The Formation of Quantum Dots - Liquid Crystal monolayers by Langmuir-Blodgett method

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Abstract. The article describes the features of the formation of CdSe/CdS/ZnS quantum dots - liquid crystal Langmuir monolayers on a water subphase surface by different temperature value. Monolayers structure was investigated by analyzing the compression isotherms and surface potential value. Films on the solid substrate (glass plates) were investigated by atomic force microscopy method for morphology, thickness and roughness. Film structure was studied as a function of the pressure at which the transfer was carried. It is shown that the structure of films obtained by a higher temperature of subphase is more perfect. The film is monolayered and uniform in thickness.

1. Introduction

Nowadays one of the fastest growing areas in nanotechnology is provide materials for biological applications and purposes of electronics. Colloidal quantum dots (QDs) of the semiconductor materials are one of the most interesting materials for research and applications projects. They are used extensively for the modification of biological objects [1], as well as photovoltaic devices and as a promising material for solar cells [2]. And one of the critical issues for practical using of QDs is obtaining ordered structures with them.

One method, which allows obtaining the ordered layers of nanoobjects, is a Langmuir-Blodgett method. It allows to obtaining the ordered layers of amphiphilic substances or objects using self-assembly principle. This method is not expansive and not required specific conditions in process of organization of layers.

In our work we obtained Langmuir monolayered films consisting of CdSe/CdS/ZnS QDs and 4′-octyl-4-biphenylcarbonitrile (8CB) liquid crystal (LC). We choose these materials by few reasons. In one hand semiconductor QDs is photoactive material perspective for solar cells and photovoltaic devices in other hand 8CB is material which can change properties (by phase shifting) in temperature near to normal room. And we can control structure of monolayers (and films) by changing temperature in Langmuir trough. Molecules of 8CB have large dipole moment [3] and we can get information about orientation molecules on the surface by measuring surface potential value.

We study formation of QDs-8CB monolayers by changing few control parameters: temperature of subphase, concentration of QDs in monolayer and surface pressure of deposition monolayers to solid substrate.
2. Materials and methods
In all experiments we use deionized water (R about 18 Mom×cm) as a subphase. QDs obtained by chemical reduction method and have three-layered structure with CdSe/CdS/ZnS composition. Diameter of QD is about 7-8 nm and they stabilized by oleic acid [4]. Solution of 8CB (was purchased from Sigma-Aldrich) prepared in chloroform (Vector, Russia) with concentration 10⁻³ M. We used different ratios QDs:8CB (4:1, 2:1, 1:1 1:2, 1:4) as material of monolayers. For formation, deposition and measure surface potential of monolayers we used KSV Nima LB trough KN 1003 (KSV Nima, Finland). Temperature in the trough was controlled by LOIP thermostat (18 and 35°C). Deposition of monolayers was realized by different value of surface pressure: 3, 6, 9, 12 mN/m. Glass plates (previously cleaned) was used for substrates. Atomic force microscopy (AFM) picture taken in semicontact mode by Nanoeducator II AFM microscope.

3. Results and discussion
In few series of experiments (with different temperatures of subphase and ration of QDs:8CB) we received a series of monolayers compression isotherms. Most interesting result we obtain by ratio QDs:8CB 4:1 and 35°C temperature of subphase. We choose these parameters of LB process for deposition because the compression isotherm not shown strongly breaking point (figure 1) which is typical for 8CB monolayers and corresponds formation of three-layers complex LC structure [5].

And at 35°C, 8CB molecules change their orientation on the water surface. We can assert this for the reason, because at higher temperatures the sign of the surface potential was reversed (figure 2).

![Figure 1. Compression isotherms for QD:8CB 4:1 and 2:1 ratios](image1)

![Figure 2. Surface pressure isotherms (blue curves) and surface potential of monolayer graph (red) for 8CB by 18°C (left) and 35°C (right)](image2)
Moreover, after passing through the phase transition pressure at 35°C (about 5 mN/m) the absolute value of the surface potential increases. This indicates the compaction of molecules in the monolayer in the same orientation. On the contrary, at 18°C after the phase transition point the absolute value of the surface potential short time is constant and decreases after. This can be due to a decrease in the surface density of the molecules (which is impossible - with the decrease in the working area surface of the Langmuir trough, the surface density of the molecules increase, if we have surfactant molecules) or due to changes in the orientation of molecules. Thus, as the temperature rises, the molecules of a liquid crystal behave like typical surfactant molecules (the same behavior of 8CB molecules we can see at 18°C in first part of isotherm before breaking point) and we can obtain monolayered structure with them. Thus in our experiment we obtain complex organic-inorganic films by using high temperature and specific ration of QDs:8CB.

For further study monolayers were deposited on glass substrates and studied by AFM method by semicontact mode. The transfer was carried out at different values of surface pressure: 3, 6, 9, 12 mN/m by Langmuir- Schaefer method and dried at room temperature.

For each sample we study morphology of surface and structure, height profiles were measured. On figure 3 and figure 4 shown AFM picture for few samples. Film obtained by different value of surface pressure at deposition.

Figure 3. AFM pictures and hight profile for films deposited at 3 mN/m (A) and 6 mN/m (B)

These pictures shown that in the case of transfer a monolayer at 3, 6 or 9 mN/m surface pressure value, the resulting films has an island structures. Moreover, as the value of the pressure of transport increases, the boundaries of the islands became clearer and the size of the islands is larger. However,
in each case the thickness of the film in the island is of the order of the diameter of the quantum dot used in the monolayer. This fact allows us to say that the resulting films are monolayers. When the film is transferred at 12 mN/m, it covers almost the entire sample and has a smaller roughness. However, it has some heterogeneity in the morphology of the surface, in contrast to films with a island structure.

Figure 4. AFM pictures and hight profile for films deposited at 9 mN/m (A) and 12 mN/m (B)

4. Conclusion
Research results allow us to say that an increase in temperature in Langmuir trough and changing ratio of QDs:8CB allows us obtaining a film with monolayer structure. It was confirmed by analysis of compression isotherms and using AFM method. Structure of the film dependent on the surface pressure by deposition, and if we transfer monolayer by surface pressure more 10 mN/m we will obtain monolayer structure.

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