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Luminescence enhancement of water soluble CdTe quantum dots by proper surface modification with ethylene diamine

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ABSTRACT

Thioglycolic acid (TGA) capped CdTe quantum dots (QDs) have been synthesized in aqueous media. The effect of diamine on luminescence property of TGA capped CdTe QDs has been investigated and it has been found that the diamine significantly affects the optical properties of CdTe QDs. Luminescence efficiency as well as lifetime of CdTe QDs have seen to be enhanced notably up to certain concentration of the ethylene diamine added and the observation is much more pronounced in case of smaller size QDs. The results indicate that the local surface-trap states of CdTe QDs reduced effectively by the EDA treatment.

1. Introduction

Semiconductor quantum dots (QDs) have received much attention over past couple of decades because of their tunable sizes and interesting optical properties that are distinctly different from conventional bulk materials [1–3]. Nanometer sized semiconductor particles and their size dependent physicochemical properties are currently of much interest to the scientific community for their immense technological applications as sensors [4,5], solar cells [6,7], and luminescence devices [8,9] etc. Due to small size, brightness, luminescence tunability and exceptionally high photostability, QDs have been adopted for *in vitro* bioimaging as an alternative to commonly known organic fluorophores [10–12]. Optical properties of QDs have been observed to be strongly sensitive towards their local environments including surface properties. Studies focusing on controlling the optical and photophysical properties of QDs by proper surface modification with various organic and inorganic functional molecules [13] have been found in literature.

Great efforts have been devoted by various research groups to synthesizing QDs through various physical and chemical routes, among which the colloid chemical route is one of the most successful methods, characterized by the capability to tune the sizes, shapes, and surface chemistries of QDs [14–18]. The colloid chemical method is also flexible for synthesizing QDs either in coordinating solvents or in aqueous media [19,20]. Both organometallic and aqueous synthetic routes have their own advantages and disadvantages, because of the differences in starting materials, growth media, and especially growth kinetics mechanism [18,21]. The aqueous synthetic routes have advantages over organometallic synthesis because of the cost, safety, and easy to apply in biological fields [10]. QDs synthesized in aqueous media inherently possess a broader luminescence properties, lower quantum yield (QY) and lesser photostability [21,22]. Various auxiliary techniques have been attempted to improve the quality of aqueous synthetic QDs [18]. The nature and strength of the interaction between the capping ligands and the surface atoms of QDs determine the stability of the QDs [21,23,24]. The stability of QD-ligand complexes has become a focus of study because of its promising applications in various fields [10,25–27]. Ligands attached to the surface of the colloidal QDs strongly affect the photophysical properties of QDs. Some groups have examined the system of CdSe QDs in the presence of electron donors such as amines [23,24]. Fluorescence is a useful tool for monitoring electronic changes at the QDs surface. Dannhauser and co-workers [28] have observed emission enhancement of CdS QDs in the presence of very low concentrations of triethylamine (NEt_3). The authors suggested that this enhancement effect is due to binding of the amine to surface defect sites that otherwise would trap excited electrons and prevent luminescence of QDs. Cowdery-Corvan et al. [29] studied photoluminescence (PL) quenching effects of CdS QDs at higher amine concentrations. They proposed that after the initial traps were saturated with amine molecules, the excess amine could quench the luminescence of QDs. In this way, the amine effectively blocks charge recombination and decreases the photoluminescence quantum efficiency of CdS QDs.

In the present study we have investigated the effect of externally added amine on the optical properties of water soluble TGA capped CdTe QDs by steady state and time resolved spectroscopy. We found that at moderate amine concentration, PL intensity is

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maximized due to the surface passivation of CdTe QDs. The QY as well as luminescence lifetimes of CdTe QDs are highly sensitive to the amine concentration. We also found that the effect depends on the size of the CdTe QDs studied here. Therefore, studies of surface structure of thiol-stabilized QDs continue to be a great importance in controlling the optical properties of semiconductor QDs.

2. Materials and methods

All chemicals were of the highest purity available and were used as received. Cadmium perchlorate hexahydrate [$Cd(ClO_4)_2 \cdot 6H_2O$] was obtained from Chameleon Reagent, Japan. Thioglycolic acid (TGA) was purchased from Aldrich Chemical Co. Aluminum telluride (Al_2Te_3) was purchased from MP Biomedicals Inc. Ethylenediamine (EDA) was obtained from Wako Chemicals, Japan. Milli-Q water (Yamato Millipore WQ 500) was used throughout this study.

Water-soluble CdTe QDs capped with TGA were prepared according to the procedure reported earlier in the literature [21]. 2.35 mmol of $Cd(ClO_4)_2 \cdot 6H_2O$ is dissolved in 125 mL water and then 5.7 mmol TGA was added followed by adjusting the pH at around 11.0 by the addition of 1 M NaOH solution under vigorous stirring. The solution was continuously stirred until the solution became optically clear. Next 0.2 g of Al_2Te_3 was placed in a 50 mL three-necked flask. Then around 20 mL of concentrated sulfuric acid was introduced to the Al_2Te_3 chunks to produce H_2Te gas, which passed through the previous resulting mixture in N_2 atmosphere for about 20 min. The CdTe precursors are formed at this stage, which is accompanied by faint orange color. In this study the molar ratio of Cd^{2+}:TGA:Te^{2-} was 1:2.4:0.5. After few days later the QDs solution turned to yellow color showing clear exciton peak at 475 nm. This sample is called as-prepared CdTe QDs. The size of the QDs is controlled by the duration of reflux time and can easily be monitored by absorption and emission spectra.

The luminescence quantum yields (QY) of different sized CdTe QDs were determined at room temperature. QYs were measured by comparing the integrated emission of the CdTe QDs in solution to the emission of rhodamine B according to the previously described methods [30]. UV–vis absorption and luminescence spectra were measured using U-3210 (Hitachi) and FluoroMax-2 (Jobinyvon-Spex) spectrophotometers, respectively. Luminescence decays were measured by picosecond single-photon counting technique. The excitation was done at 400 nm obtained by focusing the output (800 nm, pulse width <100 fs) of a cavity dumped Ti:sapphire laser (Cascade, KMLabs Inc.) on a BBO crystal. Thesetup was operated at an average repetition rate of 2 MHz with temporal resolution of 40 ps. Decays were deconvoluted using a non-linear least-square iterative convolution method based on Marquardt algorithm. The quality of fit was judged in terms of Durbin–Watson parameter, weighted residuals, and reduced χ^2 values. The NT-MDT (Smena) AFM was employed to study the morphology of the CdTe QDs. Noncontact mode is used for the AFM measurements.

3. Results

It has been observed that the luminescence intensity as well as quantum yield of CdTe QDs is very sensitive towards synthesis procedures. We also observed that the luminescence intensity of TGA capped CdTe QDs are sensitive to the externally added amine. Firstly, we checked the effect of amine on luminescence properties of as-prepared CdTe QDs of 2.7 nm size. The addition of the amine slightly increases the absorbance of the CdTe solution as shown in Figure 1A, but this effect is due to the additional absorbance of the added ethylene diamine. PL intensity of CdTe QDs increases with increases in EDA concentration up to a certain concentration. Beyond that the luminescence intensity decreases with further increase in amine concentration. The increase in the luminescence intensity is thus due to an increase in the QY.

The similar phenomena were observed for different size (3.2 and 3.8 nm) of CdTe QDs as illustrated in Figures 2 and 3. In all cases the luminescence intensity increases with increase in amine concentration, and there is also a slight red shift of the luminescence peak. The largest enhancement of the QY 0.74 was achieved with ethylene diamine in case of larger sized (3.8 nm) QDs. The luminescence intensity is maximized at an amine concentration of 1 mM. Further addition of amine decreased the luminescence intensity as well as and QY of particular QDs. Point to be noted here is that during the increase of amine concentrations the luminescence spectral shift is very prominent in case of smaller sized CdTe QDs. We also performed the AFM measurements for TGA capped CdTe QD before and after the addition of EDA [26]. Pattern on the substrate of CdTe QDs suggest a good dispersion of the particles and negligible aggregation in both cases. In Figure 4 the luminescence quantum yield is plotted against the concentration of ethylene diamine for three different sizes of CdTe QDs. It is clear from this figure that in case of smaller size QDs (2.7 nm) the change of QY is very sensitive towards increase concentration of amine. Point

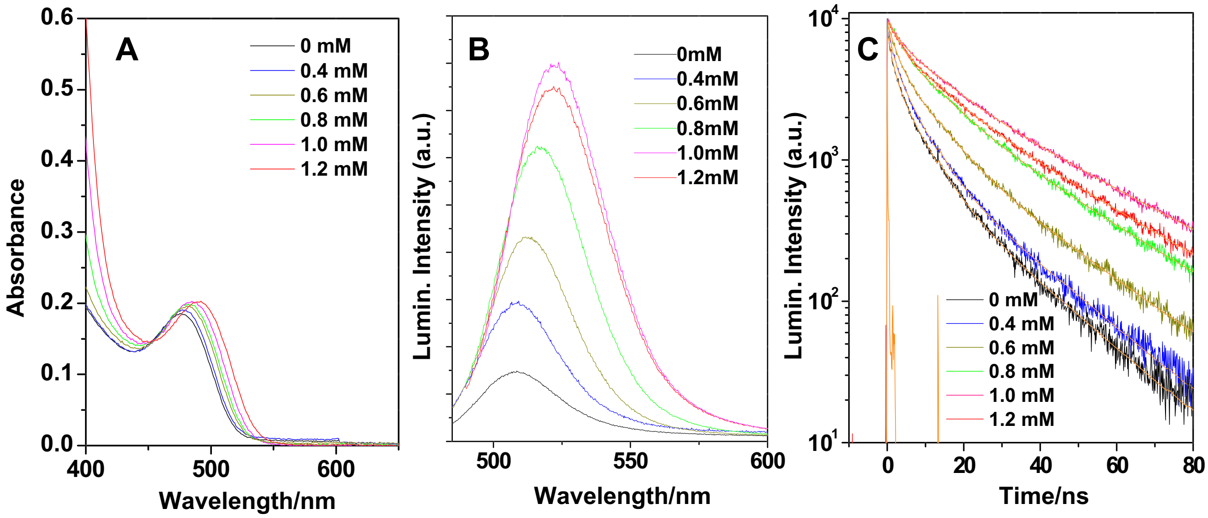

Figure 1. (A) Absorption spectra, (B) luminescence spectra and (C) decay profiles of 2.7 nm CdTe QDs recorded at different amine concentrations.