Fabrication, Characterization and Photophysical Investigation of Organic and Organic-Inorganic Nanoassemblies in Aqueous Medium

M.Sc. Thesis

Submitted By YESHVIR YADAV



DISCIPLINE OF CHEMISTRY INDIAN INSTITUTE OF TECHNOLOGY INDORE

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NDIAN INSTITUTE OF TECHNOLOGY INDORE CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in the thesis entitled "Fabrication, Characterization and Photophysical Investigation of Organic and Organic-Inorganic Nanoassemblies in Aqueous Medium" in the partial fulfilment of the requirements for the award of the degree of MASTER OF SCIENCE and submitted in the DISCIPLINE OF CHEMISTRY, Indian Institute of Technology Indore, is an authentic record of my work carried out during the time period from July, 2018 to June, 2020, under the supervision of Dr. Tushar Kanti Mukherjee, Associate Professor of IIT Indore.

The matter presented in this thesis has not been submitted by me for the award of any other degree of this or any other institute.

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71. Tushar Kanti Mukherjee

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Signature of PSPC Member #1 Date: 02/07/2020

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Convener,

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Signature of PSPC Member #2 Date: 02/07/2020



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ACRONYMS

QD	Quantum Dot
CdTe	Cadmium telluride
MSA	Mercaptosuccinic acid
PEI	Polyethylenimine
NPs	Nanoparticles
SPR	Surface Plasmon Resonance
UV-vis	Ultraviolet- Visible
PL	Photoluminescence
FTIR	Fourier Transform Infrared
CLSM	Confocal Laser Scanning Microscopy
DIC	Differential Interference Contrast
λ_{em}	Emission wavelength
λ_{ex}	Excitation wavelength
FESEM	Field Emission Scanning Electron Microscope
GD	Green Droplet
Au NPs	Gold Nanoparticles

Chapter 1

Introduction

Nanoscience and Nanotechnology

Nanoscience, as the name suggests is an emerging area of science that involves the study of materials mainly in the nanoscale range. These materials exhibit a large range of novel properties because of their ultra-small size which makes them highly suitable for various kinds of applications. It is also a quickly growing field that can shape a new world around us and could lead to overwhelming development in fields that vary from manufacturing to health care.

The range of nanoscale is considered to be around 1 to 100 nanometers. A nanometer (nm) is equal to 10^{-9} m (meter) or equal to 10^{-3} (µm) micrometer. We measure molecules and atoms in the scale of nm and µm. For example if we laid 10 hydrogen atoms side by side, it measures in nm scale, a strand of DNA has diameter 2.5 nm whereas the thickness of red blood cell is 7,000 nm wide.

Nanotechnology, on the other side, is the drawing, manufacturing, and use of structures, devices, and systems at the nanoscale. So actually one is studying nanomaterials and their properties and the other is make use of those materials and properties to fabricate something new or different.



Scheme 1. Illustration of applications of nanotechnology in various fields

Nanoparticles

A NP is generally defined as a small particle that ranges from 1 to 100 nanometres in size. They are invisible to the naked eye and reveals notably different chemical and physical properties to their bulk counterparts.

Most NPs are made up of several hundred to thousand of atoms. The surface of NPs in general is functionalised with various moieties such as

- Surface molecules = organic and inorganic molecules.
- Organic molecules coating over inorganic nanoparticles are known as stabilizers, capping and surface ligands, or passivating agents.

Types of Nanoparticles

Designing NPs with different structures and functions became a primary interest. One of the most important parameters in designing the NPs is to control and tune their morphology and size, which are very important in biomedical, electronic, optical and technical fields. Therefore, interests in the fabrication of organic and inorganic NPs with different compositions, shape, and particle size rise rapidly, leading to the emergence of nanotechnology research field.



Scheme 2. Classification of NPs on the basis of compositions.

In recent times, scientists have focused their attention towards developing organic nanoparticles as these materials self-assemble into highly aligned superlattice at room temperature that has potential applications in organic light-emitting diodes (OLED), sensors, and medical diagnosis.⁽²⁻³⁾ Various nanoparticles have been fabricated during the last two decades. The structures of these materials can be zero (0D), one (1D), two (2D), and three (3D) dimensional.^(4,5) The synthesis, photophysical properties as well as applications of metal NPs, semiconductor NPs or quantum dots (QDs) are described below.

Metal Nanoparticles (NPs)

Metal NPs are nanoscopic materials with a general measurement underneath 100 nm. The physical and optical properties of metal NPs is credited to their little size and the emormous surface area to volume ratio.⁽⁷⁻⁹⁾ NPs have a significant job in various scientific branches for example, medicication, material science, mechanics, pharmaceutics, and others. As of late, analysts discovered the colossal potential in metal NPs synthesis and their applications.



Scheme 3 - Schematic diagram illustrating the surface plasmon resonance in metal NPs.

Metal NPs have unique light scattering properties and they exhibit Surface Plasmon Resonance. SPR is a characteristic phenomenon of metal NPs, which is observed if the size of the NPs is smaller than the wavelength of the incident light. As in SPR, the electromagnetic field of the incident light excites the surface electrons of a metal NP; this results in coherent localized oscillation of the electron density with a resonant frequency that depends upon size and shape of NPs as well as dielectric of metal and surrounding medium. The SPR band of metal NPs can be tuned from visible to near-infrared regions by varying the size of the NPs; this makes them highly suitable for imaging and sensing applications in the field of biomedical science.⁽¹⁰⁾ Several transition metal NPs including gold (Au), silver (Ag), iron oxides (FeO), copper (Cu) have been designed for medical applications.⁽¹¹⁾ However, Au and Ag NPs have gained special attention because they can absorb in the visible region of the solar spectrum and show low cytotoxicity.

Quantum dots

In the year of 1980, the Quantum Dots (QDs) were first found in glass crystals by Russian physicist Alexey I. Ekimov . It took one more decade for the discovery of colloidal QDs with size-tunable optical properties.⁽¹²⁾ In brief, QDs are exceptionally little particles in the scope of just a few nanometers. They are little to such an extent that their optical and electronic properties contrast essentially from those of their bigger particles. These nanoscale particles, which are usually made of semiconductor materials, firmly bind either electrons or electron holes. QDs discharge light of explicit frequencies when power or light is concerned with them. In semiconductor materials, absorption of light excites an electron from the valence band to the conduction band thus generating a hole in the valence band. The hole and the electron generates exciton which is essentially an electron-hole pair. At the point when the excited electron relax back to the ground state and the exciton's energy is emmitted as light or fluorescence, this whole phenomenon is known as exciton recombination. As the confinement energy depends upon the size of various QDs, both absorption as well as the emission of these QDs can be optimized by varying the size of the QDs during its synthesis.⁽¹³⁻¹⁵⁾ The larger size dots absorb and emit lower energy and the spectrum shift towards the orange-red region whereas the smaller size dots absorb and emit at higher energy i.e. bluer light. As a result, heterogeneous mixture of particles with different sizes manifests excitation wavelength dependent emission, which is commonly known as multicolor emission. These size-tunable optical properties provide the QDs a great advantage over the common organic fluorophores⁽¹⁴⁾.

Moreover, they are bright and much more photostable than most of the available fluorescence probes. They have been used in various applications to develop QD-optoelectronics, QDlasers and bioimaging probes. However, there are serious limitations of semiconductor QDs in a biological application. QD tests display in-vivo harmfulness. For instance, QD nanocrystals are exceptionally harmful to cells and tissues. When the UV light is incident on the particles they break up and the procedure known as photolysis which results in the discharge of poisonous cadmium particles into the way of life. To circumvent this problem of toxicity, small size carbon nanoparticles with an average size approximately ~2-5 nm were introduced as carbon quantum dots. They were found to possess several advantageous properties over QDs, such as low cytotoxicity, good biocompatibility, high solubility, and easy surface functionalization.



Scheme 4 - Illustration of the influence of particle size on the band gap and quantum confinement effect in semiconductor.

CdTe QDs

CdTe QDs are the most imperative semiconductor material because it shows narrow bandgap of 1.47 eV as well as a large exciton Bohr radius of 7.3 nm, which makes them widely applicable in various filed. CdTe QDs show quite good crystallinity and emit in the whole region of the electromagnetic spectrum i.e. from green to red region (450–700 nm) with high luminescence quantum yield (QY) of 20–90%. CdTe QDs can be synthesized in aqueous as well as in organic medium. The ligands which are generally utilised during the synthesis of CdTe QDs in aqueous medium are thiol-containing compounds namely, 3-mercaptopropionic

acid (MPA), glutathione (GSH), cysteine (CYS) and thioglycolic acid (TGA). The pH of the medium greatly influence the QY of QDs, in acidic medium excess ligand and Cd²⁺ in the reaction medium will deposit on the surface of QDs and lead to the formation of a shell-layer structure which comprises of the ligand-Cd complexes. These complexes of ligand-Cd effectively eliminate the nonradiative pathway for excitons and enhance the QY of QDs. ⁽¹⁶⁻¹⁹⁾

Polyelectrolytes

Polyelectrolytes are simply the polymers which are water soluble due to the presence of ionic charge along their polymer chain. They are commonly used in the research of complex coacervation. They are classified as the linear or branched macromolecule chains which have a large number of ionic groups in their structure. They are usually soluble in polar solvent, generally water. In positively (or negatively) charged polyelectrolyte solution, a single species polymer with random polydispersity and one species of counter-ions which are small ions with oppositely charged sign to that of macromolecular charge are present. The charge of counter-ion and macromolecular structure must be equivalent to attain the condition of electroneutrality.

The commonly used polyectrolytes are polyethylenimine (PEI), poly(diallyldimethylammonium chloride) (PDADMAC), poly(acrylic acid) (PAA) and poly(sodium 4- styrene sulfonate) (SPS).

Few characteristics of PEI are as follows

- It is a polymer which is composed of a repeating unit that contains amine group and two carbon aliphatic CH₂CH₂ group.
- The branched PEIs are liquid at room temperature while the linear PEIs are solid at room temperature.
- The repeating monomer unit in PEI is $(C_2H_5N)_n$.



Scheme 5. (A) Structure of single monomer unit of linear PEI. (B) Structure of single monomer unit of branched PEI.

QD-Polymer Self-Assembled Coacervates

The expression "coacervates" alludes to organic/inorganic rich droplets shaped by liquid-liquid phase separation in macromolecular systems. Coacervation is a process that generates coacervate colloidal droplets. At the point where coacervation takes place, two phases of liquid co-exist simultaneously: a thick phase which is polymer-rich (coacervate phase or coacervate droplets) and a very dilute phase which is polymer-deficient known as dilute phase. (20-22) An assortment of materials with different structures and properties can be shaped because of electrostatic cooperations between oppositely charged macromolecules. Under characterized conditions, complexation between oppositely charged polyelectrolytes can prompt a phase separation phenomenon, alluded to as complex coacervation. The QD and polymer self-assembled nanostructures show enhanced thermal, mechanical, and optoelectronic properties due to their unique properties which originates from the combination of both inorganic nanomaterial and polymer. The inorganic components exhibit large surface area, excellent thermal stability, and size-dependent optoelectronic properties, on the other hand, organic polymer including mechanical flexibility, and good processability. Therefore, these self-assembled nanostructures with unique physical and biological properties have allured a lot of attention due to their potential applications in drug delivery, catalysis, chemical storage, bioimaging and biosensors.⁽²³⁻²⁹⁾

Chapter 2

Experimental Section

2.1 Materials

Sodium tellurite (Na₂TeO₃), cadmium chloride (CdCl₂), mercaptosuccinic acid (MSA) (C₄H₆O₄S), sodium borohydride (NaBH₄), tri-sodium citrate (Na₃C₆H₅O₇.2H₂O), sodium hydroxide (NaOH), sodium chloride (NaCl), polyethylenimine (PEI, MW = 50,000), hellmanex III and Pur-A-Lyzer dialysis kit (molecular weight cut-off 3.5 kDa) were obtained from Sigma-Aldrich. Milli-Q water was obtained from a Millipore water purifier system (Milli-Q integral).

2.2 Synthesis Procedure

2.2.1 Synthesis of MSA-Capped CdTe QDs

CdTe QDs were synthesized using a reported method.⁽³⁰⁾ In a 100 ml round bottom flask, 0.04 M cadmium chloride in 4 ml was added to 50 mL distilled water. Then in a stepwise manner 100 mg trisodium citrate dihydrate, 50 mg mercaptosuccinic acid, and 100 mg sodium borohydride were added to the reaction mixture at room temperature with constant stirring. The solution was allowed to mix for 5 min and then the reaction mixture was refluxed for 30 min at 100 °C to obtain the green luminiscent QDs. The finally obtained CdTe QDs were then purified using dialysis (24 h). The concentration of CdTe QDs were estimated using the equation proposed by Peng.⁽³¹⁾



Scheme 6. Schematic representation of synthesis of MSA-capped CdTe QDs

2.2.2 Synthesis of CdSe QDs

CdSe QDs were synthesized using the reported method.³² 456.7 mg of CdCl₂.2.5H₂O (2 mmol) and 480.5 mg of MSA (3.2 mmol) were mixed in 100 mL deionized water in a 250 mL round bottom flask. NaOH solution was used to maintain the pH of the reaction mixture to 11.8. Then 352.2 mg of ascorbic acid ($C_6H_8O_6$) and 0.2 mmol (22.2 mg) of SeO₂ were added to the reaction mixture under constant stirring. The pH of the resultant solution was again maintained to 11.8. The reaction mixture was then refluxed at 100 °C at constant stirring. The obtained CdSe QDs were purified using dialysis (24 h).



Scheme 7. Schematic representation of synthesis of MSA-capped CdSe QDs

2.3 Sample Preparation

2.3.1 Microscopy Experiment

For all the Confocal and AFM experiments, the samples were drop casted over clean cover slides. All the cover slides were cleaned in a stepwise manner using chromic acid (15 min) then using 2% Hellmanex III (15 min). After every cleaning step cover slides were washed using Milli-Q water. At last, all the cleaned slides were finally rinsed with methanol and dried in a vacuum oven.

2.3.2 Preparation of the binary mixture

Different mixtures of QD^{518} and PEI were generated by varying the concentration of PEI from 0.05-100 μ M while keeping the concentration of QD^{518} fixed at 0.58 μ M. All the binary mixtures were kept for atleast 12 h before doing any experiments. The pH of all the binary mixtures were maintained by using an appropriate quantity of diluted HCl solution (1M) and NaOH solution (1M).

2.4 Characterization Techniques

The UV-vis spectra of synthesized CdTe QDs were measured in a quartz cuvette with 10 mm path length using Carry 100 Bio, a Varian UV-vis spectrophotometer and the PL spectra were measured in a quartz cuvette with 10 mm path length with Fluoromax-4 Spectrofluorometer (HORIBA Jobin Yvon, model FM-100) at emission and excitation slit widths of 5 nm. FTIR spectrum was recorded to confirm the formation of CdTe QDs using a Bruker (Tensor-27) spectrometer on a thin KBr pellet in the range of 800 to 4000 cm⁻¹. The FESEM images were recorded using Supra 55 Zeiss, a field-emission scanning electron microscope. The Confocal images were taken using an inverted confocal microscope (Olympus, model no. FV1200MPE, IX-83). A 100X resolution objective with oil immersion was used (1.4 NA) with a 488 nm diode laser as the source to excite the samples using appropriate dichroic and emission filters along the optical path. AFM images were recorded on a clean glass coverslip using AIST-NT microscope (model SmartSPM-1000). The PXRD pattern of CdTe QD⁵¹⁸ was measured using the lyophilized sample of CdTe QD⁵¹⁸ with a Bruker D8 Advance X-ray diffractometer. The X-rays were generated using a sealed tube with a Cu K α source.

Chapter 3

Results and Discussion

3.1 Characterization of CdTe QDs

The dialysis purified CdTe QDs were studied using various techniques like UV–vis spectroscopy, PL spectroscopy, AFM, FTIR and zeta (ξ) potential. Figure 1A shows the excitonic emission and absorption spectrum of MSA-capped CdTe QD in Milli-Q water. The exciton band maximum at 485 nm in Figure 1A corresponds to the broad absorption spectrum of CdTe QDs and the sharp emission spectrum corresponds to the PL band centered at 518 nm obtained upon excitation at 450 nm. In the AFM image of Figure 1B a range of well dispersed spherical QD⁵¹⁸ can be observed with an average size of 2.3 ± 0.1 nm. The structural aspects of CdTe QDs were studied using powder XRD pattern as shown in Figure 1C. The PXRD pattern of CdTe QDs depicts three peaks at 20 values of 24.8, 42.4, and 47.3°, corresponds to the (111), (220), and (311) crystalline planes, respectively. The estimated ξ potential for QD⁵¹⁸ was found to be -24.8 ± 1.1 mV. (Figure 1D)



Figure 1. (A) Absorption and Emission spectra of QD^{518} ($\lambda_{ex} = 450$ nm). (B) AFM image of MSA-capped QD⁵¹⁸. (C) PXRD pattern of MSA-capped CdTe QD⁵¹⁸. (D) Zeta (ξ) potential of QD⁵¹⁸. (E) FTIR spectrum of CdTe QD⁵¹⁸.

The surface functionalization of QDs were estimated through FTIR measurement. Figure 1E shows the FTIR spectrum of MSA capped CdTe QDs. The broad peak observed at 3451 cm^{-1} is due to the O-H stretching vibration and the band at 1560 cm⁻¹ is due to C=O stretching vibration of -COOH group present at the surface of QDs. The band at 1415 cm⁻¹ is due to C-H bending vibration. The earlier reported literature shows that S-H stretching vibration peak of the free MSA ligand is present at 2500 cm⁻¹. The absence of an S-H stretching peak and the presence of the free carbonyl peak in the spectrum indicates that MSA is bound to the surface of Cd²⁺ site through Cd-SR bond formation.

3.2 QD-PEI Nanocomposite Formation

A series of different binary mixtures of QD^{518} and PEI were made by varying the concentration of PEI and keeping the QD concentration constant. The concentration of QD^{518} used was fixed at 0.58 μ M, while concentration of the PEI monomer was changed between the range of 0.05- 60 μ M. Although the absorption maximum of QD^{518} does not change much after adding the initial amounts of PEI but at higher concentrations of PEI the absorption band starts to get broadened (Figure 2A). In contrast, notable changes were seen in the PL behaviour of QD^{518} after the addition of PEI. The PL peak position of QD^{518} was observed to shift from 518 to 527 nm after the addition of 2.5 μ M PEI with a red shift of 8 nm which is due to the increase in the size of QD upon the formation of QD-PEI nanocomposite from few nm to thousand of nm (Figure 2B). The lowering of the PL intensity of QD^{518} after the addition of PEI (Figure 2B) can be attributed to the phenomenon of exciton–exciton coupling among the closely placed QD⁵¹⁸ in the QD-PEI droplets.

Phase behaviour of the different binary mixtures in case of QD-PEI nanocomposite formation changes from various phases like from clear (C₁) to turbid (GD) to precipitate (P₁) and finally to clear (C₂) on varying the concentrations of PEI in the range of 0.05 - 60 μ M. Figure 2C shows the turbidity vs concentration plot of QD-PEI binary mixtures with varying the amount of PEI. These results definitely point us towards the formation of supramolecular structures and that they constantly undergo various structural rearrangements in the reaction mixture. The phase behaviour of these binary mixtures was studied using the turbidity measurements as shown in Figure 2D. In this current study all our focus was centered on the turbid region (GD) of the binary mixture that was obtained after the addition of 2.5 μ M PEI. Figure 2E depicts the FESEM image of GD which clearly reveals well defined spherical droplets with an average size of 2335 ± 80 nm.



Figure 2. (A) Changes in electronic absorption spectra of QD^{518} after formation of GD. (B) Changes in emission spectra of QD^{518} after formation of GD. (C) Plot of turbidity (600 nm) against PEI molar concentrations at pH 7. (D) Photographs of QD-PEI binary solution after the addition of different concentrations of PEI. (E) FESEM image of GD at 2.5 μ M PEI concentration. The inset shows size distribution histogram of GD⁵¹⁸. (F) Confocal fluorescence image of GD.

3.3 PL Behaviour of Hybrid Droplets

These QD-PEI nanocomposite droplets are anticipated to be intrinsically luminescent due to the presence of CdTe QD⁵¹⁸ inside these spherical structures. To prove this fact, we studied the PL nature of these hybrid coacervate droplets through confocal microscopy. The Figure

2F shows the CLSM images of GD obtained from the turbid region of the binary solution and as expected, distinct green luminescent droplets were seen in confocal images.



Scheme 8. Illustration of Formation of QD-PEI Nanocomposite Droplet in the Turbid Region via QD-PEI Nanocomposite Formation.

Droplet formation between different oppositely charged aqueous polyelectrolytes is a common phenomenon which has been already reported in our previous studies.²⁶⁻²⁸ The present hybrid nanocomposite system has been formed utilizing a very simple single step mixing of negatively charged MSA-capped CdTe QDs and positively charged polyethylenimine (PEI) polyelectrolytes in water (Scheme 8).

3.4 Droplet formation at different pH

The pH effect on the formation of QD-PEI nanocomposite was studied for pH 5, 7 and 10. Figure 3A and 3B shows the turbidity versus PEI molar concentration plot for pH 5 and pH 7, respectively. The maximum turbid point for pH 5 and pH 7 was observed to be 1.5 and 2.5 μ M, respectively depicting the possible formation of supramolecular structures in these binary mixtures. In the case of pH 10 no clear turbid point was observed showing that no supramolecular structures are formed.



Figure 3. Plot of turbidity (600 nm) versus PEI molar concentration at (A) pH 5, (B) pH 7 and (C) pH 10.

The PL behaviour of the nanocomposite formed at pH 5 and 7 was studied using confocal microscopy (Figure 4). The results obtained from CLSM matched with our expectations and the spherical nanostructures were found to be inherently luminescent which was due to the presence of CdTe QDs inside these spherical structures. The merged images in Figure 4 clearly shows that the green luminescence originates exclusively from the QD-PEI coacervate droplets. Figure 4A and 4B clearly demonstrate that assemblies formed at both, pH 5 and pH 7 are similar in structure as well as show similar PL behaviour whereas in Figure 4C no clear formation of droplets was observed.



Figure 4. Confocal image (DIC, Merge and PL) of GD at (A) pH 5 and (B) pH 7, respectively.

The pKa value of -COOH groups present over the surface of QD^{518} is around 4.19 and 5.64 thus above pH 5, QD^{518} has deprotonated COOH groups and due to which it has negative charge over its surface. The pKa value of -NH₂ group of PEI is around 9 thus PEI at pH 9 and

above has negative charge over its surface and PEI at pH 8 and below has positive charge over its surface.

At pH 5 and pH 7, QD⁵¹⁸ has negative charge whereas PEI has positive charge. The electrostatic interactions between negatively charged QD⁵¹⁸ and positively charged PEI monomers results in the formation of spherical QD-PEI nanocomposite structure in case of pH 5 and pH 7 (Figure 4A&B). At pH 10 both QD⁵¹⁸ as well as PEI monomers are negatively charged due to which there is no electrostatic attraction rather electrostatic repulsion might take place due to which no clear turbid point was observed at pH 10 in the turbidity plot (Figure 3C). Also, no spherical structures were observed in pH 10 (Figure 4C) that were earlier observed in case of pH 5 and pH 7. In case of pH 10 few larger structures were observed in CLSM which may be due to the aggregation of PEI monomers with some QDs present in these aggregated structures.

3.5 In-Situ Synthesis of AuNPs

The GD were used to carry out the in-situ synthesis of gold nanoparticles (Au NPs) in aqueous medium. On addition of 2.5 μ M HAuCl₄ in 0.58 μ M GD solution, the white turbid solution first turned into purple color and then precipitates were observed which clearly shows that some type of interaction took place in the reaction mixture between GD and HAuCl₄ solution. Upon separating these purple precipitates, a pink color solution was obtained.



Figure 5. (A) Changes in absorption spectra of GD upon addition of HAuCl₄. (B) Absorption spectrum of pink color supernatant obtained. (C) Daylight photograph of GD before and after addition of HAuCl₄.

Figure 5A depicts the changes in absorption spectra of GD on addition of HAuCl₄. The broadening of absorption spectra resembles the absorption spectrum of larger size Au NPs as well the purple color (Figure 5C) obtained also hints towards the formation of Au NPs. Figure 5B shows the absorption spectra of supernatant obtained which shows an absorption peak at 535 nm that resembles with the absorption spectrum of medium sized Au NPs. These observations though not conclusive still point us towards the formation of Au NPs. The plausible reason behind the in-situ synthesis of Au NP might be the electron transfer from N atom of -NH₂ group of PEI on the surface of GD which helps in the reduction of Au⁺³ to Au⁰. Figure 5C shows the daylight photograph of GD before and after the addition of HAuCl₄. Further in-depth analysis of these solutions using TEM, DLS, elemental analysis can provide us with better explanation and proof towards the in-situ formation of Au NPs.

3.6 Characterization of CdSe QDs

The formation of the dialysis purified CdSe QDs were confirmed using UV-vis and PL spectroscopy. Figure 6A depicts the absorption spectrum of MSA-capped CdSe QDs in Milli-Q water with an absorption maximum at 480 nm. Figure 6B shows the emission spectrum of CdSe QDs with PL maximum at 532 nm obtained upon exciting the sample at 450 nm. Figure 6C shows the time dependent synthesis study of CdSe QDs at 30min, 1h, 1.5h, 3h, and 5h. It shows that as the reaction time increases from 30 min to 5 h, a bathochromic shift is observed in the PL emission of CdSe QDs from 513 nm to 575 nm, respectively. This result agrees well with our expectations and previous reported literature as with with increase in the reaction time size of semiconductor QDs increases and a red shift in emission is observed.



Figure 6. (A) Absorption spectrum of MSA-capped CdSe QDs. (B) Emission spectrum of MSA-capped CdSe QDs. (C) Time dependent emission spectra of CdSe QDs.

Chapter 4

Conclusion

In summary, using different types of spectroscopic techniques, we have characterized the proper synthesis of MSA-capped CdTe Quantum dots and also demonstrated the formation of QD-PEI nanocomposite. The basic mechanism behind the formation of these droplets was ascertained to be electrostatic interaction between negatively charged Quantum dots with oppositely charged polymer PEI at pH 5 and pH 7. This unique binary system is composed of spherical coacervate droplets in acidic as well as aqueous medium. These green droplets were found to be inherently luminiscent. The inability to form QD-PEI coacervate droplets at pH 10 is mainly due to the lack of electrostatic attraction between similarly charged QD and PEI. The dropets were further utilized as a reaction center for the in-situ synthesis of AuNPs. The unique luminescence properties observed for these droplets have profound implications in various applications such as sensing, bioimaging, drug delivery and light-emitting devices.

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