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The Surface Plasmon Resonance Effect on the Defect-Mode Cholesteric Liquid Crystals Doped With Gold Nanoparticles

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Abstract: Cholesteric liquid crystals exhibit the characteristics of photonic crystals with a photonic bandgap. A defect-mode cholesteric liquid crystal module was assembled in this study, and laser dye and gold nanoparticles are mixed into this module. With the help of localized surface plasmon effect induced by the gold nanoparticles, the fluorescence was significantly enhanced at both the band edges and the defect spectrum dip.

Index Terms: Photonic crystals, photonic bandgap materials, defect mode laser, cholesteric liquid crystals, periodic structures, surface plasmon resonance, gold nanoparticles, fluorescence.

1. Introduction

Cholesteric liquid crystals (CLCs) have received much attention in recent years due to its flexible molecular structures, which can be controlled and tuned by external influences such as optical excitations, electrical field induction, thermal heating, mechanical forces and then offer diverse application possibilities. Chiral molecules are added into nematic liquid crystal media to form the CLCs. The rotating and periodic structure of CLCs results from the twisting power of chiral molecules. The spatial period of CLC structure is termed pitch, which influences the reflective wavelength of the material. CLCs have many uses in the reflective liquid crystal displays [1]–[3] and have also been investigated as a potential material for distributed feedback lasers [4]. Liquid crystal incorporated optical devices have also been widely studied in the metamaterial-based applications, which were achieved by the easily reconfigurable permittivity of liquid crystals [5]–[7].

However, it has been found that high lasing threshold hindered them from being used commercially in CLC laser applications. Many ways to lower the lasing threshold included increasing cavity length by using an in-plane helical structure CLCs [8], developing highly efficient luminescence dyes [9] or introducing a defect in cavity to form so-called defect mode lasers [10]–[15]. However, little attention has been paid to the effect of gold nanoparticles on the CLC lasers. The present paper uses the surface plasmon resonance effect of gold nanoparticles to enhance the fluorescence of dyes in order to lower the threshold. The aim of this study is to incorporate both the localized surface plasmon resonance and the defect structure of cholesteric liquid crystals to improve the
enhancement of dye fluorescence. The gold nanoparticles and laser dye were mixed in the defect layer. The fluorescence was significantly enhanced at the defect mode and band edges.

2. Theory

2.1 Photonic Bandgap of Cholesteric Liquid Crystals

CLCs exhibit a local planar structure composed of nematic liquid crystals, whose average orientation on the plan is characterized by the so-called director, and the director rotates to form a helical structure with the helical axis perpendicular to the director. This helically twisted birefringent structure possesses a spatial period (or termed pitch) close to optical wavelength. Therefore, CLC films show the characteristic of one-dimensional photonic crystals. When electron waves transvers in periodic crystal structures, an energy bandgap emerges at the edges of the first Brillouin zone. Similarly, the propagating of light with wavelengths ranging in the photonic bandgap is limited in the photonic crystals. The photon group velocity \( v_g = \frac{d\omega}{dk} \) approaches zero near the band edge, which means an exceedingly long optical path length in this structure. The photon life time at the band edge is significantly increased and results in a very high density of states of photons, which benefits the enhancement of light intensity [16]. No extended electromagnetic modes with frequency \( \omega \) in the photonic bandgap are allowed to exist in the photonic crystal material. However, when a defect layer is introduced in the CLC photonic crystals, localized modes are allowed and appear as a spectrum dip in the photonic reflection band, which are also termed defect-modes.

2.2 Localized Surface Plasmon Resonance

Localized surface plasmon resonance (LSPR) is a photon-driven coherent oscillation of metallic nanoparticles with a negative real and small positive imaginary dielectric constant. Recent advances that allow the controlled synthesis of nanoscale gold make gold nanoparticle a promising candidate for LSPR. When incident light interacts with gold nanoparticles dispersed in dye molecules, LSPR is induced and significantly enhances the electromagnetic field on the gold particle surface. When the photon to plasmon transformation satisfies conservation of momentum and energy in the coupling process, the large resonant optical fields induced by the gold nanoparticles excite the proximate dye molecules to produce strong fluorescence. The fluorescence emission rate \( F_{em} \) in this case can be expressed as

\[
F_{em} \propto q \cdot |E_{LSPR} \cdot p_{mol}|
\]

where \( q \) is the emission quantum yield and \( E_{LSPR} \) represents the local electric fields caused by LSPR, and \( p_{mol} \) is the transition dipole moment of dye molecules causing the fluorescence emission [17]–[23].

3. Experiments

3.1 Materials

For preparing CLC defect modules, the following materials were used: nematic liquid crystal E7 (compositions and molecular structures as shown in Fig. 1), chiral molecule S811, diacrylate monomer (bisphenol-A-dimethacrylate) and photoinitiator Irgacure 651 (2,2-dimethoxy-2-phenylacetophenone). The defect layer is composed of E7, laser dye PM597 (pyrromethene 597) and gold nanoparticles (optional). The rubbing layer is prepared from the polyvinyl alcohol (PVA) dissolved into the de-ionized water.

3.2 CLC Defect Module Assembling

Fig. 2 shows the formation of CLC defect module. As shown in Fig. 2(a), the PVA solution was spin-coated onto two pieces of indium tin oxide (ITO) glass substrates. The substrates were dried
Surface Plasmon Resonance Effect on the Defect-Mode CLCs

Fig. 1. The compositions and molecular structures of liquid crystal E7.

Fig. 2. Three forming stages of a CLC defect module (a) shows two polymer CLC cells, (b) shows the semi-finished cells, which are made by peeling off one ITO glass in (a), (c) is a complete CLC defeat module. Three main layers are sandwiched with two ITO glass substrates. The first and third layers are polymerized CLCs. The second layer is the defeat layer.

by hot-air circulation oven and rubbed for homogeneous alignment. A 3 μm cell gap was made up by stacking the two rubbed PVA sides of two glass substrates and dispersing 3 μm spacers inside. The monomer and CLC mixture was then filled into the 3 μm cell gap. Next, the cell was thermally annealed to CLCs' clearing temperature and soon restored at room temperature so the CLCs could be well aligned. Later, the cell was polymerized by UV curing. After UV polymerization, one of the glass substrates was peeled off and the PVA layer was exposed to the air, as shown in Fig. 2(b). The sample at this stage was a semi-finished cell. When a pair of semi-finished cells were prepared, we stacked two PVA sides of two semi-finished cells face to face and dispersed 3 μm spacers inside to form a gap. The mixture of E7 liquid crystals, laser dye and gold nanoparticles was filled into this gap and formed a defect layer after the sample sides were all sealed, as shown in Fig. 2(c). The final finished sample is called a CLC defect module.

3.3 Experiment Setup

The spectrum measurement system is shown in Fig. 3. A 532 nm continuous light from a diode-pumped solid-state laser was used as an excitation light source. The laser passed a half-wave plate (for 532 nm), a light shutter, a polarizer, an aperture and finally reached the sample. The fluorescence spectra emitted by the CLC samples were measured with a spectrometer (Ocean Optics USB2000+) and processed by a computer.

4. Results and Discussion

Fig. 4 shows the cholesteric liquid crystal (CLC) reflection spectra. CLC is reflected in a specific wavelength range in the planar state texture, which is caused by the Bragg reflection. The center reflection peak, full width at half maximum (FWHM), and reflectivity are 680 nm, 100 nm, and 0.5, respectively. Applying a large voltage to CLC will change it from a planar state to a homeotropic
Fig. 3. The spectrum measurement system for laser-dye doped CLC defect module excited with 532 CW laser.

Fig. 4. CLC reflection spectra.

Fig. 5. Absorption spectrum (blue curve) of gold nanoparticles and the absorption (black curve) and excited fluorescence (red curve) spectra of laser dye PM597. The sharp and narrow spectrum (green curve) is the excitation laser, CW 532-nm laser.

state. Upon taking a reflected light measurement of the homeotropic state, we found that the original reflection band disappears. As shown by the red curve in Fig. 4, the application of high electric fields on the ITO glass substrates will align the orientation of CLC molecules from being parallel to glass substrate into being perpendicular to the glass substrates, which can be penetrated by light.

Fig. 5 presents the absorption spectrum of gold nanoparticles, and the absorption and excited fluorescence spectra of laser dye PM597. Since PM597 has an absorption peak around 532 nm, a 532-nm CW laser can be used as the excitation light source, while the fluorescence emission peak of the laser dye itself is around 575 nm, as shown by the red spectra in Fig. 5. Since CLCs behave as a one-dimensional photonic crystal structure, strong fluorescence is expected to be produced if PM597 laser dye is incorporated into CLCs. As already mentioned in the previous
paragraph, as the group velocity at the edge of a photonic crystal gap approaches zero, the photon states with wavelengths near the photonic band edge have a quite long lifetime, resulting in its fluorescence spectra having a strong enhanced effect. All of the CLCs used in the next experiment was incorporated with PM597 laser dye.

In Fig. 6, the blue curve is the reflection band of the nano gold-doped CLCs. The center reflection peak, FWHM, and reflectivity are 647 nm, 85 nm, and 0.5, respectively. Its high energy band edge inside the reflection band is located at about 617 nm. At the high energy band edge near 617-620 nm, since the group velocity is close to zero, the enhanced photon state is expected to produce a strong lasing spectrum. Therefore, in this paper, both the nano gold-doped CLC and the undoped CLC are excited with a 532 nm laser at the same intensity, and the comparison of their fluorescence spectra intensities is shown in Fig. 6.

In Fig. 6, the black curve is the fluorescence spectrum of the undoped CLC excited by a 532-nm laser with a peak at the band edge near 617-620 nm, an intensity of about 1641 au, and a FWHM of about 8 nm. The fluorescence peak intensity around 575 nm of the undoped CLC laser dye itself is about 1146 au.

Meanwhile, the red curve is the fluorescence spectrum of the nano gold-doped CLC excited by a 532-nm laser with a peak at band edge near 617-620 nm, an intensity of about 2265 au, and a FWHM of about 8 nm. The fluorescence peak intensity around 575 nm of the laser dye itself in the nano gold-doped CLC is about 1791 au. Since the CLC has a nano gold dopant, its reflection band is slightly red-shifted by about 4 nm, so the fluorescence spectrum peak of the nano gold-doped CLC at the band edge is slightly offset compared to that of the undoped CLC. In comparing the undoped CLC with the nano gold-doped CLC, the fluorescence peak intensity at the band edge of the nano gold-doped CLC is stronger than that of the undoped CLC by 624 au. After the laser dye is excited by the laser of the nano gold-doped CLC, the fluorescence around 575 nm emitted by the laser dye itself is also 645 au higher than the laser dye of the undoped CLC. This is due to the nano gold-doped CLC's effect creating surface plasma resonance, which results in the increase of the fluorescence peak at band edge around 620 nm and its original fluorescence intensity around 575 nm.

The comparison of experimental results between the undoped (without nano gold-doped) and nano gold-doped CLC defect modules are shown in Figs. 7 and 8, respectively. The production method of the defect modules has been previously described in the experiments, in which the thickness of the CLC polymer layer is 3 μm, and the thickness of the defect layer is also controlled at 3 μm. Upon comparing the reflection spectra of the undoped CLC defect module (red curve in Fig. 7) with the nano gold-doped CLC defect module (red curve in Fig. 8), the center reflection wavelength of both is 625 nm, the reflection band width of both is about 70 nm, and the peak reflectivity is about 0.47 au. A significant defect dip phenomenon is found in the vicinity of the 635 nm wavelength, and the depth of the defect dip is about 0.4 au. A comparison of the reflectivity
spectra of the nano gold-doped CLC and undoped CLC shows that the reflectivity spectrum of the nano gold-doped defect module is relatively imperfect because the defect configuration with the nano gold-doped CLC is more difficult to fabricate.

The black curve in Fig. 7 shows the emission spectrum of undoped (without nano gold-doped) CLC defect module excited by the CW laser. The CW laser intensity is controlled at 200 mW/ cm² with an ambient temperature of 28 °C. Fig. 7 shows that the red curve is in the stop band reflection spectrum of the CLC defect configuration. The concave defect wavelength is around 635 nm. The black curve represents the fluorescence spectrum of the same sample excited by the laser pump. Because the concave defect wavelength is near 635 nm, the fluorescence peak at defect will be excited in the vicinity of 635 nm, and its intensity is about 2500 au. Fluorescence peaks are also produced at both the high and low energy band edges of the CLC stop band reflection spectrum; the low energy band edge intensity is about 700, less pronounced. For the high energy band edge (short wavelength side), the original laser dye fluorescence at the high energy side is itself stronger, and its intensity at the band edge is also enhanced much, about 2200 au.

The black curve in Fig. 8 shows the emission spectrum of nano gold-doped CLC defect module excited by CW laser. The CW laser intensity is controlled at 200 mW/ cm² with an ambient temperature of 28 °C. Fig. 8 shows that the red curve is in the stop band reflection spectrum of the CLC defect configuration. The concave defect wavelength is around 635 nm. The black curve represents the fluorescence spectrum of the same sample excited by the laser pump. Since the concave defect wavelength is near 635 nm, the fluorescence peak at defect will be excited in the vicinity of 635 nm, and its intensity is about 2700 au. Fluorescence peaks are also produced at both the high and low energy band edges of the CLC stop band reflection spectrum; the low energy band edge intensity is about 750 au, less pronounced. For the high energy band edge (short wavelength side), the laser dye fluorescence at short wavelength side itself is relatively strong, so its intensity at the high energy band edge is also relatively strong, about 1300 au. Upon comparing the fluorescence
efficiency of the undoped CLC with the nano gold-doped CLC at concave defect, we found that the fluorescence spectrum of the nano gold-doped defect module is stronger, and its intensity is about 250 au higher than that of the undoped CLC.

5. Conclusion
The defect-mode CLC module was assembled and the laser dye and gold nanoparticles were mixed and incorporated into its defect layer so the laser dye could be dispersed to its proximate gold nanoparticles. The fluorescence was significantly enhanced at both the band edges and the defect dip because of the photonic crystal characteristics of CLCs. With the help of localized surface plasmon resonance effect induced by the doped gold nanoparticles, the fluorescence efficiency of the nano gold-doped CLCs was obviously enhanced at the defect dip compared with that of the undoped CLCs. This study therefore indicates the possibility of commercial CLC lasers. Most notably, this is the first study to our knowledge to investigate the fluorescence enhancement by dispersing gold nanoparticles with laser dyes in defeat-mode CLCs. Future work should include exploiting the adjustable refractive index of liquid crystals by externally optical, electrical, thermal, or mechanical influences to implement wavelength-tunable CLC lasers, and studying the effects of gold nanoparticle size, geometry, concentration, and its interaction with photons and dye molecules on the fluorescence enhancement.

References