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L-glutathione Capped CdSeS/ZnS Quantum Dots as an Environmentally Hazardous Chemical Sensor

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^{1,2}Department of Physics and Material Science and Engineering JIIT Noida, Sec-62, U.P E-mail: ¹meenakshirana123@gmail.com, ²papia.chowdhary@jiit.ac.inAbstract

Abstract—Sensing ability of fluorescence based L-glutathione (L-GSH) capped CdSeS/ZnS Core-Shell quantum dots (QDs) has been investigated for environmentally hazardous metal ion (Zn²+). A "Turn-On" response for Zn²+ions has been observed through the enhancement of fluorescence intensity with the increasing concentration of Zn²+ ions. The CdSeS/ZnS Core-Shell quantum dots (QDs) coated with L-GSH were synthesized and characterized using UV-Visible and fluorescence spectroscopy. The influencing factor in the determination of fluorescence was studied for both the CdSeS/ZnS QDs and L-GSH capped CdSeS/ZnS QDs. The surface modification of QDs with L-glutathione makes them available for interaction with the targeted materials and it further increases the emission quantum yields of QDs.

1. INTRODUCTION

The present age is an explosion of research in nanomaterial fields. As the size of the organic/inorganic material becomes smaller on the nanometer scale, their electronic and optical properties vary largely from those of bulk materials, hence, they become size or shape dependent [1]. These properties of nonmaterials are the key point of nanoscience. QDs are semiconductor nanocrystals that exhibit unique electronic and optical properties. QDs is known as zero dimensional and they exhibit well separated and discrete quantized energy states due to their smaller number of atoms compared to bulk materials. QDs are typically made up of a core of a semiconductor material and they are usually coated with a three shell of another semiconductor, which exhibits wider band gap energies [2-4]. QDs have been used in many fields such as photocatalysis [5,6], molecular biology, quantum devices and electroluminescence applications. In the recent years, QDS are also investigated for chemical sensing applications [7,8]. Sensing of environmentally hazardous metal ions is one of the most important challenges [9]. Out of different hazardous metal ions, Zn²⁺ is one of the toxic to living organism.

In this paper, we reported a novel fluorescence material using L-glutathione functionalized CdSeS/ZnS core shell QDs. L-glutathione is water-soluble and used as a capping agent. L-glutathione and its polymeric form, phyotochelatin are more stable and by nature to detoxify heavy metal ions. Characterization of the prepared functionalized CdSeS/ZnS QDs was carried out with various techniques including UV—

Vis absorption spectroscopy and fluorescence spectroscopy. It was found that functionalized CdSeS/ZnS QDs are more stable. Therefore, the development of this sensor is simple for detection of the Zn^{2+} ion.

2. EXPERIMENTAL

2.1 Apparatus

The UV-Visible absorption spectra were recorded at 300 Kelvin by a Perkin Elmer spectrophotometer (model Lambda-35) with a varying slit width. All luminescence measurements were made with a Perkin Elmer spectrophotometer (Model Fluorescence-55) with a varying slit width (Excitation slit=10. 0 nm and Emission slit=5nm) ranging from 190-900 nm. The Model LS 55 Series uses a pulsed Xenon lamp as a source of excitation. Deionized water (Millipore) was used for measuring absorption and emission spectra. All optical measurements were performed at room temperature under ambient condition.

2.2 Reagents

All reagents were of analytical grade and were used without further purification. Deionized water (Millipore) was used for solution preparation. N-dimethyl formamide (DMF), L-Glutathione and CdSeS/ZnS QDS were purchased from Sigma-Aldrich.

2.3 Procedure

2.3.1 Synthesis of L-GSH Capped CdSeS/ZnS Core-Shell Quantum Dots:

In the synthesis of QDs, we took already prepared CdSeS/ZnS quantum dots purchased from Sigma Aldrich. QDs were dissolved in 1mg/ml in toluene. DMF reagent was used for all synthesis. The reason for choosing DMF reagent is its miscibility in water and toluene both.

The synthesized CdSeS/ZnS Core-Shell QD were coated with L-GSH uses a modified version of the protocol reported in the literature. [10-13]. CdSeS/ZnS core shell QDs was dispersed in a solvent DMF (N- dimethylformamide). The mixture was

stirred until it became transparent and was stored for 1 week at room temperature. To make the CdSeS/ZnS QD water soluble already prepared CdSeS/ZnS core shell QDs was mixed with 3 ml of deionised water.

For synthesis of L-GSH Capped CdSeS/ZnS Core-Shell QD L-GSH were dissolved in DMF solution and stirred properly until the solution became transparent. Finally, L-GSH and DMF mixture added to CdSeS/ZnS core shell QDs to make it capped. The obtained L-glutathione-capped CdSeS/ZnS quantum dots became stable in size in aqueous solution for more than 1 month without any precipitation when preserved in the dark and under ambient conditions. The synthesized L-GSH Capped CdSeS/ZnS Core-Shell QDs were characterized throughout in all measurements.

3. RESULTS AND DISCUSSION

3.1 UV-Vis absorption and fluorescence spectroscopy:

The comparative absorption and emission spectra of CdSeS/ZnS QDs and L-GSH Capped CdSeS/ZnS Core-Shell QDs are shown in figure1 & Fig. 2. We observed a narrow absorbance band at 217.17 nm and a broad band at 233.58 nm for CdSeS/ZnS QDs. From the absorption spectra of L-GSH Capped CdSeS/ZnS. We found a sharp absorption peak at 204 nm and a wide absorption band at 230 nm. The blue shift of 13.7 nm in the lower wavelength band in L-GSH Capped CdSeS/ZnS Core-Shell QDs reveal the stability of QDs size. Similarly, in the fluorescence spectrum of uncapped CdSeS/ZnS QDs shows a wide emission band at ~400-450 nm with excitation wavelength 265 nm. The shape of the emission spectrum is very unique in nature compared to other other organic fluorophores, which generally have broader and asymmetric emission spectra.

The symmetric nature of the emission spectrum of CdSeS/ZnS QDs indicates these QDs are nearly uniform in shape.

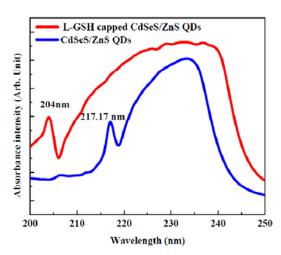


Fig. 1: Absorption spectra of L-GSH Capped CdSeS/ZnS QDs and CdSeS/ZnS QDs

In presence of L-GSH the fluorescence spectrum of CdSeS/ZnS QDs shows no specific change in position of emission wavelength, but emission quantum yields of L-GSH capped CdSeS/ZnS QDs increases a lot.

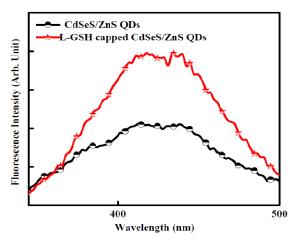


Fig. 2: Emission spectra of L-GSH Capped CdSeS/ZnS QDs and CdSeS/ZnS QDs

3.3 Optical sensing by fluorescence

 ${\rm Zn}^{2+}$ ion is the second most abundant transition metal found in our human body [14]. It plays a vital role in many biological processes, such as, catalytic activity, immune function etc. Imbalance of zinc levels in the human body can create several neurological disorders, such as Alzheimer's disease, Parkinson's disease, ischemia, epilepsy etc. [15]. Strong efforts have been devoted in recent past to develop sensitive chemical sensors for detection of trace amounts of ${\rm Zn}^{2+}$ ions in both biological and environmental systems.

Fluorescence "Turn On" and "Turn Off" process has been used to detect many hazardous ions in recent years. The effect of Zn²⁺ ions on fluorescent emission of L-GSH Capped CdSeS/ZnS Core-Shell QDs is shown in Figure.3.

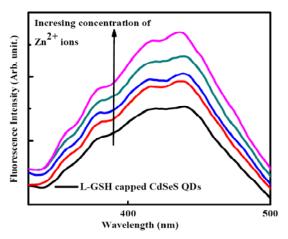


Fig. 3: Emission spectra of L-GSH Capped CdSeS/ZnS QDs in the presence of Zn²⁺ ions.

L-GSH Capped CdSeS/ZnS Core-Shell shows remarkable sensing response to Zn^{2+} ions by creating fluorescence enhancement with the continuous increase of Zn^{2+} ions concentration (Figure.3). Therefore, this system can be used for the development of a sensitive and selective method for the determination of Zn^{2+} ions in aqueous phase.

4. CONCLUSION

In this work a water-soluble L-GSH capped CdSeS/ZnS nanoparticles were synthesized in aqueous solution at room temperature through a straightforward process by using safe and low-cost method. Beside this we have investigated the possibility of using L-GSH-capped-CdSeS/ZnS QDS as an efficient fluorescence chemical sensor for Zn²⁺ ions in aqueous medium. From all the above experimental results, we can strongly establish that L-GSH-capped CdSeS/ZnS can be used as highly sensitive "Turn-On" fluorescent sensor for Zn²⁺ ion in aqueous environment. The present work opens a door to study of new water-soluble and biocompatible QDs due to its vast applicability in metal ion detection.

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