CHEMICALLY-DRIVEN FORMATION OF SILVER NANOPARTICLE DIMERS WITH TUNED INTERPARTICLE DISTANCE FOR SERS SENSING APPLICATIONS

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Surface-enhanced Raman scattering (SERS) has attracted a renewed interest in recent years due in part to single molecule detection and the fabrication of new metal nanostructured substrates [1,2]. The optical properties associated with the excitation of plasmon resonances on metal nanoparticles (NPs) are known to be crucial in providing large local electromagnetic fields [3], as required in SERS spectroscopy [2].

We obtain silver nanoparticle dimers in a colloidal suspension, chemically driven by a molecular linker (diamine) with appropriate concentration. The interparticle distance of the nanoparticle dimers is tuned in the ~2 nm range through this molecular linker, its length being chemically controlled and the surface coverage. This is revealed by red-shifted plasmon resonances in the absorption spectra for closing distances, in agreement with theoretical calculations. The molecular linker in turn forms intermolecular cavities within the dimer gap, suitable to host molecular analytes for nanosensing applications, as evidenced by SERS detection of polychlorinated pesticides at the trace level.

Methods

Silver hydroxylamine nanoparticles (Ag NPs) were prepared by reduction of silver nitrate with hydroxylamine hydrochloride at room temperature. The average size of the prepared NPs was 50 nm displaying an almost spherical shape. SERS measurements on silver colloidal suspensions were performed by adding a chloride solution and subsequently by adding an AD_n solutions up to desired concentration.

In order to calculate the plasmon resonances in our dimer configurations, we make use of the hybridization method [4]. This numerical method has been successfully applied by the authors to other experiments in silver aggregates [5].

Results

In fig. 1 we show the calculated dependence of the Ag NP dimer resonances on the interparticle distance; the radius of the two identical dimer NPs is 25nm. We have fixed the bulk plasmon resonance (needed in the theoretical calculations) in order to match the wavelength of the single particle resonances to that experimentally obtained from the absorption spectra (λ_1=355nm). We only consider the contribution to the dimer resonance of the lower (longitudinal) symmetric mode. The theoretical calculations reproduce fairly well the trend of the experimental measurements, thus providing further evidence that colloid NP dimers with chemically tuned interparticle distances are being synthesized [6].

In addition to sticking NPs together, diamines play another role which is crucial to employ dimers as nanosensors. SERS data suggests the formation of intermolecular cavities in between the dimer NPs that are able to host a target molecule for sensing, precisely where the hot spots associated to the dimer plasmon resonance occurs [6].

References

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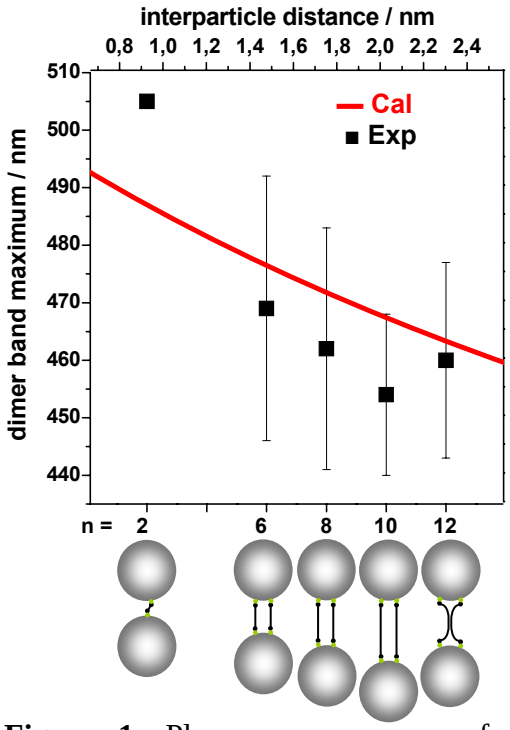

Figure 1. Plasmon resonances of NPs dimers in the absorption spectra, and schematic representations of MA_8 and AD_n molecules adsorbed on the NP surface, below.