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The Influence of Aliphatic Diamine on Optical and Dynamics Properties of Water Soluble CdTe Quantum Dots

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Introduction

The study of semiconductor nanocrystals has received wide interest in past few decades. Semiconductor particles and their size dependent physicochemical properties are currently a vital field in various branches of chemistry, physics and biology. Particularly semiconductor quantum dots (QDs) are of great interest owing to their potential application in electrical, optoelectronic devices and biological fields because of their emission tunability, superior photostability and longer photoluminescence (PL) decay times in comparison with commonly known organic fluorophores. The most interesting subject is to understand the size and shape dependence on optical properties of semiconductor nanomaterials. The single chromophore optical microscopy and spectroscopic techniques have allowed us to study the optical properties without the blurring effects of size distribution. These techniques have lead to the discovery of new phenomena in optical properties of semiconductor QDs, such as blinking and spectral diffusion that are not at all observed on the ensemble level.

CdTe QDs were synthesized in aqueous solution. The interaction between CdTe QDs and some amines were systematically investigated by using steady state and time resolved spectroscopy. One of the interesting photophysical properties of the CdTe QD is the blinking behavior. The luminescence intermittency (blinking) of single CdTe QDs was investigated in presence and absence of ethylenediamine (EDA). The results showed that amine could prevent the aggregation of CdTe nanocrystals beside thioglycolic acid as a capping reagent of CdTe QDs. The coordination between amine and CdTe nanocrystals resulted in increasing both the PL intensity and the stabilization of CdTe-amine conjugate.

Experimental

Firstly, highly luminescent CdTe QDs were synthesized in aqueous media at different pH. The size of the QDs is controlled by the duration of reflux time. UV-Vis absorption and photoluminescence spectra were measured using HITACHI U-3210 and Fluoro Max-2 spectrophotometer, respectively. The fluorescence lifetimes were measured with a picosecond Ti:Sa cavity dumped laser by TCSPC method. Optical microscopy is used to study fluorescence intermittency of individual CdTe QDs excited at 532 nm by using CW Nd:YAG laser. For single particle measurements CdTe solution was diluted by 1% PVA. Spin coating solution was prepared by 3000 rpm on a clean cover glass slip. Under continuous excitation the luminescence emission switches 'On' and 'Off' by sudden stochastic jumps. The intermittency was detected only in the single nanocrystal fluorescence experiments. In the ensemble, this phenomenon is averaged out. Ethylenediamine is used as a diamine through out the experiments

Results and discussion

As prepared TGA capped CdTe QDs show a well-resolved absorption maximum of the first electronic transition indicating a sufficiently narrow size distribution of the CdTe QDs, which shifts to the longer wavelengths with increasing size of the QDs. Luminescence maxima of CdTe QDs increases with increase in particle size. Similarly average lifetime is increased by increase in particle size. The modified CdTe QDs with ethylenediamine enhanced its luminescence intensity upto a certain concentration of amine (Fig. 1). However, CdTe QDs luminescence quenching is observed at relatively higher concentration of amine. Amine could

passivates the surface trapping state and can have noticeable influence on the luminescence properties of QDs. When the as prepared CdTe nanoparticles reacts with ethylene diamine the free COOH groups at the surface of CdTe QDs may interact with -NH_2 groups in one end of ethylene diamine by hydrogen bond. This direct interaction between the CdTe surface and the amine functional group passivates the surface and helps to block the trapping of electrons at the defect sites and hence luminescence intensity as well as quantum yield increased very much. We further probe the interaction between CdTe QDs and EDA by monitoring the lifetimes using 400 nm pulse laser as an excitation source. In presence of amine the emission lifetimes did not exhibit any noticeable change.

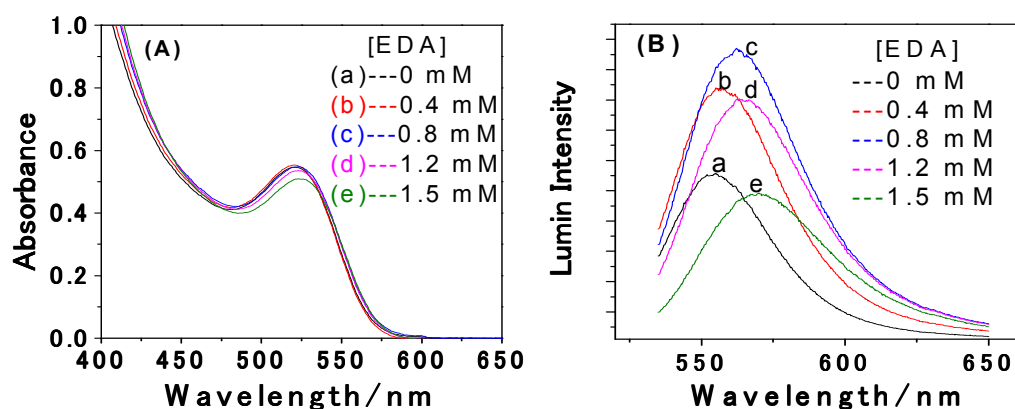


Fig.1: Absorption (A) and luminescence (B) spectra of CdTe QDs in presence of diamine (EDA). The concentrations of EDA were (a) 0, (b) 0.4, (c) 0.8, (d) 1.2 and (e) 1.5 mM.

Typical photoluminescence time trace trajectories for individual CdTe QD and amine modified CdTe QD are shown in Fig. 2. Qualitatively, it can be seen that the effect of surface passivant (EDA) is to increase the length of ‘on’ time events. The analysis of fluorescence intermittency has led to the conclusion that such “blinking” events occurs due to discrete electron transfer events that sequentially ionize and neutralize the QDs turning it ‘on’ and ‘off’. Our results can be interpreted by considering that surface passivation by amine saturates some of trapping centers. As a result the probability of electron capture is lowered. As a result extended ‘on’ times are observed. We have observed that by passivating the dangling bonds at the surface of the QDs can modify the blinking behavior.

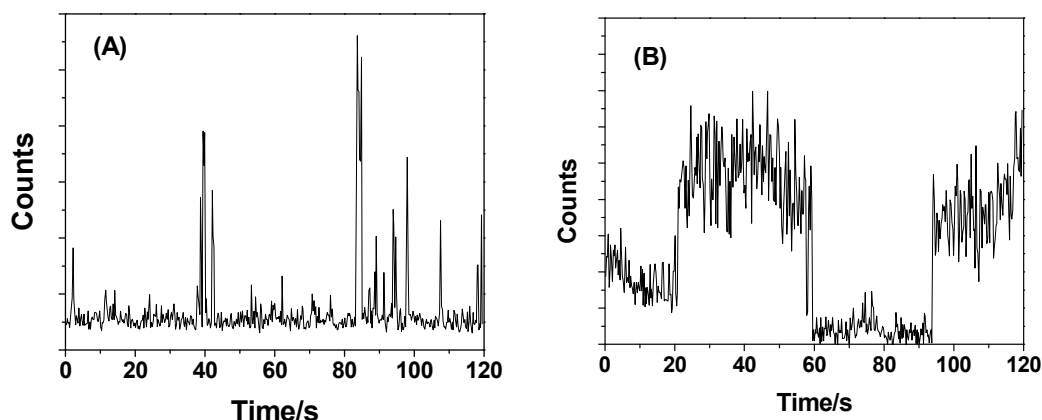


Fig. 2: Typical luminescence intensity trajectories of a single CdTe QD (A) and diamine (EDA) coated CdTe QD.

References:

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