Spectroscopic study of defect states in CdSe nanoplatelets

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Abstract. Here we report investigation of red-shifted defect photoluminescence observed in two-dimensional colloidal cadmium selenide nanoplatelets. We used absorption, photoluminescence and photoluminescence excitation measurements to show that red-shifted photoluminescence bands are related directly to nanoplatelets and may originate from surface imperfections as well as be a result of interaction between different nanoplatelets in the solution. We also found that the defect photoluminescence may be easily altered by simple mechanical treatment, including sonication and stirring, thus disclosing the ways to control nanoplatelets emission over time.

1. Introduction

Colloidal two-dimensional (2D) nanoplatelets (NPLs) emerged more than 10 year ago [1] and have been extensively studied for the past 10 years. Strong two-dimensional confinement results in special physical and optical properties of these structures, including narrow-line emission with very short lifetime [2]. Convenient 2D geometry, along with the ability to control nanoplatelets thickness on the atomic scale, made them a promising material for various photonic applications [3].

A standard colloidal high-temperature synthesis of CdSe NPLs is quite good established [4]. Nevertheless, chemical liquid-phase methods could never be as precise as, for instance, epitaxial methods, which were used to produce quantum wells yet before colloidal synthesis was developed. Impurities and small changes in synthesis conditions could lead to nanocrystals with different imperfections in arrangement of inner and/or surface atoms, which reflects on its electronic structure and thus optical properties. For instance, it is well known that quantum dots surface is far from ideal crystal lattice, and it has already been reported, that an opening of the subband gap state may occur due to surface relaxations [5]. Concerning the nanoplatelets, not only structure, but also morphology and architecture may affect their behavior. Due to pronounced 2D geometry NPLs tend to form stacks in the solution [6], which changes their emission properties. For example, stacked CdSe NPLs were found to expose red-shifted LO phonon line emission at low temperatures [7]. Another example is that stacking of NPLs of the same thickness may lead to energy transfer between them, resulting in the decrease of photoluminescence (PL) quantum yield [8]. Expectedly, when NPLs with different thicknesses are involved, nonradiative fluorescence resonance energy transfer (FRET) within standard donor-acceptor scheme could be observed [9].

In this paper we report spectroscopic study of additional photoluminescence bands with the lower energies compared to exciton emission line in CdSe nanoplatelets of various morphology. We describe several observed band morphologies: slide-shaped PL, multiple peaks and broad background. We also confirm FRET between two NPLs populations within one solution. In some cases, simple mechanical
treatment reduces the intensity of defect PL and increases the intensity of main excitonic peak, thereby showing its interaction-based nature.

2. Materials and Methods

We investigated photoluminescence of three different CdSe nanoplatelets samples (thicknesses are expressed here in monolayers, ML):

- 6 ML nanoplatelets, emitting at 513 nm;
- 5 ML nanosheets with giant lateral dimensions, emitting at 464 nm;
- mixture of 5 and 6 ML nanoplatelets.

NPLs with thicknesses of 5 and 6 monolayers and sizes which are not exceeding 100 nm were prepared by the standard synthetic procedure which could be found elsewhere [10]. The approach to obtain 5 ML nanosheets (i.e. nanoplatelets with lateral dimensions up to 700 nm) is referred to [11]. NPLs in all cases were dissolved in pure chloroform and had oleic acid as a stabilizing agent.

We used simple mechanical treatment to change NPLs conditions in every sample and find out how it could affect its optical properties. The treatment included precipitation/redissolution, as well as stirring and sonication. All these actions are widely used for colloidal nanocrystals to manipulate interaction of dissolved particles. Precipitation/redissolution was performed by adding isopropanol to nanoplatelets and subsequent centrifuging at 13000 rpm for 5 minutes until NPLs precipitate. After that, the supernatant was removed and NPLs were dissolved again. This technique is analogous to those used for ligand exchange or nanocrystal separation as described here [12,13]. Where mentioned, stirring was performed at the rate of 800 rpm for approximately 10 minutes.

Absorbance, photoluminescence and photoluminescence excitation measurements were held for every sample before and after treatment. Absorbance spectra were registered on Shimadzu UV-3600 spectrophotometer with integrating sphere, while PL and PLE spectra were registered on Cary Eclipse (Agilent) spectrofluorometer. For all presented absorbance spectra baseline was subtracted, and all PL spectra were divided by the absorbance at the excitation wavelength (400 nm for all measurements).

3. Results and Discussion

3.1. 6 ML NPLs with slide-shaped defect PL

On the Figure 1(a) one can see absorbance, emission and PLE spectra of 6 ML thick NPLs. The first pronounced absorption peaks at 479 and 507 nm correspond to the excitonic transitions from light and heavy hole subbands, respectively [14]. A long featureless tail is observed at lower energies, which has already been reported in [15]. Authors note that it could be attributed to the light scattering by NPLs aggregates. Interestingly, the slide-shaped tail can also be seen on PL spectrum. PLE spectrum registered at 555 nm does not expose any transition-like features, indicating that the slide-shaped emission could not be attributed to individual nanoplatelets.

After 60 seconds of sonication NPLs emission increased by 39% without any change of slide-shaped tail intensity, as follows from Figure 1(b), while absorbance spectrum stayed absolutely the same. To explain the effect of PL enhancement, let us consider the stacked form of NPLs in the solution. According to [8], when NPLs are stacked, energy transfer decreases the excitonic emission. Sonication leads to destruction of stacks, which results in higher quantum yield. Since nothing happened to the low energy tail in absorbance, one may conclude that it is not scattering which is responsible for.
3.2. 5 ML nanosheets with defect PL originating from thicker domains

Nanosheets are nanoplatelets with lateral dimensions which could be two orders of magnitude greater than their thickness. Because of increased area, behavior of nanosheets in solution may be different from that of small NPLs. For example, it is known that nanosheets tend to form scrolls [11,16]. Our study shows yet another one effect related to large surface area of nanosheets. Absorbance, PL and PLE spectra of 5 ML nanosheets sample are presented on Figure 2(a). Absorbance spectrum contains small peaks at lower wavelengths, which could be interpreted as originating from different populations of NPLs. The same is true for PL spectrum: it shows several “impurity” peaks, corresponding to different NPLs thicknesses [14], and a broad background band at 500-700 nm. However, PLE measurements reveal that “impurity” emission always gains energy from the main nanosheets in the ensemble, emitting at the shorter wavelengths.

To find out whether “impurities” are individual particles, we used a standard precipitation/redissolution technique, which was described earlier. After the procedure, absorbance spectrum of the sample stayed absolutely the same, but PL spectrum changed drastically, as can be seen on Figure 2(b).
Defect PL bands intensity decreased up to 85%, while exciton PL corresponding to the main population of nanosheets insignificantly increased. Demonstrated results lead us to hypothesis that the “impurity” bands could originate from small island-like CdSe particles bound to the large surface of nanosheets. When mechanically destabilized (e.g. due to precipitation/redissolution), these particles unstuck from the nanosheets surface, and do not emit light, although continue to absorb it. When bound to nanosheets, they form thicker domains, thus resulting in appearance of PL bands corresponding to thicker NPLs. Described idea, however, could not be treated more that just an assumption and requires additional research to approve or reject it.

3.3. Mixture of 5 and 6 ML NPLs with energy transfer

Finally, we studied a mixture of NPLs with thicknesses of 5 and 6 ML, where non-radiative energy transfer is observed [9]. Absorbance, PL and PLE spectra of the sample, presented on Figure 3(a), clearly show existence of two populations: 5 ML thick NPLs emitting at 466 nm and 6 ML thick NPLs emitting at 513 nm. PL and PLE spectra, registered at different wavelengths, prove the presence of energy transfer. Broad PL band at 500-650 nm probably originates from surface defects and is related to thicker particles. To demonstrate it, we used precipitation/redissolution method. As follows from the previous section, this method leads to nanoplatelets separation, and thus reduces FRET efficiency.

![Figure 3(a, b)](image)

Absorbance spectrum of the sample after the treatment did not change, and PL spectra are presented on Figure 3(b). It is seen that the emission of 6 ML thick NPLs has almost disappeared, as well as broad defect PL band. This confirms that 513 nm band and broad defect band are originating from the same particles in the solution. The fact that these particles can emit much more efficiently when FRET requirements are met denotes that interaction between NPLs is a complicated process which may affect quantum yield of both donor and acceptor.

4. Conclusions

In summary, colloidal CdSe nanoplatelets of various morphology exhibit additional PL bands, which may originate from surface defects or be a result of NPLs interaction. We have confirmed that, in general, NPLs interaction affects greatly their luminescent properties, especially when there are several NPLs populations in the solution. Moreover, we have demonstrated how simple mechanical treatment may alter primary and defect PL bands, thus disclosing the ways to control NPLs emission. To obtain more information on the nature of CdSe NPLs defect states, additional research is required.
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