Luminescence properties of II/VI semiconductor colloidal nanocrystals at collective and single scales

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Abstract. Colloidal nanocrystals are crystalline spheres of semiconductors of a few nanometers, obtained by chemical synthesis. At this size scale, lower than Bohr radius of the exciton, emission properties are dominated by quantum confinement effects and depend crucially on the nanocrystal radius, which can be controlled by adjusting the synthesis parameters. Nanocrystals present high photostability and good quantum efficiency, even at room temperature. Their emission wavelength can be tuned over the whole visible range, making them very attractive solid state light sources which are already used in optoelectronic devices or for biological labeling. The luminescence properties of CdSe colloidal nanocrystals synthesized at the Institute of Materials Science in Hanoi are presented. At collective scale, the emission properties reveal the synthesis quality. Temperature effects from ambient to 4 K on spectra and decay rates will be presented and analyzed in terms of emitting level fine structure. The study of CdSe colloidal quantum dots at the single emitter scale is of great interest as it reveals properties which are hidden by collective studies, such as luminescence “blinking”, a random switching from a fluorescent to a non fluorescent state, which is closely related to the crystalline defects of a nanocrystal and its interaction with its environment. We will present the blinking properties of the prepared nanocrystals, and relate them to the nanocrystals synthesis quality and shell quality.

Keywords: Nanocrystals, CdSe, quantum dot, single scale emitter, luminescence.

1. Introduction
Colloidal CdSe nanocrystals (NCs) have attracted growing attention due to their size-tunable optical properties and ease of chemical manipulation into structures of varied complexity using a bottom-up approach. They can be synthesized with a narrow size distribution (<5% rms) and the diameters are tunable during the synthesis (between 1.5 and 10 nm). In this size range, where the nanocrystal is smaller than the exciton Bohr diameter (11.2 nm), the confinement energy of the electron and hole is stronger than their Coulomb interaction, making them true zero-dimensional structures. The spectral properties and the photostability at room temperature make them promising light sources for a large range of applications, including quantum cryptography [1], optoelectronic devices [2, 3], or biological labeling [4]. The study of their optical properties has greatly benefited from the advent of single
molecule techniques. When observed individually, NCs have, indeed, proved to be more complex than ensemble-averaged studies could have inferred. Studies at single scale have revealed striking phenomena such as fluorescence “blinking” [5], spontaneous spectral shifts [6], and lifetime fluctuations [7]. Most of these phenomena are due to the crystalline defects of a nanocrystal and strong interactions with their surrounding environment. In the last few years the synthesis quality has largely improved to limit crystalline defects and partially removes the interactions between the core and the environment by adding a passivating shell of ZnS or CdS.

In the first part, we present study of CdSe colloidal nanocrystals, synthesized at the Institute of Materials Science in Hanoi, at collective scale. Temperature effects from ambient to 4 K on spectra and decay rates will be presented and analyzed in terms of emitting level fine structure. The effect of a ZnS shell will be shown. In the second part, the properties of CdSe colloidal quantum dots at the single emitter scale will be presented and discussed. Single scale studies such as luminescence “blinking”, a random switching from a fluorescent to a non fluorescent state will be present and discussed. The blinking properties of the prepared nanocrystals will be related to the synthesis quality.

2. Ensemble measurements

Two different types of nanocrystals are compared in this article: CdSe nanocrystal in toluene covered by trioctylphosphine oxide (TOPO), to prevent from oxidation and solubilized them in organic solvents (574 nm peak at 300 K), and ZnS-coated CdSe NCs in toluene (585 nm peak emission at 280 K).

We first study the temperature dependence of nanocrystals luminescent spectra and lifetimes in the range 4 - 300 K. Samples of nanocrystals were prepared by depositing a solution of NCs and PMMA (2% in mass) in toluene on a clean glass substrate. The low temperature experiments were carried out in a Janis Supertran-VP cryostat with a variable temperature controlled between 4 and 300 K.

The photonic excitation at 400 nm was obtained with a dye laser pumped by a pulsed nitrogen laser (0.14 mJ energy per pulse, pulse width 0.6 ns). The visible emitted light from the sample, collected by an optical fiber, was analyzed with a Spectrometer and a multichannel CCD detector (2000 pixels). The decays were analyzed with a Photo Multiplier Hamamatsu R5600U and a scope Tektronix TDS 784A with a time resolution of the order of 1 ns.

Figure 1. a) Luminescence spectra of CdSe/ZnS nanocrystals at different temperature and variation of the position of the maximum of luminescence with the temperature. b) Luminescent decays curves of CdSe/ZnS nanocrystals.

The figure 1 presents the luminescent spectra and decay variation with temperature of the CdSe/ZnS nanocrystals. The maximum of the luminescent spectra stays stable until 60 K and is then linearly red-shifted as the temperature increases. The FWHM decreases when the temperature
decreases as phonons broadening are limited at low temperature. These results are in agreement with previous studies on temperature dependence luminescence of CdSe/ZnS emitters [8]. The NCs emission wavelength presents a redshift of about 17 nm. This temperature dependence is directly related to the temperature dependence of the energy gap of bulk CdSe semiconductors as given by Varshni [9]. The temperature coefficient is found to be $(4\pm0.3)\times10^{-4}$ eV/K as given in literature for bulk CdSe.

The excited-state lifetime $T_1$ increases as the temperature decreases, from 17.5 ns at 300K to more than 200 ns at 4 K (see figure 1b). This variation is well known, and understood considering the fine structure of the emitting level. The emitting level $(1S_{3/2}1S_e)$, having electron spin $1/2$ and hole momentum $3/2$, is eightfold degenerate. This degeneracy is known to be due to three perturbative effects: the hexagonal crystalline structure (Wurtzite), the slightly prolate shape of the nanocrystal, and the exchange term in the electron-hole coulombian interaction, which is enhanced by confinement. A full mathematical treatment of the band edge exciton degeneracy can be found in ref [10]. The figure 2a presents the results for a CdSe/ZnS nanocrystal of diameter 3.5 nm. The exciton lowest sublevel has a total spin projection on the crystal hexagonal axis $J = \pm 2$ (twofold degenerate), cannot emit light through a linear process and is located a few meV below the lowest-energy optically active $(J = \pm 1L)$ exciton states.

![Figure 2a](image.png)  
![Figure 2b](image.png)

**Figure 2.** a) Fine structure of the emitting $(1S_{3/2}1S_e)$ level of a 1.8 nm radius CdSe nanocrystal calculated from [8]; b) Variation of lifetime with temperature (log-log scale) for NCs of CdSe/TOPO: red line and CdSe/ZnS: dotted blue line. Inset: The three states model as proposed in [9].

The scheme is simplified on the basis of a three level system (see inset in figure 2b): a zero exciton ground states $|G\rangle$, the $|B\rangle$ state representing the bright $(J = \pm 1L)$ exciton, and the $|D\rangle$ state representing the “dark” $(J = \pm 2)$ exciton. The energy splitting $\Delta E$ between the dark and bright states is in a few meV ranges, depending on the size and the shape of the QDs. After excitation, the system relaxes rapidly to the dark exciton state; it is later excited to the bright state through the phonon bath, and emits a photon [11]. This process is faster at high temperature, which explains the observed dependence of the excited states lifetime $T_1$ as a function of the temperature.

Figure 2b presents the variation of decays with temperature for the CdSe/ZnS and CdSe nanocrystals. The temperature dependence is modeled by the three level system as done in reference...
The experimental results are well fitted leading to the parameters $\Delta E$, $\Gamma_B$, and $\Gamma_D$ respectively the decay rates of the dark and the bright sates in good agreement with previous studies [11, 12]. From the model, two characteristic times are revealed, a short one, present only at low temperature, and a long one. This model reproduces then satisfactorily the decay curves presented on figure 1b. At low temperature ($<30$ K) two characteristic decay times are found, one lower than 2 ns and one larger than 100 ns. The short decay disappears with growing temperature.

Figure 1b presents the luminescence decay of an ensemble of nanocrystals recorded at 4 K and 280 K. It presents a multi-exponential behavior distributed over a large time scale. This can be due either to an inhomogeneous distribution of lifetimes or emitters containing a large amount of defects. To discriminate between these two causes, experiments at single emitter scale are essential as they can reveal fundamental features otherwise masked in ensemble experiments.

3. Single scale characterisations
CdSe/ZnS core-shell nanocrystals are spin coated on silica layer with a very low density (0.1/m$^2$), adjusted by different dilutions. Indeed, the distance between each nanocrystal should be higher than 1 μm to be excited and detected at single scale. The nanocrystals are then covered of a polymethyl (methacrylate) PMMA layer (50 nm thick). The optical emissions at single scale were characterized by micro-photoluminescence resolved in time at room temperature [13]. The excitation was made using a 400 nm pulsed laser diode focused onto a single NC via an oil objective lens (1.4 NA, x100). The fluorescence photons were collected by the same objective lens and sent to an avalanche photodiode (PerkinElmer SPCM-AQR-14) followed by a time-resolved photon counting card (Picoquant, Picoharp 300) (see the scheme in figure 3a). The photoluminescence intensity and decay were recorded in time-resolved acquisition mode.

![Optical Setup Scheme](image)

**Figure 3.** a) Schematic overview of the optical setup for collecting single NC fluorescence. (b) An ensemble measurement at 280 K gives a multi-exponential decay (blue line). The decay is bi-exponential at 4 K (red line): the short time is within our time resolution (<2 ns) and the long time decay is around 240 ns. Single NC decay (black line). The mean lifetime is found to be 19.5±2 ns (mean from 10 measurements).

Inset: single NCs lifetimes distribution.

On figure 3b, the decay of single NC (black line) can be compared to the ensemble decay at 280 K. The decay is monoexponential at single scale while it is multi-exponential at collective scale. The monoexponential decay suggests that there are few defects and the NC is of good quality. The multi-exponential decay at collective scale is then due to an inhomogeneous distribution of lifetimes.
Actually, the distribution of lifetimes measured on 16 single NCs gives a mean lifetime of 19.5 ns with a standard deviation of ±2 ns (see inset figure 3b).

It was seen for the first time in 1996 [5] that the light emission from single nanocrystals under continuous excitation turns on and off intermittently.

Indeed, QDs significantly interact with their local environment due to their high surface to volume ratio. The interaction of charges with their surroundings directly translates to fluctuations of their properties, particularly in the form of fluorescence intermittency. Most blinking-statistic models associate dark states with the presence of a charge in the dot’s core, which quenches the fluorescence emission by Auger processes [14]. On figure 4a, the fluorescent blinking of single CdSe/TOPO and CdSe/ZnS emitters are compared. Statistics made over more than 20 NCs shows that the CdSe NCs are in the “on” state 5 to 30% of the total time, whereas 70% of “on” states are recorded on CdSe NCs with ZnS shell. ZnS shell acts as an effective barrier to ionization and passivate potential surface trap sites [14]. This blinking behaviour is a good indication of the core/shell NCs synthesis quality.

**Figure 4.** a) Fluorescence intensity versus time trace of a CdSe nanocrystal compared to ZnS covered nanocrystal: three typical trace for each type of nanocrystal recorded with CCD camera; b) From left to right: Intensity fluctuations of single CdSe/ZnS NC measured with avalanche photodiodes. Intensity distribution for the NC trace: the two peaks correspond to off and on intensities; the threshold used is 20 photons per 6.25 ms time bin. Cumulative distributions of on (red line) and off times (blue line) in a logarithmic scale.
Due to the binary nature of the switching process, we can consider the time trace of each NC as a sequence of on and off times from which the statistical distributions $P_{\text{on}}(\tau)$ and $P_{\text{off}}(\tau)$ can be determined. The figure 4b presents the cumulative distributions of the on and off times obtained for one of our CdSe/ZnS emitters. The on and off durations do not follow an exponential statistics, Kuno and al. confirmed this observation in 2001 showing that off states are power law distributed \[15\]. The cumulative probability density $P(\tau_{\text{on,off}} > \tau)$ decreases in time according to a power law decay $p(\tau) \propto \tau^{-\beta}$, with a power exponent $\beta_{\text{on,off}} \approx 0.76$ and $\beta_{\text{on}} = 0.67$ are found in good agreement with previous studies. This kind of distribution is called “broad distribution” (or Lévy distribution) because it yields formally infinite averages for $\tau_{\text{on}}$ and $\tau_{\text{off}}$; in other words, the signal is dominated by a few rare long events \[16\]. Accounting for this surprising behavior in nanocrystals remains challenging \[17\], although some satisfying models were recently proposed \[18, 19\]. The cutoff (i.e: the truncation of the power-law statistics for long $\tau$) for “off” states, as it can be seen on figure 4b, is an artifact due to the finite duration of the acquisition, whereas the cutoff for on states at shorter times is a “true” cutoff, as already seen in references \[20\] and \[21\]. This implies that NC will be off most of the time although the exponents of on and off states are the same. The exponent $\beta_{\text{on,off}}$ and $\beta_{\text{on}}$ are independent of the power of the continuous optical excitation, of temperature, or of eventual NCs capping layer, whereas the cutoffs strongly depends on the experimental conditions \[20, 21\].

Recently, CdSe-CdS core-shell NCs with thick crystalline shells have shown a complete absence of blinking when observed at acquisition rates of 33 Hz, suggesting that well designed shells are a key parameter for obtaining non-blinking NCs \[22\].

It was shown in 2000 \[23\] that single nanocrystals, like single molecules and other nano-emitters, exhibit emission antibunching : their emission intensity correlations vanish at zero delays, meaning that photons are emitted one by one, and never two photons at the same time. Under pulsed excitation, a single nanocrystal constitutes a highly efficient triggered source of these so-called “single photons”, one laser pulse leading to one single-photon emission \[1\], which could be used in quantum cryptography protocols and other quantum optics experiments.

![Figure 5](image_url)

**Figure 5.** Histogram of the time intervals between detection events on start and stop detectors. No peak can be seen at time delay $\Delta t = 0$. Photon antibunching is evidenced using a Hanbury-Brown and Twiss-type photon correlation setup \[24\]. We realized such an experiment with our CdSe/ZnS nanocrystals. The luminescence collected by the objective is separated by a beamsplitter into two beams, each one detected by a single-photon detector, connected respectively to the start ($t_1$) and stop ($t_2$) inputs of the time-interval counter (see scheme figure 3a. This counter builds a histogram of the time intervals $\Delta t = t_2 - t_1$ between start and stop detection events. Figure 5 presents a typical histogram; it consists of a series of peaks separated by the period of pump cycle (400 ns). The absence of the correlation peak at $\Delta t = 0$ is the signature of single-photon emission.
4. Conclusions

To conclude, we underline the importance of characterizing the properties of emission at single scale, such as blinking statistics or decay profiles, as they are strongly related to synthesis quality. The CdSe/ZnS nanocrystals synthesized at the Institute of Materials Science in Hanoi are found to be of good quality at ensemble and single scales. Indeed, the same behaviors as in previous studies were found for experiments at collective scale: variation of lifetimes with temperature from 4 to 300 K, and single scale: single scale decays profiles, statistics of on and off states, photon antibunching. The synthesis of good quality nanocrystals, especially the suppression of blinking, is an important goal for bio-optics use as fluorescent labels, as well as for single-photon quantum optics experiments and applications.

References
[1] Brokmann X, Giacobino E, Dahan M, and Hermier J P 2004 Appl. Phys. Lett. 85 5
[2] Schmidt R, Scholz U, Metzner C, Wieck A, Zrenner A, et al. 2006 Appl. Phys. Lett. 88 121115
[3] Hikmet R A M, Chin P T K, Talapin D V and Weller H 2005 Adv. Mater. 17 1436
[4] Dahan M, Lévi S, Luccardini C, Rostaing P, Riveau B, Triller A 2003 Science 302 442
[5] Nirmal M, Dabbousi B O, Bawendi M G, Macklin J J, Trautman J K, Harris T D and Brus L E 1996 Nature 383 802
[6] Empedocles S A, Norris D J, and Bawendi M G 1996 PRL 77 3873
[7] Schelgel G, Bohnonberger J, Potapova I, and Mews A 2002 PRL 88 137401
[8] Valerini D, Creti A, Lomascolo M, Manna L, Cingolani R and Anni M 2005 Physical Review B 71 235409
[9] Varshni Y P 1967 Physica (Amsterdam) 34 149
[10] Efros A L, Rosen M, Kuno M, Nirmal M, D Norris J and Bawendi M 1996 PRB 54 4843
[11] Labeau O, Tamarat P and Lounis B. 2003 Phys. Rev. Lett 90 2575404
[12] Crooker S A, Barrick T, Hollingsworth J A and Klimov V I 2003 Appl. Phys. Lett. 82 2793
[13] Tamarat Ph, Maali A, Lounis B, and Orrit M 2000 The Journal of Physical Chemistry A 104 1
[14] Cichos F, Borczyskowski C von, Orrit M 2007 Current Opinion in Colloid and Interface Science 12 272
[15] Kuno M, Fromm D P, Hamann H F, Gallagher A and Nesbitt D J 2000 J. Chem. Physics 112 3117
[16] Brokmann X, Hermier J P, Messing G, Desbiolles P, J Bouchaud P and Dahan M 2003 PRL 90 120601
[17] Kuno M, Fromm D P, Johnson S T, Gallagher A and Nesbitt D J 2003 PRB 67 125304
[18] Tang J and Marcus R A 2005 The J. Chem. Phys. 123 054704
[19] Frantsuzov P A and Marcus R A 2005 PRB 72 155321
[20] Chung and Bawendi M 2004 Phys. Rev. B 70 165304
[21] Chung, Witkoskie J B, Cao J, and Bawendi M 2006 Phys. Rev. E 73 011106
[22] Malher B, Spinicelli P, Buil S, Quelin X, Hermier J P, and Dubertret B 2008 Nature Materials 7 659
[23] Michler P, Imamoglu A, Mason M.D, Carson P.J, Strouse G F, and Buratto K 2000 Nature (London) 406 968
[24] Hanbury-Brown R and Twiss R Q 1956 Nature (London) 178 1447