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Effect of capping agent on selectivity and sensitivity of CdTe quantum dots optical sensor for detection of mercury ions

Mohmed Labeb[a], Abdel-Hamed Sakr[b], Moataz Soliman[a], Tarek M. Abdel-Fettah[c], Shaker Ebrahim[a,*]

[a] *Department of Materials Science, Institute of Graduate Studies and Research, Alexandria University, P.O Box 832, Egypt*
[b] *Physics Department, Faculty of Science, Damanhour University, El-Behara, Egypt*
[c] *Applied Research Center, Jefferson National Lab and Department of Biology, Chemistry and Environmental Science, Christopher Newport University, Newport News, VA 23606, USA*

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ABSTRACT

Cadmium telluride (CdTe) quantum dots (QDs) were prepared from an aqueous solution containing $CdCl_2$ and Te precursor in the presence of thioglycolic acid (TGA) or L-cysteine as capping agents. Two optical sensors have been developed for Hg^{2+} ions with very low concentration in the range of nanomolar (nM) or picomolar (pM) depending on the type of capping agents and based on photoluminescence (PL) quenching of CdTe QDs. It was observed that low concentrations of Hg^{2+} ions quench the fluorescence spectra of CdTe QDs and TGA capped CdTe QDs exhibited a linear response to Hg^{2+} ions in the concentration range from 1.25 to 10 nM. Moreover, it was found that L-cysteine capped CdTe QDs optical sensor with a sensitivity of $6 \times 10^9\ M^{-1}$, exhibited a linear coefficient of 0.99 and showed a detection limit of 2.7 pM in range from 5 to 25 pM of Hg^{2+} ions was achieved. In contrast to the significant response that was observed for Hg^{2+}, a weak signal response was noted upon the addition of other metal ions indicating an excellent selectivity of CdTe QDs towards Hg^{2+}.

1. Introduction

The two main parameters of chemical sensors to detect the highly toxic heavy metal cations are high sensitivity and selectivity [1]. Mercury cation ion (Hg^{2+}) is a well-known chemical pollutant and possesses serious menaces to human health and the environment. Hg^{2+} is highly toxic for its bioaccumulative and persistent character, which causes serious damage to the central nervous and endocrine systems [2,3]. The United States environmental protection agency has mandated a limit of 10 nmol/L for Hg^{2+} in drinking water [4]. Consequently, it is paramount to develop a simple and reliable method for rapid and sensitive determination of Hg^{2+} ions. Several conventional Hg^{2+} detection techniques have been developed including atomic fluorescence spectrometry, atomic absorption spectroscopy, inductively coupled plasma-mass spectrometry and enzyme linked immune sorbent assay. Most of these detection techniques require highly precise sample preparation, expensive equipment, and long turnaround time [4–6].

Several of optical sensors for Hg^{2+} detection based on the fluorescence property have been developed. These fluorescent sensors depend on the change of fluorescence intensity of small organic molecules to determine the Hg^{2+} concentration. Small organic molecules showed some inevitable problems, such as most of them are water insoluble. Although metal ions can be chelated in organic solvents, it is rather difficult to directly recognize them in aqueous solution because of their strong hydration. Furthermore, these fluorophores exhibited a low signal intensity and photobleaching. In addition, most of them have narrow excitation spectra and broad emission band with red tailing, which influence the detection of Hg^{2+} ions. These disadvantages can be avoided by using semiconductor nanocrystals or quantum dots (QDs) [7–9].

Quantum dots can be defined as the bridge between cluster molecules and bulk materials. They can be prepared by several of physical and chemical approaches. QDs have interesting optical properties such as narrow, tunable and symmetric emission spectra and broad absorption spectra. Their emission can also cover a broad range of the light spectrum from visible to infrared depending on their types and crystal sizes [10–17]. Therefore QDs can be used in a wide range of applications including solar cells, light-emitting devices, bioimaging and sensors [18–23].

Tingting Gong et al. [24] developed L-cysteine capped CdTe QDs as a sensor platform for sensitive and selective silver, mercury and copper ions. Excellent linear relationships were found between the quenching

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[*] Corresponding author. Institute of Graduate Studies and Research, Alexandria University, PO Box 832, 163 Horreya Avenue, El-Shatby, Alexandria, Egypt.
E-mail address: shaker.ebrahim@alexu.edu.eg (S. Ebrahim).

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degree of the sensing platform and the concentrations of Ag^{+}, Hg^{2+} and Cu^{2+} ranging from 0.5 to 40 ng mL^{-1}. Hu Tianyu et al. [25] prepared aptamer-based aggregation assay for mercury (II) using gold nanoparticles (Au NPs) and fluorescent CdTe QDs. The red Au NPs/aptamer system reduced the green fluorescence of cysteamine-capped CdTe QDs. Fluorescence intensity was linearly proportional to the concentration of Hg^{2+} in the range from 50 pM to 1.0 nM. In this work water-soluble CdTe QDs with different capping agents of L-cysteine and thioglycolic acid (TGA) were prepared and evaluated to be acting as fluorescence probes for Hg^{2+} ions in the concentrations range of nM and pM. The proposed mechanisms of the interactions between Hg^{2+} ions and CdTe QDs are suggested. The selectivity of CdTe QDs probe towards Hg^{2+} ions are compared with other metals ions such as Zn^{2+}, Se^{2+}, Cu^{2+}, Cd^{2+}, Al^{3+}, Fe^{3+} and Pb^{2+} solutions at the same concentration.

2. Materials and methods

2.1. Materials

Sodium borohydride was purchased from Merck. Cadmium chloride (20% hydrate) and L-cysteine was received from Sigma chemical Company. Tellurium powder (99.99%) was obtained from Microphysic. TGA was received from Merck Schuchardt OHG. Isopropanol and ethanol were bought from Aldrich. Mercury chloride (99.9%) was brought from Merck Company.

2.2. Preparation of CdTe QDs with different capping agents

2.2.1. Preparation of NaHTe solution

NaHTe solution was prepared by mixing of 40 mg of tellurium powder and 45 mg of $NaBH_4$ in a three neck flask and then 5 ml deionized water were added. This mixture was kept at 60 °C for appropriate time under N_2 flow to get a deep purple clear solution.

2.2.2. Preparation of TGA or L-cysteine capped CdTe QDs

CdTe QDs dissolved in water were prepared by the following method. A capping agent (TGA or L-cysteine) (3.0 mmol) and $CdCl_2$ (20% hydrated) (330 mg) were dissolved in 100 ml of ultrapure water. The pH of this mixture was adjusted to 12.0 b y dropwise addition of NaOH solution (1.0 M) with continuous stirring in a conical flask to obtained clear solution. Then, the fresh NaHTe solution was injected at 80 °C through a syringe promptly under continuous stirring to the above $CdCl_2$ solution. In the case of using L-cysteine as a capping agent the injection was conducted at 70 °C. The CdTe QDs solution was boiled under reflux at 90 °C for 60 min. The CdTe QDs solution was purified and separated by adding isopropyl alcohol and by centrifugated at 10,000 rpm for 5 min. The last step was repeated several times to remove unreactants.

2.2.3. Detection of Hg^{2+} by CdTe QDs

To 5 ml volumetric flasks, the luminescent CdTe QDs solution (2 ml) and various amounts of freshly prepared Hg^{2+} ions solution were sequentially added. This mixture was diluted to 5 ml with ultrapure water and was incubated under darkness for 20 min at room temperature. The fluorescence spectra of this mixture were measured in the range from 470 to 700 nm with an excitation wavelength of 450 nm. PL measurement was carried out at room temperature with a (Perkin Elmer LS-55) spectrometer. For selectivity measurement, the Hg^{2+} solution was replaced by Zn^{2+}, Se^{2+}, Cu^{2+}, Cd^{2+}, Al^{3+}, Fe^{3+} and Pb^{2+} solutions with the same concentration.

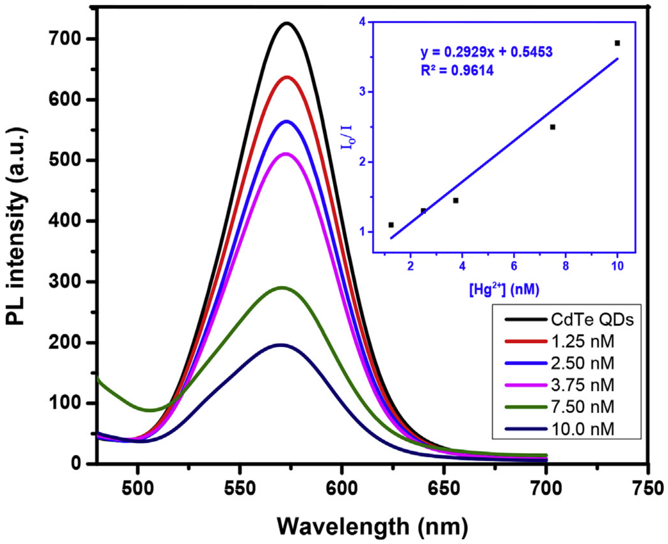

Fig. 1. Effect of Hg^{2+} concentrations on PL spectra of TGA capped CdTe QDs. Insert: Stern-Volmer relationship between PL intensity of CdTe QDs and concentration of Hg^{2+}.

3. Results and discussion

3.1. Emission properties of TGA capped CdTe QDs and detection of Hg^{+2}

Fluorescence quenching process is a reaction between fluorescent molecules and the quencher molecules to induce a decay in the fluorescence intensity [26]. The maximum PL intensity of TGA capped CdTe QDs was used for the detecting low concentrations of Hg^{2+} ions in aqueous medium. The pristine CdTe QDs have a symmetric emission peak at about 550 nm as shown in Fig. 1. When the excitation energy had a photons energy that exceeded the bandgap, they were absorbed by CdTe QDs and the electrons were promoted from the valence band to the conduction band. These excited electrons then are relaxed to their ground state by the emission of other photons with energy equals to the band-gap. The influence of Hg^{2+} ions on the PL intensity of TGA capped CdTe QDs is presented Fig. 1. It is observed that the presence of small concentration of Hg^{2+} ions produced a quenching in the fluorescence of the TGA capped CdTe QDs. The PL intensities of TGA capped CdTe QDs have gradually declined as the concentration of Hg^{2+} ions have increased. PL spectra have a nonzero tail at longer wavelength, suggesting the presence of surface energy traps and surface defects. This fluorescence is attributed to the recombination of the charge carriers at surface states [27]. For the concentration in the range of nM of Hg^{2+}, the maximum intensities of the emission wavelength did not shift and this is confirmed the fixed size of CdTe QDs [28]. The five proposed mechanisms explaining the fluorescence quenching by metal ions are cation-exchange [29], competition of ligands [30], electron transfer [31], binding with surface ligands [32] and inner filter effect [33]. The fluorescence of TGA capped CdTe QDs is sensitive to the surface states. The surface charges of TGA capped CdTe QDs can modify their photophysical properties. Hg^{2+} ions quench the PL intensity of the CdTe QDs through the interacting of metal ions with the capping layer of CdTe QDs [34,35]. The fluorescence quenching is also attributed to the non-radiative electron-hole recombination on the surface of the TGA capped CdTe QDs. This takes place through an effective electron transfer process between the surface functional groups of capping agent and Hg^{2+} ions based on the strong affinity with the functionalized TGA capped CdTe QDs [36–39] as illustrated in the schematic diagram of Fig. 2. The fluorescence intensity of CdTe QDs and the concentration of Hg^{2+} ions can be described by Stern-Volmer equation [22,40,41] as follows: