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Optical and Dynamic Properties of Water-soluble CdTe Quantum Dots

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Introduction: The study of semiconductor nanocrystals has received wide interest in past two decades. Nanometer sized semiconductor particles and their size dependent physicochemical properties are currently a vital field in various branches of chemistry, physics and biology. In particular semiconductor quantum dots (QDs) are very attractive as biological labels, because of their small size, emission tunability, superior photostability and longer photoluminescence (PL) decay times in comparison with dyes. One of the major challenges is to obtain water soluble QDs with a high PL quantum yields. 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 nanoparticles, such as blinking and spectral diffusion, that are not at all observed on the ensemble level. One of the technological challenges of dealing with quantum-size materials, both in synthesis and application, is to limit the size of growing clusters and to prevent them from interacting with each other. If clusters do interact, they condense and collapse into the bulk solid. This interaction must be prevented for the clusters to exhibit quantum confinement. In our case for single molecule measurements the quantum confinement has been done by around 1% Trehalose or PVA polymer.

Experimental: All chemicals used were of the highest purity commercially available. Firstly, highly luminescent CdTe QDs were synthesized in aqueous media at different pH. In a typical synthesis 2.35 mmol of $\text{Cd}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ is dissolved in about 125 ml water and 5.7 mmol of the thioglycolic acid was added followed by adjusting the desired pH by addition of 1M NaOH solution. Under this condition, H_2Te gas is passed through the resulting solution with a slow N_2 flow for ~20 minutes. CdTe precursors are formed at this stage, which is accompanied by orange color. The size of the QDs growing is controlled by the duration of reflux time and can easily be monitored by absorption and emission spectra. 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 ($\lambda_{\text{ex}}=410$ nm, 2 MHz repetition rate) by TCSPC method. 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. Confocal microscopy is used to study fluorescence intermittency of individual CdTe QDs excited at 524 nm.

Results and discussion: All samples 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 nanocrystals. Emission maxima of CdTe QDs increases with increase in particle size. Similarly average lifetime is increased by increase in particle size.

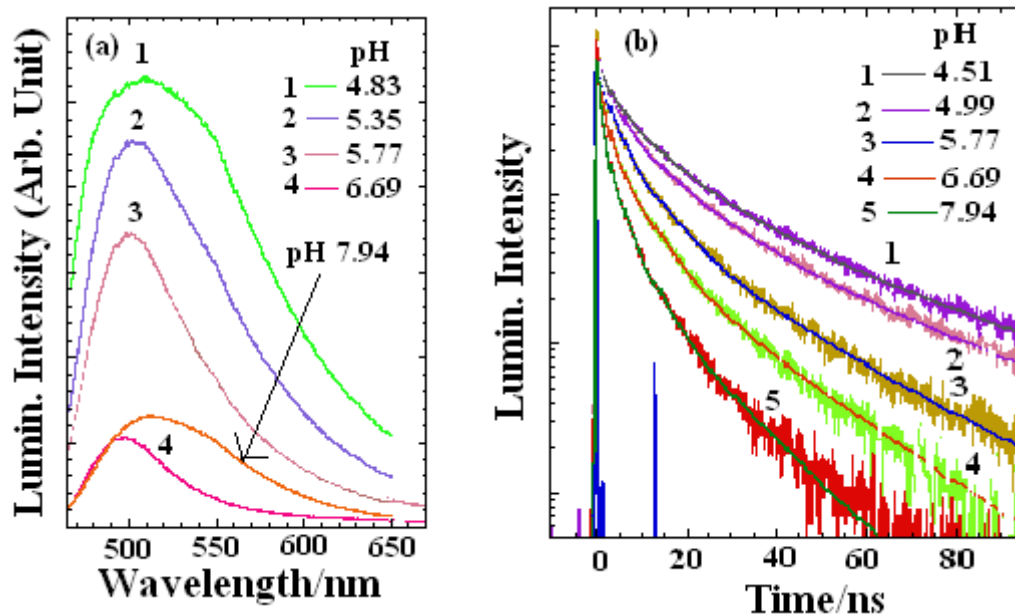


Fig. 1: Emission spectra (a) and decay profiles (b) of CdTe QDs in presence of acid and base.

The photoluminescence of TGA capped CdTe QDs were investigated before and after addition of inorganic acid and base. By addition of dilute acid the PL intensity as well as quantum yields of the CdTe is enhanced (Fig.1a). Intensity reaches maximum and then decreases with further decrease of pH. By using time resolved study we observed that by lowering the pH of the solution average lifetime increases upto a certain pH (Fig.1b). The changes of fluorescence intensity were reversible when the pH of the solution is increased by using NaOH solution. We observed that spectra are simply enhanced during the pH decrease but the peak position of the emission remains fixed. This indicates that the changes of pH mainly influence the surface and not the size of the QDs. Confocal microscopy is used to study fluorescence intermittency of individual CdTe QDs. 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. The analysis of fluorescence intermittency has lead 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". Effect of environments on luminescence properties of CdTe single QDs will be discussed on the basis of these results.