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Enhancement of Photoluminescence Intensity of CdSe Nanorods Doped in Cholesteric Liquid Crystals

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Abstract The enhancement of photoluminescence (PL) signals of CdSe nanorods caused by embedding in the cholesteric liquid crystals (CLCs) is demonstrated in this article. Three kinds of different CLCs have been used in this experiment, and the results have shown that the phenomenon of PL enhancement generally occurs in each sample. Moreover, the relations between the enhancement and the pitch of CLCs have been analyzed as well. It displays an inversely proportional property, that is, a greater enhancement of the PL signal is achieved in the samples with shorter pitches of CLCs. The highest PL amplification acquired in this study is 3.31 times. The enhancement phenomenon is attributed to the presence of oily streaks in CLCs, which possess advantages due to the excitation of CdSe nanorods. With the versatile properties that CLC have, this study suggests that the method could provide a potential way for PL signal manipulation in many optical fields.

Keywords Cholesteric liquid crystal · CdSe nanorods · Photoluminescence · Oily streak

1 Introduction

Cholesteric liquid crystal (CLC) is a quite interesting mesophase material that has been drawing many researchers' attentions. The most general method to obtain such kind of material is by adding chiral molecules in nematic liquid crystals. The presence of chiral molecules induces the LC directors to twist and rotate in a helical arrangement, forming a periodically layer-like structure. Such structure makes CLC behave as a one-dimensional photonic crystal and display valuable optical properties such as selective reflection [1]: the light possessing the same handedness as CLC helicity and the wavelength equal to the optical pitch of the CLC would be mostly reflected. Such optical property has been widely applied in the research of reflective LC displays [2], dye lasers [3], etc. Moreover, there is an interesting structure in CLCs. The line defects in CLCs named "oily streak" is a stripe-like pattern jointing each other and forming a complex network. They occasionally coarsen or shrink with time [4], but, however, it can be useful if we kept them present and stable. A notable example is the CLC structure stabilization by doping nanoparticles or polymerization that expanded the temperature range of blue phases [5, 6]. Current studies focus on the doping technique to improve the behaviors of LCs [7, 8], but, in contrast, would LCs conversely empower the performance of the doped material? In this study, we show that the use of CLCs as the matrix could also be advantageous to the amplification of photoluminescence (PL) signals.

The analysis of PL signal is an important technique that has been employed in many research fields. Considering the fact that PL signals might not always be strong enough, introducing a feasible amplification method would thus be important and necessary. The methods aiming at the PL signal enhancement have been widely studied and reported for several years. As far as we know, the most adopted method is through the utilization of surface plasma resonance (SPR) effect [9–11]. According to the reports, the resultant enhancement could reach to more than double. This method is quite effective but it generally requires two strict restrictions: one is the metal layer whose dipole vibration energy should match the fluorescence energy of material, and another one is a required proper distance that separates the metal layer from the fluorescence material. Satisfying these restrictions in an experiment is not a simple task. Recently, Park's group has tried to dope gold nanoparticles in CLCs in order to substitute the metal layer

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Table 1 The categorized three kinds of CLC sample sets

Set	Nematic LCs	Optical pitch length of CLCs (nm)	
		Long pitch	Short pitch
1	ZCE-5099LA	655	405
2	ZCE-5352LA	789	402
3	MJ99	792	426

[10]. The required optimization of the proper distance therefore changes into the adjustment of fluorescence/gold nanoparticle fraction. This method has eased the hardship of the restriction and successfully achieved the enhancement effect, but the mixture of metal nanoparticles and the fluorescence particles would increase the uncertainty of the separation distance, and result in the decrease of the entire performance. There are many other methods reported so far, such as constructing photonic crystal structures [10], elongating the excitation time [12]. These methods are functional but, however, the sophisticated structures of the photonic crystal or the heat problem resulting from laser stimulation are still obstacles that need to be overcome. Here, we provide an effective and practical way to achieve the PL enhancement effect by embedding fluorescence particles into the CLC materials. In this paper, we succeed to enhance the PL signal of CdSe nanorods. The effect is found to be related to the pitch of CLCs, and the highest PL amplification could reach to more than three times. With the versatile properties that CLCs hold, our results suggest that the technique could be a convenient and potential method for PL signal manipulation in many optical fields.

2 Experimental Methods

The CLCs used in this study were the mixtures of nematic liquid crystal and chiral dopants. In our experiment, the nematic liquid crystals, ZCE-5099LA (Chisso), ZCE-5352LA (Chisso), and MJ991597 (Merck, MJ99 for abbreviation) were used for fabricating different kinds of CLCs, and the chiral dopant used here was benzoic acid, 4-(*trans*-4-pentylcyclohexyl)-,1,1′-[(1R)-1-phenyl-1,2-ethanediyl] ester (R1011, Fusol Material Co., Ltd.). Varying the concentration of the chiral dopant in nematic LCs will result in the different helical pitch of CLCs, and in this study, two different concentrations were prepared to generate long pitch and a relatively short pitch CLC samples. The optical pitch of as-prepared CLCs were identified by the spectrometer (SD1200-LS-HA, OtO Photonics) with respect to their own reflection bands. These CLCs were classified into three kinds, sets 1, 2, and 3 as shown in the Table 1, according to which nematic LC was used.

The CdSe nanorods were prepared according to the method by Meijerink's group [13], and were dispersed and stirred in toluene with concentration 0.22 wt% in advance. The sample cells with 9.3 μm thickness and anti-parallel rubbed polyimide layers in the inner surfaces of the substrate were used in the experiment. In order to prevent the side effects of the organic solvent to the liquid crystals [14], we first injected the mixed CdSe:toluene suspension into the prepared CLC cell along. The CdSe nanorods then gradually spread out with the filling of the suspension. The toluene solution was then driven out by applying a gentle vacuum with several hours. After the toluene thoroughly evaporated, the prepared CLCs were subsequently injected into the cell before sealing. All of the samples were sonicated for an hour, and then stood at room temperature a while before the measurement.

3 Results and Discussion

The absorption and PL spectra of the CdSe nanorods in toluene suspension were acquired by the UV-vis spectrometer (JASCOV V-670) and the fluorescence spectrophotometer

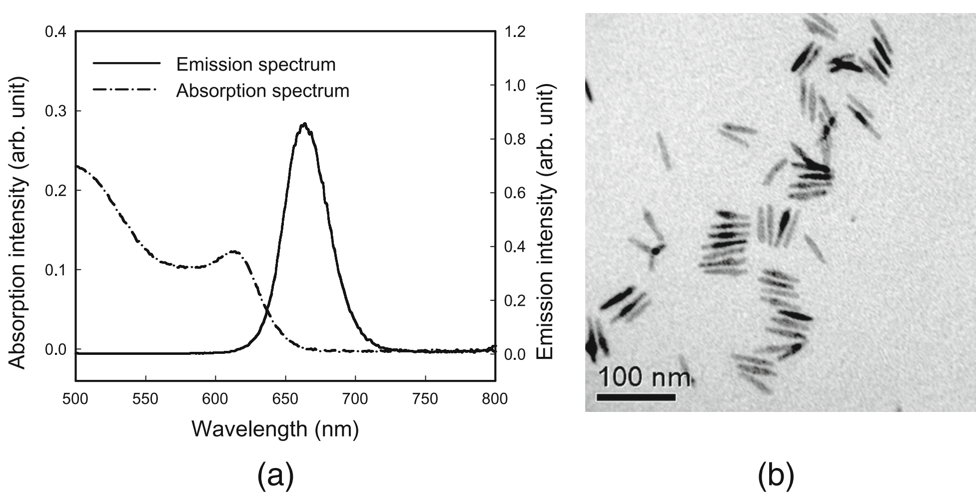


Fig. 1 **a** The absorption and emission spectrum of the CdSe nanorods dispersed in toluene. The PL emission spectrum was acquired under the illumination of 500 nm excitation light. **b** TEM image of the CdSe nanorods. The length and the diameter of these nanorods are around 40 and 6 nm, respectively

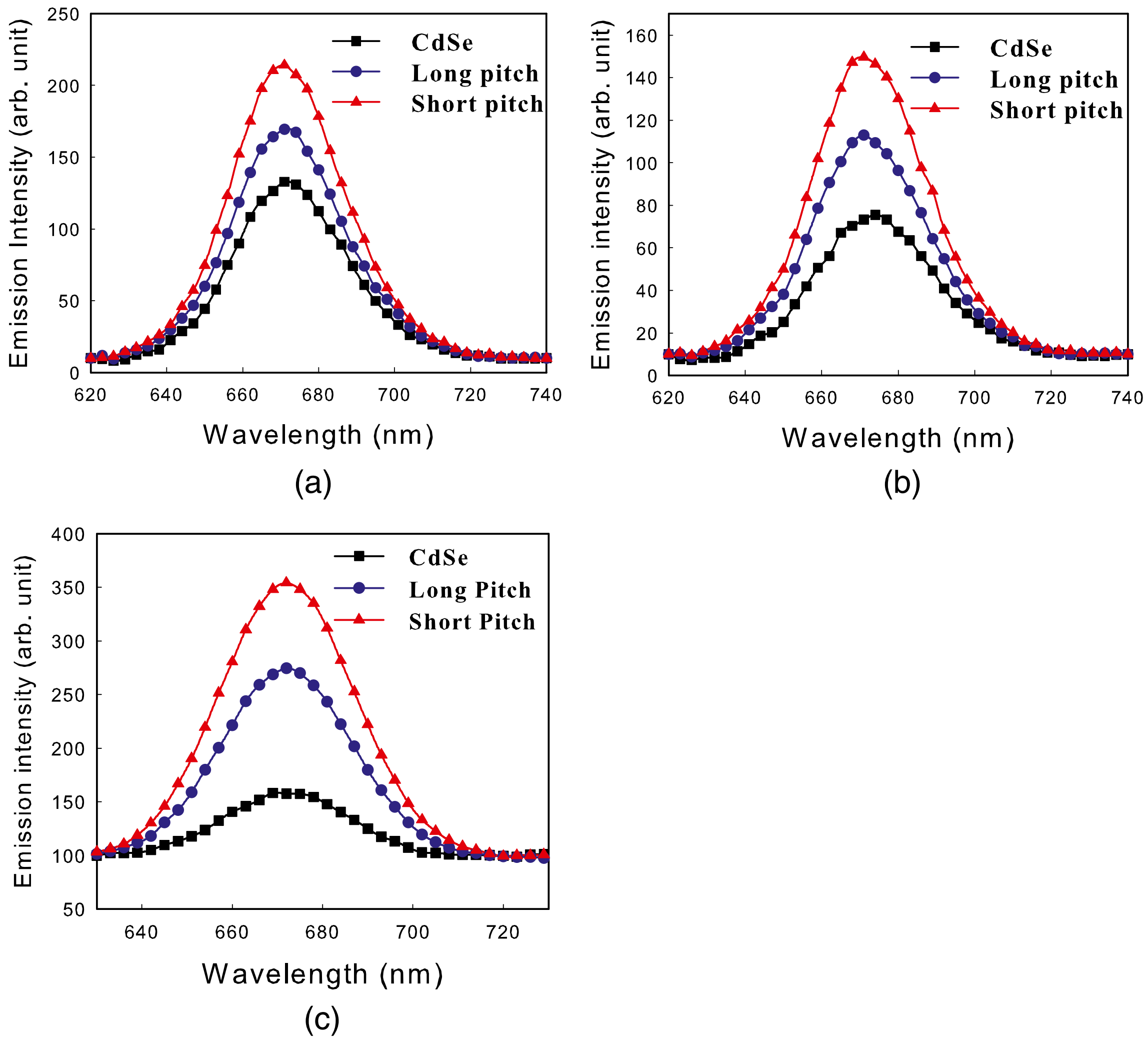


Fig. 2 The PL intensities of sample **a** set 1, **b** set 2, and **c** set 3. The *red*, *blue*, and *black curves* denote the samples with short pitch, long pitch CLCs filled, and the sample without any host material, respectively

(Fluorolog-3, Horiba Jobin Yvon) with xenon excitation lamp, respectively. The spot size is a square area about 4 mm× 9 mm, and the collection mode is front-face collection, which viewing angle is 22.5°. The obtained results were shown in Fig. 1a. With the illumination of 500 nm excitation light, the emission spectrum (the solid line) of CdSe nanorods in toluene exhibits an obvious emission peak at 663 nm. The transmission electron microscopy (TEM) image of the nanorods is shown in Fig. 1b. The average diameter and the length of these nanorods are about 6 and 40 nm, respectively.

Table 2 The increasing folds of PL signals of each sample set

Set	Folds of PL enhancement	
	Long pitch	Long pitch
1	1.32	1.69
2	1.56	2.14
3	2.94	3.31

The sample set 1 (refer to Table 1) was used in the first experiment. In order to exclude the influence from the intrinsic properties of different LCs, such as birefringence, dielectric anisotropy, we have set the first experiment within the same sample set rather than compared to other sample sets, i.e., others made from different LCs. The intensities of PL signals had been measured at room temperature, and the results are shown in Fig. 2a. The curves present in this figure include CdSe nanorods sample (without CLCs injected) and the CdSe suspended in CLCs with long and short pitch. The black, blue, and red curves in Fig. 2 denote three different conditions of CdSe nanorods: the black curve represents the sample without any host material injected; the blue curve is for the sample with long optical pitch (605 nm) CLCs filled; as to the red curve, it was filled with short optical pitch (405 nm) CLCs. It should be noticed that the CLC pitches mentioned in the following study are optical pitches. According to Fig. 2, the PL intensities obviously increased while they were suspended in the CLCs. Comparing to the black curve, the

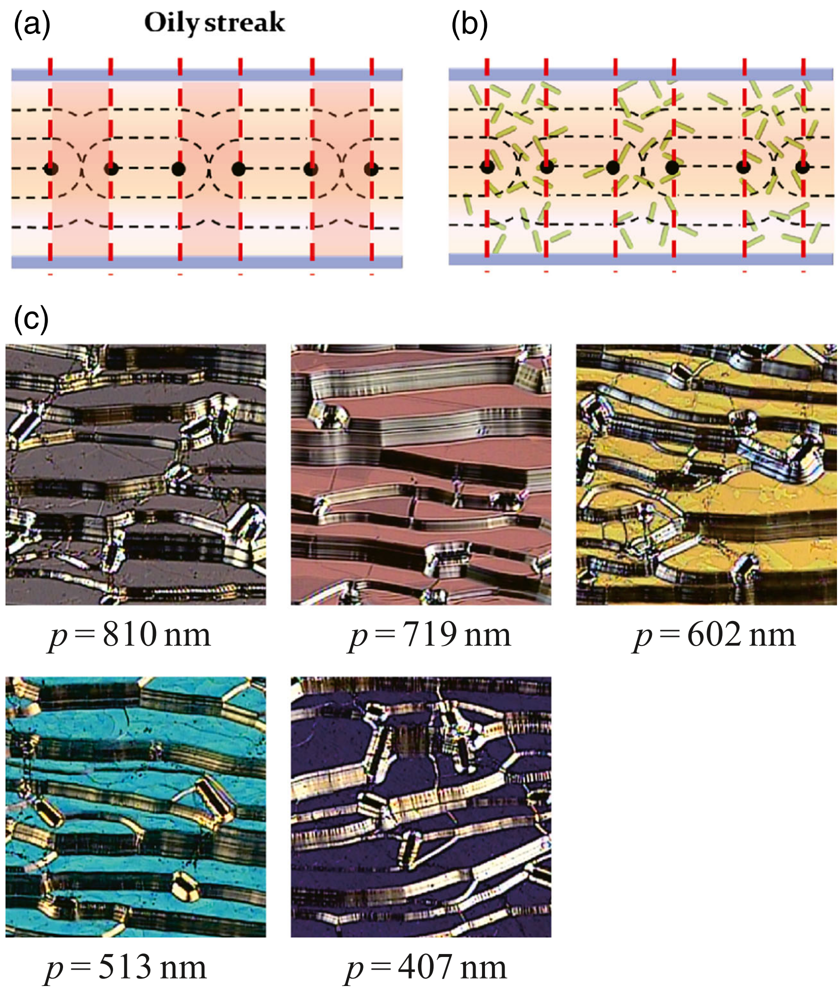


Fig. 3 **a** Schematic diagram of the arrangement of CLC layer-like structures in the area of two adjacent disclinations. The disclinations are represented by *black full circles*. The region between two *red dash lines* which displays a streak of pattern under the optical microscope is called oily streak. **b** Schematic diagram of the dispersed nanoparticles being attracted and trapped by the oily streak. **c** Polarized optical microscope (POM) image of oily streaks in CLC cells with various pitches. The networks are "oily streaks," and the various background colors resulted from the selective reflection of the CLC planar structure

increase of the peak values is about 1.32 times for the blue curve and 1.69 times for the red curve, respectively.

Moreover, the graph also clearly reveals that the enhancement property is related to the pitch of CLCs. To verify the generality of such PL enhancement property, we have performed additional experiments with two other different materials. Sample sets 2 and set 3 are different CLCs made from different kinds of nematic LCs, ZCE-5352LA, and MJ99 LC, respectively. The corresponding materials and pitches are listed in Table 1. The PL enhancement property has shown its generality in the sample sets 2 and 3, and their results are shown in Fig. 2b, c. For sample set 2, the amounts of signal increases are about 1.56 times for the long pitch sample and 2.14 times for the short pitch sample, and for set 3, the long pitch sample displayed 2.94 times increase and 3.31 times for the short pitch sample. Through the analyses of these results, we can find that the CdSe nanorods sample with short pitch CLCs exhibits stronger PL enhancing ability than

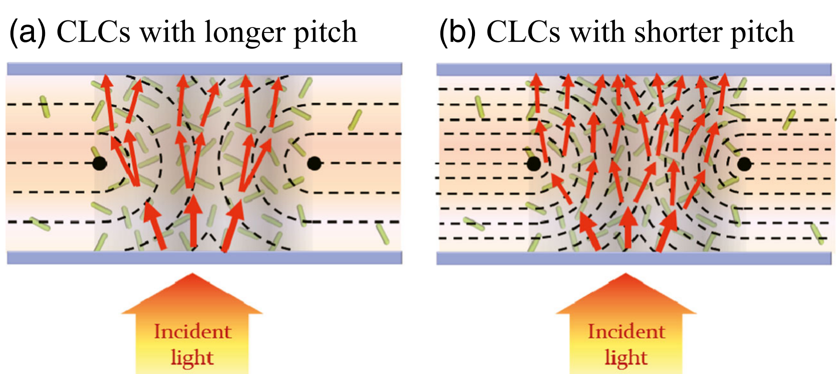


Fig. 4 Illustration of the scattering conditions of **a** a longer pitch and **b** a shorter pitch CLC sample when an incident light passes through an oily streak (*grey-shaded area*). The *red arrows* in the illustration symbolize the forward scattering of the incident light

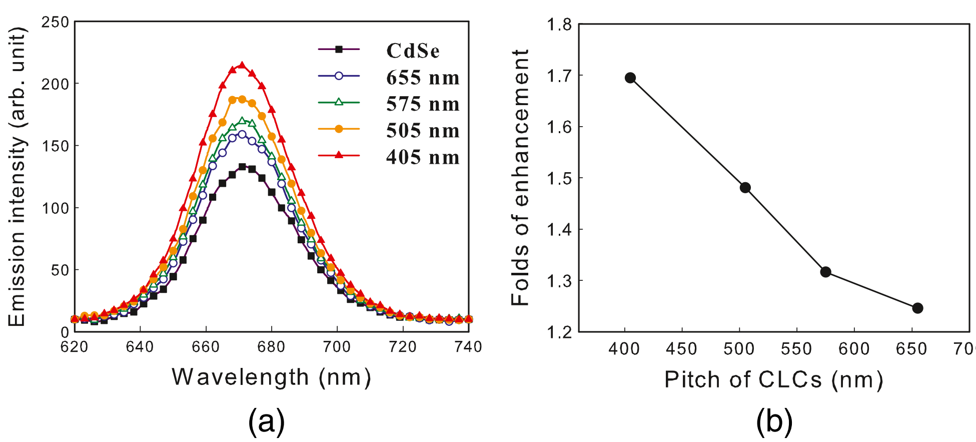
the one with long pitch CLCs. The results of PL enhancement of each sample set are summarized and listed in Table 2. In this table, the relations between the amplitude of enhancement and the pitch of CLCs could be obviously noticed. The enhancement phenomenon is consistently found in each sample set, which was made from different nematic LCs.

The optical properties of nanomaterials doped in CLCs had been greatly investigated and reported these years [15–17], including methods of manipulation of PL signal intensity [18]. Most of these researches enhanced the PL signal by switching CLC into focal conic phase, a scattering phase which could increase the possibility for excited photons been absorbed, but few studies reported on the relationship with the pitches. Therefore, it would be necessary to start from the planar structure of CLCs. The planar phase is one of those particular phases in the CLC family. It is known for the unique property of selective reflection which is induced by its photonic crystal-like molecular orientation. The molecules in CLCs rotate in a helical manner to form a periodic layer structure. This structure terminates at the boundary of two or more homogeneous domains and forms a discontinuous area. The layer structure in this area undergoes a half circle rotation. Two adjacent disclinations constitute a symmetric defect area called "oily streak" (see Fig. 3a). Earlier theoretical investigations have reported that the disclination lines possess an ability of trapping freely moving particles within them due to the elastic interaction [4, 19]. Many other researches have demonstrated this effect as well, and they have shown that, not only for colloidal particles, but also the mechanism still works on nanoparticles or gel-like materials [4, 5, 20]. Moreover, these trapped nanoparticles are not just gathered in disclinations; they also act as stabilizers maintaining the stability of CLC structure [5]. According to these studies, it is plausible that the dispersed CdSe nanorods in CLCs should be trapped and accumulated in the disclination lines as Fig. 3b illustrates. Figure 3c shows the polarized optical microscope (POM) image of oily streaks with different pitches. The various background colors are resulted from the property of selective reflection of the CLC planar structure. From these POM images, we could find that the oily streaks largely covered the planar area, which would therefore result in the attraction of most of the CdSe nanorods into these regions. Estimated area ratios of oily streaks in each picture are about 60.5 % for 407 nm pitch, 57.4 % for 513 nm, 61.6 % for 602 nm, 58.1 % for 719 nm, and 59.8 % for 810 nm. These ratios show no regular trend and are closed to each other, which imply that the densities of oily streaks are not obviously related to the pitch. It could be also found that the sizes of oily streak within a sample cell are not constant. According to these reasons, we chose not to measure a single streak but a constant area to represent a macroscopic effect of enhancement.

Not only capable of trapping nanoparticles, disclination lines also hold another notable optical property. The oily streaks, which are singularities composing of conjugated pairs of disclinations, serve as the frames of focal conic domains [21, 22]. Inside the streaks, due to the severely bent and rotated neighboring directors, forward scattering of light would therefore occur. The scattering property has been reported previously [23], and in our experiment, this property would result in the increasing of the length of light path within the oily streaks. Recalling the ability of attracting and trapping nanoparticles that oily streaks possess, the fluorescent nanoparticles gathering within the oily streaks would have more chances of being stimulated. By benefiting from these two specific properties, the intensity of PL signals of CdSe nanorods would thus increase accordingly.

Additionally, the experiments have shown another phenomenon: shorter pitch samples exhibit stronger PL enhancement ability than the longer ones. That is to say, the pitch of CLCs has some advantageous relationship to the PL enhancement effect. The schematic illustration is depicted in Fig. 4. Microscopically, the CLC directors experience the rotation more severely in the shorter pitch sample than in the longer one. The span layers between horizontal dashed lines in Fig. 4 are defined as those wherethe CLC director of each span layer has the same progressive twisted angle, thus the CLC with shorter pitch can build up more span layers in a confined space. Therefore, for such tightly twisted directors of the short pitch sample, the streaks would have higher scattering

Fig. 5 **a** The variation of PL intensity with different pitch lengths of CLCs. **b** The relation between folds of enhancement and various CLC pitch lengths. Each dot represents the PL amplification with distinct pitch length in **a** to the sample without CLCs filled



property. As the excitation light passes through a short pitch sample (see Fig. 4b), it would be more diffracted and leads to the increase of light path, the PL enhancing property would therefore be highly increased.

Further experiments on the connection between the PL emission intensity and the pitch had been performed. The detailed experimental results are shown in Fig. 5. The nematic LC used here is ZCE-5099LA, and the CLC pitch increment is set to be about 70 to 100 nm—they are 405, 505, 575, and 655 nm. The results of PL spectrum are gathered and displayed in Fig. 5a together with the sample without host material injected (black curve). The benefit from the short pitch effect is quite obvious. The decrease of CLC pitch can efficiently enhance the PL signals, and the enhancement could up to about 1.7 times for this CLC sample with 405 nm pitch. The relations between the PL enhancing times and the various pitches are summarized in Fig. 5b. It shows that the decreasing CLC pitch efficiently increases the PL signal strength of the CdSe nanorods.

4 Conclusions

In summary, an effective and practical way to achieve PL signal amplification by embedding the fluorescence particles, CdSe nanorods, into CLCs has been reported. The results showed that the presence of oily streak defects in CLCs, which has nanomaterial-attracting and light-scattering properties increases the PL signal strength and the enhancement is related to the helical pitch of CLCs. The highest PL amplification obtained in this study could reach to more than three times. With the versatile properties that CLCs hold, our results suggest that the technique could be a convenient and potential method for PL signal manipulation in many optical fields.

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