Size selective photoluminescence excitation spectroscopy in CdTe quantum dots

Yury Rakovich[*a], Laura Walsh[a], Louise Bradley[a], John F. Donegan[a], Dmitri Talapin[b],
Andrey Rogach[b], Alexander Eychmüller[b]

[a]Semiconductor Photonics Group, Physics Department, Trinity College, Dublin,
Ireland; [b]Institute of Physical Chemistry, University of Hamburg, Germany

ABSTRACT

We present a photoluminescence and photoluminescence excitation study of CdTe quantum dots, prepared via a novel organometallic approach. The global photoluminescence (excited at the energy above the absorption edge) showed a red shift of 75 meV with respect to the first absorption peak. This band edge emission was found to be strongly dependent on the excitation photon. Resonant emission spectra showed a pronounced spectral shift and line narrowing with decreasing excitation energy. The resonant Stokes shifts were extracted from photoluminescence and photoluminescence excitation data. The minimum magnitude of the resonant Stokes shift of 14 meV was obtained at room temperature.

Keywords: CdTe, nanocrystals, quantum dots, luminescence, Stokes shift

1. INTRODUCTION

Semiconductor nanocrystals or quantum dots have attracted much attention recently because they exhibit strongly size-dependent optical and electronic properties. These systems have been studied from the viewpoints of fundamental physics and possible applications. The size of the nanocrystals in all three dimensions is less than the de Broglie wavelength of the electronic subsystem excitation. Therefore, many properties of these materials can be described and understood in terms of quantum confinement effect[1,2]. Much of the work on nanocrystallites has centered on CdS and CdSe. Unlike these quantum dots whose luminescence properties have been examined and reviewed with great thoroughness[3-5], cadmium telluride nanocrystals are much less studied although this compound is the basis for development of long wavelength photodetector technologies[6]. CdTe quantum dots prepared by chemical way generally exhibit a significant size distribution that depends upon the synthesis conditions and post-synthesis treatments[7-9]. The absorption spectrum of such a quantum dots shows a very broad peak even at low temperature[10] and this broadening leads to an ambiguity in estimating the resonance position. As a result, the electronic structure in CdTe quantum dots cannot be described correctly. To overcome the inhomogeneous broadening due to the inherent size distribution, size-selective technique has to be applied to examine the energy level structure[4,5]. By restricting the excitation photon energy to the red side of the absorption band, one can excites only the lowest-energy transitions of the biggest nanocrystals. This technique has come to be known as fluorescence line narrowing (FLN) because the width of the PL band is considerably narrower in comparison with non-resonance excited photoluminescence. Another related technique, which can be used to examine the level structure of quantum dots is photoluminescence excitation spectroscopy (PLE), in which the intensity of photoluminescence (PL) at selected emission photon energy is controlled, whereas the excitation photon energies are scanned to produce the PLE spectrum. The results of these two techniques can be combined to determine basic optical properties of quantum dots and first of all to estimate the shift of the band-edge emission as a function of excitation emission[11].

In the present work we first describe the synthesis of the highly lyminescent CdTe nanocrystals with very small size distribution. The electronic and optical properties are studied by size-selective spectroscopic technique including fluorescence line narrowing and photoluminescence excitation in terms of the resonant and non-resonant Stokes shift. Finally, radiative decay of PL was studied in order to check the validity of the usual three-level model proposed to explain the non-resonant Stokes shift.

2. METHODOLOGY

CdTe nanocrystals were were synthesized by reacting dimethylcadmium with trioctylphosphine telluride in mixtures of dodecylamine and trioctylphosphine[12]. The method of size-selective

---

[*] Yury.Rakovich@tcd.ie; phone +353-1-608-2193; fax +353-1-671-1759; Physics Department, Trinity College, Dublin 2, Ireland

precipitation was used to separate a CdTe fraction with relatively narrow (< 10%) size distribution. The fraction of CdTe QDs with a mean size of 5.1 nm and room temperature PL quantum yield of ~ 60% was used for spectroscopic measurements.

Absorption spectra were measured using a Shimadzu UV-3101 PC spectrometer. The PL spectra were recorded using a Spex Fluorolog spectrometer (1680-B monochromators with a dispersion of 1.70 nm/mm) equipped with a cooled R943 Hamamatsu photomultiplier. The PL and PLE spectra were obtained by exciting the samples with a Xenon lamp (output power of 40 μW $\rightarrow$ 0.1mW, depending on the wavelength and a spot area ~ 10 mm^2) in perpendicular collection mode. The absorbance (optical density) of sample was kept below 0.1 at the first absorption feature for 1 cm path length cuvete. The small values of optical densities guarantee that no artefacts can arise from different light penetration length. The PL spectra have been corrected for the sensitivity of the detection system. For time-resolved PL measurements the sample was excited by 70 ps pulses of the second harmonic of a Nd:YAG laser (Antares) at 75 MHz repetition rate. The PL signal after dispersion by the detection monochromator, was measured by a Hamamatsu microchanel plate detector provided a typical instrument response function of 70 ps. About 5000 counts in a peak channel were used for obtaining one decay curve.

3. RESULTS AND DISCUSSION

The Figure 1 shows the room temperature absorption spectra and PL spectra. The absorption spectrum shows structure, which is typical for quantum confinement. At room temperature first absorption peak is at 2.05 eV, higher in energy than the band gap in bulk CdTe (1.5 eV)[13]. The non-resonance excited photoluminescence exhibit a one sharp peak of band-edge emission cenetred at 1.96 eV and shows a shoulder at the low-energy side, which arises from recombination of carriers in the surface traps[14,15]. Non-resonant Stokes shift between the absorption and the emission is about 90 meV.
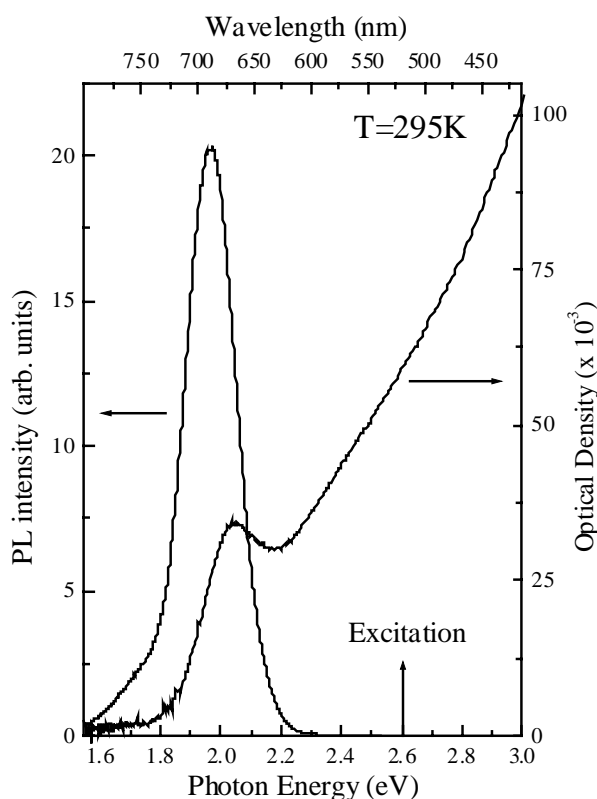

Fig. 1: Room temperature absorption and luminescence spectra of CdTe nanocrystals in toluene.

At first glance the correspondence between the spectral position of the peaks in absorption and PL spectra confirms the origin of the Stokes-shifted PL band as the radiative recombination of a confined electron in a nanocrystal. In support of this interpretation we obtained PLE spectra showing several well resolved lines (Figure 2), which were only suggested by the usual absorption spectra (Figure 1) at

room temperature. However it turns out that shape and position of spectral lines in the PLE spectrum depends strongly on detection energy. Figure 2 shows PLE spectra obtained for several detection energies selected across PL band. It can be seen that PLE spectra detected at different energies are blue shifted as detection energy increases. For detection energy below the main photoluminescence peak we observed a PLE spectrum with broad peaks, whereas for detection energy at the high-energy side we observed PLE spectra with well-resolved peaks. Such a result is expected for an inhomogeneous broadened single state system. In our case the PLE detects photoluminescence coming from all nanocrystals with the first band-to-band transition energy higher, but not lower than the detection energy. As a result the PLE spectra obtained at the high-energy side of PL peak probe a narrower size distribution with better resolved lines than the low-energy one. The sole exception is spectrum measured at detection energy of 2.26 meV. In this case PLE spectrum detects photoluminescence coming or from very small nanocrystals or from higher excited states of all quantum dots. In either case density of emitting states is very low.
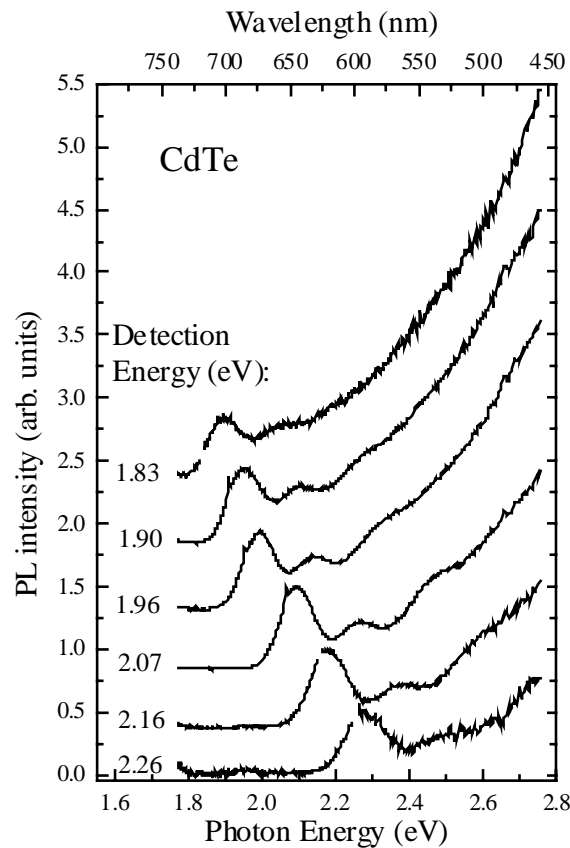

Fig. 2: Room-temperature photoluminescence excitation spectra of CdTe nanocrystals obtained for several detection energies.

It is well known that size dispersion of nanocrystals is the source of the inhomogeneous broadening of absorption and luminescence bands[1,2]. It hides information about the spectrum of a single size nanocrystal. However, as is evident from the foregoing, by tuning the detection energy through the energy range of the photoluminescence peak we can probe the quantum dots of different sizes within the only one sample. And vice versa, it is possible to select a set of nanocrystals with a well determined size by tuning the excitation energy through the absorption peak, because in inhomogeneous broadened systems the dependence of lineshape and peak position of Stokes-shifted PL on excitation photon energy can be also observed[5]. Figure 3 shows the evolution of the luminescence spectra when the excitation photon energy is tuned from 2.60 to 1.94 eV.

Global emission spectra excited at 2.50 eV consist of one peak cenetred at 1.96 eV. The full width at half-maximum (FWHM) was about 195 meV which reflect substantial inhomogeneous line broadening arising from size distribution. This broadening is due fact that the higher the excitation energy the better the PL spectrum reflects the entire size distribution of nanocrystals in the sample.
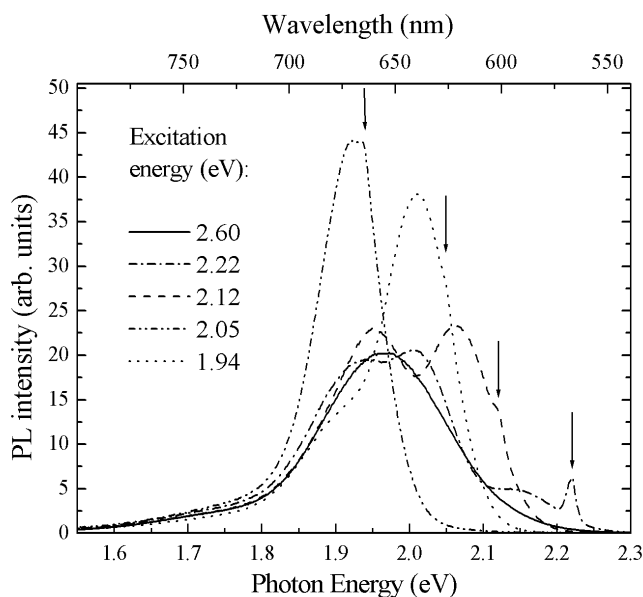
Fig.3: Room temperature nonresonant and resonant PL spectra of CdTe nanocrystals for several excitation photon energies.

For lower energy excitation (2.22 eV) PL spectrum consists of three well resolved peaks centred at 2.15, 2.03 and 1.93 eV. Such multi peak structure can be explained as result of size selective excitation. Because of the existence of a size distribution of dots, each emitting at its own characteristic energy, the measured PL intensity represents an ensemble average. For excitation at 2.22 eV the largest nanocrystals can be excited into their third excited state, nanocrystals of medium size can be excited in their second excited state, while a quantum dots of a smaller size is excited into their first excited state. As a result PL spectrum consist of three peaks. The width of the PL peaks decreases considerably (FWHM is 105 meV, 75 meV and 116 meV, respectively) demonstrating PL line narrowing, because of only nanocrystals of certain size within the finite size distribution are excited. The similar multi peak structure have been observed recently in resonantly excited PL spectra of CdTe nanocrystals embedded into glass matrix at T=2K[16]. The high-energy peak was attributed to a trap emission, 120 meV deep, as in bulk CdTe[16]. The two other peaks were attributed to the 1LO and 2LO phonon replica of the first PL peak. In our case the pattern is complicated by the significant homogeneous broadening which takes place at room temperature, which does not allow to observe any phonon replica. Moreover the energy distance between these peaks increases when the excitation photon energy is changed from 2.22 to 2.12 eV.
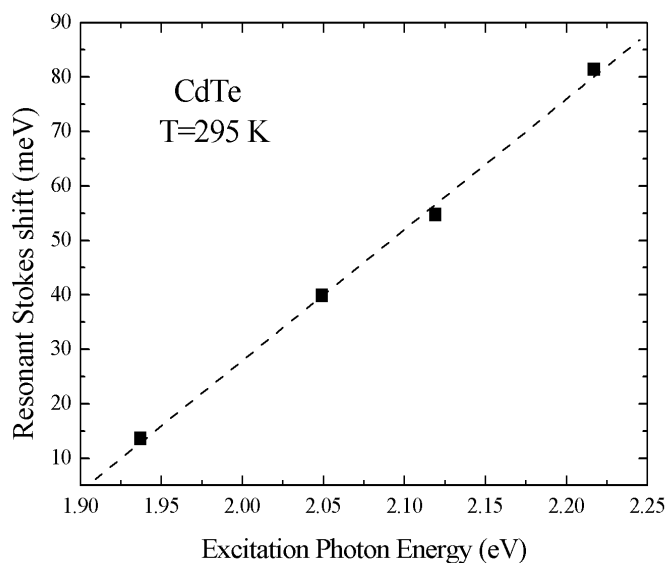

Fig. 4: The resonant Stokes shift for CdTe nanocrystals at room temperature.

As the excitation photon energy is decreased down to 2.12 eV, the PL spectrum consist of two peaks which can be attributed in similar way to second and first excited states of nanocrystals of smaller and largest size, respectively. Dual peak structure can be observed even with excitation at 2.05 eV, which corresponds to the position of the absorption maximum. For excitation at 1.94 eV the PL spectra consists one narrow peak (FWHM is 94 meV) cenetred at 1.92 eV, because only the largest particles in the size distribution is selected to be excited.

As the excitation photon energy is decreased below the first absorption maximum the energy difference between the first PLN peak and excitation photon energy (resonant Stokes shift)[11,17] decreases significantly (Figure 4). The minimum magnitude of the resonant Stokes shift D = 14 meV was obtained at room temperature when sample was excited at 1.94 eV. This value agrees very well with value of resonant red shift which has been observed in CdTe nanocrystals at very low temperature[10]. The theoretical analysis indicates that the observed Stokes shift in CdTe nanocrystals arises from the electron-hole-exchange interaction[10] and therefore the luminescence is emitted from an optically forbidden state lying at a lower energy. In order to verify this assumption and investigate the radiative lifetime, we also measured the decay of the luminescence at detection energy 1.92 eV.
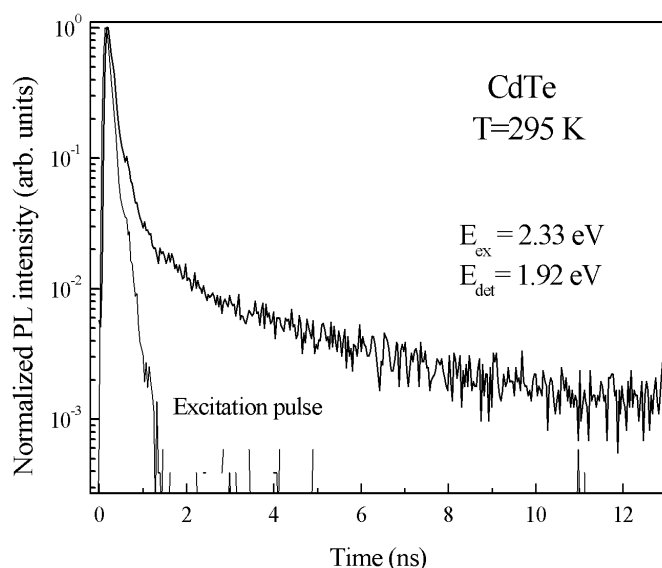

Fig. 5: Room temperature luminescence decay of CdTe nanocrystals.

At the energy of detection we have a superposition of the transitions from nanocrystals of different sizes and it is difficult to assign the decay time to one particular line. As shown in Figure 4, the decay curve is clearly non-exponential, which results from the dispersion in trap energy levels[18]. Decay was reconvoluted using a sum of two exponential decay functions with characteristic decay times τ_1=230 ps and τ_2 = 1.7 ns. The small value of decay time observed at room temperature is inconsistent with the long decay time of a weakly allowed optical transition. On the other hand the resonant Stokes shift in our CdTe nanocrystals (D=14 meV) agrees well with the magnitude of extremely shallow surface fluctuations (~ 10 meV) obtained from analysis of the temperature dependence of the Stokes shift and PL decay in CdSe nanocrystals[19]. We propose that the most likely the lowest emitting state in CdTe nanocrystals originate from interfacial disorder or from surface induced intrinsic gap states rather then from weakly allowed optical transition due to electron-hole exchange ineraction.

4. CONCLUSIONS

We present PLE and FLN measurements in CdTe free standing nanocrystals at room temperature and we show that by tuning the detection or excitation energy through the energy range of the photoluminescence peak we can probe the quantum dots of different sizes. Luminescence excitation spectra of CdTe nanocrystals reveal different maxima within the first absorption feature. Analysis of resonant Stokes shift at different excitation energies combined with data of time resolved PL measurement shows that the level structure in our samples cannot be assigned using the model of

electron-hole exchange interaction alone. We propose to assign the small value of resonant Stokes shift and small decay time to optical transitions including extremely shallow electronic levels.

REFERENCES

1. L. Brus, "Quantum Crystallites and Nonlinear Optics," Appl. Phys. A. **53**, pp. 465-474, 1991.
2. S.V. Gaponenko, *Optical Properties of Semiconductor Nanocrystals*, Cambridge University Press, Cambridge, 1998.
3. A. Eychmüller, A. Hasselbarth, L. Katsikas, H. Weller, "Photochemistry of Semiconductor Colloids. 36. Fluorescence Investigations on the Nature of Electron and Hole Traps in Q-Sized Colloidal CdS Particles**,"** Ber.Bunsenges.Phys.Chem. **95**, pp. 79-84, 1991.
4. D.J. Norris, M. Nirmal, C.B. Murray, A. Sacra, M.G. Bawendi, "Size dependent optical spectroscopy of II-VI semiconductor nanocrystallites (quantum dots)," Zeitschrift fur Physik D. **26**, pp. 355-357, 1993.
5. W. Hoheisel, V.L. Colvin, C.S. Johnson, A.P. Alivisatos, "Thereshold for quasicontinuum absorption and reduced luminescence efficiency in CdSe nanocrystals," J.Chem.Phys. **101**, pp.8455-8460, 1994.
6. S.V. Kershaw, M. Burt, M. Harrison, A. Rogach, H. Weller, A. Eychmüller, "Colloidal CdTe/HgTe quantum dots with high photoluminescence quantum efficiency at room temperature," Appl. Phys. Lett. **75**, pp. 1694-1696, 1999.
7. M. Mullenborn, R.F. Jarvis, B.G. Yacobi, R.B. Kaner, C.C. Coleman, N.M. Haegel, "Characterization of solution-synthesized CdTe and HgTe," Appl. Phys. A. **56**, pp. 317-321, 1993.
8. R.J. Bandaranayake, G.W. Wen, J.Y. Lin, H.X. Jiang, C.M. Sorensen, "Structural phase behavior in II-VI semiconductor nanoparticles," Appl. Phys. Lett. **67**, pp. 831-833, 1995.
9. A. A. Lipovskii, E. V. Kolobkova and V. D. Petrikov, "Formation of II-VI nanocrystals in a novel phosphate glass," J. Cryst. Growth **184-185**, pp.365-369, 1998.
10. J. Pérez-Conde, A.K. Bhattacharjee, M. Chamarro, P. Lavallard, V.D. Petrikov, A.A. Lipovskii, "Photoluminescence Stokes shift and exciton fine structure in CdTe nanocrystals," Phys. Rev. B. **64**, pp. 3303-1 – 3303-4, 2001.
11. O. I. Mićić, H. M. Cheong, H. Fu, A. Zunger, J. R. Sprague, A. Mascarenhas, and A. J. Nozik, "Size-Dependent Spectroscopy of InP Quantum Dots," J. Phys. Chem. B. **101**, pp. 4904-4912, 1997.
12. D.V. Talapin, S. Haubold, A.L. Rogach, A. Kornowski, M. Haase and H. Weller, "A Novel Organometallic Synthesis of Highly Luminescent CdTe Nanocrystals," J. Phys. Chem. B. **105**, pp. 2260-2263, 2001.
13. J.I. Pankove, *Optical Properties in Semiconductors*, Dover, New York, 1975.
14. M.G. Bawendi, P.J. Carrol, W. Wilson, L. Brus, "Luminescence properties of CdSe quantum crystallies: Resonance between interior and surface localized states," J. Chem. Phys. **96**, pp. 946-954, 1992.
15. M.G. Bawendi, W.L. Wilson, L. Rothberg, P.J. Carroll, T.M. Jedju, M.L. Steigerwald, L.E. Brus, "Electronic structure and photoexcited-carrier dynamic in nanometer-size CdSe clusters," Phys.Rev.Lett. **65**, pp. 1623-1627, 1990.
16. M. Chamarro, P. Lavallard, J. Pérez-Conde, A.K. Bhattacharjee, V.D. Petrikov, A.A. Lipovskii, "Electron-Hole Exchange Induced Stokes Shift in CdTe Nanocrystals," Phys. stat. sol. B. **229**, pp. 453 – 456, 2002.
17. H. Fu, A. Zunger, "InP quantum dots:Electronic structure, surface effects, and the redshifted emission," Phys. Rev. B. **56**, pp. 1496 – 1508, 1997.
18. A. Eychmüller, A. Hasselbarth, L. Katsikas, H. Weller, "Fluorescence mechanism of highly monodisperse Q-sized CdS colloids," J. Lumin.**48/49**, pp. 745-749,1991.
19. M. Nirmal, C. B. Murray, and M. G. Bawendi, "Fluorescence-line narrowing in CdSe quantum dots: Surface localization of the photogenerated exciton," Phys. Rev. B. **50**, pp. 2293-2300, 1994.