# AN ENHANCEMENT OF PbS QUANTUM DOT PHOTOLUMINESCENCE BY LSPR IN SEMICONDUCTOR NANOCRYSTALS

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## Abstract

In the present study we analyzed an influence of adding of $Cu_{2-x}Se$ nanocrystals (NCs) to PbS quantum dots (QDs) prepared in colloidal solution, in organic matrices and on glass substrates. We found that photoluminescence (PL) signal from QDs is considerably affected by $Cu_{2-x}Se$ NCs, which results in slowdown of PL decay and change of PL intensity. The behavior of PL signal drastically depends on the surrounding matrix and QD-NC separation distance. Despite $Cu_{2-x}Se$ NCs provide an enhancement of PbS QDs PL, they also caused and acceleration of QD degradation when QDs and NCs interact.

**Keywords:** Photoluminescence, quantum dots, PbS, LSPR, doped semiconductor nanocrystals

## 1. INTRODUCTION

Heavy doped semiconductor nanocrystals show unique optical features which make them attractive for photonic applications [1, 2]. In particular, they possess localized surface plasmon resonances (LSPRs) which arise from oscillation of excess charge carriers. High concentrations of excess charge carriers in semiconductor nanocrystals are reached via ionized dopant or self-doping through the deviation from stoichiometric phase [3]. The self-doping is used to reach LSPRs in the near-infrared region (NIR) for copper chalcogenide ($Cu_{2-x}Se$) plasmonic nanocrystals (PNCs). In comparison with noble metals nanoparticles with LSPRs in NIR, semiconductor PNC demonstrates some important advantages: small size (5-11 nm), tunability of LSPRs energy, low cost of materials for colloidal syntheses and comparative simplicity of syntheses technique [1, 4].

LSPRs effect is widely used in different photonic and photoelectric applications [2, 5]. Electric field arising from LSPRs modifies optical properties of nanoscale objects which are located near the PNC surface. In particular, LSPRs can lead to an enchantment of photoluminescence from organic molecules and quantum dots (QD) [6, 7]. Semiconductor QD is nanometer size object with energy structure determined mostly by the size of QD due to the quantum confinement effect [8]. Due to their unique properties, QD have become a building block for various photonic devices. Interaction between LSPR, arising from metals, and QDs were studied well and has several applications [9-11], but the interaction of LSPRs, arising from semiconductor PNC, with different fluorophores is still poorly understood.

In this work we studied an interaction of LSPRs in $Cu_{2-x}Se$ PNCs and PbS QDs, which has attractive features, including bandgap energy that covers all NIR regions by varying QD size, high absorbance and emitting efficiency. These features make them a promising material for light harvesting devises [12]. We analyzed an influence of adding of $Cu_{2-x}Se$ PNCs to PbS QDs prepared in colloidal solution, in organic matrices and on glass substrates. We found that photoluminescence (PL) signal from QDs is considerably affected by $Cu_{2-x}Se$ PNCs, that results in slowdown of PL decay and change of PL intensity. The behavior of PL signal drastically depends on the surrounding matrix and QD-PNC separation distance. Despite $Cu_{2-x}Se$ PNCs provide an enhancement of PbS QDs PL, they also caused and acceleration of QD degradation when QDs and PNCs interact. This process was analyzed in details for colloidal QD solution.

## 2. EXPERIMENTAL

Oleic acid capped PbS QDs with the average diameter of 4 nm were synthesized via well-established organometallic synthesis, the details described elsewhere [13]. Oleylamine (OAm) capped $Cu_{2-x}Se$ PNCs were synthesized via Cu vacancies boost cation exchange reactions in copper selenide nanocrystals describes in [4]. Absorption and PL spectra from PbS QDs dissolved in tetrachloromethane, and absorption spectrum from $Cu_{2-x}Se$ PNCs dissolved in toluene are shown in **Figure 1**. LSPRs from PNCs cover broad spectral region and centered at ~ 1.16 eV, QDs bandgap width is about 1.19 eV and match well with LSPR.

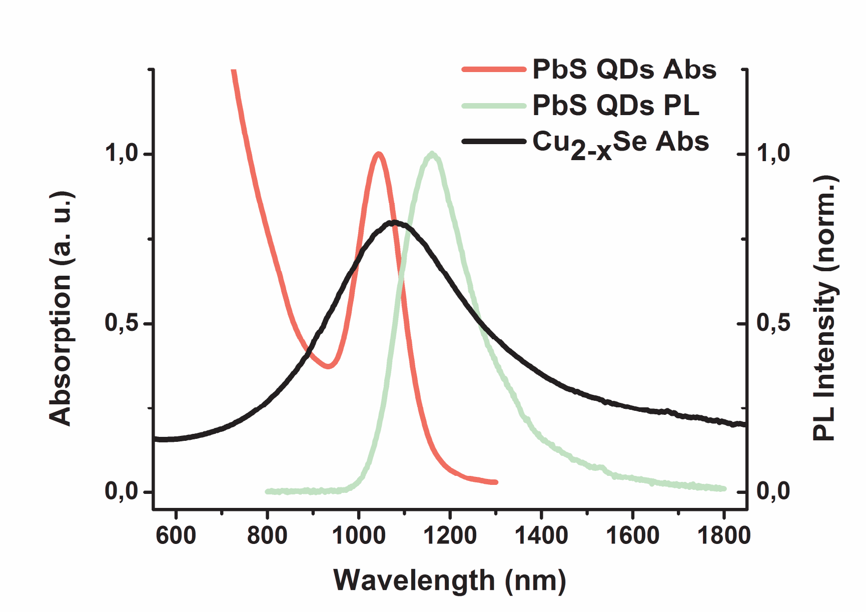

**Figure 1** Absorption spectra of Cu2-xSe PNC dissolved in toluene (black), absorption (red) and PL (green) spectra of PbS QDs dissolved in tetrachloromethane

To explore QD-PNC systems, we used PL and absorbance spectroscopy. Shimadzu UV-3600 spectrophotometer was used to measure absorbance spectra, and home-build measuring system described in [14] was used to obtain the steady-state PL spectra. Briefly, an excitation was realized by using He-Ne laser at 633 nm. PL signal was collected in 90° geometry. Acton SP-2558 monochromator, with a relative aperture of 6:5, a focal length of 0.5 m and spectral resolution of about 6 nm, equipped by InGaAs photodiode Hamamatsu G585221 with spectral range of 900-2100 nm, was used for detection of PL radiation. To study PL kinetics, we used self-build measuring setup analogues to that described in [4]. Laser-Export DTL-339QT pulsed laser with a pulse duration of 10 ns was used for excitation at 527 and 1053 nm wavelengths. High-frequency InGaAs photodiode was used for PL detection.

## 3. RESULTS AND DISCUSSION

First, we studied an interaction between $Cu_{2-x}Se$ PNCs and PbS QDs distributed in an organic matrix. PbS QDs were dissolved in 5 wt% solution of Poly(methyl methacrylate) (PMMA) in toluene. 10 µl of this solution was drop-casted on cover slips and dried at 50 °C during 1 hour. 10 µl of PNC solution was then dropped on the top of the layer of QDs in PMMA. **Figure 2a** shows PL spectra of QDs in PMMA layer before (green line) and after (black line) PNCs were added. As one can see from the **Figure 2a**, we observed 35% enhancement of PL signal. An enhancement of PL from QDs is caused by the coupling with LSPRs which are resonantly excited by the QDs PL. When we used 8.5 nm PbS QDs with PL at ~0.65 eV we did not observe any enhancement of QD PL. To examine sample stability, we repeated the measurement on the next day and performed heat treatment at 50 °C during 1 hour. **Figure 2a** shows that an enhancement factor reduces after storage at ambient conditions and after heating. These finds agree well with data reported in [15] where the coupling of LSPRs in $Cu_{2-x}Se$ PNCs and upconversion luminescence from $NaYF_4:Yb^{3+}$, $Er^{3+}$ was studied. The degradation of LSPRs in $Cu_{2-x}Se$ PNCs was explained in terms of destruction of OAm capping layer by the oxidation reaction.

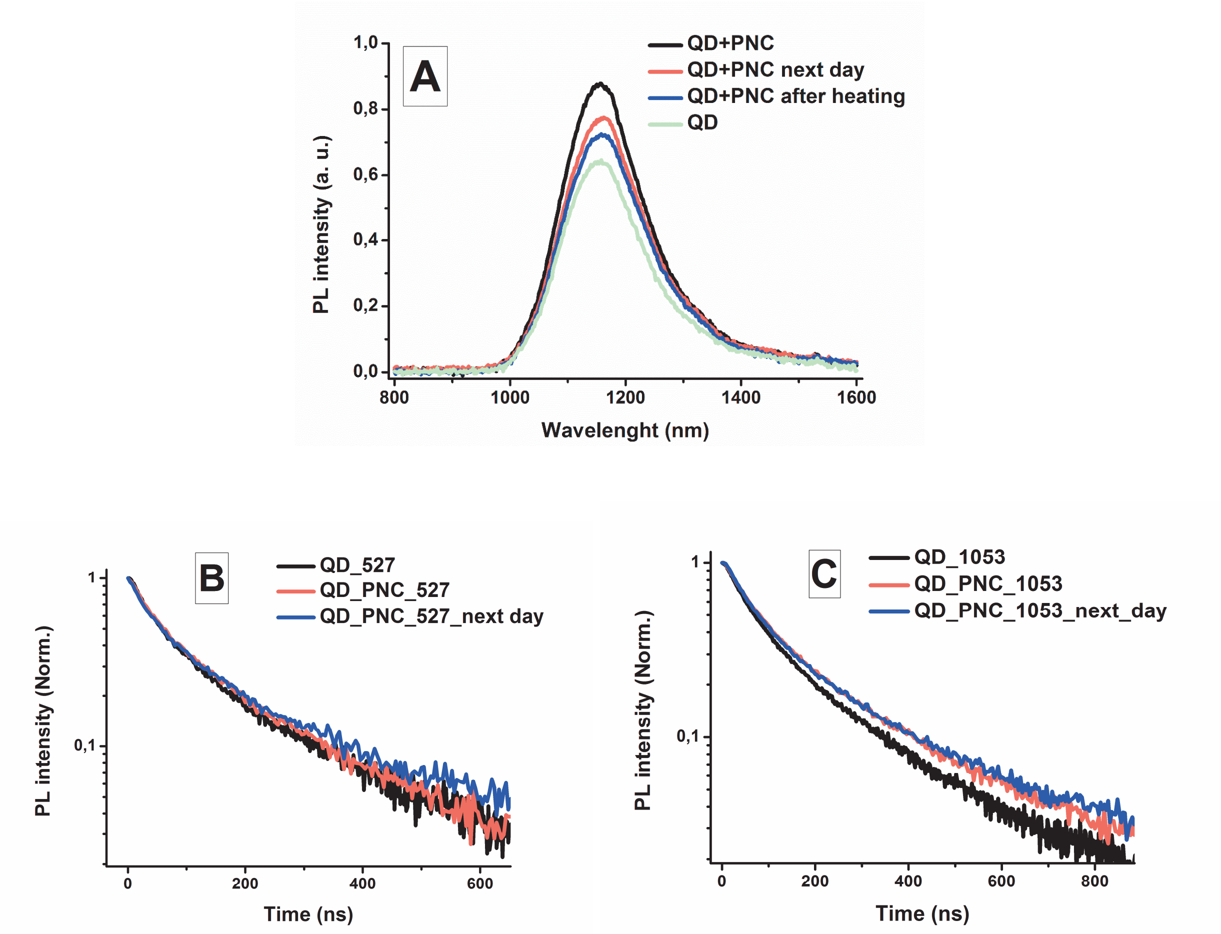

**Figure 2** a) PL spectrum of PbS QDs in PMMA: before (green line) and after (black line) PNCs were added, after day of storage (red line), and after heating (blue line); b, c) PL decay curves for QD in PMMA: pure (black), after PNC application (red) and after heating (blue), using 527 nm (b) and 1053 nm (c) laser excitation

**Figure 2b** and **c** shows PL decay curves for QD in PMMA, which were measured using 527 and 1053 nm laser excitation. We observed slight increase of PL decay times which is more pronounced for the resonant excitation at 1053 nm. It is known that LSPR can affect the photoluminescence by the modification of recombination rate and by local field enhancement, and the second mechanism does not lead to variation of the PL decay time. An increase of PL decay time caused by the plasmon enhancement has been previously observed for $NaYF_4$:Yb,Tm hybrid nanostructures [16] and for Sm complexes [17] when they interact with noble metal NPs, and was ascribed to the redistribution of the exciton population between emitting states. PbS QDs possess complicated energy structure which involves long-lived emitting state [4]. If LSPR effect is more pronounced for the excitons at the long-lived state, we can expect an increase of the average PL lifetime. Similar, Ozel et al. have demonstrated that coupling of CdS QDs with localized plasmon can lead to both acceleration of the band-edge emission and to slowdown of the defect-related emission [18]. To deeper understand our observations further experiments are required.

For a series of the samples prepared by that method we observed an enhancement in the range of 35-50 % and slight red shift of PL spectra after PNCs have been deposited. Relatively small value of enhancement factor can be explained by long distance between PNCs and QDs dissolved in polymer matrix. To explore the interaction in case of direct contact of QDs and PNCs, 10 µl of QDs solution with concentration of $8.1\times10^{-5}$ M was deposited on glass substrate by drop-casting method and dried at 50 °C. After that, 10 µl of PNC solution was drop-casted on QD layer and dried for 1 minute at 45 °C. **Figure 3a** shows QDs PL spectra before (blue line) and after (red line) PNCs were added. As shown, an enchantment factor reaches 12 times value. We can conclude that penetration of PNCs into QDs layer and, consequently, smaller QD-PNC distance, leads to more effective interaction between QD and LSPRs from PNCs. In contrast to the case of QDs in PMMA, a pronounced blue shift of PL spectrum is observed. After a day of storage, we found totally disappearance of PL response from the sample. These features may be explained by degradation of QDs. It is known that oxidation lead to degradation of QD surface which is accompanied by blue shift and weakening of PL signal [19, 20].

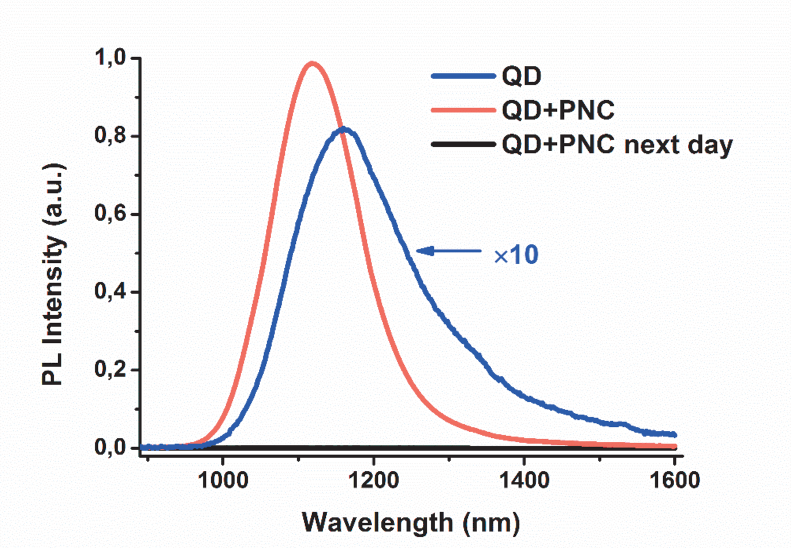

**Figure 3** a) PL spectra of PbS QDs: blue line - QD drop (10 times magnification), red line - after PNCs were dropped onto QD layer, black line - PL signal from the sample after day of storage at ambient conditions

To better understand the mechanisms that lead to fast destruction of PbS QDs, we watched the evolution of absorption and PL spectra of QD solution with PNCs. 20 µl of QD and PNC stock solutions were added to 3 mL of tetrachloromethane. **Figure 4a** shows that even after 15 minutes the position and magnitude of the first excitonic peak in absorption spectrum changed, and after 1 day of storage all features of QD absorption are vanished from the spectrum. Similar tendency was observed for the PL spectra. At the first moment after PNCs were added to QD solution, slight enhancement of PL signal was observed. Then we observed blue shift and weakening of PL signal, which were progressing during the time (the details are shown in **Figure 4b**).

Then we watched the evolution of absorbance and PL spectra of QD solution with OAm only. When we added 20 µl of 20 wt% solution of OAm in toluene into QD solution, no noticeable change in neither absorption nor PL spectra were observed. The specified amount of OAm is close to that used in studied QDs+PNCs mixture. Then we increased concentration of OAm and added 300 µl of 20 wt% solution of OAm in toluene into QD solution. **Figure 4c** and **Figure 4d** show that excess of OAm also leads to the blue shift of absorption and PL spectra of PbS QDs. However, the weakening of excitonic absorption and emission is not as fast as in case of PNCs. After day of storage we still we able to detect absorption and PL signal from the solution. The degradation of QDs in presence of OAm excess took about a week. That let us conclude that $Cu_{2-x}Se$ PNCs act as a catalyst and drastically accelerate the degradation of QDs. It is known that copper ions are very mobile in the selenides, and thus may lead to corrosion of QD surface.

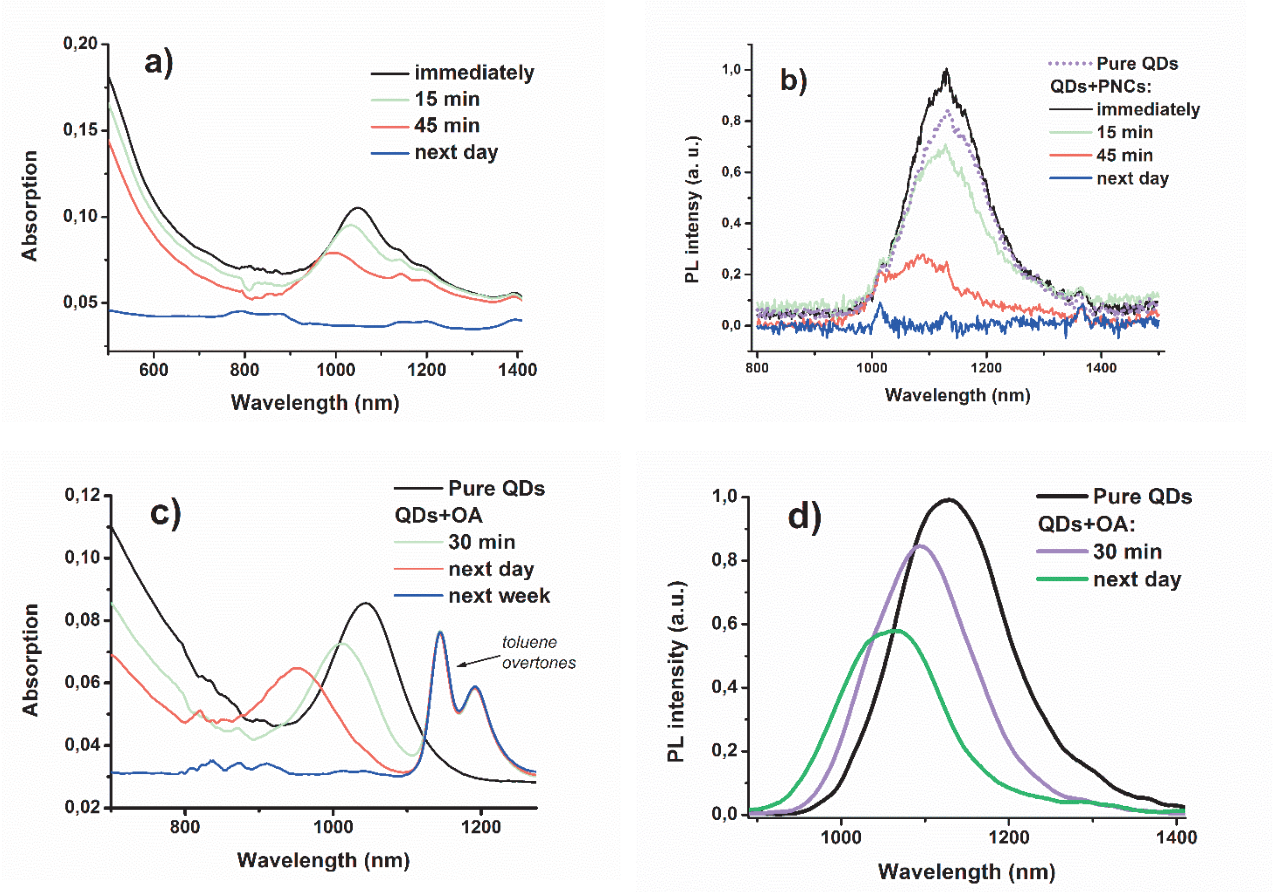

**Figure 4** Evolution of absorption and PL spectra of QD solution: a) absorption spectra of QDs with PNCs; b) PL spectra of QDs and PNCs; c) absorption spectra of QDs with OAm; d) PL spectra of QDs with OAm

## 4. CONCLUSION

To conclude, we have investigated an interaction between near-infrared emitting PbS QDs with plasmonic $Cu_{2-x}Se$ doped semiconductor nanocrystals. We found an enhancement of PL from QDs when they interact with $Cu_{2-x}Se$ PNCs. The features in PL responses that we have observed depend on the distance between QDs and PNC. We found, that $Cu_{2-x}Se$ can accelerate QD destruction when they are in a direct contact. Present study revealed further routes to optimize an enhancement of optical responses in QDs-PNCs systems.

## ACKNOWLEDGEMENTS

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