

Probing plasmon resonance's dependence on gap size in silver dimers by EELS

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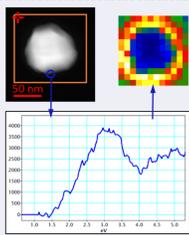
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Improvement in the energy resolution of modern analytical transmission electron microscopes (TEMs) has enabled electron energy-loss spectroscopy (EELS) in the visible light energy range and below. Aggregates of multiple silver nanoparticles, in which coupling of the particles results in highly confined and enhanced local fields in the nanometre size gaps between them, are of particular interest for various applications, including surface enhanced Raman spectroscopy [1]. While, most optical techniques do not hold the spatial resolution to image such small dimensions, EELS combined with scanning TEM (STEM) can probe Ångström-scale dimensions. We have studied silver dimers, as the simplest multiparticle plasmonic structure, with EELS. Changes of the dipolar plasmon resonances in EELS spectra of dimers as a function of the interparticle distance are monitored. Experimentally observed shifts of plasmon resonance are compared with computations, using a multiple-scattering simulation formalism [2]. The measurements and calculations were carried out for spherical particles ~20 – 30 nm in diameter.

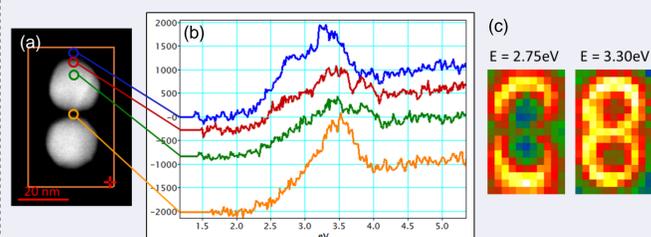
Seeing plasmon resonances with electrons

Plasmon resonances in metallic nanoparticles can be excited as the result of interaction with an electron beam, as well as being excited optically. This provides the opportunity to study plasmon resonances with Ångström spatial resolution and to correlate the results with theoretical calculations.

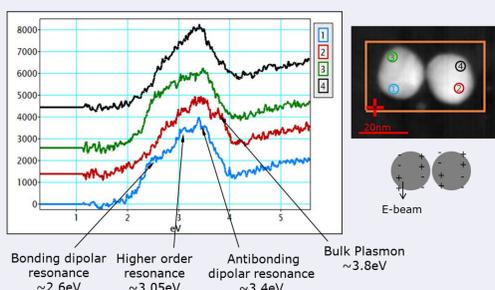
- STEM image, EELS spectrum and EELS intensity map of the surface plasmon resonance ($E = 3.05$ eV) of a single silver particle.



- Coupling between nanoparticles in dimers results in the appearance of different plasmon resonances in EELS, (plasmon hybridisation model [3]).
- Resonances at 2.75 eV and 3.30 eV (their intensities at different beam positions mapped in (c)) correspond to the bonding and antibonding dipolar plasmons.



- Higher order modes can also be observed in EELS.



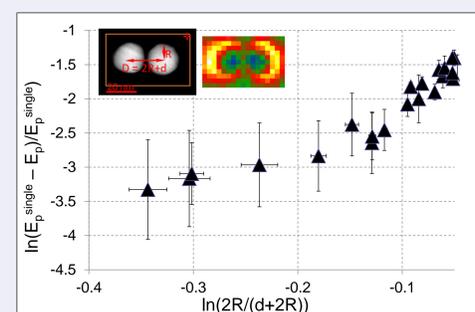
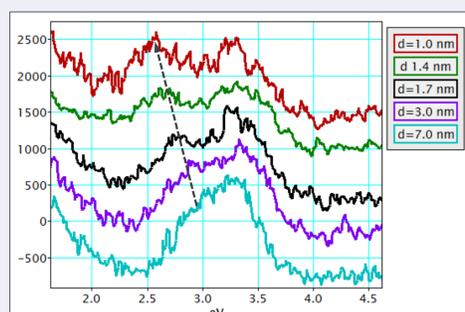
Acknowledgements

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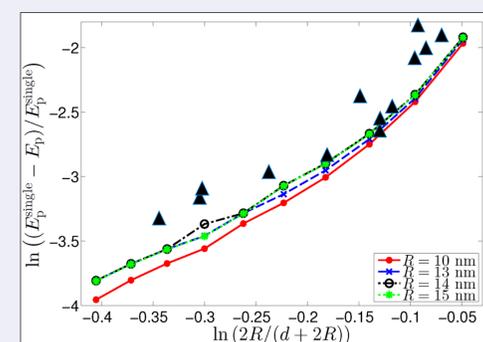
Plasmon resonance's dependence on gap size in silver dimers

As the separation distance between two nanoparticles decreases, the coupling between them strengthens and in the regime where quantum and non-local effects can be ignored, results in a redshift in the dipolar plasmon resonance. Understanding the scaling of the dipolar plasmon resonance with interparticle distance is relevant for various plasmonic structures, as discussed in the context of plasmonic rulers [4].

- Redshift of the dipolar plasmon with gap size in EELS from silver spheres of diameters 20 – 25 nm.
- The dipolar plasmon redshift ratio $(E_p^{\text{single}} - E_p)/E_p^{\text{single}}$ of silver dimers of 20 – 30 nm diameter, as a function of the diameter to the centre to centre distance ratio $(2R/(d+2R))$ (E_p^{single} is plasmon energy of a single particle of the same dimensions).



- EELS measurements are compared with simulations of optically excited dipolar plasmons of silver dimers, using a multiple scattering formalism based on the Lippmann-Schwinger equation and the electromagnetic Green's tensor [2].
- A linear fit for the logarithmic plot of the measurements can be considered (giving a scaling to the power 6.6 of plasmon energy with gap size) but the plots indicate a stronger redshift in dipolar plasmon energy for smaller gaps (below ~ 2 nm surface to surface gap here).



Conclusions

- High energy-resolution EELS is a powerful technique for probing the plasmonic properties of nanostructures with a high spatial resolution.
- The scaling of the dipolar plasmon resonance in silver dimers was investigated with EELS and computations. Experimental measurements are in good agreement with electromagnetic calculations for gaps down to ~1 nm.

References

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