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Charge carrier dynamics in CdSe nanocrystals: implications for the use of quantum dots in novel photovoltaics

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Abstract. The dynamics of photo-generated electrons and holes in CdSe quantum dots have been studied using the femtosecond fluorescence upconversion technique, permitting an unambiguous examination of the excited state. The band edge emission shows an expected size dependence on the decay rate. We find that the deep trap emission is coupled to the band edge fluorescence, implicating surface states as important factors in the excited state lifetime of the hole. As a factor of the overall efficiency of solar cells, the rate of charge separation and the fate of the exciton are important considerations in the design of nanocrystal-based photovoltaic devices.

PACS. 81.07.Ta Quantum dots – 82.53.Mj Femtosecond probing of semiconductor nanostructures – 84.60.Jt Photoelectric conversion: solar cells and arrays

1 Introduction

Recently nanocrystal/polymer photovoltaic devices have been successfully constructed by Greenham *et al.* [1] and Huynh *et al.* [2]. The impetus for seeking alternative solar cell strategies stems from the fact that currently, manufacturing costs for silicon solar cells outweigh their practical benefit, and they have theoretical power conversion efficiencies of only 26% [3]. The active layer of the nanocomposite photovoltaic can be prepared by benchtop techniques and the device itself can be prepared inexpensively without high temperature or high vacuum. Subsequent to photo-excitation, holes migrate to the device anode *via* a hole conducting polymer and electrons ultimately reach the cathode by 'hopping' between nanocrystals. Quantum dots have advantages in solar cell applications, including: their robust inorganic nature, large extinction coefficient resulting from quantum confinement, and intrinsic dipole moment which may lead to rapid charge separation similar to the photosynthetic reaction center in plants. In addition, quantum confinement allows for band gap tunability across the solar spectrum. One complication that may arise from their use in photovoltaics is that mid-gap surface states may localize carriers, reducing the overall efficiency of the device. The goal of this work is to study the ultrafast dynamics of charge carriers in CdSe nanocrystals and determine the effects that surface states play on the ultimate fate of the exciton.

2 Experimental

2.1 Femtosecond fluorescence upconversion spectroscopy

Fluorescence upconversion is a technique used to unequivocally determine the nature of the excited state, as the signal is not obfuscated by stimulated emission or ground state recovery [4]. It is a two-pulse experiment; one excites the sample, which is time-delayed by use of a linear translation stage, the other acts as a gate beam. The sample fluorescence is mixed in a nonlinear mixing crystal ($LiIO_3$ in our case) with the gate beam, and the sum frequency is produced which is the signal ultimately measured. We utilize an argon-ion pumped, Ti:Sapphire oscillator/amplifier/optical parametric amplifier system (Coherent, Inc.) which produces 175 fs tunable-visible pulses [5].

2.2 Synthesis of CdSe nanocrystals

A series of narrow size-distributed (± 5%) CdSe nanocrystals were prepared in the strict absence of oxygen using the method of Murray, Norris, and Bawendi [6], as modified by the Alivisatos group [7]. The nanocrystals were characterized by static absorption and emission spectroscopy, powder X-ray diffraction, and high-resolution transmission electron microscopy. The stoichiometry and surface composition of the nanocrystals was determined by Rutherford backscattering spectroscopy [8]. When synthesized in absence of oxygen, our nanocrystals larger than

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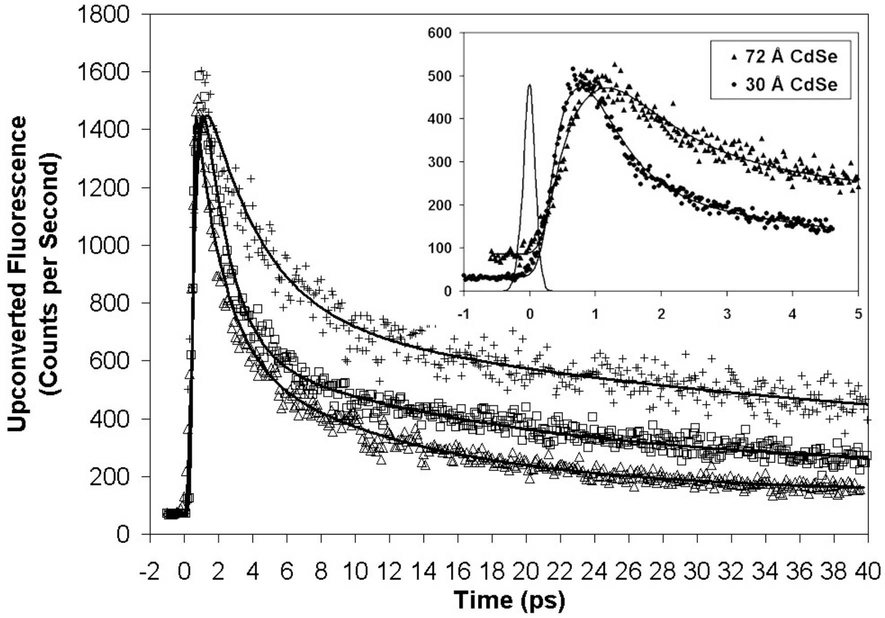

Fig. 1. Size dependence of band edge emission for 72 (+), 52 (□), and 30 Å (△) CdSe nanocrystals in toluene, with solid lines representing fit results. The inset shows scans of the same sizes with higher time resolution and the instrument response function at *Time* = 0.

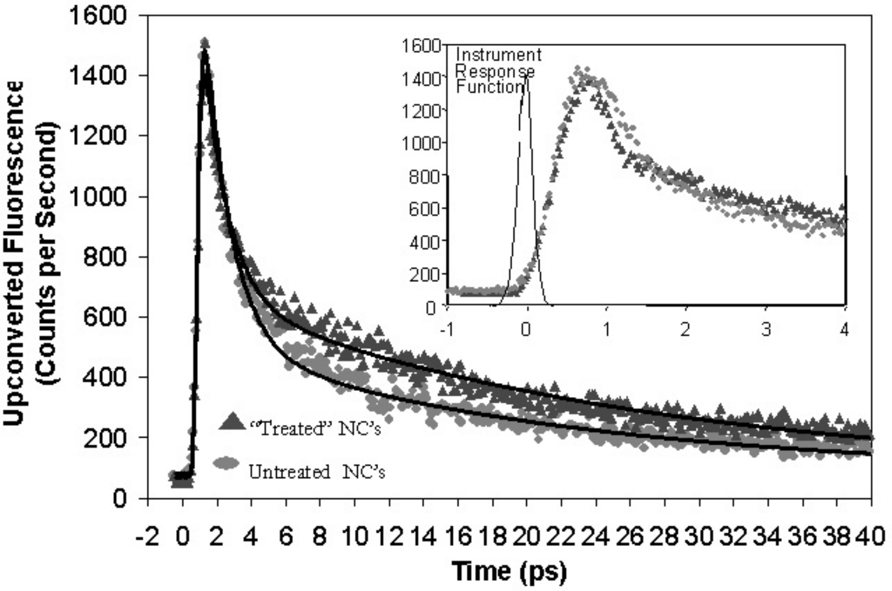

Fig. 2. Effect of surface oxidation on the band edge emission. The results show similar time constants, but differ in relative amplitude. The inset shows the dynamics on the short time scale.

~ 45 Å display no static emission at either the band edge or red-shifted surface emission wavelengths. Upon photo-irradiation with a CW argon ion laser in presence of air both emission features began to grow in, and with time the intensity of both features increased until the emission stabilized at its maximum. The absorption spectrum of the sample did not change and the sample remained optically clear, indicating the photo-oxidation treatment of the surface did not remove TOPO capping ligands or degrade the nanocrystals. The extent of photo-oxidation is being determined by nuclear reaction analysis using ^{15}N.

3 Results

3.1 Size and surface dependence of band edge emission

Figure 1 shows the effect of the band edge emission upon reducing the nanocrystal size from 72 to 30 Å. As expected, based on the argument that smaller dots force electron/hole wavefunction overlap more so than larger ones, faster decay dynamics are seen for the smaller dots; this could also be attributed to increased interaction with the surface. The decays in Figure 2 illustrate that the

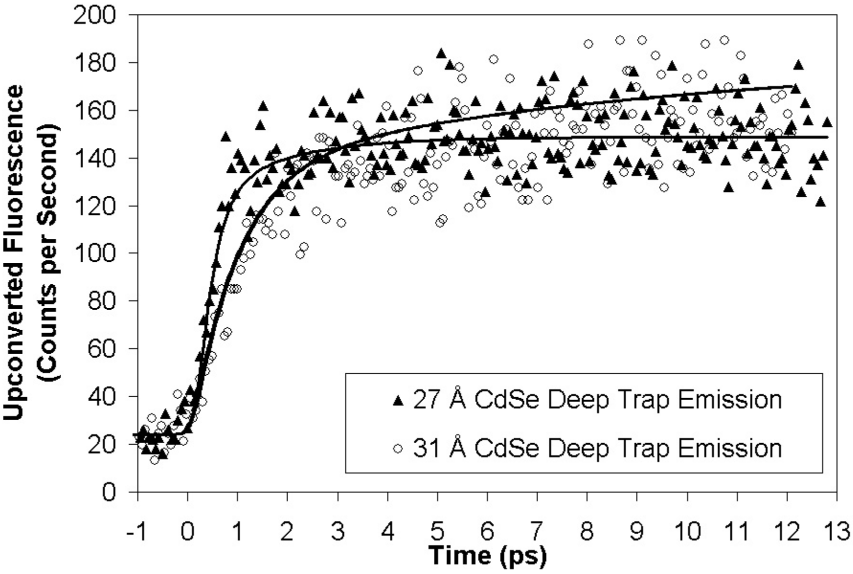

Fig. 3. Upconverted 885 nm deep trap emission from 27 and 31 Å CdSe nanocrystals in toluene.

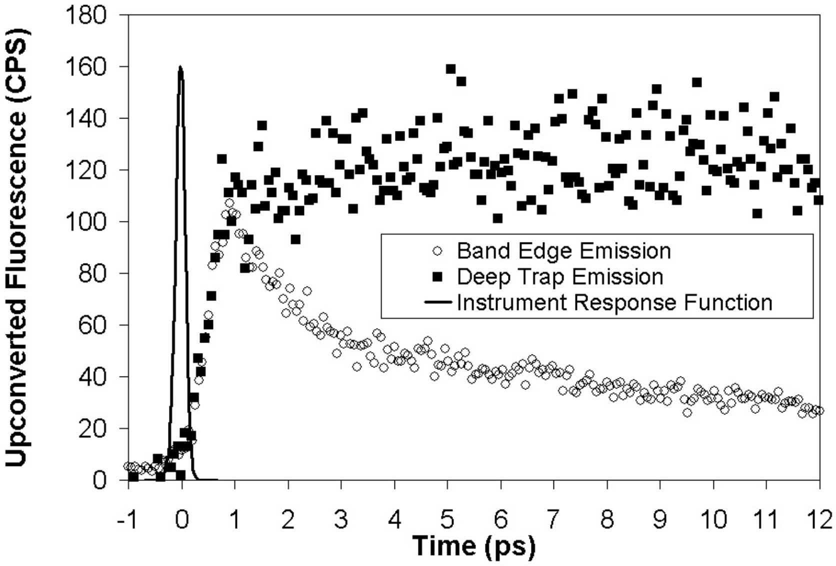

Fig. 4. Band edge and deep trap emission from 27 Å CdSe nanocrystals.

time constants for surface-oxidized (hereafter referred to as "treated") and normally passivated nanocrystals are the same but differ in relative amplitude. This is a manifestation of the decrease in electron/hole traps and more of the charges are allowed to radiatively recombine, resulting in higher fluorescence.

3.2 Implications of the surface on exciton lifetime

We attribute the broad, strongly red-shifted emission at wavelengths greater than 700 nm in static fluorescence spectra to Se dangling bond surface states (potential hole traps), whose energetic positions relative to the band gap have been calculated by Pokrant and Whaley [9]. Situated exactly mid-gap, these states have been largely excluded in theoretical models attempting to explain the behavior of the band edge exciton. While the emission is extremely weak compared to band edge wavelengths, we have successfully upconverted the 885 nm deep trap emission, shown in Figure 3. As is the case for the band edge emission, there is a size dependence on the deep trap dynamics that can be explained by the same geometric arguments. Fit results yield an extremely fast rise time for the emission on the order of 300 fs for the 27 Å sample and 650 fs for the 31 Å sample (both are fully populated within $\sim$ 2 ps). An overlay of the band edge and deep trap emission (Figure 4) illustrates two distinct features: (1) the rise times are identical, and (2) the deep trap emission grows in as the band edge fluorescence decays. This result inherently couples the two dynamics.

4 Discussion and conclusions

Our data show that holes populate surface states within 2 ps. This appears to be the dominant decay pathway for band edge emission followed by a longer-lived time component, which likely involves an optically "dark" state [10, 11]. The ultrafast interaction of the surface with the exciton has important implications for the overall efficiency of a photovoltaic device: if the surface states lie energetically well below the HOMO of the hole conducting polymer, holes photo-generated in the nanocrystals may remain trapped at the surface defeating their migration to the anode.

We have measured the size dependence of the exciton lifetime and found shorter lived components for smaller nanocrystals, as would be expected based on geometrically forced overlap of the wavefunctions and increased surface interaction. Likewise, by removing surface Se dangling bonds (passivating with oxygen [12]), an increase in relative fluorescence is seen as fewer holes are annihilated by surface electrons. The deep trap emission dynamics show a direct correlation with the band gap emission, leading us to conclude that the surface plays an integral role in the final fate of the exciton. Surface states are populated on a timescale of 2 ps; therefore, either the hole surface traps must be passivated completely, or hole-to-polymer charge transfer must occur faster than 2 ps in order to maximize device efficiency.

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