

A Plasmonic Ruler at the Liquid-Liquid Interface

Vladimir A. Turek, Michael P. Cecchini, Jack Paget, Anthony R. Kucernak, Alexei A. Kornyshev*, and Joshua B. Edel*

*Department of Chemistry, Chemical Physics Section, Imperial College London,
Exhibition Road, South Kensington, London, SW7 2AZ, United Kingdom*

*Corresponding authors: a.kornyshev@imperial.ac.uk, joshua.edel@imperial.ac.uk

Abstract

We report on a simple, fast, and inexpensive method to study adsorption and desorption of metallic nanoparticles at a liquid/liquid interface. These interfaces provide an ideal platform for the formation of two-dimensional monolayers of nanoparticles, as they form spontaneously, cannot be broken, and are defect-correcting, acting as 2D ‘nanoparticle traps’. Such two-dimensional self-assembled nanoparticle arrays have a vast range of potential applications in displays, catalysis, plasmonic rulers, optoelectronics, sensors and detectors. Here, we show that 16 nm diameter gold nanoparticles can be controllably adsorbed to a water/1,2-dichloroethane interface, and we can direct the average inter-particle spacing at the interface over the range 6-35 nm. The particle density and average inter-particle spacing are experimentally assessed by measuring the optical plasmonic response of the nanoparticles in the bulk and at the interface, and by comparing the experimental data with existing theoretical results.

Keywords: liquid-liquid interface, Plasmonic Ruler, Nanoparticles, Self Assembly, Centrifugation.

Nanoparticle (NP) adsorption at liquid-liquid interfaces (LLI) is a well established phenomenon that was first reported independently more than a century ago by Ramsden and Pickering.^{1,2} More recently, plasmonic NPs at LLIs have been reported to possess novel “metal liquid like” properties³ that have sparked a renewed interest. Driven by the growing need for cheap, fast and reproducible bottom-up assembly for nanotechnological applications, the unique optical,⁴ magnetic,⁵ electrical⁶ and chemical⁷ properties of such films has attracted intensive research in a rapidly growing field.

NP assemblies at LLIs hold great promise in diverse fields ranging from electro-variable optics⁸ to templates for hierarchical self assembly,⁹ and plasmonic rulers.¹⁰ One of the main benefits of localising NPs at a LLI for these applications is the aforementioned self-assembly.¹¹ Currently, most technological applications of nano-assemblies are based around solid-state fabrication. Although the control that the solid interface offers is unparalleled, it does have several drawbacks when compared to a LLI. One such drawback is topological defects – these can be introduced either during or post-manufacturing and are extremely difficult to correct. In fact it is often easier to fabricate a new device rather than attempting to repair defects. Conversely, a LLI system has the ability to self-correct without any external manipulation.¹²

An additional drawback of a solid state system becomes clear when introducing the exciting concept of a plasmonic ruler.¹³⁻¹⁵ The coupling between excitations of localized plasmons in NPs can allow for precise spatial information. This concept has been demonstrated between 2D arrays,¹⁰ particle dimers¹⁴ at solid interfaces and tethered NPs in bulk solution.¹⁶ It has even been recently demonstrated to provide 3-dimensional structural information.¹⁷ The use of plasmonic particles at the LLI should therefore provide information on the structural characteristics of these assemblies. The large body of work on plasmonic NPs at LLIs has typically focused on close packed arrays and is broadly divided into spectroscopic studies for sensing^{18,19} (e.g. SERS and SPR) or use of the LLI as a template for 2D self-assembly.²⁰

Despite our growing theoretical understanding of these assemblies,²¹ there are numerous questions that remain unanswered. It has become evident through theory,^{22,23} simulation^{24,25} and key experiments²⁶⁻²⁸ that the simple electrostatic and van der Waals forces that DLVO (Derjaguin Landau Verwey Overbeek) theory considers for NPs in bulk solution, is not sufficient to explain the stability of NPs at the LLI. NP interactions at the LLI are governed by the interfacial tension stabilization,⁸ long range dipole-dipole interactions resulting from an asymmetric counter-ion cloud,²⁹ hydration forces for the NP immersed in the two fluids,³⁰ capillary forces resulting from deformations of the interface,³¹ van der Waals forces that differ to those in the bulk,³² as well as thermal fluctuations.³³ It is beyond the scope of this work to give a detailed account of these forces, especially when comprehensive review articles have been published on these interactions.^{11,34,35} However, for clarity the balance of forces and a pictorial representation of NP adsorption to the LLI are shown in Figure 1.

From an experimental perspective, characterizing these interfaces can be an equally challenging task. For example, invaluable insight has come from experiments utilizing grazing-incidence small-angle X-ray scattering to study the assembly of small CdSe nanocrystals at a toluene-water interface³⁶ in which it was determined that the particles form a close packed, but disordered liquid-like structure. Furthermore, fluorescence loss induced by photobleaching and fluorescence recovery after

photobleaching on the same system revealed that the lateral diffusion of these assemblies is 4 orders of magnitude slower than its bulk counterpart.³⁶ Second harmonic generation,³⁷ surface plasmon resonance³⁸ and ellipsometry³⁹ have also been shown as a characterization method for NPs at the LLI. More recently, freeze-fracture shadow-casting cryo SEM has been performed with single-particle resolution of these assemblies.⁴⁰ However, most of these techniques are time consuming and require specialized equipment. There exists a need for a fast, *in situ* technique that would probe, with nanometer resolution, the structural characteristics of these films.

In this paper we develop techniques for characterizing and controlling the spacing of NPs at a LLI. In order to use the plasmon ruler at these interfaces, one needs to first control the adsorption of NPs to the LLI and prevent aggregation-induced close packing. Diffusion-driven, electrochemical⁴¹ and ethanol induced⁴² adsorption to the liquid interface are amongst the most widely used strategies. Out of these techniques, spontaneous self-assembly is the most convenient for the plasmon ruler; however, the assembly time is generally limited by diffusion. We build on this by using centrifugation as a means to controllably adsorb a 2D array of 16 nm Au NPs to a water/1,2-dichloroethane (DCE) LLI. Furthermore, spectroscopic techniques are used to characterize the plasmonic ruler properties of the NPs by controlling the centrifugal force, centrifugation time, salt concentration, interfacial area and pH. The methods utilized are simple, fast, and inexpensive and can be used to characterize and control the plasmonic properties at the interface.

Results and Discussion

Centrifugation as a means of kinetic control of NP assembly at the LLI

The simplicity and flexibility of centrifugation was a key motivation for applying this technique to kinetically control the self-assembly of NPs at the LLI. As our main goal is to demonstrate NP assemblies whose plasmonic properties suggest changes in the spacing between the particles, we will forgo a comprehensive study on the effects of centrifugation of the NPs, focusing instead on the experimental observation arising from NP assembly, dis-assembly and controlled spacing at the LLI. The reader is referred to the ESI for a detailed discussion on the physical background behind centrifugation speed and time dependence on NP adsorption.

Unless otherwise stated, the procedure for NP assembly describing all the steps is shown in Tables 1 and 2. A general experimental schematic of the protocol for assembly and the detection of the NPs at the LLI are shown in Figure 2. After centrifugation all but 100 μL of the aqueous solution was removed. This resulted in the 100 μL solution forming a droplet with the assembled NPs at the DCE boundary. Notably a distinct red colouration close to the interface could be seen post centrifugation, indicating that the NPs have successfully migrated to the LLI (Figure 2b). The NPs are known to provide an interfacial tension stabilisation between the oil and water⁴³ – this stabilization also prevents the particles from crossing the LLI and sedimenting at the bottom of the DCE. However, as described, nanoparticles are charged and repel each other electrostatically unless this repulsion is substantially screened.⁸ Consequently, these NPs could be visibly re-dispersed back into the bulk

by gentle agitation at NaCl concentrations below 50 mM, while no visible change in the bulk occurred at NaCl concentrations above 50 mM. Notably, the NaCl concentration had a large effect on the visual appearance of the LLI. Between approximately 40 – 150 mM a highly glossy reflective film was observed at the LLI, at concentrations above 150 mM a matt appearance was observed while at concentrations below 40 mM only faint colouration was observed. It should be stressed that the transitions do not have clear boundaries.

The remaining 100 μL of the aqueous phase formed a truncated oblate ellipsoid droplet whose surface area was estimated to be $1.071 \pm 0.01 \text{ cm}^2$ in the cell holder (see ESI for more details). Optical transmission spectra of the NPs at the aqueous droplet / DCE interface (Figure 2e) were measured to determine the localised surface plasmon resonance (LSPR) maxima, with a beam diameter of 1.5 mm at the sample interface. Before each reading, the sample height was adjusted so that the incident light would pass at approximately normal incidence – this was monitored by the intensity of the collected light, which decayed rapidly at non-normal incidences. The tube holder was tilted to approximately 5° , which was intended to minimize variations in the droplet shapes in the set of performed experiments. This tilt also helped to pin the droplets by buoyancy to an approximately constant position with respect to the incident light, while still allowing for normal incidence of the light to the droplets' surface.

NP Functionality

It was found that functionalisation groups play a large role in controlling the assembly of NPs at the LLI, shown schematically in Figure 1c. The critical role of the functionality is well documented in the literature, with several works focusing on the role of the particle's surface chemistry on adsorption and behavior at the LLI.⁴⁴⁻⁴⁶ For example, MDDA functionalised particles do not spontaneously assemble in large quantities at the LLI at low salt concentrations. This is evidenced from the fact that the centrifugation and homogenization process leaves the vast majority of the NPs in the bulk solution. On the other hand, performing an identical experiment with citrate stabilised particles results in the majority of the available NPs adsorbed to the LLI. Unfortunately agglomeration readily occurs for citrate stabilized particles due to their ease of dissociation from the NP's surface, for this reason, they were not used for further experiments. The MDDA functionality prevents the adsorbed NPs from agglomerating as the carbon chain provides approximately a 1.5 nm steric coating which circumvent short range van der Waals interactions inducing aggregation. Furthermore, the dissociated carboxyl groups at the end of the carbon chain provide a Coulombic repulsion. This stabilising technique was extremely successful, so much so that no irreversible aggregation was observed at any conditions tested. The stabilizing effect of steric repulsion for particle suspensions is consistent with the literature.⁴⁷ It is known that purely electrostatically stabilized gold particles aggregate at salt concentrations of greater than 20 mM,⁴⁸ this is a result of the Debye-screening caused diminishing of the electrostatic repulsion, so that it could no longer beat the van der Waals attraction between the NPs. However, due to the interplay of the additional forces that takes place at the LLI, as well as the interface caused modification of electrostatic and van der Waals interactions, the signatures of the bulk aggregation cannot be directly used to extrapolate the salt effect on the electrostatic

repulsion at a LLI.^{34, 49} It is beyond the scope of this work to further investigate this interplay, as well as accurately describe the local ionic concentration surrounding NPs at the LLI. However invaluable insight can be found in other works^{34, 50}. As for the effects of the steric and electrostatic stabilization, provided by the MDDA functionality, in comparison with a predominantly electrostatic stabilization by mercaptosuccinic acid for NPs at the LLI, they are qualitatively compared in Fig. S3 of the ESI.

Salt concentration dependence on NP adsorption and plasmon resonance

The effect of ionic strength on the number of particles assembled at the LLI is shown in Figure 3a-d. This latter value can be assessed from both the residual NPs in the aqueous phase (Fig. 3b) and the LSPR spectra (Figure 3a). A clear shift to the red was observed as the NaCl concentration was increased gradually from 1 mM to 200 mM. Between these NaCl concentrations, the Debye screening is reduced from approximately 9.6 to 0.7 nm. It should be noted that the Debye screening may affect not only the NP population at the interface, but their precise position relative to the boundary. However, estimates show that the shift is rather small and can be disregarded. We can thus attribute the observed shift in the plasma frequency to the change of the average distance between the NPs.

It is important to note that there are two further sources of red-shifting in these experiments. The first is a change in the dielectric constant of the surrounding medium of the NPs, while the second is plasmon coupling. The dielectric constant of pure water and a 2M NaCl solution is 1.78 and 1.80 respectively. Therefore, even if the local salt concentration at the interface in the electrical double layer is 10 times that of the bulk, a negligible positional change of the LSPR maximum would be observed. DCE on the other hand has a dielectric constant of 2.09; therefore, a more substantial effect could result from the NPs position shifting from the aqueous to DCE phases. However, if even mild changes took place, as we have already mentioned, the shift in the position of the LSPR would be minor in contrast to the shift caused by the resulting change of the distance between the NPs at the LLI.

With no addition of NaCl (i.e. intrinsic ionic strength equivalent to 1 mM NaCl), the number of NPs that could be adsorbed to the LLI under an RCF of 9391g in 10 minutes was $4.0 \pm 0.1 \times 10^{10}$ NPs from a bulk aqueous solution containing 2.75×10^{11} NPs in total. The low ionic strength of the solution means that the electrostatic repulsion acts over a longer distance inhibiting oncoming particles from adsorbing to the interface. At these conditions the LSPR maximum was 524 ± 3 nm which corresponds to the LSPR maximum of the NPs in the bulk aqueous solution. This suggests that little to no plasmonic coupling occurs due to a large separation between NPs. Based on both the empirical plasmon ruler equation as well as mean-field theory, the spacing is expected to be larger than 30 nm (Figure 5).^{51, 52} Increasing the salt concentration decreases the effective distance over which electrostatic repulsion takes place. As a result a greater number of particles can be accommodated at the LLI. Since the surface area of the droplet and total number of particles in solution are roughly uniform, the spacing between NPs can be directly controlled by the addition of salt. This leads to a linear red-shift in the plasmonic response and a linear increase

in the number NPs adsorbed to the LLI between 1-75 mM NaCl. Between 75-125 mM NaCl both the LSPR maxima and the number of adsorbed particles plateaus at ≈ 555 nm and $\approx 2.75 \times 10^{11}$ particles respectively. This is due to all of the particles in the solution being collected at the interface. Under these conditions the average inter-particle spacing remains constant. Finally at concentrations above 150 mM NaCl a further red-shift is observed. As the number of particles at the interface is already saturated, the red-shift is attributed to inhomogeneities and clustering of the NPs. This is supported by observing an increase in broadening of the plasmon spectra as NaCl is increased, Figure 3c. At lower salt concentration (1 – 50 mM) a linear dependence on the FWHM is observed which is followed by a plateau between 50 – 110 mM and finally a second increase at concentrations >110 mM. By taking these observations into account along with the LSPR maxima and NP surface coverage, a possible explanation of these trends is shown in Figure 3d. As the NaCl is increased, NP coverage at the LLI will gradually go from a relatively ordered state to a disordered agglomerated state. This is further supported by the visual appearance of the LLI which at low/moderate salt concentrations appears golden mirror-like which becomes matt in appearance at higher concentrations. The qualitative trends for red-shifting and peak broadening are as expected from the literature (although broadening at higher NaCl concentrations is likely to be a combination of closer spacing and irregularities in the structure of the monolayer of NPs).^{8, 53}

In summary, based on the experimental results, NaCl concentrations of 1-75 mM give rise to controlled spacing with a relatively homogenous NP distribution – the observed LSPR maximum at 75 mM NaCl is 555 ± 5 nm that corresponds to a $\Delta\lambda/\lambda_0$ of ≈ 0.057 . Coupled dipole approximation (CDA) simulations⁵² suggest that a $\Delta\lambda/\lambda_0$ of 0.057 correlates to a gap distance/diameter of ≈ 0.65 which for the 16 nm diameter particles used here, corresponds to ≈ 10 nm surface-surface NP separation in a hexagonal lattice (preferred packing geometry for a two dimensional array of NPs with predominantly repulsive interactions). While mean-field theory⁵¹ suggests that LSPR maximum of 555 nm corresponds to ≈ 4 nm. Our experimental data at these conditions suggests a surface-surface NP separation of $\approx 6 \pm 1$ nm (or a gap distance/diameter of ≈ 0.37) which lies between simulations and theory (Figure 5). Taking the steric coating of MDDA to be ≈ 1.5 nm and the debye screening length to be 1.1 nm, then the minimum separation between 2 NPs is expected to be 5.2 nm – this is within experimental uncertainty of the experimentally determined values for NP separations at 75 mM. To the best of our knowledge, this is the first time that a plasmonic ruler has been experimentally demonstrated at the LLI.

Centrifugation speed and time dependence on NP adsorption and plasmon resonance

Centrifugation speed and time can also be used to control adsorption and the plasmonic properties of the NPs at the LLI (Figure 4). In Figure 4a and c the only parameter that was changed when compared to the NaCl results was the centrifugal force. The data shows very predictable behavior with a strong correlation between particles adsorbed and the plasmon red-shifting with both parameters increasing until a plateau is reached (all particles adsorbed to the interface). For example, the plasmon maximum at a RCF of 13,523 g is 556 ± 2 nm ($\Delta\lambda/\lambda_0 \approx 0.059$), which corresponds to a 30 nm red-shift. Based on the plasmon ruler equation, $\Delta\lambda/\lambda_0 \approx 0.059$ suggests a ≈ 0.64 gap distance/diameter (or a ≈ 10 nm gap), while mean-field theory predicts a LSPR Max of 556 nm corresponding to ≈ 4 nm surface-surface NP separation (Figure 5a and

b). Much like previously described, the experimental results lie in between mean-field theory and simulations.

The time dependent studies (Figure 4b and d) show that at short centrifugation times, a sharp increase in the number of particles adsorbed at the LLI is observed. This is followed by a plateau after 10 minutes where $2.2 \pm 0.1 \times 10^{11}$ NPs are adsorbed to the LLI. This is followed by a gradual decrease to a value of $1.8 \pm 0.2 \times 10^{11}$ NPs at 30 minutes is observed. This decrease could be attributed to heating of the samples which takes place during centrifugation, as dissociation is believed to be more efficient at higher temperatures, although further experiments are needed to verify this. (c.f. Figure 4d).

Combining the experimental data from Figure 4 and Figure 3 (1-75 mM NaCl data), a plot of surface-surface NP separation can be drawn as a function of plasmon maximum (Figure 5a). Results from Figure 3 at NaCl concentrations of >75 mM were excluded due to the evidence of an inhomogeneous NP environment. The data presented is compared to two models. One of them was developed by Ben *et al.*⁵² where a coupled dipole approach was used to calculate the plasmon frequency of an ordered 2D array of dipole scatterers. The results of these numerical calculations were then fit to a simple exponential function. However, one must be aware that the model cannot be directly applied to our system, because it was developed for an array of nanoparticles in vacuum; therefore only the medium-independent $\Delta\lambda/\lambda_0$ can be used to compare qualitative trends (Figure 5b). In addition, we compare the results with a simple mean-field quasi-static dipolar theory developed by Kornyshev *et al.*⁵¹ where we numerically determine the position of the plasmon resonance as a function of the distance between NPs (Figure 5a and b). The experimentally observed general trend is very similar to that predicted by both models. It is worth noting, that deviation between the predictions of the mean-field theory and experimental RCF/time data becomes significant at larger interparticle separation, due to breakdown of the ‘continuous film’ representation of the nanoparticle array.⁵¹ The combined results from the RCF and time dependent studies suggest that the surface-to-surface separation between NPs can be precisely controlled between 7 - 30 nm, solely based on the centrifugation speed and time. Similar spacing can be achieved by varying the NaCl concentration.

Volumetric dependence on NP adsorption and LSPR

Given that the results obtained from Figure 3 and Figure 4 suggest that controlled spacing can be achieved, it follows naturally that one would expect to find a dependence on the LLI interfacial area for a constant total number of NPs at the interface. If the NPs’ Coulombic as well as the long range dipole-dipole repulsion lead to the NPs being spaced as far away from each other as possible at the LLI, then spacing should increase if the LLI area also increases. To verify this hypothesis, experiments were performed increasing or decreasing the total aqueous droplet volume by pipetting fluid in or out of the droplet (Figure 6). The results suggest a clear dependence on the plasmon maximum with respect to the volume within a range of 100 to 200 μL . This is followed by a plateau at higher volumes. As expected, increasing the volume of the droplet causes a blue-shift in the LSPR maximum. For example, the LSPR maximum within 100 μL was found to be 560 ± 3 nm while at 200 μL droplets had plasmon maxima of 546 ± 2 nm.

The comparison of our experimental data with both models suggest that the surface-to-surface separation between NPs lies in the range of 6 to 13 nm. The decrease of the droplet volume, which results in a decrease of the LLI surface area, causes a red-shift in the LSPR-maximum. It is important to note what happens when the volume is reduced below the initial 100 μ L volume – the compression experienced by the particles initially leads to the expected red-shift, both visually and by transmission measurements, however, if the system is allowed to reach an equilibrium either by agitation or by waiting for a short period of time, then desorption of the ‘excess’ NPs occurs. This is evidenced by both the LSPR maximum returning to ≈ 560 nm (i.e. same as for 100 μ L) and the fact that after homogenisation the NPs in the bulk aqueous phase is greater than before homogenisation. This is in marked contrast to close packed citrate stabilized arrays which are known to form ‘3D interfaces’ and show buckling when the area of 2D NP array becomes larger than the area of the LLI.^{54, 55}

Reversibility of NPs at the LLI

NP adsorption at the LLI is impeded by electrostatic repulsion between the particles. For highly charged NPs there may be a barrier for individual NPs caused by resolution. Both factors depend on the square of the charge of the NPs. Therefore we investigated the effect of changing the charge on the NPs in order to facilitate adsorption/desorption (Figure 7). NPs were assembled as described in Table 2. At this point, UV-Vis spectroscopy showed a negligible bulk absorbance (Figure 7a). The LSPR maximum was measured to be 567 ± 3 nm (consistent with the value at 165 mM NaCl from Figure 3b). To achieve desorption, 5 μ L of 5 mM NaOH was added to the droplet resulting in a final pH of approximately 9. This resulted in complete desorption of NPs from the LLI which was evidenced by an increase in the bulk absorbance at 530 nm (Figure 7b). A blue-shift of the LSPR maximum (533 ± 3 nm) was also observed which corresponds to the peak maxima for NPs in the bulk (530 nm).

Subsequent acidification of the aqueous solution with 10 μ L of 5 mM HCl to a pH of approximately 2 and removal of the 10 μ L ‘excess’ aqueous phase to ensure a constant volume ensures almost complete re-adsorption of the NPs (Figure 7c). The LSPR maximum returned to 563 ± 3 nm with UV-Vis confirming that there was a negligible NP concentration in the bulk. Though this adsorption-desorption-adsorption cycle essentially suggests that full reversibility can be achieved, subsequent cycles could only demonstrate partial reversibility. The following desorption steps lead to a LSPR maximum from transmission of only 550.8 ± 5.2 nm and a bulk absorbance at 530 nm of ≈ 0.4 , while the adsorption steps lead to negligible bulk NP concentration and an LSPR maximum of 570 ± 2 nm. This demonstrates an important step forward to providing perfect control of NP assemblies at the LLI, with the goal of coupling reversible adsorption with the plasmonic ruler by electrochemical means, i.e. applying voltage across the ITIES, as suggested previously.⁸

Conclusions

We have demonstrated novel plasmonic properties of NPs localised at a LLI. Experimental results suggest that these properties arise from controlled spacing and

that this spacing is affected by a set of controlled parameters. This was observed *indirectly* by normalized transmission spectroscopy. Importantly, experimental results qualitatively agree with mean-field theory, as well as the empirical plasmon ruler equation. The unique properties of homogenous, controlled, sub-monolayer coverage NP assemblies at the LLI open routes for many potential applications ranging from plasmonic rulers to detectors and electro-variable optics.

Whereas, the *indirect* imaging is, as demonstrated, a fast and convenient way to probe the structural properties of these assemblies, further experiments with *direct* imaging will be crucial to prove/disprove the spacing hypothesis as well as to provide a reliable reference point for the exact spacing. We believe that the results that we presented in this paper give motivation and framework to such studies. Aside from demonstrating a novel centrifugation based assembly method and a non-invasive, *in situ* optical characterization of the forming assemblies, we have also shown reversibility of the adsorption of 16 nm diameter gold particles. Finally, we have obtained results suggesting that the structural properties of NPs that are already localized to the LLI can be fine-tuned by the LLI area.

It is hoped that due to the simplicity of the experimental procedure developed here to achieve adsorption, desorption and controlled spacing, this work will provide convenient techniques to study the details of these assemblies, as well as pave the way to control these features via electrochemical means.

Experimental

Equipment used: UV-Vis measurements to quantify the number of particles assembled at the interface were performed with a Nanodrop 2000c spectrometer using PMMA cuvettes. An Eppendorf 5424 centrifuge was used to aid in self-assembly of Au nanoparticles using 2 mL polypropylene centrifuge tubes. A FA-45-24-11 rotor with a radius of 8.4 cm was used and is capable of holding 24×2 ml centrifuge tubes at an angle of 45° with a maximum relative centrifugal force (RCF) of 20,238 g (14,680 RPM). A Beckmann Coulter DelsaNano C dynamic light scattering machine was used for hydrodynamic particle sizing and zeta potential measurements. Broadband transmission spectra were obtained with a home-built optical setup with the core components consisting of a miniature fiber optic spectrometer (Ocean Optics, S2000) and a Tungsten halogen light source (Micropack, HL-2000). This setup was used to measure the localised surface plasmon resonance (LSPR) spectra and approximate the inter-particle spacing. It is important to note that due to the geometry of the setup, the incident light passed through two NP interfaces (i.e. the interface was elliptical). A Leo Gemini 1525 FEGSEM scanning electron microscope was used to size the NPs as well as provide evidence of monolayer formation (rather than multilayers). A Mettler-Toledo SevenGo Duo pro pH/ion/conductivity meter was used for conductivity measurements.

In all cases, ultra-pure water with a resistivity of $18.2 \text{ M}\Omega\cdot\text{cm}$ was used. All chemicals were purchased from Sigma-Aldrich UK and used without further purification. Chemicals used: $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ (f.w. 339.79 (anhydrous), 99.999% trace metal basis). Trisodium citrate dihydrate (f.w. 294.10, $\geq 99\%$). 12-Mercaptododecanoic acid (MDDA, f.w. 232.38, 99%). Ethanol (molecular biology,

absolute grade). Methanol (MeOH, CHROMASOLV, HPLC grade, $\geq 99.9\%$). Sodium chloride (f.w. 58.44, $\geq 99.5\%$). 1,2-Dichloroethane (DCE) (ACS reagent, $\geq 99.0\%$)

MDDA stabilized Gold Nanoparticle synthesis

Gold NPs were synthesized based on the Turkevich-Frens recipes:^{56, 57} 8.6 mg $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ (5 mg gold) was dissolved in 95 ml H_2O and brought to 100 °C. Under stirring, 5 ml 13.6 mM sodium citrate solution was then added to the refluxing mixture. The initially faint-yellow solution gradually turned dark-blue followed by wine-red over a period of 10 minutes. At this point the NPs were measured to have a hydrodynamic diameter, electrophoretic mobility, and zeta potential of 20 ± 4 nm, $-3.60 \times 10^{-4} \text{ cm}^2/\text{Vs}$, and -47.0 mV respectively. The size of the particles was verified to be $\approx 16 \pm 3$ nm using a SEM. Once the reaction had gone to completion (typically less than 15 minutes), the temperature was reduced to 60 °C. This was followed by the addition of MDDA (5 mg) dissolved in MeOH (0.5 ml). The functionalization was allowed to continue for at least 1 hour to ensure complete monolayer coverage, after which the mixture was allowed to slowly cool under stirring for at least an extra hour. The excess MDDA precipitated out and was removed by filtration. The functionalized NP typically had a hydrodynamic diameter of 26 ± 7 nm, a conductivity of 217 $\mu\text{S}/\text{cm}$, electrophoretic mobility of $-4.37 \times 10^{-4} \text{ cm}^2/\text{Vs}$ and a zeta potential of -57.0 mV. The concentration of the NPs was then increased by centrifugation to the desired value. The ‘stock’ NP solution used for the experiments had an absorption of 0.890 at 525 nm. Taking an extinction coefficient of $4.92 \times 10^8 \text{ M}^{-1} \text{ cm}^{-1}$ ⁵⁸ the concentration of NPs was determined to be 1.8 nM or 1.09×10^{12} NPs/ml.

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Supporting information available: A discussion of centrifugation, SEM images of dried nanoparticle arrays, the effects of the dielectric constant on the LSPR maximum, a comparison between mercaptosuccinic acid and MDDA and details of the calculation of the interfacial area and HWHM. This information is available free of charge via the Internet at <http://pubs.acs.org>

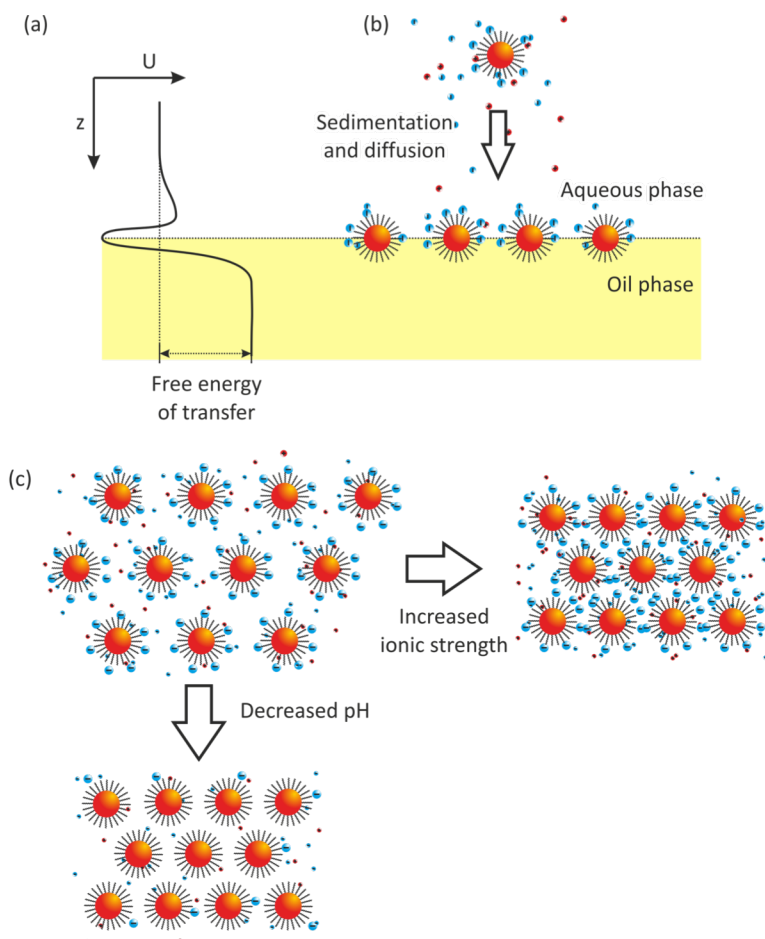


Figure 1 The main factors that influence localization of NPs functionalized by charged ligands at the LLI.

- The free energy profile, $U(z)$, for a single NP at the LLI is dominated by an interfacial stabilization well caused by the reduction of the system free energy when the NP blocks some parts of the energetically unfavorable interface between the aqueous and organic phases. For highly charged NPs, the combination of interfacial stabilization and Born resolution may give rise to a barrier on the aqueous side separating the well. The ratio of the height of the barrier to the depth of the well should grow with the size of the NP, as long as the amount of charge on an NP scales as its surface area.
- The particles reside on the interface driven by the interfacial stabilization but they feel this force at the distances of the order of their size. They thus approach the surface at a rate determined by Brownian diffusion and free- or centrifugation-promoted sedimentation (where the gravity+centrifugation force compete with the Stokes friction force). See text for further details.
- NPs at the water/oil interface with a viewpoint normal to it. The inter-particle separation is controlled by the ionic strength of the solution and also the charge on the particles which is controlled by the pH of the solution.

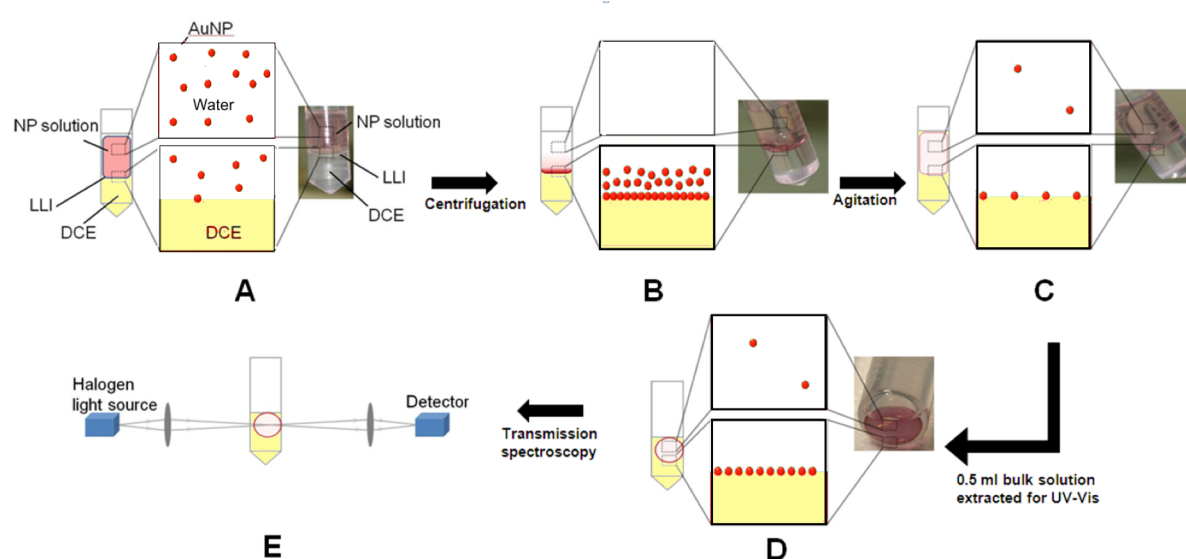


Figure 2 Schematic of the experimental procedure. All experiments were carried out with 0.5 ml DCE with 0.6 ml aq. NP solution (**A**). Upon centrifugation (**B**) the centripetal driving force provided a means to speed up NP adsorption at the LLI. (**C**) 0.5 ml of the aqueous phase was then removed, from the tubes, followed by gentle agitation of the remaining phases, re-addition of the removed aq. phase, followed again by removal of 0.5 ml aq. phase for UV-Vis measurements (**D**). The remaining 100 μ L droplet was then imaged by transmission spectroscopy in the geometry shown in (**E**).

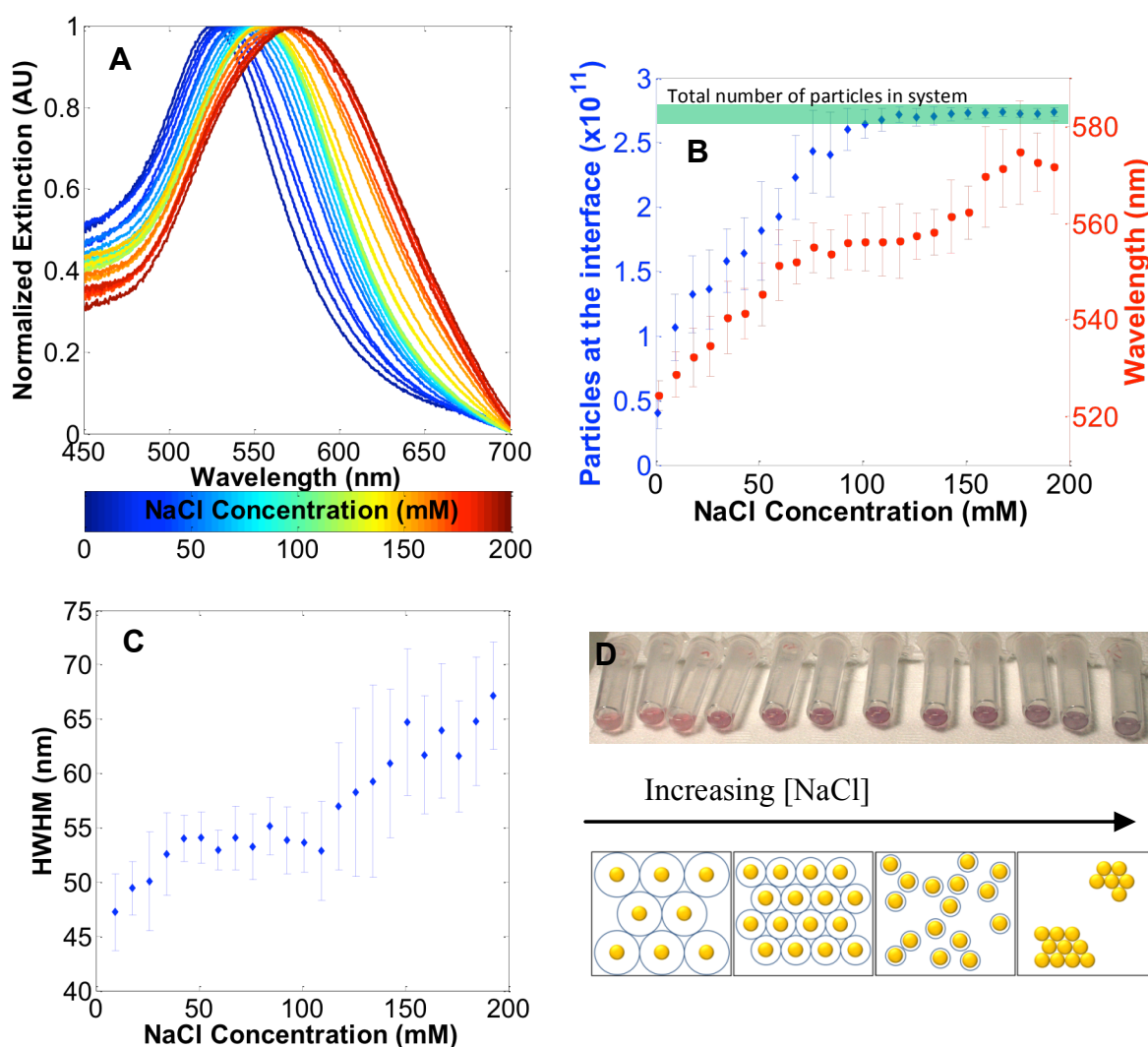


Figure 3 Dependence on plasmonic properties of 16 nm diameter gold NPs. (A) Full normalized spectra of samples. The spectra show a red-shift and peak broadening as the [NaCl] is increased. For clarity, the plasmon maximum with the number of particles adsorbed to the interface and half width at half maximum are plotted in (B) and (C) respectively. A photograph of the samples is shown in (D) with the hypothesis for what is causing the shift as the schematic.

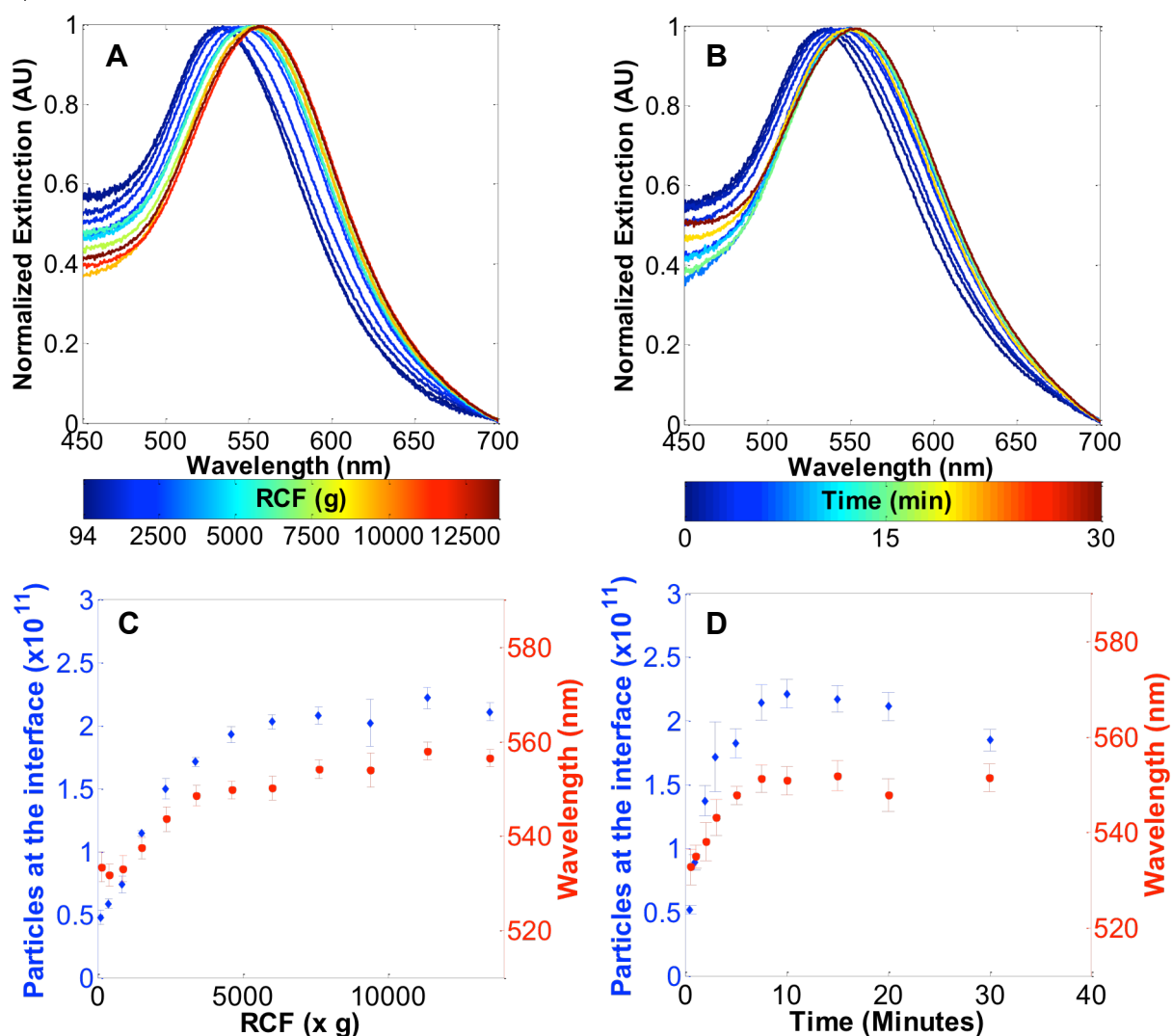


Figure 4 Particle adsorption to the LLI and corresponding LSPR maxima as a function of RCF (left) and time (right) of centrifugation. Full transmission spectra of RCF (A) and Time (B) experiments. It is clearly evident from (C) and (D) that the plasmon maximum is strongly dependent on the number of particles adsorbed. As the RCF or time is increased, more particles have time to reach and adsorb to the LLI, leading to more close packed assemblies.

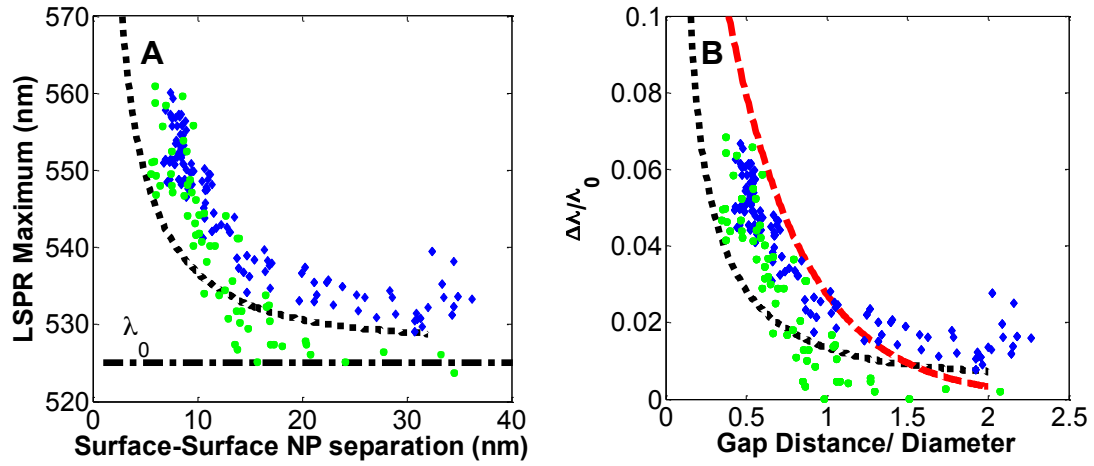


Figure 5 Demonstration of the plasmon ruler at the LLI for time and RCF dependant experiments (blue diamonds). NaCl dependant experiments for concentrations ≤ 75 mM are also shown (green circles). The results from mean-field theory from are shown as a black dotted line (A). Experimental results and theory are compared to CDA simulations (red dashed line). The LSPR shift is given as $\Delta\lambda/\lambda_0$ making the results applicable to Au NPs in any medium. The x -axis shows the dimensionless $a/2R$, the surface-to-surface separation divided by the diameter. λ_0 was taken to be 525 nm, as this represents the LSPR maximum of NPs in bulk water for the experimental results (B).

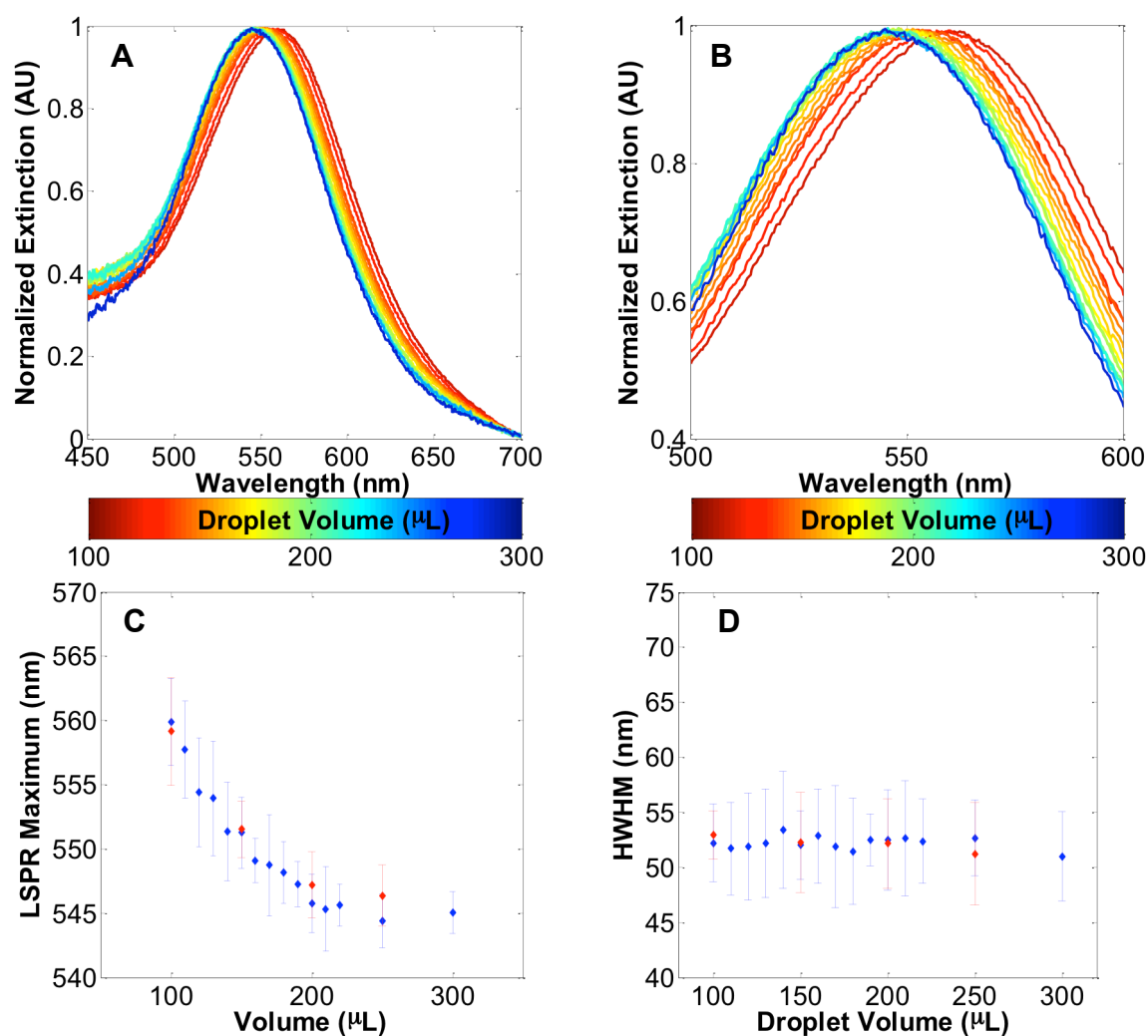


Figure 6 Volume dependence on transmission spectra (A & B), LSPR max (C) and FWHM (D). Increasing the volume of the 100 μL droplet leads to a blue-shift of the plasmon resonance. This shift is reversible and a reduction of the volume (red data points) leads to comparable maxima at set volumes. If the volume is reduced to below 100 μL , a further red-shift is observed temporarily, however, the ‘excess’ NPs are gradually desorbed until the maximum equilibrates to ≈ 560 nm, it is probable therefore that the minimum spacing of the NPs at these assemblies is dependent on the ionic strength of the solution.

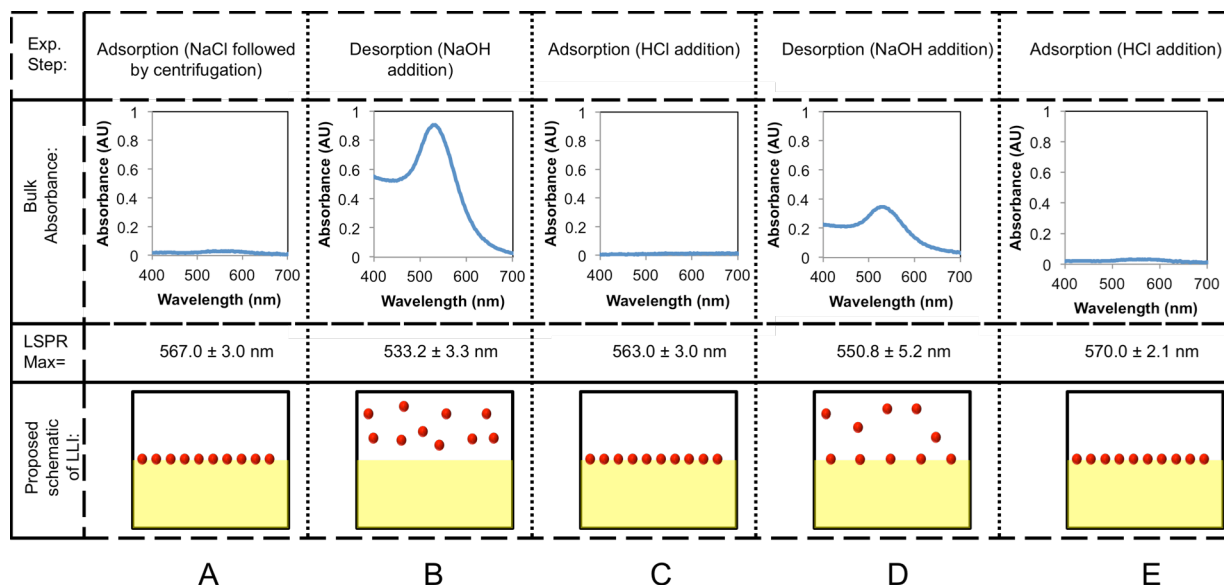


Figure 7 Demonstration of reversibility of NP adsorption/desorption. After assembly, the bulk salt was diluted in the aqueous phase 100x (A). Addition of 5 μ L 5 mM NaOH, followed by removal and combination of 5 μ L from each of the 24 samples (B), with the plasmon maximum decreasing from 567.0 ± 3.0 nm to 533.2 ± 3.3 nm and the bulk absorbance from UV-Vis of ≈ 0.9 . After the addition of 10 μ L 5 mM HCl, vigorous shaking of the sample and removal of 10 μ L of the aqueous phase (C), the LSPR maximum from transmission returns to approximately the same value as the first adsorption step, while the bulk absorbance is negligible. Subsequent HCl/NaOH additions (D) and (E) show only partial reversibility.

Experimental Step	DCE volume (μL)	Aqueous Volume (μL)	Description
(1) DCE saturation with H ₂ O	500	100	H ₂ O is added to DCE aliquot and emulsified by vigorous shaking.
(2) NP/NaCl solution preparation	0	1000	Separately, 500 μL NP solution is added to 500 μL NaCl solution (for NP/NaCl concentrations see Table 2).
(3) Addition of NP solution to water-saturated DCE	500	600	500 μL of solution (2) is added to mixture (1) [the remainder of (2) is used to estimate the bulk NP concentration by UV-Vis spectroscopy].
(4) Centrifugation	500	600	Mixture (3) is centrifuged, followed by gentle inverting to homogenize the bulk concentration of NPs.
(5) Estimation of the number of NPs adsorbed at LLI	500	100	500 μL of mixture (4) is removed and used for UV-Vis to measure the residual bulk NP concentration, which allows estimation of the number of adsorbed NPs.
(6) Background transmission measurement	500	100*	Mixture (1) is used to measure background transmission spectrum.
(7) LSPR at LLI measurement	500	100	The mixture remaining after stage (5) is used to measure LSPR of the NPs adsorbed to the LLI by transmission spectroscopy.**

Table 1: Point by point summary of experimental procedures for the assembly of NPs to the LLI and measuring LSPR maxima. * For transmission of droplets with a volume greater than 100 μL, the background was measured with the greater volume. ** For volume and pH dependent experiments, these steps were initially carried out, followed by additional procedures as highlighted in the main text.

Experimental Variable	Total NPs in Solution	NaCl conc. (mM)	Centr. Speed - RCF (g)	Centr. Time (min)	Aq. Droplet Volume (μL)	pH
NaCl Concentration	2.75x10 ¹¹	(1-193)	9391	10	100	5.5
RCF	2.75x10 ¹¹	75	(93-13523)	10	100	5.5
Centrifugation Time	2.75x10 ¹¹	75	9391	(0.5-30)	100	5.5
Droplet Volume	2.75x10 ¹¹	75	9391	10	(100-300)	5.5
pH	2.75x10 ¹¹	165	9391	10	100	(2-9)

Table 2: Experimental conditions – the number of NPs, the NaCl concentration, RCF, time of centrifugation, aqueous droplet volume and pH – for the results shown in Figures 3, 4, 6 and 7.

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