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Incorporation of luminescent semiconductor nanoparticles into liquid crystal matrix

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ABSTRACT

Characterization of size of synthesized semiconductor copper indium sulfide ($CuInS_2$) nanoparticles used for doping liquid crystal E7 is presented. The method of production of uniform dispersions of the nanoparticles in liquid crystals avoiding aggregation of the nanoparticles is discussed. It was possible to prepare doped liquid crystal with almost uniform dispersion of nanoparticles in the cell, which are visible as defects in homogenous liquid crystal phase. Electrorefractive and photo-electrorefractive characterizations of the mixtures have been done with pure E7 sample as a reference and the results are discussed.

1. Introduction

Optically Addressed Spatial Light Modulators (OA SLMs) require light-sensitive material, that is able to change its refractive properties upon light irradiation. Commonly used materials for OA SLMs are liquid crystals, because of their ability to change upon electric field applied. In OA SLMs it is not necessary to use substrates covered by series of electrodes, required to address every pixel. The light beam is directly used for selective addressing of desired regions of OA SLM. Certain voltage is applied to the panel and upon the light irradiation the electrorefractive effect is amplified only at irradiated places.

Recently, it was shown that doping of liquid crystal or photoconducting layer with semiconductor CdS or CdSe nanoparticles, can improve photo-electrorefractive effect in liquid crystal cells, when resonant light wavelength is used [1,2]. The semiconductor quantum dots used for doping liquid crystals are usually made from elements from groups II and VI (e.g. CdSe), III and V (e.g. InP), IV and VI (e.g. PbS) [3]. In this work copper(I) indium sulfide—a ternary mixture based on the elements from groups I, III and VI was used.

We present results of the determination of the size of synthesized copper indium sulfide ($CuInS_2$) nanoparticles capped with long alkyl chain surfactant (1-dodecanethiol) and studies of the mixing ability of liquid crystal with the nanoparticles. Size of the nanoparticles was determined by four different methods: UV–vis absorptiometry, spectrofluorimetry, X-ray diffractometry (XRD) and transmission electron microscopy (TEM). The semiconductor nanoparticles were incorporated into liquid crystalline matrix (commercially available liquid crystal mixture-E7, composed of molecules of 4-cyano-4′-*n*-pentyl-1,1′-biphenyl (known as *5CB*), 4-cyano-4′-*n*-heptyl-1,1′-biphenyl (*7CB*), 4-cyano-4′-*n*-octyloxy-1,1′-biphenyl (*8OCB*) and 4-cyano-4″-*n*-pentyl-1,1′,1″-terphenyl (*5CT* or *T15*)).

Possible optical applications, like liquid crystal displays (LCDs) or SLMs, require uniform material and uniform response on the entire panel, therefore a method of fabrication of liquid crystal cells with uniform concentration of the nanoparticles should be provided. Solubility of the nanoparticles in liquid crystal matrix is limited [4–6]. Authors of article [4] dissolved 0.3% of ferroelectric $Sn_2P_2S_6$ nanoparticles capped with oleic acid in liquid crystal and claimed no aggregation effect, however no photos of the mixtures were provided. Elongated particles of diameter from tens to hundreds of nanometers: MoSI and Ag nanowires, MnO_2 nanorods, WS_2 nanotubes, synthesized and used without surrounding ligands, added to liquid crystal at weight fraction in range 0.1–0.5%, caused aggregation effect and formation of two phase composition [5]. Usage of ligands with enhanced compatibility with liquid crystal molecules for gold nanoparticles made possible to dissolve maximum 0.2% of the nanoparticles in liquid crystal matrix [6].

Doping of the liquid crystals cause also change in Freedericksz threshold, which is one of key factors for control of liquid crystal

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setups and devices. The reports related to the threshold state that it could be much lower in case of doping with metal nanoparticles [7] or ferroelectric nanoparticles [4] and slightly lower or comparable in case of doping with semiconductor nanoparticles [8–10].

If the complete mixing of the two components is not possible and two phases appear, then uniform response of the sample upon light irradiation in presence of electric field can be given only if the dispersed phase is uniformly distributed in the host phase. We found that with ultrasonication procedure the nanoparticle material appears in mixture as separated defects of liquid crystalline phase, distributed in nearly-uniform fashion.

In this work the nanoparticles are characterized in terms of their properties, like: light absorption, fluorescence and size. The procedure of the preparation of the material and selection of proper range of concentration of the nanoparticles in liquid crystal is presented. The mixtures of liquid crystal with the nanoparticles are characterized by electrorefractive and photo-electrorefractive properties.

2. Experimental section

$CuInS_2$ quantum dots were synthesized from indium(III) acetate, copper(I) iodide and 1-dodecanethiol, acting as precursors of: indium, copper and sulfur, respectively. The reaction was carried out in one pot in 1-octadecene solution with an excess of 1-dodecanethiol. The detailed protocol of the synthesis is described in the article [11]. After synthesis, the nanoparticles dispersed in chloroform solution were purified several times from the excess of 1-octadecene and 1-dodecanethiol by the following method: precipitation in methanol, centrifugation (10,000 rpm, 3 min), decantation of supernatant and dissolution of precipitate in chloroform.

The size of $CuInS_2$ nanoparticles were determined by following methods and instruments. UV–vis absorption spectra were registered on Evolution 300 UV–vis spectrophotometer (Thermo Scientific). Photoluminescence excitation and emission spectra were collected on FLS 980 spectrofluorometer (Edinburgh Instruments). X-ray diffractograms were collected on Empyrean X-ray diffractometer (PANalytical) for CuKα radiation line, $\lambda = 0.15418$ nm. TEM observations were performed on FEI Tecnai G^2 20 X-TWIN microscope.

The mixtures of liquid crystals with nanoparticles were prepared according to the following protocol. The nanoparticles were dissolved in chloroform, ultrasonicated for 30 min and both were mixed with liquid crystal. Then the mixture with all the components was ultrasonicated for another 30 min at temperature about 50 °C in order to mix the components and evaporate the rest of the chloroform. The mixture was heated for a short time above the boiling point of the chloroform (about 70–80 °C) and placed immediately on the balance. A constant weight value shown by analytical balance, indicated no more evaporation of the solvent. Next, the mixture was heated again to the temperature above 70 °C and used to fill the cell by means of capillary action, being also above this temperature. Simultaneously, the reference sample —liquid crystal E7 was mixed with chloroform and prepared according to the same procedure. The cells were of thickness 5 μm, having rubbed polyimide inner surfaces, creating homogenous planar orientation of liquid crystalline molecules. Initial weight fraction of $CuInS_2$ nanoparticles material to liquid crystal, used for mixing was 1% and 5%. Our studies shown, that the concentration is too high and samples in range of concentration 0.01–0.16% were prepared.

For the microscopic observations of the liquid crystal mixtures in thin cells, polarized optical microscope-DM2700P (Leica) was used. The transmission-AC voltage characteristics and photo-electrorefractive dynamics (at constant DC voltage) of the liquid crystalline mixtures were registered in parallel polarizers setup. Alternating voltage of $f = 1$ kHz frequency, modulated with triangular function from 0 to ± 10 V was used to register transmission AC voltage characteristics. Time period of 40 s was used for one measurement cycle (which include increase and decrease of $|U|$). Polarized HeNe laser radiation ($\lambda = 633$ nm) was probing the material. Electric function generator was used to drive the voltage applied to the sample. The sample with homogenous planar orientation of liquid crystal molecules were rotated about 45° with respect to the polarizers, both set at angle 0°. The photo-electrorefractive effect was induced in the sample at constant voltage, by focused beam from unpolarized 532 nm laser diode, incident at angle about 20°. Light intensity at the sample was in the order of 5 W/cm^2.

3. Characterization of the size of $CuInS_2$ quantum dots

After synthesis and purification the $CuInS_2$ quantum dots were dispersed in chloroform and characterized by UV–vis absorption and fluorescence spectroscopy. Fig. 1 presents the results of the measurements.

The absorption band of the nanoparticles may overlap in the low wavelength regime ($\lambda < 300$ nm) with the signal from scattering of light on small particles. The end of absorption band lies roughly near the emission peak maximum (about 710 nm). On the basis of empirical dependence of the size of the nanoparticles on the long-wavelength end of the absorption band wavelength found in art. [12], we estimated the size of $CuInS_2$ nanoparticles as 3.3 nm. The method for determination of edge of absorption band was not provided and may be differently interpreted, so we estimated the uncertainty of this determination as 0.5 nm.

The nanoparticles upon excitation at $\lambda = 400$ nm, exhibit a broad band emission from about 550 nm to over 900 nm, with maximum at $\lambda_{em,max} = 713$ nm. An empirical dependence of size of the chalcopyrite $CuInS_2$ nanocrystal capped with similar ligand and having similar XRD pattern, on position of photoluminescence emission peak maximum was provided in Ref. [13], as

$$d = 68.952 - 0.2136\lambda_{em,\,\max} + 1.717\cdot 10^{-4}\lambda_{em,\,\max}^{2}. \qquad (1)$$

Determined average size, expressed as the length between apex and center of opposite side of the triangle of the studied nanoparticles by this relation is 3.9 ± 0.7 nm. The uncertainty was estimated from the error made by determination of the maximum and uncertainty of the relation, which may be found in the reference.

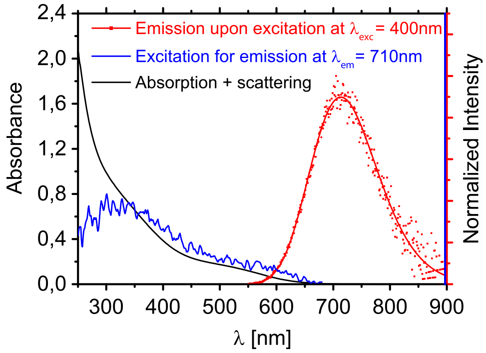

Fig. 1. Absorption spectrum (black), excitation spectrum for emission at $\lambda_{em} = 710$ nm (blue) and emission spectrum upon excitation at $\lambda_{exc} = 400$ nm (red) of $CuInS_2$ quantum dots dispersion in chloroform. Emission was fitted with a peak function with center positioned at $\lambda_{em,max} = 713$ nm. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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