

Color-Tunable Light-Emitting Device Based on the Mixture of CdSe Nanorods and Dots Embedded in Liquid-Crystal Cells

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A newly designed color-tunable light-emitting device based on the mixture of CdSe nanorods and quantum dots embedded in liquid-crystal cells has been developed. The underlying working principle is derived from a large alignment energy due to the enhanced anchoring force of liquid-crystal molecules through the amplified surface area of nanorods. After they are embedded into a liquid-crystal cell, nanorods will align along the orientation of liquid-crystal molecules. As the external bias is applied, nanorods would be driven in the direction according to the orientation of liquid-crystal molecules. The nanorods possess optically anisotropic properties, whereas quantum dots are spherically symmetric. Accordingly, the relative ratio of the emission intensity between quantum dots and nanorods can be manipulated by an external bias, and the emission color of the device is, therefore, tunable. Our work shown here may pave a new route for the future development of smart optoelectronic devices.

Introduction

One-dimensional nanostructures, such as nanorods, nanowires, nanotubes, etc., have become a class of attractive materials as their geometric anisotropy gives rise to unique physical properties.^{1–9} For example, the emission and absorption spectra arising from one-dimensional semiconducting wires can be highly anisotropic and, hence, serve as an excellent candidate for the application in polarized optoelectronic devices. On the other hand, liquid crystal (LC) is an anisotropic fluid, which is thermodynamically between isotropic fluids and crystalline solids. The most useful property of LC lies in the fact that its molecular orientation can be easily controlled via an external bias. On this basis, numerous applications have been established, among which one prominent case should be ascribed to the liquid-crystal display (LCD). Combining zero- and one-dimensional semiconductor nanostructures with the well-developed LCD technology, herein, we propose the feasibility of designing a novel color-tunable light-emitting device. We ingeniously demonstrate a color-tunable emission device by embedding semiconductor nanorods and quantum dots in a LC cell. The underlying mechanism is as follows. Nanorods will align along the orientation of LC molecules due to a large alignment energy caused by the enhanced anchoring force through ample surface area in nanomaterials. When the orientation of LC molecules is altered by an external bias, the reorientation of the nanorods will follow that of liquid crystal through the minimized elastic energy of interaction via the electric field. Because the emission of nanorods is strongly anisotropic and that of quantum dots is spherically symmetric, that is, isotropic, we, therefore, can fine-tune the ratio of the emission intensity between nanorods and quantum dots. If we

intentionally select nanorods and quantum dots with different emissive wavelengths, the resulting emission color of this newly designed device could thus be manipulated. Our result elaborated here should be very useful for the future development of smart optoelectronic devices.

Experimental Section

Syntheses of CdSe quantum dots and nanorods have been well-documented.^{10–13} In this study, CdSe quantum dots were synthesized by a previously reported protocol,¹³ and CdSe nanorods were synthesized according to the reported method, except for a slight modification regarding the usage of surfactants.¹⁴ In brief, a selenium (Se) injection solution containing 0.073 g of Se was prepared by dissolving Se powder in 1 mL of tri-*n*-octyl phosphine. CdO (0.20 g) and 0.71 g of tetradecyl phosphonic acid (TDPA) were loaded into a 50 mL three-neck flask and heated to 200 °C under an Ar flow. After the CdO was completely dissolved, judging by the vanishing of the brown color of CdO, the Cd-TDPA complex was allowed to cool to room temperature. Subsequently, 3.00 g of tri-*n*-octyl phosphine oxide (TOPO) was added to the flask, and the temperature was raised to 320 °C to produce an optically clear solution. At this temperature, the Se injection solution was swiftly injected into the hot solution. The reaction mixture was maintained at 320 °C for the growth of CdSe crystals. After 5 min, the temperature was quenched to 40 °C to terminate the reaction. A 5 mL portion of toluene was then introduced to dissolve the reaction mixture, and a brown precipitate was obtained by adding 5 mL of isopropanol and centrifuging at 3000 rpm for 5 min. The precipitate was dispersed in toluene for the transmission electron microscopy (TEM) characterization. As the TEM image of CdSe nanorods show in Figure 1a, the length and diameter of CdSe nanorods are 25 and 7 nm on average, respectively. The TEM image for the studied CdSe quantum dots is revealed in Figure 1b, showing that the size of CdSe quantum dots is about 5 nm. The corresponding photolumines-

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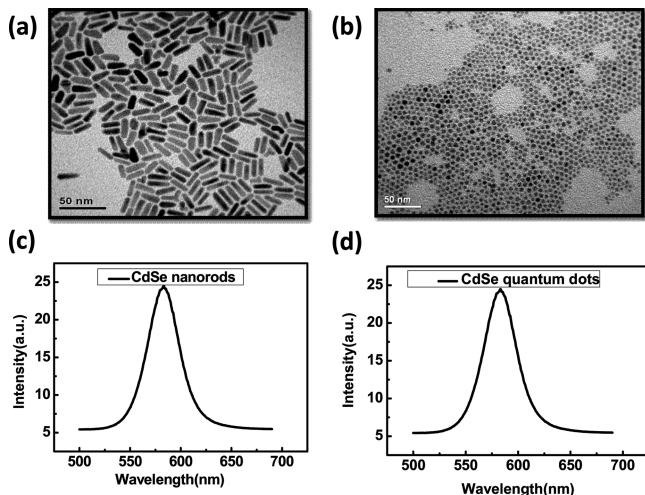


Figure 1. (a, b) Transmission electron microscopy (TEM) images of CdSe nanorods and quantum dots, respectively. (c, d) Photoluminescence (PL) spectra of CdSe nanorods and quantum dots, where the maximum PL intensity is at 650 nm (1.9 eV) and 580 nm (2.1 eV) approximately.

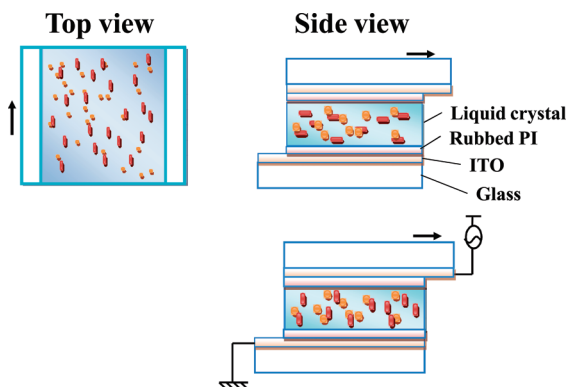


Figure 2. Schematic showing the structure of the fabricated sample with and without an external bias. The arrow is the rubbing direction. The external field will drive the direction of LC molecules perpendicular to the cell plane, and it will also drive nanorods along the same direction due to the interaction between LC molecules and nanorods.

cence spectra of CdSe nanorods and quantum dots are shown in Figure 1c,d, respectively.

A drawing of the LC cell is depicted in Figure 2, in which the top-view and side-view structures of the LC cell, consisting of embedded nanorods and quantum dots, are presented. The LC cell is composed of two glass substrates with indium tin oxide (ITO) on the surface, coated by a polyimide (PI, AL21004, Japan Synthetic Rubber Corp.) alignment layer. The PI layer, after it was spin-coated on the clean ITO glass substrate, was then soft baked at 70 °C for 110 s and hard baked at 240 °C for 8 min. Subsequently, the PI-coated ITO glass was rubbed to serve as a homogeneous alignment layer for arranging the direction of LC molecules. After preparation of lower and upper treated substrates, a mixture composed of nematic LC E7 (Merck), CdSe nanorods, and CdSe quantum dots was injected into the cell through a shot syringe. The distance between lower and upper substrates was about 7 μm . Owing to the capillary force, the cell could be thoroughly filled with LC and CdSe nanocomposites. The device was then sealed for further measurement. In this study, the concentration of CdSe nanorods and quantum dots was about 8.5×10^{10} and $4 \times 10^{10} \text{ cm}^{-3}$, respectively. As the top view shows in Figure 2, the nanorods will align with LC molecules along the rubbing direction due

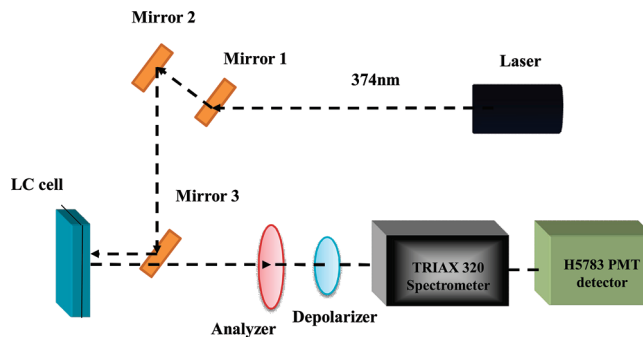


Figure 3. Experimental setup for photoluminescence measurements.

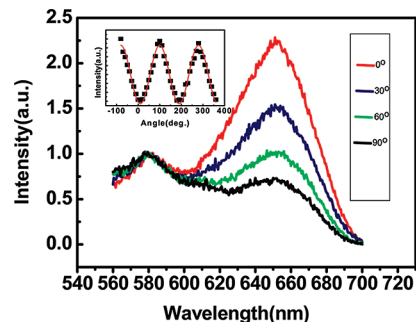


Figure 4. Dependence of photoluminescence spectra of CdSe nanorods and quantum dots on the angle of the analyzer without an external bias. The inset is the variation of the emission intensity of CdSe nanorods versus the analyzer angle.

to the surface coupling between LC molecules and nanorods. When the applied external bias is large enough, the orientation of LC molecules would be forced to align perpendicular to the cell plane, and the reorientation of nanorods would follow that of LC molecules, as shown in Figure 2.

Photoluminescence spectra were used to analyze the emission characteristics of the device containing LC and CdSe nanocomposites. The schematic plot of the experimental setup is shown in Figure 3. A 374 nm laser was used for the pumping source, which will stimulate the emission of CdSe nanocomposites. The emission from CdSe nanocomposites passes through the analyzer and depolarizer, and the signal was detected by a photomultiplier tube (PMT). The analyzer was mounted in front of the entrance slit of the spectrometer in order to distinguish the orientation of the polarized electric field. The depolarizer was placed between the entrance slit and the analyzer of the emission signal in order to eliminate the possible error in the detected polarization due to the measuring equipments. To avoid the induced separation of charged impurities, forming an electric double layer in the LC cell, we apply an alternating square wave voltage at a frequency of 1 kHz across the sample compartment.

Results and Discussion

Figure 4 shows the polarized behavior of the photoluminescence spectra arising from CdSe nanorods and quantum dots embedded in the LC cell. The maximal photoluminescence intensities of nanorods and quantum dots are at 580 nm (2.1 eV) and 650 nm (1.9 eV), respectively. When the analyzer angle is rotated with respect to the rubbed PI direction, the emission intensity from CdSe nanorods is then changed accordingly, while that of CdSe quantum dots remains constant. This result indicates that CdSe nanorods embedded in the LC cell are well-aligned with the LC molecules along the rubbed direction. It is a consequence of the minimization for the elastic energy due

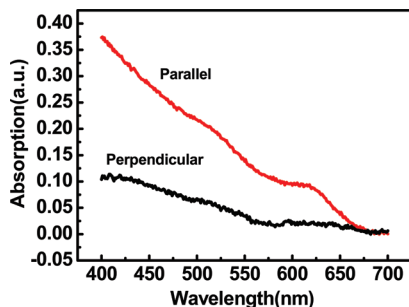


Figure 5. Absorption spectra of CdSe nanorods without an external bias in the case of the analyzer parallel (red line) and perpendicular (black line) to the rubbed PI direction.

to the interaction between LC molecules and nanorods.²² The inset in Figure 4 shows the emission intensity of CdSe nanorods as a function of the analyzer angle, which exhibits a periodic function and follows the $\cos^2 \theta$ rule. It is worth noting that this result is a fully reversible process. To confirm the fact that the observed anisotropic emission indeed arises from the interaction between LC molecules and nanorods, we have fabricated CdSe nanocomposites in a rubbed PI cell without LC infiltration, and the result shows the disappearance of emission anisotropy.

To gain an understanding of the emission anisotropy in a quantitative manner, the polarization ratio of CdSe nanorods can be calculated by $\rho = (I_{\parallel} - I_{\perp}) / (I_{\parallel} + I_{\perp})$,^{15–17} where I_{\parallel} and I_{\perp} represent the intensities of emission parallel and perpendicular to the rubbed PI direction, respectively. The large optical anisotropy could be rationalized in terms of the differences in the dielectric constant between the nanorods and its surroundings.¹⁹

According to the model developed previously, when the electromagnetic field is polarized parallel to the nanorod, the electric field inside the nanorod is not reduced. In contrast, when it is polarized perpendicular to the cylinder, the electric field amplitude is attenuated by a factor, δ , according to the equations given by

$$E_i^{\parallel} = E_e^{\parallel} \quad (1)$$

$$E_i^{\perp} = \delta E_e^{\perp}, \quad \delta = \frac{2\varepsilon_s}{\varepsilon + \varepsilon_s} \quad (2)$$

$$\rho = \frac{I_{\parallel} - I_{\perp}}{I_{\parallel} + I_{\perp}} = \frac{|E_i^{\parallel}|^2 - |E_i^{\perp}|^2}{|E_i^{\parallel}|^2 + |E_i^{\perp}|^2} = \frac{1 - \delta^2}{1 + \delta^2} \quad (3)$$

where E_i is the electric field inside the nanorod, E_e is the excitation field, and ε and ε_s are the dielectric constant of the nanorod and surrounding, respectively. Consequently, by applying the dielectric constant of CdSe nanorods (bulk $\varepsilon = 10.2$)¹⁸ and LC E7 ($\varepsilon_{\parallel} = 3.02$), we then deduce a theoretical value of the polarization ratio of 0.65. In comparison, according to the experimental result shown in Figure 5, the polarization ratio is calculated to be 0.53. The discrepancy between theoretical and experimental values may be attributed to the fact that CdSe nanorods in our study are not an ideal infinite dielectric cylinder, as proposed in the theoretical model.¹⁹

To further examine the dielectric cylinder model for the explanation of the optical anisotropy of CdSe nanorods, the polarization-dependent absorption spectra were recorded. The recorded spectra for the absorbance of CdSe nanorods parallel and perpendicular to the rubbed PI direction are shown in Figure 5. Clearly, large absorption anisotropy was observed, and the

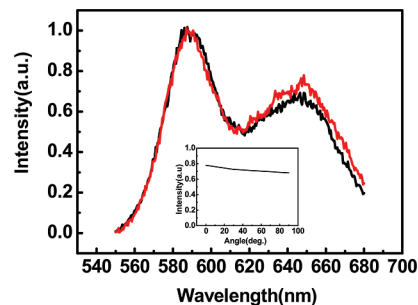


Figure 6. Photoluminescence spectra of CdSe nanorods and quantum dots with an external bias of about 20 V. The inset is the variation of the emission intensity of CdSe nanorods versus the analyzer angle.

polarization ratio at 620 nm is deduced to be 0.54, which is about the same as that measured from photoluminescence spectra.

Figure 6 shows the polarization dependence of the emission spectra of CdSe nanocomposites embedded in the LC cell under an ac square wave voltage of about 20 V. It is found that the emission spectra almost remain the same when the polarization is parallel and perpendicular to the rubbed PI direction. The inset shows the emission intensity of CdSe nanorods as a function of the analyzer angle. The intensity roughly keeps constant with respect to the change of the analyzer angle. The slight decrease with the illumination time of the laser has been observed frequently in the study of CdSe nanostructures previously.^{20,21} The result implies that, when the measurement of the emission intensity is perpendicular to the cell plane, the emission spectrum is isotropic for the LC cell under an external bias of 20 V. This behavior can be rationalized as follows. It is well-known that the LC director can be driven by an external bias to minimize the electrostatic energy of the system, and the director of the nematic LC (E7) with a positive dielectric anisotropy will be parallel to the electric field. The anchoring force between nanorods and LCs can provide a large alignment energy,²² which will drive nanorods along the orientation of LC molecules. If the nanorods are now well-aligned perpendicular to the LC cell plane, the emission detected in front of the cell plane, as in our experiment, should be isotropic. Consequently, the reduced optical anisotropy is mainly due to the reorientation of CdSe nanorods driven by biased LC molecules. Quite interestingly, it is found that the ratio of the relative emission intensity between CdSe nanorods and quantum dots can be manipulated by an external bias. When there is no external bias, as shown in Figure 4, the emission intensity from CdSe nanorods is larger than that of CdSe quantum dots for the polarization parallel to the rubbed PI direction. In contrast, the emission intensity from CdSe nanorods is smaller than that of CdSe quantum dots when the external bias is applied, as shown in Figure 6. The results establish the external bias fine-tuning emission color in this newly developed device.

Conclusions

We have successfully demonstrated a color-tunable light-emitting device by incorporating semiconducting nanorods and quantum dots in a liquid-crystal cell. The underlying mechanism is based on the large alignment energy resulting from the enhanced anchoring force of LC molecules through the amplified surface area of nanorods. In view of the well-established liquid-crystal technology, our approach elaborated here may be very useful for the development of smart optoelectronic devices in the near future.

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