Measuring attogram masses of elemental mercury using individual gold nanorods

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Supplemental Data

1. Bimetallic alloy LSPR model

We modelled the wavelength dependence of the extinction coefficient for amalgam nanoparticles to better understand the blue shift upon mercury adsorption. Bimetallic nanoparticles have been found to have LSPR wavelengths with a linear dependence on alloy fraction.[1] Given the initial LSPR peak ($(\lambda_{LSPR})_{Au}$) and the predicted peak for a pure mercury nanorod ($(\lambda_{LSPR})_{Hg}$) $(\lambda_{LSPR})_{Hg}$)of the same dimensions and surrounding media, the mass fraction of mercury (w_{Hg}) can be calculated from the observed amalgam LSPR peak ($(\lambda_{LSPR})_{Au\text{-}Hg}$)$(\lambda_{LSPR})_{Au\text{-}Hg}$):

$$w_{Hg} = \frac{(\lambda_{LSPR})_{Au}\text{-}(\lambda_{LSPR})_{Au\text{-}Hg}}{(\lambda_{LSPR})_{Au}\text{-}(\lambda_{LSPR})_{Hg}} \quad (1)$$

To complete our model we need a prediction of the pure gold and pure mercury LSPRs. Link et al. presented a model for extinction from noble metal nanorods based on Gans theory:[2]

$$\gamma = \frac{2\pi N V \epsilon_m^{3/2}}{3\lambda} \sum_j \frac{\left(\frac{\epsilon_2}{P_j^2}\right)}{\left(\epsilon_1 + \frac{1\text{-}P_j}{P_j}\epsilon_m\right)^2 + \epsilon_2} \quad (2)$$

γ is the extinction coefficient, N Nthe number of particles per unit volume, V the particle volume, $c_m\epsilon_m$ the dielectric constant of the surrounding media, λ the wavelength of the interacting light, and c_1 and c_2 are the real and complex parts of the material dielectric function. Link et al. refer to P_j as the depolarization factors for the three axes A, B, and C of the rod.[2] Because of the axial symmetry two of these are equal and A refers to the length of the rod. The depolarization factors are calculated using the following equations:

$$P_A = \frac{1\text{-}e^2}{e^2}\left[\frac{1}{2e}\ln\left(\frac{1+e}{1\text{-}e}\right)\text{-}1\right] \quad (3)$$

$$P_B = P_C = \frac{1\text{-}P_A}{2} \quad (4)$$

$$e = \sqrt{1\text{-}(B/A)^2} \quad (5)$$

where A/B is the aspect ratio.

To calculate the LSPR of an average particle (62 nm long, 20 nm diameter) we input the metal's known complex dielectric[3] and the refractive index of the environment. The model does not provide for the heterogeneity of the particle's immediate surroundings (a particle with an attached ligand on a substrate in air). We use an average index of 2 to match the calculated pure gold peak with the experimentally observed peak. The predicted longitudinal LSPR peak wavelength of the 20x62 nm mercury nanorod (HgNR) is 480 nm, and 756 nm for the AuNR. The chromatic distribution of the extinction coefficient for a nanorod of each material is presented in figure SD.1.

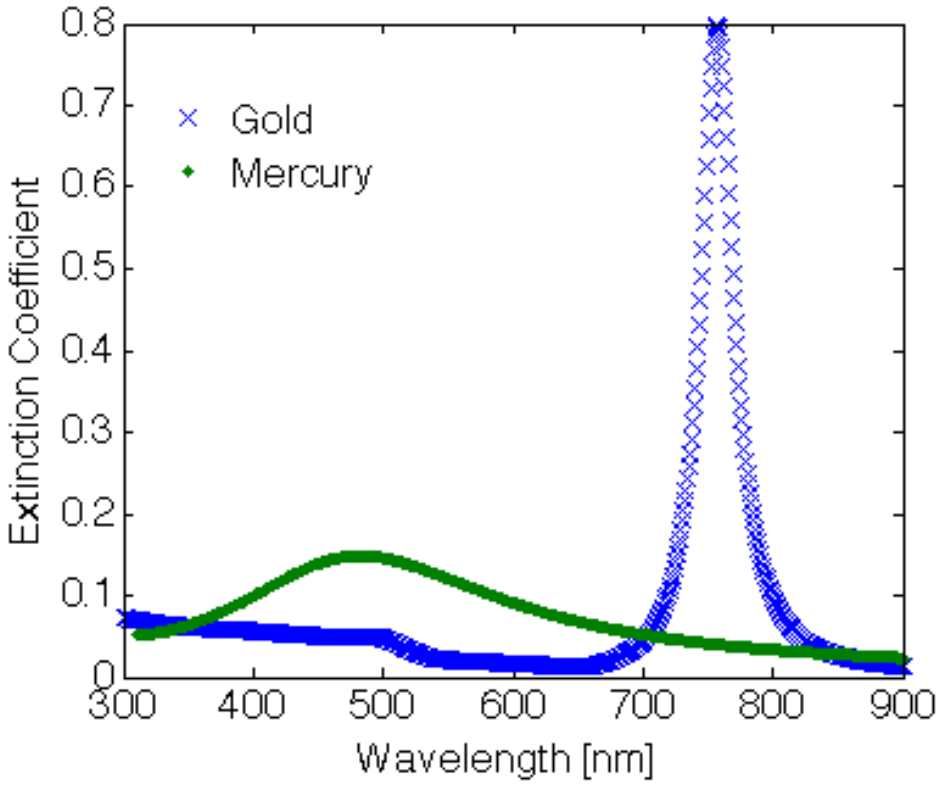

Figure SD.1 Predicted absorption spectra for gold and mercury nanorods (20x62 nm).

We observed saturated particles of this size shift 3 nm, or 1% the difference between the LSPR wavelengths of an AuNR and an HgNR of those dimensions. This suggests that these saturated particles consists of 1% Hg and 99% Au. The EDX data, size measurements, and LSPR model are all in agreement that the mass of mercury in a saturated AuNR is on the order of 1% the rod mass. Previous work by Levlin et al. found that single crystal gold surfaces exposed to mercury vapour saturate before formation of a complete of monolayer, with saturation at approximately 40% of a monolayer.[4] In the case of our particles a complete monolayer would result in a mass fraction of 2.5% Hg, so the observed 1% Hg agrees with the 40% monolayer coverage value. Our model has an obvious linear relationship with SA:V from equation 1 with the assumption of a consistent submonolayer coverage at saturation. Fixing the model inputs to a constant SA:V and varying the aspect ratio fits with the monotonic relationship between shift at saturation and aspect ratio.

To directly compare the experimental results and model we can input the observed particle dimensions into the model and predict the shift at saturation. We assume that mass fraction of mercury at saturation is equivalent to a 45% monolayer surface coating of mercury. The results of this prediction are plotted against the experimental data in figure SD.2. For the 12 particles tested, the average percent difference between the model and experimental results is 5%.

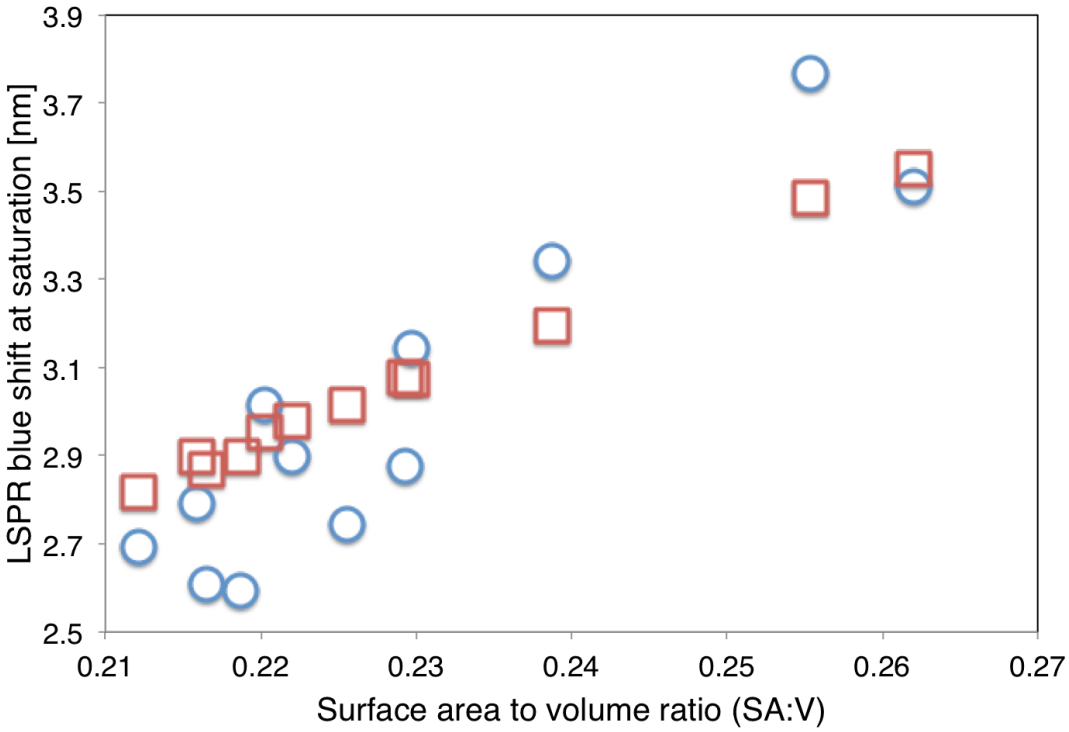

Figure SD.2 Comparison of model predicted LSPR-shifts at saturation with those found experimentally.

2. Core/Shell model prediction of geometric effects

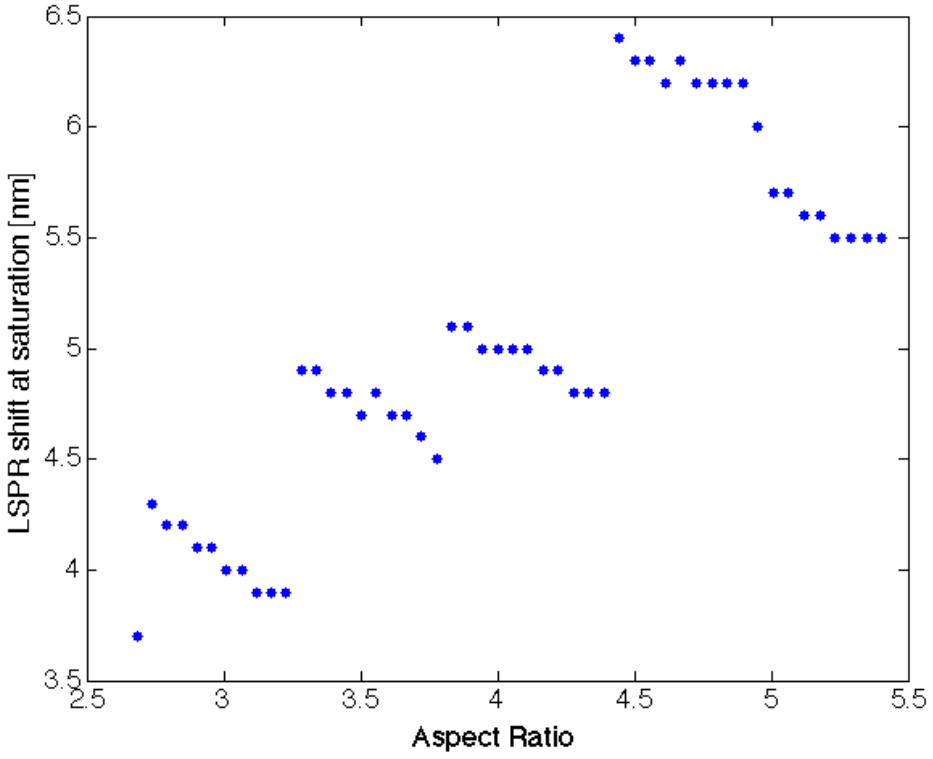

Figure SD.3 Core/shell model approximation of shifts at saturation for a range of aspect ratios with a constant surface area to volume ratio.

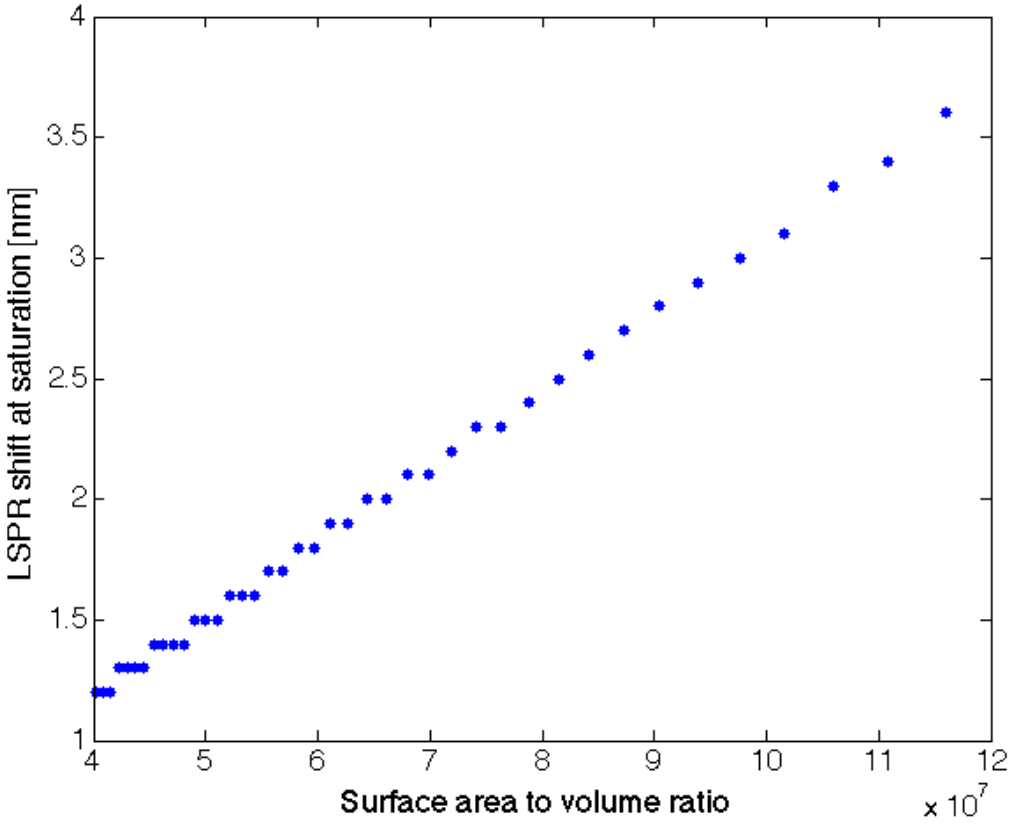

Figure SD.4 Core/shell model approximation of shifts at saturation for a range of surface area to volume ratios and a constant aspect ratio (3).

1. S. Link, Z. L. Wang, and M. A. El-Sayed, *The Journal of Physical Chemistry B*, 1999, **103**, 3529–3533.
2. S. Link, M. B. Mohamed, and M. A. El-Sayed, *The Journal of Physical Chemistry B*, 1999, **103**, 3073–3077.
3. E. Arakawa and T. Inagaki, in *Handbook of optical constants of solids II*, Academic Press, 1991, pp. 467–470.
4. M. Levlin, E. Ikävalko, and T. Laitinen, *Fresenius' Journal of Analytical Chemistry*, 1999, **365**, 577–586.