Electronic Supplementary Information

Single Particle Study: Size and Chemical Effects on Plasmon Damping at the Interface between Adsorbate and Anisotropic Gold Nanorods

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This document contains detailed experimental methods and additional supplementary figures (Fig. S1 to S5).

Experimental Methods

Discrete Dipole Approximation (DDA) Calculations

Modelling the optical properties of AuNRs is of paramount importance in tailoring conditions to exploit performance optimally in these applications. Furthermore, comparison of experimental data with simulated optical properties is a means of characterizing samples of nanoparticles in terms of the various parameters such as size, geometry, concentration, etc.

Of the various numerical methods available, the Discrete Dipole Approximation approach implemented in the publicly available DDSCAT code is a powerful method to simulate the extinction spectra of AuNRs.[1-4] DDSCAT is a FORTRAN package that implements the DDA method to simulate interaction of electromagnetic radiation with particles of arbitrary shape and composition. The method is described in detail elsewhere.[1-4] In the present study, we used DDSCAT to study the relative contributions of scattering and absorption to the extinction as a function of medium refractive index. Briefly, the particle is subdivided into N polarizable points, located on a cubic lattice with an interdipole distance d given by $V = Nd3$ where V is the volume of the particle. The radiation scattered and absorbed by the target is computed taking into consideration dipole-dipole interactions. For this study, the AuNRs were represented as hemispherically-capped cylinders, and the dielectric function of gold was chosen from Johnson and Christy.[5]

References

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2. W. –H. Yang, G. C. Schatz, R. R. van Duyne, *J. Chem. Phys*., 1995, **103**, 869-875.
3. N. Félidj, J. Aubard, G. Lévi, *J. Chem. Phys*., 1999, **111**, 1195.
4. A. L. Gonzalez, C. Noquez, *J. Compt. Theor. Nanosci*., 2007, **4**, 231-238.
5. P. B. Johnson, R. W. Christy, *Phys. Rev. B*, 1972, **6**, 4370-4379.

Supplementary Figures

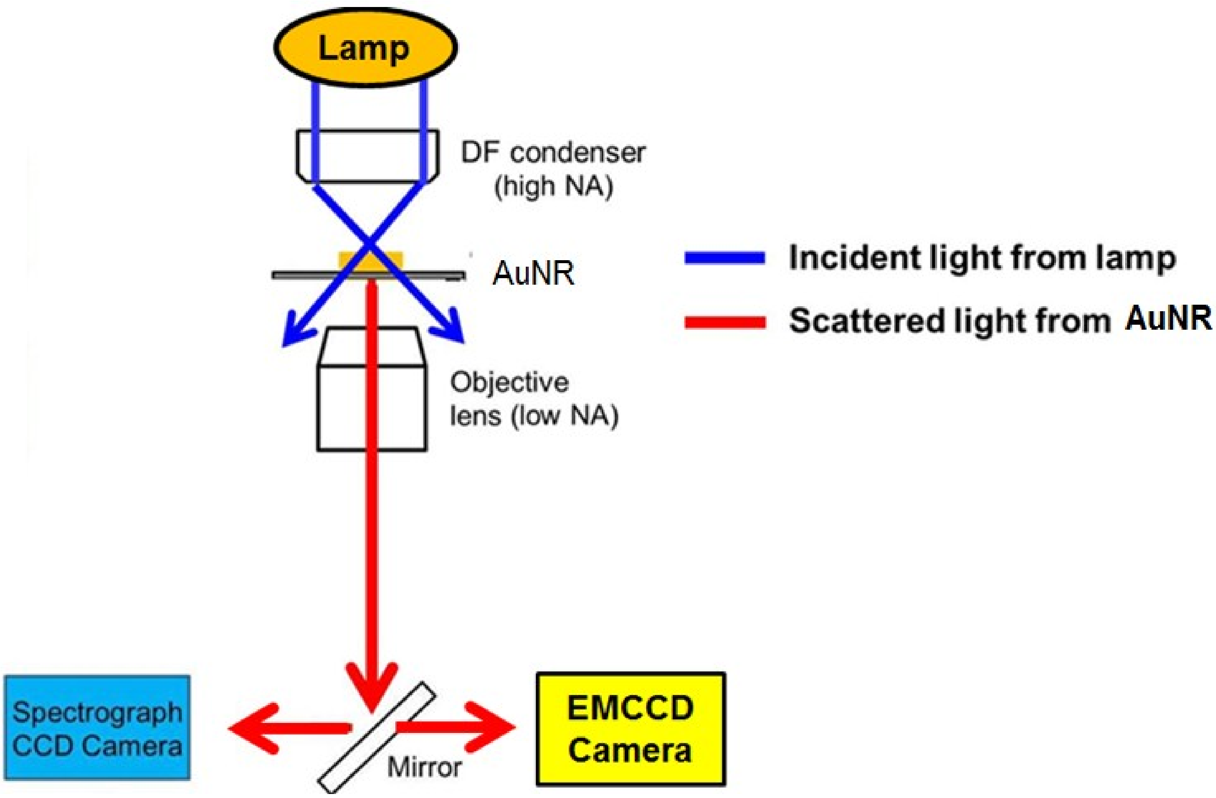

Fig. S1 Experimental setup for DF scattering microscopy and spectroscopy. The blue-line shows incident light from lamp, while the red-line indicates the scattered light from AuNR.

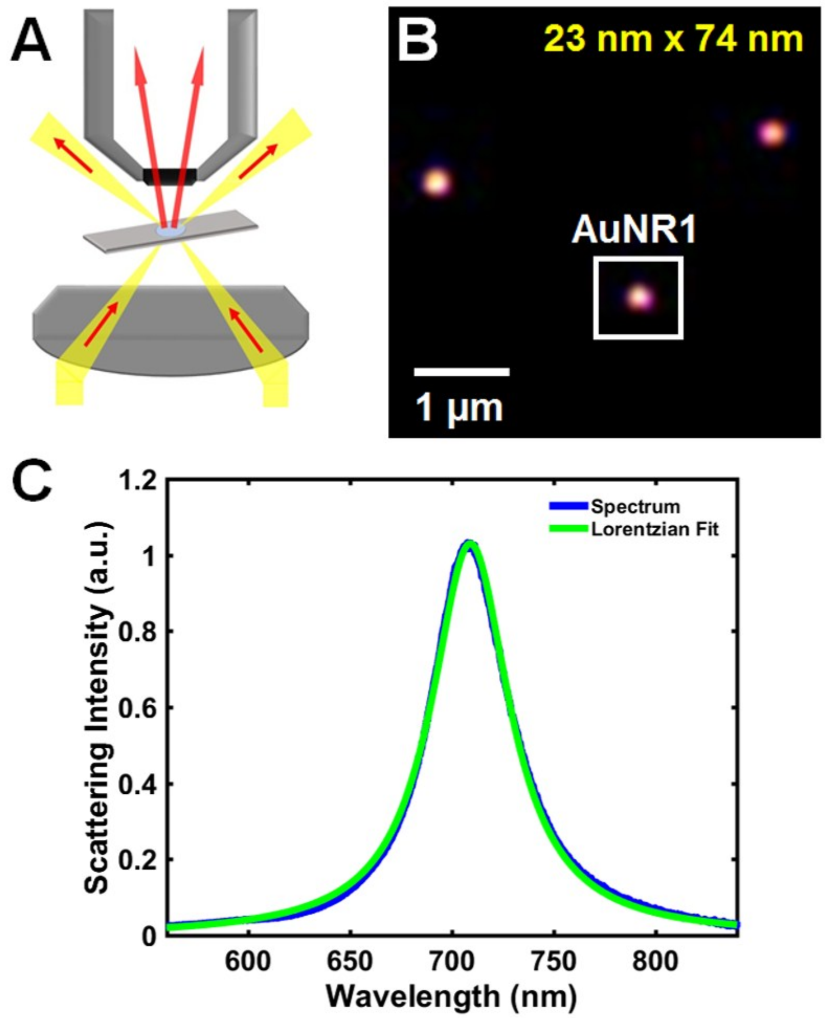

Fig. S2 (A) The working principle of DF microscopy. (B) DF scattering image of single AuNRs with an average size of 23 nm × 74nm. (C) Single particle scattering spectrum of AuNR1 indicated in (B). The longitudinal LSPR peak for the AuNR1 is observed at approximately 716 nm. The green curve shows a fit to Lorentzian function.

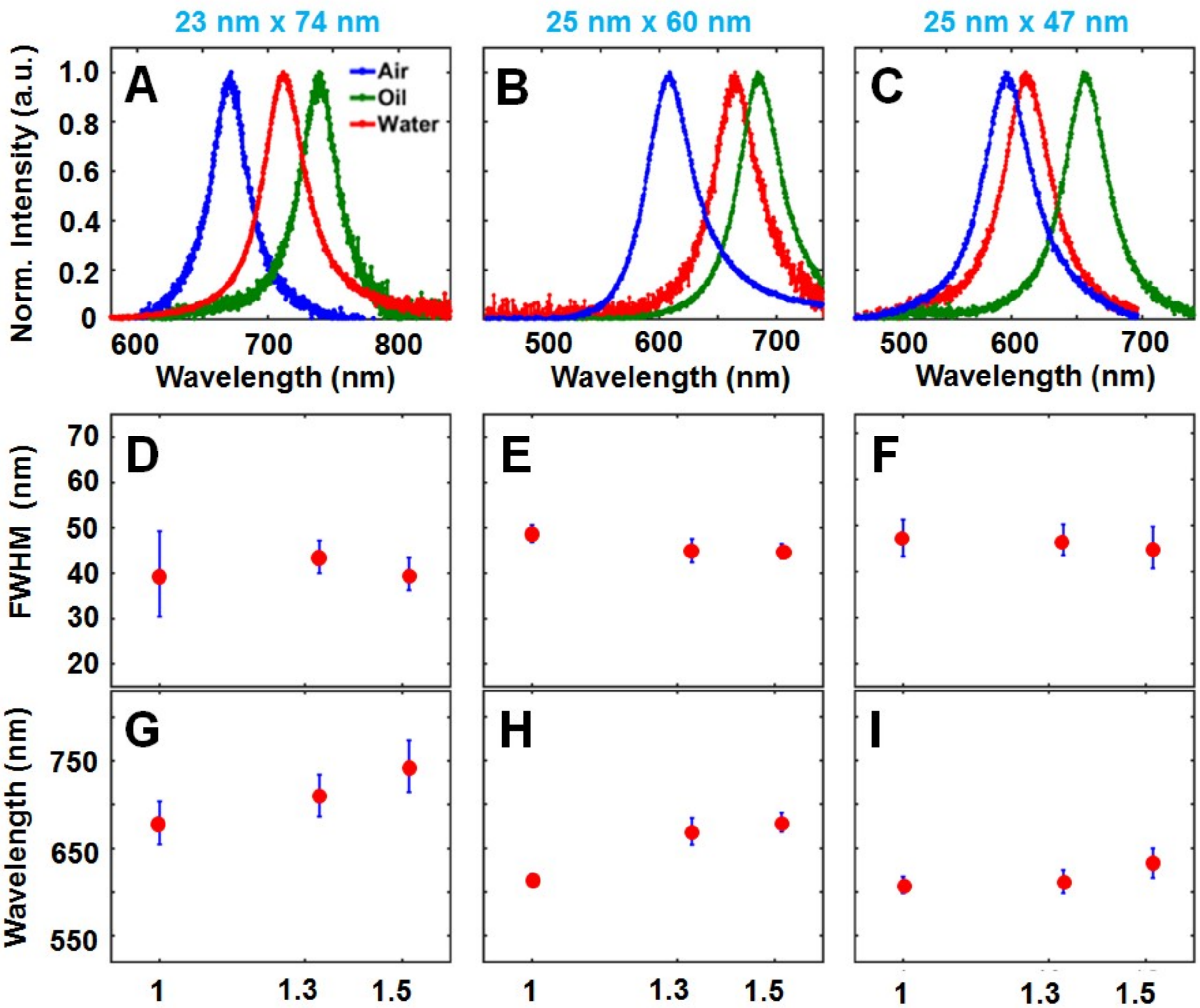

Fig. S3 (A, B, C) **S**cattering spectra of single AuNRs with three different ARs (1.88, 2.4, 3.22) in air (blue), water (red), and oil (green). (D, E. F) Change in the LSPR linewidth of single AuNRs with different ARs while varying the medium dielectric environment from air to oil. (G, H, I) Change in the LSPR wavelength of single AuNRs with different ARs while varying the medium dielectric environment from air to oil.

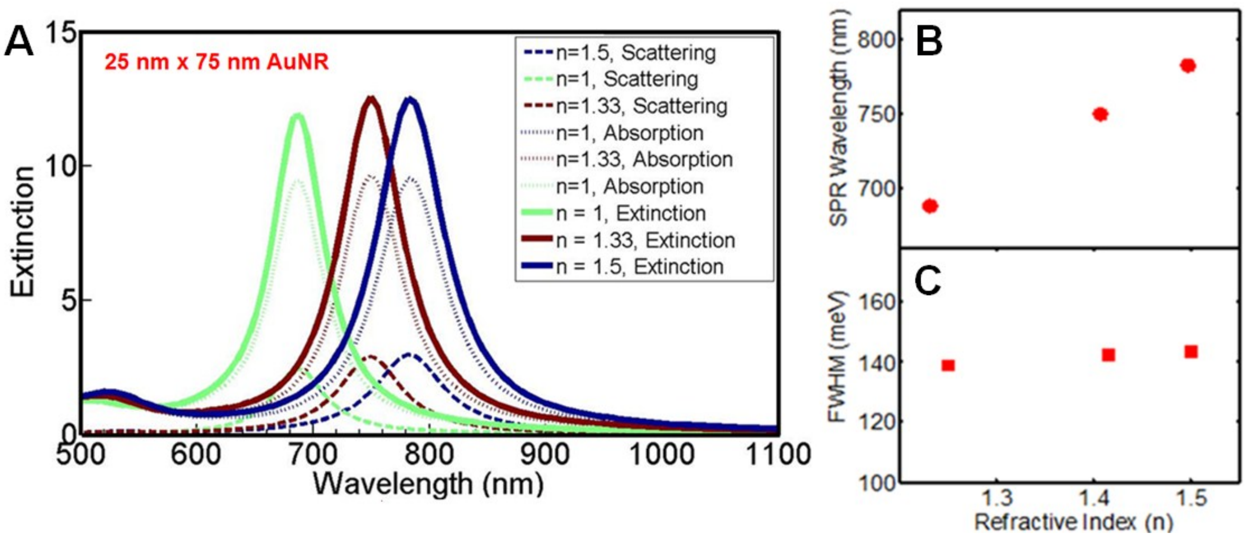

Fig. S4 (A) DDA calculation on the extinction, absorption, and scattering spectra of AuNR (25 nm × 75 nm) as a function of the medium refractive index (air, water, oil). (B) Change in the LSPR scattering wavelength in a different medium. (C) Change in the SPR linewidth as a function of refractive index from air to oil.

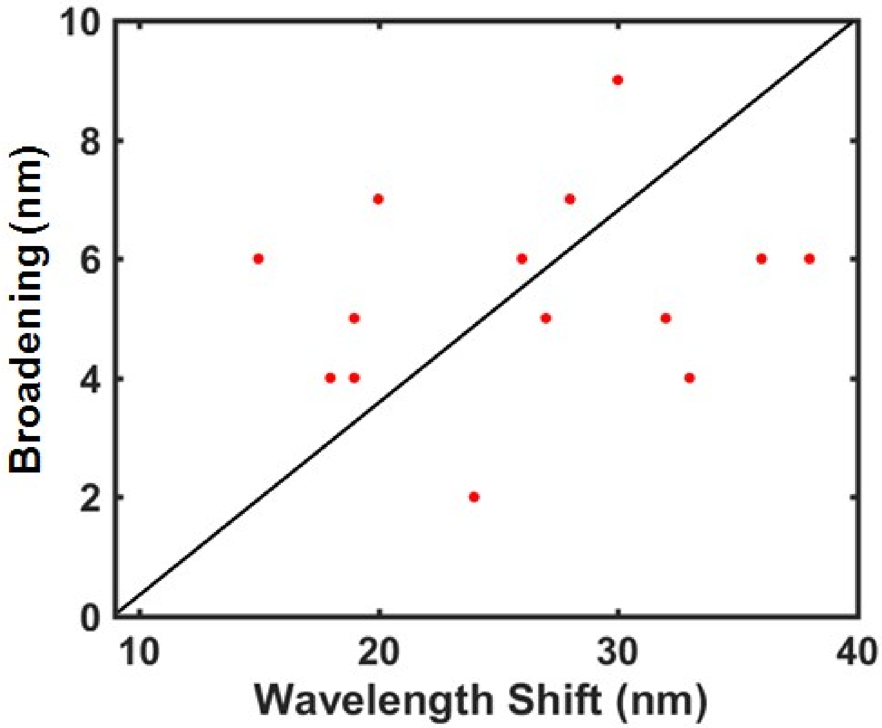

Fig. S5 Linear illustration of the non dependence character of the of the redshift caused by the refractive index change and the broadening of the full width at half maximum caused by the retardation of decay time due to the interaction of adsorbate with AuNR surfaces.