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We present a new technique to perform high resolution resonant photoluminescence excitation of CdSe/ZnS nanocrystals. The method takes advantage of the long photoluminescence decay times (~ 1 μs) observed in this system at liquid helium temperatures. Resonant photoluminescence excitation can be performed using a tunable pulsed excitation and a time-gated detection. Spectral hole burning investigations on an ensemble of CdSe/ZnS nanocrystals lead to homogeneous linewidths of ~100 μeV for the band edge exciton state.

Semiconductor nanocrystals (NCs) featuring atomic-like electronic energy level structures can be used in a wide variety of applications, such as nanoscale electronics[1] and biological labelling[2]. In particular, colloidal CdSe NCs are promising for many of these applications due to their bright luminescence which is tunable across the visible spectrum[3].

Photoluminescence from single CdSe NCs exhibit a strong photon antibunching[4], making these particles good candidates for the realization of triggered single photon sources[5]. For certain applications[6] in quantum information such as linear optics quantum computing[7], the single photons should display a Fourier-limited spectrum which is determined by the lifetime of the excited state. The case of pure radiative decay of an ideal two-level system leads to perfectly indistinguishable photons. However, dephasing and spectral diffusion, which manifest as fast and slow fluctuations of the transition frequency, introduce distinguishability between photon wavepackets. It is therefore of crucial interest to investigate the homogeneous linewidth, and thus the coherence decay time, of the transition involving the band edge exciton.

Spectral hole burning is a powerful method to investigate the homogeneous linewidth of organic molecules in the condensed phase at liquid helium temperatures[8]. Since the molecules emit in a wide spectral range of vibrational lines (~ 10-350 meV) which are red-shifted with respect to the zero phonon line (ZPL), the separation of the fluorescence photons from the excitation light can easily be performed using appropriate optical filters. Direct implementation of this technique on CdSe NCs is not possible because of a very small red shift of the luminescence spectrum with respect to the absorption transition, as shown by fluorescence line narrowing experiments[9]. This red shift is only a few meV (depending on the particle size) for the sharp ZPL. The luminescence spectrum of the NCs also displays a longitudinal optical (LO) phonon replica of the ZPL, with a ~25 meV red shift[10] which makes very difficult the spectral filtering of the luminescence from the scattered excitation light.

In this letter, we present a new experimental method to perform high resolution spectroscopy of the CdSe NCs band edge exciton. This method is a spectral hole-burning technique based on "time filtering" of the luminescence photons from the excitation light. It exploits the long photoluminescence decay times (~ 1 µs) observed in this system at liquid helium temperatures.

In order to measure the homogeneous width of the $1S_e1S_{3/2}$ band edge exciton transition, we first irradiate an ensemble of CdSe NCs with a fixed frequency cw beam delivered by a single longitudinal mode dye laser. The spectral hole burnt in the red wing of the lowest absorption band is then probed by recording a photoluminescence excitation (PLE) spectrum using an optimized combination of pulsed excitation and time-gated detection. The pulses are prepared from the same cw laser with two acousto-optical modulators in double pass configuration and the hole burning spectra are recorded by scanning the laser frequency around the burning wavelength. In practice, we prepare rather long pulses of 20 ns duration which offer a good spectral resolution of 35 neV and efficient excitation of the NCs. Time-shifted detection of the emitted photons is performed during the inter-pulse period (see Fig. 1.a) by a triggered single photon counting avalanche photodiode synchronized with the excitation pulses. A compromise between a high excitation rate of the NCs and a long detection time window has to be found for an optimum detection rate. Indeed, for experiments performed at 3 K where the average NCs lifetime[11] is 300 ns, the collection of the luminescence is optimum at a repetition rate of 1 MHz. Nearly half of the emitted photons are collected in the 800 ns detection time window.

We studied ZnS coated CdSe NCs (1.9 nm radius, 565 nm peak emission) dispersed in a thin polymer (PMMA) film. The sample is prepared by depositing on a silica plate a small drop of a solution of NCs (10^{-4} M) in toluene containing 2% by weight PMMA. It is then placed in a helium flow cryostat at the focal region of a high numerical aperture parabolic

mirror, used in a confocal configuration to excite and collect the luminescence from the NCs. Fig.1.b shows a luminescence excitation spectrum recorded at 3 K after a 30 minutes irradiation at 571.63 nm laser wavelength. The burning intensity was set to 500 $W.cm^{-2}$, below the saturation intensity to ensure that the photon absorption rate of the NCs is well below their average luminescence decay rate. The reading intensity was fifty times weaker (peak intensity 10 $W.cm^{-2}$). The spectrum shows a hole at the burning laser frequency with a relative depth of about 10 %. Similar results were also observed at other burning frequencies within the inhomogeneously broadened $1S_e1S_{3/2}$ absorption band. The spectral hole is well fitted by a lorentzian shape with a total width at half maximum of 200 µeV, corresponding to a homogeneous width of 100 µeV (half of the measured value[8]). Reducing the burning intensity by a factor of ten led to spectral holes with the same width, confirming the absence of power broadening in the presented spectra. The spectral holes disappear several hours after the irradiation, showing that the mechanisms involved in hole burning are due to photo-induced spectral jumps.

In order to explain the observed hole width one has to take into account the fine structure of the band edge exciton which consists of five sublevels. Three of them are optically active (bright). The two others including the ground state are optically passive (dark). Since the spectral hole is burnt in the red wing of the lowest absorption band,, the resonant laser light creates preferentially the excitons in the lowest energy active state $\left|\pm 1^L\right\rangle$, from which fast relaxation to the dark ground state $\left|\pm 2\right\rangle$ occurs at low temperatures. While luminescence from the ground state is normally forbidden within the electric dipole approximation, radiative recombination is made possible through coupling to phonons, spin flip transitions induced by paramagnetic defects, or mixing of bright and dark excitons induced by surface states[12]. The measured homogeneous width should give access to the bright exciton optical coherence lifetime. Dephasing processes due to phonons vanish at

liquid helium temperatures, but a contribution of spectral diffusion to this width cannot be excluded[13]. Therefore from our measurement we can conclude that the coherence lifetime is longer than 13 ps, which sets a lower limit for spin relaxation within the band-edge exciton manifold.

We also investigated the effect of the hole burning in the emission spectrum of NCs. The photo-induced spectral dispersion of the emitting states gives photoluminescence spectra broader than the excitation spectra. Nevertheless, interesting informations can be extracted by comparing luminescence spectra before and after a burning irradiation. Fig. 2 shows the differential emission spectrum (difference between the luminescence spectrum taken after and the one taken before irradiation) of the sample at 3 K after the irradiation described in Fig. 1. The luminescence is excited at the fixed wavelength 514 nm. Spectral holes in the luminescence spectra appear with a red shift compared to the burning frequency. The observation of a hole which is 6 meV red-shifted with respect to the burning frequency supports the picture that excitation creates the exciton in the $\left|\pm 1^{L}\right\rangle$ state and luminescence arises from the "dark" exciton ground state $\left|\pm 2\right\rangle$. The holes (ii) and (iii) display a progression energy of 25 meV, attributed to the longitudinal optical (LO) phonon mode[10].

A characteristic feature of the differential emission spectrum is the increase of the luminescence intensity in the blue side of the burning frequency. This anti-hole, accompanied with phonon replica, can be interpreted as follows. Let us assume that the photo-induced spectral jumps responsible for hole burning are spectrally symmetric (blue shifts and red shifts of the NC absorption lines occur with equal probabilities). While the red-shifted NCs can still interact with the burning laser via absorption in the upper fine structure sub-levels ($\left|\pm 1^{U}\right\rangle$, $\left|0^{U}\right\rangle$), the blue-shifted NCs are out of resonance and cannot be re-excited by the burning beam. The latter will therefore lead to the observed increase of the blue shifted luminescence.

In summary, we have developed a new method to perform resonant photoluminescence excitation of NCs with a high spectral resolution, based on the long emission decay of CdSe/ZnS NCs at low temperature. Although measured at low saturation intensity, the 100 µeV homogeneous linewidth found for the first excitonic state cannot exclude a contribution from spectral diffusion. This open question can be adressed by extending the presented method to perform time-gated PLE of individual NCs.

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Figures

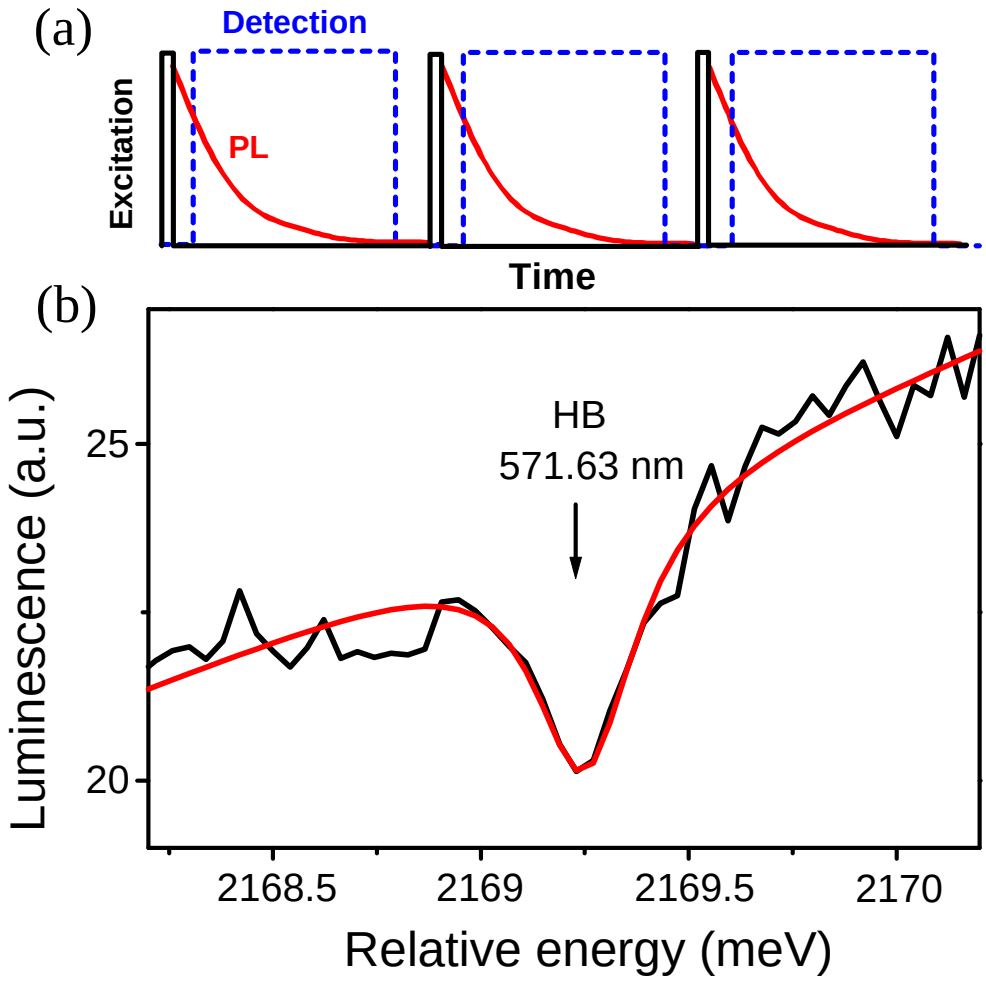

FIG. 1

a) Principle of the resonant photoluminescence excitation method, showing the schematic temporal profile of pulsed excitation, emission decay (PL) and synchronized time-gated detection. The pulse width of 20 ns offers a high spectral resolution. With a luminescence lifetime of 300 ns at 3 K, a repetition rate of 1 MHz ensures an optimal detection of the emitted photons. The time-shifted detection is active for 800 ns after each pulse.

b) Excitation spectrum at 3 K for a collection of CdSe/ZnS NCs, recorded after a 30 minutes hole burning at 571.63 nm with an irradiation intensity of 500 $W.cm^{-2}$. The deduced homogeneous linewidth is 100 µeV.

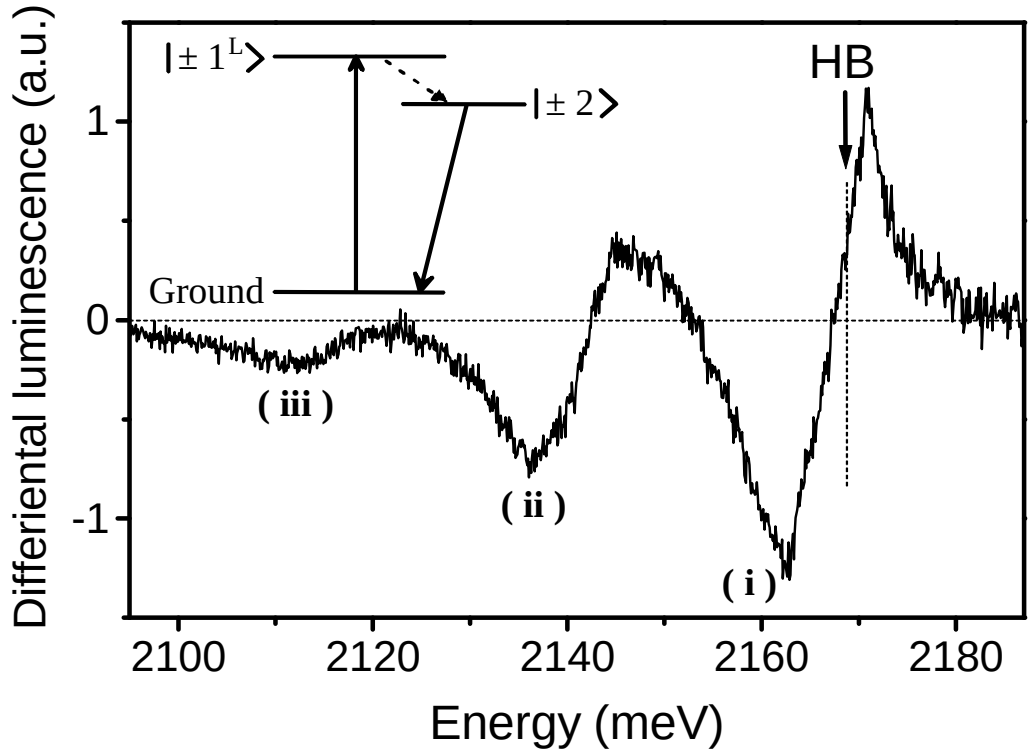

FIG. 2

Inset: Three state model for a CdSe NC, showing resonant excitation of the band edge exciton in the lowest energy active state $\left|\pm 1^{L}\right\rangle$, followed by fast relaxation to the dark ground state $\left|\pm 2\right\rangle$ at low temperatures. Luminescence stems from this ground state with a lifetime of a few hundred ns.Main figure: Difference between luminescence spectra recorded after and before hole burning, at 3 K. The main spectral hole (i) is red-shifted compared to the burning energy, evidencing burning in the “bright” state and emission from the “dark” state. Red-shifted replicas (ii) and (iii) of the main spectral hole (i) are attributed to a LO phonon mode at 25 meV.