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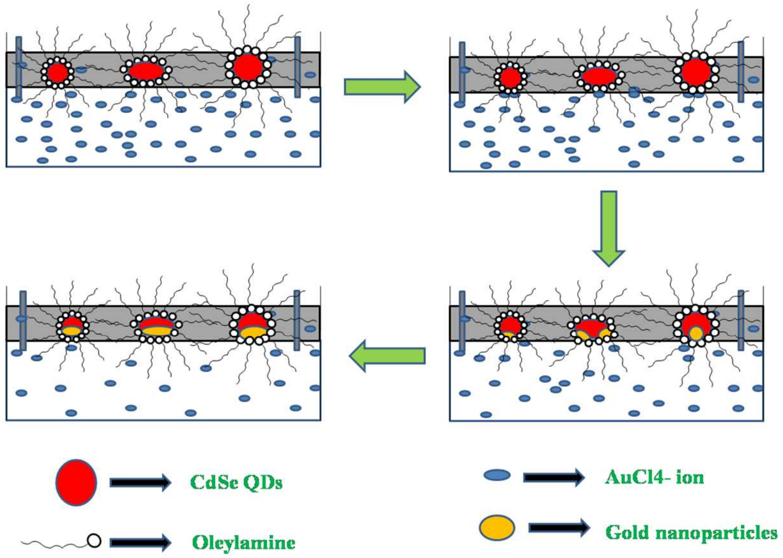

Oleyl amine capped CdSe quantum dots are allowed to form monolayer on aqueous $HAuCl_4$ subphase and Langmuir-Blodgett technique is used judicially to grow Au tips in a directed fashion on CdSe quantum dots.

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ARTICLE TYPE

Preferential growth of Au on CdSe quantum dots using Langmuir-Blodgett technique

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Abstract: Oleyl amine capped CdSe quantum dots (QD) were synthesised by hot injection technique. These QDs formed a self assembled monolayer on aqueous subphase of Langmuir-Blodgett (LB) trough. Here, in this report we introduced a simple but very efficient route to form metal (Au)-QD hybrid nanostructure via LB technique. In this method, metal counterpart of hybrid nanostructure could be deposited exclusively on one side of QDs. Formation of stable monolayer of QDs was evidenced from surface pressure-area (Π-A) isotherm. Development of gold tip was confirmed and monitored by detailed TEM study on the monolayer deposited on TEM grids from LB trough. Other characterizations like UV-Vis spectroscopy, FTIR, XPS and EDX also suggested the same. Oleyl amine was proved to act both as reducing agent as well as capping agent in this strategy.

1. Introduction:

In past few decades, semiconductor quantum dots (QDs) have been studied extensively due to their atypical electronic and optical properties. Spatial confinement of excitons dictates the physical properties of QDs. There occurs an increase of HOMO-LUMO gap with decrease in crystallite size due to quantum confinements, and its implications in photophysics have already generated special interest. Hybrid metal-semiconductor nanostructures have also gained importance due to better tunability in optical and electronic properties, which is controlled by their shape, size and nature of tipping. Intraband excitation of collective charge oscillation of metal nanoparticle and interband excitation of semiconductor quantum dots both play an important role in modern optics.

The interface between metal-semiconductor shows light induced charge separation[1-6] resulting in formation of a Schottky barrier. This leads to a deviation of optical properties when compared with the pristine semiconductor QDs.[7-9] Light–induced charge separation ability makes them a potential candidate to be used as a photocatalysts[10-14] and/or as key materials of solar cells and photovoltaics. Exciton-plasmon interaction resulted in the formation of a new quasiparticle which showed non-linear effect.[15]

Various synthetic routes have already been reported for different composition of hybrid nanostructures.[15-22] Usually, quantum dots are synthesized first and then metal tip is introduced. Banin *et.al.* have reported a room temperature method for depositing gold onto the CdSe nanocrystals, nanorods and tetrapods.[19] Several other protocols are published regarding the tip formation with single and double sided anisotropic growth of Au nanoparticles on semiconductor nanorods.[23-29] Most of these methods show multiple Au islands formation at the initial step which migrate slowly towards both ends of the nanorods or sometimes to a particular end. Same sequence is observed for QDs as well, where multiple tips are generated at the initial stage of the reaction.

In this paper we demonstrated a facile method for the synthesis and assembly of Au-CdSe hybrid with preferentially grown Au-tip on CdSe in a well controlled manner via Langmuir-Blodgett (LB) technique. In the field of materials science, LB technique had been used mainly for self-assembly of nanoparticles and easy control in film thickness made it popular.[30,31] The technique had also been exploited for the deposition of various materials including QDs on solid surface to generate long range assembly on substrate.[32,33] Here, oleyl amine capped CdSe QDs were assembled on water subphase of LB trough. The formation of stable monolayer helped to explore the system further by introducing $HAuCl_4$ in the subphase. The oleyl amine present on CdSe surface assisted in the reduction of chloroaurate ion into Au^0 resulting in Au tipped CdSe. Here oleyl

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† Electronic Supplementary Information (ESI) available: [TEM images for as synthesized CdSe QDs, CdSe spread over water subphase in LB (along with EDX) and Au-CdSe hybrid formed by beaker based synthetic method were provided.]. See DOI: 10.1039/b000000x/

amine had dual roles: capping agent, as well as reducing agent. The issue of multiple tips formation on various sites of the nanoparticle was tactfully handled by this new approach. QDs and metal-QD hybrid nanostructures were characterised by using UV-Vis spectroscopy, XPS and TEM, whereas formation of stable monolayer of QDs on LB trough was established from surface pressure-area (Π-A) isotherm.

2. Experimental Section:

Chemicals used:

Cadmium oxide (CdO, 99.5%), oleic acid (90%), oleyl amine (70%), 1-octadecene (90%) and trioctylphosphine oxide (TOPO, 99%) were purchased from sigma Aldrich, USA. Selenium powder (Se, 99.99%) was from Strem chemicals, USA. Anhydrous toluene and methanol were purchased from Thomas baker, India. All chemicals were used as received.

Preparation of Oleyl amine capped CdSe QDs:

CdSe QD seeds were prepared following a recent report by Chauhan et al.[34] CdO 1.0 mmol (0.128 g), oleic acid 6.3 mmol (2 ml), trioctylphosphine oxide 5.17 mmol (2.0 g) and 1-octadecene 15.6 mol (5 ml) were loaded into a 50 ml three necked round bottom flask and heated to 150 ^{o}C for 1 h under vacuum. This mixture was heated to 300 ^{o}C under N_2 atmosphere. At this temperature a well dispersed solution of elemental Se (1.5 mmol, 0.118 g) in 1mL of oleyl amine (from glove box under N_2 atmosphere) was injected through big needle syringe to the above mixture. The heating mantle was instantly removed at 30 min and anhydrous toluene (5 ml) was added to the reaction mixture to stop the reaction and allowed the reaction mixture to cool to room temperature. The orange-red precipitate obtained on the addition of anhydrous methanol was centrifuged repeatedly and redispersed in 1 ml of anhydrous toluene for further use.

Study of surface pressure-area (Π-A) isotherm of QDs:

The as synthesized CdSe QDs were centrifuged several times to remove uncoordinated organic molecules and the mass collected from pellet was rotary evaporated and dried thoroughly to make it free from solvents. These QDs were dispersed in chloroform with a concentration 1 mg/ml. The KSV NIMA medium trough was thoroughly cleaned with water and iso-propyl alcohol (IPA) and then the dry trough was filled with deionised water. The surface of water was made free from dust particles before spreading 5 µl solution of 1 mg/ml CdSe QDs taken in chloroform solvent. Given a time of 10 min for complete evaporation of solvent, before recording the surface pressure-area (Π-A) isotherm. Π-A isotherms were recorded increasing the volume of CdSe spread over water subphase as well as at different time interval.

Formation of metal-QDs hybrid nanostructure:

Keeping all other experimental conditions same as before the trough was filled with 5×10^{-5} M aqueous solution of $HAuCl_4$. Π-A isotherms were recorded with 30 µl of CdSe in $CHCl_3$ when the barriers were compressed at a rate 10 mm/min, following 2 min of standing time for solvent evaporation after spreading the sample. The evaporation time was modified as compared to pristine CdSe over water subphase, since here the monolayer was already in contact of the reactant, the reaction was expected to start immediately after spreading. The barriers were kept a position of maximum surface pressure ensuring most compact monolayer formation, for 2 h. The monolayer of Au-QD hybrid was deposited at a rate 5 mm/min at constant surface pressure of 7 mN/m on various substrates like Si(111) and quartz for characterization. 25 monolayers were deposited with a gap of 10 min between successive dipping to dry it up on the substrates for various characterizations.

3. Characterisation:

UV-Vis-NIR Spectroscopy:

The spectra were measured by depositing CdSe QDs on a clean quartz plate from the monolayer formed on the water subphase in LB using a Jasco UV-Vis spectrophotometer (V570 UV-VIS-NIR) operated at a resolution of 2 nm. Similar measurements were done after the formation of Au-QD hybrid nanostructure in LB trough which was deposited on a quartz plate.

Fourier Transform Infrared spectroscopy (FTIR):

FTIR spectroscopic measurements were performed using Perkin Elmer-Spectrum One FTIR Spectrometer operated at a resolution of 4 cm^{-1} on samples deposited on Si(111) substrate from LB trough and then dried in air.

X-ray Photoelectron Spectroscopy (XPS):

XPS measurements were made using a custom built ambient pressure XPS system from Prevac and equipped with VG Scienta monochromator (MX650) using Al Kα anode (1486.6 eV).[35] The energy of the photoelectrons were analyzed using VG Scienta's R3000HP differentially pumped analyzer. The spectra were recorded at pass energy of 50 eV.

Transmission Electron Microscopy (TEM):

Transmission electron microscopic (TEM) images were recorded using a FEI, Tecnai G^2 F30, S-Twin microscope operating at 300 kV. The microscope is equipped with a high-angle annular dark field (HAADF) detector from Fischione (model 3000) and a scanning unit. The compositional analysis was performed using energy dispersive X-ray (EDX, EDAX Inc.) attachment in the same microscope. Samples for the analyses were prepared by depositing Langmuir film on carbon-coated copper grids at different time interval to assess the growth of Au tips on CdSe QDs and then were dried in air.

4. Results and discussion:

The initial concern of the scheme was to form stable monolayer of hybrophobized CdSe QDs. Synthesis of CdSe was carried out with oleyl amine as major capping agent via hot injection technique where the average particle size was ~ 10.4 nm as observed by the TEM image and particle size histogram, Supporting Information, SI-1. On spreading these as-synthesized particles on water subphase in LB, the surface pressure-area (Π-A) isotherms showed the ability of oleyl amine capped CdSe QDs to form stable monolayer, Fig. 1A. Typical surface pressure-area (Π-A) isotherms of CdSe QDs with increasing volume spread over the subphase illustrated the surface pressure could reach as much as 13 mN/m. Further trial to increase surface pressure disrupted the monolayer. Fig 1B demonstrated surface pressure-area (Π-A) isotherms at t=10 min, t=90 min and t=2 h with 15 µl of the sample. The nature of all the three curves remained almost unaltered except a small shift in gas phase region of Π-A isotherm with time. This may be due to dissolution of a very small fraction of the monolayer in the subphase.[36] Overall, these curves warranted the stability of the monolayer over water subphase. On measuring the surface pressure for full cycle, hysteresis observed only insignificantly which actually substantiated the previous conclusion (Supporting Information SI-2). The TEM image obtained from the deposited CdSe monolayer spread over water in LB trough verified the observation further where long range assembly of the QDs was found to be generated quite effortlessly, Supporting Information SI-2. The EDAX analysis showed the presence of Cd and Se, Supporting Information SI-2.

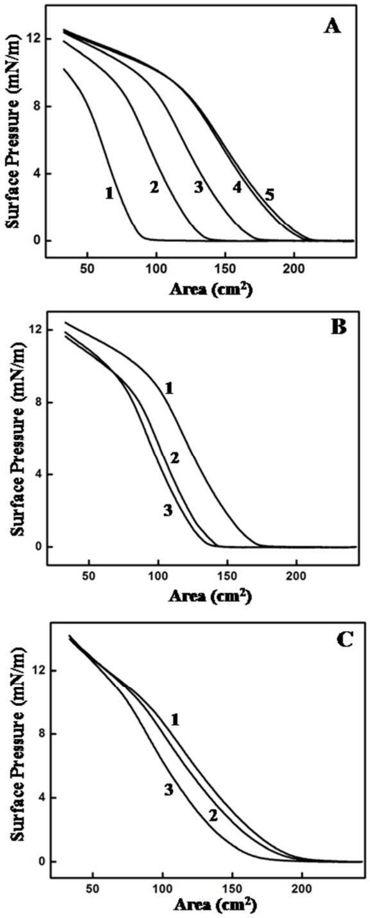


Fig. 1: (A) Surface pressure-area (Π-A) isotherms of CdSe QDs on water subphase by adding successively increased volume: 5, 10, 15, 20 and 25 µl of sample corresponding to the curve numbers 1-5. **(B)** Π-A isotherms of CdSe QDs with 15 µl of sample at t=10 min (Curve 1), t=90 min (Curve 2) and t=2 h (Curve 3). **(C)** Π-A isotherms of CdSe QDs with 30 µl of sample at t=10 min (Curve 1), t=90 min (Curve 2) and t=2 h (Curve 3) over $HAuCl_4$ subphase.

In order to further verify the stability of oleyl amine capped CdSe QDs in LB, the subphase of water was replaced with 5×10^{-5} M aqueous solution of $HAuCl_4$. The capping agent of QDs was selected judicially so that the same molecules of oleyl amines could act as the reducing agent towards $HAuCl_4$ to form gold tip on the QDs. Since the overall experiment time as demonstrated in this paper was limited to 2h, the stability of CdSe monolayer over aqueous solution of $HAuCl_4$ was also verified for the above mentioned time interval, Fig. 1C.

Definitely the oleyl amine molecules helped to render the CdSe QDs thoroughly hydrophobized so that they could form the monolayer on pure water/ water based subphase. The presence of oleyl amine was attested by FTIR study (Fig. 2A) before and after the formation of Au-CdSe hybrid. Similar nature of both the spectra suggested the presence of significant amount of oleyl amine capping even after the formation of Au-QD hybrid nanostructures. It could be noted that the bands at 1557 cm^{-1} (N-H bending mode) and 1644 cm^{-1} (combined motion of NH_2 scissoring and N-H bending) damped down significantly in Curve 2, Fig. 2A i.e. after the reduction of $HAuCl_4$ by oleyl amine. The stretching vibration of N-H band at 3278 cm^{-1} was already very feeble in oleyl amine capped CdSe QDs (Curve 1, Fig. 2A) and completely absent in Curve 2, Fig. 2A. The band at 2852, 2920 cm^{-1} could be assigned to -C–H stretching modes and 2970 cm^{-1} to =C-H stretching vibration.[37] The bands at 1086 and 1236 cm^{-1} might arise from P=O of TOPO,[38] indicating presence of TOPO on to the surface of CdSe QDs.[39,40]

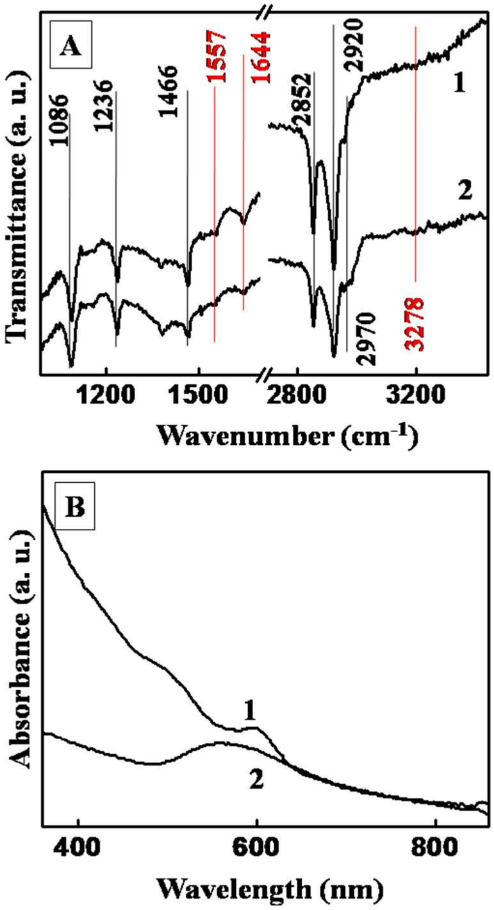


Fig. 2: (A) FTIR spectra of oleyl amine capped CdSe QDs (Curve 1) and oleyl amine capped Au-CdSe hybrid nanocomposite (Curve 2) obtained by depositing the monolayer on Si (111) substrate. **(B)** UV-Vis-NIR spectra of CdSe QDs (Curve 1) and Au-QD hybrid (Curve 2) obtained by depositing the samples on quartz plate from LB monolayer.

CdSe QDs and Au-QD hybrid nanostructures were primarily characterised by UV-Vis spectroscopy. Two sharp absorption peaks 598 nm and 495 nm (Curve 1, Fig. 2B) were characteristics to CdSe QDs.[41] The nature changed prominently after the formation of Au-QD hybrids when a broad peak was observed within the wavelength region 490 nm to 600 nm (Curve 2, Fig. 2B) indicating the formation of Au-CdSe, since the surface plasmon resonance peak for Au nanoparticles generally centered around this wavelength.[42]

Further confirmation came from the XPS studies on the Au-CdSe hybrid. XPS analysis showed Cd 3d of Au-CdSe hybrid could be fitted with two components corresponding to $3d_{5/2}$ and $3d_{3/2}$ at 405.4 and 412.1 eV binding energy (BE) respectively, Fig. 3A. The fitting clearly showed the presence of single species for Cd^{2+} coming from CdSe QDs even after the hybrid formation. The deconvolution of Se 3d peak showed the presence of two decoupled components at 54.3 and 55.2 eV (Fig. 3B) due to $3d_{5/2}$ and $3d_{3/2}$ which had come from CdSe QDs. Absence of any extra components in the fitted curve ruled out the possibility of the presence of unreacted Se in the system. The Au 4f peak obtained from the hybrids was fitted with $4f_{7/2}$ and $4f_{5/2}$ components at 83.7 and 87.5 eV respectively with a energy gap of 3.8 eV (Fig. 3C). The slender fitted graph indicated the presence of metallic Au^0 species in the hybrids.[43]

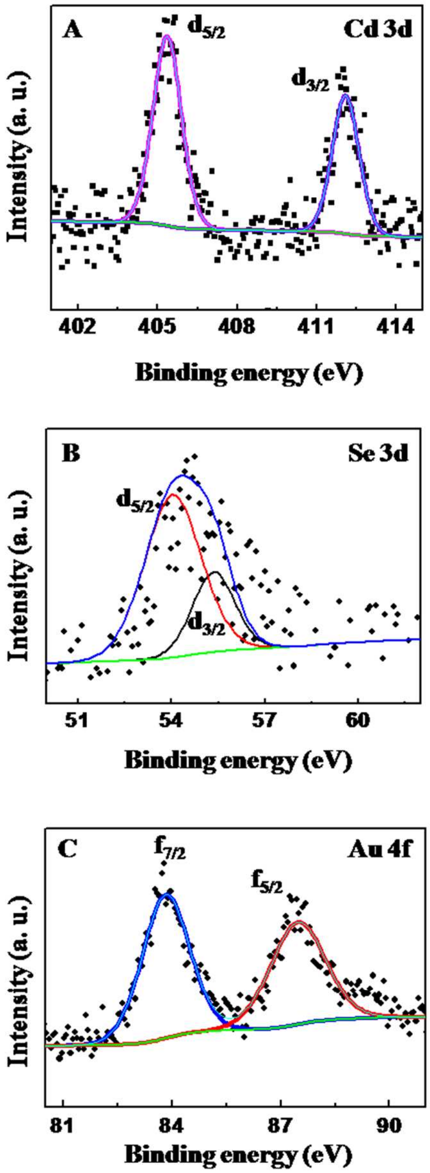


Fig. 3: XPS analysis of CdSe-Au hybrids for **(A)** Cd 3d, **(B)** Se 3d and **(C)** Au 4f.

TEM images at various magnifications (Fig. 4) confirmed the formation of Au-CdSe hybrid and also clearly envisaged the site selective growth of Au^0 on CdSe when the sample was collected at t=20 min. The low magnification image showed long range assembly of these particles when maintained at a reasonable surface pressure of 10 mN/m, Fig. 4A. EDX from the area also indicated signals from Cd, Se and Au with reasonably good intensity, Fig. 4B. It may be noted that C and Cu signals observed in the EDX spectrum are due to the carbon-coated Cu-grid used in the analysis. The closer view clearly revealed the presence of Au at one side of the particle only which was expected while designing the experiment on LB, Fig. 4C. The interplanar spacing (d-spacing) for both CdSe and Au respectively indicated the highly crystalline nature of both the components of the hybrid, Fig. 4C. The d-spacing was calculated on a single particle in a highly magnified image in Fig. 4D. CdSe had d=3.37 Å, closest match was found with (002) plane of hexagonal lattice [44] where as for Au interplanar distance d=2.32 Å corresponded to (111) plane of face centered cubic (fcc) crystal lattice. There was large lattice mismatch between CdSe and Au [32.85% between Au (111) and CdSe (002)]. Several misfit dislocations could be seen at the interface (Inset, Fig. 4D) and in this way huge strain was partially relaxed at the interface.[45-47] However, the white contrast at the interface was due to the remaining strain.

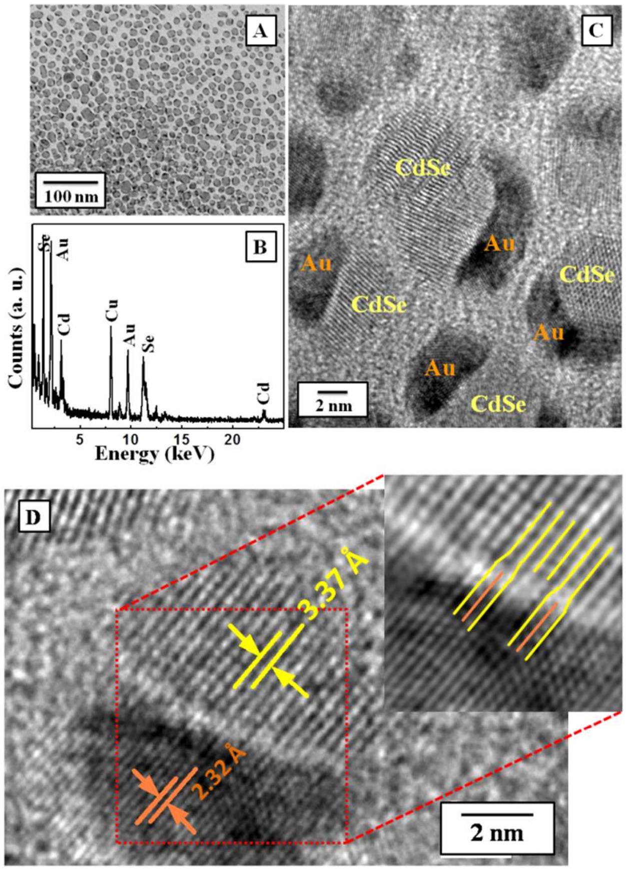


Fig. 4: **(A)** Transmission electron microscopic image at low magnification for Au-CdSe hybrid formed via LB technique. **(B)** EDX as obtained from this region of the sample. **(C, D)** HRTEM image of hybrid nanostructure: the lattice planes of Au and CdSe were clearly visible. Fourier-filtered image in the inset of (**D**) showed misfit dislocations at the interface.

For a detailed distribution of atomic content inside the nanocystals, elemental mapping of Cd, Se and Au was performed using drift corrected EDX spectrum imaging using STEM-HAADF mode, Fig. 5. The STEM-HAADF image in Fig. 5A and the corresponding chemical maps for Cd, Se and Au acquired using Cd L, Se L and Au L energy, were presented in Fig. 5B-D**,** respectively. EDX maps (Fig. 5B-F) were collected while beam of about 2 nm was scanning across about 60 nm X 30 nm area. In this process X-rays were collected point by point from 50 points in x-direction and 25 points in y-direction from the STEM-HAADF image shown in Fig. 5A. Composite maps of Cd-Au and Se-Au were presented in Fig. 5E and Fig. 5F, respectively. Composite maps confirmed the anchoring between Au and CdSe.

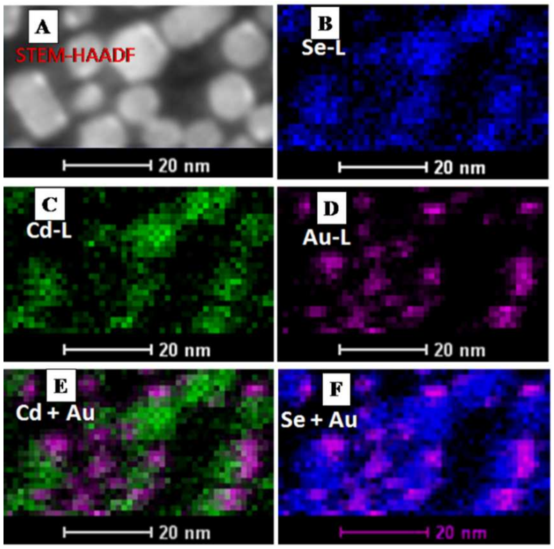


Fig. 5: (A) Scanning TEM-HAADF image of CdSe-Au which was deposited at t=20 min after exposure of CdSe to aqueous $HAuCl_4$ subphase. **(B-D)** EDX maps obtained from same area in A using Se L, Cd L and Au L energy, respectively of the representative elements in Au-CdSe. **(E, F)** Overlay of Cd - Au and Se - Au.

The TEM images in Fig. 4 were obtained for deposition at t=20 min of exposure of CdSe monolayer to aqueous $HAuCl_4$ subphase. The images evidenced moderately colossal Au tips. It can be safely concluded the tip formation was quite rapid; the exposure of single monolayer of CdSe to huge amount of chloroaurate ions in the subphase could be the plausible reason for such a speedy reaction. Thus the monolayer was deposited at a range of time intervals (2 min, 5 min, 10 min, 15 min, 20 min and 90 min) from LB. The Au deposition could be clearly seen even at t=2 min (Fig. 6A), which on the other hand assured the efficient reducing ability of oleyl amine. The growth was found to concentrate on a particular spot on CdSe surface till t=5 min, (Fig. 6A and 6B). Afterwards the growth started spreading over the surface which was in contact with the reactants in the subphase (Fig. 6C-F). The deposition continued in the same fashion and remained unaltered even on maximum time for exposure t=90 min in this study. It was important to note that the deposition occurred extremely site selectively on CdSe QDs. In general the beaker based approach to the similar reaction lacked such selectivity resulting in multiple tips on all over the surface of CdSe QDs. Many times these isolated islands migrated to the end of CdSe to form the major Au tip at one end keeping few smaller islands all over the surface, this observation is very common for CdSe nanorods.[48] In this beaker based approach, on continuing the reaction for longer time Au was found to cover up the entire surface of the CdSe particles, since in this approach the reactant $HAuCl_4$ could access CdSe surface from all possible direction leading to an envelope. The observation could be evidenced by a detailed TEM analysis on beaker based approach as a parallel experiment to this, Supporting Information SI-3.

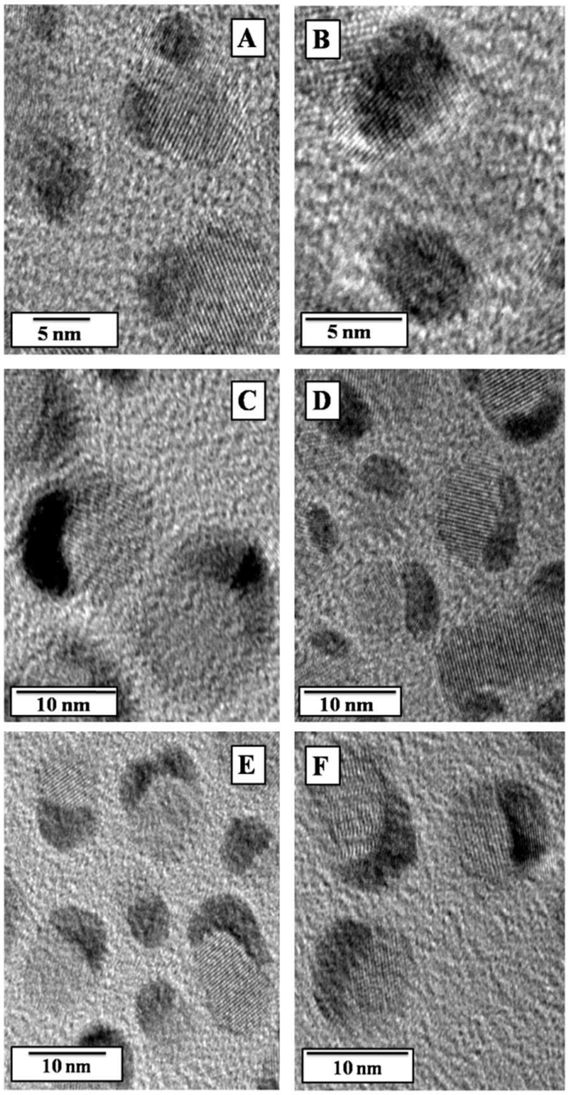
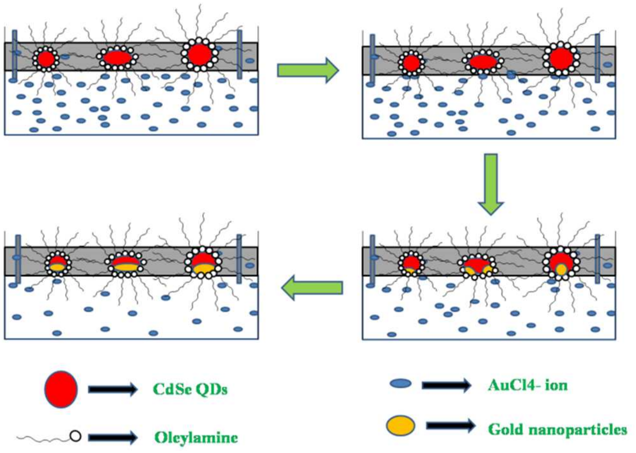


Fig. 6: (A-F) Transmission electron microscopic images taken after spreading the QDs on $HAuCl_4$ subphase in LB trough for t=2 min, 5 min, 10 min, 15 min, 20 min and 90 min respectively

The plausible mechanism was delineated in Scheme-1. The formation of stable CdSe QD monolayer could be attributed to competent capping ability of oleyl amine which made the particles hydrophobic. When these particles were exposed to aqueous $HAuCl_4$ at a reasonably good surface pressure (where the monolayer was in the most compact arrangement), the movement of the CdSe QDs was restricted. Thus only a fraction of the surface of the particle was unveiled to chloroaurate ions present in the subphase. Oleyl amine acted as reducing agent and nucleation of Au^0 started only at one point on CdSe surface. The growth continued with time – initially the small spots were amplified and then it was spread on the exposed semi circular surface of CdSe. The other half of CdSe particle never saw the reactants (AuCl$_4^-$) and hence no sprout of Au appeared there. This approach could definitely be a cleaner approach to the existing one to have controlled deposition of Au or other element during formation of hybrid structures and a similar study with nanorods which is under consideration presently is believed to produce interesting results as well.



Scheme 1: Schematic diagram for plausible mechanism of formation of Au tip selectively at one side of CdSe QD via LB technique.

Conclusion:

In this work Au-CdSe (metal-QD) hybrid nanostructure was formed where Au tipping was carried out in absolute directed fashion on CdSe QDs using Langmuir-Blodgett technique. The capping of oleyl amine on CdSe QDs was judicially chosen which could also be exploited for reduction of HAuCl$_4$ to Au^0. The success of application of these materials would definitely depend on the assembly of particles in the desired fashion and particularly long range assembly would encourage a number of potential applications. Here we carried out the synthesis on LB, thus the long range assembly could be effortlessly achieved. This method of tipping was found to be simple, selective and reproducible. Entire synthesis procedure was carried out at an ambient temperature without the use of any hazardous chemicals. The success of such reaction on LB was definitely encouraging enough to extend the study for other systems.

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