Supporting Information

Extinction and Extra-High Depolarized Light Scattering Spectra of Gold Nanorods with Improved Purity: Direct and Inverse Problems

Boris N. Khlebtsov,[a,b] Vitaly A. Khanadeev,[a,b] and Nikolai G. Khlebtsov[a,b,*]

[1] *Institute of Biochemistry and Physiology of Plants and Microorganisms, Russian Academy of Sciences, 13 Prospekt Entuziastov, Saratov 410049, Russia*

[2] *Saratov State University, 83 Ulitsa Astrakhanskaya, Saratov 410026, Russia*

* Corresponding author: khlebtsov@ibppm.sgu.ru

S1. Depolarization setup calibration

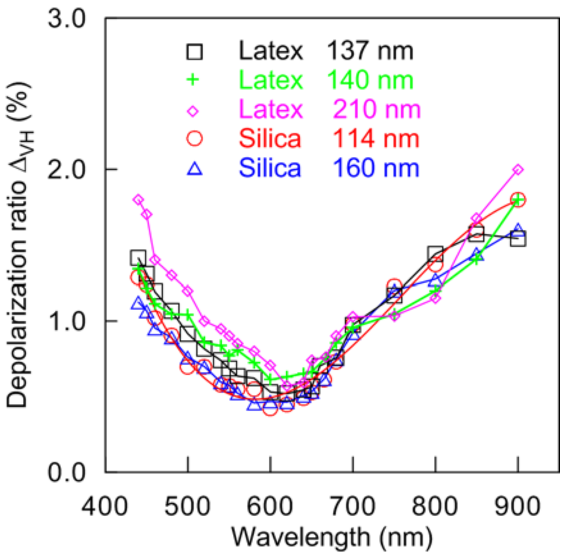

Figure S1. Depolarization spectra of 137-, 140-, and 210-nm polystyrene latexes and of 114- and 160-nm silica nanospheres.[1] Because of the small depolarization scattering from particles, the average course of the measured spectra gives an estimate of the instrumental error as a function of the wavelength.

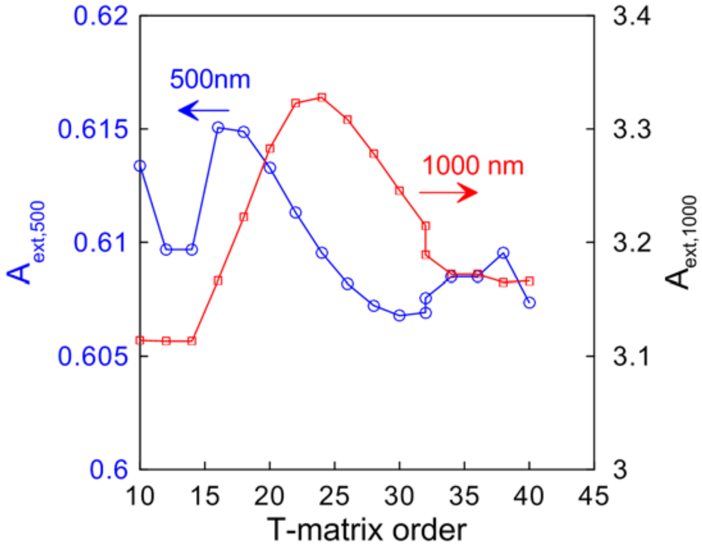

Figure S2. Oscillating convergence of the extended-precision T-matrix codes with an increase in the T-matrix order. Calculations for randomly oriented GNRs with an average length of 82.4 nm, an average aspect ratio of 5.27 (log-normal distributions, $\sigma_r = 1.16$), and hemispherical end-caps ($\chi_c = 1$). The percentage and radius of the impurity particles are 2% and 16 nm, respectively. Extinctions at 550 and 900 nm are normalized to the gold mass-volume concentration $c_g = 57$ µg/mL, corresponding to the reduction of 0.01% $HAuCl_4$.

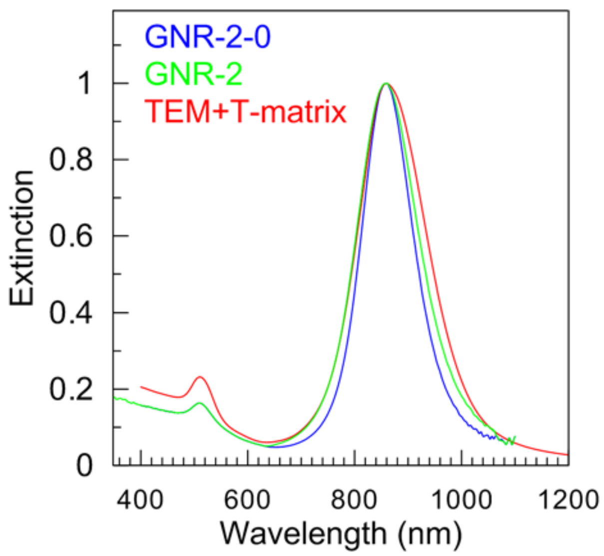

Figure S3. Extinction spectra of as-prepared GNR-2-0 rods (blue) and GNR-2 rods one week after preparation (green, TEM sample), as well as TEM-based T-matrix calculations (red). The FWHMs of GNR-2-0, GNR-2, and the calculated spectra are 120, 140, and 156 nm, respectively.

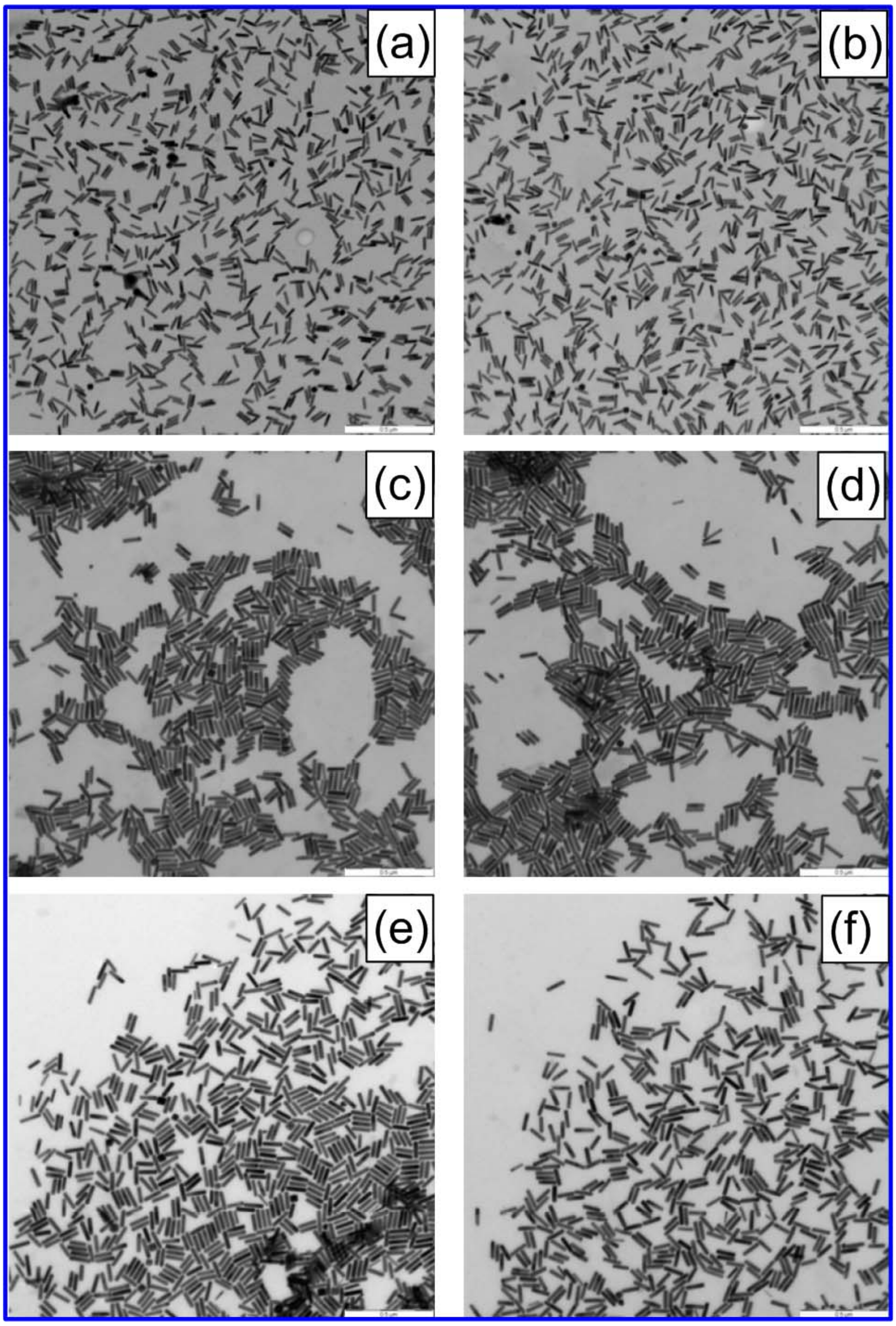

Figure S4. Overview images of GNR-1 nanorods with percentages of impurity particles of 6.5 (a), 4.8 (b), 2 (c), 2.6 (d), 1.7 (e), and 1% (f). Each image represents about 900-1200 particles.

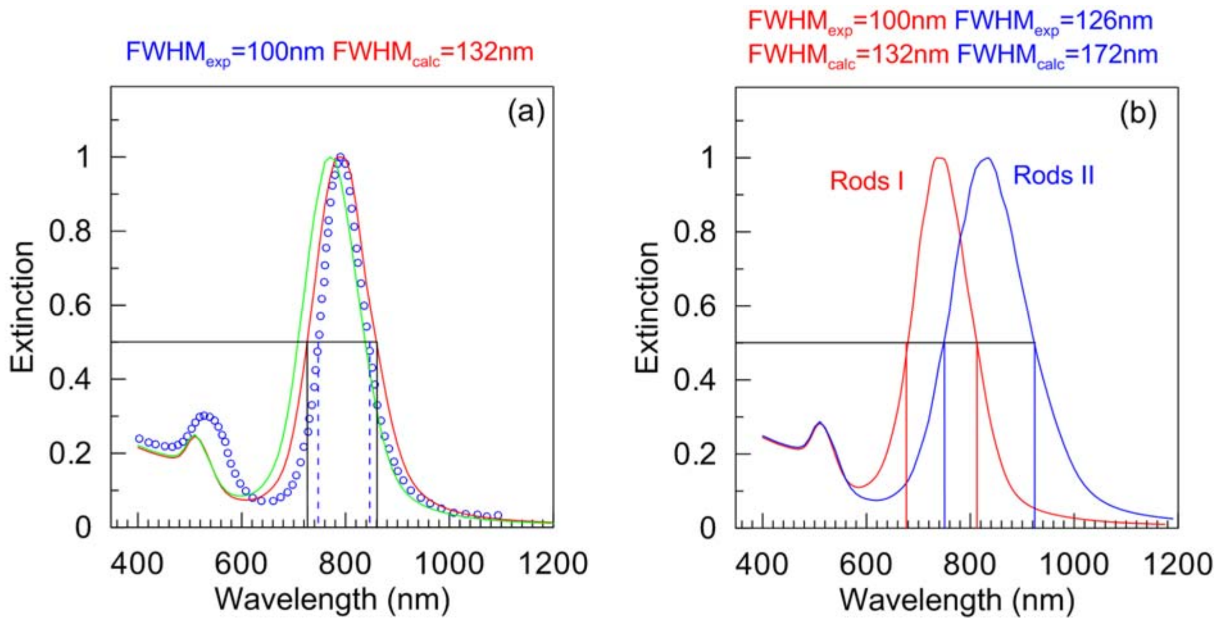

Figure S5. (a) Experimental (circles)[2] and calculated (red and green) extinction spectra of Gem1-NRs. The T-matrix calculations are based on the average geometrical TEM parameters of the rods: $r_{av} = 3.6 \pm 0.4$, $L_{av} = 43 \pm 8$ nm, and $d_{av} = 12 \pm 2$ nm. The hemispherical end-cap shape of Gem1-NRs with $\chi_c = 1$ gives a slightly blue-shifted spectrum (the dashed green line, $\lambda_{max} = 770$ nm), whereas the end-cap parameter $\chi_c = 0.5$ gives much better agreement between the calculated (red line) and the measured peak position ($\lambda_{max} = 795$ nm). The FWHMs for the measured and calculated spectra are 100 and 132 nm, respectively. (b) T-matrix calculations for Gem1-NRs-I and Gem1-NRs-II with the following TEM parameters:[2] (I) $r_{av} = 3.1 \pm 0.4$, $L_{av} = 34 \pm 7$ nm, $d_{av} = 10 \pm 2$ nm (red) and (II) $r_{av} = 4.1 \pm 0.6$, $L_{av} = 42 \pm 7$ nm, $d_{av} = 10 \pm 2$ nm (blue). The hemispherical end-cap shape of Gem1-NRs with $\chi_c = 1$ was used for the type II rods ($\lambda_{max} = 840$ nm), whereas the best-fitting $\chi_c = 0.5$ was used for the type I rods to give $\lambda_{max} = 748$ nm. Note that the calculated FWHMs (132 and 172 nm) for Gem1-NRs-I and Gem1-NRs-II are greater than the experimental ones (100 and 126 nm, respectively). For calculations, log-normal distributions for the aspect ratio and length of the rods were used with the corresponding standard deviations. The impurity particle fraction was assumed to be as small as in the case of GNR-1 rods.

S6. Light scattering by small anisotropic particles with random orientations

In the general case, the intensity of scattered light with a polarization vector $\mathbf{e}_s$ can be represented as the sum of three independent components corresponding to scalar, symmetric, and antisymmetric contributions,[3]

$$I = I^{(0)} + I^{(s)} + I^{(a)} = G_0 \left|\mathbf{e}_s^*\mathbf{e}_0\right|^2 + \frac{1}{10} G_s \left[1 + \left|\mathbf{e}_s\mathbf{e}_0\right|^2 - \frac{2}{3}\left|\mathbf{e}_s^*\mathbf{e}_0\right|^2\right] + \frac{1}{6} I_0^{(a)} \left[1 - \left|\mathbf{e}_s\mathbf{e}_0\right|^2\right], \quad \text{(S1)}$$

where $\mathbf{e}_0$ defines the incident light polarization and G_0, G_s, and G_a are given by the expressions in Eq. (4). In the case of a linearly polarized wave, the polarization vector $\mathbf{e}_0$ is real and the scattered light is partially depolarized and can be decomposed into two incoherent components, one ($I_{\|}$) polarized in the plane $(\mathbf{e}_o, \mathbf{k}_s)$ and the other ($I_{\perp}$) polarized perpendicularly to the plane $(\mathbf{e}_o, \mathbf{k}_s)$. In terms of the a and b constants [see Eq. (4)], we have[3]

$$I_{\|} = I_0 \left[a(\mathbf{e}_0\mathbf{e}_s)^2 + b \right], \quad I_{\perp} = I_o b \,. \quad \text{(S2)}$$

For our scattering geometry, $(\mathbf{e}_0\mathbf{e}_s) = 1$ and $\Delta_{VH} = I_{\perp} / I_{\|} = b/(a+b)$, which coincides with Eq. (3) at $\theta=90^{\circ}$.

In our previous paper[1], we derived the following expression for axially symmetric particles:

$$\Delta_{VH} = \frac{\chi^2}{5 - 2\chi^2}, \quad \chi^2 = \frac{\left|\alpha_1 - \alpha_2\right|^2}{\left|\alpha_1\right|^2 + 2\left|\alpha_2\right|^2}. \quad \text{(S3)}$$

At first glance, Eq. (S3) looks somewhat different from the first expression in Eq. (10) of the main text:

$$\Delta_{VH} = \frac{3}{4 + 5\dfrac{\left|\alpha_1 + 2\alpha_2\right|^2}{\left|\alpha_1 - \alpha_2\right|^2}}. \quad \text{(S4)}$$

To show the equivalency of both expressions, we note that

$$(\alpha_1\alpha_2^* + \alpha_2\alpha_1^*) = \left|\alpha_1\right|^2 + \left|\alpha_2\right|^2 - \left|\alpha_1 - \alpha_2\right|^2 \quad \text{(S5)}$$

and

$$\left|\alpha_1 + 2\alpha_2\right|^2 = 3(\left|\alpha_1\right|^2 + 2\left|\alpha_2\right|^2) - 2\left|\alpha_1 - \alpha_2\right|^2 \quad \text{(S6)}$$

After substitution of these expressions into (S4), we have

$$\Delta_{VH} = \frac{\left|\alpha_1 - \alpha_2\right|^2}{\frac{4}{3}\left|\alpha_1 - \alpha_2\right|^2 + \frac{5}{3}\left[3\left(\left|\alpha_1\right|^2 + 2\left|\alpha_2\right|^2\right) - 2\left|\alpha_1 - \alpha_2\right|^2\right]} = \frac{\left|\alpha_1 - \alpha_2\right|^2}{5\left(\left|\alpha_1\right|^2 + 2\left|\alpha_2\right|^2\right) - 2\left|\alpha_1 - \alpha_2\right|^2} = \frac{\chi^2}{5 - 2\chi^2}. \quad \text{(S7)}$$

This proves the equivalence of both expressions in Eq. (10).

References

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3 L. D. Landau, E. M. Lifshitz. *Electrodynamics of Continuous Media*, Second ed., Amsterdam: Elsevier Butterworth-Heinemann, 2004.