Detection of lead Using Thioglycolic Acid Capped ZnSe and ZnSe@ZnS core-shell Quantum Dots

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Abstract. Herein, we proffer a sensitive and selective sensor using ZnSe and ZnSe@ZnS quantum dots (QDs), for detection of toxic metal ions at nm level. It has been found that the TGA capped ZnSe and ZnSe@ZnS QDs were apparently sensitive to Pb²⁺ ions as perceptible from their fluorescence quenching measurements. However, in case of few common heavy metal ions such as Zn²⁺, Co²⁺, Fe²⁺, Mg²⁺, Ni²⁺ and Cd²⁺ ions, negligible quenching compared to Pb²⁺ ions was noted. Hence, we have successfully detected Pb²⁺ ions in aqueous solutions based on the photoluminescence (PL) spectroscopy. The observed linearity range was from 10 NM to 100 nM for both Pb²⁺ ions. An alternative QD based sensor for the spectroscopic detection, and concentration quantification of Pb²⁺ ions is proposed.

Keywords: Quantum dots, Photoluminescence, Metal ions, Thioglycolic acid, Core-shell QDs.

1. Introduction
Luminescent quantum dots (QDs) have attracted the interest of current researchers, due to their unique photophysical properties[1]. Selective and specific sensing abilities of nanostructures for biomolecules and metal toxic ions have attracted the tremendous attention of current researchers because of their societal importance. Huang et.al., Mir et.al., and Chakraborti et.al, proposed that QDs based optical sensor could be development for detection of bioanalytes, metal and other environmental pollutants [2–4]. Metal contaminated water is a source of innumerable diseases and therefore become a major threat for the humans related to their health issues. Among the heavy metals Lead ions present in drinking water can cause, coma, convulsions nausea, cancer , renal failure, and subtle effects on metabolism and intelligence[5]. But one of the major issues related to the quantum dots research is their toxicity. Unfortunately, the extensively studied Cd based QDs could hardly be used in medical fields because of their known toxicity[6]. To overcome these issues herein, we proposed ZnSe based QDs as an alternative to the Cd-based toxic QDs. To improve the photophysical properties such as PL quantum yield and stability against the oxidation, ZnSe@ZnS core-shell structures were developed. These core and core-shell nanostructures were used shows improved optical sensing of lead in lead contaminated water samples. It was found that the QDs were very specific for sensing of lead. Therefore, an optical sensor for the detection of lead at nM level has been proposed here.
2. Materials and Methods

Thioglycolic acid and Zinc acetate were acquire from central drug house, India; powdered selenium (~100 mesh, 99.999%), sodium borohydride (NaBH₄, 99%), and thiourea (99%), were acquire from SD-fine chemicals, India and Sigma-Aldrich, USA, respectively.

A facile and feasible cadmium-free approach for the preparation of ZnSe and their core-shell particles is already reported in our previous work [7]. Typically, zinc acetate (0.2 mmol) in presence of 20 ml aqueous solution TGA (0.24 mmol) at pH 11.5 was made to react with 2 ml NaHSe solution (0.08 M) in a reaction beaker. NaHSe solution was made by reacting selenium powder with NaBH₄. The reaction mixture was then heated to 90°C for 1hr followed by immediate cooling to room temperature.

Core-shell derivatives was obtained by using 20 ml of ZnSe prepared solution in presence of a 10ml mixed solution that containing Zinc acetate (0.12 mmol) and 2, TGA (0.18 mmol) of, and thiourea (0.12 mmol) at a pH of 10.2. This solution was kept under magnetic stirrer at 90°C for 2 h and followed by immediate cooling to room temperature.

3. Characterization and discussion

3.1 Characterization

After the successful synthesis TEM was employed for size analysis of these QDs. The TEM images of these core and core-shell nanostructures are shown in Figure 1. The average size of these ZnSe core only (inset Figure 1A) and ZnSe@ZnS core-shell (inset Figure 1B) QDs obtained from the TEM analysis using Imagej software were found respectively, as 3.60 ± 0.12 and 4.80 ± 0.20 nm. The stability analysis of nanostructures was confirmed from the electrophoresis measurement. It was found that zeta potential of -38 mV assigned for ZnSe QDs, whereas as for core-shell ZnSe@ZnS QDs as -45 mV [7]. UV-Vis and fluorescence measurements were used to find the photoluminescence quantum yield (PLQY) of these ZnSe QDs and their core-shell QDs. It was seen that the PLQY increase from 13% to 32% while shifting from core to core-shell structures [7]. XRD measurement shown in inset Figure 1B shows the shifting of XRD peaks of ZnSe@ZnS towards the higher 2θ value compare to ZnSe nanocrystals. This peak shifting of is a consequence of development of ZnSe@ZnS structures. Detailed analysis of physical measurements of synthesized QDs has been described in Mir et.al. 2017[7].

3.2 Detection of Toxic Metal Ions

The effect of metal ions adsorbed onto the surface of ZnSe and their core-shell nanostructures may be different from that expected from the bulk samples. It is evident from Figure 2(A) fluorescent intensity
of TGA modified ZnSe and ZnSe@ZnS QDs was quenched by 90% in solution after addition of Pb2+ ions with varies concentration from 10 to 100 nM.

In order to understand the selectivity of QDs towards detection of Pb2+ ions, the quenching response of QDs in presence of other relevant metal ions was analysed. The detection responses were found up to 1 mM level. The luminescence intensity was minimally affected by Cd2+, Cu2+, Fe2+, Zn2+, Co2+, Mg2+ and Ni2+ ions.

The Pb2+ ions effectively quenches the fluorescence intensity (Figure 2) of TGA capped ZnSe and ZnSe@ZnS core-shell nanostructures by easing the electron-hole non-radiative recombination. The fluorescence quenching is a consequence of the formation simple QD-metal complex. Therefore this quenching data was used to determine the binding parameters of the complex by using Stern Volmer Equation (1)

\[
\log \left( \frac{I_0 - I}{I} \right) = \log K_b + n \log [Q]
\]

The binding plot of log \((I_0 - I)/I\) against to log [Q] as seen in Figures 2 C, are used to find the binding parameters. The binding constant \(K_b\), and corresponding occupied number of binding sites \(n\), were calculated from the intercept and slope of the Figure 2C, which yielded the binding constant \(K_b \approx 9.8 \times 10^{-10}\) for ZnSe and \(2.9 \times 10^{-8}\) M ZnSe@ZnS samples. The corresponding average number of binding sites are \(n=1.4\) and 1.1, respectively.

**Figure 2.** Fluorescence quenching spectra of ZnSe QDs (A) and ZnSe@ZnS core-shell QDs (B) in presence of varied concentration of lead (0, 10, 20, 30, 40, 50, 60, 70, 80, 90, 100 nM). (C) Stern Volmer binding plot of QD-Lead complex.

4. Conclusion

This work describes the sensing potential of ZnSe and ZnSe@ZnS core-shell QDs for heavy metal ion detection. The luminescence response of QDs was investigated in presence of these toxic ions. These core and core-shell structures manifested a selective detection response towards lead ions, and overt minimal sensing response to other metal analytes. As per the WHO norms, lead ion concentration in the drinking water should be 0.01 mg/L (0.48 µM). With TGA capped ZnSe and ZnSe@ZnS QDs, we could detect lead ion at 10 nM level. We propose a sensing platform for the quantification of Pb^{2+} ions.
in water samples. Since lead is a major pollutant mostly available in industrial affluent, but the attention for their detection and remediation can hardly be stressed. Binding constant of $9.8 \times 10^{-10}$ and $2.9 \times 10^{-8}$ M was estimated, respectively for ZnSe-Pb$^{2+}$ and ZnSe@ZnS-Pb$^{2+}$ complex. To the best of our knowledge, ZnSe and ZnSe@ZnS QDs are the first reported system used for the detection of toxic lead ions. The simplicity, rapidity and cost-effectiveness make the present system quite efficient for the detection of lead ions. The corresponding average number of binding sites are $n=1.4$ and 1.1.

Acknowledgments

This work was financially supported by the grants from the Science and Technology Innovation Commission of Shenzhen (Grant No. ZDSYS201707271554071; We also acknowledge Project supported by GDHVPS (2016) and the Basic Research Plan Program of Shenzhen City in 2016 (Grant No. JCYJ20160509100737182).

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