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Femtosecond dynamics of CdTe quantum dots in water

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Abstract

We present studies on femtosecond to nanosecond fluorescence dynamics of aqueous solutions of cadmium telluride (CdTe) quantum dots (QDs) with diameters of 3.1 and 3.6 nm. Ultrafast times in the range 200–320 fs and 1.6 ps were determined, and assigned to electron relaxation to the bottom of the conduction band and to recombination of trapped electrons and holes. These times are common to the relaxation mechanisms of QDs in solution, and therefore suggests that intrinsic mechanisms for electron and hole relaxation dominate over surface effects, in agreement with other reports. Additionally, times of ∼40 ps, ∼600 ps and ∼20 ns due to radiative transitions were recorded. These results are relevant to understanding the photodynamics of CdTe and other QDs in water which should play a fundamental role in their signal when used in biological media.

Keywords: Femtosecond; Cadmium telluride; Quantum dots; Fluorescence; Ultrafast dynamics; Electron; Holes; Relaxation; Recombination

1. Introduction

Within the last two decades, the interest in semiconductor quantum dots (QDs) has increased rapidly [1]. The physical and chemical properties of semiconductor QDs differ from those of the bulk materials. Due to quantum size effects, the bandgap energy can be tuned and the formation of atomic like levels occurs at the edges of the bandgap [2]. Therefore, many properties of these materials can be systematically described and understood in terms of quantum confinement effects [3–6]. These special properties have turned semiconductor nanocrystals into promising materials for many potential technological applications [7–12].

Though the basic properties of II–VI nanocrystals including electron–hole energy states and optical transition probabilities are well established and understood [13–15], there are a number of important issues relevant to primary photophysical and photochemical processes that require further studies. Photoluminescence properties of nanocrystals typically depend on surface structure, chemical environment, migration of carriers and a number of interactions [16]. An understanding of these properties beyond simplified quantum dot considerations is necessary for establishing photoluminescence mechanisms and developing highly efficient light-emitting nanocrystalline devices or solar cells.

Unlike nanocrystals of CdS and CdSe, whose structural and luminescence properties, as well as their surface-related emission, have been examined in detail [2,17–21] considerably less attention has been paid to cadmium telluride (CdTe) nanocrystals. Several groups have performed the synthesis of CdTe nanocrystals in various environments, showing that thiol-capped CdTe QDs are some of the most robust and highly fluorescent nanoparticle materials synthesized in aqueous medium and in other solvents [22–29]. However, the study of their ultrafast luminescence properties is still in an early stage [27–32].

Recent studies of CdTe nanoparticles in the fs-regime have been carried out in chloroform [30], using CdSe/CdTe tetrapods [30,31] and CdTe/CdSe core–shell quantum dots in toluene [32]. At the best of our knowledge, there is no report on the fs-regime of CdTe nanoparticles in aqueous solutions.

Unlike femtosecond transient absorption or pump–probe laser spectroscopies, fluorescence up-conversion is unique in its ability to probe the excited state without interference from

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other processes such as excited-state absorption or ground-state recovery.

In this paper, we report on studies of time-resolved photoluminescence transients of thioglycolic acid-capped CdTe nanoparticles in a neutral aqueous solution. The obtained results show a rich dynamics with transient times ranging from 200 fs up to 20 ns. We discuss the nature of the related events and propose an energetic scheme for these excited QDs in water.

2. Experimental

Thioglycolic acid-stabilized (TGA) CdTe QDs were synthesized as described elsewhere [16]. The duration of the heat treatment was 1.5 h for sample 1 and 20 h for sample 2, resulting in CdTe QDs with average diameters of approximately 3 and 3.6 nm for samples 1 and 2, respectively, as determined by high-resolution transmission electron microscopy (HRTEM). Prior to the measurements, the samples were diluted by adding an aliquot of a stable and concentrated aqueous solution of CdTe to neutral water (Mili-Q) and D_2O (Aldrich, 99.9%).

Taking into account the following equation: $D = (9.8127 \times 10^{-7})\lambda^3 - (1.7147 \times 10^{-3})\lambda^2 + ((1.0064)\lambda - 194.84))$ [33] where D (nm) is the diameter of the nanocrystal sample, and λ (nm) is the wavelength of the first excitonic absorption peak of the corresponding sample, we calculated the average values of nanoparticle size. The reported function provided fitting functions of the experimental data which are valid from a nanocrystal size range of 3–8 nm. We obtained diameters of 3.1 and 3.6 nm for the QDs with the excitonic first peak of 543 and 588 nm, respectively, a very similar result to that determined by HRTEM.

The UV–vis absorption and emission spectra were recorded on Varian (Cary E1) and PerkinElmer (LS-50B) spectrophotometers, respectively. Picosecond time-resolved emission decays were obtained using a time-correlated single-photon counting spectrophotometer (FluoTime 200, Picoquant) described earlier [34]. The excitation was performed at 371 nm and the emission was detected at magic angle. The instrumental response function (IRF) was typically 65 ps. Time-resolved emission transients were observed by using the fluorescence up-conversion technique [35]. Briefly, the system consists of a femtosecond (fs) Ti:sapphire oscillator (Tissa 100, CDP) pumped with a 5-W diode laser (Verdi 5, Coherent). The pulses (60 fs, 450 mW) were centred on 736 nm at 82 MHz repetition rate. The light beam was doubled in 1-mm BBO crystal and a dichroic mirror was used to separate the fundamental from the doubled beam (368 nm) sent for sample excitation. Typically, the energy of the excitation pulse at the sample was ~0.5 nJ. The remaining fundamental light was used to gate the emission of the sample flowing in a 1-mm quartz-rotating cell. The emission was collected and focused into a 0.3-mm BBO crystal (type I) using reflective optics. The gating pulse was time delayed and focused into the nonlinear crystal to overlap with the sample fluorescence. The resulting up-converted signal in the UV region was filtered, entered to a double monochromator and detected with a photomultiplier tube. The IRF of the apparatus measured by gating the Raman signal from solvent is 170 fs for a 1-mm sample cell. The data were deconvoluted with the IRF signal of the apparatus and fitted to a multi-exponential function using the Fluofit package. The quality of the fits was characterized in terms of residual distribution and reduced χ^2 values. All experiments were carried out at 293 ± 1 K.

3. Results and discussion

3.1. Steady-state and ps-resolved observation

The quantum yield of CdTe nanocrystals is directly related to the used TGA/Cd ratio. Our particles were synthesized following a previous procedure and using the same chemical precursors, capping agent (TGA: size of the thioglycolic acid ligand ~0.47 nm) and solvent (water) [36]. Therefore, our particles prepared with a TAG/Cd ratio of 2 should have a quantum yield of 15%, which also agrees with the 13.6% reported earlier for CdTe QDs using the same TGA/Cd ratio [37].

Fig. 1 shows a TEM micrograph of the ~3.6 nm diameter CdTe QDs, while Fig. 2 gives the absorption and photoluminescence spectra of both CdTe particles having diameters of 3.1 and 3.6 nm. The absorption spectra indicate that CdTe nanoparticles have a wide range of absorption. Emission spectra (characterized by Gaussian lineshape and relatively narrow spectral width, FWHM ~190 meV) show only a band-edge fluorescence peak, which is slightly red-shifted from the absorption onset (global Stokes shift ~1.6 eV) indicating that surface defects, rather than lattice defects, must be responsible for trapping the exciton. The same behaviour was observed for TGA, mercaptopropionic acid (MPA) [26] and TOP/DDA (trioctylphosphine/dodecylamine) capped CdTe QDs upon transfer into water [28].

Our emission spectra exhibit the band-edge emission. In a previous work, its presence has been explained by invoking different recombination mechanisms, such as recombination of the delocalized electron–hole (e–h) pairs strongly coupled to

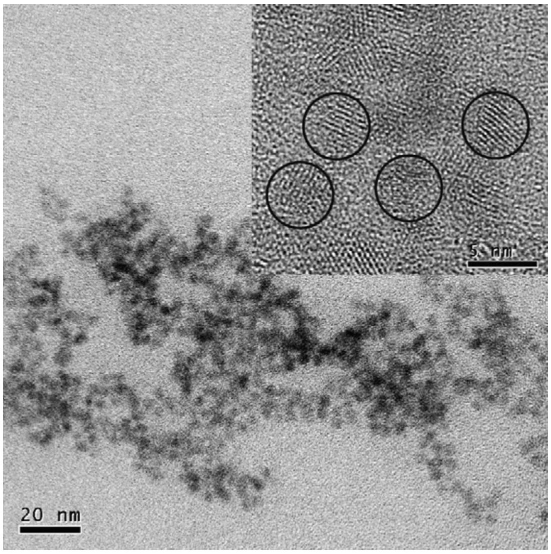

Fig. 1. TEM micrographs of 3.6 nm in diameter CdTe quantum dots (QDs). The inset shows a high-resolution image demonstrating good crystallinity of the single QDs. In order to improve the contrast on the TEM microscope, the samples were washed with isopropanol and redispersed in a water/DMF (1:100) solution.