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Size dependent ratiometric detection of Pb (II) ions in aqueous solution by light emitting biogenic CdS NPs

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ABSTRACT

We have synthesized water soluble CdS quantum dots (QDs) in different sizes (~ 3, 10 and 25 nm) via a green rout using pomegranate peel extract as a reducing and stabilizing agent. The particles with the size of ~ 3, 10 and 25 nm respectively exhibit blue, green and yellowish red emission under UV light. We have utilized the NPs for the discrimination of metal ions in aqueous solution. Interestingly, the fluorescence from the NPs undergoes a ratiometric variation *only* in presence of Pb^{2+} ions, indicating that the system can act as a potential Pb^{2+} ion sensor. There was a remarkable size dependent stock shift (~ 270 nm) upon the addition of Pb^{2+} ions, which enables the detection by naked eye. DLS study indicates that Pb^{2+} ions induce aggregation in the system owing to the complex formation between the capping agent and the metal ion. The aggregation, in turn, generates inter plasmon coupling and results in emission color variation. The naked eye detection limit of Pb^{2+} ions in solution was found to be 10^{-9} M. This is the first study of Pb^{2+} ion sensing using CdS quantum systems and the detection procedure is easy-to-make, less time consuming and highly re-producible. The present method enables direct application of the system for detecting Pb^{2+} ions due to the presence of ratiometric fluorescence, leading to a large Stokes shift and associated color change in the visible region.

1. Introduction

Quantum dots and nanoparticles have been extensively used for bio-labelling [1], tissue engineering [2], sensing applications [3], light harvesting [4], photo-catalysis [5], developing photo-electronic devices [6], enhancing the contrast of MRI images [7], and targeted drug delivery [8]. Numerous synthetic methods were developed towards preparing quantum dots and nanoparticles due to their wide range of potential applications. The available methods for the preparation of CdS NPs/QDs are biosynthesis [9,10], chemical precipitation [11], sol gel [12], micro emulsion [13], reverse micelles [14], hydrothermal [15], laser irradiation [16], template method [17], micro wave irradiation [18], micro capillary reactor [19], sonochemical reduction [20] and solvothermal [21]. Among them, biosynthesis of QDs/NPs by plant or its fractions receives much attention in recent years due to its simple, eco-friendly, non-toxic nature [22]. More importantly, utilizing bio-friendly species to prepare and stabilize QDs/NPs will reduce nanoparticle's toxicity and make them more useful for biological applications [23,24]. In this framework, we described the synthesis of CdS QDs and NPs using pomegranate peel extract. The nanoparticles were expected to be stabilized by the phytochemicals (punicalagin and punicalin) [25] present in the aqueous pomegranate peel extract.

Semiconductor quantum dots or nanoparticles have been utilized for the development of sensors because of their high surface area, desired optical and electronic properties which include a broad excitation spectra, narrow emission, color tunability as a function of size and resistance to photo bleaching [26–29]. The luminescence of QDs/NPs emerge, mainly from the recombination of the charge carriers. The alterations of surface charge or ligand components of the QDs/NPs would influence the efficacy of the electron–hole recombination and accordingly the luminescence efficiency. Hence, a chemical sensor constructed on QDs/NPs can be established using fluorescence changes, made by the direct physical adsorption or chelation of ions or small molecules on the exterior of the QDs/NPs, stimulated by the exchanged ligand [30].

Herein, we synthesized a fluorescent probe based on CdS QDs which is stabilized by pomegranate peel extract as a fluorescent sensor towards toxic Pb^{2+} ions. While a few quantum dots have been utilized for detecting toxic metal ions, CdS based QDs have not been utilized for detection of Pb^{2+} ions, till date. Lead is a toxic heavy metal, which is wildly spread and associated with environment pollution. Detection of Pb^{2+} ions in water is important because lower level of exposure of lead ions can cause adverse health effect to living and eco-system. Lead ions affect the central nervous system, gastrointestinal track and human growth [31]. According to World Health Organization (WHO) a limiting concentration of Pb in drinking water is as 10 ppb [32]. The fluorescent based sensors for Pb^{2+} are attractive because of their sensitivity, and

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selectivity [33–35].

We hypothesis that, the capping molecules on the CdS QDs surface can interact with metal ions which leads to aggregation and associated shift in the fluorescence of the QDs. In this context, we have examined the selectivity of Cds QDs/NPs towards the binding of Pb^{2+} ions. We also monitored the detection as well as the aggregation of QDs in presence of Pb^{2+} by photoluminescence spectroscopy, dynamic light scattering method and transmission electron microscopy. Since CdS QDs are known for their good emission quantum yields, possibility of a naked eye detection of the toxic metal ions by the system was investigated. Naked eye detection of the analyte will be more attractive and convenient since it eliminates the involvement of expensive equipment.

2. Experimental

2.1. Biosynthesis of water soluble CdS quantum dots and nanoparticles

The materials are gotten from Sigma-Aldrich (USA) and used as acknowledged. The experiment was performed using deionized water. The pomegranate (local market, Chennai, TN, India) peel extract was prepared by adding the peels into the deionized water and the mixture was heated for 5 min. The resulted solution was filtered using Whatman filter paper and used it for the experiments [25]. Aqueous solutions of $CdCl_2$ (0.5×10^{-2} M to 1×10^{-3} M) and Na_2S (0.5×10^{-2} M to 1×10^{-3} M) were prepared. Na_2S (5 mL) was mixed into a stirring solution of $CdCl_2$ (5 mL). Pomegranate peel extract (3 mL) was added into the reaction mixture, after that the addition of distilled water (5 mL) into the reaction mixture so as to elude the agglomeration. The solution was stirred for 30 min at room temperature. The as-synthesized nanoparticles were centrifuged and washed with distilled water in order to eliminate the unreacted precursors and biomolecules from the extract.

2.2. Colorimetric evaluation

Colorimetric detection test in existence of different metal ions (Na^+, Mg^{2+}, K^+, Zn^{2+}, Li^+, Ca^{2+}, Cu^{2+}, Mn^{2+}, Co^{2+}, Pb^{2+}, Cd^{2+}, Hg^{2+}, Ni^{2+}, UO_2^{2+}, Ba^{2+}, Fe^{2+}, Bi^{3+}, Fe^{3+}, As^{3+}, Al^{3+}, Cr^{3+}, Ce^{4+}, V^{4+}, As^{5+}) were performed in aqueous solution by biosynthesized CdS quantum dots and nanoparticles at room temperature. The metal ions concentration were varied from 10^{-2} M to 10^{-9} M. Metal ion (100 μL) was added to CdS (200 μL), along with the addition of ~ 1 mL of water. Fluorescence spectroscopy was used to observe the changes in the peak position of as-synthesized CdS QDs/NPs with the addition of analyte.

2.3. Characterization of CdS QDs and NPs

UV–visible absorption measurements were done on UV-3100 Hitachi spectrometer. Zeta potential and particle size measurements were recorded by Malvern-zeta sizer. The IR spectra have been studied by Perkin-Elmer FT-IR spectrometer. Photoluminescence experiments were carried out by HORIBA Jobin Yuvin Fluoromax-4 spectrofluorometer. The morphology and size of CdS NPs was analysed using transmission electron microscopy (TEM-Philips Tecnai 12). Energy dispersive X-ray spectroscopy (EDAX) and selected area electron diffraction (SAED) study were recorded by TEM, furnished with an EDAX and SAED accessory. X-ray diffraction analysis was done by advance powder X-day diffractometer (Bruker D8) with Cu Kα radiation. The pictures were clicked with digital camera (Canon A3200 IS).

3. Results and discussion

3.1. Influence of precursor concentration

The objective of the work is to synthesize different sized CdS nanoparticles using aqueous pomegranate peel extract and use the system as a sensor for toxic metal ions. In our method, the synthesis of CdS NPs involves addition of $CdCl_2$ and Na_2S followed by the mixing of pomegranate peel extract at room temperature. We have changed the concentration of the precursor from 0.5×10^{-2} M to 1×10^{-3} M which resulted in CdS QD and CdS NP. Table S1 summarizes the various precursor concentrations used for the present study. The UV–vis absorption spectra of synthesized nanoparticles at various concentration of precursor are given in Fig. S1. The nanoparticles have shown size dependent UV–vis absorption spectrum which is comparable with the hydrothermal synthesis of CdS nanoparticles by Schneider research group [36]. The variations in the emission color of the nanoparticles indicate that the size of the nanoparticles is different and the precursor concentration plays a role in controlling the size (Figure in Table S1). The DLS measurement and zeta potential results also revealed that the CdS nanoparticles prepared with higher concentration of the precursors lead to aggregation of the particles which reduce the fluorescence intensity of the sample. The CdS QDs/NP prepared from 10^{-2}:10^{-3}, 10^{-3}:10^{-3}, 0.5×10^{-3}: 10^{-3} M of $CdCl_2$:Na_2S (sample D, G and H) are relatively stable and have shown interesting photophysical properties. Hence, we have chosen these three samples for further studies.

3.2. Characterization of CdS QDs and NPs

Fig. 1a-f represent TEM images of three different CdS nanosystems synthesized using 0.5×10^{-3} M of $CdCl_2$ and 10^{-3} M of Na_2S produced monodispersed spherical quantum dots with a width of ~3 nm (CdS QDs). Increasing the concentration of the precursor such as $CdCl_2$ and Na_2S (10^{-2}:10^{-3} and10^{-3}:10^{-3}) led to spherical, monodispersed nanoparticles with the size of ~10 nm (CdS NP1) and ~25 nm (CdS NP2). The average diameter of the CdS particles are given in fig. S2. The high resolution TEM image shows that the lattice planes of CdS QDs and NPs are well determined. From the lattice fringes of the micrograph (Fig. 1d-f), the interplanar spacing (d) of CdS QDs, NP1 and NP2 was estimated as 0.31 nm which is associated to the d value of (111) plane in cubic CdS [36]. The resultant selected area electron diffraction pattern of CdS samples also confirmed the crystalline nature of the nanoparticle (Fig. 1g-i). Fig. S3 shows the EDAX pattern acquired from CdS QDs, CdS NP1 and CdS NP2, which confirms the presence of Cd and S in the sample. The XRD pattern of CdS QDs and NPs show diffraction peaks located at 2θ equal to 26.4°, 43.8° and 51.6° corresponding to the planes (111), (220) and (311) which suggests that all the formed CdS particles are cubic zinc blende structure [37] (Fig. 2a).

Fig. 2b shows the UV–vis absorption spectra of as-synthesized CdS NPs (sample D, G and H). The biosynthesized CdS QDs, CdS NP1 and CdS NP2 have shown the absorption peak at 357 nm, 369 nm and 371 nm, respectively. The change in the absorption peak from 357 nm to 371 nm indicates that increase in the particle size of the CdS nanoparticles [36]. It can be seen that there is a formation of hump at 418 nm in the case of CdS NP2 which indicates the formation of bigger size of nanoparticle through agglomeration of the sample. Fluorescence spectra of as-synthesized CdS nanoparticles are given in Fig. 2c. CdS QDs, CdSNP1 and CdSNP2 have shown emission at 450 nm, 546 nm and 610 nm, when the samples were excited at 335 nm, 350 nm and 380 nm, respectively. It is visible that the emission peak position differs in three different samples in a comparable way as the absorption peak position. We observed a blue shift in the case of CdS QDs relative to CdS NP1 and CdS NP2 due to its smaller size. The noticed broad emission peak is ascribed to the recombination of charged carriers trapped in the surface states, which is associated to the size of CdS particles [38,39].

3.3. Mechanism for the generation of CdS QDs and NPs

Aqueous pomegranate peels extract are abundant in source of phytochemicals for example punicalagin and punicaline [40,41]. These biomolecules are bound on the exterior of CdS nanoparticles and stabilized them in the solution [36]. The functional groups which are