

Supporting Information

In Situ Plasmonic Counter for Polymerization of Chains of Gold Nanorods in Solution

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EXPERIMENTAL SECTION

Materials

Hexadecyltrimethylammonium bromide (BioUltra, $\geq 99.0\%$), benzyldimethylammonium chloride hydrate (BDAC), gold (III) chloride trihydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$), sodium borohydride (98%), *L*-ascorbic acid (99%), and silver nitrate (99%) were purchased from Sigma-Aldrich Canada. Thiol-terminated polystyrene ($M_n = 12000$, $M_w/M_n = 1.09$) was purchased from Polymer Source Inc. Deionized water (18.2 M Ω) was used in all the experiments.

Methods

Synthesis of gold nanorods. Gold NRs with a mean diameter and length of 12 ± 1.8 and 99 ± 10.2 nm, respectively, were synthesized by the seed-mediated growth method.¹ The NRs were stabilized with a CTAB/BDAC binary surfactant. The synthesis was scaled up to obtain a 100 mL dispersion of the NRs. Seed gold NPs were prepared by mixing chloroauric acid (HAuCl_4) (0.12 mL, 15mM) with an aqueous solution of CTAB (2.5 mL, 0.20M), 1.0 mL of deionized water, and sodium borohydride (NaBH_4) (0.50 mL, 10mM) in ice-cold water. For the preparation of a growth solution, CTAB (2.0 g, 0.20 M) and BDAC (2.97 g, 0.25 M) were dissolved in 90 mL of DI water at 60 °C. After cooling down to room temperature, the solution of CTAB/BDAC was mixed with aqueous solutions of silver nitrate (AgNO_3) (5.0 mL, 4.0 mM) and HAuCl_4 (5.0 mL, 15mM). Following the addition of ascorbic acid (1.24 mL 0.788M), the dark-yellow solution turned colorless. Finally, 0.10 mL of a 60-min-aged seed solution was added to the growth solution and the mixture was incubated at 27.0 °C for over 20-24 h.

Monitoring nanorod self-assembly. The self-assembly of the NRs was monitored by acquiring time-dependent ultraviolet-visible-near infrared (UV-vis-NIR) spectra of the NR solution, by using a

Varian Cary 5000 UV-Vis-NIR Spectrophotometer and cuvettes with 1.0 cm path length. Transmission Electron Microscopy (TEM) imaging was performed on Hitachi HD-2000 and H-7000 transmission electron microscopes. The self-assembly of the NRs was characterized by determining the time-dependent number average degree of polymerization, X_n , of the NR chains. We examined randomly selected locations on the TEM grids. Both the NR chains and the individual NRs were included in the analysis. The total number of NRs counted for each sample was ~ 1500 .

Variation in the number density of x -mer nanorod chains at different conversion

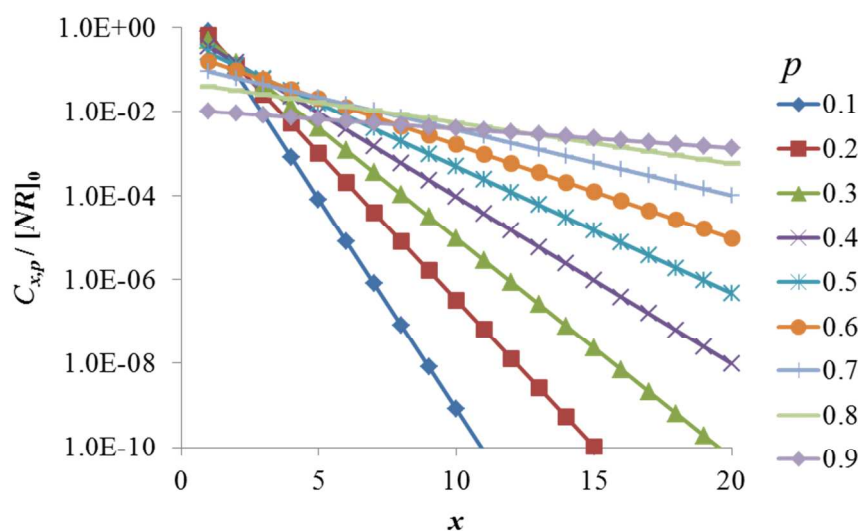


Figure S1. Calculated number density of chains at different conversion p . Conversion p is designated with different colors in the legend.

FDTD simulated extinction spectra of nanorod chains

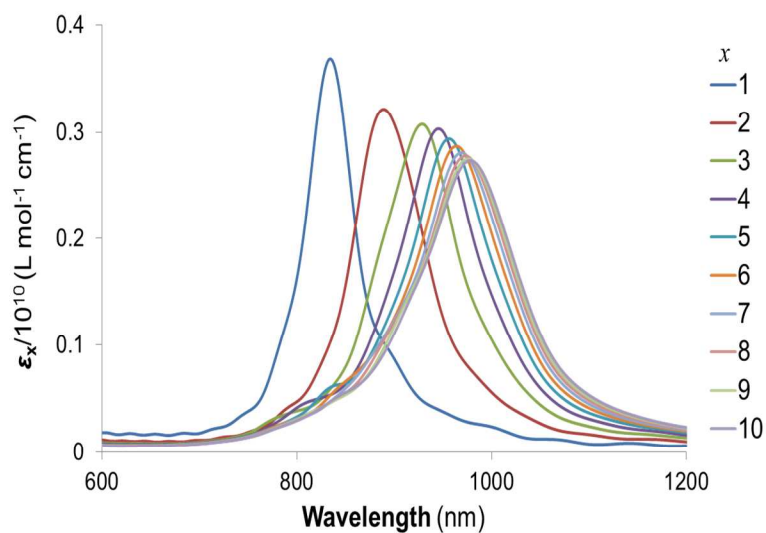


Figure S2. FDTD Simulated extinction spectra (ϵ_x) normalized by x for individual NR50-12K chains with the number of NR (x) varying from 1 to 10. The colors of lines correspond to the different values of x .

Distribution of sizes of gold nanorods

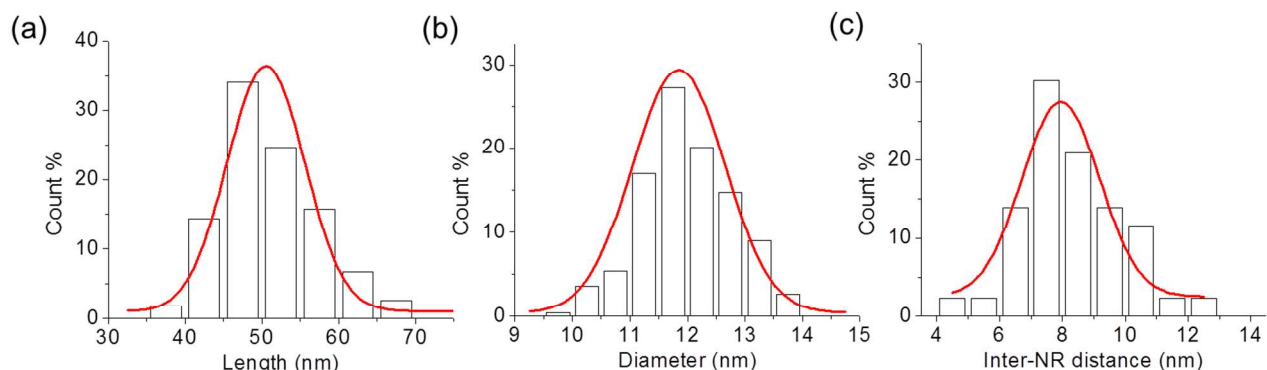


Figure S3. Distribution of (a) NR lengths, (b) NR diameters, and (c) inter-NR distances of NRs in dried NR50-12k samples.

Experimental and simulated extinction spectra of gold nanorods

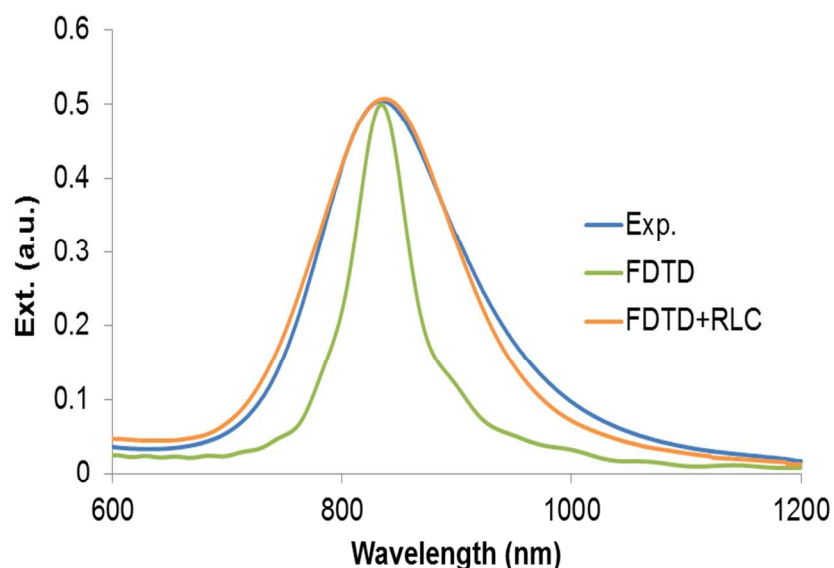


Figure S4. Experimentally measured (blue line), FDTD simulated (green line) and combined FDTD and RCL simulated (orange line) extinction spectra of the individual NR50-12k. In experiments, the average length and diameter of the NRs were 50 ± 6.1 and 12 ± 1.6 nm, respectively. In the FDTD simulation, the length and diameter of the NRs were 50 and 12 nm, respectively. The orange line shows the combined FDTD and RLC simulation with considering the size distribution of the NRs. The spectra were normalized to have some peak height.

References

1. Nikoobakht, B.; El-Sayed, M. A. Preparation and Growth Mechanism of Gold Nanorods (NRs) Using Seed-Mediated Growth Method. *Chem. Mater.* **2003**, *15*, 1907-1962.