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Citation: *APL Materials* **5**, 076104 (2017); doi: 10.1063/1.4991029

View online: <http://dx.doi.org/10.1063/1.4991029>

View Table of Contents: <http://aip.scitation.org/toc/apm/5/7>

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## Hybrid fluorescent layer emitting polarized light

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(Received 3 May 2017; accepted 19 June 2017; published online 18 July 2017)

Semiconductor nanorods have anisotropic absorption and emission properties. In this work a hybrid luminescent layer is produced based on a mixture of CdSe/CdS nanorods dispersed in a liquid crystal that is aligned by an electric field and polymerized by UV illumination. The film emits light with polarization ratio 0.6 (polarization contrast 4:1). Clusters of nanorods in liquid crystal can be avoided by applying an AC electric field with sufficient amplitude. This method can be made compatible with large-scale processing on flexible transparent substrates. Thin polarized light emitters can be used in LCD backlights or solar concentrators to increase the efficiency. © 2017 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>). [<http://dx.doi.org/10.1063/1.4991029>]

Semiconductor nanorods (NRs) have a needle-like structure and their light absorption and emission properties are anisotropic.<sup>1–4</sup> Aligning nanorods collectively along a preferred axis is attractive for photovoltaic energy conversion, light-emitting devices, optical sensors, or switches.<sup>5–9</sup> Several techniques for aligning NRs have been explored and it was found that electric-field-driven deposition from a colloidal suspension is efficient for many kinds of anisotropic particles: nanowires,<sup>10</sup> carbon nanotubes,<sup>11</sup> gold NRs,<sup>12,13</sup> and semiconductor NRs.<sup>3,6,14–16</sup> Zonghai *et al.* reported on the alignment of CdSe and CdTe NRs along the applied electric field and the accumulation of NRs near the electrodes after drop-casting from a solution.<sup>17</sup> Ryan *et al.* used a combination of a DC electric field and the slow evaporation of toluene to generate superlattices of semiconductor nanorods with orientation perpendicular to the substrate.<sup>18</sup>

In these papers, good alignment is obtained, but the methods are not always compatible with cheap, reproducible, and homogeneous deposition on large substrates as required for large size applications such as solar cells or OLEDs. In previous work, we presented a novel technique for the homogeneous deposition and efficient alignment of CdSe/CdS NRs on a glass substrate which is based on applying an electric field between electrodes during dip-coating.<sup>19,20</sup> In this approach, the alignment of the NRs requires electric fields with amplitude up to 20 V/μm, and alignment is only possible on substrates with appropriately patterned electrodes. An alternative, electrode-independent approach involves the formation of films made of aligned polyvinylpyrrolidone nanofibers, containing silica-coated CdSe/CdS NRs oriented parallel to the nanofiber axis, with polarization ratio 0.45.<sup>21</sup>

Liquid crystals (LCs) combine properties such as long-range orientational order and optical and electrical anisotropy while remaining fluid. The self-organizing nature of LCs has been demonstrated in different configurations<sup>22,23</sup> and proved to be instrumental in the alignment of anisotropic objects such as nanowires, nanotubes,<sup>20</sup> and metallic<sup>22</sup> and semiconducting<sup>24</sup> nanorods. Hybrid materials combining different types of building blocks may display interesting properties that can be used in novel applications. Unfortunately, it is very difficult to disperse high concentrations of nanoparticles in anisotropic fluids without the problem of aggregation. For example, the work of Tao Du *et al.*<sup>24,25</sup> in which photo-alignment is used to align NRs in LC, mentions the presence of clusters of NRs in

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LCs. Often surfactant stabilization is applied to reduce clustering as, e.g., for the case of gold NRs in lyotropic LC.<sup>22,23,26</sup>

In this work, we show that the application of an AC electric field can effectively disperse existing clusters of CdSe/CdS NRs in the nematic LC mixture. In addition, by mixing NRs into reactive mesogens instead of regular LC, the configuration of aligned nanorods in LC without aggregations can be fixed by UV polymerization. The resulting polymer film can be detached from the ITO-coated substrates. When illuminated with unpolarized blue light, it emits mainly linearly polarized green light by photoluminescence, with polarization contrast ratio 0.60 (intensity ratio 4:1).

The CdSe/CdS NRs used here have been synthesized using an established colloidal synthesis method<sup>3</sup> and have an average length of 51 nm and an average diameter of 4.8 nm (see the [supplementary material](#), CdSe/CdS dot in rod synthesis). Figure 1 shows (a) a transmission electron microscopy (TEM) image of NRs on a substrate and (b) a sketch of the synthesized NRs. The NRs have an emission spectrum centered around 580 nm when excited with a wavelength of 365 nm (see the [supplementary material](#), optical properties of CdSe/CdS NRs and Fig. S1).

In a first experiment, two glass substrates (one without and one with interdigitated ITO electrodes) are used to make a LC device with 10  $\mu\text{m}$  spacing between the substrates. The cell has 2 times 25 ITO finger electrodes with length, width and thickness equal to respectively 2600  $\mu\text{m}$ , 4  $\mu\text{m}$  and 30 nm, while the gap between two electrodes is 20  $\mu\text{m}$ . The experimental setup and ITO pattern are schematically shown in Figs. 2(a) and 2(b). A suspension of 1 wt. % NR in non-reactive LC (MDA-00-3536) is filled into the cell without alignment layers by capillary force.

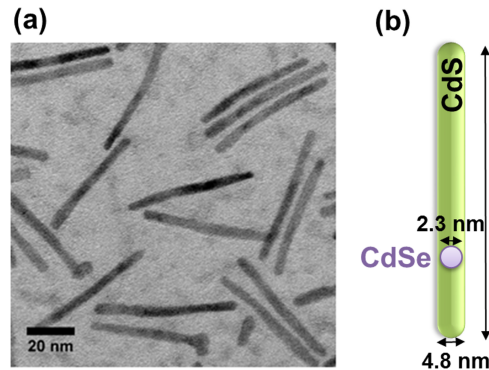


FIG. 1. (a) TEM micrograph of CdSe/CdS nanorods. (b) Sketch of the CdSe/CdS nanorod structure.

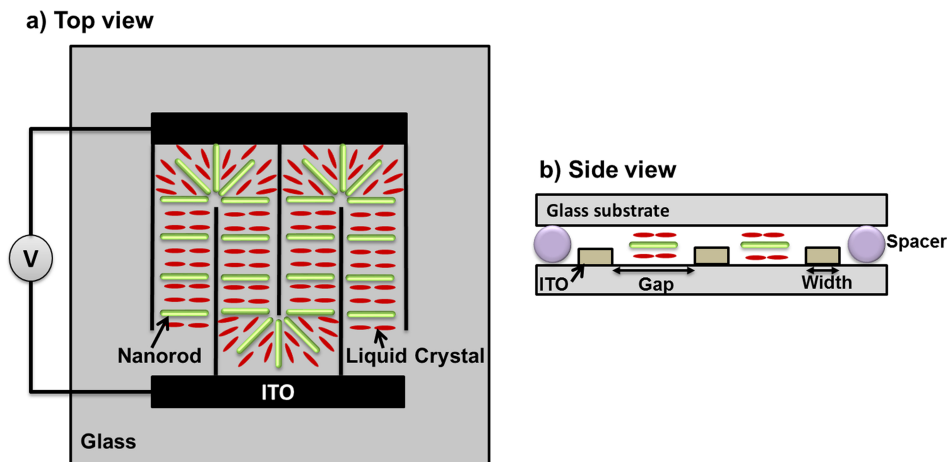


FIG. 2. (a) Sketch of the experimental setup: a device with two parallel glass substrates with interdigitated ITO electrodes on one substrate, is filled with a suspension of NRs (green) in a non-reactive LC (red) in the presence of an electric field. The length of the electrodes is 2600  $\mu\text{m}$  (b) Cross-section of the cell indicating the width (4  $\mu\text{m}$ ) and the thickness (30 nm) of the ITO electrodes and the gap between them (20  $\mu\text{m}$ ) (not to scale).

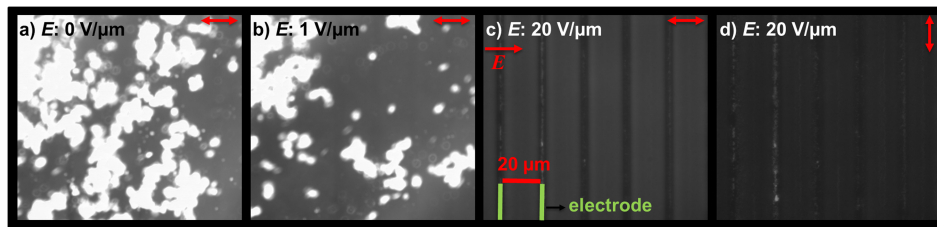


FIG. 3. Polarized fluorescence microscopy images of NRs suspended in LC, filled in a device with interdigitated electrodes. The electrode gap of  $20\ \mu\text{m}$  is indicated by a red line. The electric field is (a) absent (many clusters), (b)  $1\ \text{V}/\mu\text{m}$  (less clusters), [(c) and (d)]  $20\ \text{V}/\mu\text{m}$  (no clusters) with the polarizer (c) parallel and (d) perpendicular to the applied electric field.

Polarization fluorescence microscopy can provide information about the average NR orientation. The NRs are excited in the UV band (330–380 nm) using a xenon lamp. The photoluminescent intensity of the NRs, integrated over the emission spectrum is detected by an Andor CCD camera after passing through a dichroic mirror and a rotatable linear polarizer. Figure 3(a) shows that before any voltage is applied to the device; the fluorescence (unpolarized) is dominated by NRs that are aggregated in clusters. When we apply a 1 kHz voltage with amplitude 20 V over the gap of  $20\ \mu\text{m}$  (average electric field  $1\ \text{V}/\mu\text{m}$ - see [supplementary material](#), application of an AC fields) most of the aggregates remain visible [Fig. 3(b)]. With polarization microscopy, we have observed (not shown) that at this voltage the LC director aligns along the field lines. By applying an AC electric field with higher amplitude ( $20\ \text{V}/\mu\text{m}$ ), we can make the clusters disappear and obtain a good dispersion of the NRs, which remain stable after switching off the voltage. The fluorescent emission in the presence of a field of  $20\ \text{V}/\mu\text{m}$  is strongly polarized [compare Figs. 3(c) and 3(d) with different orientation of the polarizer], indicating good alignment of the NRs.

Clustering of NRs in LC originates from the increase in elastic energy in the LC in the neighborhood of a NR due to frustrating boundary conditions. By forming clusters of NRs the number of regions with high elastic energy decreases, which reduces the total LC elastic energy. In addition, the permanent dipole moment of NRs (which is known to be along the long axis<sup>27</sup>) results in an attractive force when two NRs are oriented head-to-tails. The fact that clustering disappears when the amplitude of the ac field is sufficiently high, may be explained by the alignment of the NRs in the applied AC electric field. If the field is sufficiently high, the NRs will tend to align their dipole moment in the same direction as the electric field, and this leads to a repelling force between NRs that lie next to each other.

In the second experimental approach, we demonstrate how to realize a solid film containing aligned NRs, based on a suspension of 1 wt. % NR in reactive LC, and the same cell with interdigitated electrodes as in Fig. 2. The mixture of reactive nematic LC is prepared by mixing photo initiator (Irgacure 819, BASF) with a blend of different reactive mono- and di-acrylate mesogens (Merck) and photo inhibitor (tert-Butylhydroquinone, Sigma-Aldrich). The chemical structure of the materials shown in Fig. 4.

An electric field ( $20\ \text{V}/\mu\text{m}$ , 1 kHz) is applied between the electrodes and after a few seconds, the device is also illuminated with UV light for one minute in order to photopolymerize the reactive LC mixture. After polymerization is completed, the voltage is switched off. Finally, one of the two glass substrates is removed and the polymer layer remains on the other substrate.

Polarization fluorescence microscopy images of the resulting NR layer are shown for when the orientation of the polarizer is parallel [Fig. 5(a)] or perpendicular [Fig. 5(b)] to the applied electric field. The stripes with lower intensity correspond to the ITO electrode lines, which illustrates that the NRs tend to move to the region between the electrodes when a field is applied. The difference in brightness between Figs. 5(a) and 5(b) indicates that the nanorods are aligned along the electric field because the NR emission is mainly linearly polarized along the long axis.<sup>1,3,4,9</sup> We define the polarization ratio as:  $\Pi_r = (I_{\parallel} - I_{\perp}) / (I_{\parallel} + I_{\perp})$ <sup>9</sup> with  $I_{\parallel}$  and  $I_{\perp}$  the photoluminescent intensities, integrated over the spectrum and averaged over the gap area between the electrodes, when the polarizer is oriented, respectively, parallel and perpendicular to the applied field. The polarization ratio for the regions between the ITO electrodes is about 0.6, which is somewhat lower than the highest reported polarization ratio for a single CdSe/CdS NR, namely 0.75.<sup>4</sup> The fact that we find a smaller value may

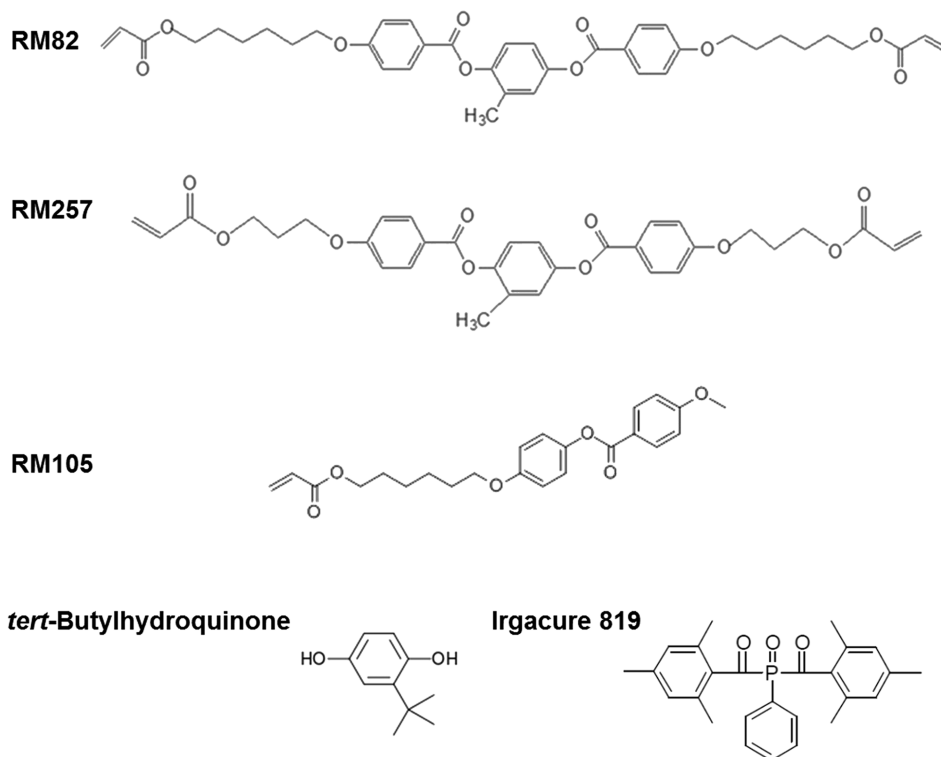


FIG. 4. Chemical structure of two liquid crystalline diacrylate monomers having side groups of different lengths (6-carbon spacers for RM82 and 3-carbon spacers for RM-257), liquid crystalline monoacrylate monomer (RM105), inhibitor (tert-Butylhydroquinone), and photo-initiator (Irgacure 819).

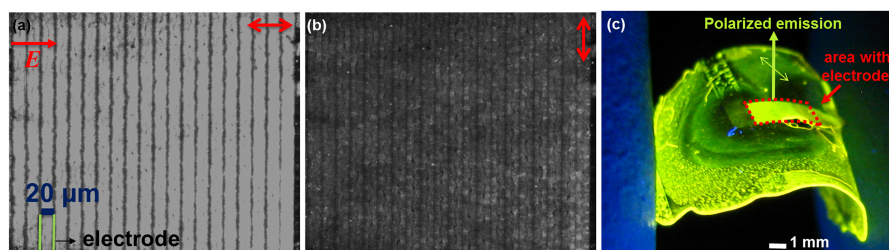


FIG. 5. Fluorescence microscopy images of a polymerized layer of NRs in LC on ITO electrodes, with the polarizer oriented (a) parallel and (b) perpendicular to the applied electric field. (c) Photograph of the detached polymer film with 10 μm thickness excited by a UV lamp. In the bright rectangle (1.2 mm × 2.6 mm), in the center of the film, the voltage was applied, the NRs have been aligned, and the fluorescent emission is polarized. The total sheet is about 8 mm × 16 mm. With this technique, we are able to control the orientation and the position of NRs in space (see [supplementary material](#), paragraph 5 and Fig. S3 for the details).

be attributed to several factors: a limited degree of alignment, loss of polarization due to scattering, or unpolarized emission from aggregates. It might also be due to the fact that the transition dipole moment of the NRs is not perfectly aligned with their long axis.<sup>24</sup> The polarization ratio obtained here (0.6) is higher than for the same experiment using UV curable glue NO68, which yielded only 0.4 (see [supplementary material](#), paragraph 4 and Fig. S2 for the details). It indicates that alignment of the LC by the electric field leads to a better alignment of the NRs. The film is chemically stable (against polar protic solvents) and therefore suitable for processing in devices as an additional film. The layers are thin and can be detached from both substrates, which may be interesting for application inside a cell or in flexible optical devices. Figure 5(c) shows a photograph of the resulting 10 μm thick film which is excited by a UV lamp.

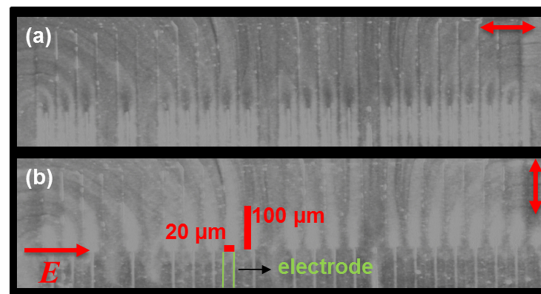


FIG. 6. Polarized fluorescence microscopy images of NRs in LC close to the edge of the electrode area while the polarizer is oriented (a) perpendicularly and (b) parallel to the line electrodes. The voltage amplitude during polymerization was 400 V, with the frequency 1 kHz.

Figure 6 shows fluorescence microscopy images of aligned NRs close to the end of the interdigitated finger electrodes. The polarizer is oriented parallel [Fig. 6(a)] or perpendicular [Fig. 6(b)] to the applied electric field between the electrodes. The intensity differences between Figs. 6(a) and 6(b) indicate that the NRs are aligned along the electric field lines, as illustrated in Fig. 2(a). Away from the end of the electrode lines, where the field lines are spread out, the electric field becomes weaker, but according to the images in Fig. 6, the NRs are still well aligned.

We have demonstrated the realization of a thin film polarized emitter with polarization ratio of 0.60 based on the alignment of CdSe/CdS NRs in LC. The NRs are aligned by an electric field between the interdigitated electrodes and the mixture is polymerized by UV illumination. This method has the potential to be compatible with large-scale processing on cheap, flexible, and transparent substrates and could be realized in a roll-to-roll process. The polarization ratio of the mixture of NR and reactive LC is higher than the mixture of NR and UV curable glue. The fact that this value is much higher is ascribed to the elastic coupling between NRs and LC and the collaborative effect of torques acting on the NRs and on the LC. We observe that the application of an AC electric field with amplitude above a few  $V/\mu\text{m}$  dramatically reduces clustering of NRs in LC.

See [supplementary material](#) for the additional information (CdSe/CdS dot in rod synthesis, optical properties of CdSe/CdS NRs, application of an AC fields, aligned NRs in polymer, control the position, and orientation of NRs and Figs. S1–S3) which is noted in the text. This material is available free of charge via the Internet.

This research was supported by the Interuniversity Attraction Poles program of the Belgian Science Policy Office, Under Grant No. IAP P7-35 and by the IWT-SBO project SECONDOS.

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