dark greenish AgNP seed solution was stored at room temperature for 2h before use.

AgNR formation. 25 μ L of 50 mM AgNO₃ solution and 250 μ L of 100 mM ascorbic acid was mixed with 5 mL of 100 mM CTAB. Vary amount of seed solutions (50-200 μ L) was added under stirring. AgNR formation was initiated by mixing 50 μ L of 1M NaOH solution with the growth solution. After gentle mixing, the reaction was left undisturbed in 27 °C water bath for 1h. The crude AgNR was centrifuged at 6,000 g for 5 min. The upper clear solution was discarded. Redissolve the precipitation into 5 mL of 1 mM CTAB solution, 0.5 mL of 25 wt% CTAC solution

was added. AgNR precipitates within one hour. Discard the up clear yellow supernatant, redissolve the precipitate into 5 mL of water for characterization.

For modified synthesis of AgNR in this research, 0.1 mL acetonitrile was added to 5 mL of 100 mM CTAB before mixing with 25 μ L of 50 mM AgNO₃ solution and 250 μ L of 100 mM ascorbic acid. All other synthesise procedures are the same as described above.

FDTD simulation. FDTD simulations were performed using Ansys' Lumerical FDTD. The silver dielectric functions was assessed from Johnson and Christy's data.¹ The simulation was discretized at 0.125nm minimum mesh step with an auto non-uniform mesh at accuracy 8 and the mesh refinement used was the conformal variant 0. A uniform mesh was applied to the nanorod with a 1nm buffer. The simulation time was set at 1000fs, in a 1.33 refractive index medium with a 1e-07 shutoff, and bordered by PML boundary conditions with 64 layers. A total field scattered field (TFSF) light source was used to excite the nanorod. The spectra are collected from cross section analysis planes placed within the TFSF.

¹ Johnson, P. B.; Christy, R. W. Optical Constants of the Noble Metals. *Phys. Rev. B* **1972**, 6 (12), 4370– 4379

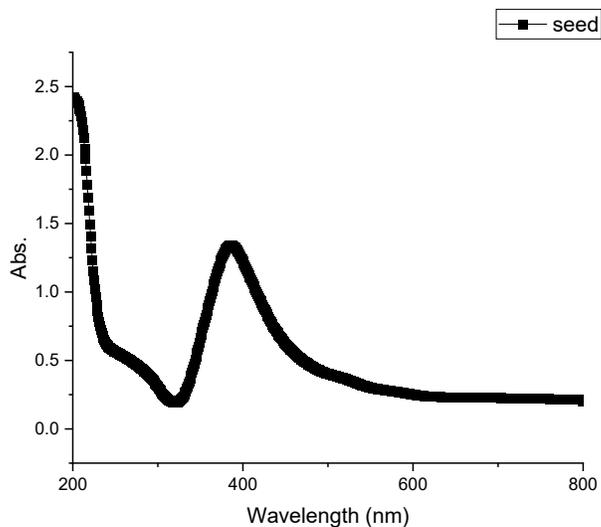


Figure S1. UV-Vis spectroscopy of AgNP seeds solution

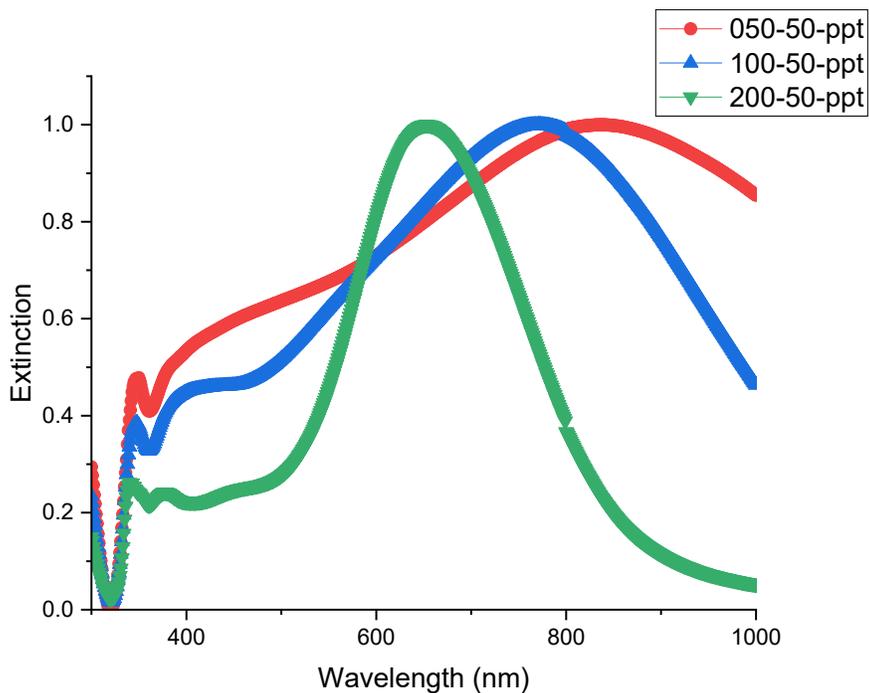


Figure S2. UV-Vis spectrum of AgNRs (after the depletion purification process) prepared using 2% acetonitrile as the co-solvent in order to increase the solubility of the CTA-Ag-Br intermediate.

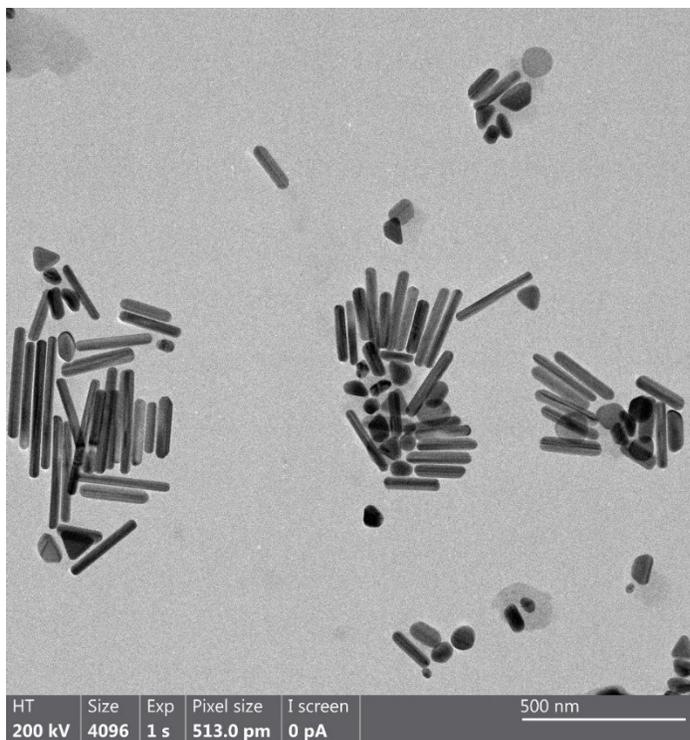


Figure S3. TEM image of AgNR with LSPR at 850 nm prepared in 2% acetonitrile/100mM CTAB.

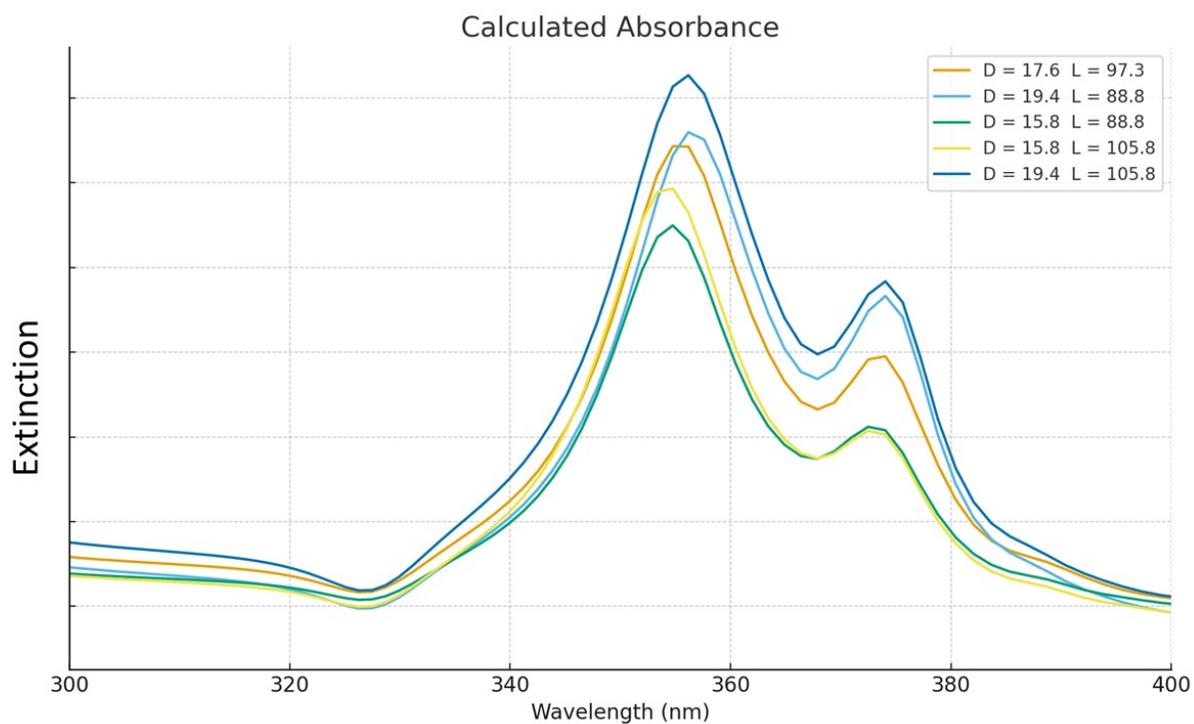


Figure S4. FDTD simulated UV-Vis spectrum of silver nanorods with different dimensions. Diameters(D) and lengths(L) are labeled in the figure: Thick Short (19.4, 88.8), Thin Short (15.8, 88.8), Thin Tall (15.8, 105.8), Thick Tall (19.4, 105.8). Two peaks due to the out-of-plane quadrupole mode and dipolar resonance mode around 350 nm and 370 nm present.