ADDITIONS AND CORRECTIONS

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S. Link and M. A. El-Sayed*: Simulation of the Optical Absorption Spectra of Gold Nanorods as a Function of Their Aspect Ratio and the Effect of the Medium Dielectric Constant

We previously reported[1] the simulation of the optical absorption spectrum of gold nanorods using Gans theory[2] according to the following set of equations:

$$\gamma = \frac{2\cdot\pi\cdot N\cdot V\cdot\epsilon_{\mathrm{m}}^{3/2}}{3\cdot\lambda}\cdot\sum_j \frac{(1/Pj^2)\cdot\epsilon_2}{\left(\epsilon_1 + \frac{1-P_j}{P_j}\cdot\epsilon_{\mathrm{m}}\right)^2 + \epsilon_2^{\,2}} \qquad (1)$$

γ is the extinction coefficient, N the number of particles per unit volume, V the particle volume, ϵ_{m} the dielectric constant of the surrounding medium, λ the wavelength of the interacting light, and ϵ_1 and ϵ_2 are the real and complex parts of the material dielectric function taken from ref 3 and interpolated to give a smooth absorption band. P_j represents the depolarization factors for the three axes A, B, and C of the rod with $A > B = C$.

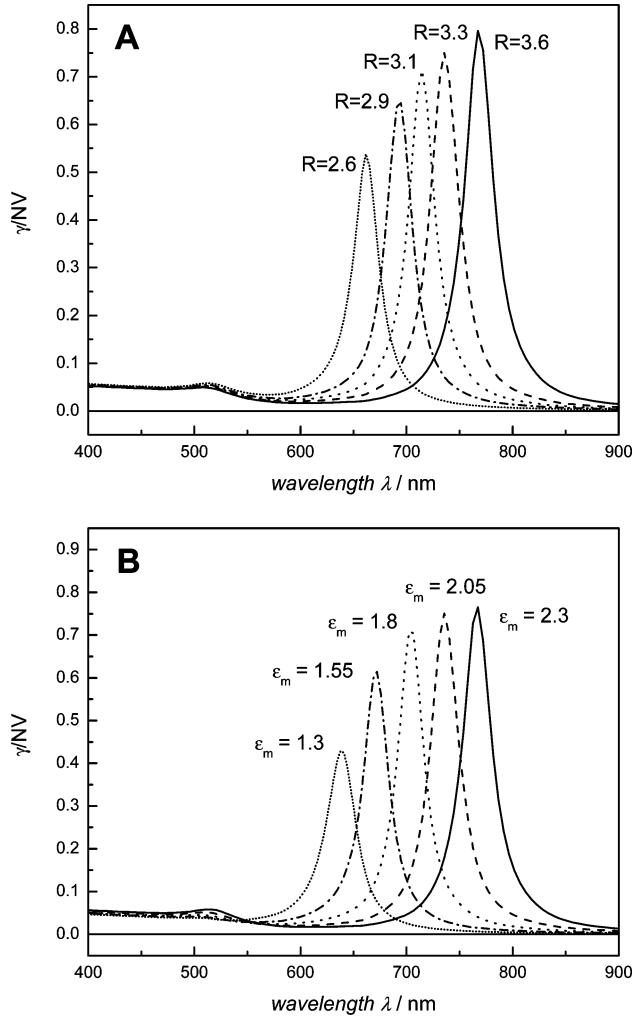

Figure 1. (A) Calculated absorption spectra of elongated ellipsoids with varying aspect ratios R using eq 1. The medium dielectric constant was fixed at a value of 2.05. (B) Calculated absorption spectra of elongated ellipsoids with varying medium dielectric constant ϵ_{m} using eq 1. The aspect ratio was fixed at a value of 3.3.

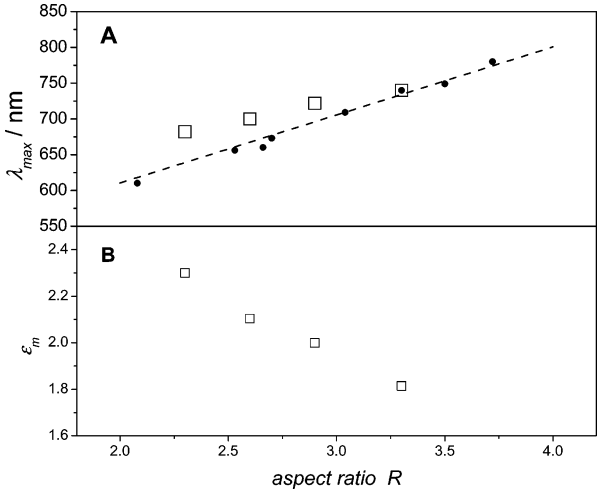

Figure 2. (A) Plot of the absorption maximum of the longitudinal plasmon resonance against the aspect ratio as determined by TEM. The circles correspond to different nanorod preparations, while the squares are the results obtained by thermal reshaping. The line corresponds to eq 5 with a medium dielectric constant of 1.77. (B) Dependence of the medium dielectric constant on the aspect ratio obtained if the medium dielectric constant is used as a variable parameter to match the experimental absorption maximum of the longitudinal plasmon resonance for thermally reshaped rods.

$$P_A = \frac{1-\mathrm{e}^2}{\mathrm{e}^2}\cdot\left[\frac{1}{2\cdot\mathrm{e}}\cdot\ln\left(\frac{1+\mathrm{e}}{1-\mathrm{e}}\right) - 1\right] \qquad (2)$$

$$P_B = P_C = \frac{1-P_A}{2} \qquad (3)$$

$$\mathrm{e} = \sqrt{1-\left(\frac{B}{A}\right)^2} \qquad (4)$$

The ratio A/B is the aspect ratio R.

In our previous work, eq 2 was mistakenly computed according to

$$P_A = \frac{1-\mathrm{e}^2}{\mathrm{e}^2}\cdot\left[\frac{1}{2}\,\mathrm{e}\cdot\ln\left(\frac{1+\mathrm{e}}{1-\mathrm{e}} - 1\right)\right] \qquad (2b)$$

By correcting this error, one obtains the absorption spectra shown in Figure 1 for different aspect ratios and medium dielectric constants. For the derived relationship between the absorption maximum of the longitudinal plasmon resonance λ_{max} as a function of R and ϵ_{m}, we now find

$$\lambda_{\mathrm{max}} = (53.71\cdot R - 42.29)\cdot\epsilon_m + 495.14 \qquad (5)$$

instead of the previously reported result (eq 8 in ref 1). The

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correct form of this relationship between λ_{max}, R, and ϵ_m has been pointed out by Yan et al.[4] and is in agreement with eq 5.

The error in eq 2 leads to incorrectly high values for ϵ_m. The spectra shown in Figure 1 are recalculated with an ϵ_m varying between 1.3 and 2.3. Using $\epsilon_m = 1.77$ and eq 5, we can fit the experimentally found relationship between λ_{max} and R for the electrochemically prepared gold nanorods (see Figure 2A) without assuming that ϵ_m varies with R. A value of $\epsilon_m = 1.77$, and therefore a refractive index of $n = 1.33$ ($\epsilon_m = n^2$), is in good agreement with the refractive index of the solvent (water). For the thermally reshaped nanorods, however, one still has to assume that ϵ_m varies with R (see Figure 2B) in order to find agreement between the experiment and the theoretical prediction. This is not surprising as the rods with different aspect ratio were prepared by changing the temperature.[5] Temperature effects on the dielectric constant and on the structure of the capping material around the rods is to blame for this observation. This assumption makes good physical sense, as in the thermal reshaping, increasing the temperature dissolves the larger micelles (rods) and leaves behind the smaller rods at higher temperatures. It is possible that the smaller micelle structure around the rods has less water content leading to an increase in the refractive index (and thus to the value of the dielectric constant).

In conclusion, the mistake in eq 2 leads to unreasonably high values for ϵ_m. However, our previous main conclusions, that (1) Gans theory can be used to model the optical absorption spectra of nanorods predicting a linear dependence of λ_{max} on R and ϵ_m and (2) the thermal reshaping process alters the local surrounding environment of the nanorods (e.g., the capping material), have not changed.

References and Notes

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(4) Yan, B.; Yang, Y.; Wang, Y. *J. Phys. Chem. B* **2003**, *107*, 9159.
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