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Calibrating Au and Ag plasmonic rulers with EELS

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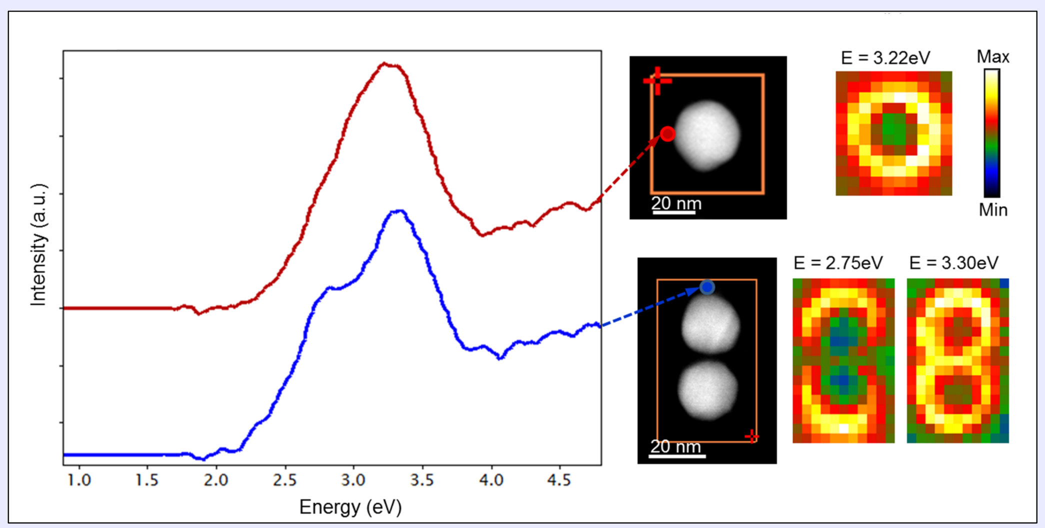
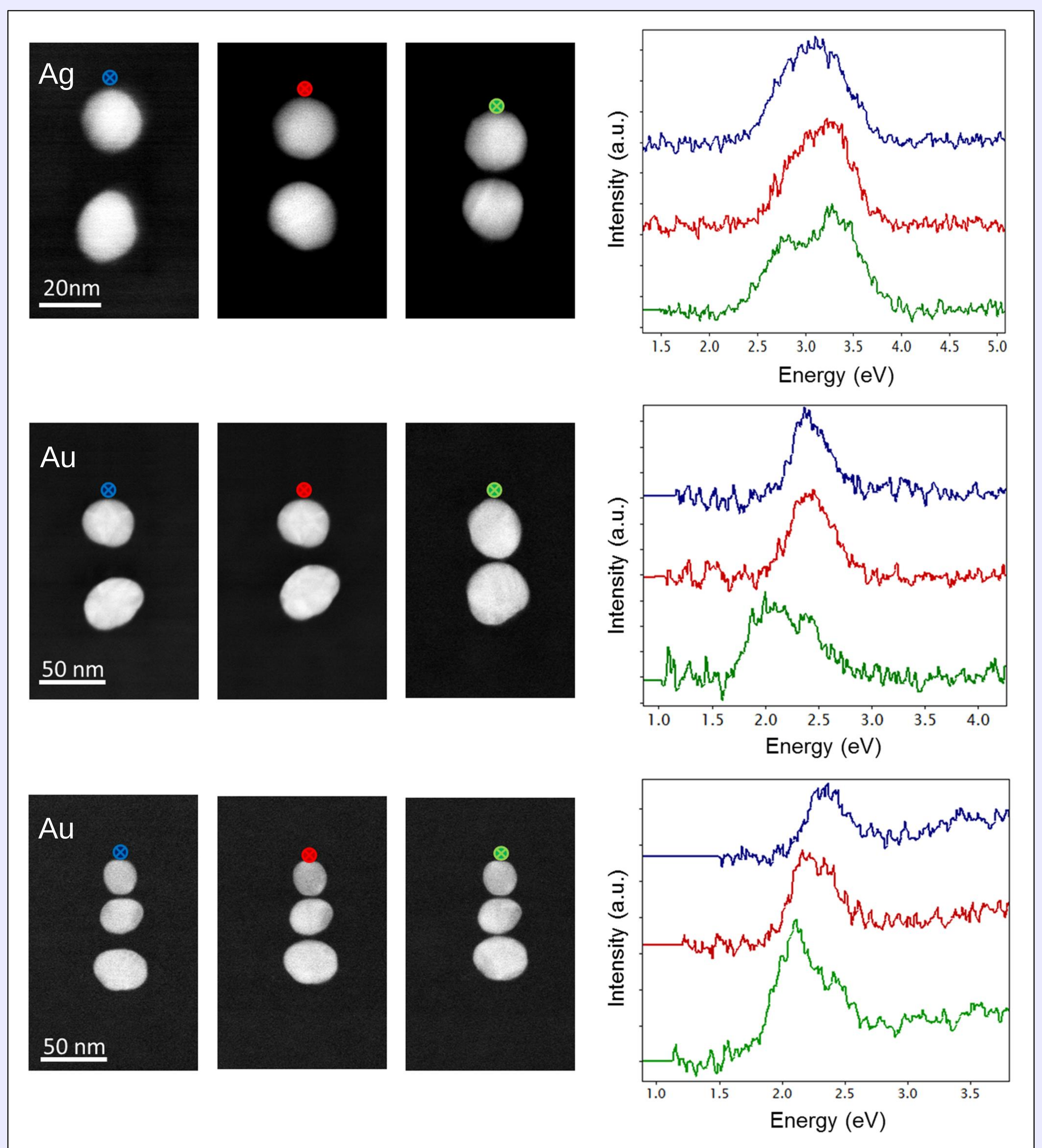
The concept of plasmonic rulers is being explored as a biosensing tool, in which the recorded shift in the plasmon resonance of dimers or aggregates of nanoparticles, caused by change in interparticle distance, is used for sensing of certain biological targets [1, 2]. A challenge in successfully implementing plasmonic rulers is the accurate calibration of them. Here we have employed scanning transmission electron microscopy (STEM) imaging and electron energy-loss spectroscopy (EELS) to investigate the scaling of the plasmon resonance energy with interparticle distance in dimers of gold and silver particles. The experimental results are compared with three-dimensional optical scattering calculations [3].

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. Studying surface plasmons with EELS in an electron microscope offers the possibility of simultaneously imaging structures with sub-nanometre resolution.

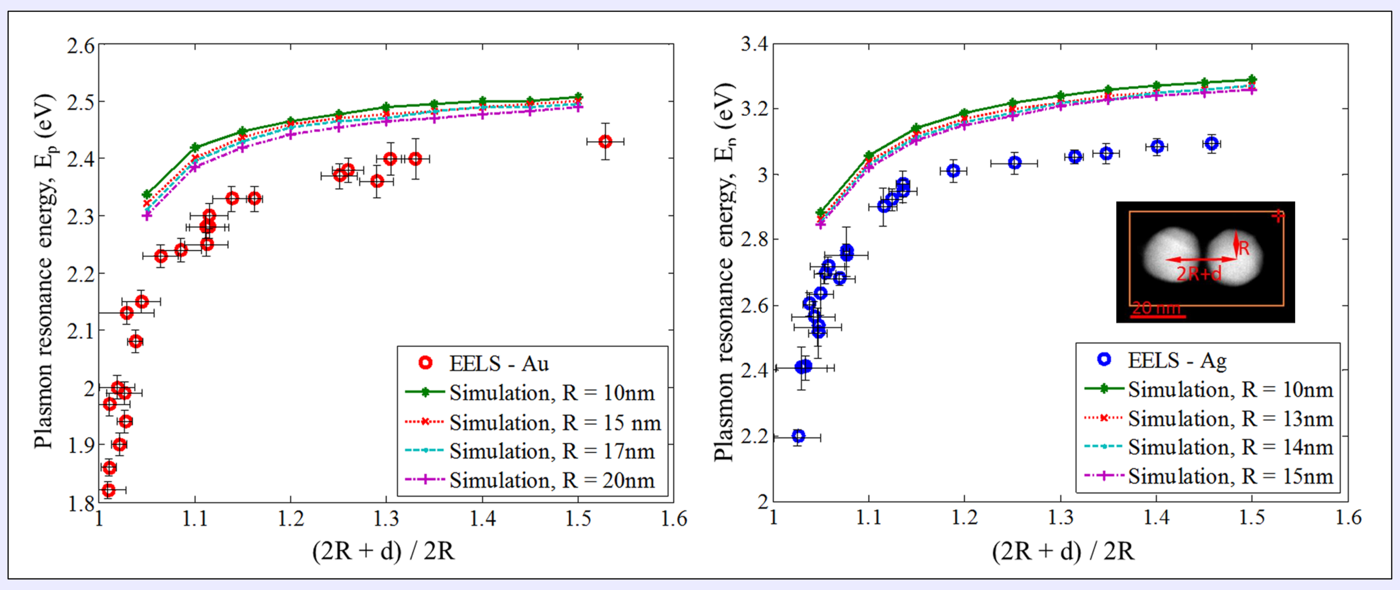


- EELS measurements were recorded from different sets of dimers. However, in some cases it was possible to move the particles with the electron beam [4] and hence, measure on the same dimer but with varying interparticle distances.

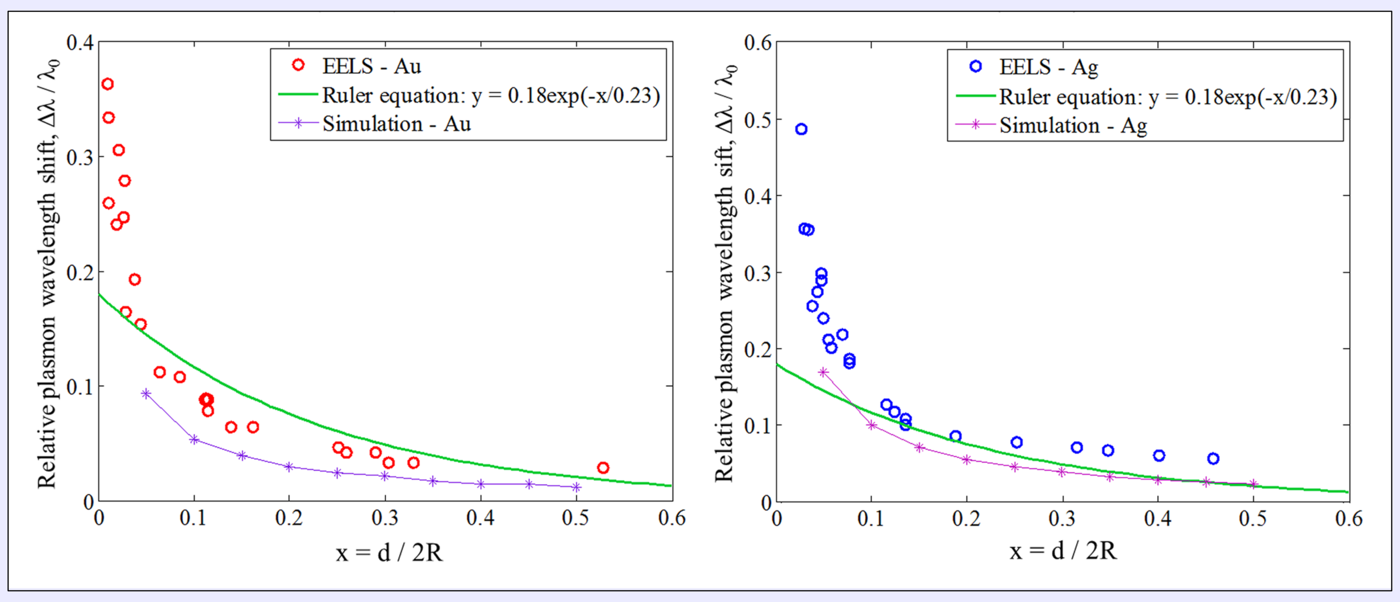


Scaling of the plasmon resonance energy in gold and silver dimers

- Only dimers with surface to surface distances larger than 1 nm are considered here to avoid regimes where quantum and non-local effects become significant [5, 6]. A good qualitative agreement is observed between the simulated and EELS measurements of plasmon resonance energy, E_p, as a function of interparticle distance.

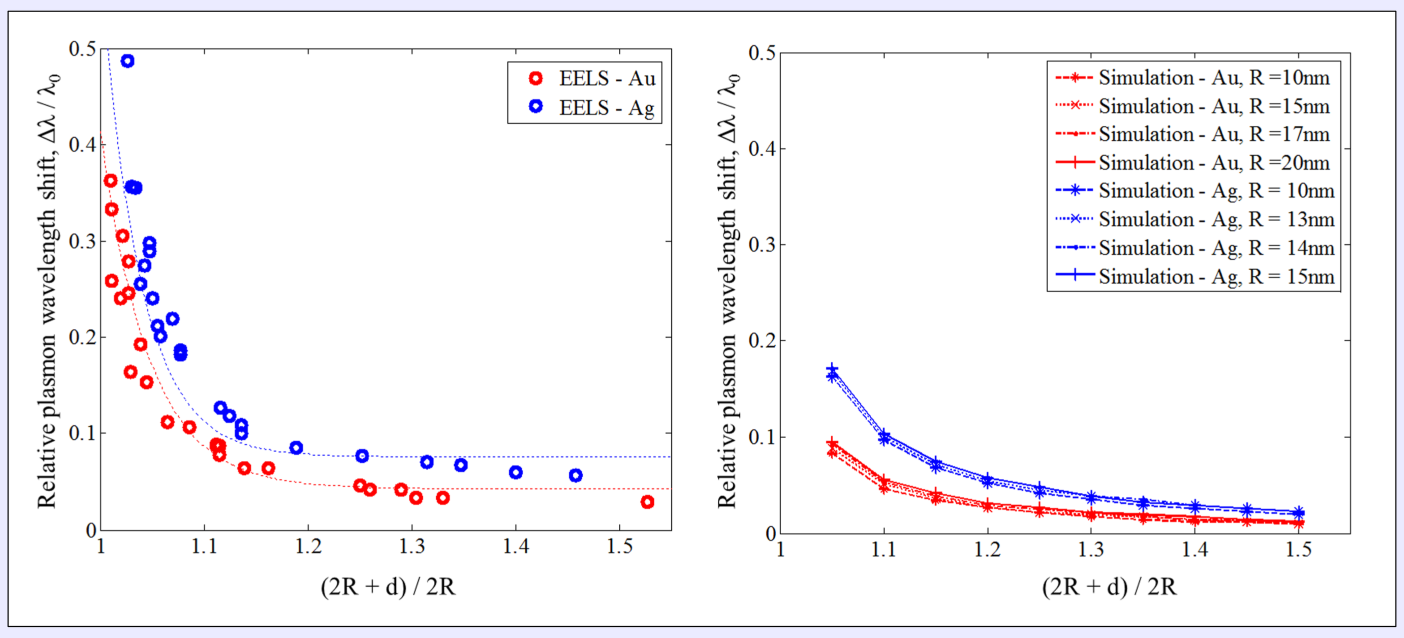


- The simulations do not take into account the presence of a substrate below the particles. This can explain the observed redshift of the measurements compared to the simulated values [7].



- When attempting to fit a single exponential decay function through the data, very different decay constants are found than what has been reported in the literature [2].

- A smaller decay constant is found for silver than for gold both experimentally and theoretically, implying that silver can act as a more sensitive plasmon ruler than gold.



Conclusions

- The high spatial resolution in STEM imaging combined with EELS can be exploited to accurately calibrate the scaling of surface plasmon resonance energy in plasmonic rulers.
- The shift in the plasmon resonance energy as a function of interparticle distance could be well described by three-dimensional, fully-retarded optical scattering simulations. When applying a single exponential fit, significantly different decay constants had to be used compared to previous reports, nor was the decay constant found to be universal. Our data show that silver might have advantages compared to gold for building sensitive plasmonic rulers.

References

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