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Anomalous carrier life-time relaxation mediated by head group interaction in surface anchored MnSe quantum dots conjugated with albumin proteins

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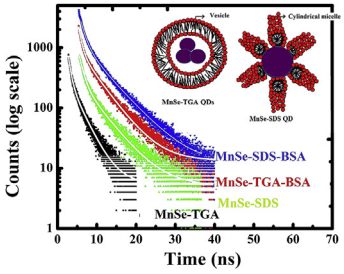
HIGHLIGHTS

- Surface anchored manganese selenide quantum dots (MnSe QDs) have been synthesized via a physico-chemical reduction route.
- Time resolved luminescence spectra of the QDs have displayed bi-exponential decay trend.
- Thioglycolic acid (TGA) coated QDs exhibited shorter lifetime as compared to sodium dodecyl sulfo-succinate (SDS) coated ones.
- Upon BSA conjugation, the average life time is four-fold enhanced in MnSe-SDS QDs.
- An efficient FRET process has been revealed in BSA conjugated TGA coated MnSe QDs.

GRAPHICAL ABSTRACT



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ABSTRACT

We report on the radiative emission decay dynamics of a less known, γ-phase manganese selenide quantum dot system (MnSe QDs) subjected to bio-functionalization. A short-ligand thioglycolic acid (TGA), and a long-chain sodium dodecyl sulfate (SDS) surfactants were used as surface anchors prior bioconjugation with albumin proteins (BSA). Time resolved photoluminescence (TR-PL) spectra of the QDs have revealed bi-exponential decay trends with the fast (τ_1) and slow (τ_2) decay parameters assigned to the core state recombination and surface trapped excitons; respectively. The average lifetime (τ_{avg}) was found to get shortened from a value of ~0.87 ns–0.72 ns in unconjugated and BSA conjugated MnSe-TGA QDs; respectively. Conversely, MnSe-SDS QDs with BSA conjugation exhibited nearly four-fold enhancement of τ_{avg} with respect to its unconjugated counterpart. Moreover, a considerable amount of Förster resonance energy transfer (FRET) was found to occur from the TGA coated MnSe QDs to BSA and with an ensuing efficiency of ~61%. The origin of anomalous carrier life-time relaxation features has also been encountered through a simplified model as regards head group interaction experienced by the MnSe QDs with different surfactant types. Exploiting luminescence decay characteristics of a magneto-fluorescent candidate could find immense scope in diverse biological applications including assays, labeling and imaging.

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1. Introduction

Nanoscale research, with nano-biotechnology implications, has been regarded as one of the fastest growing fields across the globe. This has become possible due to the advent of semiconductor quantum dots (QDs) and their practical relevance in numerous technological assets: from luminescent probes to display devices, from bio-markers to multiplex imaging agents, from sunscreen lotion to environmental remediation, etc [1–5]. The role of QDs has been remarkable owing to their broad absorption response over a wide electromagnetic spectrum, narrow emission line-width, high photoluminescence (PL) quantum yield, size dependent tunable color as well as resistance to photo-bleaching [5]. In addition, owing to strong multiplex capabilities of the QDs over conventional organic dyes, the former can play as an extremely versatile candidate in bio- labeling, sensing, imaging, immunoassay etc.

Amidst transition metal chalcogenides, manganese sulfide (MnS) and manganese selenide (MnSe) have raised immense interest because of its magnetic, optoelectronic and light emission properties [6–8]. The unique, cooperative magnetic and light emission property of the MnSe system, is due to the exhibition of pronounced carrier recombination events and availability of ample localized magnetic ions with unpaired spins. This helps in realizing strong *sp–d* exchange interaction between electron/hole band states and 3*d* electrons of Mn^{2+} ions [8–10]. Unlike most of the conventional fluorescent QDs (such as, CdS, CdSe, ZnO, CdSe/ZnSe etc.), MnSe bears a low toxicity level, and is therefore, less hazardous to environment [11–13]. This is because, under UV illumination, photo-degradation response of the metal ion core (Mn^{2+}) in MnSe, is comparatively slower than that of the Cd^{2+} in CdSe system [13–15]. Several issues, such as, size selectivity, bio-specificity and bio-functionalization efficacy, need to be suitably addressed while considering safe handling of the QDs in cellular environment [5,14,16]. It is worth mentioning here that, excellent QD solubility and bio-conjugation could be achieved through surface functionalization of the QDs with a ligand/cap by employing techniques that include passive adsorption, multivalent chelation, and/or covalent bond formation [17]. In fact, the use of amphiphillic and surfactant molecules provides a complementary doorway for improving QD biocompatibility as well as environmental stability. In this regard, the QDs functionalized with ligand molecules allow dispersal of nanocrystals with their polar-terminated head groups responsible for efficient biomolecular binding [18–20]. With the emerging concepts pertinent to diagnostics and therapeutics in biomedical engineering and nano-biotechnology, magneto-fluorescent MnSe QDs with passable surface functionalization could act as an alternative, yet valuable candidate over traditionally used organic fluorophores.

In this communication, we assess on how carrier lifetime relaxation involved in the radiative recombination emission process is influenced by the nature of surface functionalization of the MnSe nano-bioconjugates. First, the MnSe QDs are made water-soluble by coating with two different surface ligands, such as, an anionic surfactant of sodium dodecyl sulfate (SDS) and an amphiphilic ligand molecule of thioglycolic acid (TGA). Subsequently, the surface functionalized QDs were conjugated with bovine serum albumin (BSA) proteins for successive studies. In particular, the nature of carrier life-time decay aspects as well as Förster resonance energy transfer (FRET) from the MnSe QDs to BSA molecules have been discussed in great detail.

2. Experimental: Materials and methods

The protocols used for synthesizing and characterizing surface functionalized, BSA conjugated MnSe QDs are as detailed below.

2.1. Synthesis and surface functionalization of MnSe QDs

In a typical synthesis procedure, 0.62 g of manganese chloride-tetra hydrate [$MnCl_2 \cdot 4H_2O$, 99% pure, Merck] and 0.11 g SeO_2 were dissolved in 22 ml Millipore water® followed by the addition of 0.1 g $NaBH_4$. The pH of the solution was adjusted to ~11 by adding a few drops of aq. NaOH followed by vigorous stirring (~250 rpm) at a temperature of 60 °C, for 300 s [15]. Then, one of the surfactants, either TGA (or, SDS) of 10% concentration is added to the above mixture. Finally, the solution was transferred to a 50 ml capacity teflon-lined stainless steel autoclave. The autoclave was sealed airtight and subjected to oven heating at a temperature of ~180 °C, for 6 h. On completion of the reaction, the autoclave was allowed to cool down to room temperature. In subsequent step, the precursor extract was subjected to high speed centrifugation (~6000 rpm) followed by filtration using a Whatman filter®. The as-received precipitate (residue) was then repeatedly washed with distilled water and finally cleansed with ethanol. It is worth mentioning here that, the TGA and SDS surfactant coated MnSe QDs were synthesized independently and kept ready for subsequent experiments.

2.2. Bioconjugation of water-soluble MnSe-QDs with albumin proteins

The freshly prepared (TGA and SDS coated) MnSe QDs have been considered for bio-conjugation with BSA. At first, lyophilized BSA powder (69 *kD*, Sigma-Aldrich, 99.9% pure) was subjected to denaturing in 1 mM aqueous $NaBH_4$ and at a temperature of 60 °C. The excess borohydride was removed by spontaneous decomposition by heating. For effective bio-conjugation, the denatured BSA (prepared with concentrations 10 μg/ml), was allowed to mix with 7 ml TGA and SDS capped MnSe QDs independently. The test tubes containing MnSe-TGA-BSA and MnSe-SDS-BSA mixtures, were teflon-sealed after being shaken for several minutes. After incubation (at a temperature of 37 °C) for a time duration of 1 h, the samples were subjected to centrifugation (~6000 rpm), for 10 min. The final residue as obtained through the filtration step was washed with deionized water several times. The centrifugation and filtration steps have been repeated several times to yield bio-conjugated QDs free from excess TGA and SDS molecules.

2.3. Analytical equipment employed

A high resolution transmission electron microscope (HRTEM, JEOL, JEM-2100) working at an accelerating voltage of 200 kV) was employed to reveal information as regards the size and morphology of the MnSe QDs. The *ImageJ* software® was used [21] to carry out fast Fourier transform (FFT) analysis of the captured images. The characteristic optical absorption features were recorded through the UV–Visible optical absorption spectroscopy (UV 2450, Shimadzu Corp.), whereas photoluminescence (PL) spectra were obtained by employing a PerkinElmer LS 55 spectrophotometer. The data acquisition was obtained through a computer controlled standard monochromator based photodetection system. On the other hand, carrier life time measurement of the QDs was performed by a time resolved photoluminescence spectroscopy system (TR-PL, LifeSpec II, Edinburgh Instruments, UK).

All the experiments were carried out at room temperature.

3. Results and discussion

3.1. Microscopic analysis of the surfactant coated MnSe QDs

To assess size, shape and size distribution, electron microscopy