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Enhanced birefringence for metallic nanoparticle doped liquid crystals

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ABSTRACT

Birefringence of metallic nanoparticle doped liquid crystals is investigated theoretically based on the Maxwell-Garnett effective medium theory. The scattering influence for metallic nanoparticles are considered associated with anisotropic permittivities of liquid crystal. Improved birefringence for E7 liquid crystals with doped metallic nanoparticles could be obtained in the whole visible wavelength range. High birefringence is realized based on high birefringent undoped liquid crystals. The sizes and volume fraction of metallic nanoparticles affect the birefringent enhancement.

1. Introduction

Liquid crystals (LCs) are extensively used in many kinds of optical devices owing to its anisotropic properties of refractive indices. As well known birefringence is defined by $\Delta n = n_e - n_o$ (n_e and n_o are the extraordinary refractive index and ordinary refractive index respectively). Except for commonly use in flat panel display, high birefringence is a very important factor in many applications such as phase modulator in liquid crystals adaptive optics. Phase modulated quantity is $\Delta n \times d$, where d is the thickness of LCs cell. When d is fixed, higher Δn is required to obtain larger phase modulated quantity [1–5]. Furthermore, high birefringence is helpful to reduce the cell gap when phase modulated quantity is fixed, as a result faster response can be achieved [6]. In addition, the beam steering effect can be performed in LCs, such as negative refraction. Because LC is not full angle negative refraction material, larger negative refraction angle can be realized by applying high Δn LCs material [7,8]. Finally, due to the features of compatibility with almost all materials and tunable permittivity, LCs are employed widely for tunable devices and materials [9–12].

The common approach for achieving high Δn is molecular design, in which large molecule electric polarizability is designed as possible as one can [13]. Due to the limitations of other material properties, LCs with super high Δn becomes very difficult to be designed. In this paper, an approach in which metallic nanoparticles are dispersed randomly into LCs is proposed to achieve super high Δn. Under the consideration the influence of anisotropic permittivity of liquid crystal for metallic nanoparticles, the enhancement of birefringence is investigated analytically. Birefringence in commercial E7 LCs and high-birefringence LCs with metallic nanoparticles is analyzed theoretically and larger improvement values is demonstrated according to the variation of structure parameters.

2. Theory

When electromagnetic wave propagate with wavelength λ in the material composed of isotropic spherical particle of radius R and uniaxial liquid crystal host with dielectric function characterized by the diagonal elements $\varepsilon_x = \varepsilon_y = \varepsilon_\perp$ and $\varepsilon_z = \varepsilon_{||}$, in the long wavelength limit condition ($\lambda \gg R$), there has been an approach to deal with this problem that isotropic host permittivity is considered for different polarized light [14]. This theory cannot consider scattering effect of anisotropic liquid crystal for metallic spherical particles. In this work, an alternative Maxwell-Garnett effective medium theory reflecting the anisotropic scattering of metallic spherical nanoparticles is used on account of anisotropic permittivity of liquid crystal. As shown in Fig. 1, the dielectric response of composite material can be described by effective dielectric tensor and it is found that the dielectric tensors remain uniaxial symmetry. So, the effective permittivities tensors $\varepsilon_x = \varepsilon_y = \varepsilon'_\perp$ and $\varepsilon_z = \varepsilon'_{||}$ are given as follows [15]:

$$\varepsilon'_i = \frac{\varepsilon_i[\varepsilon_i - L_i(\varepsilon_i - \varepsilon_m) - f(1 - L_i)(\varepsilon_i - \varepsilon_m)}{[\varepsilon_i - L_i(\varepsilon_i - \varepsilon_m) + f L_i(\varepsilon_i - \varepsilon_m)} \quad (1)$$

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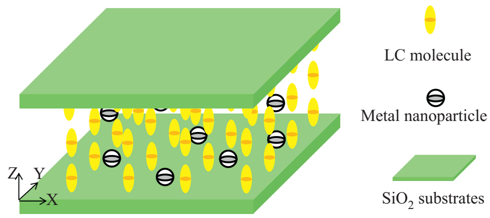

Fig. 1. Schematic diagram of LCs structures with randomly doped metallic nanoparticles.

Table 1
Three-coefficient Cauchy model. The Cauchy coefficients B and C are in units of μm^2 and μm^4, respectively. Temperature is 25 °C.

Coefficients	A_e	B_e	C_e	A_o	B_o	C_o
E7	1.6933	0.0078	0.0028	1.499	0.0072	0.0003

where ε_i and ε_m are the permittivities of liquid crystal and metallic particles. f is the volume fraction of metallic particles. The depolarization factor L_i for positive liquid crystal ($\varepsilon_e > \varepsilon_o$) is

$$L_{||} = \frac{1+e^2}{e^3}(e - \tan^{-1} e) \qquad L_{\perp} = (1 - L_{||})/2 \tag{2}$$

Here parameter e is written as

$$e = \sqrt{\frac{\varepsilon_{||}}{\varepsilon_{\perp}} - 1} \tag{3}$$

In formula (1), the scattering influence of metallic particle due to anisotropic dielectric properties of liquid crystal are considered sufficiently associated with the distinction of depolarization factor along different directions. The effective complex refractive index $n_i' = n_i' + i n_i''$ can be obtained from following formulas:

$$n_i' = \sqrt{\frac{\mathrm{Re}(\varepsilon_i') + \sqrt{\mathrm{Re}(\varepsilon_i')^2 + \mathrm{Im}(\varepsilon_i')^2}}{2}} \qquad n_i'' = \sqrt{\frac{-\mathrm{Re}(\varepsilon_i') + \sqrt{\mathrm{Re}(\varepsilon_i')^2 + \mathrm{Im}(\varepsilon_i')^2}}{2}} \tag{4}$$

Due to the emergence of imaginary part, the birefringence is redefined as $\Delta n' = n_e' - n_o'$.

3. Calculations and analysis

3.1. E7 liquid crystals

Firstly, commercial E7 LCs is chosen for nanoparticles doping. Considering wavelength effect of n_e and n_o, the refractive indices are described as a three-coefficient Cauchy model which fits the experimental values well in the visible spectrum with the following form [16]:

$$n_e = A_e + \frac{B_e}{\lambda^2} + \frac{C_e}{\lambda^4} \qquad n_o = A_o + \frac{B_o}{\lambda^2} + \frac{C_o}{\lambda^4} \tag{5}$$

The corresponding coefficients A_e, B_e, C_e, A_o, B_o, and C_o are listed in Table 1.

Owing to small energy dissipation for noble metals, silver is chosen as the doped metallic nanoparticles. Considering the size effect of nanoparticle, the permittivity of silver is written as follows [17–19]:

$$\varepsilon_{Ag} = \varepsilon_{\infty} - \frac{\omega_p^2}{\omega^2 + i\omega\gamma_s} \tag{6}$$

where $\gamma_s = \gamma_0 + 4V_F/3R$. $V_F = 1.39 \times 10^{10}$ m/s is the Fermi velocity of silver [20]. The plasmonic frequency $\omega_p = 1.5 \times 10^{16}$ rad/s, the damping frequency $\gamma_0 = 7.73 \times 10^{13}$ rad/s and high frequency permittivity $\varepsilon_{\infty} = 6$ correspond to bulk silver. These parameters are taken from the literature [17]. The refractive index is $n_{Ag} = \sqrt{\varepsilon_{Ag}}$.

According to formula (1)–(4) discussed above, the calculated refractive indices for doped E7 LCs are shown in Fig. 2. The peaks of $\mathrm{Re}(n_o')$ and $\mathrm{Re}(n_e')$ emerge in the range 400–500 nm, and strong energy dissipation exists as shown in Fig. 2(a), which arises from the surface plasmonic resonance in the interface between silver nanoparticle and LCs host. Compared with E7 LCs, the birefringence of LCs with silver nanoparticles is promoted in the >450 nm wavelength range, shown in Fig. 2(b). There are large imaginary parts of refractive indices in the 460–500 nm wavelength range. In order to be far from energy dissipation, reasonable wavelength range can be chosen as practical applications corresponding to smaller imaginary part values. The birefringence decreases as the wavelength increasing, but theΔn remains higher than that of E7 LCs in the long wavelength side of visible spectrum. The variations of refractive indices are attributed to distinct polarizabilities along long axis and short axis of LCs molecules for isotropic silver nanoparticles. The contributions of effective electric polarizability for n_e exceed that for n_o, so, this is the reason why the birefringence can be improved in silver nanoparticle doped LCs.

Additionally, in the wavelength range 400–450 nm, the birefringence decreases even the Δn values are transferred from positive to negative which is the results of the difference for resonant peaks of n_o and n_e. As a result of plasmonic resonance, the effect would go with strongly energy dissipation.

3.2. Super high birefringence LCs

We investigate birefringence improvement for high birefringent LCs (undoped). We take the parameters $n_o = 1.5$ and $n_e = 2$ from Ref. [21], corresponding to $\Delta n = 0.5$ in the whole visible range. Silver nanoparticles are doped into the LCs and the volume fraction is 0.05. As shown in Fig. 3, birefringence is improved in the wavelength range 500–800 nm and the imaginary parts of index is less than 0.1 in this range (not shown). The Δn value decreases from 0.558 to 0.5031 with wavelengths increasing, which is due to the scattering strength of metallic nanoparticles becomes weak with increasing wavelength. In contrast to undoped LCs, birefringence for doped LCs is promoted approximately 0.0031–0.058.

3.3. Particle size and volume fraction

Different sphere radius results in different birefringence for doped LCs. We choose two different radius silver nanoparticles with $R = 5$ nm and $R = 10$ nm. High birefringence LCs with $n_o = 1.5$ and $n_e = 2$ is used. As shown in Fig. 4, birefringence for $R = 10$ nm is better improved compared with $R = 5$ nm. The reason is that larger nanoparticle produces strong electric polarizability.

Next, we consider the effect of volume fraction. As shown in Fig. 5, higher Δn is obtained for larger volume fraction when $R = 5$ nm is fixed. Δn could be enhanced greatly when volume fraction increases one time from 0.05 to 0.1. Nevertheless, for larger volume fraction LCs phase could be more difficult to be formed. So modest volume fraction must be chosen to ensure the forming of LCs phase and higher Δn in actual experimental operations.

Finally, it is noted anisotropic scattering is more proper to the research of birefringent improvement in anisotropic liquid crystal with metallic nanoparticles, in contrast to the consideration of isotropic scattering. The approach also can be used to control the refractive indices and improve the birefringence for any nanoparticle doped LCs. The material of nanoparticle can be metals and dielectrics.

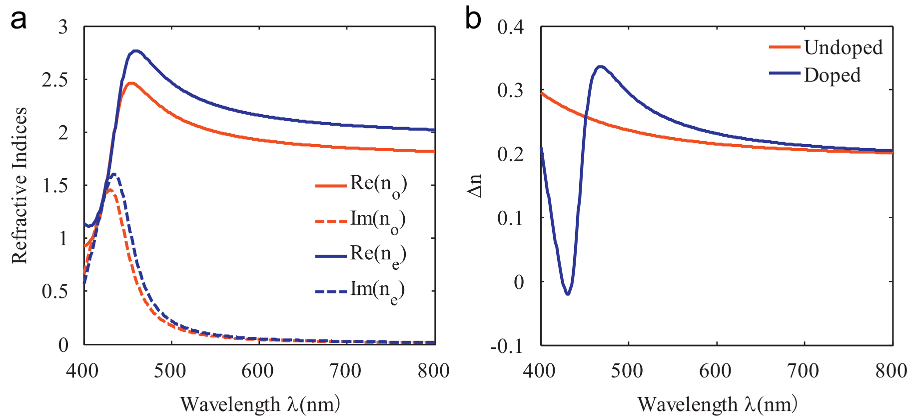

Fig. 2. (a) Real part and imaginary part of effective refractive indices n_o and n_e for doped E7 LCs with silver nanoparticles and (b) the birefringence for undoped and doped E7 LCs. The radius of silver nanoparticle is $R=5$ nm and small volume fraction is $f=0.05$.

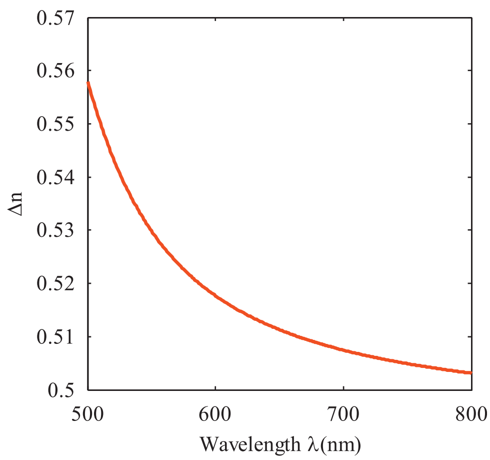

Fig. 3. Birefringence for doped LCs corresponding to undoped LCs with $n_o=1.5$ and $n_e=2$. The radius of silver nanoparticle is $R=5$ nm and volume fraction is $f=0.05$.

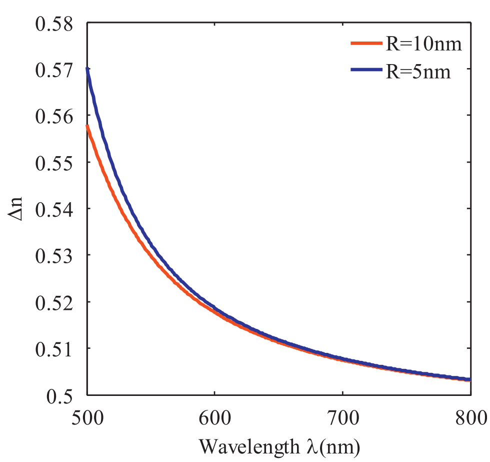

Fig. 4. Birefringence Δn for different nanoparticle radius $R=5$ nm and $R=10$ nm. The volume fraction is $f=0.05$.

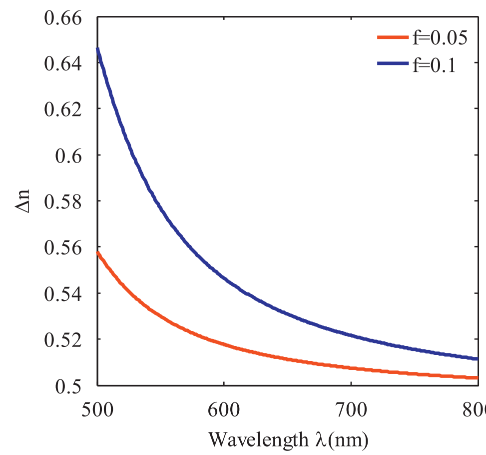

Fig. 5. Δn for different volume fraction ratio $f=0.05$ and $f=0.1$. The nanoparticle radius is 5 nm.

4. Conclusions

In this paper, we propose an approach to enhance the birefringence of LCs by metallic nanoparticles doping. The effective refractive indices of nanoparticles doped LCs are described by the Maxwell-Garnett effective medium theory under long wavelength limit condition. Improved birefringence for silver nanoparticles doped E7 LCs is obtained in the whole visible wavelength range. Larger birefringent improvement is achieved for liquid crystals with high birefringence. Lager nanoparticle radius and higher volume fraction are beneficial to more improvement of birefringence. The metallic nanoparticles greatly improve the optical properties of LCs and offer an opportunity to design novel optical devices.

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