Ligands Exchange, Studying the Stability and Optical Properties of CdSe/CdS/ZnS Quantum Dots with Liquid Crystal

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\textbf{Abstract.} Liquid crystal (LC) ligands have the ability to control the dispersion and the homogeneity of quantum dots (QDs) in solution. LC phase transition can be used as a tool to control the assembly of dispersed QDs. Comparing the results before and after the ligands exchange (oleic acid to liquid crystal) highlights some important differences in optical and morphology properties of QDs. We have studied changes in optical properties and a shift in the spectral wavelength band of QDs with LC ligands. Application of LC ligands leads to quenching of the emission and excitation spectra intensity of CdSe/CdS/ZnS QDs. Such hybrid materials have interesting potential for usage in a variety of applications such as photonic materials or (bio) chemical sensors.

1. Introduction

Quantum dots (QDs) have a significant advantage because of their unique tunable properties due to quantum confinement effects. Also, the emitted wavelength range depends on the size of the quantum dot. The properties of desired thin film structure can be controlled by using various types of QDs or using different stabilizer molecules, etc. \cite{1}. Liquid crystals (LC) can also be used as stabilizers and have the potential to control the dispersion of quantum dots (QDs) in liquid crystal phase. The challenge in creating hybrid material based on QDs incorporated to LC (QD:LC) is their stabilization as a composite material over time. QDs without stabilizer (not surface-functionalized) are strongly attracted to each other by electromagnetic forces lead to aggregates and separation from an organic solvent. Recently, there are some studies have been carried out on developing LC /nanoparticle materials hybrid \cite{2, 3}. But these studies didn't cover the properties of nanoparticles in 2 dimensions (2D) form. The 2D monolayer study can provide information about the interaction between molecules and homogeneity of monolayer surface. The dispersed QDs in the LC material will respond to the local order phase and have been found that QDs preferentially located in the low molecular order such as isotropic phase \cite{4, 5}. LC was used to organize the QDs in the form of their self-assembly \cite{6}. We have studied the designing system of the QDs:LC mixture, the ligands of LC can act as a surfactant between QDs and solvent. We used core/shell/shell system CdSe/CdS/ZnS QDs stabilized by oleic acid (OA).Some studies are reported that various ligands of fatty acid could effects on the optical
properties of QDs [7]. Previously we have studied the influence of separation excess ligands of oleic acid from QDs solution on the morphology and optoelectronic properties of QDs thin film [8]. QDs were separated from ligands of OA and investigated their dispersion in the LC solution after ligand exchange. The LC phase, structure and intermolecular interactions depends on different parameters such as temperature, electric field, concentration, etc., these could be tuning properties of hybrid materials. The using of stabilizer can enhance the dispersion and control the assembly of QDs [9]. Moreover, the existence of LC in the QDs solutions can modify their optical properties (emission and excitation). LC mixture can be tuning QDs properties for a particular application such as chemical and biochemical optical sensing, etc. [10].

Therefore, in this work we have studied the formation of the 2D monolayer at air-water interface by Langmuir-Blodgett (LB) technique and investigated an influence of LC on the properties of QDs solution and structure of their monolayers.

2. Materials and methods

4′-octyl-4-biphenylcarbonitrile (8CB) was purchased from (Sigma-Aldrich) and dissolved in chloroform at a concentration of \(10^{-3}\) M. CdSe/CdS/ZnS QDs were prepared by hot-injection method [11]. We have replaced the ligands (OA) with mesogenic ligands of LC to produce QDs stabilized by LC ligands (see figure 1). QDs were washed by using a precipitation and re-dispersion. 2 mL of QD solution was precipitated with 2 mL of toluene and centrifuged. The OA ligands were removed by two times rinsing with centrifugation at 6000 rpm for 8 mins. Afterward, the precipitate was washed by adding ethanol solution and finally resuspended in 2 ml chloroform with concentration about \(10^{-7}\) M – such low concentration was used to ensure a uniform dispersion of CdSe/CdS/ZnS QDs in the LC phase. A mixture of QD:LC was prepared at a different ratio 1:1 and 1:2. The QD:LC mixture in bath sonicated at temperature 45°C for 4 hours to obtain QDs dispersion in the isotropic LC medium. The mixture of QD:LC is then taken away from the heating and was left to cool at room temperature. The formation of the monolayer at air-water interface was performed by LB bath (KSV Nima LB trough KN 1003, Finland). A 50 µl of QD solution was spread on the sub-phase surface of the deionized water (18.2 Ω × cm). Surface pressure isotherms of the monolayers were recorded at room temperature. The movable barriers compressed monolayer at a specific area with constant rate 12 mm/min. The same LB experiments were done for LC and a mixture of QDs:LC at ratio (1:1 and 1:2). The monolayers were transferred on a glass substrate and their morphology was studied by atomic force microscope (AFM) (Nanoeducator II AFM microscope). The emission and excitation spectra of solutions were obtained using Cary Eclipse Fluorescence Spectrophotometer (Agilent Technologies).

![Figure 1](image-url)

Figure 1. Schematic representation of ligands exchange of QDs that was performed by oleic acid (OA) substitution with liquid crystal (LC) molecules.

3. Results and Discussion

The replacement of ligands capped QDs by chemical treatments was investigated. The estimated areas of monolayers (when monolayer in solid state) for LC, QDs and QDs: LC at ratio (1:1 and 1:2) solutions are equal to 164.1, 41.41, 108.91 and 141.5 cm², respectively (figure 2). LC isotherm (curve 1) shows higher occupied area and lowest surface pressure 7.5 mN/m. The isotherm of QDs (curve 2) shows low occupied area with the high surface pressure of 29 mN/m. We assume that the
changes in surface pressure ($\pi$) and occupied area of QDs:LC monolayer (curve 3 and 4) are influenced by LC ligands, and then isotherms proportionally shift towards the larger area with increasing the concentration of LC (figure 2). The isotherms areas (curve 2, 3 and 4) before collapse point region II indicate formation homogeneous monolayer solid-like state.

Figure 2. LB isotherms of LC (1), QDs (2), QDs:LC 1:1 (3) and QDs:LC 1:2 (4).

After the collapse point region III, the surface pressure of LC raised slightly (the plateau region), we postulate the existence of a bilayer on top of a monolayer (trilayer) [12]. The isotherm (curve 4) shows increased in occupied area and surface pressure due to presence higher concentration of LC. The shape of the isotherms (curve 3 and 4) of the QDs:LC monolayer reveals that the surface pressure rises monotonically instead of creating the plateau region and didn’t show second collapse similar to pure LC (region IV) (see figure 2). This result indicates the enhancement of the mixture molecular compression and stability, the mixture highly compressed and formed a densely packed multilayer.

The structure of the hybrid material depends on the surface properties of QDs and the liquid-crystalline properties of the host phase. The thin films of QDs and QDs:LC (1:1 and 1:2) transferred on glass substrates at surface pressure 22, 6.9 and 6.9 mN/m, respectively (see figure 3). AFM images in figure 3(b) and 3(c) show the more homogenous morphology of QDs:LC monolayer compared with the morphology of only QDs monolayer and the occupied area of QDs decrease with increase the concentration of LC.

Figure 3. AFM images of QDs at 22 mN/m (a), QDs:LC 1:1 at 6.9 mN/m (b) and QDs:LC 1:2 at 6.9 mN/m (c).
Emission and excitation spectra of the solutions before and after the ligand exchange are shown in (figure 4). The QDs were capped with OA ligands have an optical emission band at 618 nm and excitation band at 597 nm. When surface capping ligands of oleic acid are separated, the emission and excitation spectra of QDs solution have shown red shifting to 623.5 and 640 nm, respectively. The emission and excitation spectra band are shifted to longer wavelength thus can emphasize that QDs became un-stabilized and aggregated after separating OA thus lead to increasing the physical size of QDs. However according to the previous study reported that the possibility of induced red shift in absorption and emission spectra band due to aggregation of QDs [13].

![Figure 4](image.png)

**Figure 4.** Emission spectra (a) and excitation spectra (b) for solutions of QDs with OA stabilizer (1), QDs solution without OA stabilizer (2), QDs:LC 1:1 (3) and QDs:LC 1:2 (4).

Figure 4a and 4b depict that the emission and excitation intensity of QDs:LC at a ratio (1:1 and 1:2) (curve 3 and 4) shifted to 621.2 and 634 nm, respectively. This result due to the influence LC phase on the surface properties of QDs, and according to the previous study the changing in the “refractive index” can cause a red or blue shift in spectra of QDs [14,15].

The intensity of emission and excitation spectra of QDs after ligand removal integrated intensity increased. The peak excitation spectra (figure 4b) were expanded could be explained by such ligands have an influence on the surface charges, interparticle separation and carrier mobility [16]. The understanding and designing surface-modified QDs in LC phases is an important role in the photonic applications that require soft-switchable materials.

**4. Conclusion**

This study provides a procedure of ligand exchange that plays an important role in control the stability and optical properties of CdSe/CdS/ZnS QDs. We compared the effects of removing and exchanging the ligands on the stability, morphology, emission and excitation spectra of QDs. We have studied the formation of QDs and LC mixture monolayer in 2D by LB method which helps our understanding of QDs organization within the host material of LC phase. CdSe/CdS/ZnS QDs solution incorporating the LC ligand show good dispersion in the isotropic phase and give enhancement in optical properties of QDs. Increases the concentration of LC lead to decrease the intensity of emission spectra of QDs solution and reduce the occupied area of the gas phase in QDs: LC monolayer. CdSe/CdS/ZnS QDs exhibit a significantly red shift in both the emission and excitation spectra after removing the ligand of OA. The results could be useful in the creation of optical, photonic device or molecular encapsulation applications.
Acknowledgments
This work was supported by grants from the Russian Foundation for Basic Research project № 16-07-00093/16 and № 16-07-00185/16.

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