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To cite this article: E. O. Gavrish, I. F. Galin, E. A. Konshina & D. A. Vakulin (2015) Comparison the Properties of LC Cells with CdSe/ZnS QDs Embedded Into Nematic LC Matrix and the Polyimide Alignment Layer, Molecular Crystals and Liquid Crystals, 615:1, 50-56, DOI: 10.1080/15421406.2015.1066954

To link to this article: <http://dx.doi.org/10.1080/15421406.2015.1066954>



Published online: 21 Aug 2015.



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Comparison the Properties of LC Cells with CdSe/ZnS QDs Embedded Into Nematic LC Matrix and the Polyimide Alignment Layer

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We compared electro-optical characteristics of LC cells with 0.05 and 0.1 wt.% semiconductor quantum dots (QDs) CdSe/ZnS embedded into nematic liquid crystal and polyimide layers. The phase delay of the LC cells increased with addition of the QDs into the liquid crystal layer. Also we observed decreasing the phase delay of the LC cells with QDs embedded into the polyimide layer. The threshold voltage reduced in case of doping LC with QDs, in contrast to the LC cells with QDs in the polyimide layers. The optical response times of LC doped with QDs were less than in case of adding the same into the polyimide layer.

Keywords Semiconductor quantum dots (QD); electro-optical characteristics; polyimide alignment layer (PI); phase delay; dielectric permittivity

Introduction

Semiconductor quantum dots (QDs) are one of the well-studied classes of nanoparticles and widely used material. Doping liquid crystals with QDs have an impact on the properties of LC cells [1]. Threshold voltage of electro-optical effect, pretilt angle, phase retardation, dielectric permittivity of the doped LC can vary on size and concentration of nanoparticles. The threshold voltage decreases, when CdSe and CdTe nanoparticles were added to LCs due to lowering elastic coefficient [2]. The effective permittivity, the phase retardation and the threshold voltage decreased, when 0.1 and 0.2 wt.% 3.5 nm CdSe/ZnS QDs embedded into the nematic liquid crystal as a result of director pretilt angle variation [3]. The threshold voltage of 5CB twisted-nematic cells reduced up to 25% when 0.1 – 0.2 wt.%, 3 and 5 nm CdSe/ZnS were used [1]. The turn on time of cells with nematic liquid crystal doped with QDs reduced too [4].

Changing phase delay, threshold voltage and other optical and dynamical characteristics of LCs cells are conforming to variation of a pretilt angle. The adsorption of the surfactants or nanoparticles on the substrates can mediate and lower the surface tension of

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the substrates, consequently modifying the pretilt angle of LC molecules take place. The addition of 0 to 0.16 wt.% Polyhedral Oligomeric Silsequioxanes (POSS) in the homogeneous PI changes the surface energy of the alignment layer and generates a variable pretilt angle continuously over the range of $0^\circ < \theta_p < 90^\circ$. This technique is very simple and is compatible with methods familiar in the current LCD industry [5].

The main goal of our research is to compare the electro-optical characteristics of the LC cells with quantum dots (CdSe/ZnS) embedded into the LC and the polyimide alignment layer. In this work we study the effect of semiconductor quantum dots on phase delay, threshold voltage and optical response of LC cells.

Experimental Setup and Materials

The experiments were performed on plane-parallel electrically controlled LC cells with homogeneous orientation made-up of two glass substrates with a diameter of 35 mm coated with transparent conducting layers of indium tin oxide and alignment polyimide layers. The nematic LC of ZhK-1282 type (NIOPIK, Moscow) with positive dielectric anisotropy equals to 9.9 and isotropic nematic phase transition temperature about 62°C was used. The colloidal semiconductor QDs CdSe/ZnS of the core/shell type with a diameter of ~ 3.5 nm were used in this work. Each QD comprised of CdSe core passivated by ZnS and covered by a layer of trioctylphosphine oxide molecules. The concentration of CdSe/ZnS nanoparticles in LC and PI alignment layer was 0.05 and 0.1 wt.%.

We blended the suspensions of the QDs with the LC in its nematic phase using an ultrasonic bath for 1.5 hour prior to filling the cells. QDs mixed with LC poorly and tended to precipitate. Nanoparticles were injected directly into a solution of PI in dimethylformamide in case of doping PI layers. The solution was mixed in an ultrasonic bath for 1.5 hour and was deposited by spin-coating of the substrates. Whereupon substrates with the PI layers doped with QDs were annealed at 180 degrees for 10-15 minutes and then rubbed in one direction to create the anisotropy of surface properties. The cells were filled by the capillary technique in air at room temperature.

The optical transmission of LC cells on a wavelength of $0.65 \mu\text{m}$ were studied using an experimental setup described elsewhere [6]. The cell was placed between two crossed polarizers. The optical signal detected by photodiode is measured by an oscilloscope and the special computer program. The phase delay is calculated from the experimental curves of cells transmission on voltage. The maximum phase delay and threshold voltage of the electro-optical effect are evaluated as described elsewhere [7]. The threshold voltage is determined by extrapolating the linear part of the phase delay. Pretilt angle is determined by calculating the theoretical dependence of the phase delay for a given thickness of the cell using its maximum value. LC cells capacitance and resistance were measured using a special computer-controlled electric circuit on a sinusoidal voltage with a frequency of 1 kHz and a voltage variable within 0.3–10 V. The permittivity of the cells was experimentally determined via the ratio of capacitances of the filled and empty cells. All electrical and optical measurements were performed at a room temperature. A quality of liquid crystal orientation was assessed using the polarization microscope.

Results and Discussion

The dependencies of the phase delay from the voltage for the LC cells with 0.05 and 0.1 wt.% QDs in LC layer and PI alignment layer are shown in Figure 1 (a, b). We observed

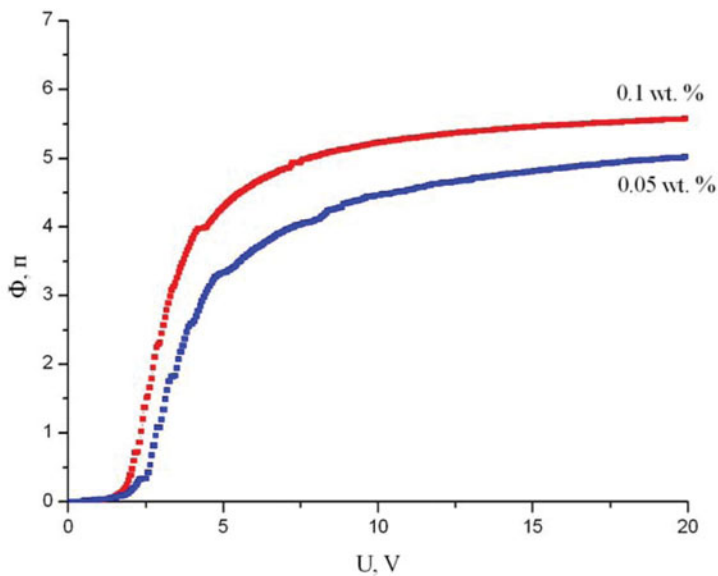
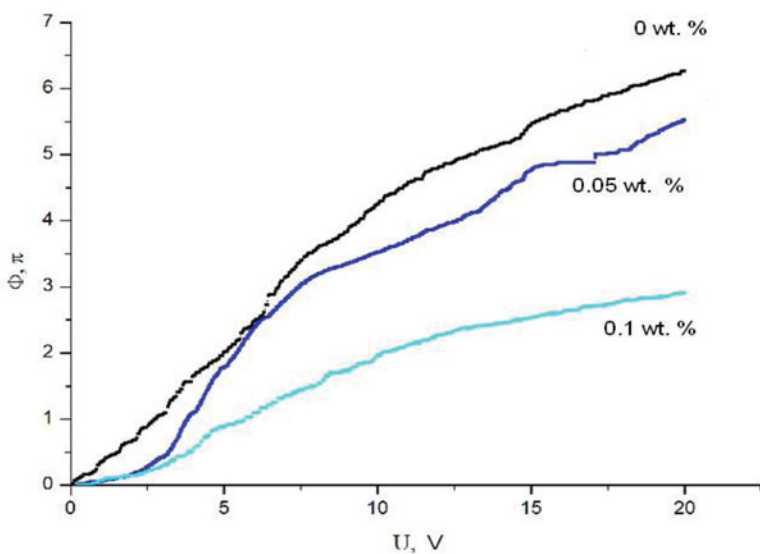
**a****b**

Figure 1. Dependencies of the phase delay on voltage for the LC cells with the polyimide alignment layer: (a) CdSe/ZnS QDs embedded into the nematic LC; (b) CdSe/ZnS QDs embedded into the polyimide layer. The QDs concentration were 0.05 and 0.1 wt.% and the thickness of the LC layer was about 12 to 13 μm .

insignificant increasing the phase delay of LC cells with addition of quantum dots (Figure 1, (a)), but one decreased with QDs embedded into the polyimide layer (Figure 1, b). Adding the QDs into PI layer increased the threshold voltage (Figure 1, (b)), but it is unchanged in the cells the same concentration of nanoparticles in the LC (Figure 1, (a)). The influence

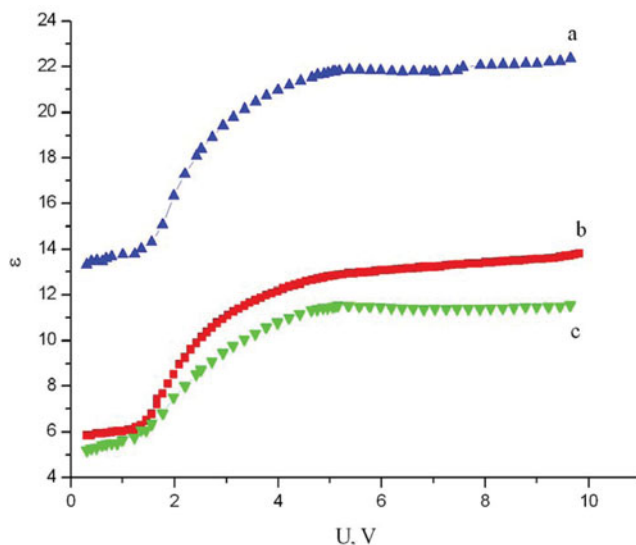


Figure 2. The permittivity ε as a function of applied voltage with frequency 1 kHz under temperature about 25°C for the LC cells without QDs (a), with 0.1 wt.% QDs in LC layer (b), and 0.1 wt.% QDs in PI layer (c). The LC layer thickness were (a) 14.5 μm , (b) 13.4 μm , and (c) 14.7 μm .

of the cells boundary conditions on the phase delay is larger in case of doping PI layer (Figure 1, (b)), unlike doping the liquid crystal (Figure 1, (a)). While the phase delay decreased in two time the QDs concentration increased from 0.05 wt.% to 0.1 wt.%. The reason for the reduction of the phase delay is the variation of the order parameter, which leads to change in the initial angle and the effective dielectric constant.

Decreasing the threshold voltage correlates with reducing the screening effect. As it is known, the process of separating ions by the action of an external electric field leads to the formation of space charge at the interface, which induces an occurrence of a screening

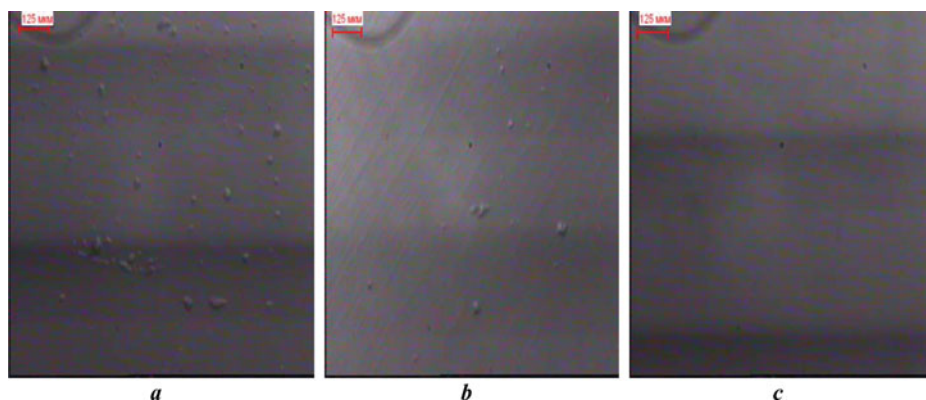


Figure 3. Micrographs of the LC cells with homogeneous aligned polyimide layer doped with QDs: 0.1wt.% (a), 0.05 wt.% (b) and without QDs (c) in the crossed polarizes. Magnification of the microscope was 2.5.

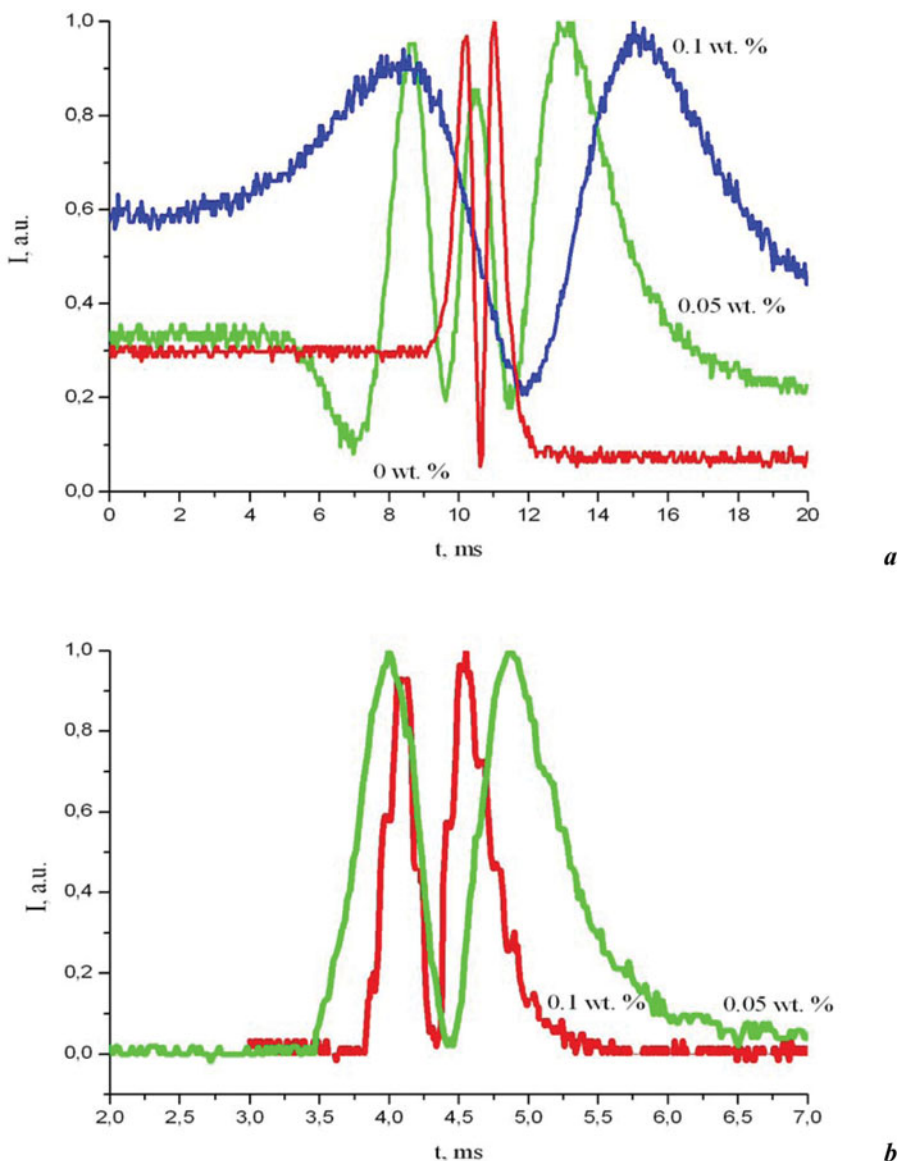


Figure 4. Optical response of homogeneously oriented LC cells with 0.05 wt.% and 0.1 wt.% CdSe/ZnS QDs doped PI layers (a) and liquid crystal layer (b). Frequency of the applied electric field was 1 kHz and voltage was 30 V.

effect. The drop of a voltage depends on the thickness and permittivity of the liquid crystal and the alignment layer. Nanoparticles in the liquid crystal can serve as traps for ions. Trapping of ions leads to fast run-off and reduces the space-charge of cells [8]. The space charge near the alignment layer surface can cause in an increase the polar component of the surface energy and the polar angle of LC director. Doping polyimide layer with QDs may increase its density and the screening effect of alignment layers.

Table 1. Response time for 2π phase modulation of the LC cell with liquid crystal and alignment layers doped with quantum dots

Alignment layer and liquid crystal	The response time of the phase modulation 2π , ms
PI+LC	1.68
(PI+0.05 wt.% QDs)+LC	2.17
(PI+0.1 wt.% QDs)+LC	7.82
PI+(0.05 wt.% QDs+LC)	1
PI+(0.1 wt.% QDs+LC)	0.53

Dependencies of the effective permittivity ε as a function of applied voltage are shown in Figure 2. The LC cells permittivity reduced in the result of doping LC and PI layers with QDs in comparison with the LC cell without nanoparticles. Adding QDs in the PI layers reduces ε of the LC cell more essentially (Figure 2, (b)).

Figure 3 shows micrographs of the homogeneous aligned LC cells. The quantum dots can be combined into the clusters during polyimide drops spin coating (Figure 3, (a, b)). Thus clusters of QDs in polyimide can create defects on the surface of the alignment layer. The higher the concentration of QDs, the bigger clusters in size. Cluster size can be up to several tens of microns.

Adding QDs leads to acceleration of the LC cell optical response, but the relaxation is slowing [9]. We observed slowing of the LC cells optical response with PI layers doped with QDs (Figure 4, (a)). The higher the concentration of QDs in PI, the longer the response time. The increase in the threshold of an electro-optical effect may adversely affect on slowdown of optical response. In contrast, with increasing QDs concentration in the liquid crystal we observed optical response acceleration in Figure 4, (b).

Increasing the threshold of an electro-optical effect (Figure 1, (b)) and decreasing the permittivity of the LC cell (Figure 2, (b, c)) may affect on the optical response slowdown. In contrast, the optical response time of the LC cells with QDs in the liquid crystal decreased with increasing of the concentration up to 0.1 wt.% in Figure 4, (b). To explain this phenomenon carrying out additional researches is necessary. Response time for 2π phase modulation of the LC cell with liquid crystal and alignment layers doped with quantum dots are shown in the Table 1. The response times of the cells with QDs in the LC (table 1) decreased with increasing the concentration from 0.05 wt.% to 0.1 wt.%.

Summary

We studied variation of the LC cells electro-optical characteristics in the result of doping with 3.5 nm CdSe/ZnS quantum dots liquid crystal and alignment layers. It has been shown that, doping semiconductor nanoparticles reduces dielectric permittivity of the LC cells. Adding of quantum dots into the liquid crystals decreases a screening effect of LC layer resulting in lower threshold voltage of the cells and decreasing the optical response time with increasing the concentration from 0.05 wt.% to 0.1wt.%. The same QDs doped in PI layer slowdown the optical response of LC cells due to increasing of the alignment layer screening effect and the threshold voltage. The experimental results on QDs doping the LC cells with the PI alignment layer contribute to the understanding of the semiconductor QDs action on behavior and characteristics of the LC cells.

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