ENHANCEMENT OF PHOTOLUMINESCENCE INTENSITY OF CdS(Se) NANOCRYSTAL THIN FILMS

S. A. Filonovich, Yu. P. Rakovich, A.G. Rolo, M. V. Artemyev[a],
G. Hungerford, M. I. Vasilevskiy, M. J. M. Gomes, J. F. A. Ferreira

Departamento de Física, Universidade do Minho, 4700-320 Braga, Portugal
[a]Physico-Chemical Research Institute, Belarussian State University, Minsk, Belarus

The influence of atmospheric pressure on the optical spectra of thin matrix-free (MF) films of nearly close-packed CdS nanocrystals (NCs) and CdSe NCs embedded into a polymethylmethacrylate (PMMA) matrix was examined. A considerable increase (29 – 35%) in the photoluminescence (PL) intensity was observed for all samples on reduction of the pressure to 10^{-4} mbar. This pressure-induced enhancement of the PL intensity was also found to be reversible. An interpretation of the results is given in terms of a pressure-induced change in the adsorption/desorption equilibrium of molecules of atmospheric gases (most likely oxygen) at the surface of the nanoparticles. The sensitivity of the optical properties of NCs to the change of the pressure gives rise to the possible device application as a semiconductor gas sensor.

Keywords: Nanocrystals, Photoluminescence, Surface states, Atomic adsorption/desorption

1.Introduction

Within the last few decades the PL behaviour of small semiconductor particles has been intensively studied in order to obtain information on the energies and dynamics of photogenerated charge carriers, as well as on the nature of the emitting states [1-4]. Whereas in a single crystal charge carriers are trapped in defect states or by doping ions in the bulk, in small particles these traps are most likely located at the surface [3, 4]. The extremely small size and high surface to volume ratio of the quantum-confined semiconductor NCs means that there is a strong influence of surface molecules or ions (i.e. stabiliser, solvent or solute molecules, as well as molecules of surrounding media) on their optical spectra [5, 6]. Since the wavefunction of electrons and holes in NCs extends across the particle surface photoexcited carriers may be easily captured at the surface traps, where they recombine non-radiatively. Such a mechanism was proposed to be mainly responsible for the reduced PL intensity in NCs [1]. For a certain nanoparticle size, both the spectral position and PL yield of NCs can be modified by changing the surface conditions [1, 3, 4].

In this work, we report the dependence of the optical spectra of MF films of CdS NCs and CdSe NCs embedded in a PMMA matrix on the change of pressure. Using time-resolved PL spectroscopy under different excitation conditions we have tried to examine the contribution of surface states to the radiative and non-radiative recombination in II-VI quantum-dots. The high sensitivity of the PL intensity to change pressure is discussed in terms of the adsorption of atmospheric gases (principally oxygen).

2. Experimental procedure

CdS NCs were prepared by mixing, at room temperature, two equimolar (10^{-2}M) solutions of 1-thioglycerol cadmium salt and sodium sulfide. Both were dissolved in dimethylsulfoxide (DMSO). Two parts of the colloid solution of CdS NCs were heated to $170°C$ under nitrogen with an excess of

cadmium ions. To remove the residual components, the resulting NC colloid solutions were precipitated using acetone and re-dissolved in fresh portions of DMSO. Thin solid films of MF CdS nanocrystals on quartz substrates were then prepared by spin-coating using the colloid solutions. After drying, CdS NCs formed a random almost close-packed structure of nearly spherical particles separated by surface monolayers of thioglycerol.

CdSe nanocrystals were synthesized according to the well-known procedure of high-temperature thermolysis of Cd and Se organometallic precursors in a highly coordinating solvent [7]. Briefly, a solution of dimethylcadmium and elemental selenium in trioctylphosphine was injected into hot (360^0C) trioctylphosphine oxide. The CdSe colloidal solution formed was refluxed at 300^0C in order to obtain the nanocrystals of the desired size, as CdSe nanocrystals grow slowly during refluxing. After this, the CdSe phase was precipitated with methanol at room temperature and redissolved in chloroform containing appropriate amount of dissolved PMMA. Thin films of PMMA doped with CdSe nanocrystals were prepared by casting from a chloroform solution onto quartz glass and drying at room temperature [7].

Optical absorption spectra in the wavelength range 250-2700 nm were measured using a Shimadzu UV-3101 PC spectrometer. The PL spectra were recorded using a Spex Fluorolog spectrometer equipped with an R943 Hamamatsu photomultiplier. The PL spectra were obtained by exciting the samples with a Xenon lamp (output power 0.5-2mW, depending on the wavelength, and spot area $10mm^2$).

The time-resolved fluorescence measurements were made using the single-photon counting (SPC) technique [8]. The SPC fluorometer was equipped with an LED excitation source with a peak emission at 490 nm (IBH, NanoLED), which gave an instrumental response (full width at half maximum) of $ca.$ 1.4 ns. The excitation wavelength was selected by a double monochromator with an 8nm band-pass and the emission was monitored, via either a cut-off or interference filter, using a Hamamatsu R2949 side window photomultiplier. The high repetition rate used (800kHz) meant that the data acquisition was made in the 'reverse mode'. Decays were measured to 10,000 counts in the peak and reconvoluted using non-linear least squares analysis (IBH Consultants Ltd), using an

equation of the form $I(t) \propto \sum_i \alpha_i \exp(-t/\tau_i)$, where τ_i are the PL decay times, with the

instrumental response obtained sequentially using scattered excitation light. The pre-exponential factors α_i are presented normalised to unity. The goodness of fit was judged in terms of a χ^2 value (usually less than 1.2 for an acceptable fit) and weighted residuals.

3. Results

In the absorption spectra (Fig.1), the lowest-energy quantised e-h transition is clearly seen at the energy $E_1^{CdS} = 2.89$ eV and $E_1^{CdSe} = 2.42$ eV for CdS MF film and CdSe/PMMA sample respectively. This reveals the strong effect of quantum confinement in these NCs. The mean particle size, d ≈ 2 nm and d ≈ 4 nm for the MF film of CdS NCs and CdSe/PMMA films, respectively, was estimated from the value of E_1 and confirmed by Small Angle X-ray Diffraction data analysis. A pronounced emission peak centred at 545 nm with a full width at half-maximum (FWHM) of 30 nm (124 meV), was observed in the spectra of CdSe NCs (Fig. 2 a)). The PL spectra of CdS NCs exhibit two peaks (Fig.2 b)), one close to the absorption edge (high-energy (HE) peak, λ_{max} at 460 nm, FWHM of 46 nm (270 meV)) and a very broad low-energy (LE) one.
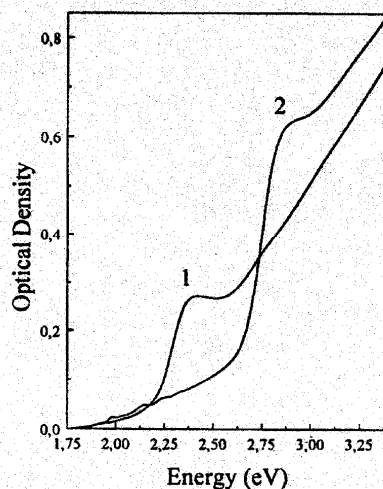
Fig. 1. Absorption spectra of a PMMA film containing CdSe NCs (1) and a MF film of nearly close-packed CdS NCs.
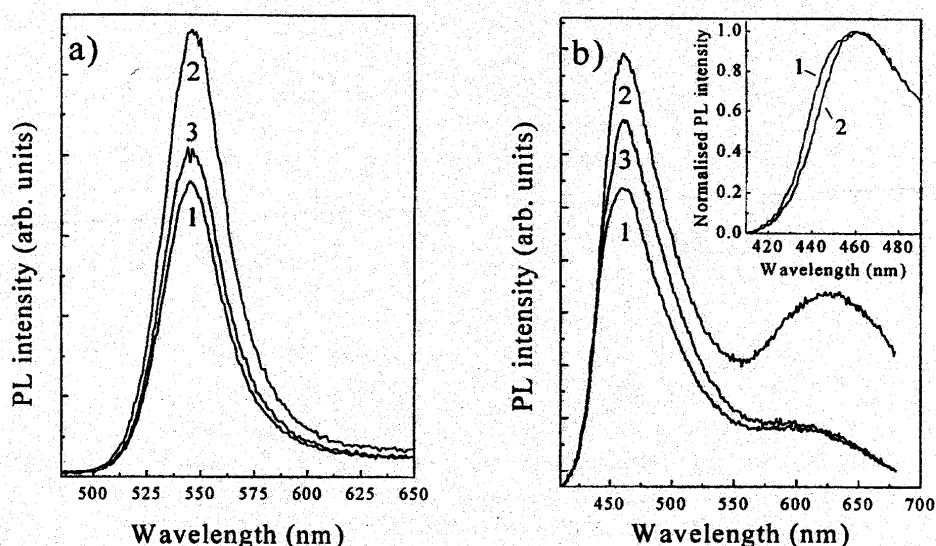

Fig. 2. PL spectra of CdSe NC in PMMA matrix (a) and MF film of CdS NCs (b). 1–at atmospheric pressure; 2 – under vacuum $(P = 10^{-4}$ mbar); 3 – after returning to atmospheric pressure. Inset – PL lineshape at atmospheric pressure (1) and under vacuum (2).

It was also found that the shape of the PL band in the spectra of CdSe/PMMA films depends on the excitation conditions. We observed a pronounced blue shift in the PL band with increasing excitation wavelength (Fig.3). As the excitation wavelength was increased from 420 to 510 nm, the shift in the maximum of the PL band was found to decrease from 140 meV to 120 meV, with respect to the absorption peak of the corresponding electron-hole transition. In order to elucidate further the recombination processes occurring under various excitation conditions, measurements of the temporal dependence of the PL decay were performed by using two different excitation wavelengths, namely, $\lambda_{exc} = 375$ nm and 485 nm (Fig.4). The PL decay was found to be multiexponential for both excitation wavelengths. Table 1 gives the recovered decay parameters.

Table 1. Multiexponential fit parameters to the observed PL decay in CdSe/PMMA film at the emission wavelength 550 nm. The time increment was 0.0523 ns/channel.

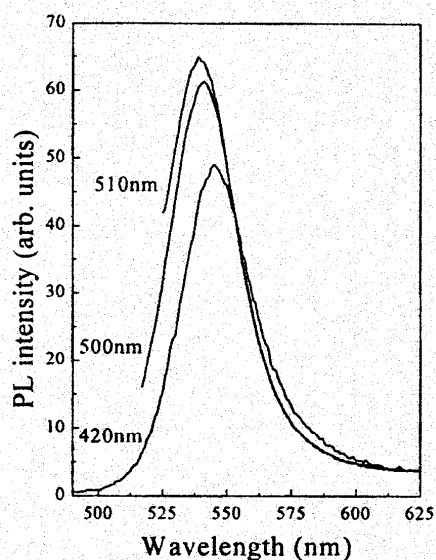| λ_{exc} (nm)	τ_1 (ns)	α_1	τ_2 (ns)	α_2	τ_3 (ns)	α_3	χ^2
375	0.74±0.05	0.77	4.11±0.15	0.19	26.66±0.68	0.04	1.13
485	0.88±0.15	0.70	3.45±0.36	0.23	13.43±0.91	0.07	1.00

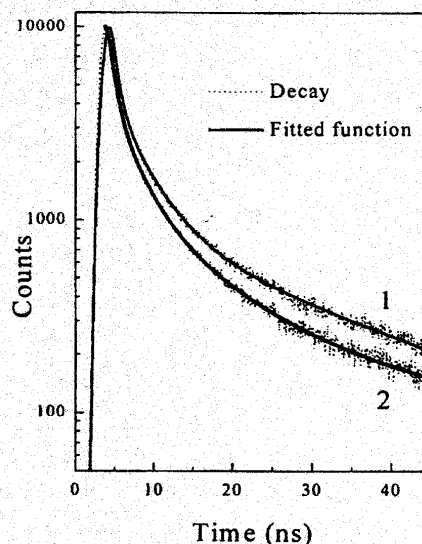Fig. 3. PL spectra of MF film CdS NCs measured at different excitation.

Fig. 4. Luminescence decays and fitted function CdSe NCs in a PMMA matrix at λ_{exc} = 375 nm (1) and 485 nm (2).

Finally, a considerable increase in the PL intensity was observed for all samples on reducing the pressure to 10^{-4} mbar. The maximum increase in PL (ΔI) was estimated to be 35% of the initial intensity of the band-edge peak in spectrum of CdSe NCs. For CdS this increase was 29% and 62% of the initial intensities of the HE and LE peaks respectively. Within the experimental error, we did not detect an influence of pressure reducing on the lineshape of the PL band in CdSe/PMMA films. At the same time, the HE band in the PL spectrum of the MF film of CdS NCs became narrower in vacuum (see inset in Fig.2 b)). The decrease in the FWHM was about 50 meV, which considerably exceeds the experimental error (~ 2 meV). An attempt was made to observe the effect of pressure on the absorption spectra of both kind of samples, however this did not yield such a pronounced effect as found in case of the PL.

The pressure-induced enhancement of the PL intensity was found to be reversible. On return to atmospheric pressure a gradual decrease towards the initial PL intensity was observed. However the final intensity (Fig.2, spectrum 3) was found to remain higher than the initial value.

4. Discussion

The large FWHM of the PL band and the significant shift of the PL lines with respect to the absorption peaks, allow us to conclude that the PL peaks cannot be attributed to direct electron-hole recombination, otherwise we have to explain the large Stokes shift (about 190 meV for MF films of CdS NCs and at least 120 meV for CdSe/PMMA films). Such large Stokes shifts have been previously observed for CdS/glass [9] and CdSe/glass systems [10]. Sometimes they were explained by a strongly enhanced electron-LO-phonon coupling in NCs [9]. However, in this case unrealistic values of the Huang-Rhys parameter would be required and this explanation appears very unlikely. Another explanation [10] stresses the effect of broad NCs size distribution. Larger NCs (with smaller

confinement effect) contribute more to the emission ($\sim R^3$) when the whole ensemble is excited (non-selective excitation). On the other hand, all NCs contribute to the absorption according to the distribution of their sizes. Finally, there is an explanation of the Stokes shift in terms of the 'dark' (ground) and 'bright' exciton states [10, 11]. The splitting between them can be as large as several tens of meV [11]. However, none of these effects can explain such a shift of more than 100meV for the moderate size NCs in our case.

We suggest that the HE PL peak in the spectra of the MF film of CdS NCs and the PL band in the CdSe/PMMA film, both originate from the radiative recombination of a confined electron in a NC and a hole captured at a shallow acceptor level. Because of the large surface-to-volume atomic ratio in NCs, an excited electron or hole may be easily captured at the surface traps. The surface can contain adsorbed foreign atoms or molecules, which can create such shallow traps.

It is important to note that surface states must be of the acceptor type, because the PL peak is located at an energy higher than the bulk band gap energy. Only confinement of electrons, not holes, can explain this blue shift. So, the hole must be the trapped particle.

The capture process should be faster than the direct e-h recombination, which implies that the latter should not seen in the stationary PL spectra. This explanation has been previously proposed, in ref. [12], on the basis of a time-resolved PL study. The data from our time-resolved PL measurements confirm this interpretation, since all characteristic decay times obtained are in the nanosecond time-scale. Direct recombination is characterised by a decay time of the order of ten picoseconds [13], which is beyond the resolution of our equipment. The overlap of electron states of NCs with surface states leads to a significant increase in the PL decay time [14], such as what we observe in our measurements.

The blue shift of the PL peak with increasing excitation wavelength (Fig. 3) can be explained by the NC size dispersion in CdSe/PMMA films. If different size nanocrystals are contributing to different parts of the emission spectrum one can expect a change of the PL spectrum with changing the excitation wavelength, a different resonant sizes are selected from the size distribution. This explanation is confirmed by the fact that the characteristic PL decay time reduces as the excitation wavelength increases (Table 1), because the decay time decreases with NC size [3].

What remains to be discussed is the mechanism of the increase in the PL intensity as the pressure reduces. It has been shown that, in the case of bulk CdS crystals, the quantum efficiency of the PL depends on the concentration of chemisorbed oxygen molecules [15]. Atmospheric oxygen can easily adsorb to the semiconductor surface in the form of a weakly bounded physisorbed complex or strongly chemisorbed O^- or O_2^- anions [16]. As the PMMA film is permeable to air, oxygen can reach the NC surface. We suggest that the physisorbed oxygen effectively captures the electron from a photogenerated e-h pair and reversibly transforms into an oxygen anion (chemisorbed state). Then, the remaining hole recombines non-radiatively with the captured electron, thus reducing the radiative recombination rate. The combined action of reduced pressure and UV excitation can cause a decrease of steady-state concentration of oxygen on the NC surface [17].

The reverse adsorption process can take place within a few minutes after returning to atmospheric pressure, which can explain the gradual recovery of the initial PL intensities.

If the proposed model is valid, one should not expect to see a pressure effect on the recombination rate. In order to verify this assumption, additional measurements (not shown) of the PL decay were performed at atmospheric pressure and under vacuum. No well-defined changes in the values of the characteristic decay time with reduction of pressure were detected. This implies that the principal recombination mechanism does not change. Thus, the effect of pressure is related to adding/removing concurrent non-radiative recombination centres without affecting directly the radiative recombination.

5. Conclusion

It follows from our studies of the absorption, stationary and time-resolved PL spectra of two kinds of nanocrystalline samples that the intense PL peak in the vicinity of the absorption peak most likely originates from the recombination of an electron confined in a NC and a hole trapped in a shallow acceptor state.

We suggest that a pressure-induced desorption of molecules of atmospheric gases (probably oxygen) from the nanoparticle surface is responsible for the observed increase in the PL intensity in MF films of CdS NCs and CdSe NCs in PMMA matrix when the pressure is reduced. This effect is reversible and could be used to make gas sensors. For this purpose, matrix-free nearly close packed films of nanocrystals would be preferable.

Acknowledgements

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