Unfolding the contents of sub-nm plasmonic gaps using normalising plasmon resonance spectroscopy

Bart de Nijs,[a] Richard W. Bowman,[a] Lars O. Herrmann,[a] Felix Benz,[a] Steve J. Barrow,[b] Jan Mertens,[a] Daniel O. Sigle,[a] Rohit Chikkaraddy,[a] Anna Eiden,[c] Andrea Ferrari,[c] Oren A. Scherman,[b] Jeremy J. Baumberg*[a]

[a] *NanoPhotonics Centre, Cavendish Laboratory, Department of Physics, JJ Thompson Ave, University of Cambridge, Cambridge, CB3 0HE, UK. Tel: 01223 760945; E-mail: jjb12@cam.ac.uk*
[b] *Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EW, UK. Tel: 01223 331508; E-mail: oas23@cam.ac.uk*
[c] *Cambridge Graphene Centre, University of Cambridge, 9 JJ Thomson Avenue, Cambridge CB3 0FA, UK. Tel: 01223 748351; E-mail: acf26@cam.ac.uk*

Electronic Supplementary Information

Supplementary figures

Depositing 80 nm gold nanoparticles (Au NPs) on a glass cover slip shows no coupled (C) mode as shown in figures S1 where only the transverse (T) mode is visible at 533 nm. This shows that the coupled (C) modes shown in figures 2, 3, 5 and S2 are the result of the interaction between the gold nanoparticles and the substrate.

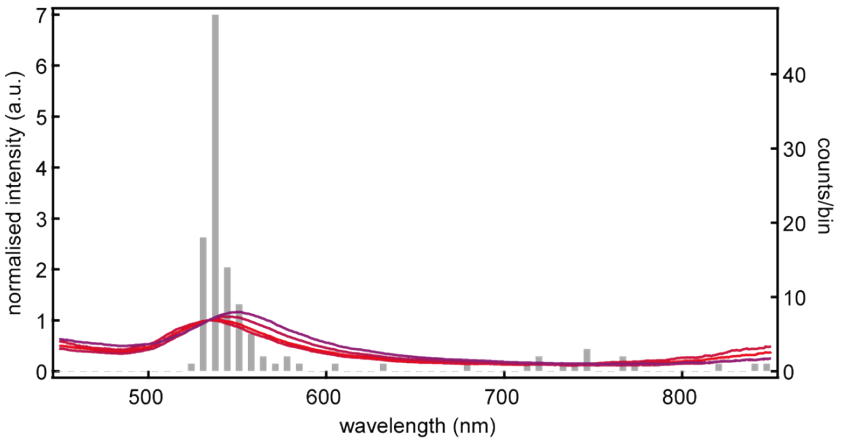

Figure S1: Scattering spectra of 80 nm Au NPs on glass, corrected for chromatic aberration with statistical peak distributions shown in grey. The scattering spectra of Au NPs on silica do not show a c-mode showing that the modes between 600-800nm are the result of coupling between Au NPs and the substrate.

Using smaller nanoparticles, 60 nm instead of 80 nm, resulted in a blue shift of the c-mode with respect to the larger nanoparticles as is shown in figure S2. Figure S2 shows distributions for both 60 nm and 80 nm Au NPs on a gold surface with cucurbit[7]uril (CB[7]) as a molecular spacer. Using larger nanoparticles (i.e. 100 nm) will result in a further red shift of the c-mode, moving it further towards the infrared.

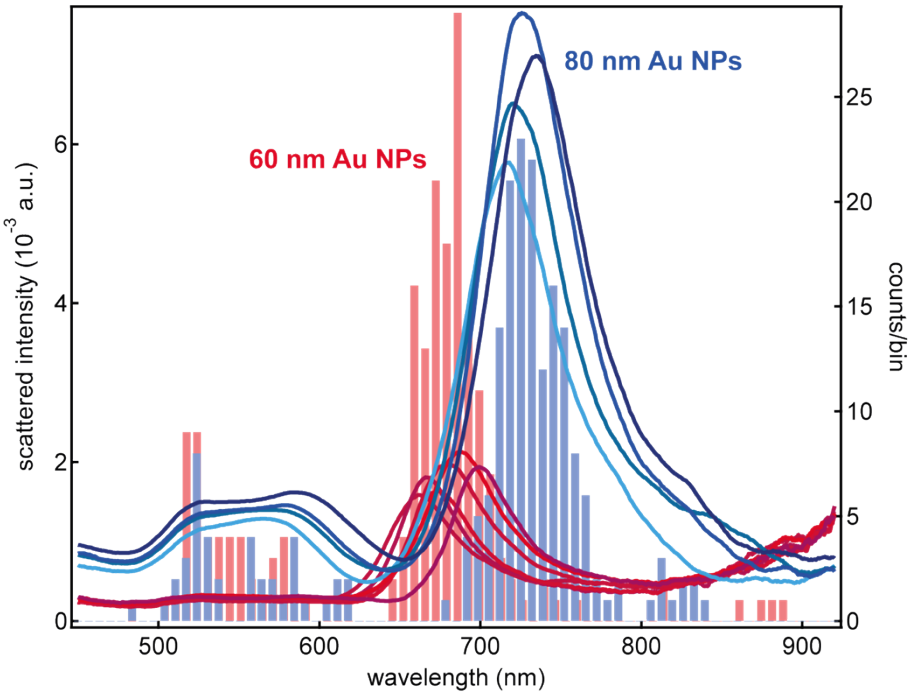

Figure S2: Averaged chromatic aberration corrected scattering spectra of 60 nm and 80 nm Au NPs on Au with a cucurbit[7]uril as a molecular spacer. A clear difference in scattering intensity can be observed as a result of the difference in NP size. Additionally the coupled mode shows a blue shift for the smaller 60 nm Au NPs with respect to the 80 nm Au NPs.