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Correction: Plasmonics in the ultraviolet with the poor metals Al, Ga, In, Sn, Tl, Pb, and Bi

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Correction for 'Plasmonics in the ultraviolet with the poor metals Al, Ga, In, Sn, Tl, Pb, and Bi' by Jeffrey M. McMahon *et al.*, *Phys. Chem. Chem. Phys.*, 2013, **15**, 5415–5423.

In ref. 1, hereon referred to as **I**, we reported the results of a fit of a dielectric model to experimental optical data for indium (In).² We then reported additional results based on this fit, such as nanoparticle cross sections. Since publication, we have come to realize that the experimental data that we used for this (e.g., see Fig. 2 of **I**) does not correspond to the actual data reported in ref. 2.

In this correction article, we report the results of a new fit (of the same dielectric model used in **I**) to the correct experimental optical data for In.² Following this, we calculate the optical properties of spherical In nanoparticles. Finally, we correct a few other minor errors that we have noticed with **I**.

Recall the dielectric model $\varepsilon(\omega)$ used in **I**:

$$\varepsilon(\omega) = \varepsilon_\infty - \frac{\omega_D^2}{\omega(\omega + i\gamma)} + \sum_{n=1}^2 \frac{\Delta\varepsilon_n \omega_{Ln}^2}{\omega_{Ln}^2 - \omega(\omega + i2\delta_n)} \quad (1)$$

which consists of ε_∞ , the high-frequency limiting dielectric constant, along with one Drude pole and two Lorentz oscillator poles. The Drude model accounts for intraband electron motion, with plasma and collision frequencies of ω_D and γ , respectively; the Lorentz oscillator model accounts for interband transitions (and similar effects), each occurring at ω_{Ln} with an electron-dephasing rate of δ_n , resulting in a corresponding shift in permittivity of $\Delta\varepsilon_n$. Fitting eqn (1), without restriction of its parameters (e.g., as done in ref. 3 and 4), to the experimental optical data for In in ref. 2 using simulated annealing results in $\varepsilon_\infty = 1.232$, $\omega_D = 10.936$ eV, $\gamma = 0.359$ eV, $\Delta\varepsilon_1 = 1.152$, $\omega_{L1} = 4.065$ eV, $\delta_1 = 2.710$ eV, $\Delta\varepsilon_2 = 27.868$, $\omega_{L2} = 1.137$ eV, and $\delta_2 = 0.554$ eV. Unlike in **I**, only a single fit over the entire ultraviolet (UV)-visible (Vis) spectral range is found to be necessary to accurately describe the experimental data,² as is apparent below.

Fig. 1 shows eqn (1) evaluated over the range 1.5 to 12.5 eV, in comparison to the experimental data² points used for the fit. As can be seen, the model in eqn (1) is remarkably accurate. Moreover, comparing to Fig. 2 of **I**, it can be seen that the correct magnitude of the real part of $\varepsilon(\omega)$ is much lower than used for the fit in **I**. This is the reason that only a single fit is necessary in the present case, as opposed to the two in **I**.

To illustrate how this correction affects the optical properties of small particles, such as those reported in **I**, we recalculated the extinction efficiencies of spherical nanoparticles with diameters of 20, 50, 100, and 200 nm, using Mie theory.⁵ As can be seen in Fig. 2, they are quite different than those reported in the center panel of Fig. 6 of **I**. Rather than occur above 12 eV, the peak resonance (dipolar) now occurs in the UV, extending into the Vis with increasing particle size. This is consistent with the results seen for the other poor metal nanoparticles reported in **I** (Fig. 6–8 therein). It is interesting to note that the extinction efficiencies are in fact similar to gallium (Ga) (Fig. 7 of **I**), except narrower. The shift of the resonances to lower energies (from above 12 to near 7 eV, for the 20 nm diameter particle, for example) arises from the reduced magnitude in the real part of $\varepsilon(\omega)$, which causes the resonance condition $\text{Re}[\varepsilon(\omega_{\text{res}})] \approx -2$ to occur at lower energies.

It is also important to also discuss the impact that the corrected model will have on the electric field enhancements ($|\mathbf{E}|^2$), a topic discussed in Section 3 of **I**. Therein, extinction cross sections and $|\mathbf{E}|^2$ enhancements occurring at the junction between a dimer of 20 nm diameter nanoparticles were calculated. Considering that the extinction efficiencies of the isolated In particles are similar to Ga, as discussed above, as is the permittivity (compare Fig. 1 to Fig. 3 of **I**, for example), it is reasonable to expect similar qualitative behavior of the dimer cross sections. Instead of occurring in the far UV and beyond, as reported in **I** and the top panel

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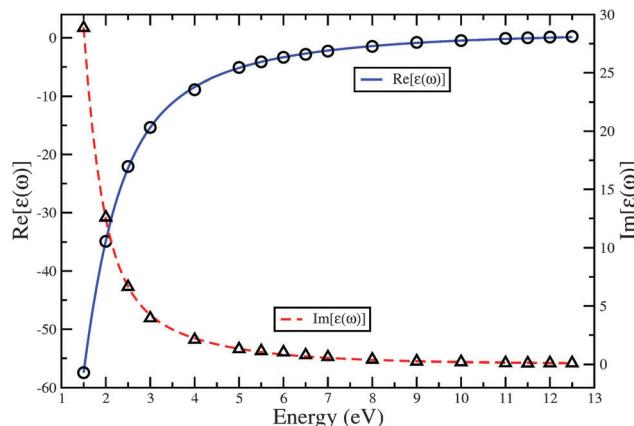


Fig. 1 Relative permittivity $\varepsilon(\omega)$ of In from 1.5 to 12.5 eV, evaluated using eqn (1) with the parameters in the text. The real and imaginary parts of $\varepsilon(\omega)$ are shown as blue solid and red dashed lines, respectively. The corresponding parts of the experimental data² used for the fitting of eqn (1) are also shown as circular and triangular symbols, respectively.

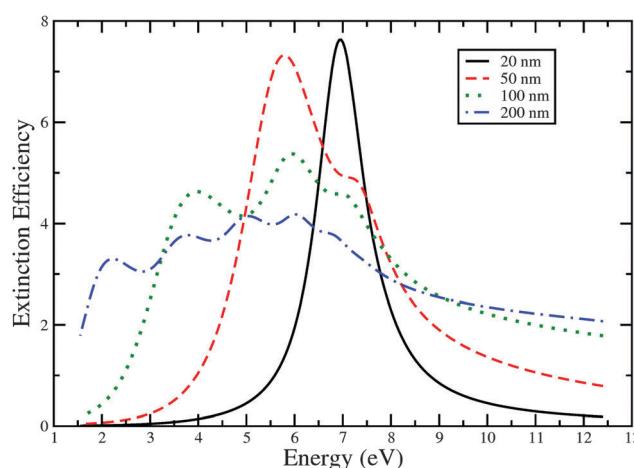


Fig. 2 Extinction efficiencies for spherical In particles with diameters of 20, 50, 100, and 200 nm.

of Fig. 11 of **I**, they are actually more likely to occur in the middle to far UV. Considering further that the width of the resonances of the isolated In particles are narrower relative to Ga, it is expected that the $|\mathbf{E}|^2$ enhancements of the former should be stronger, though still less than aluminum (Al), which has very strong and narrow single-particle resonances (see the top panel of Fig. 6 of **I**).

In addition to our incorrect use of the In experimental optical data² in **I**, we have also noticed three other errors, though they do not (significantly) affect the results. First of all, $\Delta\varepsilon_2$ for Al in Table 2 of **I** should be 0.070, not 0.069. Secondly, γ_{Ln} in the text in Sections 2.1 and 2.2 of **I**, as well as γ_{L1} and γ_{L2} of Table 2 of **I** are typos; they should be δ_{Ln} , δ_{L1} , and δ_{L2} , respectively. Finally, in Section 2.2 of **I**, we reported that Ga was experimentally measured at 140 and 77 K at low- and high-energies, respectively. However, it was actually thallium that was measured at these temperatures.^{6,7} Ga was measured at 300 K.^{8,9}

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References

1. J. M. McMahon, G. C. Schatz and S. K. Gray, *Phys. Chem. Chem. Phys.*, 2013, **15**, 5415, DOI: 10.1039/c3cp43856b.
2. R. Y. Koyama, N. V. Smith and W. E. Spicer, *Phys. Rev. B: Solid State*, 1973, **8**, 2426.
3. J. M. McMahon, S. K. Gray and G. C. Schatz, *Phys. Rev. Lett.*, 2009, **103**, 097403.
4. J. M. McMahon, S. K. Gray and G. C. Schatz, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2010, **82**, 035423.
5. C. F. Bohren and D. R. Huffman, *Absorption and Scattering of Light by Small Particles*, John Wiley & Sons, Inc., New York, 1983.
6. G. Jézéquel, J. Thomas and I. Pollini, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1988, **37**, 8639.
7. H. P. Myers, *J. Phys. F: Met. Phys.*, 1973, **3**, 1078.
8. O. Hunderi and R. Ryberg, *J. Phys. F: Met. Phys.*, 1974, **4**, 2084.
9. G. Jézéquel, J. C. Lemonnier and J. Thomas, *J. Phys. F: Met. Phys.*, 1977, **7**, 1613.

The Royal Society of Chemistry apologises for these errors and any consequent inconvenience to authors and readers.

