

CHM 2990 Project Report:

Electrolyte Assisted Self-Assembly of Gold Nanocubes at a Liquid | Liquid interface

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Abstract:

Precise control over the assembly of nanoparticles at liquid | liquid interfaces is imperative to their success at integrating into electronic, photonic and optical devices. The self-assembly of nanoparticles also has important applications to medicine and catalysis. However, many difficulties arise in trying to control the precise properties of the nanoparticles, as these are strongly dependent on the size, shape and interparticle separation of the nanoparticles.

In this report, we use 11-mercaptoundecanoic acid (MUA) to functionalise gold nanocubes and attempt to assemble them at a water | 1,2-dichloroethane interface. Interfaces provided molecularly flat, self-healing surfaces that are ideal for 2D assembly of nanoparticles. We found that there was no noticeable difference between samples with different concentrations of electrolyte: indicating an issue with the functionalisation, an insufficient concentration of electrolyte or a lack of adsorption caused by an acidic pH.

1. Introduction

1.1 Introduction to metal nanoparticles

The unique chemical and physical properties of matter when it is reduced to nano-dimensions, between 10-100nm, have led to the development of several disciplines such as nanoengineering,¹ nanoelectronics² and nanobioelectronics.³ Particles of matter within these dimensions are typically referred to as nanoparticles (NPs),⁴ and it is the use of these upon which the aforementioned fields were developed. Most of these fields require the ability to precisely control the properties of the NPs used. As many of these properties are related directly to the size and geometry of the particles, the ability to control these aspects is crucial.

The assembly of NPs into macroscopic structures promises to revolutionise a range of fields through the development of devices such as magnetic, electric and photonic sensors.^{5,6} NPs also show promising applications in catalysis⁷ and the field of nanomedicine has applicability from diagnosis to therapy.⁸ Many of these applications require light to be absorbed or scattered within a specific energy band, usually achieved through the use of gold NPs (Au-NPs) since

the optical properties of Au-NPs are strongly geometric and size dependant.⁹ Therefore, a great deal of work has been done to develop syntheses which precisely control the size and geometry of the resultant particles. Noble metal NPs can be synthesised in a variety of media, with the aqueous based synthesis being the most ideal as they are highly reproducible in the laboratory.

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There are three general processes employed in these syntheses: template-assisted, adsorbate-directed and seed-mediated synthesis, the latter has been the most popular as it is able to consistently produce geometries such as spheres,¹¹ rods¹² and cubes.¹³ Figure 1 illustrates the general mechanism for seed mediated growth. The process of seed mediation requires two steps, the first of which is the generation of small particles, referred to as “seeds”,¹⁴ under supersaturated conditions. The result is the fast generation of uniformly spherical NPs between 1 and 5nm.

The second step, is the growth step, where the geometry of the resulting particle is controlled.¹⁵ The reaction conditions are altered, at this stage, and more Au-NPs are added, along with a reductant and a template molecule, which is specific to the desired geometry.

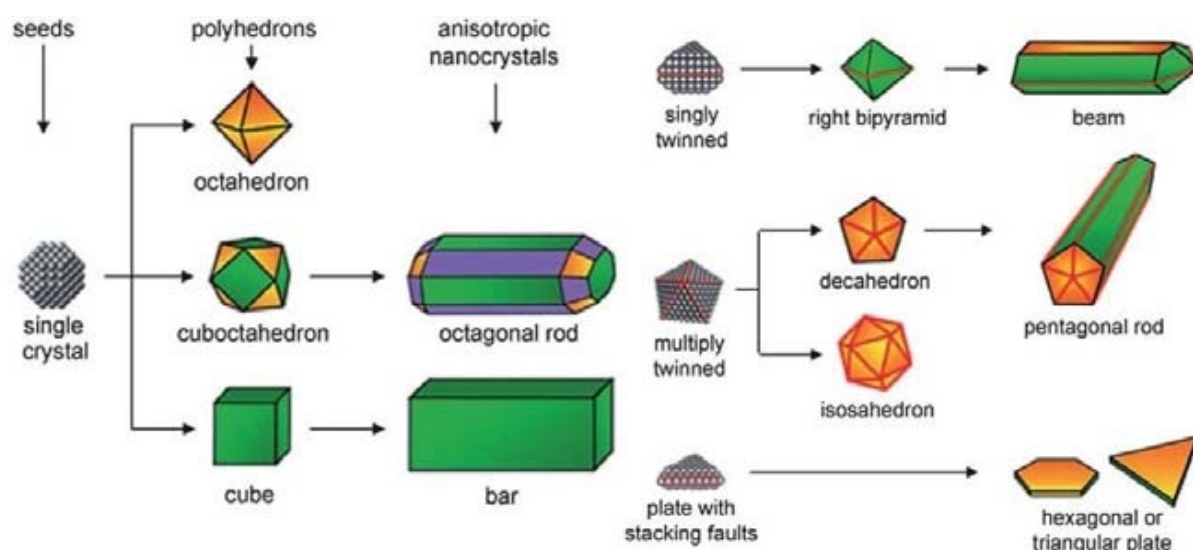


Figure 1. Schematic illustrating the general process of seed mediated growth, producing NPs of a variety of geometries. Reproduced from ref. 16.

1.2 Optical properties of noble metal nanoparticles

As mentioned previously, Au-NPs are of particular interest for optical applications due to their high stability and strong optical absorption in the visible and near infrared regions.¹⁷ Most of the optical properties of metal NPs are the result of an optical phenomenon, termed a surface plasmon resonance (SPR): in which the collective valance electrons of the metal NP are in resonance with the electric field of the incident light.¹⁸ The conduction electrons in metal NPs are confined to the volume of the particle^{13,19} and as a result the electron oscillation is confined to the surface of the particle, hence the SPR is also known as a localised surface plasmon resonance. For spheres, the near-field is localised to about 10nm from the surface of the particle.²⁰

The SPR results in strong absorption and scattering as the SPR interacts with light, and such processes dominate the interactions.²¹ For small NPs, it is worth noting that the magnetic field of light interacts only weakly with the electron's spin, therefore the electrical interaction dominates the interaction with light. The interactions between non-spherical NPs and light are more complex than those of spherical NPs and a number of studies have revealed the geometric dependence of a NP's optical character.²²

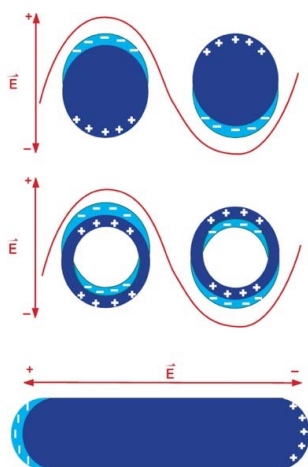


Figure 2. Schematic illustrating the surface plasmon resonance for nanospheres [top], for hollow nanospheres [middle], and nanorods [bottom] in the electric field of light.

For the nanorod, only the longitudinal mode is shown. The transverse ‘end on’ mode is more or less the same the nanosphere resonance, illustrated by the topmost image. Reproduced from ref. 23.

For example, the SPR manifests as two peaks in an ultraviolet-visible spectrometer (UV-Vis) for a nanorod, one representing an oscillation across the face of the rod (transverse), the other, along the length (longitudinal).²⁴ This demonstrates the dependence of the SPR on the geometric environment of the NP, and it is thought that a shift in the SPR frequency observed in ensembles of metal NPs are able to be modified by interparticle distance.^{25,26} At distances

of less than about 5nm, an absorption band appears in the spectra of the NPs, which is often attributed to the coupling of neighbouring plasmons.²⁷ The coupling of plasmons occurs when interparticle distance is comparable to, or smaller than, the incident wavelength, and occurs in conjunction with a drop in electrical resistance, which has important implications for electronic applications.²⁸

The analytical techniques usually used to characterise NPs and their optical properties are: UV-Vis, dark field microscopy (DFM) and scanning electron microscopy (SEM).²⁹ Transition electron microscopy (TEM) is also often used for high resolution imaging; however, TEM can cause severe sample damage due to the intensity of the electron beam when compare to SEM.³⁰ The UV-Vis absorption spectrum for a NP sample is usually broad and asymmetrical as the particles in a sample usually have slightly different sizes and shapes, therefore leading to different responses. However, the red-shift of a spectra is a useful in determining the geometries of a larger sample,²⁹ and will be used herein for that purpose.

Precisely correlating the optical properties of a NP with its specific size and geometry requires single particle spectroscopy. It is to this end that DFM and SEM are applied. A dark field microscope focuses light on a sample via a dark field condenser, the scattered light resulting passes through an objective lens and is then recorded on a CCD camera to give scattering spectrum.³¹ DFM is often used to characterise the assembly of NPs.

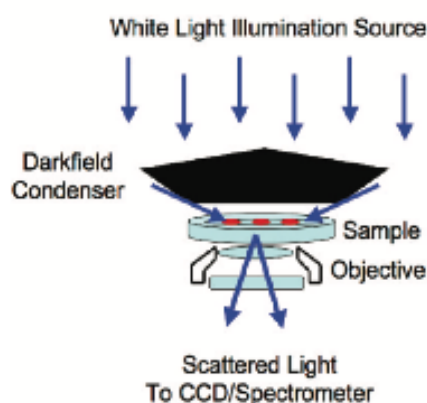


Figure 3. Schematic representing the typical instrumentation of a dark field microscope. Reproduced from ref. 32

The limitation of DFM is that it cannot give detailed information about the morphology of the particles being analysed; it can only give the optical properties of what is presumed to be a single particle.³¹ This is the reason that SEM is required for a thorough analysis of NPs as SEM can resolve the geometry of the individual particles, though if detailed structural data is required TEM must be employed.²⁹

1.3 Self-Assembly of nanoparticle films

There are two general approaches to the construction of nanodevices; the so called ‘bottom-up’ and ‘top-down’ methods. The top-down method involves the conversion of bulk materials into nanostructures, generally through physical processes, such as focused ion-beam milling.³³ The resulting structures usually have a highly damped optical response due to their low crystallinity and rough surfaces,³³ making them impractical for many optical applications. The bottom-up method, on the other hand, involves the organisation of premade NPs into superstructures via either physical or chemical methods.³⁴ The physical methods used, such as spin coating and solvent evaporation, often lead to random structures making them less suitable for the development of fine nanostructures. Therefore, the precision and control needed for most applications are difficult to achieve through the use of physical methods.

The use of bottom-up chemical assembly, especially of Au-NPS, has attracted a great deal of attention due to the high level of crystallinity which can be achieved through the use of linker molecules.³³ Linkers can also be polymers and biopolymers, such as proteins and DNA, with DNA thought to be the most versatile linking molecule.³⁵ Linkers can be small organic molecules functionalised with thiol, ammonium or a combination thereof, which are effective due to the affinity of those functional groups to the surface of Au-NP.³⁶ The advantage of these linker molecules is that they allow reliable control over interparticle distance through the length and steric bulk of the functionalised molecule.³⁶

Monolayers of NPs are essential to many of their applications and free-standing membranes of covalently bonded NPs have been reported,^{37, 38} along with synthetic monolayers, which have attracted considerable interest as they are able to be endowed with tailored properties. Aside from the size and shape of the elementary NPs, interparticle separation is an additional factor affecting the physical and chemical properties of assembled NPs.³⁹

For the assembly of monolayers, several techniques have been reported, including adsorption,^{40,41} the use of carbon⁴² and metal substrates⁴³ and the use of interfacial tension.⁴⁴ The latter, provides a suitable template for the construction of ordered NP structures, particularly when

using a liquid-liquid interface (LLI) since the NPs can readily rearrange when the equilibrium is manipulated.⁴⁵ The mobility afforded by the interface offers an environment for refined control of interparticle distance as a cross-linking agent, or other chemical species can be introduced to the system through either phase.⁴⁶

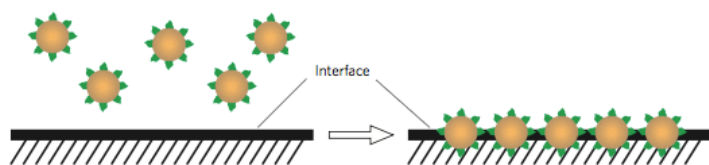


Figure 4. Schematic describing the self-assembly of NPs at an interface. Reproduced from ref 11.

Herein, we study the assembly of gold nanocubes, functionalised with 11-mercaptopundecanoic acid (MUDA) at a water | 1,2 dichloroethane interface through the use of UV-vis technique. The electrolyte concentration in each phase is systematically varied through the addition of water soluble salts. The addition of the electrolyte screens the columbic repulsion between particles, therefore allowing in-plane control over interparticle separation. It should be noted that without an electrolyte in either phase Leonora Velleman *et al.*⁴⁷ found that very few NPs assemble at the interface. The concentration of the chosen electrolyte could provide an avenue through which more precise control could be exerted over interparticle distance.

1.4 Project Aims:

There are four principle aims to this project:

- I. The synthesis of cubic gold nanoparticles (Au-NPs), suitable for used in a ligand exchange and for the formation of a film.
- II. The second aim is to perform a ligand exchange, in which 11-mercaptopundecanoic acid ligands will be used to create a covalently bonded monolayer of NPs.
- III. The third aim is to assemble a monolayer using an 1,2-dichloroethane | water interface, where the particles are to be suspended through the use both hydrophobic and hydrophilic ligands.
- IV. The final aim is to add electrolytes to the layers, varying the concentration of the salt to see if the interparticle spacing within the film can be controlled.

2. Results and Discussion:

2.1 Synthesis of Au-NPs

Systematic variation was applied to the method outlined by T.K.Sau *et al.* in the synthesis of the Au-nanocubes. Both methods utilise a seed mediated growth mechanism, requiring the preparation of both a seed and a growth solution. It is important to note that the seeds must be used within two hours of preparation, as it is likely that they form into spheres when left for longer.

The first method involved the preparation of the seed solution with room-temperature sodium borohydride (NaBH_4) and resulted in the growth of mostly spherical NPs, as indicated by their UV-Vis spectrum (figure 5a). The second method involved the preparation of the seed solution with chilled NaBH_4 and resulted in the growth of a polydispersed sample of cubic nanoparticles. The polydispersity of the sample is indicated by the UV-Vis spectrum (figure 5b.).

NaBH_4 is unstable under atmospheric conditions and therefore decomposes rapidly at room temperature. This accounts for the difference between method one and two as the cooled NaBH_4 decomposes less rapidly, hence is present longer, when added to the seed solution. This suggests that a precise synthesis of cubic NPs is assisted by the use of cooled NaBH_4 . However, the concentration of NaBH_4 in solution is more precisely known when the solution is warm, and thus when exact concentrations are required warm NaBH_4 is likely to be more accurate.

Figure 5a. UV-Vis absorption spectrum for cube sample prepared with RT NaBH_4 .

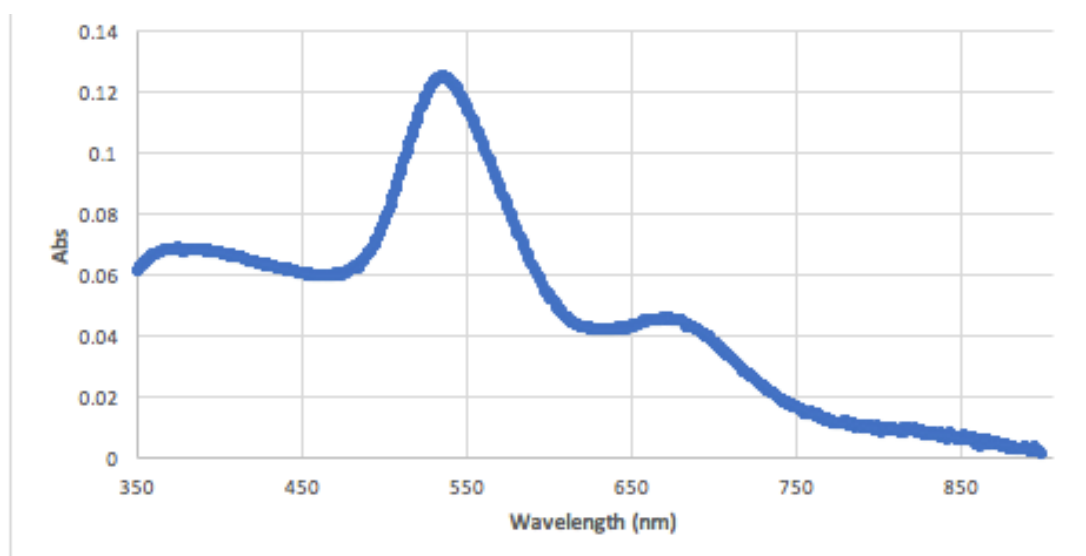


Figure 5b. UV-Vis absorption spectrum for cube sample prepared with cold NaBH_4 .

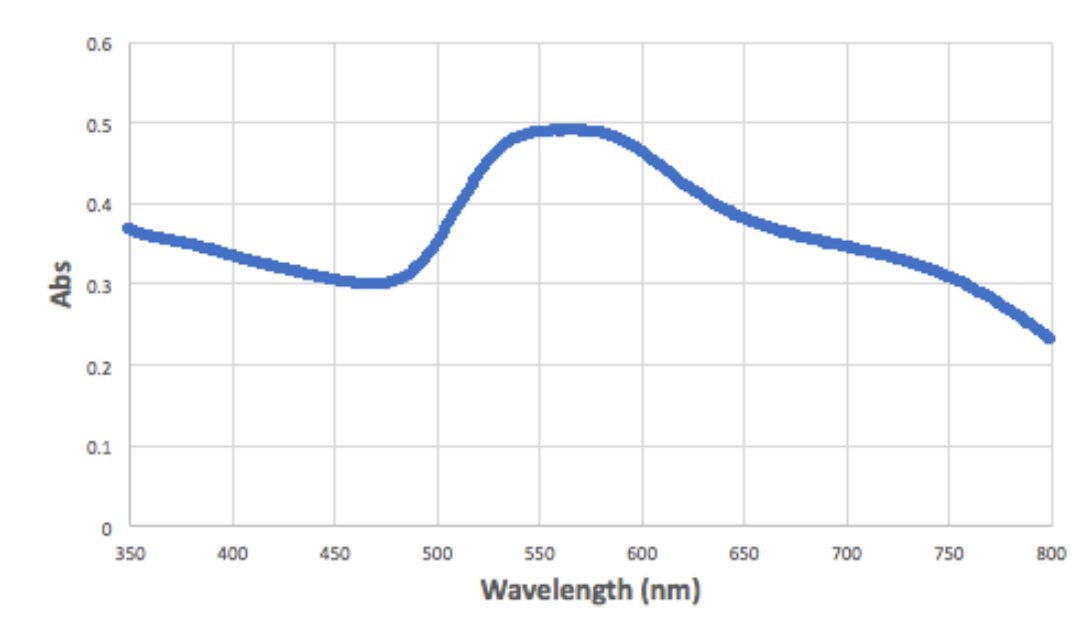
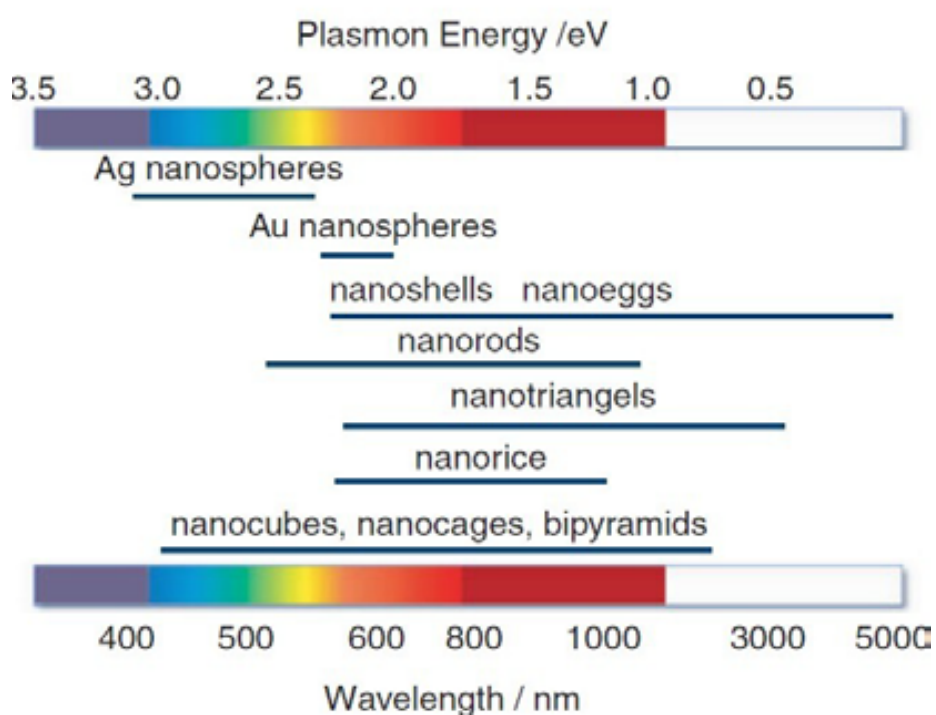


Figure 5c. Summary of the shape dependant optical properties of Au-NPs. Reproduced from ref. 49.



2.1.2 Optical properties

The UV-Vis spectra (figure 5a-c) represent the relative absorption of the sample at a particular wavelength due to the interaction of the SPR and the incident radiation. It is a non-destructive method for characterising the optical absorbance of NP samples. Typically, it is combined with SEM and/or TEM to precisely correlated the optical absorbance with the geometry of the sample. However, a number of studies have been done³⁷ that correlate ‘common’ geometries (rods, spheres and cubes) with a particular absorption spectrum. It is from studies such as these that the typical absorption value of 560nm is taken.⁴⁷

Therefore, it is likely that the RT synthetic method did not produce nanocubes: the maximum absorbance value is blue-shifted away from the expected value and the secondary absorption peak at 670nm potentially indicates the presence of another, undesired NP. This peak is too red-shifted to be the result of a cubic or spherical SPR. It is possible that it is the longitudinal mode of a rod-NP; however, this is unlikely as current research suggests that silver ions are necessary for the formation of rod-NPs.

Silver ions are proposed to play a role in affecting the symmetry and structure of the Au-NPs in an early stage of their growth.²⁹ To the authors knowledge, there is no way to produce Au-nanorods without silver ions, even if the role they play is yet to be conclusively explained. This renders it unlikely that the second peak is the result of nanorods; however, SEM or TEM would be required to confirm this.

The second peak in figure 5a. is also unlikely to be the result of Au-nanostars, which are known to have an optical response at about 720nm, the peak is blue-shifted outside this range.⁴⁸ This peak is therefore, likely a hybrid geometry or an aggregation of NPs that is small enough to remain in solution. This cannot be confirmed without imaging such as SEM, TEM or DFM.

The absorption maxima for the sample synthesised with cold NaBH_4 (figure 5b.) of 560nm indicates that nanocubes were successfully synthesised by the second method. This absorption value is in good agreement with the literature value for Au-nanocubes (figure 5c.). The broadness of the absorption peak is likely to indicate that the sample is polydispersed, and therefore that the synthesis did not produce nanocubes of a single size or, potentially, geometry. Alternatively, it could indicate a distribution in the rounding of the cubic vertices, which leads to a blue-shift in the optical response of the sample. No matter which is the case, the broadness of the peak indicates that the synthesis used did not precisely control the geometry and size of

the resulting particles.

The relative strength of the signals at 400nm should be noted, 0.07 and 0.33 for RT and cold NaBH₄ respectively. This is compared to the literature absorption value of 0.3 for 1.25*10⁻⁴ M to determine the concentration of gold in the sample. As table 1 indicates, there little difference between the methods in terms of concentration of Au-NPs synthesised. The perceived difference in their signals is simply a difference in the dilution factor when the UV-Vis was taken. This indicates both methods had similar yields.

Table 1: Au-nanocube concentration of synthesised

Sample	Absorption	Dilution Factor	Concentration Synthesised (M)
RT NaBH ₄	0.07	18.5	5.40*10 ⁻⁴
Cold NaBH ₄	0.33	5	6.88*10 ⁻⁴

2.2 Ligand Exchange with Au-nanocubes

The Au-nanocubes were functionalised with 11-mercaptoundecanoic acid (MUA). The ratio of cubes to ligand was 1:1 and the solution was left to gently stir overnight in accordance with established protocol.²⁹ The solution was observed to be dark red in colour with a tinge of purple. The functionalised cubes were washed and redispersed in the ligand solution to ensure the reaction was complete and the washed solution was observed to maintain most of its colour, though somewhat diluted, indicating the reaction was successful.

Thiol ligands are known to have a strong affinity for Au-NP and have been used in numerous ligand exchange reactions.⁵⁰ Thiols, in general, have a strong affinity for gold surfaces making them ideal functional groups for ligands to possess in such a reaction, therefore allowing us to be confident that the exchange reaction has proceeded towards completion. It is worth noting other functional groups such as ammonium have been exploited in these reactions as they bind to gold surfaces as well.

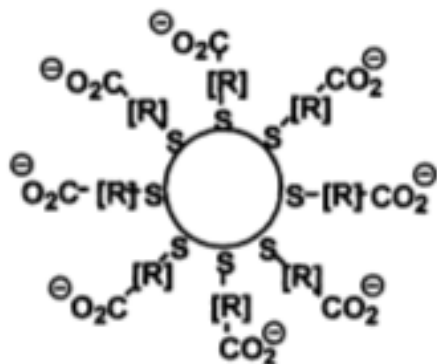


Figure 6. Schematic representing the bonding of a thiol and carboxyl functionalised ligand to the surface of a gold nanosphere. Carboxyl groups shown deprotonated. Reproduced from ref. 51.

MUA possesses both a thiol and a carboxyl group, allowing strong binding to the gold surface and for the ligand to become charged. In order to screen the electronic repulsion with an electrolyte, there first must be strong electronic repulsion between the cubes. Carboxyl groups are ideal as they deprotonate under neutral or basic conditions, leaving the resulting charge on the nanotube. The pH of the solution then becomes an important consideration, as maximum deprotonation is ideal.

The pKa of MUA is 5.7,⁵¹ and therefore careful control and modification of the pH was necessary in the preparation of the ligands. It was also necessary to readjust the pH when redispersing the sample as an acidic pH could result in the particles falling out of solution as the carboxyl groups protonated by the abundance of H^+ ions. The pH adjustment was performed by the dropwise addition of a dilute NaOH solution. Care should be taken when selecting a base, as some strong bases may have compromised the colloidal stability of the particles, causing them to fall out of solution.

The advantage of the pH dependency of the ligand is it provides another way in which to control the assembly of nanoparticles: through the relative amount of protonation. The disadvantage is that it potentially makes the layer itself sensitive to the pH and therefore limits some applications. One such area limited by this would be nanomedical sensing of acidic areas, such as the stomach.

The pH dependence of MUA, and the potential dependence of the resulting monolayer, may also serve as an avenue through which further sensing applications could be developed. If the synthesis for a precise layer were to be developed, then the damage to this layer caused by an acidic environment could be quantified and used as a pseudo-pH meter when it may be impractical to apply other sensing methods.

Leonora Velleman *et al.*⁴⁷ used 12-mercaptododecanoic acid (MDDA) when preparing functionalised nanocubes. They also mention the pH dependency of their ligand in the context of providing electrostatic repulsion to be screened, and it is likely therefore, that such dependency would arise in their assembly. Images comparing MDDA and MUA can be seen below (figure 6a-b.)

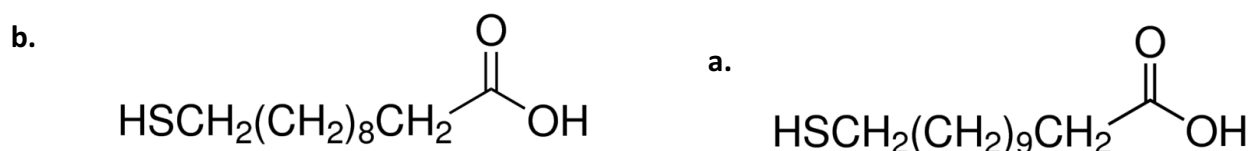


Figure 7. Comparison of the structure of MUA (a) and MDDA (b).

There is little that differentiates MUA and MDDA, except for the one carbon and the corresponding hydrogens in the carbon back bone. Given both have now been successfully used to functionalise nanocubes, we know that the single carbon did not make a difference. The limit at which the chain becomes too long or too short to properly functionalise the cube is an open question, but one which has important implications for the use of thiol-carboxyl ligands in the creation of nanoscale devices.

2.3 Interfacial Assembly

We attempted to assemble the functionalised cubes at a 1,2 –dichloroethane interface | water interface. The amount of NaCl dissolved in the water was systematically varied over a number of trials to see if a critical concentration beyond which the cubes assembled at the interface could be determined. As mentioned in the introduction, studies have found that very few cubes, functionalised with similar ligands, assemble at the interface without the aid of an electrolyte. We therefore, assumed that no cubes would be observed at a NaCl concentration of zero, and proceed with varying the amount of NaCl used.

We found no noticeable change between 20mM and 100mM. This may have been due to insufficient electrolyte in solution, or it may have been because of insufficient cubes in solution. We expected to see the red-purple colour associated with the functionalised cubes to form a 2D layer at the interface. No such layer or colour was observed, indicating that the cubes did not assemble at the interface.

It is possible that there was simply insufficient volume of cubes and interface to observe any changes. The meniscus of water was observed to dominate the interface at such a low volume (750 μ L) and it is also possible that this obscured any assembly of the cubes at the interface. The ratio of water to 1,2-dichloroethane was used as reported⁴⁷ but diluted by a factor of 100 as the volume of functionalised cube sample was small.

The pH dependency may have also factored into the failure to observe an assembly of cubes as the interface was constructed under atmospheric conditions. Under atmospheric conditions water is often mildly acidic due to dissolved CO₂ as it forms carbonic acid. This may have acidified the water and therefore caused the functionalised cubes to fall out of solution. No layer was observed on either the bottom or the sides of the vial, but there is often not visible residue when NPs fall out of solution: what is termed a ‘crash’.

It is important to note that the 1,2-dichloroethane formed the top layer of the interface, and that the Au-Nanocubes were added to the aqueous phase before the 1,2 – dichloroethane was added. It is possible that this order of addition was responsible for the failure to observe a formed layer as the cubes may have already been crashed by the pH before the interface was even formed.

Figure 8 shows the pH dependent behaviour of unfunctionalised Au-NPs. This behaviour is broadly the same across all geometries⁴⁶ but does not account for the functionalisation. Nonetheless Tomasz Andryszewski *et al* observed that at an acidic pH the particles have little tendency to adsorb to the interface. Therefore, it is also possible that the particles did not crash, but simply did not adsorb on the interface.

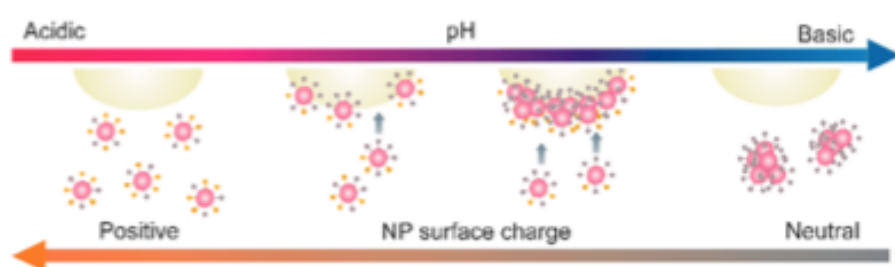


Figure 8. Chart representing the pH controlled behaviour of Au-NPs (without MUA). At low pH the particles show have little tendency to adsorb to the interface. Between pH 3-10 the particles adsorb onto the interface, as the pH has increases an aggregate layer forms and at a high pH bulk aggregation of the particles occurs. Reproduced from ref. 46.

3. Conclusions and Future Work:

3.1 Conclusions

We found that we could synthesis a polydispersed sample of cubes by modifying the synthetic method presented by T.K.Sau *et al.* with the use of cold NaBH_4 . This is thought to be more effective as the cooling prevents the decomposition of NaBH_4 therefore allowing it greater time to react with the seed solution. The UV-Vis spectra of the products produced by the two different methods clearly show that cold NaBH_4 result in a sample that is most likely cubic. The absorbance of samples, though perceptively different, actually shows that there was little difference between the concentration of Au-NPs synthesised by either method, indicating similar yields.

We found that MUA can be used to functionalised cubic NPs, as indicated by the colour of the reaction solution. The thiol and carboxyl functionalities make a ligand such as MUA ideal for an electrically assisted self-assembly; however, the pH must be carefully controlled to ensure maximum deprotonation. The pH dependency of the ligands constrains their applicability to some fields, but could potentially broaden them in others.

We found that no functionalised nanocubes assembled at the 1,2-dichloroethane | water interface, as none of the colour associated with the functionalised nanocubes was observed at the interface after mixing. It is possible that the pH of the water caused the Au-nanocubes to ‘crash’ and fall out of solution by forcing the MUA to reprotonate due to the abundance of H^+ ions resulting from dissolved CO_2 in the water. It is also possible that the electrolyte concentration [20mM – 100mM in five trails] was too low to cause the cubes to gather at the interface.

3.2 Future Work

3.2.1 Synthetic Methodology

Though cubic NPs were produced by the use of cold NaBH_4 with the method outlined by T.K.Sau *et al.* it is evident from the UV-Vis spectrum of the corresponding sample that it is polydispersed. Further work could be done to determine the reason for this polydispersity, and it could also extent to modifying the method to see if monodispersity could be achieved. A precise, monodispersed sample of Au-nanocubes is ideal for many of the applications.

As mentioned previously, the seeds of a seed mediated growth method must be synthesised and used within a few hours, otherwise the seeds grow into spherical NPs. Future work could focus on finding a method to stabilise the seed particles, allowing them to be stored for a greater length of time. Such work could perhaps focus on the use of a stabilising agent which could be easily removed to 'activate' the seeds, but would prevent further growth while in storage.

3.2.2 Ligand Exchange

As mentioned previously, the difference in the length of the carbon chain between MUA and MDDA appeared to make no difference to the ligand exchange. Future work could therefore identify within what limits the length of the chain makes no difference. Such work could move from the smallest functionalised molecule possible to large, long chain, perhaps even aromatic compounds, and identify at what point the molecules fail to bind.

Additionally, the ability to endow monolayers with tailored properties allows for a level of specificity which is difficult to achieve with conventional engineering. One avenue for endowing these properties is the functional groups attached to the ligands that create the layer. Future work could therefore assess the viability of this notion perhaps through a practical test of whether or not ligands with additional functional groups bind to the NPs. Comparing the strength of the gold-thiol bond with functionalised ligands and without may also be an important indicator of the conditions under which such a tailored layer could exist.

Therefore, it may also be important to quantify the strength of the gold-thiol bond, and compare it to other bonds to see if another functional group may also serve as a binder. Ammonium is a strong candidate, and proteins have been used for self-assembly. However, the issue with proteins is that they can be easily disrupted by temperature and pH, and therefore are suitable only to applications in which such conditions would be unlikely to be encountered.

We used carboxylic acid groups to ensure that the Au-nanocubes electrostatically repelled one another; however, there is no apparent reason why the repelling functionalities need to be carboxylic acids. Future work could perhaps focus on amine functionalised ligand as they are capable of protonation and therefore of the same electrostatic repulsion as carboxyl groups. An important point to note about this suggestion is that amine groups are also presumably capable of binding to the gold surface as they possess a nitrogen.

3.2.3 Electrically Assisted Self-Assembly

The critical concentration of electrolyte in solution that results in the formation of a monolayer at the interface is still unknown. Future work could therefore attempt to discern it, either by stepping through higher electrolyte than the ones used herein, or by attempting to dissolve salts in both phases of the interface. The degree to which the interparticle distance can be controlled by the concentration of electrolyte is also unknown. Future work could use quantitative measurements to attempt to correlate interparticle separation and salt concentration to allow for fine-tuned control over optical and electrical properties.

Covalently bonded layers of NPs have been reported; however, the construction of this layer required mechanical compression of the NPs once assembled at the interface.⁴⁶ Future work could focus on the use of charge linking agents then utilise the electrostatic repulsion to compress the layer. The strength of electrostatic force is accurately known, and is more precise than the use of mechanical compression. It is also more easily reproduced, as the device used for the mechanical compression was unique (i.e. the authors made it). Therefore, would also be more easily replicated in the both in the laboratory and, potentially, in industry.

Future work could also focus on other means of electrically assisted self-assembly such as the application of an electric field to the interface or particles already assembled at the interface. Electrical techniques such as electrophoresis are already routinely applied to the identification and characterisation of NPs, and a modification of such a technique has the potential to be useful to construction of electrically assisted monolayers.

Furthermore, future work might vary the identity of the salt used for electrically assisted self-assembly to see if that too may provide an avenue for control over the optical and electrical properties of monolayers. There is no apparent reason that NaCl and KCl would produce different results but more complex salts, such as $(\text{CH}_3)_4\text{NI}(\text{NO}_3)_4$,⁵² could produce markedly different effects. Sulphur salts, such as S_2Cl_2 , may be of particular interest as the affinity of thiol to gold surface is due to the strength of the S-Au bond. Other charged NPs themselves may also function to screen the electrostatic repulsion between ligands; however, the steric bulk of such particles hinders this line of inquiry.

4. Acknowledgements:

We would like to thank Dr Alison Funston, Anchal Yadav and Wemning Tong for their support and expertise throughout this project.

5. Materials and Method:

5.1 Reagents

All water used herein is milli-Q water unless otherwise noted. Sodium borohydride (NaBH_4 , 99%), L-Ascorbic acid (AA, >99%), 1,2-dichloroethane (DCE, >99%) and auric acid (GA) were purchased from Sigma Aldrich Co. Trisodium citrate (TSC) was purchased from Merck. Cetyl trimethylammonium bromide (CTAB, 98%) were purchased from UniLab Co. All the reagents in the experiments were used as received.

5.2 Synthesis of Au-nanocubes:

The Au-nanocubes were synthesised using the seed growth method, which has been reported previously.^{16,17} The seed solution was prepared by adding 0.3mL of NaBH_4 [0.01M] into a 4.73mL aqueous solution, containing 1.875mL of CTAB solution [0.2M], 2.83mL of MQ- H_2O and 0.025mL of HAuCl_4 solution [0.05M], which generated a transparent light yellow-brown colour in the solution. The resulting seed solution was kept in a water bath of $29\pm 1^\circ\text{C}$ for 40 minutes before used. This was to ensure complete decomposition of the NaBH_4 in the solution.

The growth solution was prepared using 11.38mL of MQ- H_2O , 1mL of CTAB solution [0.2M] and 0.1mL of HAuCl_4 solution, mixed for at least 5 minutes to ensure homogenisation, solution was dark yellow-orange in colour. Then 1.5mL of aqueous AA solution [0.1M] was added to the growth solution, the solution turned transparent and colourless upon the addition of this solution. The growth solution was mixed for at least 5 minutes to ensure that all AA was dissociated.

Next, 0.1mL of the seed solution was taken and diluted by a factor of 10 (0.9mL of MQ- H_2O was added). Finally, 0.025mL of the seed solution was added to the growth solution, resulting in a light pink tinge to the solution. Over the next 5 minutes of stirring, growth solution slowly turned a rich, dark purple. The growth solution was then placed in a water bath, of $29\pm 1^\circ\text{C}$, and left undisturbed overnight.

5.3 Functionalisation of Au-nanocubes

The UV-Vis spectrum of the sample-to-be-functionalised was taken. The absorbance at 400nm was measured to be 0.0777, which was then used in conjunction with the literature absorbance value of 0.3 for 1.25×10^{-4} M. The concentration of gold in the sample was therefore 3.24mM.

To achieve a 1:1 ratio of ligand to Au-nanocube, it was calculated that 0.009g of MUA was needed: 0.0091g was actually used. The MUA was dissolved in a 250mL beaker in 80mL of H₂O and the pH was adjusted to 8-9 through the dropwise addition of dilute NaOH (~2.5mM). The solution was then heated for 10 minutes to ensure complete dissolution. The solution was then stirred to ensure homogenous distribution of MUA. The solution was then transferred to a 100mL volumetric flask and made up to the mark with H₂O.

1.5mL of Au-nanocubes were then added to a small vial (washed with toluene, ethanol then H₂O) and the solution was stirred moderately fast. 1mL of MUA was then added dropwise over 4 minutes while the solution was being stirred. Solution turned cloudy and red with a tinge of purple in the light. The solution was then left overnight with gentle stirring.

5.4 Preparation of nanoparticle films at the liquid | liquid interface:

We added 750μL of 1,2-dichloroethane to 1mL of aqueous solution (contained 750μL of H₂O with various concentrations of NaCl and 250μL of functionalised cube sample) in a vial. Particle adsorption was promoted by vigorous shaking for 10 seconds. The emulsion was allowed to separate over the next 10 minutes. No colour was observed at the interface, which indicates the particles did not adsorb to the interface. The concentrations NaCl used were 20mM, 40mM, 60mM, 80mM and 100mM, made by weighing out appropriate mass and then dissolving that mass in ~5mL.

5.5 UV-Vis Absorption Measurements:

UV-Vis absorption spectra were recorded with Cary-60 UV-Vis spectrometer between 300-900nm, with a scan rate of 600.00 nm/min in dual beam mode. The cuvette was washed MQ-H₂O, ethanol and then MQ-H₂O again, then 0.3mL of analyte was added with approximately 3mL of MQ-H₂O, until a light pink tinge was observed. The spectra were recorded with two cuvettes, one with MQ-H₂O, to be used for baseline correction and the other with the analyte.

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