

Detecting short-chain thiol binding on CTAB-stabilised gold nanorods at single particle level

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Deeper understanding the binding of thiol molecules on CTAB-capped gold nanorods enables the rational tuning of colloidal interactions. In this study, I would like to present my last results on the adsorption of short thiol-containing molecules on gold nanorods. It is shown that plasmon peak broadening originated from the increasing chemical interface damping (CID) combined with the corresponding peak shift provide information on the ligand exchange process at the single particle level. Based on the findings, the accumulation of negatively charged 3-mercaptopropionic acid (MPA) is reduced compared to that of the positively charged cysteamine because of the interaction of the given thiol-ligand and the native CTAB layer. While cysteamine readily replaces CTAB, the adsorption of MPA leads to a self-limiting process.

Keywords: gold nanoparticles, self-assembly, plasmonics, single particle spectroscopy

Introduction

Ligand exchange using thiol-containing ligands is one of the most widespread procedure for imparting functionality to gold nanoparticles.¹ The majority of gold nanorod syntheses utilise CTAB as a stabilising ligand.^{2,3} Thus, the interaction between the thiol-molecule and the native CTAB plays a central role in surface modification. The binding can be easily monitored by spectroscopic measurements, since the optical response of the particles is extremely sensitive on the dielectric properties of the near-field region.⁴ In this work, two molecules (namely cysteamine and 3-mercaptopropionic acid) are used for ligand exchange and the modified particles are optically investigated at the ensemble and single particle levels as well⁵. By fitting the scattering spectrum of an individual gold nanorod with a Lorentzian-function the plasmon resonance energy and the damping of the dipole-oscillator model can be determined. The linewidth characterises the entire surface of the particle, while peak shift provides information on the ligand replacement just at the tips of the rod⁶.

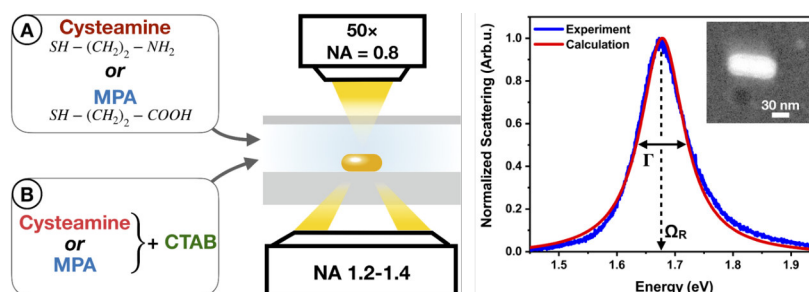


Figure 1: The schematics of the performed experiments without (A) and in the presence of CTAB (B). The obtained scattering spectra were fitted using a Lorentzian-function in order to calculate the resonance energy and the plasmon damping.

Experimental section

Gold nanorods synthesised in this study (24 x 76 nm) were prepared according to a previously published protocol². The surface modification of the CTAB-capped was carried out using similar sized but oppositely charged short-chain thiol ligands (3-mercaptopropionic acid (MPA), cysteamine). The ligand exchange procedure was monitored on the ensemble level by Vis spectrometry and electrophoretic mobility measurements. To gain a deeper insight into the surface modification process *in situ* single particle scattering experiments were performed in a liquid cell using an aberration corrected imaging spectrometer coupled with a dark-field microscope operated in trans-illumination mode.⁵

Results

In our earlier published work⁷, the ligand exchange of cysteamine on CTAB-covered gold nanorods was investigated at ensemble and single particle levels as well. It was confirmed that cysteamine forms a well-defined patch at the tips of the gold nanorods which was directly evidenced by AFM measurements and was indicated by the saturation of plasmon peak blueshift and electrophoretic mobility.

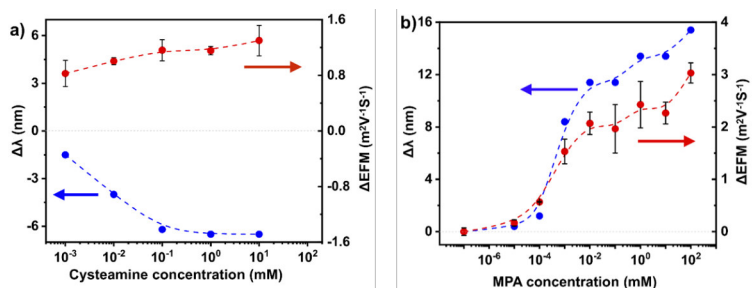


Figure 2: Plasmon peak shift and electrophoretic mobility changes upon adding different concentration of (a) cysteamine and (b) MPA

As shown in Figure 2.a the blueshift and the electrophoretic mobility converge to a limiting value as a consequence of site-selective binding of cysteamine in agreement with our earlier findings. Interestingly, the attached MPA increases the electrophoretic mobility and causes a redshift (Figure 2.b) which may indicate the accumulation of CTAB at the surface of the nanorods due to electric interactions. In order to get a deeper understanding of the ligand exchange and to corroborate the proposed mechanism of MPA-binding single particle spectroscopy experiments were performed without and in the presence of CTAB as well.

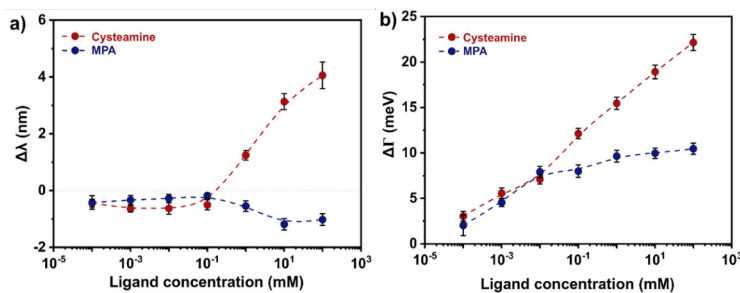


Figure 3: (a) Longitudinal resonance peak shift and (b) broadening obtained for different concentration of cysteamine and MPA

The resonance wavelength and damping change values can be seen in Figure 3. for the case where CTAB was removed. Although the peak position trends were opposite compared to ensemble measurements, the increasing damping indicates the binding of thiol ligands to the gold surface. Figure 3.b also shows the inhibited accumulation of MPA from 10⁻² mM ligand concentration presumably because of the attractive interaction with the remaining CTAB.

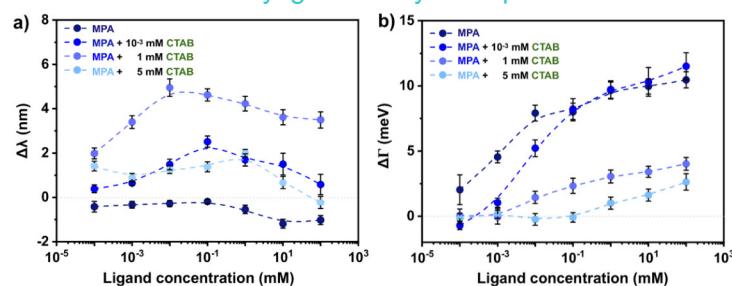


Figure 4: (a) Longitudinal plasmon resonance shift and (b) broadening induced by MPA-addition at different background CTAB concentration

As can be seen in Figure 4, *in situ* MPA-adsorption experiments were carried out with different CTAB concentrations. The magnitude of the redshift is clearly proportional to the bulk CTAB concentration up to the critical micellar concentration of CTAB ($\text{cmc} = 1 \text{ mM}$). The amount of accumulated MPA was suppressed with increasing CTAB concentration which indicates the self-limiting process of the MPA adsorption (Figure 4.b).

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