HIGHLY EMISSIVE CdTe QUANTUM DOTS PASSIVATED WITH NOVEL BRANCHED LIGANDS AS FLUORESCENT SENSORS

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ABSTRACT

Nano scale materials are the most crucial in the present era of bio and nano technology. They stand as a basic building block for the medical electronic, and various other useful applications. The nano materials can be tuned to obtain various nano scale structures or shapes. The basic significance of nano sized organic or inorganic material is that its properties vary significantly compared to its bulk counterparts. These changes in the optical and the electronic properties of the nano materials compared to its bulk counterpart could be easily noticed. These nano materials can be of metals, non-metals, alloys, polymers or so. As the bulk semiconductor material is shrunken down to its nano scale, widening of its bandgap energy happens and the phenomenon can be termed as a quantum confinement phenomenon. The confinement of materials in all the three dimensions is termed as quantum dots (QDs). Recently, nanotechnology exclusively based on QDs has successfully entered numerous electronic and biomedical industries. QDs can also act as a fluorescent probe for variety of applications. In the present study, the optical properties of the quantum dots were utilized for the sensing applications. The quantum dots are synthesized with the help of different organic ligands. The ligands stabilize the quantum dots by encapsulating it, resulting in effectively exhibiting of the quantum phenomenon. Although there was a substantial number of applications, where these nanomaterials have employed, there is still room for exploration, in terms of understanding the fundamentals, their intriguing physical and chemical nature, and fabrication of these materials on accordance with the current needs. We have synthesized a range of nanoparticles based on CdTe QDs, performed a comprehensive morphological and photophysical characterizations and demonstrated their chemical sensor applications for the detection of biological, environmental and industrially significant molecules. The studies conducted using various CdTe QDs given in this thesis is briefed below.

In the present thesis, we tried to synthesize the quantum dots using various novel ligands. The purpose of the study was to understand the significance of the branched chain ligands, where one methyl group is present in one of the branches of the ligand. This makes the ligand bulkier than the conventional linear chain ligands. For the synthesis of the quantum dots, we preferred a colloidal synthetic route over the other available methods due to the ease of its synthesis. We have made use of the three novel ligands, using which we have synthesized the CdTe quantum dots and the same quantum dots has been studied for fluorescence sensing applications.

In the first work we synthesized CdTe quantum dots using 3MIBA ligand and studied the properties of the quantum dots using various characterization techniques like TEM, XRD, XPS, UV-VIS spectroscopy and Fluorescence spectroscopy. The lifetime studies and zeta potential studies were also conducted to get more insights into

our system. The as synthesized 3-MIBA capped CdTe quantum dot (CdTe@3-MIBA) was found out to be highly fluorescent and was successfully used to detect the mercury ions at the nano-molar concentration. The performance of the sensor was found out to be linear in the range of 1.5–100 nM with an excellent detection limit of 1.5 nM. The mechanism of sensing was decoded using various studies and it was concluded that the quenching behavior of the sensor was due to the electron transfer and aggregation.

We explored the possibility of using another novel branched chain ligand namely ethyl 2-mercaptopropionate for the synthesis of CdTe quantum dots. Extensive microscopic and photo physical characterizations revealed the behavior of the synthesized QD's. In the present case, the QDs, were found out to be highly sensitive for Cu^{2+} ions. A detailed studies were performed to unearth the mechanism of quenching of the QD's in the presence of Cu^{2+} ions. The sensor was linearly responding in the range of 0.5 nM to 129.5 nM with a detection limit (LOD) of 0.5 nM, providing a pathway for the QDs based Cu^{2+} probe.

The synthesis of highly fluorescent water soluble CdTe QDs using a novel branched ligand 3-Methoxybutyl 3-mercaptopropionate (3MB3MP), by facile colloidal synthesis method. The synthesized QD shows excitation independent high fluorescent emission at 590 nm upon exciting at 360 nm wavelength. The QDs shows excellent temporal stability and a typical phenomenon of photo-brightening/photo activation effect, up to 190 minutes of continuous irradiation of UV rays. The fluorescence is then found to quench suddenly, under further irradiation. We have proposed a model for this photoactivation effect, by conducting thorough investigation. We hypothesize that, the in-situ formed ROS species may be interacting with the surface of QDs and satisfying the dangling bonds present on the surface of QDs. This can ultimately reduce the sites for non-radiative decay, and thus enhancing the fluorescence emission. The results obtained from photoactivation studies motivated us to investigate the effects of ROS, in laboratory condition as well. For this purpose, we have chosen, one of the typical ROS, H_2O_2, which is the most stable among ROS. We have observed that, in the presence of H_2O_2, even in the absence of UV radiation, the fluorescence emission of CdTe@3MB3MP QDs are found to be enhanced. Therefore, a novel label free fluorescence-based detection of H_2O_2 has been demonstrated using CdTe@3MB3MP QDs. The fluorescent emission is found to be enhanced in linear fashion within a range of 10- 250 nM concentration of H_2O_2, which then found to collapse significantly upon concentrations higher than 300 nM. A thorough photophysical and microscopic characterizations has been carried out in order to unveil the mechanism of H_2O_2 detection, including UV-Vis absorption spectral studies, FTIR, XPS, time resolved fluorescence decay studies etc.