

Up-Conversion Luminescence in Colloidal CdTe Nanocrystals

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ABSTRACT

We report on the efficient photoluminescence up-conversion in colloiddally synthesized CdTe nanocrystals. We demonstrate that the efficiency of photon energy up-conversion and magnitude of spectral shift can be controlled: (i) by the size of the nanocrystals; (ii) by the temperature dependence of the excited state absorption coefficient; (iii) by the dependence on excitation intensity. From the analysis of the experimental data we can suggest that intrinsic gap states are involved as intermediate states in the photoluminescence up-conversion rather than nonlinear two-photon absorption or Auger processes.

INTRODUCTION

Anti-Stokes photoluminescence (ASPL), or photon energy up-conversion (UC), in semiconductor compounds – a phenomenon in which the photon energy of photoluminescence (PL) output is higher than the excitation energy – has attracted much attention recently [1-8]. Such UC effects have been reported in bulk semiconductors [1,9,10], heterostructures [2, 3], quantum wells [4, 8] and self-assembled quantum dots (QDs) [5,6] at low temperatures. Recently, ASPL has been observed in Si [11], InP, CdSe [7,12] and PbS nanocrystals (NCs) [13]. The energy up-conversion is usually achieved by (i) a Auger process [14, 15], (ii) a nonlinear mechanism such as two-photon absorption [3,5,13], (iii) and thermal activation by the absorption of phonons [11, 12].

In this work we report the observation of well resolved ASPL bands at room temperature and very low excitation intensity in colloidal CdTe NCs.

EXPERIMENTAL DETAILS

CdTe NCs stabilized by thioglycolic acid were synthesized in aqueous solution by reaction of cadmium perchlorate with H_2Te gas following the method of Ref. [16]. Four fractions of CdTe NCs with sizes of 1.8, 3.0, 3.5 and 4.4 nm and PL quantum yield (QY) of ~ 20% was isolated from the crude solution by size-selective precipitation [16] and 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 1.7 nm/mm) equipped with a cooled R943 Hamamatsu photomultiplier. The PL spectra were obtained by exciting the samples with a Xenon lamp (output power of 40 μW - 0.1 mW, depending on the wavelength and a spot area ~10mm²). A Xenon lamp or He-Ne laser (λ = 632.8 nm, output power of 2 mW) were used in the ASPL experiments. When using the Xenon lamp a cut-off filter was employed in order to avoid illumination of the samples by higher

orders caused by the spectrometer grating, whilst an interference filter ($\lambda = 632.8$ nm, 10 nm bandwidth) was used in conjunction with the He-Ne laser to eliminate laser lines from appearing in the ASPL spectra. The power density of excitation was varied in the range of $0.001 - 45$ mW/cm² by neutral-density filters and controlled by Coherent Labmaster power meter. The PL spectra have been corrected for the sensitivity of the detection system. The absorbance (optical density) of all samples was kept below 0.2 at the first absorption feature for 1 cm path length. The small values of optical densities guarantee that no artifacts can arise from different light penetration length.

RESULTS AND DISCUSSION

Figure 1 demonstrates the evolution of optical properties of CdTe NCs as the size increased from 1.8 to 4.4 nm. The well-pronounced absorption peaks are indicative of a narrow size distribution of CdTe NCs, which was estimated to be about 10-12%.

The steady-state PL (SSPL) spectrum excited by the Xe-lamp ($\lambda_{ex} = 400$ nm, $\hbar\omega_{ex} = 3.1$ eV) consists of one sharp peak of band-edge emission. Shifts in the PL peak position with increasing size of CdTe NCs are somewhat smaller than shifts in absorption.

The PL spectra excited with the energies smaller than peak position of SSPL (i.e. smaller than the band-gap energy) show well resolved ASPL bands (figure 2) on the high-energy side of the spectra of all samples. The maximum efficiency for energy up-conversion in the sample of 3.5 nm CdTe NCs was estimated to be about 3.34×10^{-4} % relative to the absorbed Xenon lamp power at 625 nm ($\hbar\omega = 1.98$ eV) at room temperature.

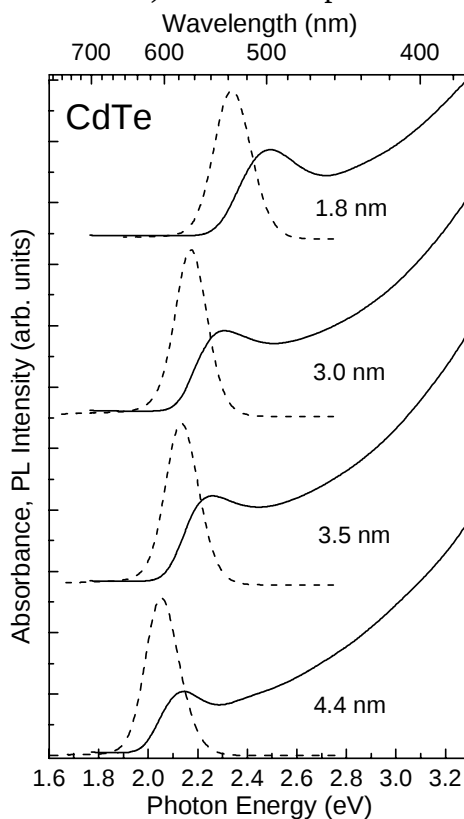


Figure 1. Room-temperature absorption and emission spectra of CdTe NCs with different sizes (in nanometers).

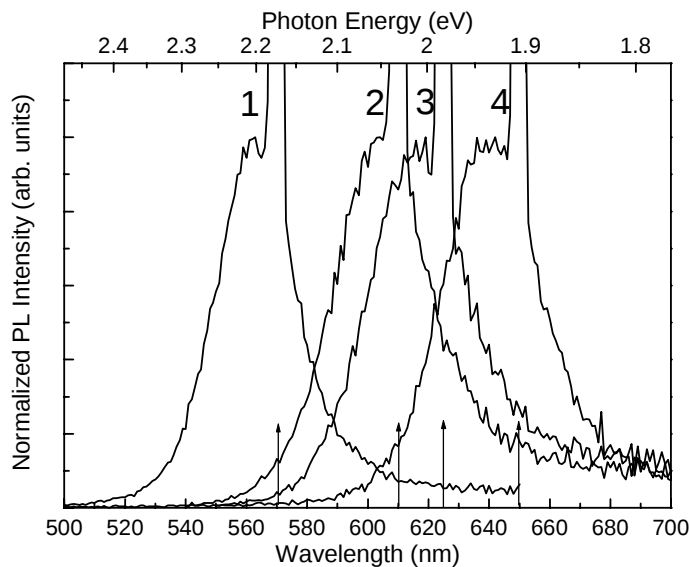


Figure 2. PL spectra of CdTe NCs with different sizes (1 – 1.8nm; 2 – 3.0nm; 3 – 3.5nm; 4 – 4.4nm). Wavelengths of excitation are indicated by arrows

According to Ref. [7] the maximum magnitude of the up-converted blue shift ($\Delta E_{UC}^{\max}$) can be defined as the difference between the excitation energy and the energy value at which an exponential fit of the ASPL spectrum crosses the average background noise level. Using this procedure a value of $\Delta E_{UC}^{\max} = 350$ meV was obtained for excitation of CdTe NCs with size 3.5 nm by a low-power He-Ne laser ($\hbar\omega = 1.96$ eV, $P=2$ mW). Exciting other samples by the Xenon lamp the value $\Delta E_{UC}^{\max}$ was obtained in a range 290 – 340 meV.

Analysis of the dependence of the ASPL intensity on excitation energy can provide information about the mechanism of transferring excitation energy to the high-energy spectral region. In most of the mechanisms of ASPL proposed recently [1-8] at least two exciting photons are supposed to be involved in generation process. As a result it is expected that the intensity of the ASPL increases nonlinearly with the excitation intensity. However, figure 3 shows that the integrated ASPL intensity (excited by a He-Ne laser) depends on excitation intensity linearly. (When using the Xenon lamp for illumination samples with other sizes of CdTe NCs the same linear dependence was showed up.) This feature clearly indicated that nonlinear two-absorption (quadratic dependence on excitation intensity) or Auger recombination (cubic dependence on excitation intensity) could not be the cause of the observed photon energy UC. Moreover, the power of He-Ne laser (or even less powerful Xenon lamp) is too weak for the generation of two-photon absorption processes.

As mentioned above ASPL can be observed as a result of energy accumulation of the excited electron-hole pair from the phonon bath. In that case the intensity of ASPL should grow with rising temperature because of the increase of the phonon occupation number. It was found indeed that the ASPL intensity increases dramatically with temperature (figure 4). At the same time, the Stokes-shifted PL shows thermal induced quenching and broadening. The spectral position of the UCPL peak is weakly depended on temperature while the position of SSPL peak changes significantly (0.6 - 0.7 meV/K), coinciding with the peak of the first optical transition in absorption spectrum (0.55 – 0.7 meV/K). Although these experimental

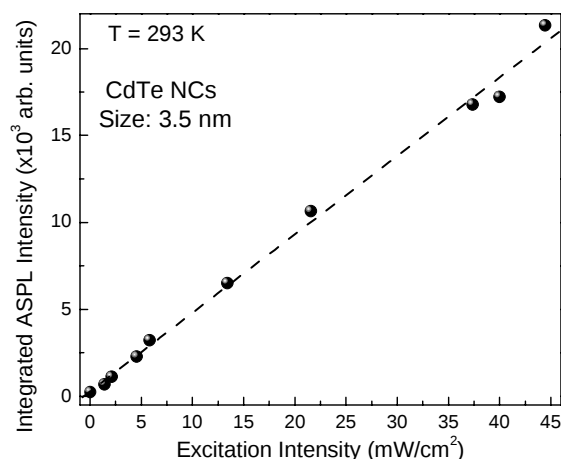


Figure 3. Dependence of the ASPL intensity in CdTe NCs on the excitation power density at room temperature. The line shows a linear fit to the data.

findings testify to an important role of electron-phonon interactions in UC processes in CdTe NCs, this mechanism alone is not a sufficient explanation of all the experimental results. The thermal energy available from the phonon bath is too small to explain the obtained $\Delta E_{UC}^{\max}$ value.

It was also found that the spectral shape of the ASPL does not reflect the size distribution of the NCs. The effect of the inhomogeneous distribution can be evident in the excitation wavelength dependence of the SSPL spectra [17, 18]. When the excitation energy is restricted to the onset region of the absorption spectra then a much narrower range of NC sizes is excited; these NCs have the largest size in the ensemble. SSPL spectra of CdTe NCs at this

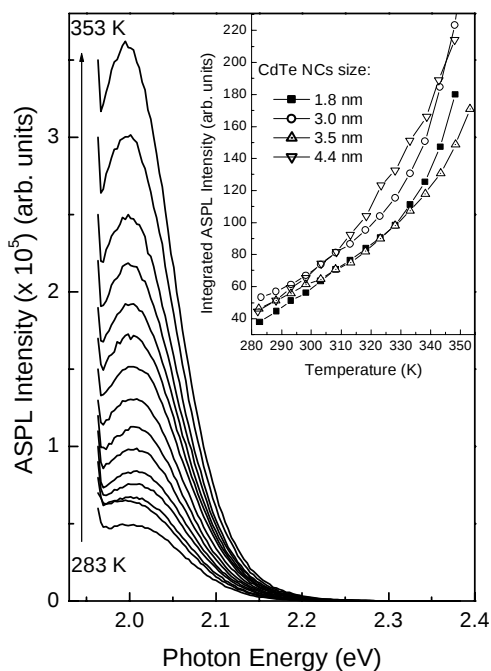


Figure 4. Temperature behaviour of the ASPL band in 3.5 nm CdTe NCs. Inset: Variation of the integrated intensity of the UCPL with temperature for all samples studied.

type of excitation show a decrease of the width of the PL peak (from 174 meV at $\hbar\omega_{ex} = 2.34$ eV to 119 meV at $\hbar\omega_{ex} = 2.17$ eV) demonstrating pronounced PL line narrowing. In contrast the ASPL linewidth shows additional broadening with decreasing excitation energy (from 120 meV at $\hbar\omega_{ex} = 2.0$ eV to 150 meV at $\hbar\omega_{ex} = 1.95$ eV).

It is well known that in addition to the quantum-confined states, there may be subgap states in semiconductor NCs [18, 19]. Recent studies of the carriers dynamics in CdSe NCs [18, 20, 21] at above-gap excitation shown that immediately after photoexcitation, the initially formed hot electrons thermalize quickly to the bottom of the conduction band (CB) and subsequently decay either into shallow trap states [18, 20] or an intrinsic "dark" exciton state [22]. This trapping of electrons is an extremely fast process occurring in the 300-500 fs time range [21, 23] providing fast thermal equilibrium between a long-lived lower state and an upper state. Moreover a thermal repopulation effect in the band gap emission has been observed previously [24, 25]. Based on the above discussed experimental results and work from previous studies we propose that the observed up-conversion PL originates from cascade phonon-assisted excitation via a set of below-gap state. Such an UC processes can be highly efficient if optical transitions and thermal coupling between electronic levels of shallow traps are conveniently exploited. The photon energy up-conversion mechanism responsible for the production of the ASPL in CdTe QDs is therefore attributed to the excitation from the valence band into one of the below-gap trap states located near the CB (CB_{trap}). Thermally activated retrapping from the CB_{trap} state causes repopulation of the trap states and possible transitions to the conduction band (detrapping), followed by recombination to the valence band. Based on the finding that the ASPL linewidth does not follow the size distribution of the NCs we suggest the involvement of shallow electron traps rather than "dark" exciton as CB_{trap} states at room temperature.

In order to explain the broadening of the ASPL linewidth with decreasing of excitation energy as well as the obtained ΔE_{UC}^{max} value we have to suggest the dispersion in trap energy levels which can explain, among other things, the multiexponential PL decay in our CdTe NCs [26]. Also the linear dependence of ASPL on excitation intensity is consistent with the assumption that there are relatively long-lived electron-hole pair states in part of the process, giving rise of the ASPL [11, 12].

At higher temperatures the thermal detrapping is more significant and it gives a rise of the ASPL intensity. It is reasonable to propose an activation energy E_{act} for the detrapping process. This activation energy should be higher, the more deeply trapped and the more localized an electron is. From analysis of the Arrhenius plots we estimated E_{act} to be in range of 300-360 meV. Although a simple model proposed in the present work describes all ASPL results very well, a complete description of the photon energy UC in CdTe NCs requires knowledge of the nature and the density of localized states as well as the corresponding electron-phonon coupling which are poorly understood so far.

CONCLUSION

We report on the efficient photoluminescence (PL) up-conversion in colloiddally synthesized CdTe NCs. We demonstrate that the efficiency of photon energy up-conversion and the magnitude of the spectral shift can be controlled: (i) by the size of the NCs; (ii) by the temperature dependence of the excited state absorption coefficient; (iii) by the excitation intensity. Much experimental evidence indicates that subband surface states are involved in the photon energy UC process. Our data are consistent with the suggestion for shallow

thermally coupled electron trap states with trap depth of 300-360 meV.

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