

Ultrafast transient absorption studies on CdTe and chiral CdSe quantum dots

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Introduction

Nanoparticulate materials are finding many applications ranging from ones in information technology (bottom up approach using arrays of particles), through biosensors (using surface modification to bind analytes) to therapeutic (with the potential of targeting particular biomolecules). Many of these uses rely on the fact that the particles have different optical properties from those of the bulk material, because of quantum confinement. This causes remarkable size-dependent photoluminescence behaviour in the case of chalcogenide semiconductors (such as CdTe, PbSe etc.) or shape-dependent wavelength tunable absorption spectra in noble metal particles. Nanoparticles are usually stabilised by so-called capping agents, which are often thiols, e.g. TGA, penicillamine (Fig. 1). Functionalisation of these capping agents facilitates delivery of the particles into cells and allows the targeting of specific components, as has recently been demonstrated by the Gun'ko team^[1]. Such targeting should be enhanced by using chiral substances and remarkably it has been found possible to prepare both gold and silver nanoparticles in chiral forms^[2] using optically-active thiol-containing stabilizers or with DNA as a template^[3]. Gun'ko's group has recently published the first reports of chiral quantum dots of II-VI semiconductors^[4]. These new nanomaterials show strong and complementary circular dichroism in the region characteristic of the CdS exciton bands. They are also strongly luminescent, emitting intense blue-white or green-white light (see Fig. 2) and thus are potentially exploitable in LED or similar devices. This emission is not due to intrinsic recombination of the hole-electron pairs as is found for the TGA capped materials but rather is believed to originate from surface-defect states. This work with racemate (R-) and enantiomers (dextrotary (D-) and levorotary (L-)) penicillamine (Pen) capping agents has subsequently been extended to CdSe, which behaved similarly, and to CdTe, which strikingly is neither chiral nor "white" luminescent. A key feature determining the photophysical properties of the nanoparticles is their surface, although in most cases this is badly characterized. Thus there is still insufficient knowledge about the types of electron (hole) surface traps, trapping mechanisms and their impact on energy relaxation and charge recombination processes. In this work we use for the first time the

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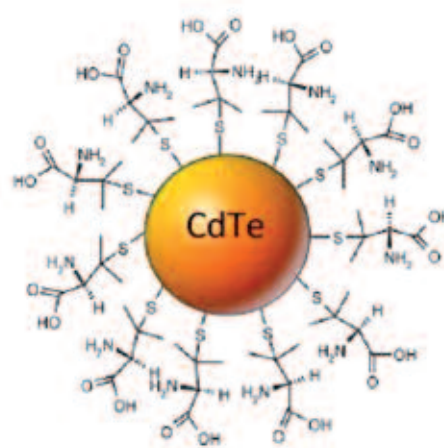


Figure 1. CdTe TGA QDs.

UV-Vis transient absorption capabilities of the ULTRA laser system to get insight into the ultrafast dynamics of CdTe and CdSe quantum dots and to compare the properties of the penicillamine stabilized QDs with those of a classic, TGA capped sample where the emission is excitonic in nature. It is also hoped that the project will provide the necessary background for time resolved resonance Raman studies of surface defect states.

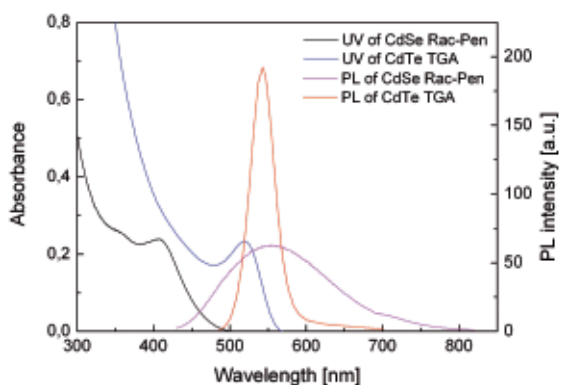


Figure 2. Absorption and emission (PL) spectra of CdTe TGA and CdSe Rac-Pen.

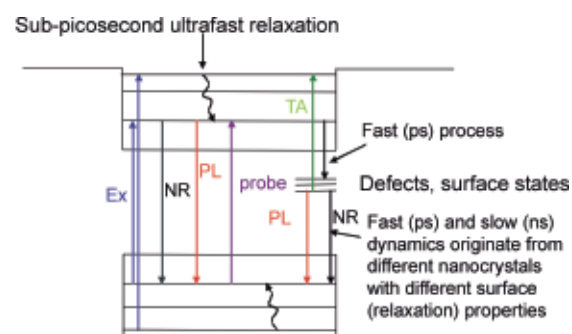


Figure 3. Single quantum well energy level diagram. Vertical arrows show possible optical transitions.

Synthesis

CdTe TGA quantum dots were prepared according to well-known procedures^[5]. CdSe quantum dots were prepared using a method similar to that previously reported for penicillamine stabilized CdS by substituting Na_2SeSO_3 for CH_3CSNH_2 as the X^{2-} source^[4,6].

Experimental

Absorption and photoluminescence measurements were conducted using commercial spectrometers in the Chemistry department of Trinity College Dublin. The picosecond transient absorption pump-probe experiments were carried out using the ULTRA time-resolved spectroscopy apparatus at the Central Laser Facility of the Science & Technology Facilities Council at the Rutherford Appleton Laboratory. Briefly, a titanium sapphire chirped pulse amplifier (Thales Laser) is seeded with a <20 fs oscillator to generate 10 kHz, 50 fs, 1 mJ pulses at 800 nm. A portion of the Ti:Sapphire laser output beam was used to generate a white light continuum (WLC) in a 2 mm thick CaF_2 plate which was continuously rotated to avoid damage and colour center formation. The WLC was focused to 150 μm in the sample then dispersed by a monochromator (Spectral Products) and detected shot by shot using a linear silicon array (Quantum Detectors).

Pump excitation light (400 nm) was generated by second harmonic upconversion of the 800 nm laser beam and focused to 200 μm in the sample. The excitation pulse energy was monitored before each experiment and set to 40 nJ using a variable neutral density filter. A 400 nm interference filter was placed in front of the monochromator slit in order to remove scatter from the excitation beam. The pump and probe beams were set at a magic angle for CdTe and 45° for CdSe samples. The samples for transient measurements were prepared by placing a small volume of solution between two CaF_2 windows of a standard solution flow cell of 500 μm path length (Harrick Scientific). During pump-probe experiments samples were rastered to minimize photodecomposition effects and to avoid eventual re-excitation. Samples were frequently checked for decomposition using standard UV/Vis spectroscopy.

Results and discussion

Possible optical transitions in confined systems are schematically illustrated in Fig 3. Transitions “Ex” corresponds to the creation of the electron – hole

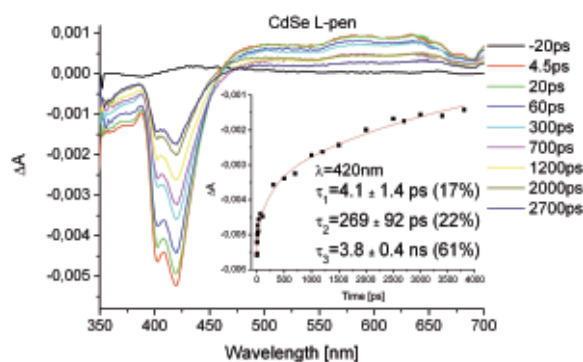


Figure 4. Transient absorption spectra following 400 nm (50 fs) excitation of CdSe L-Pen capped QDs. In the inset, kinetics of the bleach and corresponding lifetimes are presented. The signal at about 400 nm is probably due to residual scattering of the excitation line.

pairs. The fast initial process (<1 ps) just after absorption is electrons (holes) energy relaxation within electrons (holes) quantized states. Depopulation of the lowest electron quantized state may occur via direct (radiative or nonradiative) exciton recombination back to the ground state or due to electron relaxation to the surface/defect related states. In the latter case electron relaxation is dominated by trapping at the particular type of defect and emission and relaxation properties are strongly dependent on surface quality. The simplest way to distinguish between excitonic and defect related emission is to compare absorption and emission spectra. Emission from defects is very broad and its maximum is significantly shifted from the absorption maximum. Such broad emission is characteristic of the penicillamine CdSe sample (see Fig. 2). In contrast CdTe-TGA exhibit relatively narrow photoluminescence band characteristic of excitonic emission (Fig. 2). For both CdSe and CdTe QDs the emission lifetime is of the order of nanoseconds. However some nonradiative processes in QDs are much faster (ps) and can be successfully probed using ultrafast pump-probe techniques such as transient absorption spectroscopy. In order to minimize photodecomposition and multiphoton effects the utilizing of the high sensitivity and multiwavelength detection capabilities of ULTRA is of particular importance.

CdSe quantum dots

The picosecond transient absorption spectra of CdSe quantum dots capped with enantiomers (L-, D-) and racemate (R-) form of penicillamine (Pen) are quite similar. Representative spectra for CdSe L-Pen capped are presented in Fig. 4. Spectra exhibit strong bleach at about 420 nm corresponding to the depletion of the ground state via strongly allowed excitonic transitions. The broad transient absorption features above 470 nm can be tentatively identified as arising from the defect states. For all investigated samples the decay was analyzed using three exponential model assuming complete recovery. The bleach decay curve with appropriate fit, corresponding time constants and relative signal amplitudes for CdSe L-pen are collected in the inset of Fig. 4. The bleach decay shows the existence of three regions with different time

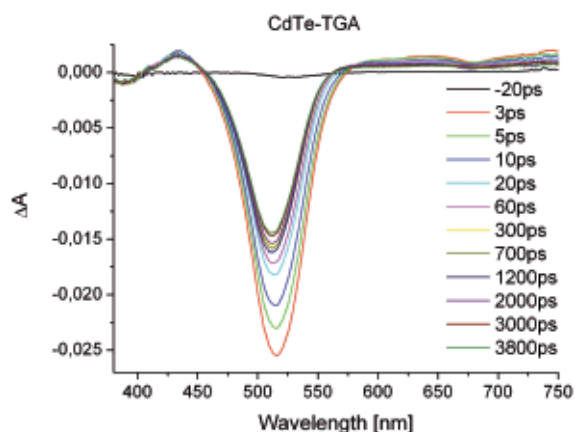


Figure 5. Transient absorption spectra following 400 nm (50 fs) excitation of CdTe TGA capped QDs.

constants: fast initial stage with time constant about 4 ps, followed by slower decay of the order of hundred of picoseconds and final slow nanosecond kinetics. As direct electron intraband relaxation is an extremely fast process (<1 ps) the bleaching decays should represent depopulation rate of the lowest electron quantized states. On the other hand initial picosecond decays are definitely too fast to be explained by direct electron-hole recombination between quantized electron and hole states. It is therefore more likely that depopulation of the lowest electron quantized states occurs via new, surface-defect related states. Spectrally uniform decay of the bleach suggest that initial ps and final ns dynamics arise from different quantum dots with different number and/or type of traps implying different relaxation (surface) properties^[7].

CdTe-TGA quantum dots

The ps transient absorption spectra of CdTe TGA capped are presented in Fig. 5. The sharp transient absorption band is centered at 435 nm. The strong bleach band at 513 nm corresponds to the depletion of the ground state. At longer wavelengths weak, broad transient absorption bands are also observed. These bands may be (tentatively) assigned as arising from the exciton state. The best kinetics fits were obtained assuming a triexponential model (see Fig. 8). A more

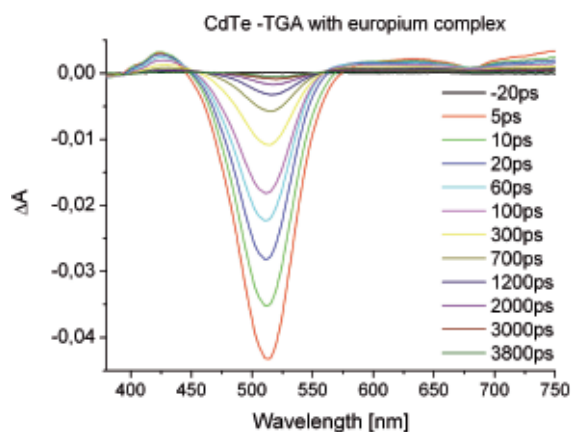


Figure 7. Transient absorption spectra following 400 nm (50 fs) excitation of CdTe TGA capped QDs in the presence of Europium complex.

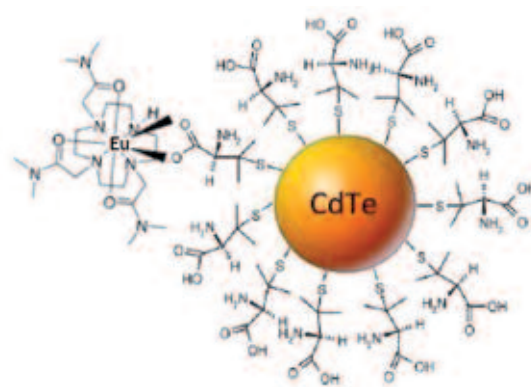


Figure 6. Association of Europium complex with CdTe nanoparticle.

detailed study will be required to determine the origin of this multicomponent decay.

Interesting behavior of CdTe-TGA QDs has been observed in the presence of a europium complex based on a tri-acetamide substituted cyclen (see Fig. 6). The titration of the quantum dots with the europium complex resulted in a dramatic effect on the emissive properties of the QDs with significant quenching observed with 1:1 equivalents. It is important to note that lanthanide complexes are typically weak emitters due to forbidden Laporte transitions. No Eu emission was found indicating that the QDs were not apparently acting as an “antenna” [8a]. The quenching effect of QD excited states in the presence of the europium complex is also clearly visible in Fig. 7 and 8. Interestingly the presence of the Europium complex leads to almost complete signal recovery (at pump-probe delay equal to 3.8 ns). Note it is assumed that water bound TGA (Fig. 6)^[8]. In as much as relaxation

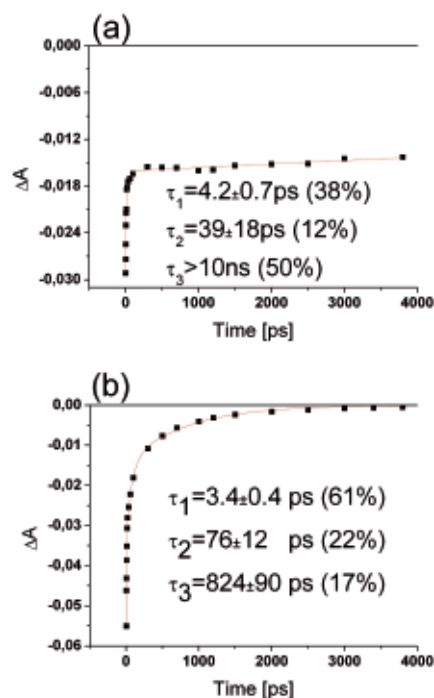


Figure 8. The bleach kinetics (at 513 nm) of CdTe TGA in the absence (a) and presence (b) of Europium complex.

properties are surface sensitive such behavior indicates that the europium complex strongly interacts with the surface of nanoparticles. However, the mechanism of quenching has not been elucidated so far.

It is worth mentioning that by contrast to the behavior of the analogous CdSe samples, only very weak transient absorption was observed for CdTe Pen capped QDs, presumably indicative of very rapid deactivation of the initially formed excited state. This observation is consistent with the non-luminescent behavior of these particles.

Conclusions

We have carried out ps studies on the energy relaxation in CdTe and chiral CdSe QDs. Our results confirmed the ULTRA system's capability to conduct high quality ultrafast transient absorption measurements in a wide spectral range using multiwavelength detection methods. Our studies show that relaxation paths involve at least three processes with different time constant. This multicomponent relaxation behavior was associated with nanocrystals with different surface properties. Transient absorption bands for CdSe samples were tentatively explained as arising from defect states. The data show that probing the surface defect states with TR³ spectroscopy should be possible. We have also shown that CdTe QD excited states are strongly quenched by a europium(III) complex. The nature of the quenching process is under investigation.

Acknowledgements

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