Abstract: A simple and general approach for controlling optical anisotropy of nanostructured semiconductors is reported. Our design involves the fabrication of liquid crystal devices with built-in semiconductor nanotubes. Quite interestingly, it is found that semiconductor nanotubes can be well aligned along the orientation of liquid crystals molecules automatically, resulting in a very large emission anisotropy with the degree of polarization up to 72%. This intriguing result manifests a way to obtain well aligned semiconductor nanotubes and the emission anisotropy can be easily manipulated by an external bias. The ability to well control the emission anisotropy should open up new opportunities for nanostructured semiconductors, including optical filters, polarized light emitting diodes, flat panel displays, and many other chromogenic smart devices.

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OCIS codes: (230. 3720) Liquid-crystal devices; (260. 5430) Polarization

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1. Introduction

Semiconductor nanostructures have generated a great deal of attraction in the last decade because of their unique physical properties as well as a wide range of potential applications [1, 2], including lasers [3, 4], solid state emitters [5, 6], and transistors [7-9]. In these applications, the ability to control the polarization of the emission from optoelectronic devices is especially critical since it represents an approach to manipulate the transport of information and images [3, 10, 11]. Unfortunately, a precise and convenient method to control the emission anisotropy from nanostructured semiconductors is still not available. Here, we report a simple and general approach involving the fabrication of liquid crystal devices with built-in semiconductor nanotubes. Our proposed devices enable to accomplish the vital goal that with an applied external bias, it is possible to fine tune the polarization of the emitted light from semiconductor nanotubes at will.

We have focused on semiconductor nanotubes rather than other kinds of nanostructured geometries since there is plenty of empty space inside a tube, which is able to be filled with liquid crystal molecules. It therefore provides a more effective way to manipulate the aligned orientation through elastic interactions between liquid crystals and nanotubes due to increasing contact areas. Consequently, the orientation of the nanotubes can be easily controlled when the liquid crystal molecules are derived by an external field [12, 13]. Liquid crystals are anisotropic fluids, and their orientation can be easily controlled by applying an external electric field. Therefore, manipulation of the orientation of semiconductor nanotubes with the assistance of liquid crystals is highly feasible [14].

2. Experiment

The semiconductor nanotubes used in this study are CdSe nanotubes, which represent one of the attractive one-dimensional materials since it can emit a wide range of energy spectra covering from visible to infrared [15-17]. To synthesize CdSe nanotubes, we used a simple route using pristine anodic aluminum oxide (AAO) membranes (Anodisc 25) as templates with pore diameters of about 200 nm and thickness of about 60 μm purchased from Whatman international Ltd (England) [18, 19]. First, 0.8 M cadmium acetate dihydrate solution (Cd(OAc)$_2$) was dropped on the surface of the AAO template and the drop was drawn by the filter under the template. Thus, parts of (Cd(OAc)$_2$) were adhered on the walls of the template pores by the electrostatic interaction. It was followed by dropping the AAO template with 0.2 M sodium selenium sulfate solution (Na$_2$SeSO$_3$), which was prepared by dissolving 3.95 g selenium (Se) and 15.75 g Na$_2$SO$_3$ in 250 mL DI water, stirring the solution at room temperature for 2 h, and filtering off the undissolved solids in order to gain a clear
After repeating the above two steps for 10 times, the CdSe nanotubes would form along the walls of AAO pores. At last, the AAO membrane was dissolved completely with a 1M NaOH solution and the remaining nanotubes were washed with a large amount of ethanol. The structure of the nanotubes was studied by the transmission electron microscope (TEM) and high resolution transmission electron microscope (HRTEM) images as shown in Figs. 1(a) and 1(b). As we can see, the tubular morphology of the one-dimensional nanostructure was obtained. The open end of nanotubes demonstrates the hollow structure of the tubular nanostructure as shown in the inset of Fig. 1(a). The inset in Fig. 1(b) is the electron diffraction (ED) pattern, which shows the wurtzite phase of CdSe nanotubes. As also shown in Fig. 1(c), the room temperature Raman scattering spectrum of CdSe nanotubes displays a Raman shift of about 210 cm$^{-1}$, which represents the longitudinal optical phonon mode of wurtzite crystal structure of CdSe. The narrow line-width indicates that the grown CdSe nanotubes have good crystalline quality. A detailed description of the synthesis and characterization of the CdSe nanotubes will be published elsewhere.

![Fig. 1. (a) The TEM shows that the CdSe nanotube has about 1.6 μm in length and two open ends. The insets show a hollow structure of the nanotube and 200 nm in diameter. (b) The HRTEM of CdSe NT and the inset is the electron diffraction (ED) pattern, shows the wurtzite phase of CdSe NTs. (c) Raman spectrum of the CdSe nanotubes. The rising line in the right side of the peak 210 cm$^{-1}$ is due to the PL signal of the CdSe nanotubes.](image)

To fabricate the liquid crystal devices with built-in CdSe nanotubes, we adopt the standard textbook procedures as follows [21]. Fig. 2(a) shows schematically the profile of the liquid crystal device with built-in CdSe nanotubes. Two indium tin oxide (ITO) glass substrates were first coated with a polyimide (PI) alignment layer. Then, the CdSe nanotubes and liquid crystal mixtures (NTs-LCs) were formulated by adding 0.1-0.2 μg CdSe nanotubes to 1 ml nematic LCs E7 from Merck and sonicating the mixtures for about 40 minutes in order to disperse them uniformly. After that, two rubbed PI-ITO substrates were combined in the
same rubbing direction and the mixtures were injected into the sandwiched PI-ITO cell with a gap of about 8 μm by capillary action.

The photoluminescence (PL) spectra were performed to determine the polarization of the emission arising from CdSe nanotubes. A 100 W Xe lamp dispersed by a monochromator was focused onto the sample with a condenser to serve as the pumping source, and the emission signal was detected by a photomultiplier tube (PMT). An analyzer was mounted in front of the entrance slit of the spectrometer in order to distinguish the orientation of the polarized electric field. Different voltages at 1 kHz frequency were applied across the sample to determine the controllability of the optical anisotropy under an external bias. A 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. All experiments were carried out at room temperature. A schematic experiment setup for the optical measurement is shown in Fig. 3.
3. Results and discussion

Figure 4(a) exhibits that the emission of the CdSe nanotubes has a maximum intensity around 550 nm and the peak around 424 nm is the signal from ITO glass. The emission of the CdSe nanotubes incorporated in liquid crystals devices is practically linearly polarized when the voltage was not applied as shown in Fig. 4(a). It indicates that the majority of the CdSe nanotubes are well aligned with their orientation along the rubbed direction of PI layer. The degree of polarization defined as the intensity ratio \( r = (I_{\parallel} - I_{\perp})/(I_{\parallel} + I_{\perp}) \) calculated from the PL intensities in Fig. 4(a) is 72\% , where \( I_{\parallel} \) is the parallel-polarized intensity and \( I_{\perp} \) is the cross-polarized intensity with respect to the rubbed direction of PI layer, respectively. For comparison, we have fabricated a sample by mixing CdSe nanotubes with DI-water. Here, the structure of the device is similar to that of the NTs-LCs device, except liquid crystals being replaced by DI-water. The corresponding PL spectra are shown in Fig. 4(b), which do not show any indication of anisotropy. Apparently, the well alignment nanotubes is promoted by the assistance of liquid crystals through the elastic interaction between nematic liquid crystals and nanotubes. Our result therefore demonstrates an easy and convenient way to obtain well aligned semiconductor nanotubes in a large area, which is very difficult to obtain according to the previous reports [1, 2]. It is worth noting that the emission at 424 nm arising from ITO glass does not show an anisotropic behavior, which provides us an excellent check point that the polarization obtained here does not arise from our measuring system.

Fig. 4. Photoluminescence spectra of the device consisting of nanotubes and DI-water or liquid crystals, where the polarization along parallel and perpendicular directions were defined with respect to the rubbed direction of PI layer. (a) The emission is linearly polarized without applying an external bias, where the polarizations along parallel and perpendicular directions were defined with respect to the rubbed direction of PI layer. It shows that nanotubes are arranged along the rubbed direction of PI layer after the composites were injected into the cell. (b) It shows that DI water has no capability in assisting to drive well-aligned nanotubes.
In order to quantitatively explain the magnitude of the measured optical anisotropy, we calculate the theoretical value in terms of the dielectric contrast between the NTs and surrounding environment as described previously [22]. Due to a large aspect ratio of 8 for the studied NTs, we assume that when the incident electric field is parallel along the axial direction, the electric field in the cylinder is not reduced. However, when the polarization is perpendicular to the cylinder, the electric field is attenuated by a factor of

\[ \sigma = \frac{2\varepsilon_{LC}}{\varepsilon_{LC} + \varepsilon_{CdSe}} \]  

(1)

where \( \varepsilon_{LC} \) and \( \varepsilon_{CdSe} \) are the dielectric constant of LC and CdSe bulk, respectively. Accordingly, the degree of polarization \( \rho = \frac{1-\sigma^2}{1+\sigma^2} \) is estimated to be 0.75, which is in good agreement with the experimental value of 0.72.

Let us now consider the effect of external bias on the polarization of the emission arising from the CdSe nanotubes incorporated in liquid crystal devices. Quite interestingly, after applying an external bias of 9V, the anisotropic behavior of the emission almost disappears as shown in Fig. 5(a). We can clearly see that the emission wavelength remains the same after the external bias is applied, but the degree of polarization changes enormously from 72% to a negligible level. It indicates that due to the reorientation of liquid crystals driven by the effect of the Freedericksz transition [23], the elastic interactions between liquid crystals and nanotubes will force nanotubes to follow this reorientation [14, 24]. According to the above result, a controllable polarization of the emission from semiconductor nanotubes has been achieved based on our proposed LCs-NTs composites.

Fig. 5. Emission spectra of the CdSe nanotubes mixed with liquid crystal and the change of the degree of polarization as a function of external bias. (a) After applying an external bias of 9V, the anisotropic property of the emission almost disappears. (b) The degree of polarization decreases gradually with external bias, and it starts to saturate when external bias exceeds 3V, which is similar to the voltage required to switch the liquid crystals from parallel to perpendicular orientation with respect to the rubbed PI direction.
Figure 5(b) shows the change of the degree of polarization as a function of external bias. It clearly indicates that the degree of polarization decreases gradually with external bias, and it starts to saturate when external bias exceeds 3V, which is similar to the voltage required to switch the liquid crystals from parallel to perpendicular orientation with respect to the rubbed PI direction [25, 26]. This result again provides an additional evidence to support the fact that the reorientation of the well aligned CdSe nanotubes is driven by liquid crystals molecules. To clearly illustrate the result shown here, a schematic diagram for the change of the orientation of liquid crystals and CdSe nanotubes is plotted in Fig. 2(b). After the external bias exceeds 3V, the arrangement of liquid crystals and nanotubes changes from the configuration shown in Fig. 2(a) to Fig. 2(b).

Finally, one may suspect that the anisotropic behavior observed here may solely arise from the reorientation of liquid crystal molecules caused by external bias. The incorporated CdSe nanotubes are randomly distributed without well alignment independent of the external bias. To rule out this possibility, we have fabricated a similar LCs device with the CdSe nanotubes replaced by CdSe quantum dots. As shown in Fig. 6, the PL spectra of the LCs-quantum-dots device do not show any indication of anisotropic effect. Even if an external bias is applied, we still can not detect a measurable anisotropic effect. Therefore, we may conclude that the detected emission anisotropy is due to the well aligned CdSe nanotubes driven by liquid crystal molecules.

![Photoluminescence spectra of the LCs-quantum-dots device. It does not show any indication of anisotropic effect with and without an external bias.](image)

**4. Conclusions**

In summary, we have demonstrated that liquid crystals device with built-in semiconductor nanotubes enable to fine tune the polarization of the emission from semiconductor nano-tubes. With an applied voltage of 3V, the degree of polarization can be dramatically changed from 72% to a negligible level. The studied CdSe nanotubes were synthesized by a novel, low-cost and time-saving method using the templation of AAO membranes. Besides, we discovered that CdSe nanotubes can be well aligned along the direction of the rubbed PI film with the assistance of liquid crystal molecules, which provides an elegant way to obtain ordered arrays of one-dimension nanostructures. We believe that this electrically driven emission polarization of LCs-NTs composite device could open up new possibilities for the application of semiconductor nanotubes in a number of areas, including polarized light emitting diodes, flat panel displays, electro-optic modulators, and many other chromogenic smart devices.

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