Supporting Information

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SI Text

Transverse Excitation of Chains with Mean Nanorod Dimensions

Longitudinal resonances generated with incident light polarized along the long axis of the chain are substantially stronger than corresponding transverse resonances generated with incident light polarized perpendicularly to the long axis of the chain. In Fig. S1, we plot the simulated extinction spectra of chains with average nanorod parameters (length of 52 nm and width of 13 nm) in both the longitudinal and transverse excitation configurations. Noting the scale in Fig. S1 *A* and *B*, it is clear that transverse resonances are more than an order of magnitude weaker than their longitudinal counterparts and peak in wavelength at around ∼500 nm, far from longitudinal resonance peaks. Transverse excitations of polydisperse nanorods have similar resonance peaks, and thus to first order we can neglect the transverse resonances altogether in the calculation of the simulated extinction spectra of ensembles of polydisperse nanorods.

Semianalytical Calculation of Single Nanorods

For the case of nanorod monomers, in which there are only 2 df (length and width), we can calculate the expected average extinction spectrum of a polydisperse ensemble, using semianalytical methods from literature. As described by Prescott and Mulvaney, the extinction spectrum of a uniform ellipsoid dispersed in a nonabsorbing medium can be described by its dielectric function and appropriate geometrical factors (1). Using the geometrical factors for cylindrical nanorods with spherical ends, we computationally averaged the extinction spectra of gold nanorods with Gaussian-distributed lengths (mean 52 nm, standard deviation 6.1 nm) and diameters (mean 15 nm, standard deviation 1.6 nm). To obtain the spectral average of this polydisperse ensemble we computed the extinction spectra of $201 \times 201 = 40{,}401$ nanorods with lengths from 39.8 nm to 64.2 nm and diameters from 9.8 nm to 16.2 nm, corresponding to a range of 4 SDs across each parameter. We then calculated the weighted average of these extinction spectra, with the weight being provided by the 2D (L, d) Gaussian distribution centered upon $L = 52$ nm and $d = 12$ nm with the respective SDs of 6.1 nm and 1.6 nm. In Fig. S2 *A* and *B* we plotted 20 individual extinction spectra for increasing nanorod diameter and length, respectively, and in Fig. S2*C* we plotted the weighted average (blue line). We fitted these data to Gaussian and Lorentzian lineshapes in wavelength and observed that the averaged extinction spectrum is substantially more Gaussian than Lorentzian in character (Fig. S2*C*). The Gaussian fit is a very good approximation at or around the resonance, although it falls off quicker than the actual weighted average of the extinction spectra.

Convergence

Evaluating the convergence of a Monte Carlo experiment is generally a challenging task. Sometimes the rate of convergence of the Monte Carlo sample mean to the true mean can be estimated using the Monte Carlo sample variance by appealing to the central limit theorem (2). Our case is somewhat complicated by the fact that we are examining the convergence of extinction spectra. Although one could estimate the convergence criterion based on point-by-point sample variances in the extinction spectra, in our case it is more appropriate to evaluate convergence of the Gaussian fits to the spectra, comparing peak wavelengths and full widths at half maximum.

Using the semianalytical framework above for the monomer case, we followed the Monte Carlo/Gaussian procedure by stochastically generating monomer geometries with lengths and widths selected from their respective Gaussian distributions, averaging their ensemble extinction spectra and fitting the resulting average spectrum to a Gaussian. For a range of 1–15 samples, we repeated this procedure 1,000 times each (i.e., 1,000 Monte Carlo simulations) and plotted the quartiles (25th percentile, median, 75th percentile) of the means and SDs of the Gaussian fits in Fig. S3. For a given number of samples, 50% of the Monte Carlo simulations produced mean or SD values that fell between the corresponding blue bars in Fig. S3.

For comparison, we performed a standard parameter sweep (i.e., a brute force non-Monte Carlo exploration of the entire parameter space) for a range of 1–15 samples. For a chosen number of samples, we selected a set of geometries with the appropriate length and width distributions centered on the average monomer geometry to calculate a weighted average extinction spectrum. The resulting average extinction spectra were fitted to Gaussians and their means and SDs are plotted in Fig. S3. Note that the geometry selection for this parameter sweep has either one or multiple reasonable choices, depending on the number of samples. For example, for 1 sample, the natural choice is that both the width and the length of the single nanorod are simply the means of their respective distribution. For 9 samples, a reasonable choice would be to take three values of the width and three values of the length (e.g., the mean, 1 SD below, and 1 SD above for each parameter). For 3 samples, one can fix the width to be at the mean only and select three values for the length or vice versa; thus there are at least two equally "reasonable" choices, both of which are shown in Fig. S3 *A* and *B*. In the case of the brute force parameter sweeps, how the sets of geometries are chosen has substantial impact on the resulting estimate of the ensemble extinction spectrum. In particular, because variability in monomer length tends to account for greater broadening in extinction than variability in monomer width, preferentially sampling lengths will be more informative than preferentially sampling widths.

From the results of Fig. S3, it is unclear whether the Monte Carlo (MC)/Gaussian approach is substantially faster than the brute force parameter sweep for the single nanorod: Sometimes the MC approach wins, and sometimes the brute force approach wins. However, two things are important to keep in mind: (*i*) To obtain a result from the brute force sweep that is comparable to the MC result, one has to intelligently choose how the samples are selected for calculation, and (*ii*) a speedup actually is not expected for such a small parameter space (two variables) with the MC approach.

We expect the real strength of the MC/Gaussian approach would be seen in situations with a large number of free parameters and limited variability in the responses of individual samples. In this regard, the MC/Gaussian procedure provides a means of approaching a complex problem for which any form of analytics or parameter sweeping is unfeasible. To better illustrate this point, in Fig. S4 we plot the number of simulations needed to perform a brute force parameter sweep with three points per parameter as a function of nanorod chain length, which is the absolute minimum number of points that could provide any meaningful information about the overall distribution. Even in the case of a dimer (two rods, one gap) that has five free parameters, performing such a limited parameter sweep would require $3^5 = 243$ simulations, whereas an octomer (eight rods) would require more than 10^{10} simulations, making it completely intractable.

In Fig. S5, we see that the relative fluctuations in the calculated peak wavelength and full width at half maximum of the extinction spectra generally decrease with increasing sample size. In particular, monomer, dimer, and trimer chains required substantially more Monte Carlo samples to achieve degrees of stability comparable to those of longer chains. We found that the extinction spectra of individual Monte Carlo samples for shorter chains were substantially less clustered than those for longer chains. This highlights the fact that the convergence of Monte Carlo experiments is situational and must be evaluated case by case. Although additional sampling is required for the solution to truly converge (Fig. 4*A* and Fig. S5 *A* and *B*), the large computational cost associated with achieving substantially finer convergence deterred us from additional sampling.

Geometrical Parameters for Nanorods Used in Simulations

The lengths and widths of each nanorod, and the gap lengths between them, were stochastically selected from Gaussian distributions where $L = 52 \pm 6.1$ nm, $d = 13 \pm 1.6$ nm, and $l = 6.7 \pm 1.4$ nm (Fig. S6).

Doppler Broadening Resulting from Thermal Motion of Chains

Because our physical system comprises nanorods and nanorod chains that are free to move around in a solution, is it natural to consider whether thermal motion of these chains leads to Doppler broadening in the extinction spectra. However, we expect this effect to be negligible in any realistic implementation of this system because of the relatively large masses of the nanorods and nanorod chains. For example, an isolated gold nanorod with mean dimensions ($d = 13$ nm, $L = 52$ nm) will have a mass of ~1.3E-19 kg, so at room temperature the broadening will be approximately $\sqrt{kT/mc^2 f_0} \simeq 6 \times 10^{-10} f_0$, where k is the Boltzmann constant, T is the temperature in kelvin, m is the mass, c is the speed of light in vacuum, and f_0 is the frequency (3).

1. Prescott SW, Mulvaney P (2006) Gold nanorod extinction spectra. *J Appl Physics* 99(12): 123504.
2. Ata MY (2007) A convergence criterion for the Monte Carlo estimates. *Simul Model Pract Theory* 15(3):237–246.
3. Siegman AE (1986) *Lasers* (University Science Books, Mill Valley, CA).

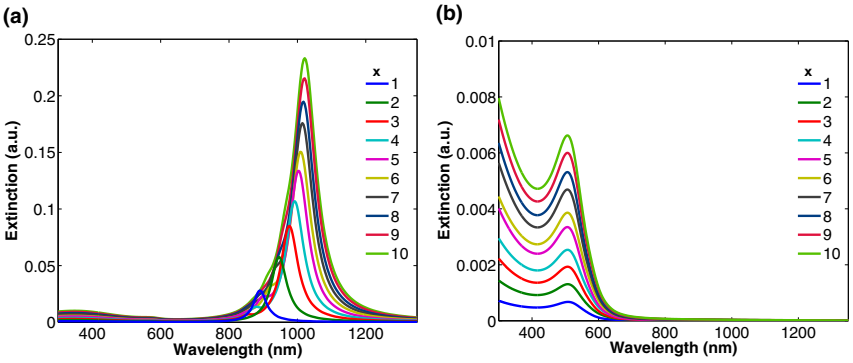

Fig. S1. Simulated extinction spectra of nanorod chains comprising *x* nanorods where all nanorods have average dimensions ($L = 52$ nm, $d = 14$ nm, $l = 6.7$ nm) for (*A*) longitudinal excitation (incident electric field polarized parallel to long axis of chains) and (*B*) transverse excitation (incident electric field polarized perpendicularly to long axis of chains).

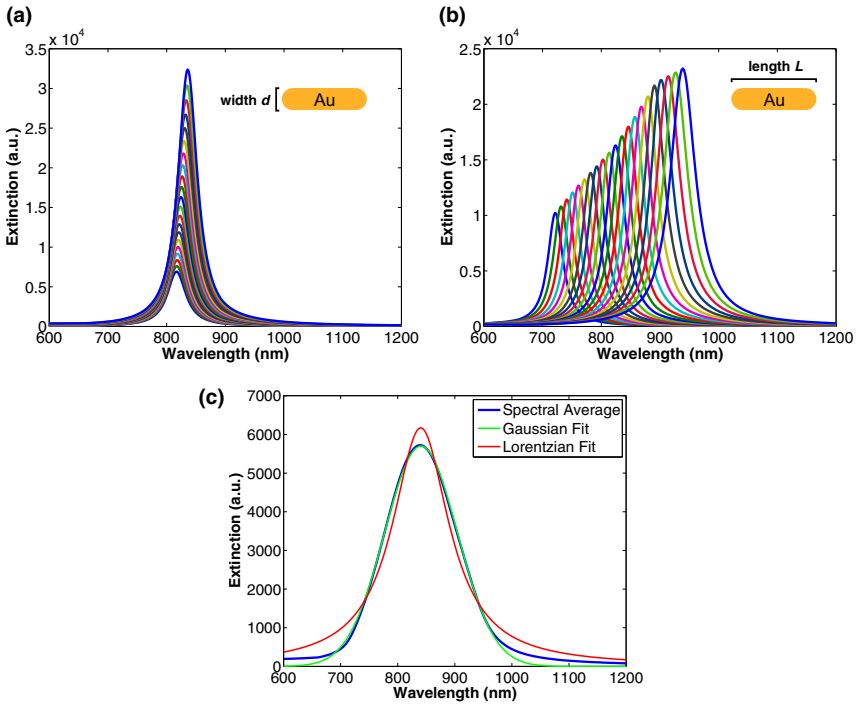

Fig. S2. (*A*) Extinction cross sections of gold nanorods with diameter d varied from 9.8 nm to 16.2 nm and length $L = 52$ nm. (*Inset*) Schematic of a nanorod of length L and diameter d. (*B*) Extinction cross sections of gold nanorods with diameter $d = 13$ nm and and length L varied from 39.8 nm to 64.2 nm. The longer lengths correspond to larger resonant wavelengths. (*C*) Average of the spectra in *A* and *B*, weighted by a Gaussian distribution, where $L = 52 \pm 6.1$ nm, $d = 13 \pm 1.6$ nm (blue), as explained in the text. Green and red curves are the Gaussian and Lorentzian fits, respectively.

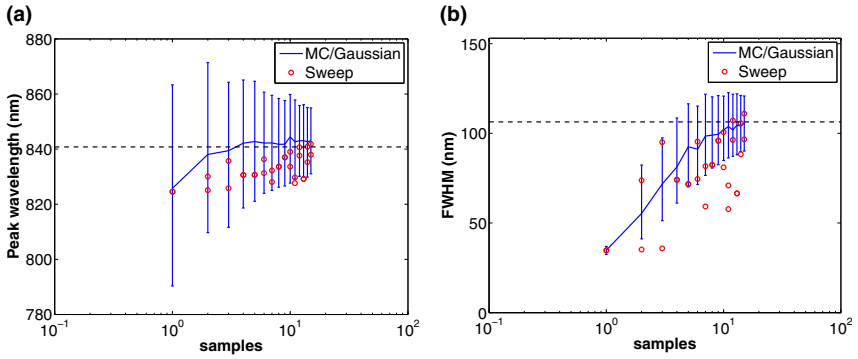

Fig. S3. Convergence of the peak wavelengths (*A*) and the full widths at half maximum (FWHM) (*B*) for the extinction spectra of polydisperse nanorods (monomers), using the MC/Gaussian approach (blue lines and markers) and a brute force sweep of the parameter space (red circles) as the number of sampled points increases. Blue bars indicate quartile values (25th percentile, median, 75th percentile) obtained from 1,000 independent MC/Gaussian trials. The horizontal black dashed lines indicate true mean and SD parameter values obtained through exhaustive averaging (shown in Fig. S2*C*).

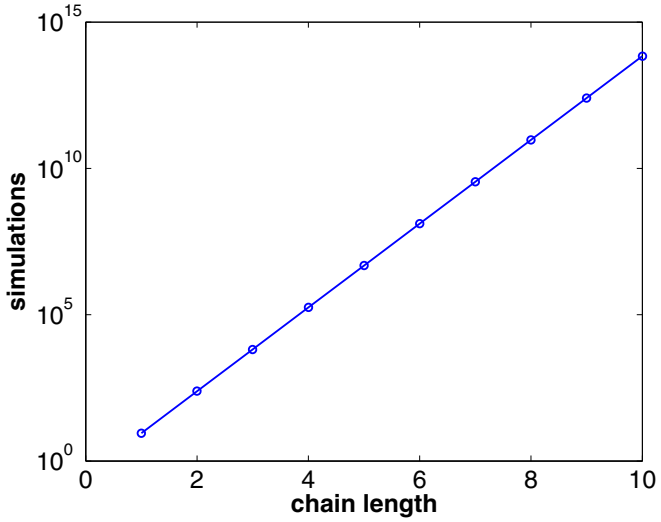

Fig. S4. Number of simulations needed to perform a parameter sweep with three points per parameter.

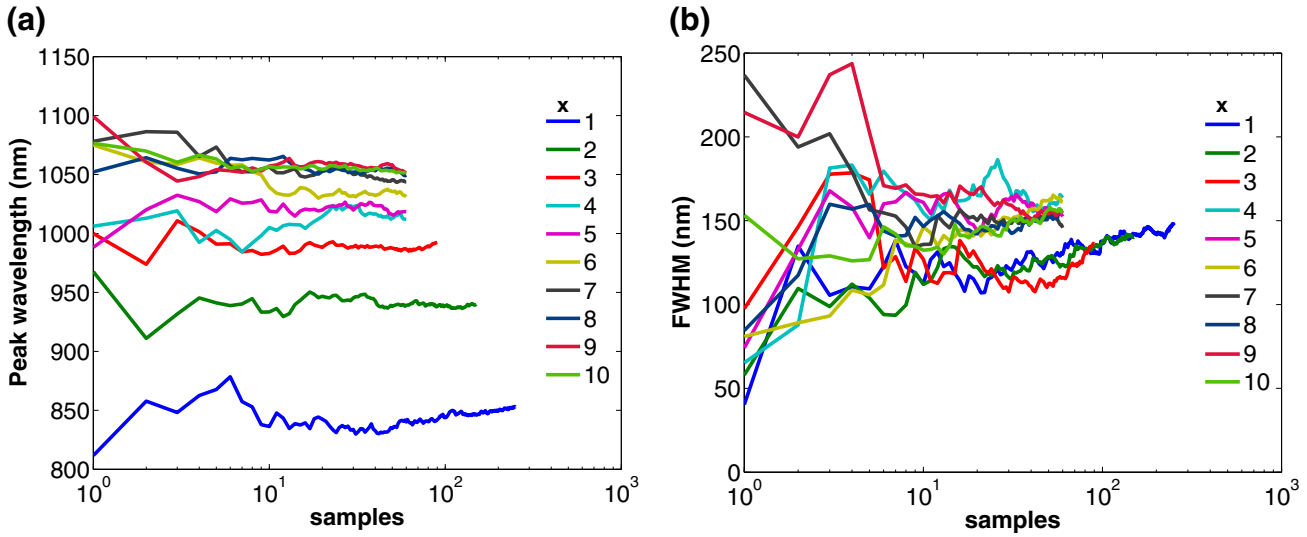

Fig. S5. (*A*) The peak wavelengths and (*B*) the full widths at half maximum (FWHM) for the extinction spectra of polydisperse ensembles of chains comprising $x = 1$–10 nanorods, as obtained from the Monte Carlo simulations with Gaussian fitting as the number of samples is increased. For a large number of samples the calculated peak wavelengths and FWHMs should converge to their true values.

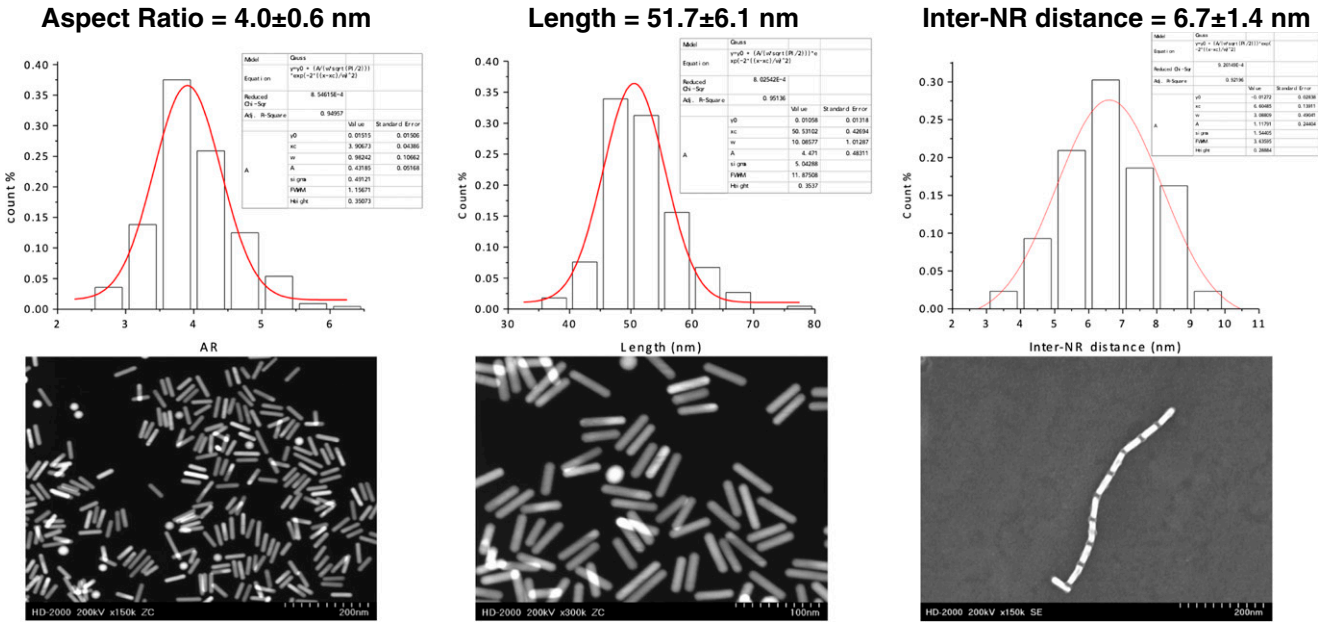

Fig. S6. Transmission electron microscope (TEM) images of gold nanorods and nanorod chains in solution. We performed statistical analysis on the lengths *L*, aspect ratios *d*/*L*, and internanorod distances *l* to obtain the distributions used in the calculations presented in the main text.