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STUDY OF THE INTERACTION BETWEEN MERCAPTOACETIC ACID (MAA) CAPPED CdS QUANTUM DOTS WITH DENATURED BOVINE SERUM ALBUMIN (dBSA)

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The highly fluorescent thiol capped CdS quantum dots were synthesized by a novel aqueous synthesis route. In this method we used $CdCl_2.2.5H_2O$ and sodium sulfide (Na_2S) as the Cd and S source, respectively with thioglycolic acid (TGA) as stabilizer. The structure of CdS nanocrystals was investigated by means of X–ray diffraction (XRD), energy–dispersive X–ray analysis (EDX), UV–visible, Fourier transform infrared (FT–IR) spectroscopy and transmission electron microscopy (TEM). The results showed the crystallinity of the CdS nanocrystals and the average size of CdS QDs was 3.15 nm. An aqueous solution of CdS capped with thioglycolic acid (TGA) shows a characteristic fluorescent peak at 560 nm, which decrease under the influence of both the pH and temperature. The interaction between water soluble colloidal mercaptoacetic acid (MAA) capped CdS quantum dots and denatured bovine serum albumin (dBSA) has been studied by using absorption and steady state fluorescence measurements. The interaction between quantum dots and dBSA occurs through static quenching mechanism.

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1. Introduction

Most of the nanocrystals possess intermediate dimensions between the molecules and the sub-micrometric crystallites. Keeping in view this we define solely particles dimension on the basis without taking into account the type of material considered and the property to be assessed. Hence it is defined on the basis of the scaling of a property of a material with nanometric dimensions that fluctuates with the particles dimensions. This is essentially different from both the macrocrystalline analogues and molecules. A crystalline arrangement based on the hundreds to thousands of atoms is known as Semiconductor Nanocrystal having a bulk structure identical to the macrocrystalline compound [1-7].

CdS is one of the most studied materials because it has a well-established relationship between the optical absorption and the size of the particle. One important type is cadmium sulfide (CdS) quantum dots which is an II–VI semiconductor having a band gap of 2.42 eV including high

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tunability. It is found in electrical and optical properties of QDs of CdS demonstrate quantum size effects. The shifting of absorption and luminescence bands toward higher energy will lead to the reduction of grain size, a discrete absorption spectrum and enhanced oscillator strength. Due to relatively large nonlinear response and photocatalytic activity cadmium sulfide is investigated among the nanocrystalline semiconductors especially as a luminescent material keeping in view their technologically relevance with the optoelectronic devices, optical data storage and high-speed optical communications. An important kind of thiolate used in preparation and assembly of cadmium sulfide (CdS) quantum dots as the stabilizer agent is called Mercaptoacetic acid (MAA). The bifunctional molecule of MAA consists of both thiols and carboxylic acid groups. The absorption of both carboxylic acids and thiols on metal surface result in the formation of well-packed monolayers.

A biomacromolecule comprising 37 thiol groups per monomer is called denatured BSA (dBSA). The method employed to prepare is through chemically reduced bovine serum albumin. The interaction of CdS QDs with dBSA in aqueous medium will represent a method to study the effect QDs on cells in vivo studies. To modify the surface of QDs chemically reduced BSA has been used. The conjugate of denatured BSA and the surface of the CdS QDs will help to improve its chemical stability and photoluminescence for the detection of metal ions in the biological systems. Many reported studies include the interaction between biomolecules and semiconductor nanoparticles using spectroscopic techniques [8-14].

In the current study, CdS quantum dots were synthesized by a novel and simple aqueous precipitation using a method which is not time consuming. This synthesis was carried out at room temperature. A stabilizing agent Mercaptoacetic acid (MAA) was used to prevent particle growth and agglomeration. We determined the interaction between quantum dots and dBSA occurs through static quenching mechanism using absorption and steady state fluorescence measurements. The object of the present study is to use protein-QDs conjugate for the application of fluorescence and also the detection of metal ions in the biological systems.

2. Materials and Methods

There are two successful routes described for the synthesis of CdS quantum dots: the first is through the synthesis in the organic phase and second through aqueous synthesis of thiol-capped CdS quantum dots. In most of the aqueous approaches, Na_2S and thioura are used as the S source, we try to report a novel aqueous synthesis of highly fluorescent thiol capped CdS quantum dots using sodium sulfide (Na_2S) as the S source. The CdS quantum dots were synthesized according to the following chemical reactions:

$$CdL + S^{2-} \rightarrow CdS + L, \text{ where L = MAA (Mercaptoacetic Acid)}$$

In this synthesis, the precursor $CdCl_2 2.5H_2O$ was dissolved in 200 ml of de-ionized water, and an sufficient amount of the thiol stabilizer (MAA) was added under stirring, then followed by adjusting the pH to the sufficient value (≈ 11.2) by dropwise adding of 2 M solution of NaOH. Sometimes, the solution can remain slightly turbid at this stage due to the incomplete solubility of Cd thiolate complexes without influencing the further synthesis. The solution is positioned in a three-necked flask fixed with a septum and valves and is deaerated by N_2 bubbling for 30 min.
The sodium sulfide (Na_2S) solution was then injected in the $CdCl_2 2.5H_2O$ solution. CdS precursors are formed at this stage which is accompanied by a change of the solution color to yellow due to the formation of thiocarboxylic acid protected CdS nanoparticles. The precursors are converted to CdS nanoparticles by refluxing the reaction mixture at 90°C for 3 h under atmospheric conditions with a condenser. The molar ratio of $Cd^{2+}/MAA/S^{2-}$ was 1:2.4:0.5. The complete procedure for the of CdS quantum dots is shown in figure 1.

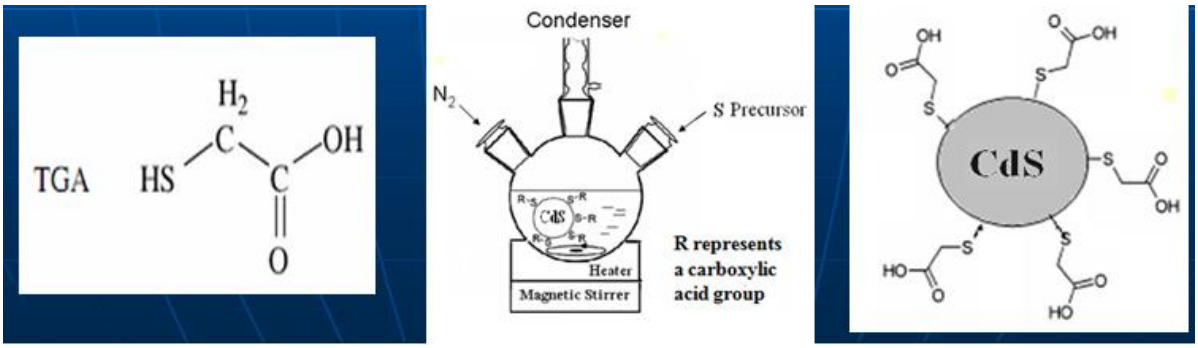

Fig. 1: Synthesis of CdS quantum dots

2.1 Interaction between CdS quantum dots and dBSA

BSA was chemically treated with $NaBH_4$ for the preparation of dBSA. The procedure was as follows. BSA was first dissolved in 100 mL of denionized water and later on $NaBH_4$ was added under stirring. This reaction continued for 1 h at room temperature and then at 70 ^{0}C till no more gas (H_2) was produced. The complete method is already reported in our previous studies [15-19].

3. Results and Discussion

3.1 X-ray diffraction (XRD)

In figure 2 the diffraction pattern of the CdS quantum dots obtained is shown and this was confirmed by comparing with the published data (JCPDS 10-454). Four intense diffraction peaks are attributed to (111), (200), (220) and (311) crystal planes of CdS, respectively. They are in the cubic form (zincblende phase) and show a good crystallinity. The average particle size obtained using the X- ray diffraction is 3.15 nm which is calculated using Scherrer equation**.**

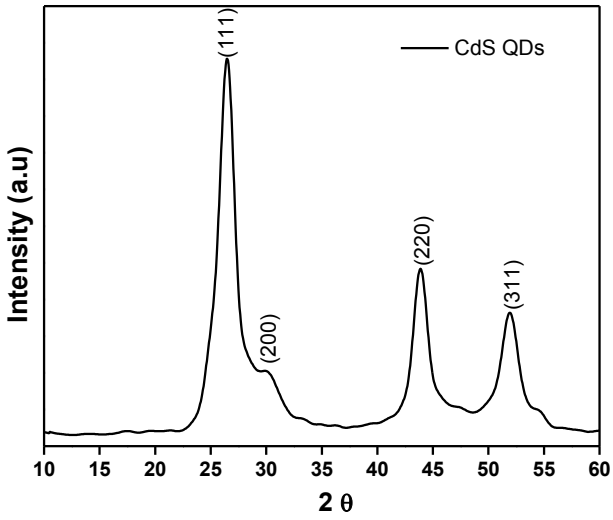

Fig. 2: XRD pattern of the CdS quantum dots

3.2 Energy-Dispersive X-ray Analysis (EDAX)

The EDAX (energy-dispersive X-ray Analysis) experimental results shown in figure 3 confirm the presence of metal ions in these nanoparticles as well as Cd and S. The Cd and S were

from CdS nanoparticles and the excess S was attributed to the stabilizer of (Mercaptoacetic Acid (MAA)).

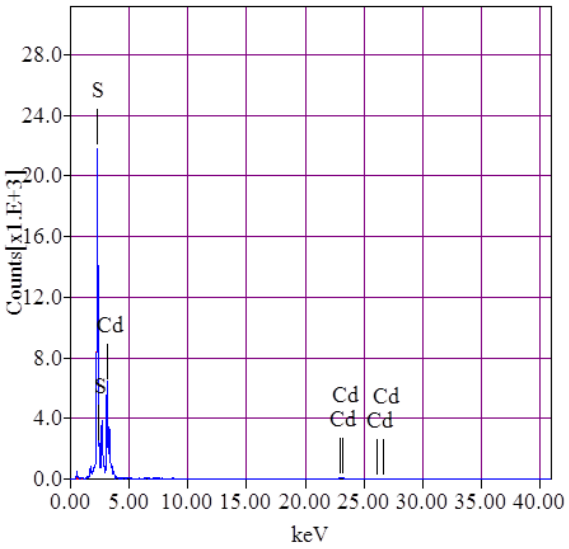

Fig. 3 Energy-dispersive X-ray Analysis of the CdS quantum dots

3.3 Transmission Electron Microscopy (TEM) Analysis

In order to analyze morphology and size distribution of CdS capped with thioglycolic acid (TGA) TEM was used as shown in figure. Cds particles TEM images showing homogenous size distribution for these nanocomposite confirming the nanoparticles size of the nanocomposite. SAED pattern of CdS QD is shown in the figure. The value of CdS QD average particle size derived from log-normal fitting to the size distribution histogram is 3.2 nm and this reflects single crystalline structure of CdS QD.

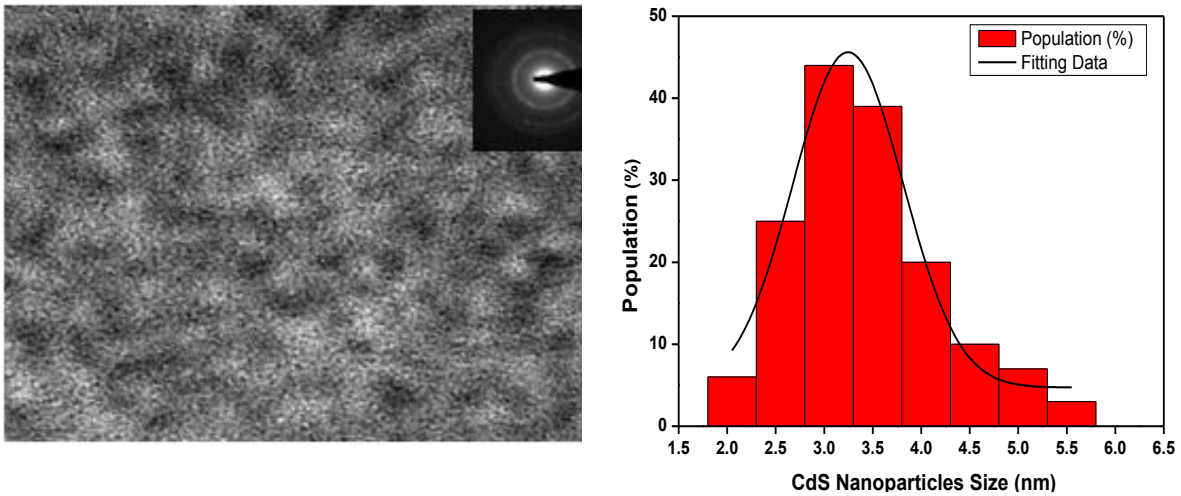

Fig. 4: TEM image and size dispersion histogram of synthesized MPA capped CdS quantum dots (The scale bar equals 5 nm)

3.4 Spectral analysis by FT-IR spectra

The broad peaks in the range from 3405 to 3432 cm^{-1} are present in each spectrum, which are corresponds to the effect of –OH stretching vibration. The active mode peaks of CH_2 (2940 cm^{-}

[1]) in the capped layer were shifted to lower frequency with respect to that of MAA. The shift in CH_2 vibrations to smaller frequency indicates that the surfactant molecules in the adsorbed state are affected by the field of solid surface. It is important to note that the S-H vibrations band located around 2565 cm^{-1} and 2665 cm^{-1} in the spectrum of pure Mercaptoacetic Acid (MAA) are disappeared completely in the IR spectrum of bare core CdS nanocrystals. The vibration band of C=O at around 1717 cm^{-1} in the spectrum of mercaptoacetic acid shifts to 1566 cm^{-1}.

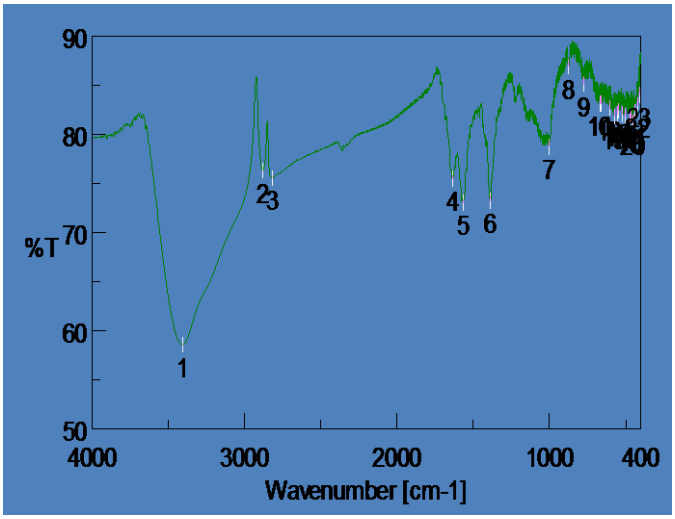

Fig. 5. FTIR Spectra of synthesized MPA capped CdS quantum dots

3.5 Optical properties of CdS QDs and CdS/dBSA

The absorption spectrum of dBSA in the absence and presence of colloidal MAA-capped CdS QDs at different concentrations is shown in figure 6. In the presence of QDs the absorbance of dBSA increased at a peak of 390 nm. This represents the addition of QDs changes the polarity of the micro-environment of dBSA which mean that there is a conformation change and the peptide strands of BSA molecules were extended leading to a decrease in the hydrophobicity [20].

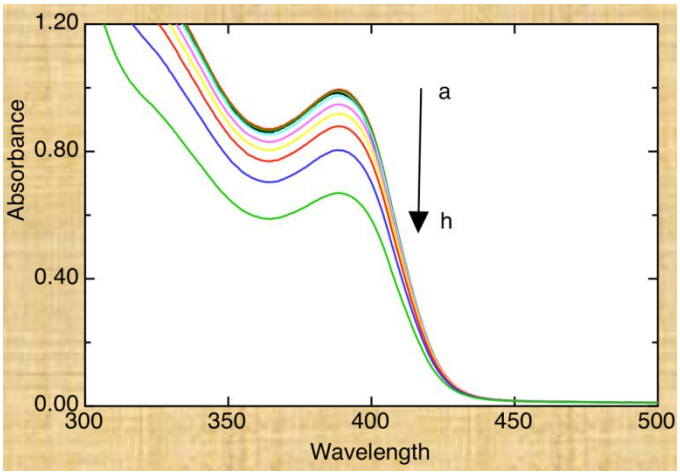

Fig. 6: Absorption spectra of a) 3 × 10^{-5} M CdS-MAA and successive concentrations of dBSA 2.5 × 10^{-7} M - 3 × 10^{-5} M, a-h respectively.

At various concentrations of CdS QDs in the range of 450–700 nm the fluorescence spectrum of dBSA is recorded as shown in figure 7. The excitation wavelength is 370 nm. It was

found from the figure that by increasing the concentration of QDs the fluorescence intensity of dBSA is decreased at a wavelength of 560 nm.

In order to confirm the interaction between QDs and protein and to exclude the interaction between protein and capping agent we have performed similar experiment which is the effect of MAA on the fluorescence spectrum of dBSA. It was found that in the presence of MAA there is no appreciable difference in dBSA emission wavelength as well as intensity (the data is not shown here) confirming the fluorescence quenching shown in Figure 7 due to the interaction between QDs and dBSA.

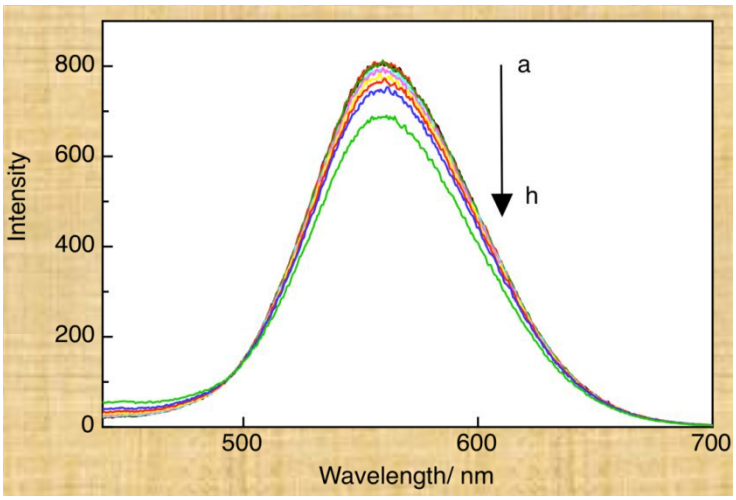

Fig. 7: Fluorescence spectra of a) 3 × 10^{-5} M CdS-MAA and successive concentrations of dBSA 2.5 × 10^{-7} M - 3 × 10^{-5} M, a-h respectively, λ_{ex} = 370 nm, λ_{em} = 560 nm.

In conclusion, the interaction between QDs and dBSA has been investigated using Uv-visible and steady state fluorescence spectroscopic measurements. The experimental results clearly show that QDs quench the fluorescence of dBSA through complex formation. Hence this paper provides a good knowledge and strategy for exploring the new dimensions of the biological activities of QDs at the protein level.

4. Conclusion

The EDAX (energy-dispersive X-ray Analysis) results indicate the presence of metal ions in these nanoparticles as well as Cd and S. The Cd and S were from CdS nanoparticles and the excess S was attributed to the stabilizer of (Mercaptoacetic Acid (MAA)). TEM images demonstrated homogenous size distribution for these nanocomposite and confirmed the nanoparticles size of the nanocomposite. From the FT-IR Spectra it is concluded that the nanoparticles were adsorbed by the –SH groups and the free carboxylic acid group exists as carboxylate ion and make the capped particles soluble in water. The interaction between water soluble colloidal mercaptoacetic acid (MAA) capped CdS quantum dots and denatured bovine serum albumin (dBSA) has been studied by using absorption, steady state fluorescence measurements. The interaction between quantum dots and dBSA occurs through static quenching mechanism.

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