

Single-nanoparticle spectroscopy in colloid chemistry

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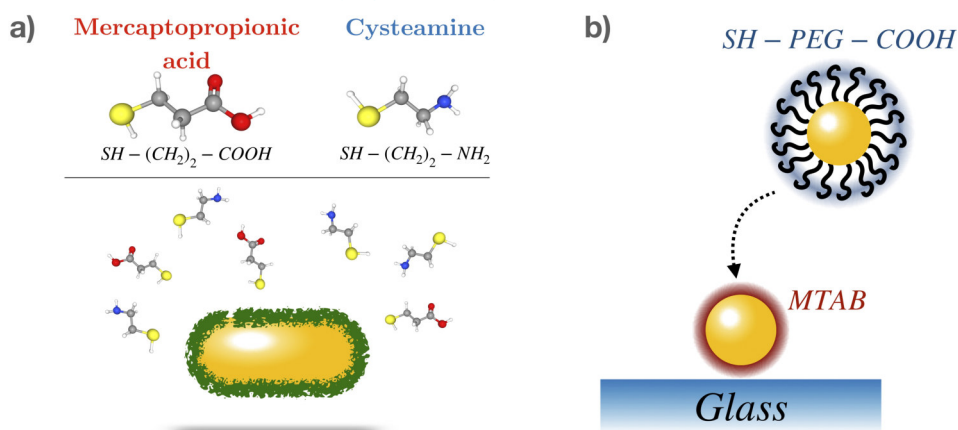
In this work we present our latest results on the possibilities to study ligand exchange and self-assembly of gold nanoparticles by optical methods, with a special focus on engineering colloidal interaction between the particles. We employ the chemical interface damping (CID) increase related scattering peak broadening of individual gold nanorods due to thiol-molecule binding to study the ligand exchange at the rods' surface. We show that the interaction between the already adsorbed and adsorbing ligands is especially important when both ligands are charged. We also highlight how ligand-exchange can be used for the controlled preparation of gold nanoparticle dimers. By analyzing the plasmon coupling upon dimer formation (plasmon ruler, deconvolution of the coupled spectrum, optical simulations), one can obtain information on the spatial arrangement of the dimers, which is largely determined by the surface grafted molecules.

Keywords: plasmonics, scattering microspectroscopy, surface-modification, self-assembly

Introduction

Noble metal nanoparticles offer a unique opportunity to study physicochemical processes at a length scale that is highly relevant for colloid science. This feature stems from the localized plasmon modes these particles can support when the conduction band electron are forced to collective oscillation upon illumination with light. The few tens of nanometres spatial extent of the optical near-field that develops as a result of this collective oscillation falls in the range typically of interest in colloid science. The associated sensitivity of the scattering spectrum of these particles on the properties of the embedding medium makes them an ideal model system to follow ligand-exchange or self-assembly processes even down to the individual nanoparticle level. This latter is especially useful as it allows – when supplemented with other high resolution investigation methods like atomic force or electron microscopy - a more rigorous interpretation of the physical and chemical processes and hence a deeper insight into phenomena that often determine the behaviour of nanosized systems.

The motivation of the current work is twofold (Scheme 1). First, recent literature results show that the binding of thiols to gold nanoparticles induces plasmon peak-broadening due to increasing CID.¹ We exploit this effect to investigate how single nanoparticle scattering spectroscopy can be used to study in detail ligand exchange reactions at the nanoparticles' surface. Second, we use this techniques to asses in-situ, in aqueous environment the effective stabilizing effect of PEG molecules, that are the prototypical molecules in nanomedicine to render the body-introduced agents 'invisible' (stealth function). For this, we design nanoparticles that form dimers – one of them having PEG molecules grafted on the surface. The nanoparticle dimers are formed in a liquid cell and studied in-situ by microspectroscopy. Upon dimer formation, the plasmon coupling can be used to extract the average equilibrium distance between the particles (plasmon ruler). By complementing the measurements with detailed colloid interaction energy calculations, the effective influence of the PEG molecules on the particle stability can be derived.



Scheme 1: a) Ligand exchange of CTAB (green) using two, oppositely charged small thiol molecules cause change in the particles optical spectrum that can reveal the details of the ligand exchange procedure. b) Assembly of oppositely charged dimers and the resulting optical changes provide information about the relevant colloidal interactions and the role of PEG.

Experimental

The nanospheres and nanorods have been synthesized according to already published protocols.^{2,3} The ligand exchange process of the nanorods' original CTAB capping layer was studied using different small-molecule thiols (cysteamine, mercaptopropionic acid) and has been followed on the ensemble level by Vis-spectroscopy and dynamic light scattering. For the single-particle experiments the nanoparticles have been first deposited on glass substrate and integrated in a liquid cell. The cell allowed changing the solution composition conveniently using a peristaltic pump. The scattering spectra of individual nanoparticles was measured on a laboratory developed, dark-field optical microscope based microspectroscopy setup.⁴

Results

CTAB itself has an interesting effect on the resonance peak of the nanorods. Recent papers state that the CTAB stabilizes silver on the rods' surface and when the CTAB concentration is varied in the bulk, this combined effect is responsible for the observed damping changes.⁵ We observe in contrast in the peak positions and damping values even when *only* the CTAB concentration is varied and no silver is added to the system (Figure 1).⁴ This indicated that that – besides the silver present directly at the interface – the negatively charged counter ions might also have a significant influence on CID, which will be the subject of our investigation in an upcoming work.

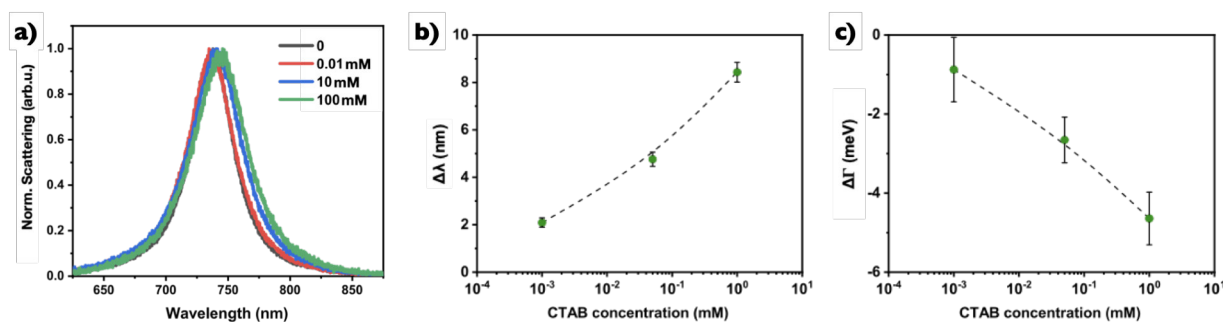


Figure 1: a) Scattering peak of a selected, individual gold nanorod at different, increasing CTAB concentrations. The wavelength (b) and damping (c) changes derived from fitting the oscillator model to the measured peaks.⁴

When the nanorods became in contact with the thiols, there is a significant difference in the damping and position change of the resonance peak. While the positively charged cysteamine was found to effectively replace the similarly positive charged CTAB, a self-limiting ligand-exchange was found for the negatively charged mercaptopropionic acid. This underlines the central importance of intermolecular interaction during ligand during the ligand exchange process.⁴

For the surface modified spherical nanoparticles, the equilibrium particle-particle distance dependent optical changes of the scattering spectrum as a result of plasmon coupling is usually represented by the so called plasmon ruler. This indicates an exponential like redshift of a coupled mode as the particles approach each

other. For our work we derived a theoretical plasmon ruler by simulating the scattering spectra of dimer nanospheres using the boundary element approach.⁶ During the retarded simulations the particle size range of interest, the presence of a substrate and the limited collection angle of our experimental setup were all taken into account. Especially for larger particles, our results show some deviation from the prediction of the classical plasmon ruler equation.⁷

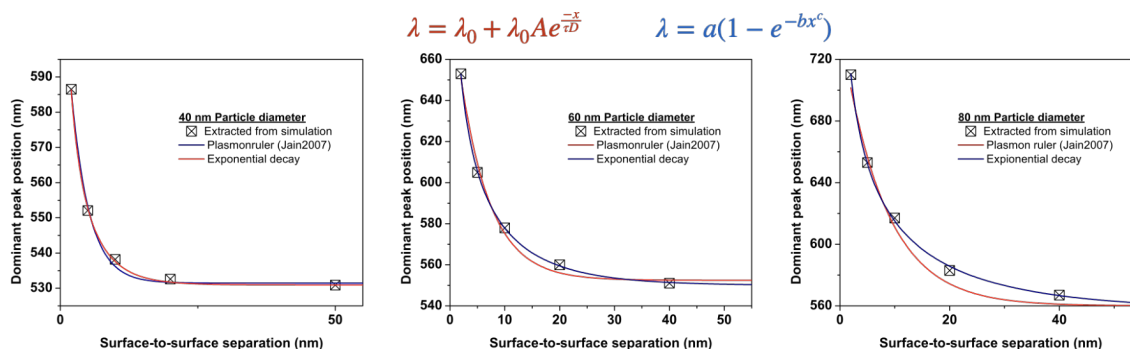


Figure 2: Simulated peak-position of a nanoparticle dimer as a function of gap size.

Figure 3 shows the experimental realization of a nanoparticle dimer with the associated spectral changes. It has to be emphasized that the optical spectra are recorded *in-situ* in the liquid cell upon dimer formation, while the inset shows the ex-situ recorded correlative SEM image. Using the plasmon ruler of given particle size, a gap size of 3.4 nm can be derived, which is reasonable for the given PEG size (3000 Da). Further work will focus on the quantification of the equilibrium particle separations under varying conditions (mainly pH and ionic strength) that affect the strength of the interaction potential and will compare the result to colloidal interaction calculations.

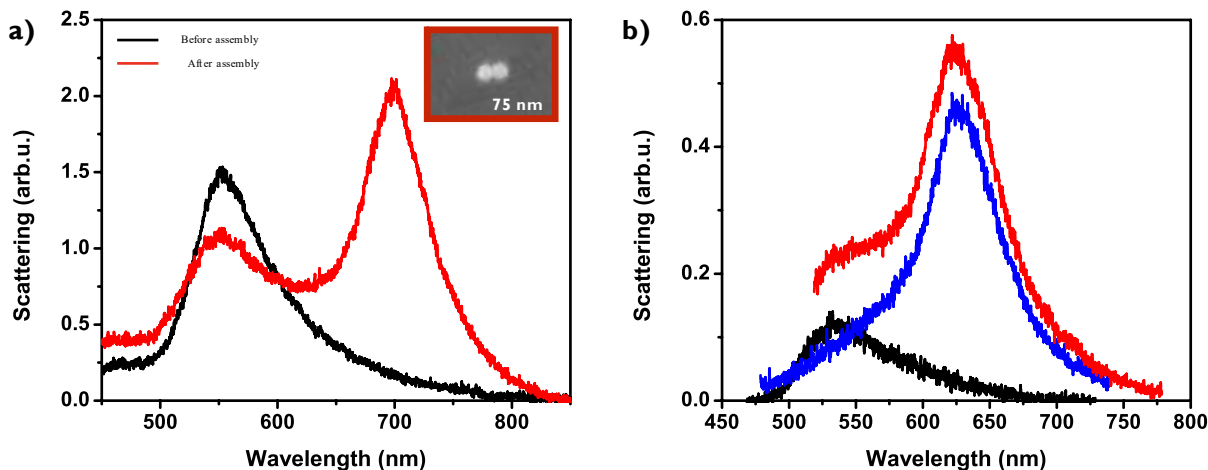


Figure 3: Scattering spectra of an individual scatterer measured before and after dimer formation for 75 nm (a) and 60 nm (b) diameter particles.

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