Synthesis and Optical Characterization of Cadmium Sulfide Quantum Dots

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Abstract:
Quantum dots, QD have generated significant interest owing to their optical properties. With enhanced research interest of with cadmium sulfide, CdS nanoparticle for optical sensors and QD probes we followed a conventional methodology to prepare colloidal CdS nanoparticles during an undergraduate chemistry curriculum's advanced chemistry course and characterized them using fluorescence in the presence of stabilizer, sodium salt of ethylenediaminetetraacetic acid [EDTA]. The influence of CdS concentration in colloidal solution indicated the quenched fluorescence at higher concentration. Additionally, we used human serum albumin [HSA] to study the interaction at varying CdS concentration. It indicates that presence of HSA molecule may serve as stabilizer agent to the colloidal solution aqueous of CdS QD. This study provides feasibility of CdS QD preparation and studying their optical properties in an undergraduate chemistry curriculum effectively.

Keywords: Cadmium Sulfide, Quantum dots, nanoparticles, quenched fluorescence

I. INTRODUCTION

Quantum dots, QDs are semiconductor nanoparticles including of elements from the periodic groups II–VI or III–V and their size are ranging between 2 and 10 nm in diameter. The CdS quantum dot, QD is a typical kind of II-IV nanoparticles, which plays an important role in the common type of core-shell QDs. It is of great practical significance to synthesize the water-soluble CdS QDs used in multicolor biomarkers and prepare core-shell QDs [1, 2]. The range of diameter is close to or smaller than the dimensions of the exciton Bohr radius. Moreover, the mobility of charge carriers (electrons and holes) is restricted within the nanoscale dimensions, and his quantum confinement effect QDs with unique optical and electronic features. Owing to this size-dependent property, the absorption and emission properties of the semiconductor QDs can be easily tuned by controlling the particle size, shape or surface structure. Compared with traditional organic fluorophores, QDs process several advantages in fluorescence properties for biological applications, that including: a high brightness because of the extinction coefficient and quantum yield, broad absorption characteristics and a narrow band width in emission spectra, independence of emission on the excitation wavelength, continuous and tunable emission maxima because of quantum size effects [3-5]. It is evident that the method for preparation of nanoparticles and the matrix, in which they are synthesized, lead to distinction not only to sizes but to properties as well. The CdS nanoparticles synthesized in the form of colloid solutions have additional level in the band gap, the concentration of nanoparticles both in composites and in colloid solution also effect the fluorescence spectrum until its shift into the longer wavelength [6]. The higher concentration of sulfides in the solution above 5mM leads to the precipitation of the deposit even on the presence of stabilizers. Previous method for preparing stable aqueous colloid of CdS upto 15mM concentration was further refined and decreased to 12.5mM [6]. Increased average sizes of the nanocrystal indicated the emission fluorescent band red shift to 540nm and different QD solutions an expansion of the emission range up to ~100 nm is evident with improved features as biomarkers [7]. Extinction coefficient QD equalization is directly linked to CdS shell growth and tunable size for high "Quantum

Yield", QY and brightness [8]. In this study we report the concentration quenching of fluorescence of colloid quantum dots of CdS in the presence of stabilizer, sodium salt of ethylenediaminetetraacetic acid [EDTA] and transport protein, HSA outlining its role in putative interaction with QDs.

II. MATERIALS AND METHODS

Materials:

Cadmium nitrate, ammonium sulfide, cyclohexane, deionized water, tetraethoxysilane, ammonia, acetone and other common reagents used in the study were of an analytical grade. The EDTA IGEPAL® (octylphenoxypolyethoxyethanol) and HSA were purchased from Sigma Aldrich.

Synthesis of bare CdS and silica-coated CdS:

The CdS QDs were synthesized using revised scheme of earlier published report [9]. First, CdS QDs were prepared via a reverse microemulsion method. Subsequently, reverse water-in-oil microemulsions were prepared using cyclohexane and IGEPAL. A total of 20 mL of cyclohexane was mixed with 8 mL of IGEPAL to form a microemulsion. An aqueous solution of cadmium nitrate (190 mg in 2 mL deionized water) was added to the first microemulsion and 2 mL of an ammonium sulfide solution (0.01 M) were added to the second and continuously stirred. The two microemulsions were mixed together after 5 minutes and the development of a yellow color was noted, indicating the formation of CdS QDs. The so-synthesized QDs were precipitated and repeatedly washed with 25 mL of ethanol, then centrifuged to obtain the QDs. For silica-coated QDs, 1 mL of tetraethoxysilane and 0.2 mL of a 28% ammonia solution were added to the CdS solution. The stirring continued for 8 hours, then precipitated with acetone, repeatedly washed with 25 mL of ethanol, and then thrice with 25 mL of double-distilled H2O. The final product was desiccated to obtain water-soluble, silica-coated CdS QDs.

Additionally the CdS quantum dots were also prepared using procedure published for comparative analysis and control [6].

III. RESULT AND DISCUSSION

X-ray diffraction characterization:

The powder XRD pattern of the CdS QDs. in the Fig. 1 shows broad peaks indicating the small sizes of the QDs. The crystallite size (Dhkl) of cadmium sulfide crystal was estimated using Debye Scherer equations.

$$Dhkl = k\lambda / \beta \cos\theta$$

Where, λ is the wavelength of radiation and β Is the full width and half maximum intensity, θ is the diffraction angle of consider diffraction peak, and K is the shape factor constant [i.e. taken as 0.90 for the almost spherical particles]. The XRD peaks at 26.5°, 43.5° and 51.5° correspond to the crystal planes (111), (220) and (311) of the cubic CdS phase respectively. The average size of the QDs calculated from (220) reflection by the Scherrer formula [10] was about 4 nm. The intensity of 111plane is relatively higher to other packing.

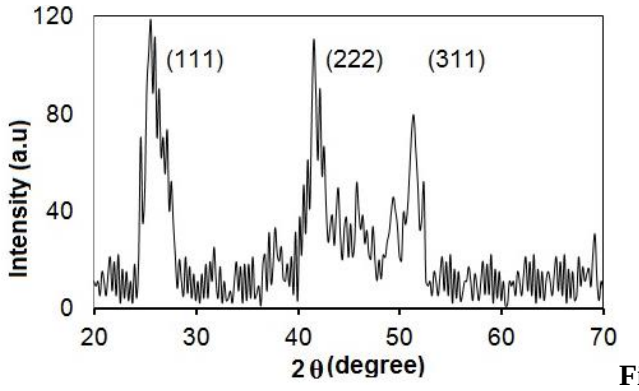


Figure 1: X-ray diffraction pattern of CdS QDs.

Optical absorption of CdS solution:

The optical properties of colloidal CdS thus prepared were investigated with different concentrations. The colloidal solution prepared with 50mM ethylenediaminetetraacetic acid [EDTA] concentration to prevent sedimentation. The colloidal solution was relatively stable in 50mM EDTA concentration and no further improvement was notice with increased, 100 mM EDTA solution. The optical absorption was measured on Thermo Evolution 3000 UV-Vis spectrophotomer in partial UV and visible range. The absorption of ultra violet or visible radiation results from excitation of bonding electrons as a consequence, the wavelength of absorption peaks can be correlated with the type of bonds in the species hence UV visible absorption spectroscopy is an efficiencies technique to monitor the optical properties of quantum size particles. Figure 2 indicate the absorption pattern of concentrated 10 mM and diluted colloidal solution of CdS.

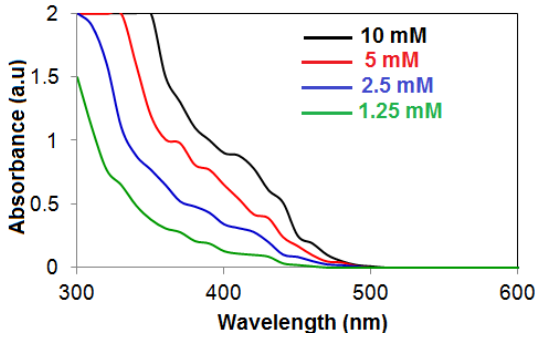
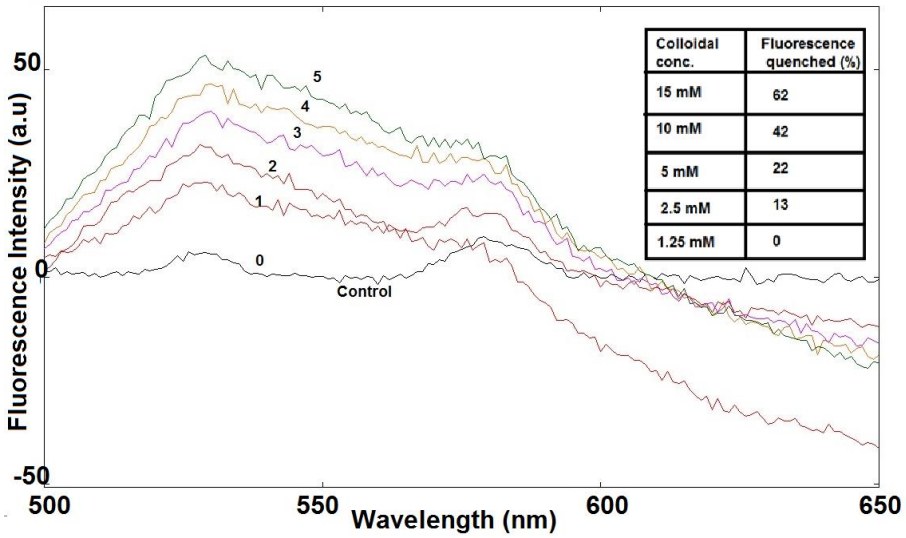


Figure 2: Optical absorption of CdS colloidal solution.

These results are consistent with earlier report [6]. The fluorescence of stable aqueous solution of CdS was investigated using Shimadzu spectrofluorometer, RF 6000 at ambient temperature. The fluorescence spectrum of CdS at varying colloidal concentration is depicted in figure 3. The emission maximum upon using excitation at 365 nm is 528 nm. As can be seen that the fluorescence intensity values quenched upon using increased concentration of CdS colloidal solution. Various concentration used in the data were subtracted from control and percent quenched using diluted 1.25 mM as minimal or zero percent. It indicates a linear relationship within the given concentration of colloidal solution.



Colloidal conc.	Fluorescence quenched (%)
15 mM	62
10 mM	42
5 mM	22
2.5 mM	13
1.25 mM	0

Figure 3: Effect of fluorescence intensity depending on the concentration of CdS QD colloidal solution. The control is represented as 0. Various spectra notation as 1 through 5 represents concentration of 1.25 mM, 2.5 mM, 5 mM, 10 mM and 15 mM respectively. The subtracted values from control value at 528 nm were tabulated in the inserted table. The concentration dependence on percent quenching is linear (data not included).

The variation in the presence of 50 mM EDTA compared to 100 mM EDTA stabilizer concentration (data not included) is negligible. The results with diverse set of CdS QD in a range of higher wavelength (red shifted) is comparable [6] suggesting that over 2 mM colloidal solution results in quenching of fluorescence intensity. It is likely that shift is directly related to the formation of

coarsened particles due to aggregation [6]. A decrease in the fluorescence intensity with an increase in the concentration is related to the group of effect called the concentration quenching. As the concentration of fluorescing centers increases, the excitations of the electron subsystem initiate to migrate over the ensemble of fluorescence centers. The resonant energy transfer from one fluorescence center to another one occurs until this energy is completely captured by quenching centers. Several mechanisms were outlined for such concentration quenching phenomenon [11].
Interestingly we have employed human serum albumin, HSA to study the binding to CdS QD and possibility to stabilize the colloidal solution. We have used 10 μM concentration of HSA in 3 pH ranges, in acidic range [pH 5] physiological relevant neutral ph 7.0 and basic pH of 9.0.

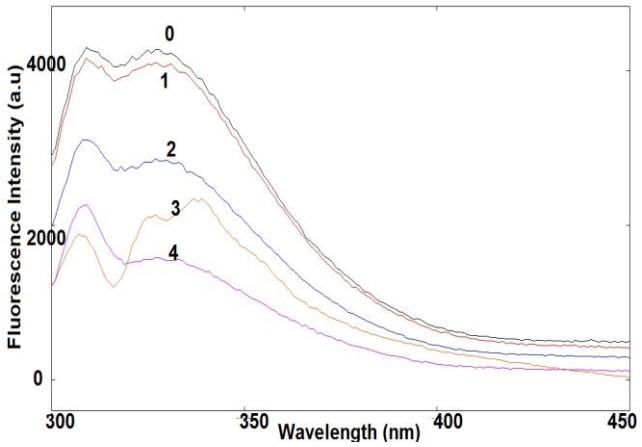


Figure 4: Binding of CdS QD suspension with HSA probed by fluorescence quenching. The excitation wavelength used was 280 nm to target lone tryptophan residue on the protein molecule. The data shown here were obtained in 50 mM phosphate buffer saline, PBS, pH 7.0. The emission maximum was 335 nm. The control HSA solution alone is represented as 0, increasing concentration to final concentration were 0.01 mM (trace 1), 0.1 mM (trace 2) 0.25 mM (trace 3) and 0.5 mM (trace 4). The decrease in fluoresce is linked to binding of CdS QD to HSA solution.

Recently the binding of HSA to poly grafted on to starch QD suing spectroscopy [12]. In this report we demonstrate the effective binding of CdS QD to HSA [Figure 4]. It is interesting that HSA undergoes native like conformation (N-state) acid induced (A-state) and basic transition (B-state) in acidic and basic pH conditions [13] of the environment. Interestingly we did not notice any significant change in pH 5 and 9 for A and B state respectively towards binding, but the aggregation of CdS QD at the either pH range is higher compared to neutral pH. It would be interesting to explore the binding with diverse size QDs with appropriate stabilizer in subsequent studies as acid induced unfolded form of protein effectively binds to CdS QD. More recent study [14] has focused on novel detection method of HSA based CuInZnD QD-cobalt divalent cation sensing system. Further advancement may support the selective QD for biological applications.

IV. CONCLUSION

According to unique properties of QDs, they are suitable alternatives to conventional organic fluorophors for labelling cells and other imaging applications. Although current synthesis methods of QDs somewhat capable to prepare appropriate QDs with enhanced quantum yield and narrower size distribution, additionally use of chemical agent, EDTA and protein such as HSA and others may act is effective stabilizer. In addition, this approach has some challenges such as scaling up of the synthesis to obtain large amount of QDs, improved control over size and shape and understanding the synthesis mechanism at the molecular level, which finally may help in providing better control over size, shapes and crystallinity in the future. It could serve as a pilot for evaluation for diverse group of stabilizer to yield the better quantum yield QDs evaluate by fluorescence spectroscopy at undergraduate level.

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 # Quincy X. Bedford, Iris S. Denmark, Xoa Pryce, Sharita Ellison carried out synthesis as part of their undergraduate CH-431 course [Advance chemistry Lab] and Aakriti Gautam assisted Dr. Trivedi and completed the work.