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Hot injection versus room temperature synthesis of CdSe quantum dots: A differential spectroscopic and bioanalyte sensing efficacy evaluation

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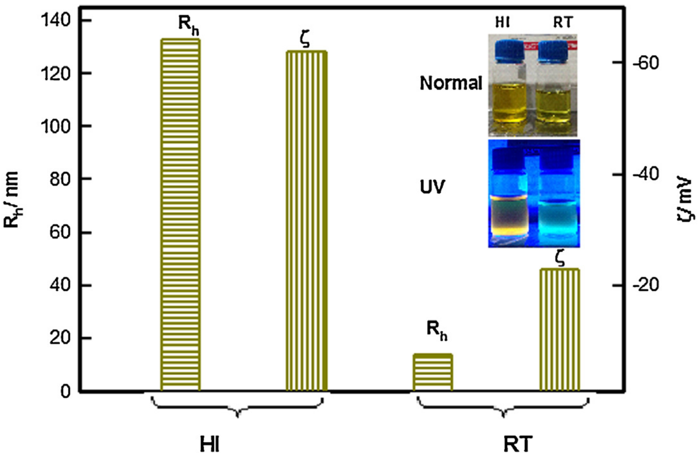
HIGHLIGHTS

- Comparative study of structural, optical, and sensing properties of CdSe quantum dots (QDs) synthesized by hot-injection (HI), and room temperature (RT) protocols discussed.
- Steady state and time resolved fluorescence spectra revealed differential quantum yield (higher photochemical stability and 10 folds quantum efficiency for HI-QDs), and life-times as function of synthesis protocol.
- HI-QDs could be synthesized in the size range of 2.5–6.3 nm whereas by RT method only fixed size (≈3.3 nm) nanoparticles could be prepared.
- HI-QDs (zeta potential, $\zeta \approx -60$ mV) protocols were electrostatically more surface active compared to their RT ($\zeta \approx -24$ mV) counter parts.
- HI-QDs have limited sensing capability as compared to the room temperature protocol QDs are concerned.

GRAPHICAL ABSTRACT



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ABSTRACT

In this work, we have performed an exhaustive comparative study of structural, optical, and sensing properties of CdSe quantum dots (QDs) synthesized by hot-injection (HI), and room temperature (RT) protocols. CdSe QDs were synthesized in aqueous solution at room temperature by reacting cadmium chloride pentahydrate ($CdCl_2{\cdot}5H_2O$) with sodium hydrogen selenide (NaHSe) in presence of capping agent 3-mercaptopropionic acid (MPA). In hot-injection (HI) method elemental Se was reacted with CdO at 225 °C. These were characterized by XRD, TEM, EDX, UV–vis, and fluorescence spectroscopy. The EDX measurements indicated that these quantum dots were highly pure, and had their composition as ≈Cd:Se = (1:1) (atomic% by weight) for both types of QD samples. These exhibited relatively narrow fluorescence band and high fluorescence intensity in the yellow spectral range. The HI-QDs exhibited high photochemical stability, and offered sufficient promise for application in design of optoelectronic devices. Steady state and time resolved fluorescence spectra revealed differential quantum yield (higher for HI-QDs), and life-times as function of synthesis protocol. However, the optical response profile revealed higher binding efficacy of RT-QDs in respect for oxalic, ascorbic acid, citric acid, and hydrogen peroxide analytes. Therefore, it is concluded that HI-QDs had rich spectroscopic signature, but poor sensing attributes (against ascorbic acid, citric acid, oxalic acid, and hydrogen peroxide) compared to RT-QDs. Further, HI-QDs could be synthesized in the size range of 2.5–6.3 nm whereas by RT method only fixed size (≈3.3 nm) nanoparticles could be prepared.

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1. Introduction

Synthesis of semiconductor nanoparticles, also known as quantum dots (QDs), is envisaged as important building blocks for fabrication of advanced optical and photonic materials because of their size-dependent optical transition properties. Because of their specific applications, the synthetic methodology, and surface engineering of these QDs must be addressed on case to case basis. Colloidal quantum dots are of interest for fabrication of optoelectronic devices such as light emitting diodes [1], and bioimaging [2] and photo-voltaics [3]. The development of such devices relies on the optimization of synthesis, and processing conditions to enhance energy transport, and their optical properties. Simultaneously, these need to be water dispersible to allow for biocompatibility for applications in biology. The quantum dots are colloidal semiconductor nanocrystals with well-developed electronic energy levels. Incidentally, these QDs are extensively studied nanostructures because of their size-dependent fluorescence (F) properties which arise from quantum-confinement that are tunable across a large part of the visible spectrum [4]. The spectroscopic attributes like absorption and fluorescence emission profiles have been characterized both experimentally, and discussed theoretically as a function of composition and their structural anisotropy [5–9]. Further, the empirical relationship between size, and absorption maximum wavelength has been established experimentally [7,8]. These features have been partially understood in the framework of effective mass approximation incorporated to solid-state electron-in-quantum-well models [10]. However, this approach is applicable to relatively large structures. Recently, more sophisticated models, and concepts have been applied to understand electronic transitions occurring in smaller structures [5,6,11].

In QD synthesis despite significant progress being achieved, the procedure is still not facile as one would like. For example, the need to use high-boiling-point solvents (organometallic route and the derivative methods), is the most general strategy to obtain high quality QDs, and high temperature over 250 °C is needed which often lead to inflammable conditions in the laboratory. Meanwhile, to avoid the oxidation of reagents and/or QDs, the reaction is conducted in vacuum. In addition, multi-step accessorial precursor preparation is required before the actual synthesis.

The core-only CdSe QDs normally exhibit low luminescence efficiency, which necessitates their appropriate surface passivation for wider applications, and enhancement of their luminescence efficiency. Numerous protocols of organic and inorganic surface modifications were employed in the past to passivate the surface defects present on these structures. For instance, organic passivation may include polymer coating, surface grafting and ligand exchange [12–14]. On the other hand, synthesis of inorganic wide bandgap shells has been used with some success. Formation of these inorganic shells must be delicately controlled to mitigate problems arising from lattice mismatch, peak broadening, and changes affecting the core dimension. Nonetheless, shelled quantum dots continue to suffer from surface state problems pertaining to the decrease in fluorescence efficiency during the ligand exchange process [15]. Even when shells are applied residual, surface ligands are present as an outcome of the synthesis conditions. A non-ambiguous understanding of the effects of these ligands on optical signatures of quantum dots is not available. Wuister et al. have found that the thiol capped ligands can act as hole-acceptor for CdSe quantum dots inducing a considerable increase in fluorescence intensity [16]. It was clearly shown that surfactant coating of QDs helped inhibit agglomeration, and thereby, facilitated the enhancement of the observed quantum yield.

For the commercial scale synthesis, establishing facile and feasible approaches are a must. Synthesis of QDs through aqueous route appears close to “green chemistry” concept, which has succeeded in producing many highly luminescent QDs, such as CdSe, CdTe, ZnSe, HgTe, CdHgTe, and so forth. Atypical synthesis known as hot injection method includes various steps: preparation of hydrogen chalcogenide; preparation of precursors by injecting hydrogen chalcogenide into metal salt aqueous solution in the presence of thio-ligands; and a thermal growth of precursors. In order to overcome the above mentioned disadvantages, a simple, low cost, and highly producible aqueous synthesis method was proposed [17–19].This method entails no pre-preparation of various precursors, N_2 protection, and energy-promoted growth (heating, microwave, and ultrasonication) and can be performed at room temperature through a stepwise addition of raw materials. A pertinent question arises here. What is the spectroscopic, structural and sensing efficacy (against routine analytes like ascorbic acid, oxalic acid, and citric acid) distinction/difference between the HI- and RT-QDs of the comparable size? Hydrogen peroxide plays an important role as a signaling molecule in the regulation of a wide variety of biological processes. A recent study [20–22] has found that hydrogen peroxide plays a crucial role in the immune system. This study suggested asthma sufferers have higher levels of hydrogen peroxide in their lungs than healthy people, which could explain why asthma sufferers have inappropriate levels of white blood cells in their lungs. Hydrogen peroxide presences inside cells increase after tissues are damaged causing pathogenic conditions. Therefore, we specifically targeted H_2O_2 as an analyte for detection. We report a comprehensive investigation to address this issue herein, and clearly differentiate between the two. Considering the wide spread applicability of quantum dots in physical and biological sciences, the importance of present study can be hardly stressed.

2. 2 Experimental

2.1. Synthesis

2.1.1. Hot injection method

CdSe quantum dots (QDs) were synthesized from the precursors CdO and elemental Se using a kinetic growth procedure pioneered by Peng and co-workers [23–32]. This approach has several advantages relative to conventional CdSe QD synthesis methods [30]. In particular, the typical precursor materials, especially dimethyl cadmium, are extremely toxic, expensive, unstable, explosive and pyrophoric in nature, making the system difficult to handle [23,31]. Although the hazards associated with the precursors may not be overlooked, the kinetic synthesis method employed is viewed as an example of closer to green chemistry when necessary care is taken for improved safety.

Briefly, a stock solution of Se precursor was prepared by adding 30 mg of Se to 5 ml of 1-octadecene (ODE) (90%) in a 10 ml round-bottom flask was clamped on a hot plate. A calibrated micro-syringe was used to draw 0.4 ml of trioctylphosphine (TOP) from its Sure-Seal bottle, and added to the reaction flask. The solution was stirred for about 15 min. It was warmed to allow for the faster dissolution of Se powder. Now, this Se stock solution was stored at room temperature (20 °C) in air tight bottles. Cd precursor was made by adding 13 mg of CdO to a 25 ml round-bottom flask containing 0.6 ml of oleic acid, and 10 ml of octadecene. The flask was heated gradually to a temperature of 225 °C, and 1 ml of previously prepared selenium solution was added to the hot cadmium solution. The physical size and morphology of the products depend on the reaction time,

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