# Understanding the formation of binary nanocrystal superlattice using metallic and semiconducting systems

A Thesis

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in partial fulfilment of the requirements for the
BS-MS Dual Degree Programme

by

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# Certificate

This is to certify that this dissertation entitled "**Understanding the formation of binary nanocrystal superlattice using metallic and semiconducting systems**" towards the partial fulfilment of the BS-MS dual degree programme at the Indian Institute of Science Education and Research, Pune represents study/work carried out by Bhaskar Saha at National Chemical Laboratory, Pune under the supervision of Dr. B.L.V. Prasad, Senior Scientist, Physical and Material chemistry department, National Chemical Laboratory, Pune during the academic year 2018-19.

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This Thesis is dedicated to Maa and Baba

# Declaration

I hereby declare that the matter embodied in the report entitled **Understanding the formation of binary nanocrystal superlattices using metallic and semiconducting systems** are the results of the work carried out by me at the Department of Physical and Material Chemistry, National Chemical Laboratory, Pune, under the supervision of Dr. B. L. V. Prasad and the same has not been submitted elsewhere for any other degree.

Bhaskar Saha

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Date: 30-03-2019

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Above all, I would like to thank my parents who were supportive throughout my career.

## Table of Content

# Abbreviations

| | |
|---|---|
| h | hour |
| g | gram |
| mg | milligram |
| µL | microlitre |
| mL | millilitre |
| mol | mole |
| M | molar |
| DDT | Dodecanethiol |
| DDA | Dodecylamine |
| DDAB | Dimethyldioctadecylammonium bromide |
| DR | Digestive ripening |
| OlAm | Oleylamine |
| Octylam | Octylamine |
| HAADF | High Angle Annular Dark-Field Imaging |
| HRTEM | High Resolution TEM |
| ITO | Indium Tin Oxide |
| FT-IR | Fourier-Transform-Infrared Spectrometer |
| NC | Nanocrystal |
| PXRD | Powder X-ray Diffraction |
| PL | Photoluminescence Spectrometer |
| RB | Round bottom |
| RT | Room temperature |

| | |
|---|---|
| SPR | Surface Plasmon Resonance |
| STEM | Scanning Transmission Electron Microscope |
| TEM | Transmission Electron Microscope |
| UV - NIR | Ultraviolet - Near IR Spectrometer |
| UV-VIS | Ultraviolet - Visible Spectrometer |
| XPS | X-ray Photoelectron Spectrometer |

## Abstract

Binary nanocrystal superlattices (BNSLs) of two different nanocrystals (NCs) with precise size and chemical composition were studied in this present work. NCs with different sizes and compositions mixed at ambient condition shows different kinds of self-assembly. These results strongly suggest that the radius ratio and the number density of individual NCs have a significant influence on the self-assembly process as mentioned in the literature. Moreover, when we performed the assembly at the different time and temperature, it was observed that single/monolayer (made of two different kinds of NCs positioned randomly) could be obtained at a lower temperature and lower time conditions. UV-Vis-NIR and XPS studies provided strong support towards the presence of an interaction between two types of NCs in the solution phase mixing also.

# 1. Introduction

Binary nanocrystal superlattices (BNSLs) are an assembly of two different monodisperse nanocrystals (NCs) in an ordered two-dimensional fashion. BNSLs with many crystalline structures that are otherwise known for atomic and molecular systems were unravelled recently prompting the notion that monodisperse NCs behave similarly to molecular and atomic systems. In the BNSLs the individual NCs are highly packed to maximise the packing density which is the driving factor for their formation. Investigating the composition and properties of BNSLs is not only interesting from the fundamental point of view, but these materials provide an inexpensive way to fabricate a large variety of metamaterials [1]. The key factors that play an essential role in the formation of the BNSLs are a) van der Waal Interactions between the neighbouring particles. b) radius ratio of the two crystals involved in the creation of the BNSLs [2-4] (as shown in **figure 1**) c) inter-particle distances. d) the nature and length of the ligand attached to the NCs. e) the entropic constraints due to ligand mixing and packing [5].

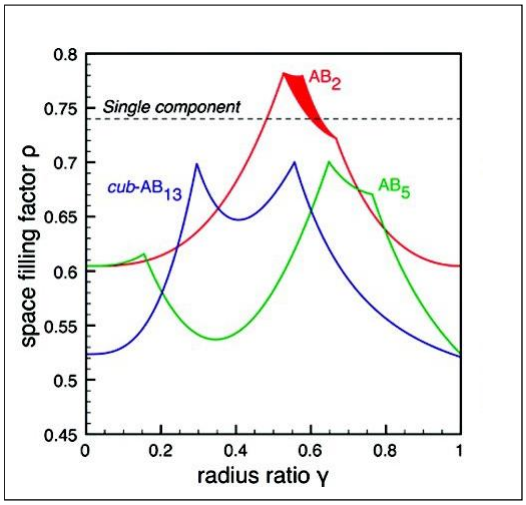


**Figure 1**. Calculated space-filling curve of different crystal packing of a two component system [6]

As a part of our project, we aimed at preparing the BNSLs using monodispersed metallic NCs like gold, silver in combination with different metal sulphides such as lead sulphide, cadmium sulphide and copper sulphide etc. We then wanted to see whether any interaction exists between them in the solution state or these interactions start manifesting in the solid state (when NCs come together in an ordered fashion) only.

Our efforts in this direction have started with the preparation of gold nanoparticles and metal sulphides NCs capped with ligands of small carbon chains (aliphatic amines).

***1.1.*** *Digestive ripening method:* DR method was used to prepare the metallic NC systems. The DR method involved three steps. In the first step, a two-phase reverse micelle method was used to synthesise the NCs. These were termed as as-prepared NCs. At this point, the NCs have a broad size distribution and are highly polydisperse. The polydispersed solution consists of NCs with different sizes, and many of are featured with crystals defects which led to lower stabilisation energy, resulting in higher chemical reactivity at these locations and more ligand-surface interaction shown in **figure 2**. The second step of this procedure involves the addition of an excess amount of organic ligand to the as-prepared solution. These organic ligands or the DR agents have a stronger interaction with the NC surface, and also the DR agent is generally added in excess (1:30). After these steps, the precipitation of the NCs from the reaction mixture is carried out. The examination of the TEM images of the NCs after the second step indicated a slight narrowing of the size distribution. It was proposed that the breaking of large NCs into smaller NCs narrows the size distribution and form metal-ligand complex on the surface [6]. The third step involves the re-dispersion of the precipitated NCs in a solvent with another dose of an excess amount of ligand (1:30) and refluxed under an inert atmosphere, which leads to the formation of monodisperse NCs stabilised by organic ligands dispersed in a non-polar solvent [7].

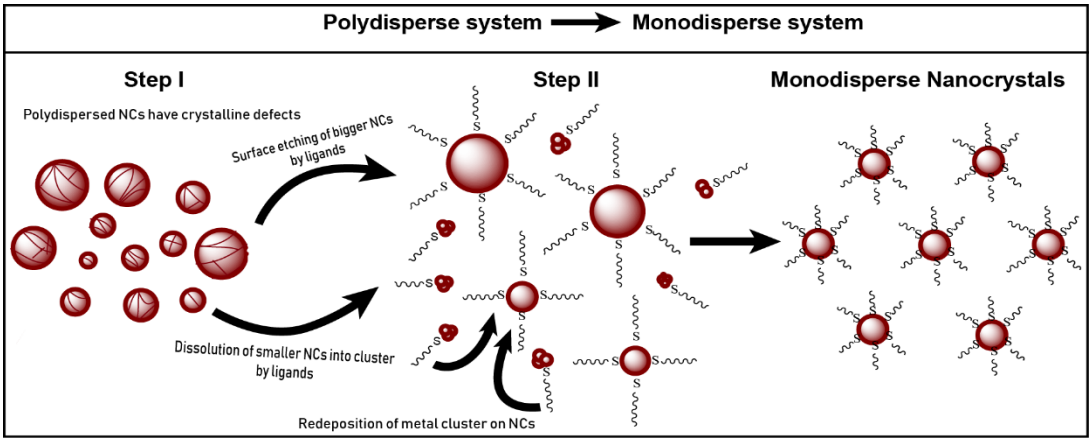


**Figure 2**. Steps involving in Digestive Ripening method (adapted from ref 8)

***1.2.*** *Hot-injection method*: This method used to prepare the metal sulphide NCs. In the procedure we followed a sulphur source was injected into the metal precursor at an elevated temperature. The formation of the monodisperse NC by this method is explained using the nucleation and the growth mechanism proposed by LaMer [9]. As we can see in **figure 3** that the monomer concentration in the solution increases and reaches a saturation point where it leads to the nucleation process followed by the growth until the monomer concentration falls belows the solubility limit in the given solvent.

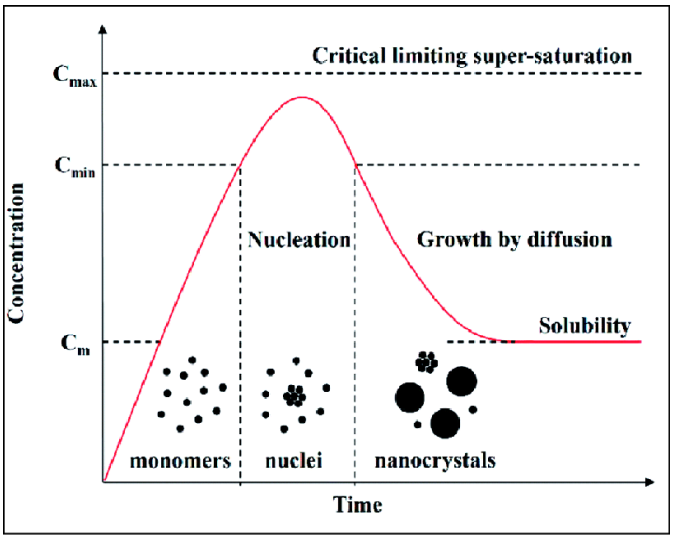


**Figure 3.** The plot of La-Mer model for the generation of atoms nucleation and subsequent growth of colloidal synthesis

Injection of reagent at an elevated temperature results in the burst of homogeneous nucleation which separates the nucleation and the growth process and quick drop in the temperature till room temperature prevents further nucleation, leading to monodisperse NC formation [8]

After ensuring the preparation of reasonably good monodisperse NCs, apart from the preparation of BNSLs, we also wanted to see how the BNSLs formation would influence the optoelectronic properties of the individual NCs. Here, our primary motivation was to check what happens to the optoelectronic properties of the individual NC systems and whether any interaction exists between them in the solution state or the interactions starts manifesting only in the solid state. Our results indicated that the

two NC systems namely the metals and metal sulphides start interacting in the solution state itself. This is a new observation and could help in devising new materials.

## 2. Materials Required

Gold (III) chloride, DDAB, $NaBH_4$, DDT, oleic acid, oleylamine (99%), $CS_2$, 1-octadecene (ODE), cadmium acetate ($Cd(CH_3COO)_2$), $(C_2H_5)_2NCS_2Na{\cdot}3H_2O$, $AgNO_3$, CuI, octadecylamine, octylamine procured from Sigma-Aldrich, and all solvents purchased from local vendors.

## 3. Experimental Methods

### 3.1 Metallic systems

#### 3.1.1. Preparation of gold NCs

45 mg of $AuCl_3$ (0.14 mmol), 150 mg of DDAB (0.32 mmol), 15 mL of toluene was loaded in a RB flask. 170 mg of $NaBH_4$ was dissolved in 500 µL milli-Q water. This was followed by the addition of 126 µL of $NaBH_4$ solution to the Au-toluene solution. The stirring was continued for 1 h at room temperature. 5 mL of the as-prepared solution, 360 µL of dodecanethiol (DDT) were loaded in a 50 mL RB and stirred for 15 minutes. This was followed by the addition of 18 mL of ethanol to the reaction mixture and keeping it aside/idle for 2 h. After the supernatant was decanted and the precipitate was dried under $N_2$ gas. This precipitate was re-dispersed in 5 mL toluene, and an excess amount of DDT (360 µL) was added to this dispersion. After that, it was refluxed under $N_2$ atmosphere for 1 h at 110 °C.

The same experimental procedure was carried out for performing the DR of Gold nanoparticles with other surface-active ligands.

#### 3.1.2. Preparation of silver NCs [10]

9 mL of oleic acid and 1 mL of oleylamine were loaded in a three-neck RB flask with 0.339 g of $AgNO_3$ (2 mmol). The RB flask with the precursor was heated to 70 °C and was degassed and dried under vacuum for 1.5 h and then filled with $N_2$ gas. The temperature was raised to 180 °C at a heating rate of 1 °C $min^{-1}$. After air-cooling to

ambient temperature, the NCs were retrieved by centrifugation using toluene and ethanol in 1:3 ratio. The centrifugation process was repeated for four times, and the sediments were re-dispersed in toluene.

### 3.2 Semiconducting metal sulphide NCs

The synthesis of monodisperse metal sulphides NCs like lead sulphide (PbS), cadmium sulphide (CdS) and copper sulphide (CuS) was carried out by the hot-injection method [12].

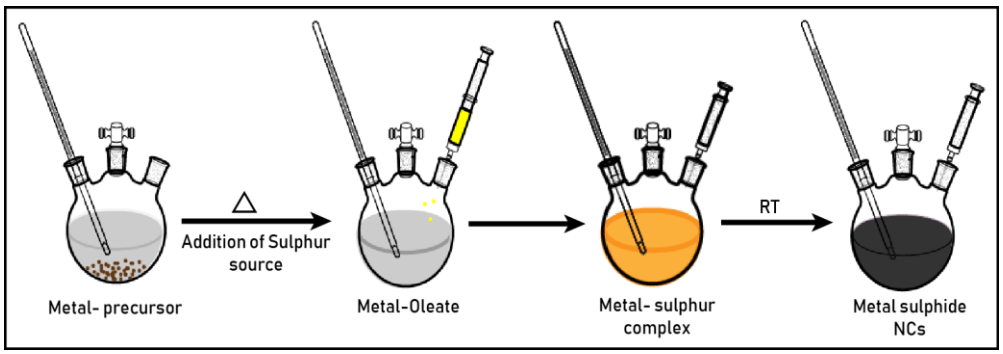


**Figure 3**. Steps involving in hot-injection method

#### 3.2.1. Preparation of Lead Sulphide (PbS)

- Preparation of Octyl Ammonium Octyl Dithiocarbamate ($C_8$DTCA)

About 10 mL of dry dichloromethane (DCM) was taken in 100 mL RB flask and cooled. To this 50 mmol of $CS_2$ (large excess) was added and stirred for some time in an argon atmosphere. After 15 min 10 mmol of octylamine $C_8NH_2$ was added drop-wise into the $CS_2$ solution and stirred for 30 min. A white coloured precipitate formed immediately. The precipitate was dried under vacuum. The powder was recrystallised from toluene.

- PbS NC preparation

0.45 g lead oxide (PbO) (2 mmol), 1.5 mL of oleic acid and 6 mL of 1-octadecene (ODE) were loaded in a three-necked 100 mL RB and heated to 110 °C for 1-2 h under vacuum to obtain a clear solution. The temperature was adjusted to desired injection temperature (120-160 °C) followed by a fast injection of octyl ammonium octyl dithiocarbamate ($C_8$DTCA) solution (70 mg $C_8$DTCA + 0.5 mL of

oleyl amine + 10 mL of ODE) at 120 °C. Immediately after injection, the heating mantle was removed, and the solution cooled naturally after the injection till room temperature. When the reaction solution cooled to room temperature (~30 °C), the PbS QDs were purified twice using acetone, centrifuged at 5000 rpm for 3 min and re-dispersed in toluene.

### **3.2.2.** Preparation of Copper Sulphide (CuS)

0.38 g copper iodide (CuI) (2 mmol), 1.5 mL of oleic acid and 6 mL of ODE was loaded in a three-necked 100 mL RB and heated to 110 °C for 1-2 h under vacuum to obtain a clear or pale orange colour solution. The temperature was adjusted to the desired injection temperature (140 -180 °C) followed by a fast injection of the sulfur solution (32 mg of elemental sulfur + 3 mL of oleyl amine + 10 mL of ODE) at 180 °C. Immediately after injection, the heating mantle was removed, and the solution cooled naturally after the injection till room temperature. When the reaction solution cooled to room temperature (~30 °C), the CuS NCs were purified twice using methanol, centrifuged at 5000 rpm for 3 min and re-dispersed in toluene.

### **3.2.3.** Preparation of Cadmium Sulphide (CdS)

0.461 g cadmium acetate ($Cd(CH_3COO)_2$) (2 mmol), 1.5 mL of oleic acid and 6 mL of ODE were loaded in a three-necked 100 mL RB and heated to 105 °C for 1-2 h under vacuum to obtain a clear or pale yellow colour solution. The temperature was adjusted to desired injection temperature (140 -180 °C) followed by a fast injection of sulphur solution (32 mg sulphur + 1.5 mL of oleyl amine + 10 mL of ODE) at 180 °C. Immediately after injection, the heating mantle was removed, and the solution cooled naturally after the injection till room temperature. When the reaction solution cooled to room temperature (~30 °C), the CdS NCs were purified twice using acetone, methanol: acetone (3:1), centrifuged at 5000 rpm for 3 min and then re-dispersed in toluene.

### **3.2.4.** Preparation of Silver Sulphide ($Ag_2S$)

*Preparation of Ag(DDTC)*: 0.05 mol of silver nitrate ($AgNO_3$) and $(C_2H_5)_2NCS_2Na{\cdot}3H_2O$ were firstly dissolved in 100 mL of distilled water, respectively. Then, the two solutions were mixed with stirring in a 500 mL beaker. After keeping at

an ambient condition for 3 h, the resulting yellow precipitate was filtered, washed with distilled water, and methanol which was further dried under vacuum for 3-4 h.

*$Ag_2S$ NCs*: A given amount ( ~25 mg) of Ag(DDTC) (0.1 mmol) was added into 10 mmol of OA, 10 mmol of octadecyl amine, as well as 20 mmol of ODE as a solvent, in a three-necked RB (100 mL) at room temperature. Then, the slurry was heated to 100 °C to remove water and oxygen with vigorous magnetic stirring under vacuum for 1-2 h in a temperature-controlled electromantle, and thus to form an optically transparent solution. Then the solution was heated to a temperature to 200 °C at a heating rate of 15 °C/min and kept for 30 min under $N_2$ atmosphere. After cooling to room temperature, the NCs were precipitated by adding an excess amount of the absolute ethanol into the reacted solution, followed by washing with ethanol and drying in air at 60 °C. The as-formed NCs were easily re-dispersed in toluene.

## 4. Fabrication of BNSLs

**4.1.** *Au-DDT/Au-OlAm*: Individual NCs were prepared separately via the DR method (mentioned above). Both the solutions were diluted 80 times with the solvent from the stock solution. Both the dispersions were then mixed in a 2 mL Eppendorf in 1:2 volumetric ratio and kept aside for half an hour. After that, the solution was drop-casted (~ 6 µL) on TEM grid which was kept for drying overnight at room temperature.

**4.2.** *Au-DDT/ PbS-OlAm*: Individual NCs were prepared separately via the DR method and hot injection method respectively (mentioned above). Both the solutions were diluted 80 and 60 times apiece with solvent from the stock solution. Both the dispersions were mixed in a 2 mL Eppendorf in a 2:1 volumetric ratio and kept aside for half an hour. After that, the solution was drop-casted (~ 6 µL) on TEM grid which was maintained for drying overnight at room temperature.

**4.3.** *Au-OlAm/CuS-OlAm*: Individual NCs were prepared separately via the DR method and hot injection method respectively (mentioned above). Both the solutions were diluted 80 and 120 times respectively with solvent from the stock solution. Both the dispersions were mixed in a 2 mL Eppendorf in 1:1 volumetric ratio and solution was immediately drop-casted (~ 6 µL) on a TEM grid and kept for drying overnight at room temperature. Further combinations were carried out by varying the time and the

temperature for the BNSLs solution. Which were further discussed in the result and discussion section.

**4.4.** *Au-OlAm/CdS-OlAm*: Individual NCs were prepared separately via the DR method and hot injection method respectively (mentioned above). Both the solutions were diluted 60 and 60 times apiece with solvent from the stock solution. Both the dispersions were mixed in a 2 mL Eppendorf in 1:1 volumetric ratio and solution was immediately drop-casted (~ 6 µL) on a TEM grid and kept for drying overnight at room temperature.

## 5. Fabrication of device

All the devices are fabricated on ITO films, the substrate (ITO films) were appropriately cleaned, and individual solution of NCs was spin coated on the substrate with a speed of 2000 rpm for 40 seconds to prepare thin films.

***5.1.****Au device:* Au as-prepared solution was used for metallic device and 0.1 % (v/v) 1,2-Ethanedithiol solution was used for ligand exchange of the surfactant present on the surface of the Au NCs. 10 layers of the solution was coated on the substrate.

***5.2.****CuS-device:* For this system, CuS NCs capped with OlAm was used and with 2% (v/v) 1,2-Ethanedithiol solution was used for ligand exchange of the OlAm present on the surface of CuS NCs. Five layers of the solution were coated on the substrate.

***5.3.****Au-CuS device:* For this system, one layer of gold was coated via spin coating then ligand exchange was done with 0.1% (v/v) 1,2-Ethanedithiol solution later on top of that CuS-OlAm solution was coated on top of the Au. and again ligand exchange was done with 0.1% (v/v) 1,2-Ethanedithiol solution. This process was continued for five layers each.

***5.4.****Ag-device:* For this system, Ag NCs capped with OlAm was used and with 2% (v/v) 1,2-Ethanedithiol solution was used for ligand exchange of the OlAm present on the surface of Ag NCs. 2 layers of the solution was coated on the substrate.

## 6. Result and discussion

All the NCs that were synthesised are duly characterised. For brevity, we are presenting only the most pertinent characterisation details here. The UV-Vis data supports the synthesis of our desired Au NC dispersions as shown in **figure 4**. Peaks at 525 nm, 526 nm and 530 nm correspond to Au-DDT, Au-DDA and Au-OlAm respectively. The other dertails like the capping agent used and the size/size distribution of the Au NCs obtained are compiled in **Table 1**.

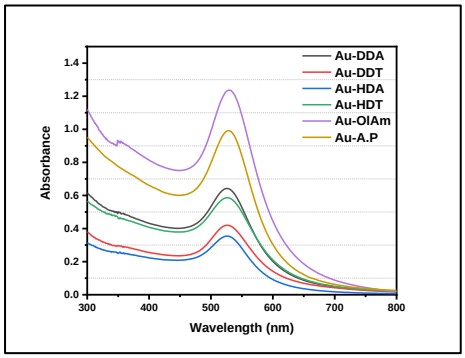


**Figure 4**. UV-Vis spectra of Au NCs capped with different surface ligand.

**Table 1:** List of different NCs synthesised with their corresponding capping agent and particle size ( measured from TEM images).

| S.no. | Sample | Capping agent | Size (nm) |
|---|---|---|---|
| 1. | Au | DDT | 5.1 ± 0.1 |
| 2. | Au | DDA | 6.1 + 0.2 |
| 3. | Au | OlAm | 6.7 ± 0.2 |
| 4. | Ag | OlAm | 6.3 + 0.7 |
| 5. | PbS | OlAm | 4.4 ± 0.5 |
| 6. | CuS | OlAm | 14 ± 0.1 |
| 7. | CdS | OlAm | 2.3 ± 0.3 |

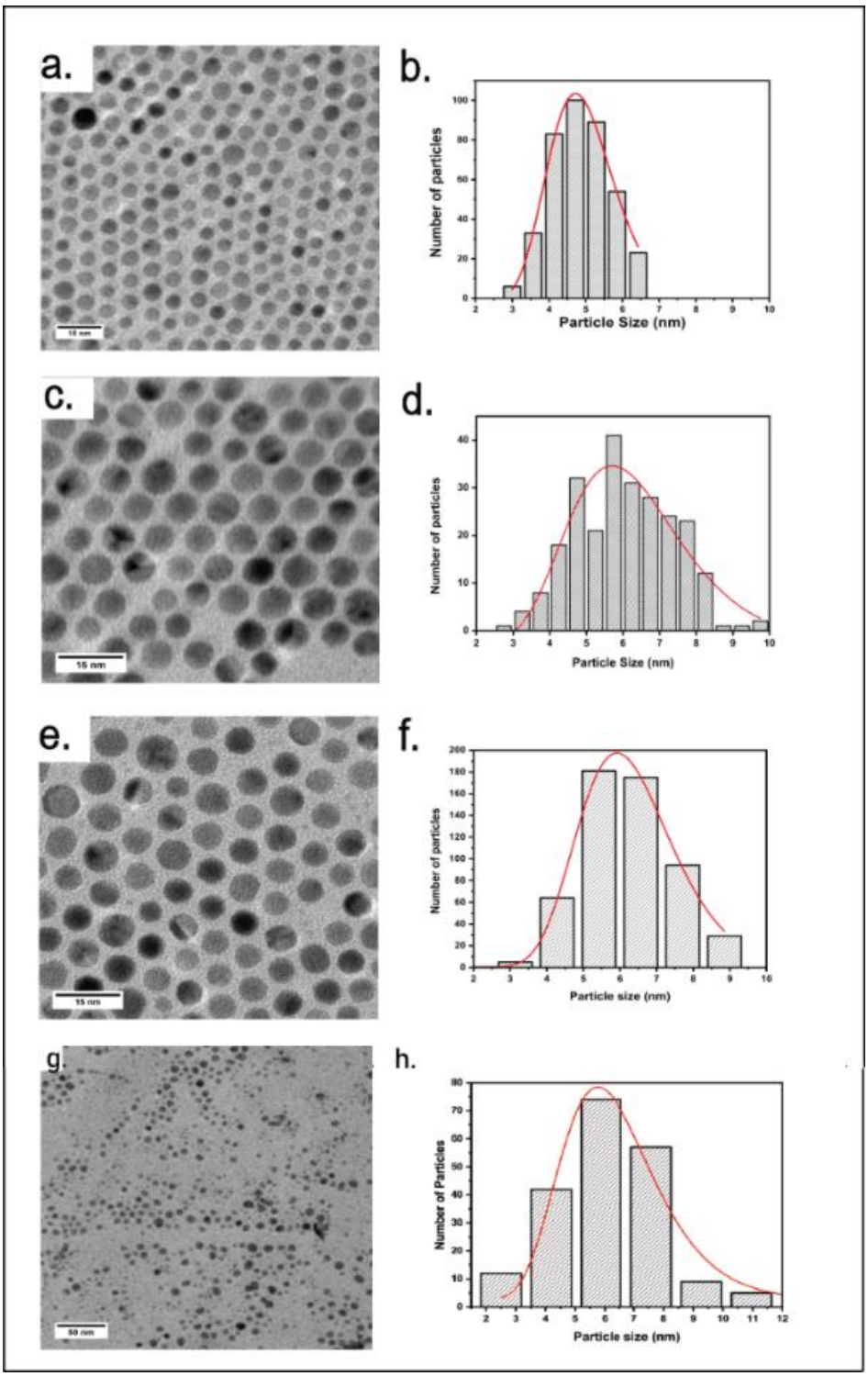


**Figure 5**. TEM images of Au NCs and their particle size histograms obtained by DR method at 110 °C (a,b) 4.4 ± 0.1 nm Au-DDT (c,d) 6.1 $\pm$ 0.2 nm Au-DDA (e,f) 6.2 $\pm$ 0.2 nm Au-OlAm (g,h) 6.3 $\pm$ 0.7 nm Ag-OlAm

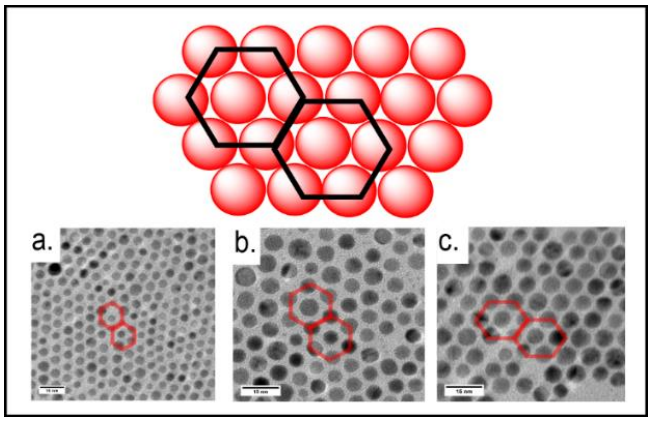


**Figure 6.** Representation of hcp packing in a) Au-DDT b) Au-OlAm c) Au-DDA

The TEM image of these individual NCs indicated that they assemble in pseudo hexagonal close packing as shown in **figure 6.** This itself exemplifies the monodispersity of these NCs.

For the synthesis of semiconducting metal sulphide NCs like PbS, CuS and CdS, we used the hot-injection method. The primary reason for opting for hot-injection method over the general heating method is that in general heating method the nucleation and the growth process are not well separated hence, NCs obtained are not highly monodispersed in nature. But in the hot-injection method, the nucleation and the growth process can be separated.

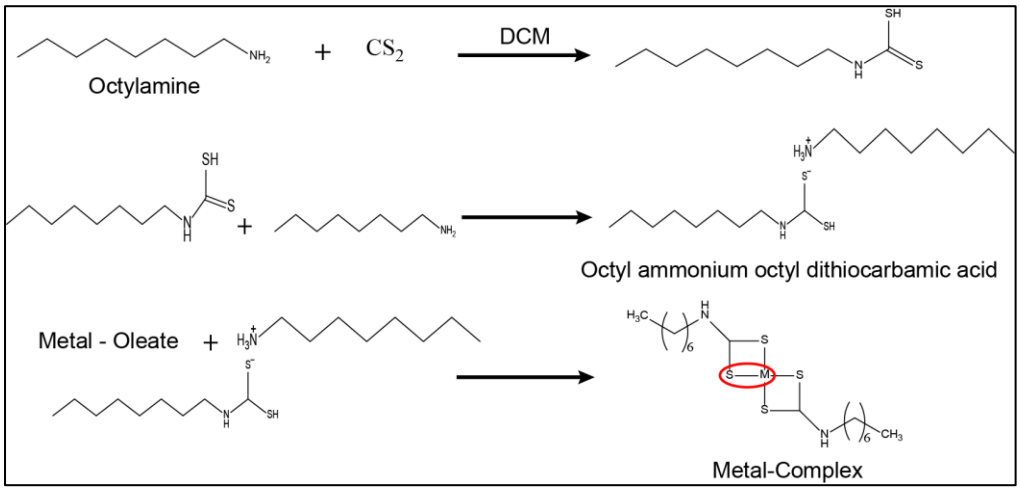


**Figure 7**. Reaction mechanism for the formation of metal complex

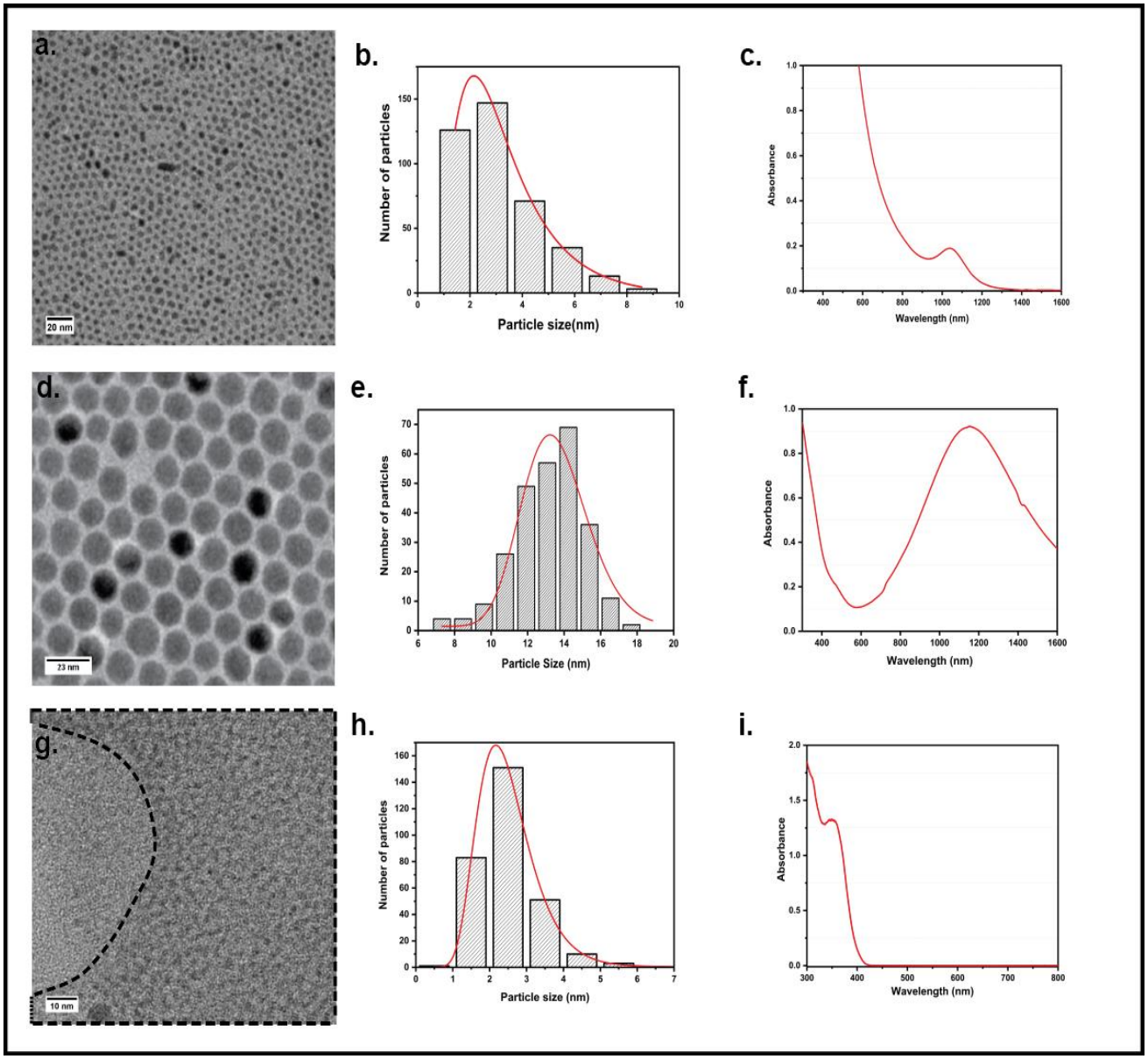


**Figure 8**. TEM image of different metal sulphides and their corresponding particle size histograms and UV-spectra (a,b,c) PbS-OlAm (d,e,f) CuS-OlAm (g,h,i) CdS-OlAm

As we had injected the sulphur source at an elevated temperature into the metal-oleate, the rate of decomposition is expected to be faster for the metal-oleate which leads to instant nucleation in the solution. At the same point of time due to drop in the temperature till room temperature, which prevented further nucleation and the growth of the nuclei formed is slowedand no new nuclei were formed which leads to the creation of the monodisperse NCs [10].

The UV-NIR spectra of PbS-OlAm and CuS-OlAm showed an absorbance peak near IR region around 1170 nm (**figure 8.c**) and 1040 nm (**figure 8.f**) respectively. Whereas, for CdS-OlAm shows an absorbance around UV-Vis region 346 nm (**figure 8.i**).

The particles of CuS NCs (CuS-OlAm) are featured with an average size of 13.7 $\pm$ 0.1 nm, which are nearly spherical (**figure 8.d**). Other characterisations like IR, PXRD (**figure 9**) have been done to confirm the phase purity of the samples as well as the presence of a capping molecule. The sharp bands at 2922 and 2854 $cm^{-1}$ are assigned to the antisymmetric and symmetric CH stretching vibrations of the $–CH_2$-groups in the oleylamine molecular [11-12] and presence of acyclic C-H stretching [13] (**figure 9.a**). The corresponding powder XRD patterns CuS-OlAm can be well indexed to the cubic phase of $Cu_{7.2}S_4$ (*JCPDS 72-1966*) (**figure 9.b**).

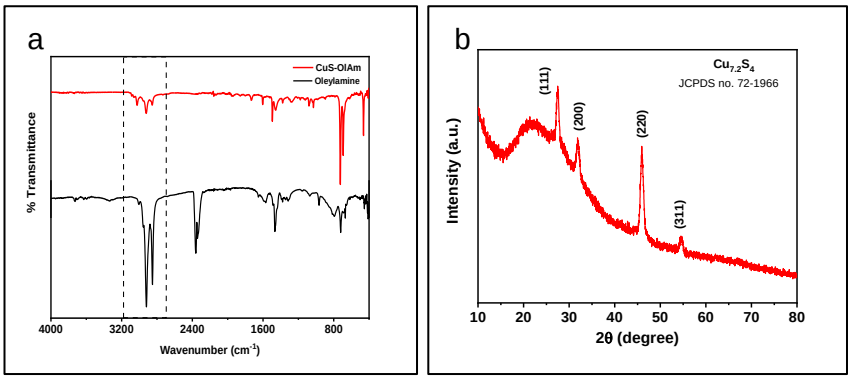


**Figure 9**. a) FT-IR spectra of CuS-OlAm and Oleylamine b) PXRD graph for CuS-OlAm

After characterising the individual NCs with TEM, we proceeded to make assemblies with two different systems, having different radius ratio. Firstly, we performed the assembly of DDT capped Au and OlAm capped Au system with different sizes (radius ratio of 0.7). In this case, we observed some indications for the formation of a superlattice as shown (**figure 10. a**). The darker region in the TEM image is plausibly due to the superlattice formation, as confirmed by the zoomed version (**figure 10.b**). We analyze this image as having two layers in ABABA stacking fashion (schematically shown in **figure 10.c.**) where red spheres can be layer A, and blue sphere can be called layer B or vice-versa. We observed an ordered pattern in this case, and more importantly, the top layer NCs were situated in a three-point saddle minima

However, from this experiment, it was difficult to tell whether the two layers are different or from the same NC's system

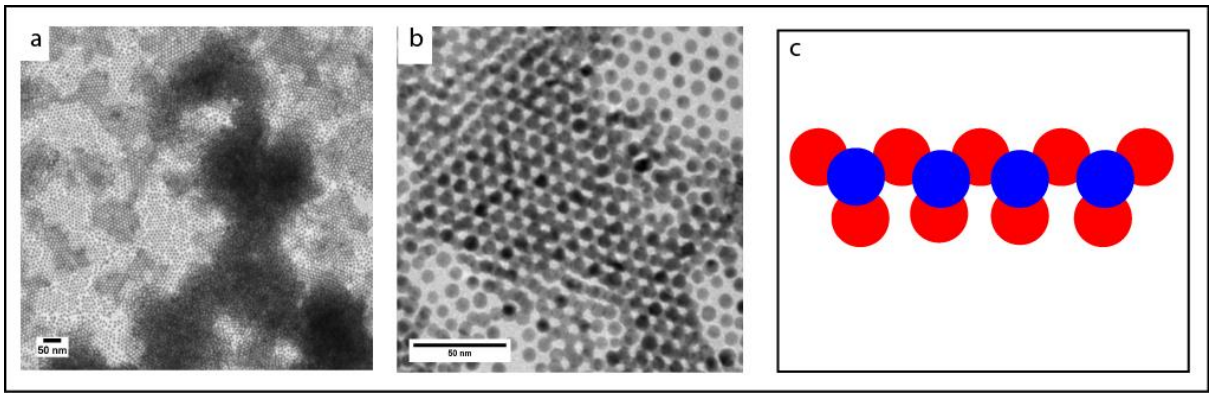


**Figure 10**. TEM images of binary superlattice formation of Au-DDT/ Au-OlAm in 2:1 volumetric ratio.

As a second attempt, we looked for BNSL formation between metal and metal sulphide systems. We tried gold NCs capped with DDT and lead sulphide capped with OlAm having a radius ratio of 0.65. Here, we observed the NCs having the darker contrast overlayed on the NCs having lighter variation. In **figure 11.a** we can see both the regions having the PbS NCs (marked area) as well as the Au NCs (dark spots) on top of the PbS NCs. Based on our previous experience we can assign the darker contrast materials as gold NCs because TEM images are generally taken in the bright field mode so, higher the electron density darker the contrast [14]. In **figure 11(b-c)** we saw few interfaces where it was observed that Au NCs are not aggregating and trying to fuse with the PbS NC surface. On a few occasions, we found that there were formation

of dark contrast fringes (**figure 11.b**) which were due to Au NCs sitting on top of the PbS NCs. However, we didn't observe any ordered pattern in between both the NCs and we propose that the van der Waal interaction between Au-Au is more than the Au-PbS, so they tend to segregate into different regions. This could be the reason why we did not observe any BNSLs for this NCs combination.

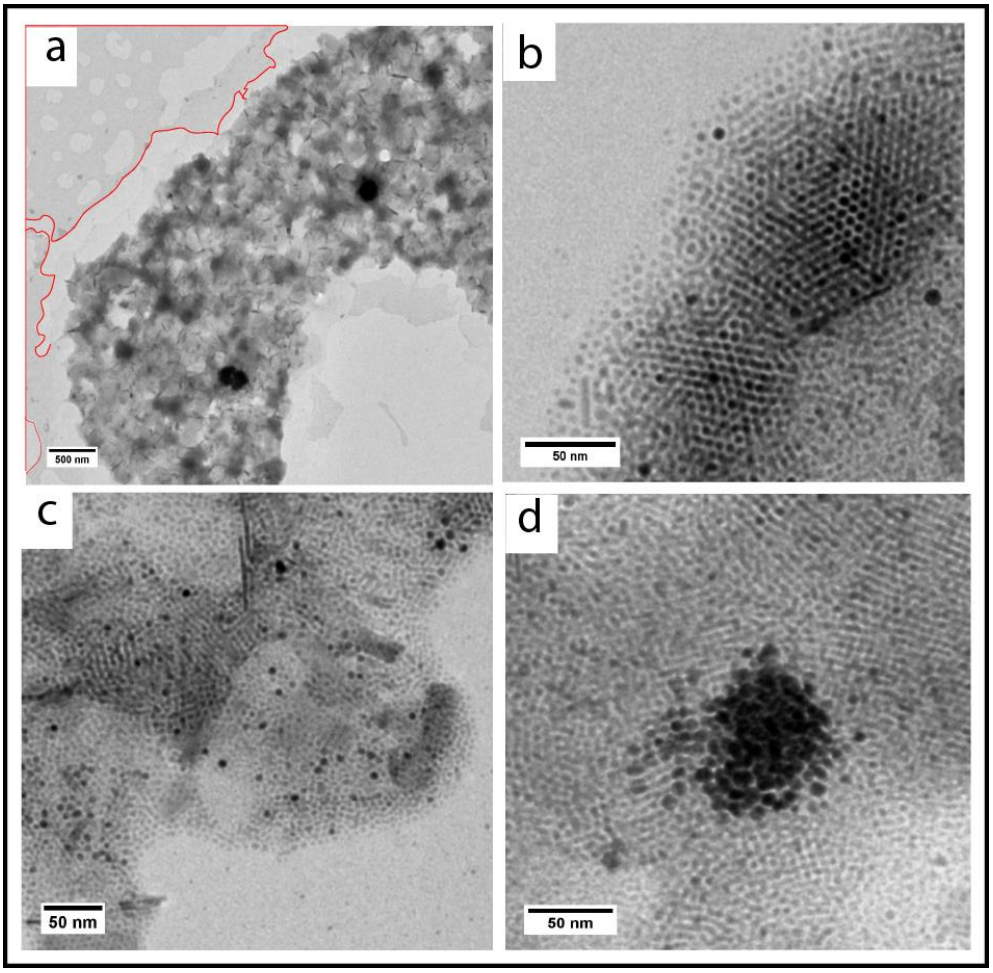


**Figure 11**.TEM images of Au-DDT/ PbS-OlAm in 2:1 volumetric ratio a) formation of two regions, (b-c) Au-PbS interface d) aggregation of Au NCs on top of PbS NCs

In another attempt to check with different size ratio we proceeded with Au-OlAm and CdS-OlAm ( radius ratio = 0.38). As there is a significant difference in the radius of individual NCs, we did observe a difference from the previous case, yet we didn't find any ordered formation of BNSL. But, the mixture showed a significant size and colour contrast in the TEM images. Additionally, from TEM images it has been observed that Au-OlAm/CdS-OlAm mixture shows aggregation (**figure 12**).

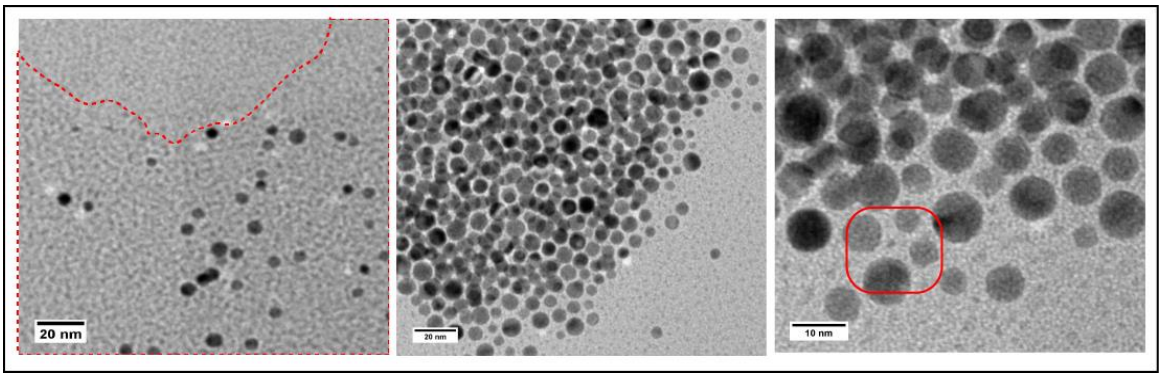


**Figure 12**. TEM images of Au-OlAm/CdS-OlAm mixture in 1:1 volumetric ratio.

So, to check whether this aggregation happens in the solution phase or due to solvent drying, we performed an experiment where we reviewed the UV-Vis spectra of the individual NCs with comparable absorbance and compared with that of when mixed. Here, we observed a decrement in the absorbance in the mixture (**figure 13.a**).To confirm the decrement in absorbance is not due to dilution, we added the same volume of solvent (500 µL, in place of 500 µL CdS-OlAm solution) to the gold solution in the cuvette (**figure 13.b**). Here, we didn't observe any significant decrement of gold SPR intensity as it was for the case of mixture (Au-OlAm/CdS-OlAm). Therefore, dilution is not playing any role in the decrement of absorbance.

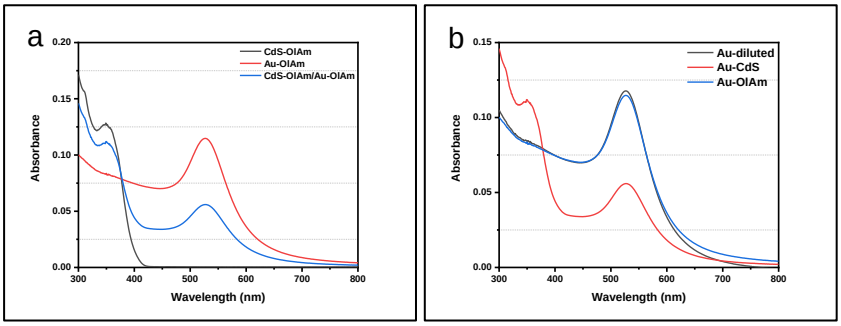


**Figure 13**. a) Comaprison of UV-Vis spectra of Au-OlAm/CdS-OlAm mixture with their individual spectra b) UV-Vis spectra for Au-OlAm dilution effect

Among other systems, we tried Au-DDA and CuS-OlAm with radius ratio of 0.45. As we know the thermodynamics of mixing plays an essential role in the self-assembly process [5], we envisaged the effect of equilibration time for the formation of BNSL. On this note, we stored the mixture solution under ambient condition for 3 min, 30 min and 3 h before drop-casting on a TEM grid. The individual monodispersed NCs were mixed in different volumetric ratio, and then the TEM images were taken (**figure 14**). It was hypothesised that if the system was given more time to equilibrate better results could be obtained. As it had been mentioned earlier, both individual NC systems are nearly monodispersed.

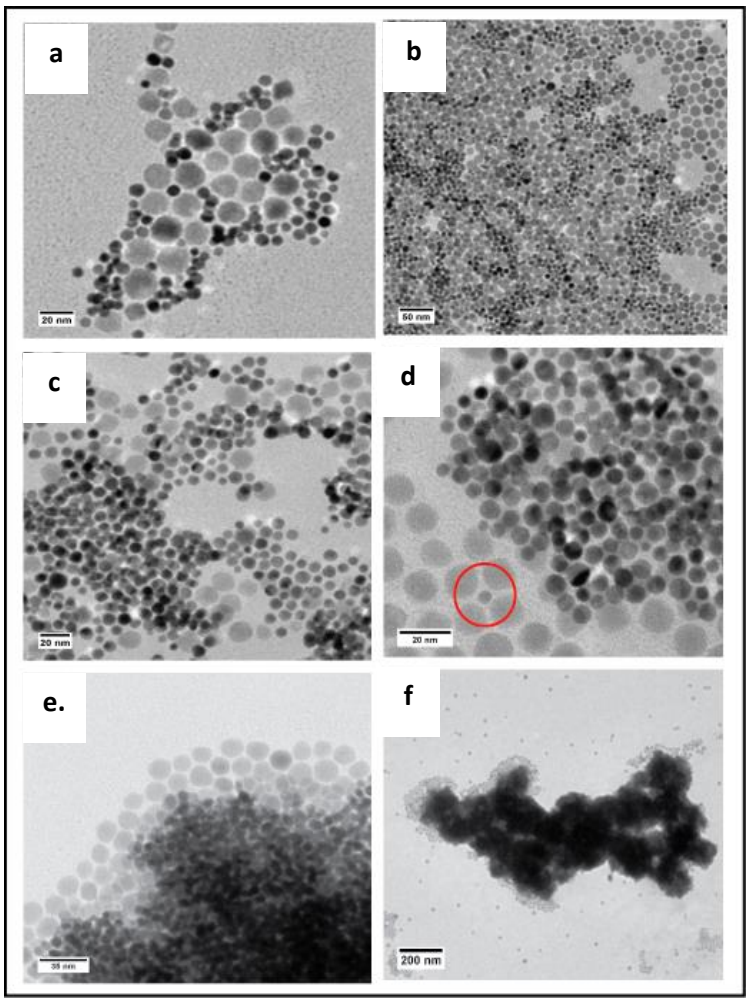


**Figure 14.** TEM images of Au-DDA/CuS-OlAm (a-b) in 1:1 volumetric ratio dropcasted with 3 mins of mixing (c-d) in 1:2 volumetric ratio and dropcasted after 30 minutes of mixing (e-f) in 1:1 volumetric ratio and dropcasted after 3 h of mixing

From the image (**figure 14.a** and **b**) the two systems can be easily identified as there is a significant size difference (regions encircled). It was also found that there was a considerable contrast between the two particles signifying their different composition. It may be recalled that in this case, we have mixed the two individual NCs in 1:1 volumetric ratio and then after mixing we drop-casted the mixture on TEM grid (**figure 14 (a-b)**)**.** In the next case, copper sulphide and gold NCs were mixed in the 2:1 volumetric ratio respectively (**figure 14 (c-d)**) and the mixture was kept for nearly 30 mins to equilibrate. For this case, we observed that the NCs are randomly assembling. On that note, further experiments were performed, and it was found that upon keeping the mixed solution for 3 h, there were more number of multilayer formation as compared to a single layer (**figure 14 (e-f)**), it can be seen from the TEM images that the Au NCs have formed a layer on top of the metal sulphide layer (CuS-OlAm), it has also been observed that there are fewer regions of single layers around the multilayer formed. As the mixture was kept for drying on TEM grid it was expected that when the solvent is evaporating the particles will tend to come closer and form some single layers of either copper sulphide, gold or mixed NCs. But, we observed that there were only multilayer formation containing copper sulphide and gold NCs.

Above mentioned all experiments were carried out at RT. So, to check how temperature and time played a role in superlattice formation which intrigued us to perform a set of experiments with systems containing gold NC capped with DDA and copper sulphide NC capped with OlAm , we observed some exciting results by changing the time and temperature of equilibriation.

In **figure 15 (a-b)** where both the NCs were mixed in 1:1 volumetric ratio and kept the resultant mixture at 0 °C for 3 h and then dropcasted on TEM grid, we observed there is less formation of multilayer and single layer formation of Au and CuS NCs which randomly assembled. For the case where we mixed the two NCs at RT and drop-casted immediately on TEM grid, it shows the random assembly of Au and CuS NCs, and we also observed the formation of both multilayer and the single layer (**figure 15 (c-d)**). Lastly, for the case where we heated the mixture of two NCs till 70 °C and allowed it cool down to RT over 3 h time period shown in (**figure 15 (e-f)**). We observed the formations of multilayer, where Au NCs have precipitated over the CuS NCs, and due to rise in temperature, there was agglomeration in the Au NCs which formed a

sheet kind of structure. That could be the free amine ligand that got detached from the NC surface due to heating.

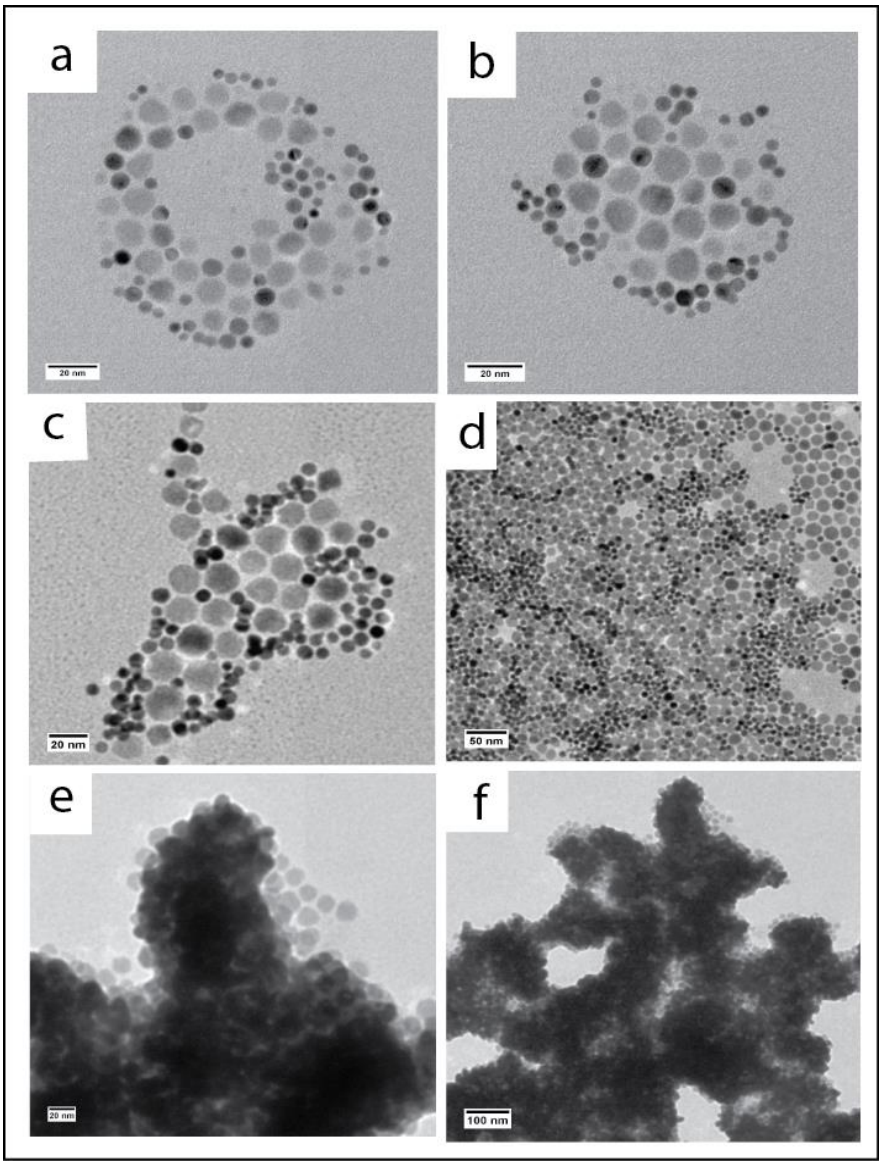


**Figure 15.**. TEM images of Au-DDA/ CuS-OlAm in 1:1 volumetric ratio (a-b) mixed at 0 °C and kept for 3 h (c-d) mixed at RT and dropcasted immidiately (e-f) heated till 70 °C and cooled down over 3 h

Likewise, we performed another set of experiment with both gold and copper sulphide NCs have same capping agent. Firstly we mixed both the NCs in 1:1 volumetric ratio

and kept it for equilibriation for 3h at RT, following that the mixture was dropcasted on TEM grid and kept for overnight drying at RT.

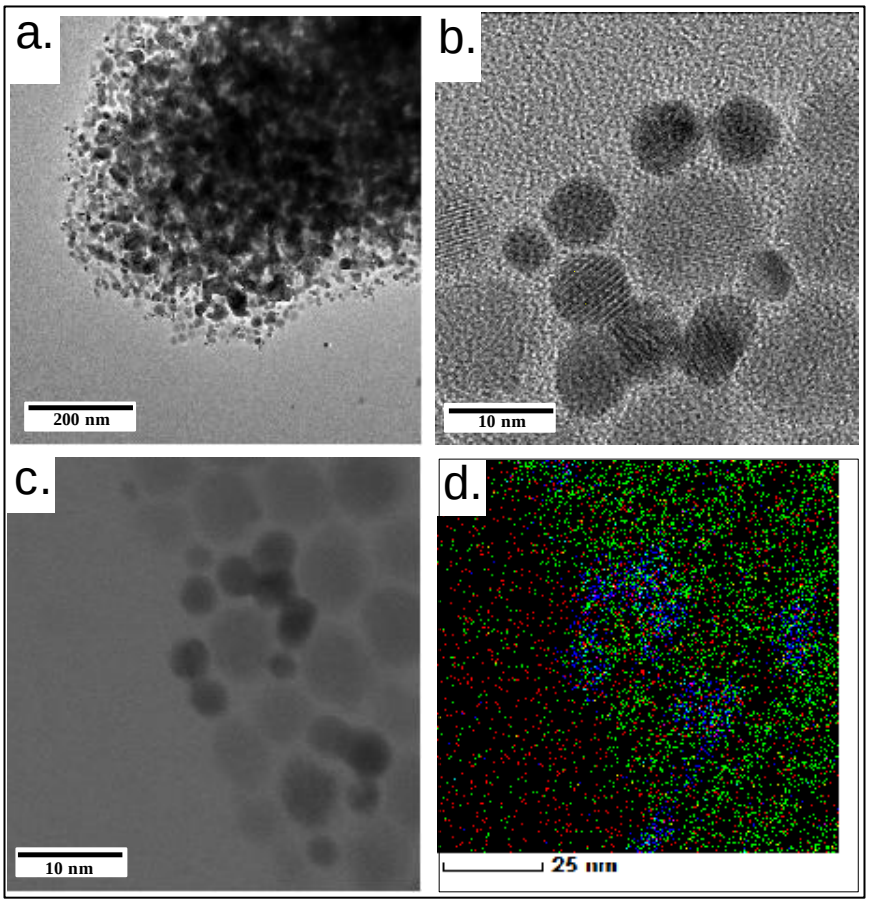


**Figure 16.** ( a-b) HRTEM image of Au-OlAm/CuS-OlAm mixture in 1:1 volumetric ratio c) HAADF image showing two distinct NC d) STEM mapping

In **figure 16.a** we observed there was thick layer formation of the capping agent i.e. same for both the NCs and also free ligand present in the system, but on the edges it was observed some arrangement of the two NCs. In some other locations of the same systems it was found single layer formation of copper and gold NC. So, on further zooming( **figure 16.b**) fringes were observed in the NCs of CuS and Au. In the HRTEM image, we have found seven NCs of Au is surrounding a CuS NC. To confirm the NC are of Au and CuS we took a HAADF image (**figure 16.c**) of that area. There we can see a colour contrast between the two NC, CuS having the lighter variation whereas Au is having the darker contrast [16]. We also did a STEM mapping of the above mentioned showed (**figure 16.d**) where the blue dot indicates the Au NC, the red dots

correspond to the Nitrogen present in the system, and the green dots represent the CuS NC in the system. For this system, the mapping for sulphur was not performed.

Following the 1:1 volumetric mixture system, we performed another set of experiment of the same materials but with a varied mixing parameters. In this system, we observed there was a thick layer of the capping agent as it formed a sheet-like structure above the NCs (**figure 17.a**), we also observed images (**figure 17.b**) with sheet kind structure in some locations with colour contrast where darker sheets corresponds to the aggregation of gold NCs and the lighter one having copper sulphide NCs. We also varied their individual's volumetric ratio in the mixture and obtained the same results that there were formation of multilayers and no formation of the single layer near the vicinity of the multilayer. For the case where the gold capped with oleylamine NCs were in excess as compared to the copper sulphides NCs capped with oleylamine (**figure 17.c**), we observed ring formation of bigger sized copper sulphides NCs around the multilayer. This is explained better by the Marangoni effect [16].

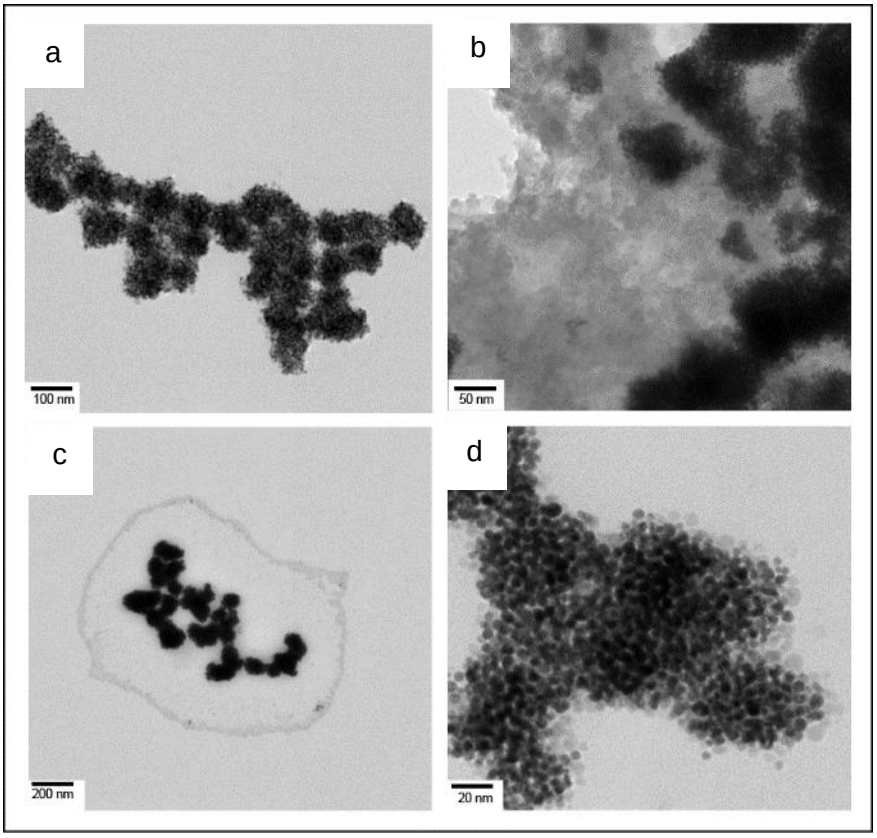


**Figure 17.** TEM images of Au-OlAm/CuS-OlAm combination in (a-b) 1:2 volumetric ratio respectively (c-d) 2:1 volumetric ratio respectively.

After observing the TEM images, we fabricated a few devices and checked for their current efficiency in the presence of light and in absence of light coated as thin films. All these devices made by spin coating the individual samples on ITO films (substrate).

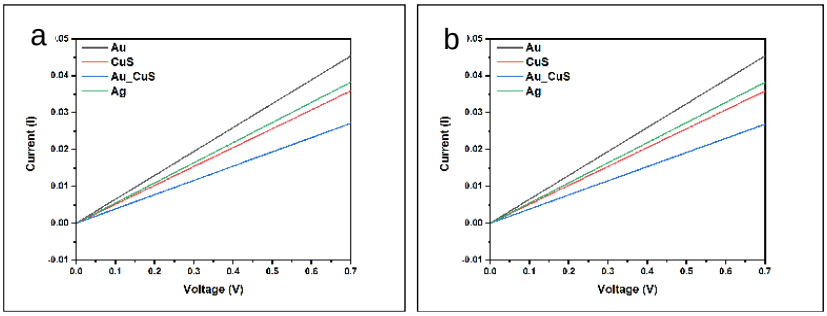


**Figure 18.** I-V characteristics of Au, Ag, Au_CuS, CuS devices a) in absence of light b) in presence of light

For the Au_CuS sample, the Au was coated on top of CuS-OlAm sample. From I-V characteristics as shown (**figure 18**), we didn't find any significant change in the current as we varied the materials and the light condition. In **figure 18.a** the current was measured in the absence of light and in **figure 18.b** the current was measured in the presence of light. We observed there is a decrement in the current as we have increased the number of layers from individual single component material to the bicomponent multilayer system. As the slope is decreasing for the latter case, this signifies the decrement in the A.C. conductance.

But none of the above experiments has indicated the formation of BNSLs. Even the device fabrication and the measurement experiments did not reveal any significant difference in terms of their performance whether the device was fabricated from a single component. Therefore, to understand how we can improve and make better devices from a mixture of NCs we have performed a series of experiments where we titrated one type of NC system with the other and systematically and measured the variation in UV-Vis-NIR spectra of the mixture.

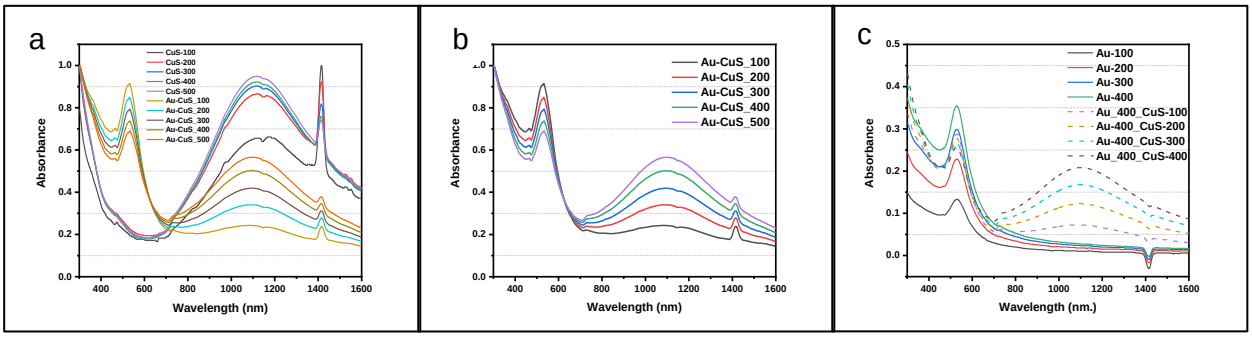


**Figure 19**. UV-VIS-NIR spectra of a) Comparing the CuS dilution effect with mixture spectra b) Au-Octylam upon addition of CuS-OlAm c) Checking the dilution effect in the Au-Octylam after addition of CuS-OlAm in small volume

We gradually added small volume of CuS-OlAm in Au-Octylam solution (**figure 19.b)** and observed there was a decrement in the absorbance of Au-Octylam. Both the NCs dissolved in toluene, i.e. good solvent for both the NCs. and it was observed there is an isosbestic point. Since, it was observed that there was a decrement in Au-Octylam absorbance, there could be a possiblity of dilution effect playing a role in the decrement of the absorbance. So, to check for dilution effect for both NCs. We took around 700 µL of toluene and added 100 µL of Au-Octylam solution and recorded the UV-Vis spectra and repeated further by adding 100 µL till 400 µL of Au-Octylam solution was added. Similarly in Au-toluene solution, 100 µL of CuS-OlAm was added, and UV-NIR spectra were recorded, this process was further continued till 400 µL of CuS-OlAm was added to the Au-toluene solution. We observed there was a decrement in the absorbance of Au-Octylam (400 µL) by 0.3 units and by theoretical calculation, it was expected that for every addition there would be a decrement in absorbance of 0.35-0.28 units. But, experimentally we observed that the decrement was of more than 0.28 units. Hence, We could say that the dilution effect is not the only factor responsible for the decrement of Au-Octylam's absorbance peak. So, we proposed that there could be some chemical interaction between the two NCs as there is an isosbestic point observed in the UV-Vis-NIR spectra [17].

These results intrigued us to further investigate for another system; we checked for Au-DDA/CuS-OlAm and Au-Oleyl/ CuS-OlAm solution.

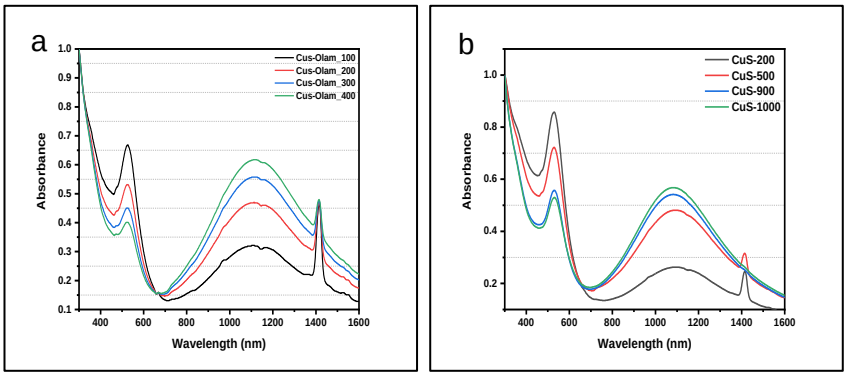


**Figure 20**. UV-Vis-NIR spectra of a) Au-DDA/CuS-OlAm b) Au-OlAm/ CuS-OlAm

After performing a series of UV-Vis-NIR experiment with different ligand capped Au-DDA/CuS-OlAm in **figure 20.a** and Au-OlAm/CuS-OlAm in **figure 20.b**. We observed that the peak corresponding to the copper sulphide was around 1170 nm increased on increasing the concentration in the solution, and there is a slight blue shift in the peak position as we increased the volume of CuS solution. The UV-Vis-NIR spectra of metal-semiconductor interaction were analyzed by varying the chain length (of the capping ligand on gold NCs; $C_8$, $C_{12}$ and $C_{18}$) which showed no significant difference somewhat similar type of isosbestic point in all the spectrum.

As we proposed, there could be some chemical interaction between the metal-semiconductor in the solution state as we observed the isosbestic point in UV-Vis-NIR spectra, we tried further to understand its nature by XPS technique. In this case, we drop-casted the same solutions used for TEM analysis, on a silicon wafer and dried at RT. Pure Au-DDA, Pure CuS-OlAm and their mixture were studied.

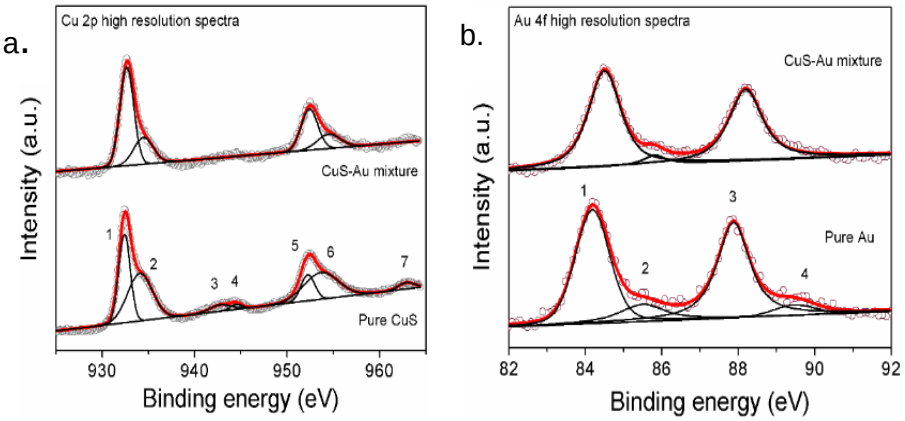


**Figure 21**. XPS high resolution spectra of a) Cu 2p orbital b) Au 4f orbital

A high-resolution scan was performed in each case for the core level Cu 2p and Au 4f regions, and the results were shown in **figure 21.a** and **b** respectively.

In the Au 4f spectra, we have observed two major peaks at 84.21 eV and 87.84 eV (peak 1 and 3 in the graph) corresponding to Au $4f_{7/2}$ and Au $4f_{5/2}$ [18-19] respectively. An energy gap of 3.63 eV which occur due to spin-orbit coupling was observed in the pure gold sample which corresponds to the bulk gold value.[20]. Interestingly a shift in Au $4f_{7/2}$ by 0.33 eV and Au $4f_{5/2}$ by 0.38 eV towards the higher binding energy were observed when this Au NCs were mixed with copper sulphide NCs This shift indicates the transfer of some electron density from the Au core [21].

On comparing the Cu 2p orbitals showed some significant difference before and after mixing. Upon deconvolution the spectra of pure CuS, we found seven peaks for $Cu^{+}$ and $Cu^{2+}$, whereas, few of them have significantly suppressed upon mixing with Au. The peaks are listed in **Table 2** and **3.** The ratio of $Cu^{+}/Cu^{2+}$ calculated from the area under the curve from the fitting analysis for both the cases is also compiled in **Table 2** and **3**. A significant increase in $Cu^{+}$ concentration was observed upon mixing, which could be due to the transfer of an electron from Au to $Cu^{2+}$.

**Table 2:** Deconvulated data of Cu 2p orbital in CuS

| Peak no. | Peak position (nm) | FWHM (nm) | Area under the curve | Oxidation state | Orbital | $I_1/I_2$ |
|---|---|---|---|---|---|---|
| 1 | 932.4 | 1.47 | 39167 | $Cu^{+}$ | $2p_{3/2}$ | 0.85 |
| 2 | 934.08 | 3.18 | 45547 | $Cu^{2+}$ | $2p_{3/2}$ | |
| 3 | 942.78 | 2.7 | 5288 | $Cu^{2+}$ | $2p_{3/2}$ | |
| 4 | 944.51 | 1.45 | 2196 | $Cu^{2+}$ | $2p_{1/2}$ | |
| 5 | 952.24 | 1.74 | 13580 | $Cu^{+}$ | $2p_{1/2}$ | |
| 6 | 953.67 | 4.36 | 35053 | $Cu^{2+}$ | $2p_{1/2}$ | |
| 7 | 962.92 | 2.05 | 3895 | $Cu^{2+}$ | $2p_{1/2}$ | |

**Table 3:** Deconvulated data of Cu 2p orbital in Au-CuS

| Peak no. | Peak position (nm) | FWHM (nm) | The area under the curve | Oxidation state | Orbital | $I_1/I_2$ |
|---|---|---|---|---|---|---|
| 1 | 932.68 | 1.77 | 22618 | $Cu^{+}$ | $2p_{3/2}$ | 2.61 |
| 2 | 934.48 | 2.49 | 8657 | $Cu^{2+}$ | $2p_{3/2}$ | |
| 5 | 952.49 | 2.13 | 11408 | $Cu^{+}$ | $2p_{1/2}$ | |
| 6 | 954.61 | 2.93 | 5476 | $Cu^{2+}$ | $2p_{1/2}$ | |

## 7. Conclusion

We have successfully synthesised NCs of different metallic and semiconducting systems using different solution chemistry routes. The as-prepared NCs were nearly monodispersed and have been characterised well by various advance instrumental techniques. This project is aimed to understand the formation of BNSLs which initially showed some promising results; 1) most of the binary systems we performed showed improper mixing of two NCs when kept for constant equilibrium time. 2) Lesser time for equilibrium leads to random mixing of NCs and formation of single layers, while greater the equilibrium time more is the multilayer formation. 3) The temperature for equilibrium also played a significant role in the final assembly type; random mixing of NCs in a single layer was mostly observed at lower (0 °C) temperature. A gradual increase in temperature led to more multilayer and ultimately precipitated product.

Based on these preliminary observations from TEM, and further from solution state UV-Vis-NIR and XPS study we concluded that there is a significant interaction between the metallic (Au) and semiconductor metal sulphide ($Cu_{7.2}S_4$) system upon simple solution phase mixing.

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