ULTRATHIN COLLOIDAL CDSE NANOPLATELETS FOR SHORT-WAVELENGTH LIGHT EMITTERS

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Abstract

Two-dimensional colloidal nanocrystals have recently revealed a great potential as optical gain media due to their remarkable optical properties. Various optoelectronic devices designed for CdSe nanoplatelets have been already introduced, such as hybrid light emitting diode and vertical cavity laser. So far these devices cover only visible spectra because they use NPLs with thicknesses of 5 monolayers or more, which optical properties are well known. We believe that ultrathin NPLs consisting of only 4 ML will show optical properties more than favorable for their use as optical gain media, providing endless opportunities for creating pure-colored light emitters for UV wavelengths. Here we have synthesized NPLs of both 5 ML and 4 ML thicknesses, studied and compared their optical properties meaning to prove that possibility.

Keywords: Nanoplatelets, CdSe, synthesis

1. INTRODUCTION

Semiconductor nanocrystals (NCs) have been highly attractive materials for research and device applications for decades now. Today much prominence is given to so called nanoplatelets (NPLs), two dimensional colloidal NCs. First acquired in 2006 in the form of nanoribbons [1] they demonstrate electronic structure similar to that of quantum wells [2]. So that optical properties of NPls depend chiefly on their thickness, which can be controlled with high precision thanks to modern colloidal synthesis methods [3]. At the same time NPLs have a great advantage over the quantum wells, being free-standing structures, with no dependence on a substrate.

This form is perfect for creating various nanoplatelet-based heterostructures that can inherit NPLs' unique characteristics and vastly improve them. These heterostructures include highly perspective core/shell NPLs, noticed to enhance quantum yield up to 80% [4]. Studies, conducted in this field demonstrate the synthesis of CdSe NPLs with epitaxially grown CdS and CdZnS shell of controlled thickness [5, 6] and later reports regarding core/crown NPLs, where CdSe serves as an exciton funnel that collects the excitons and transfers them to the CdSe core [7].

Their outstanding optical properties favorably distinguish NPLs from other colloidal semiconductor nanocrystals by high anisotropy of electron-phonon interaction [8], narrow photoluminescence maxima and near absence of the Stokes shift [9, 10]. These NCs are very promising for developing various optoelectronic devices since their two-dimensional geometry is directly compatible with established device designs and processary approaches. It was revealed that high-energy carriers in NPLs relax to the band edge with speeds highly exceeding their recombination velocity. That happens to be the exact quality required for stimulated emission and lasing [11]. Moreover, NPLs show optical gain unreachably high for any other NCs tested for this application. That's why in most recent time it was already possible to develop LEDs [12] including hybrid organic-inorganic ones [13] and semiconductor lasers [14, 15] that uses CdSe NPLs and heterostructures based on them as an active emitting layer.

While the nanoplatelets-based light emitters are undoubtedly a high demand, they can't cover all the possible applications due to the lack of spectral diversity. At the same time it was observed, that with reducing the platelet thickness, it's maxima tend to move to shorter wavelengths approaching UV range, with emitting

velocity and oscillator strength increasing on the contrary [10]. But methods for obtaining ultrathin NPLs with the thickness of only 4 ML as well as their optical properties are yet poorly studied, especially there seem to be no sufficient information about charge carriers relaxation kinetics.

We suggest that developing a stable and repeatable synthesis procedure of ultrathin NPLs and researching their optical characteristics would allow to broaden the line of pure-colored semiconductor light emitters and enrich them with devices operating in UV range. Such devices would be extremely useful for medical lasers, as well as for integrating them in optical fibers, microfabricated waveguides and lab-on-chip systems [14].

2. MATERIALS & METHODS

2.1. Chemicals

Selenium powder (Alfa Aesar, 99.99%), Oleylamine (Acros, 80-90%), Oleic acid (Fisher, 70%), Stearic acid (Fisher, >97%), Cadmium acetate dihydrate (Sigma-Aldrich, >98%), 1-Octadacene (Sigma-Aldrich, >95%), Hexane (Sigma-Aldrich, >97%), Isopropanol and Methanol (Vekton, puriss). All chemicals were used as received without further purification, except oleylamine which *was* centrifuged before use.

2.2. Nanoplatelets Synthesis

5 ML thick NPLs were obtained according to the published procedure [6] double the amount. 106.6 mg of $Cd(AC)_2{\times}2H_2O$, 8 mg of elementary Se, 28.4 mg of stearic acid and 10 ml of octadecene were mixed in three-neck flask, heated under argon flow to the temperature of 170°C and reacted for 15 min.

Preparation of 4 ML thick NPLs required several changes applied to the method. This time 106.6 mg of $Cd(AC)_2{\times}2H_2O$, 28.4 mg of stearic acid, 125 µl of oleylamine and 9 ml of ODE were mixed in three-neck flask. Separately we prepared 0.1 mmol solution Se-ODE. After Se was completely dissolved, 1 ml of this solution was added to the flask and further reaction carried the same way.

When reaction was stopped, CdSe nanocrystals were precipitated by isopropanol. Precipitate was then centrifuged and washed twice with methanol to get rid of organic compounds and unreacted precursors, and afterwards dissolved in chloroform. Oleic acid was added to stabilize colloidal nanoparticles.

2.3. Electron Microscope Imaging

For conventional TEM observations, the samples were prepared by drop-casting concentrated NPLs solutions onto carbon-coated 200 mesh copper grids, and the measurements were performed with a scanning electron microscope Merlin (Zeiss) at 30 kV accelerating voltage.

2.4. Absorbance and PL spectroscopy

We studied electronic energy structure of by means of absorbance (Abs) and photoluminescence (PL) spectroscopy. All measurements were performed at room temperature. Abs measurements were carried out with a UV-Probe 3600 (Shimadzu) specrophotometer and PL spectra with optical transitions in the visible were acquired using a Cary Eclipse (Varian) spectrofluorimeter.

2.5. *Time-resolved photoluminescence spectroscopy*

Fluorescence decay analysis was carried out with a MicroTime 100 (PicoQuant) fluorescent microscope, that adopts the principle of time-correlated single photon counting.

3. RESULTS AND DISCUSSION

Figure 1a and **1c** shows TEM images of our nanocrystals that prove in both cases we have indeed acquired square NPLs with lateral size of approximately 20 nm. Hence suggested synthesis procedure allows to obtain NPLs of desired thickness that are monodisperse by their lateral sizes. Some of NPLs in the images are standing on their edge and self-assembly of NPLs in distinguishing stack structures can be observed.

As shown in **Figure 1b**, 5 ML thick NPLs have their Abs and PL maxima at the edge of visible area with fundamental exciton transition at 460 nm. Ultrathin NPLs meanwhile have optical transitions already in UV range, and more specifically at 398 nm, as can be seen from **Figure 1d**. PL analysis shows that nanoplatelets posses extremely narrow photoluminescence maximum with full width at half maximum ~10 nm indicating that NPLs in the sample are of high quality and uniformity. Stokes shift is measured to be only 6 and 8 nm for 4 ML and 5 ML thick NPLs respectively, its near absence reveals that only a small portion of absorbed energy is lost to non-radiative processes.

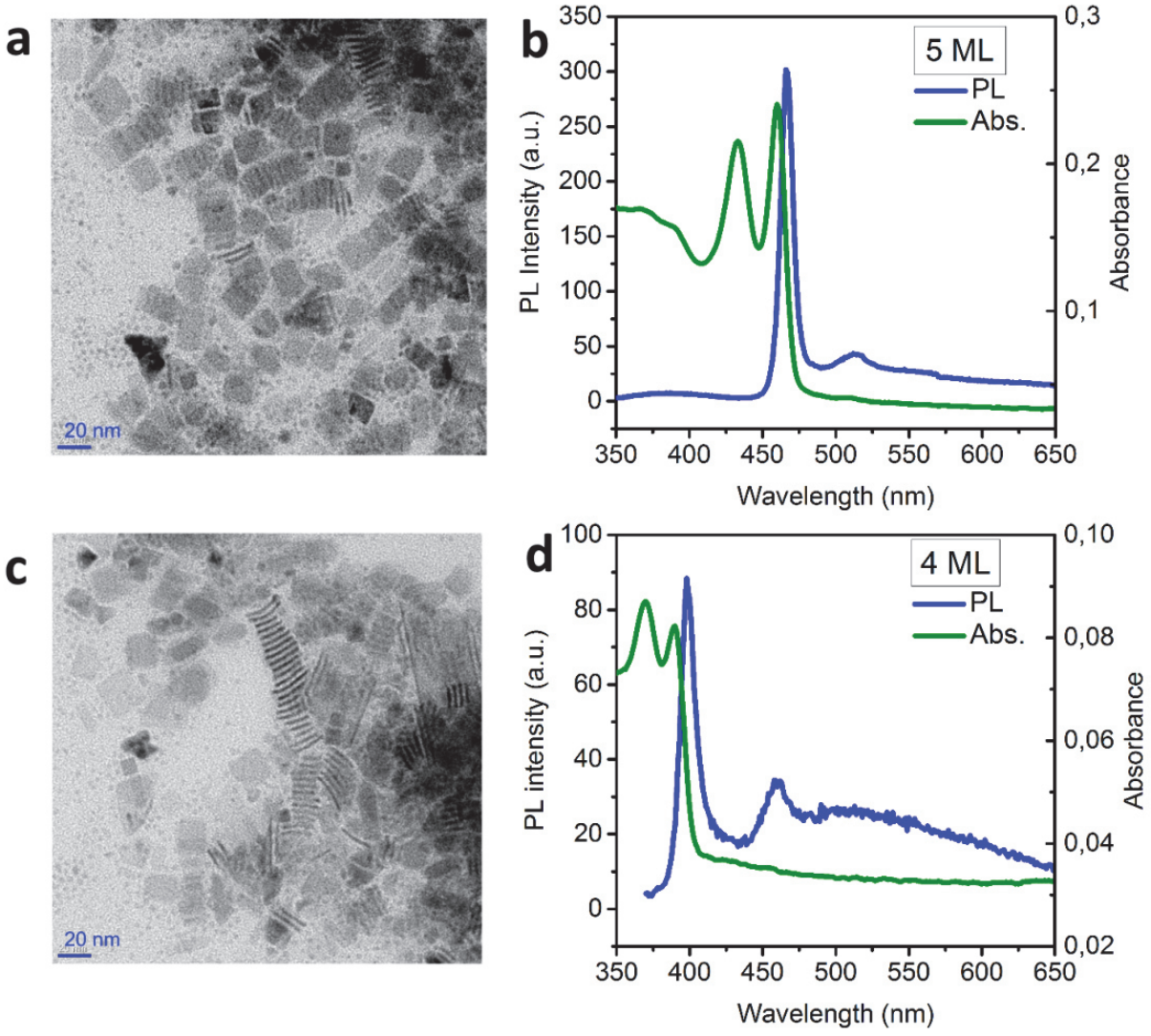


Figure 1 TEM images, PL and Abs spectra of 5 ML (a, b) and 4 ML thick NPLs (c, d)

Fluorescent decay curves are shown in **Figure 2**. Graphs marked a and c correspond to PL decay at the main maximum and those marked b and d features decay in the area of defect PL, that can be seen at **Figure 2b**

and **2d** to the right of the main maximum. Two-dimensional PL maps are also shown as little square images near the graphs. Each color stands for fluorescent lifetimes value in this area.

Decay curves of 5 ML thick NPLs demonstrate very short fluorescent lifetimes (approximately 3 ns on substrate and 10 ns in solution). For ultrathin NPLs we registered lifetimes as short as less than 1 ns on substrate and nearly 3 ns in solution. This makes 4 ML thick NPLs the fastest of so far known colloidal fluorescent emitters. Thus optical properties of ultrathin CdSe NPLs confirm that they have a giant oscillator strength, which makes them very attractive for developing pure-colored short-wavelength light emitting devices.

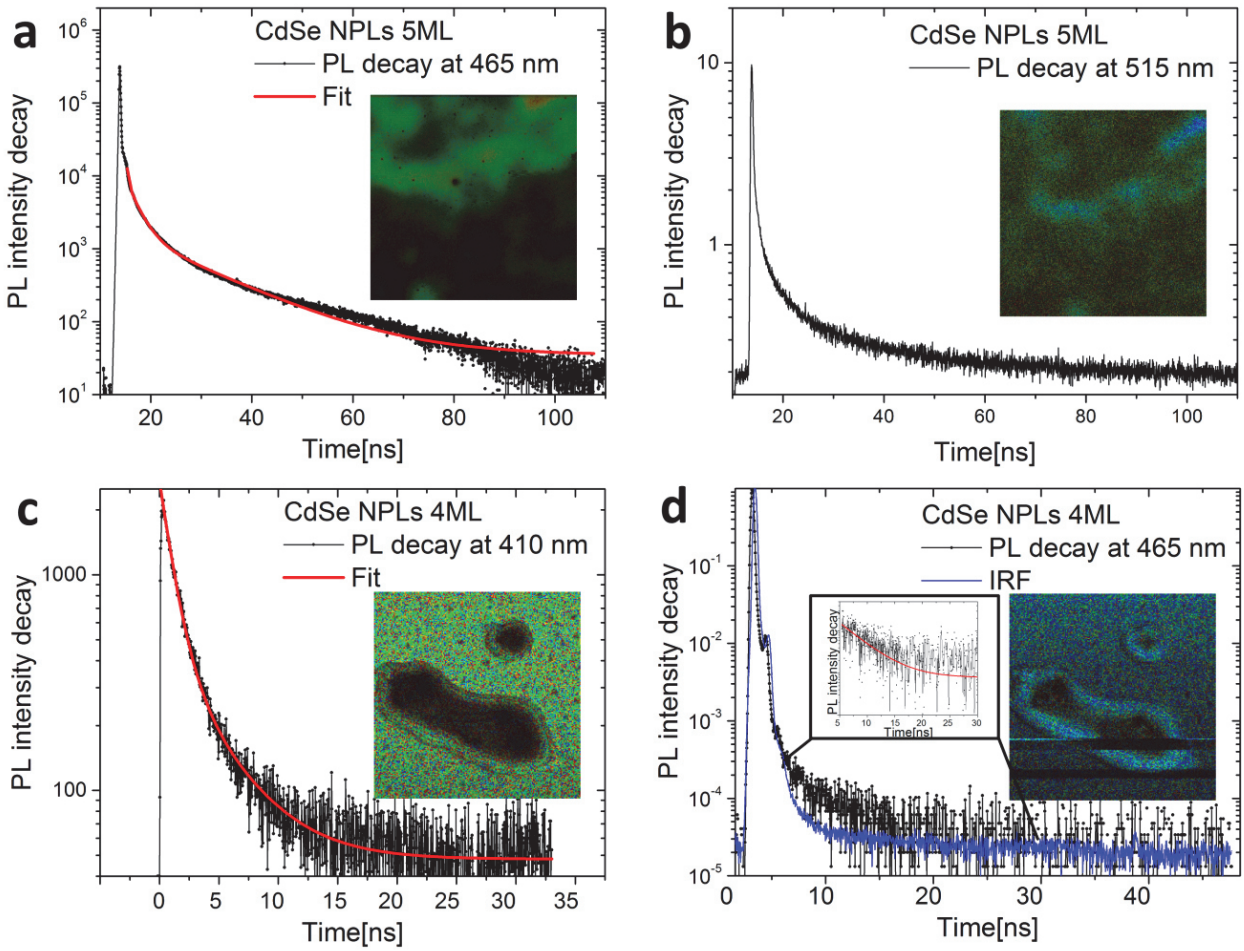
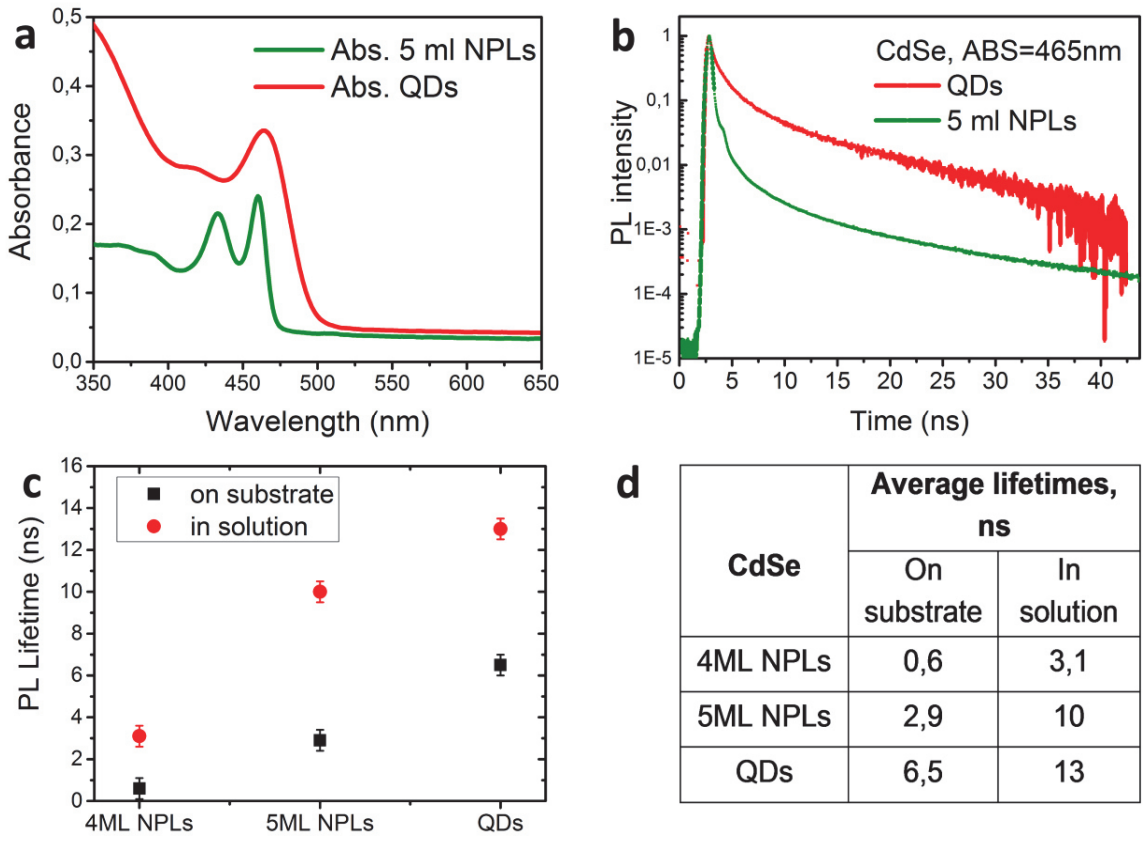


Figure 2 PL decay curves at the main maximum and in the area of defect PL of 5 ML thick NPLs (a, b) and of 4 ML thick NPLs (c, d)

We have performed additional comparison of PL decay kinetics in NPLs with that in quantum dots (QDs). For this study we used our 5 ML thick NPLs and CdSe QDs with the same absorption band and similar quantum yield, as shown in **Figure 3a**. It's well seen from **Figure 3b** that PL decay happens much faster in NPLs than in spherical nanocrystals.

Lifetimes values measured for all nanocrystals are shown in **Figure 3** in forms of **3d** table and **3c** scatter plot. Decay kinetics analysis of CdSe nanocrystal samples revealed that PL decay time depends on nanocrystal shape and size: PL decay times are shorter for NPLs rather than for spherical nanocrystals and PL decay times tend to reduce together with NPL thickness. This uncovers for us endless opportunities for developing active elements for light emitters with precisely defined PL decay kinetics parameters, only by varying shape and size of nanocrystals.



d

CdSe	Average lifetimes, ns	
	On substrate	In solution
4ML NPLs	0,6	3,1
5ML NPLs	2,9	10
QDs	6,5	13

Figure 3 Fluorescent lifetimes of NPLs and QDs: a) absorption spectra of 5 ML thick NPLs and QDs, b) PL decay curves of 5 ML thick NPLs and QDs: c) decay time dependence on the size and shape of NCs and d) table of measured numerical values for all NCs

4. CONCLUSION

Present work contains our study on optical properties of two-dimensional CdSe nanocrystals. We have developed a reproducible synthesis procedure for obtaining ultrathin NPLs with the thickness of only 4 MLs and obtained them as well as 5 ML thick ones.

We have studied absorbance and photoluminescence characteristics of these NPLs and detected narrow PL maxima and almost absent Stokes shift. Fluorescence decay times were measured for NPLs in solution and on substrate. Additional comparison of the results with such of quantum dots was performed with QDs with the same absorption band and similar quantum yield. It was revealed that PL decay happens much faster in NPLs than spherical nanocryslals. Lifetimes, registered for ultrathin NPLs are very short and scales in several nanoseconds.

Extremely narrow PL maxima indicates high quality and uniformity of NPLs in the sample and insignificant Stokes shift proves that only a small portion of absorbed energy is lost to non-radiative processes. These properties combined with fast fluorescent lifetimes verifies the prediction of a giant oscillator strength within the NPLs. That's why they seem so perspective for their use in optoelectronic devices.

Results regarding ultrathin nanoplatelets show that reducing platelet thickness allows us to reach UV spectral region while preserving optical properties typical of NPLs. We conclude that ultrathin NPLs posses all the necessary qualities to be used in short-wavelength light emitters.

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