Electronic Supplementary Material (ESI) for RSC Advances

Characterization of Gold Agglomerates: Size Distribution, Shape and Optical Properties

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Supplementary Information

Simulation of UV-visible spectra

UV-Visible spectra of agglomerated gold colloids were derived from the Mie theory in the electric dipole approximation. [1, 2] Based on transmission electron microscopy (TEM) images, agglomerates were modelled as prolate spheroids with fixed minor radii of 16.5 nm and major radius (16.5 x n) nm, with n = 1 for raw gold nanoparticles (AuNPs), then 2, 3, … for increasing agglomerate size.

The extinction cross section C_{ext} of an agglomerate is composed of the corresponding absorption and the scattering cross sections:

$$C_{ext} = C_{abs} + C_{sca} \quad \text{(S1)}$$

In terms of the electric dipole approximation, C_{abs} and C_{sca} can be calculated as follows:

$$C_{abs} = \frac{8\pi^2}{3\lambda} \mathrm{Im}(\alpha_l + 2\alpha_t) \quad \text{(S2)}$$

$$C_{sca} = \frac{128\pi^5}{9\lambda^4} (|\alpha_l|^2 + 2|\alpha_t|^2) \quad \text{(S3)}$$

where λ is the incident wavelength. Equations (S2) and (S3) indicate that this model simplifies the polarizability (α) of agglomerates into two orthogonal dipole tensor components, i.e. longitudinal (α_l) and transversal (α_t) polarizability tensor components, and ignores the contribution from higher order multiple moments. In other words, the physical model defines longitudinal and transverse eigenmodes of the chain as a whole, corresponding to the two extinction maxima discussed in the paper. This is in agreement with the characteristics of theoretical extinction spectra of planar gold agglomerates where interaction among particles is restricted to dipole-dipole coupling. [3] The method is just applicable for small agglomerates in which mainly in-phase dipolar modes are significantly excited. The polarizability tensor components are given by:

$$\alpha_{l,t} = \frac{V(\varepsilon - 1)}{4\pi + (\varepsilon - 1)P_{l,t}} \quad \text{(S4)}$$

where V is the volume of the prolate spheroid, ε is the dielectric constant (at the incident wavelength) of the metal (i.e. gold) [4] with respect to surrounding medium (i.e. water [5] in this case). $P_{l,t}$ is a shape factor given by [6]:

$$P_l = \frac{4\pi}{r^2-1}\left\{\frac{r}{\sqrt{r^2-1}}\ln[r+\sqrt{r^2-1}]-1\right\} = 4\pi - 2P_t \qquad \text{(S5)}$$

where $r = a/b$, i.e. the ratio of the semi major axis a to the semi minor axis b of the agglomerate. In our calculation b is fixed to the mean radius of the individual particles (16.5 nm).

Fig. S1 shows simulated UV intensities for a sphere of radius 16.5 nm, and for agglomerates formed from n = 2, 3, 4 and 5 spheres with a radius of 16.5 nm arranged in a chain. The wavelength of maximum intensity is plotted against n in Fig. S2. Interpolation of experimental maxima gave effective numbers of particles in the chain, and then an equivalent diameter of the sphere of equal volume to that of the prolate spheroid was calculated and compared with mean diameters measured by differential centrifugal centrifugation and particle tracking analysis (Fig. 2 in paper).

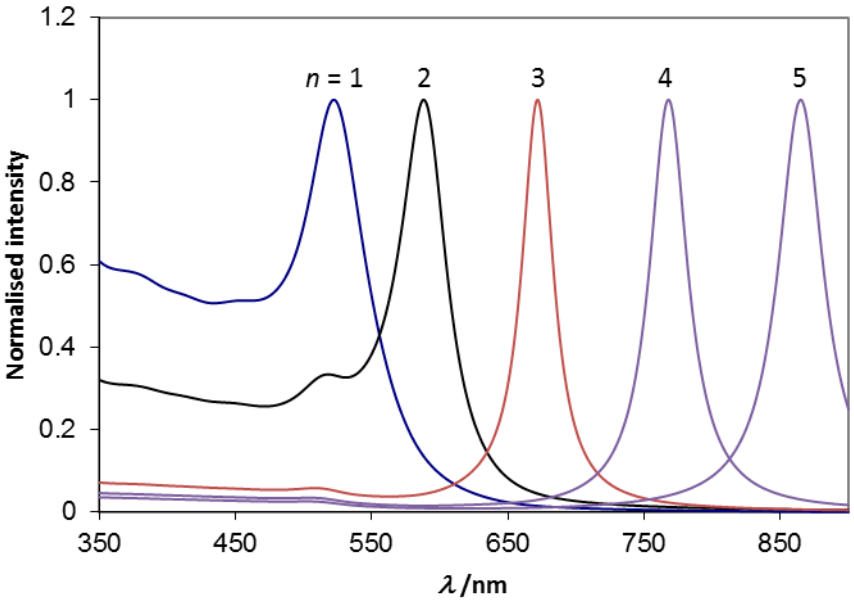

Fig. S1 Calculated UV-visible spectra of prolate spheroids having $a = b = 16.5$ nm and $c = 16.5$ nm × n, where $n = 1, 2, \ldots, 5$.

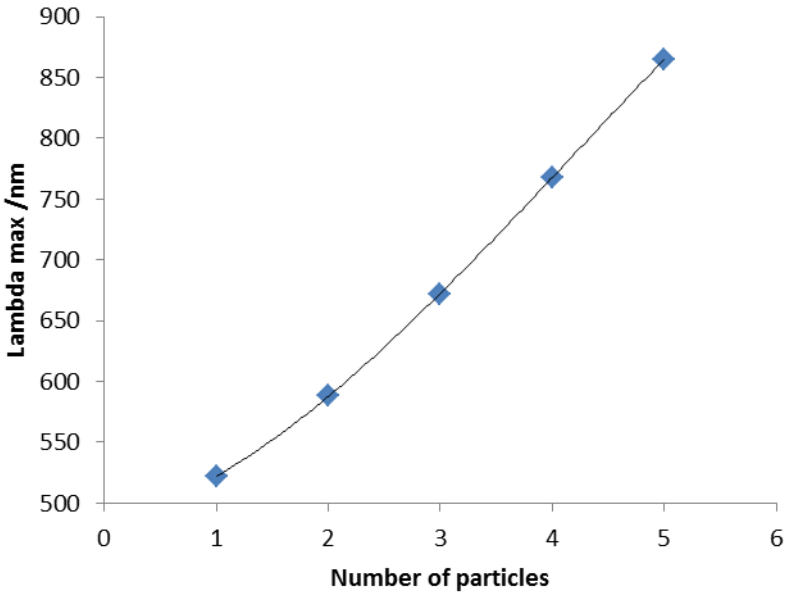

Fig. S2. Wavelength of maximum intensity of a calculated UV-visible spectrum of prolate spheroids having $a = b = 16.5$ nm and $c = 16.5$ nm $\times n$, where $n = 1, 2, \ldots, 5$.

References

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