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Comment

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Comment on "Rapid and Efficient Prediction of Optical Extinction Coefficients for Gold Nanospheres and Gold Nanorods"

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In a recent paper, Near et al.[1] discussed the connection between the 10-based molar extinction coefficient ε of a suspension of nanoparticles and extinction efficiency Q_{ext} calculated with the discrete dipole approximation (DDA). In particular, they derived an empirical relation based on comparison of experimental measurements with the simulations. This comment shows that there is no need for such empirical relations at all since an exact analytical relation is well-known.

Let us start from the 10-based attenuation coefficient $\mu = \varepsilon c$, where c is the molar concentration. On the basis of eq 3.46 of ref 2, for the e-based attenuation coefficient, we obtain

$$\mu = C_{ext}N/\ln 10 \tag{1}$$

where N is the number density (particles per volume) and $C_{ext} = AQ_{ext}$ is the extinction cross section (A is a geometrical cross section) of the nanoparticle. While C_{ext} has an unambiguous definition, different definitions have been proposed for A and hence Q_{ext}. Further we use the most common one, the cross section of a volume-equivalent sphere (with radius r_{eff}),[2] given by

$$A = \pi r_{eff}^2 = (9\pi/16)^{1/3}V^{2/3} \tag{2}$$

regardless of the particle shape (V is the particle volume). In particular, this definition is used in both popular DDA codes: DDSCAT[3] and ADDA;[4] hence, it is also used in ref 1. The only assumption required for eq 1 is that of the independent scattering; i.e., the particle concentration is relatively small.[2]

Equations 1 and 2 imply

$$\varepsilon = C_{ext}N_A/\ln 10 = (9\pi/16)^{1/3}(N_A/\ln 10)V^{2/3}Q_{ext} \tag{3}$$

where N_A is the Avogadro number. Thus, eq 3, the main motivation of this comment, provides a direct and rigorous connection between ε and either C_{ext} or Q_{ext}, computed by the DDA or any other single-particle light-scattering method.

Let us further relate eq 3 to the result of ref 1. The latter is based on the following definition (cf. equation 1 of ref 1)

$$\varepsilon\ [\mathrm{L{\cdot}mol^{-1}{\cdot}cm^{-1}}] = Q_{ext}10^{-24}N_A\ [\mathrm{mol^{-1}}]f\ [\mathrm{nm^3}] \tag{4}$$

where f is called both "a theoretical conversion function" and "a system volume".[1] The latter name is also supported by the unit of $\mathrm{nm^3}$ assumed for f. However, inconsistency of such unit is evident from eq 4 itself. Moreover, combining eqs 2−4 one can obtain

$$f\ [\mathrm{nm^3}] = \frac{\mathrm{nm^2}}{\mathrm{L{\cdot}cm^{-1}}}\frac{10^{24}}{\ln 10}A\ [\mathrm{nm^2}] = \frac{10^7}{\ln 10}A\ [\mathrm{nm^2}]$$
$$= 5.2506 \times 10^6(V\ [\mathrm{nm^3}])^{2/3} \tag{5}$$

Thus, f is directly proportional to the nanoparticle cross section; hence, a name like "system cross section" is more appropriate. More important is that the right-most part of eq 5 is exactly the empirical eq 2 from ref 1 (for spheres) with numerical values of the parameters falling in the fitted confidence bounds. Therefore, the experimental procedure and the obtained empirical relation for spheres in ref 1 are correct, but it only verifies the textbook eq 3.

Additional comments are required for the case of nanorods, which are also considered in ref 1. While eqs 3 and 5 are valid for nanoparticles of any shape, they are apparently different (by a few times) from the corresponding results (eq 3 and Figure 6) in ref 1. The reason for that is the difference in experimental and simulation conditions in ref 1. The DDA simulations were performed for incident light polarized along the nanorod length, while experimental measurements imply random orientation of the nanorods. Therefore, the empirical relation for nanorods in ref 1 can only be considered to approximately account for the difference in Q_{ext} between nanorods in fixed and random orientations. Even in a studied range of rod lengths and diameters, the fit is not perfect; i.e., there are significant errors associated with the empirical formula. More importantly, these errors may largely increase if other lengths and/or diameters are considered.

Moreover, such fixed-orientation approximation is not required since one can compute the orientation-averaged C_{ext} using any DDA code and use eq 3. The proper way to perform such averaging is outside of the scope of this comment, but it is a standard approach in DDA simulations of optical properties of nonspherical nanoparticles.[5,6] Moreover, in some cases an accurate result can be obtained by averaging over only three perpendicular incident polarizations.[5] For a nanorod the latter approach incurs only two times larger simulation time than that for a single incident polarization since both perpendicular-to-the-axis polarizations are equivalent.

AUTHOR INFORMATION

Notes

The authors declare no competing financial interest.

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