Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information: Determining Nanorod Dimensions in Dispersion with Size Anisotropy Nanoparticle Tracking Analysis

William H. Hoffmann,[†,‡,¶] Bo Gao,[†] Niall M.C. Mulkerns,[†,¶] Alexander G. Hinton,[†,‡] Simon Hanna,[†] Simon R. Hall,[‡,¶] and Henkjan Gersen[*,†,¶]

†*H.H. Wills Physics Laboratory, University of Bristol, Tyndall Avenue, Bristol BS8 1TL, UK*

‡*School of Chemistry, University of Bristol, Cantock's Close, Bristol BS8 1TS, UK*

¶*Bristol Centre for Functional Nanomaterials, University of Bristol, Tyndall Avenue, Bristol BS8 1TL, UK*

E-mail: h.gersen@bristol.ac.uk

Nanorod polarisability in the Rayleigh-Gans approximation

In SANTA, the polarisation state of light scatterered from single nanoparticles is used to interrogate nanoparticle aspect ratio. The change in the polarisation state of the scattered light comes from the change in the polarisability of the nanoparticle when its dimensions are modified. In this work, the Rayleigh-Gans prolate ellipsoid approximation[S1,S2] of nanoparticle scattering is used, which allows the calculation of the nanorod polarisabililty along its long and short axes. The polarisability components can be calculated with

$$\alpha_i = \frac{4}{3}\pi ABC \frac{\epsilon_p - \epsilon_m}{\epsilon_m + \mathcal{L}_i(\epsilon_p - \epsilon_m)} \tag{1}$$

where α_i is the polarisability along the i-th axis, ϵ_p is the relative permittivity of the nanoparticle, ϵ_m is the relative permittivity of the medium, $\mathcal{L}_i$ is a shape factor, and A, B, and C are the semiaxes of the ellipsoid along axes a, b, and c, respectively. For a prolate ellipsoid, shape factors are known analytically:

$$\mathcal{L}_a = \frac{1-e^2}{e^2}\left(-1 + \frac{1}{2e}\ln\frac{1+e}{1-e}\right), \tag{2}$$

$$\mathcal{L}_{b,c} = \frac{1-\mathcal{L}_a}{2}, \tag{3}$$

where $e = \sqrt{1-\left(\frac{C}{A}\right)^2}$. Therefore, with knowledge of the nanorod dimensions, the polarisability components can be calculated.

TEM images

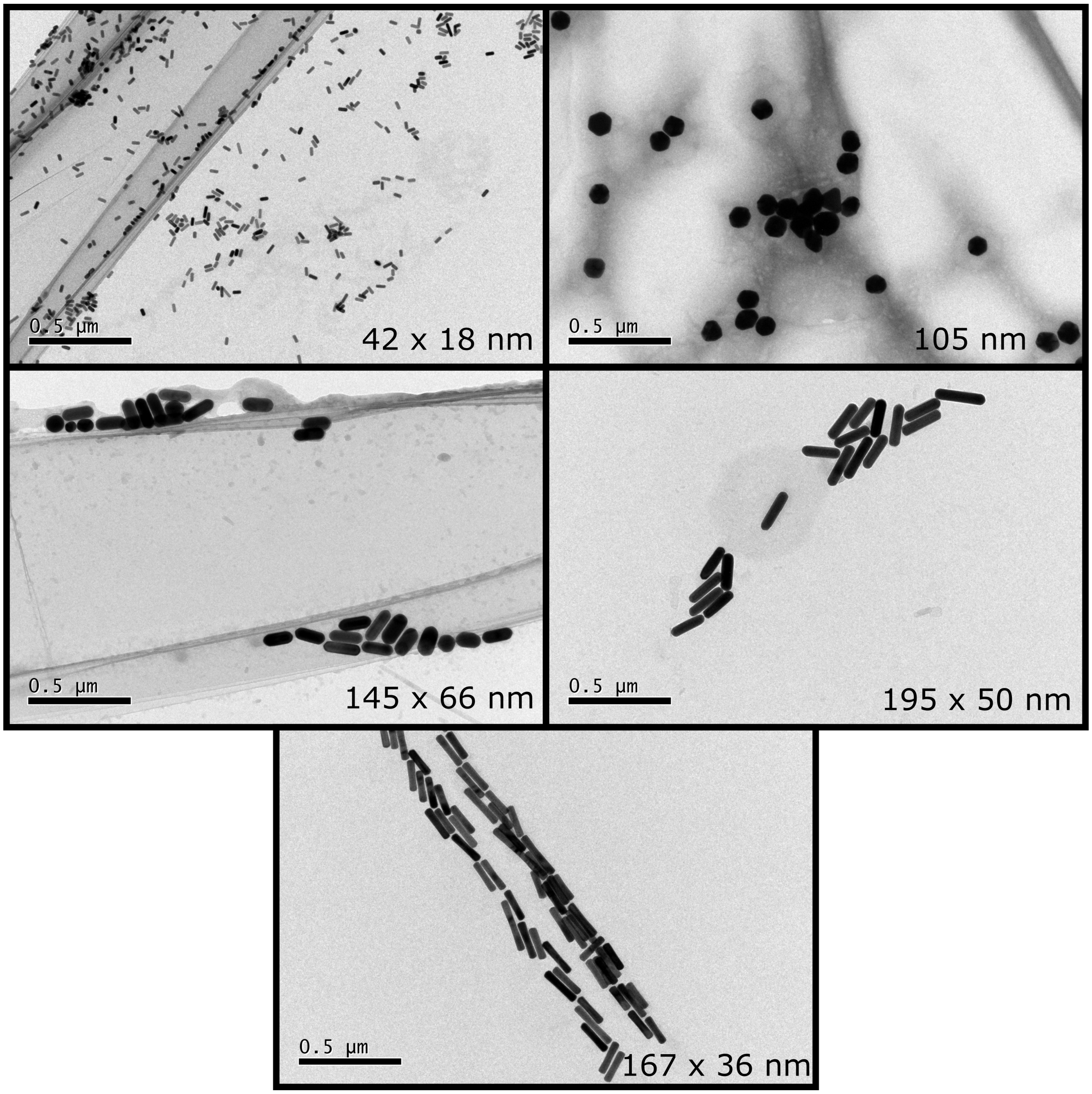

Figure S1: Example TEM micrographs of the nanoparticles used in this work.

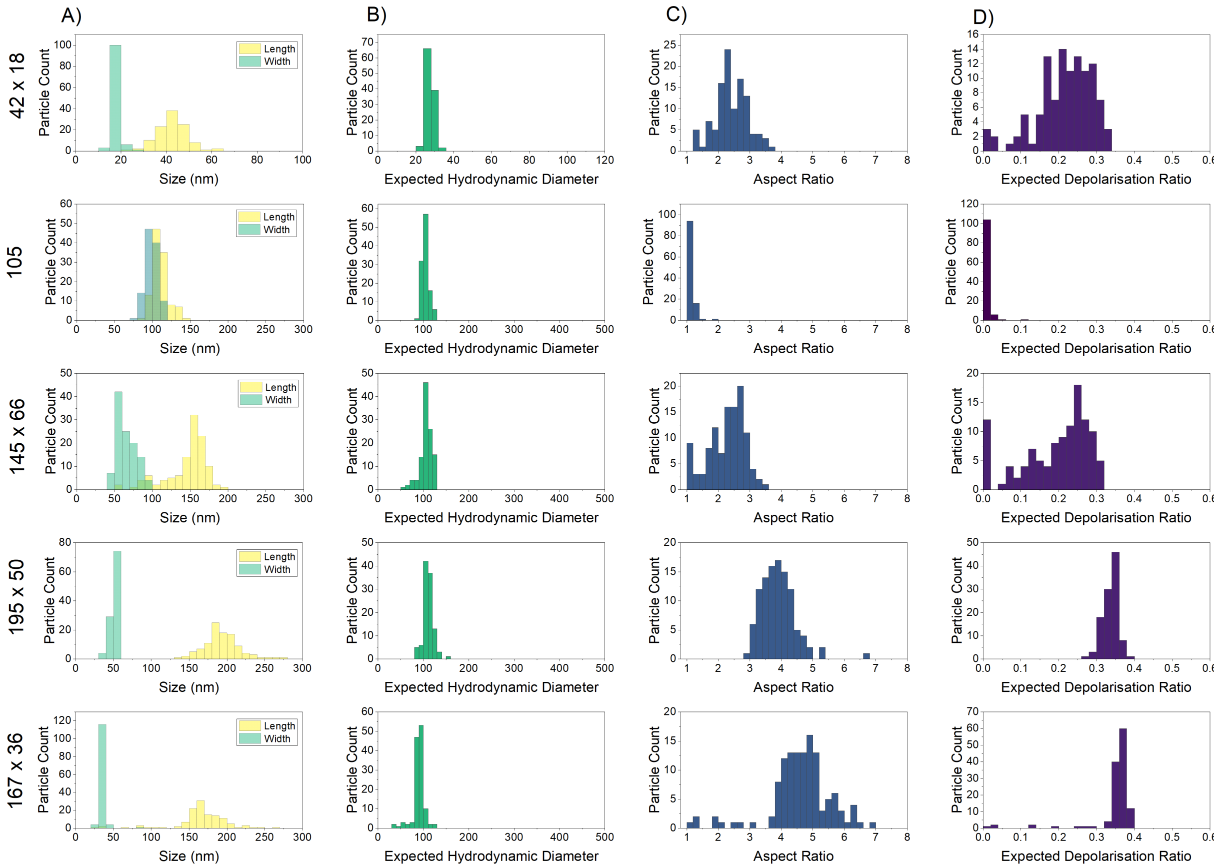

Figure S2: Plots with data collected from measuring the TEM images. Rows correspond to the sample indicated. A) Measured lengths and widths of the nanoparticles. B) The expected hydrodynamic diameter distributions calculated from the size measurements in column A. C) Aspect ratios. D) The expected depolarisation ratio distributions calculated from the values in column C.

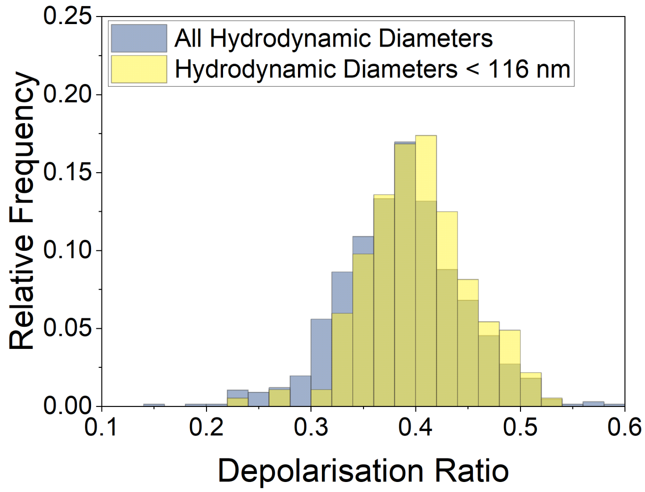

Figure S3: Depolarisation ratio distributions obtained for the 167 nm × 36 nm nanorods without filtering based on hydrodynamic diameter (grey) and with filtering out nanoparticles with hydrodynamic diameters greater than 116 nm. This value was selected as the cutoff because it is two standard deviations larger than the expected mean hydrodynamic diameter determined from TEM. Whilst there is a slight shift to higher depolarisation ratios upon filtering, the broadness of the distribution does not appreciably change, indicating that the depolarisation ratio distribution is not significantly affected by aggregation.

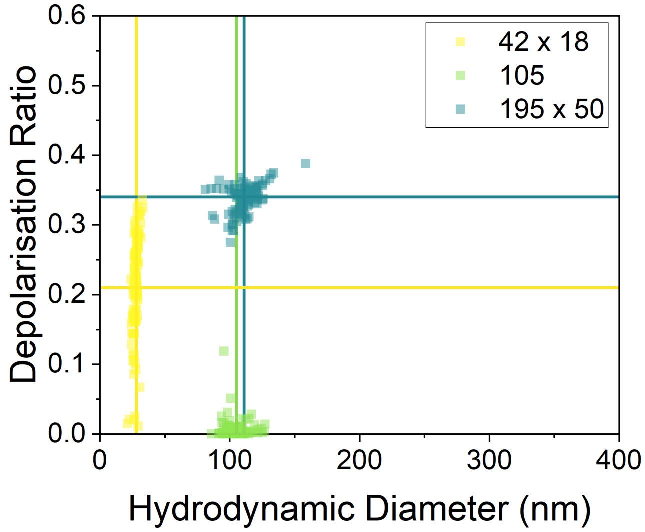

Figure S4: Expected depolarisation ratio vs. expected hydrodynamic diameter of individual nanoparticles from TEM data based on the limited number of nanoparticles imaged. The lower depolarisation ratios shown here for the 42 nm × 18 nm sample are not detected in SANTA, possibly due to the comparatively lower scattering signal from this nanoparticle size.

References

(S1) Chen, H.; Shao, L.; Li, Q.; Wang, J. Gold nanorods and their plasmonic properties. *Chemical Society Reviews* **2013**, *42*, 2679–2724.

(S2) Bohren, C. F.; Huffman, D. R. *Absorption and Scattering of Light by Small Particles*; Wiley-VCH: Weinheim, Germany, 2004.