Polymer dispersed liquid crystal-mediated active plasmonic mode with microsecond response time

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Active plasmonics combined with liquid crystal (LC) has found many applications in nanophotonics. In this Letter, we propose a fast response active plasmonic device based on the interplay of the plasmonic spectrum and Fabry–Perot (FP) modes. The plasmonic spectrum and FP modes are exited in a layer of gold nanoparticle (NP) islands and an LC microcavity, respectively. The FP mode splits the extinction spectrum of the NP to narrow bands, which are named hybrid modes (HMs). Due to multiple reflections of photons inside the cavity, the extinction coefficient is enhanced compared to a bare NP layer. An external electric field shifts the HM leading to a significant increase in the figure of merit (FoM) related to the activation ability by up to a factor of 45. Additionally, we could reduce the response time of active plasmonic. This decrease in response time is achieved through polymer-dispersed LC (PDLC) in the microcavity. Utilizing a mesogenic monomer in PDLC reduces the response time of the HM into the microsecond range, while the sample remains transparent. © 2019 Optical Society of America

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When plasmonic nanoparticles (NPs) are irradiated with light, free electrons at the interface with the surrounding environment collectively start to oscillate. The frequency of this oscillation is the same as that of the incident light. The electric field of plasmonic resonances is locally intense and confined to a sub-wavelength dimension around the NP [1]. This large electric field enhances the light–matter interaction at nanoscale. Because of this capability, localized surface plasmonic resonance (LSPR) has extensively contributed to the development of nanophotonics during the past decade. In spite of large advances in plasmonic devices, actively controlled LSPR is one of the future demanding features in plasmonic-based devices. For the activation of plasmonic absorption, multiple methods have been used. For example, high-speed switching in the extinction spectrum of an anisotropic plasmonic nanorod dispersed in organic solvent has been demonstrated. In these studies, the alignment of the nanorod is controlled in external electric field [2–4]. The LSPR wavelength based on the Mie theory is dependent on the surrounding refractive index [5]. This property can be exploited in the activation of LSPR. Due to large and controllable birefringence, liquid crystal (LC) is an excellent candidate for the activation of LSPR. So far, LC-based active plasmonic has been implemented in electro-optic and all-optical setups [6,7]. Nevertheless, due to strong radiative damping, the large bandwidth of the extinction spectrum of metal NP reduces the sensitivity and spectral shift. Recently, hybrid modes (HMs) emerging from the coupling of Fabry–Perot (FP) modes and LSPR related to NP has been observed [8–11]. In our previous report, by means of hybridization of optical FP modes and a plasmonic mode, an active plasmonic with high figure of merit (FoM) connected to plasmonic activation ability is realized [12]. The FP modes and plasmonic mode are excited in the cavity of LC and in the NP layer, respectively. The optical modes of FP have much narrower bandwidths compared to LSPR, and the overlay of the FP modes and the extinction spectrum splits the wide spectrum into narrow band modes. This narrowing makes it more sensitive to external stimuli and strong spectrum modulation. From a practical point of view, the response time is a decisive issue. In recent years LC-based control of transmission through metamaterial has been widely studied [13]. Practically, this structure could be implemented in the color tunability for display application. Therefore, high-speed tuning of color is desirable in this application. The electro-optic response time of the used LC in Ref. [12] is in the millisecond range. In this Letter, for achieving a faster response in the order of microseconds, we have used polymer dispersed LC (PDLC), which, in most cases, offers faster response-times [14]. In the PDLC layer, we expect a shorter decay time $\tau = \gamma d^2/K_{11}$ for smaller droplets, with $\gamma$ and $K_{11}$ being the viscosity and splay elastic constant of the LC, and $d$ being the average size of the LC droplets dispersed in the polymeric matrix. Using mesogenic monomers in the mixture of PDLC yields a clear device, so that light can transmit through the PDLC layer without scattering [15]. In addition, compared to the bare NP layer, we also demonstrate a high
FoM and higher absorption close to plasmonic peak of NP. The combination of the FP cavity with a plasmonic structure offers spectra with more color purity due to a narrower bandwidth, compared to a single plasmonic layer.

A mixture is prepared by mixing nematic LC 1782B (synthesized at Warsaw Military University) and a mesogenic monomer RM257 (obtained from MERCK) at weight fractions 80:20. For 1782B, the nematic to isotropic phase transition occurs at 133°C. It has positive anisotropy, and its ordinary and extraordinary refractive indices at room temperature are 1.53 and 1.81, respectively. For RM257, the refractive indices are 1.508 and 1.687, respectively. The melting and clearing points for RM257 are 66°C and 127°C, respectively. An IRGACURE 819 (BASF) photo initiator with 0.5 wt% of the total mixture was used the average refractive index of 1782B for the (LC-NP) nanocomposite.

The LC cell was assembled from the NP and the polyamide coated substrates. The cell gap was controlled by using a 3 μm micrometer spacer. The LC mixture (at clearing temperature) was filled inside the cell via capillary action. In addition, in the same way, another control sample with only nonreactive 1782B LC was prepared. The samples were slowly cooled down to room temperature to obtain perfect alignment along the rubbing direction. Finally, for curing, the cell that contained the monomer was irradiated with a 365 nm LED lamp for approximately 1 h. During this treatment, the LC molecules are placed parallel the rubbing direction and the nonreactive LC nanocomposite for polarization parallel and perpendicular to grooves which are formed along the rubbing direction. This type of nanocomposite has been used in scattering-free and phase-only modulating devices.

As clearly observable from SEM image, even though the PDLC layer has a low concentration (20 wt%) in the mixture, it is completely different from isotropic monomers, for which phase separation occurs, and polymers aggregate into thick fibrils [15]. Due to the anisotropy in the structure, the incident polarized light experiences an effective refractive index of the polymer and the nonreactive LC nanocomposite for polarization parallel and perpendicular to grooves which are formed along the rubbing direction. This type of nanocomposite has been used in scattering-free and phase-only modulating devices [17].

The simulation of the HM of the device is based on the transfer matrix method (TMM) [18]. Parameters are approximately the same as the experimental value. The incident light polarized along the rubbing direction experiences only effective extraordinary refractive index, and we could use a TMM similar to isotropic state. The LC and NPs are divided into two sub-layers. One of them is the bulk LC (BLC) layer, and the other is a nanocomposite composed of NPs and surrounding LC (LC-NP) [11, 12, 19]. The multi-layers which are used in the TMM are shown in Fig. 1(b). The red dashed box schematically represents the (LC-NP) layer. The parameters about this layer are presented in the supplementary material of Ref. [12]. As depicted inside this box, gold NPs tend to randomize and align LC molecules perpendicular to the surface of the NP. The composite (LC-NP) layer due to the random orientation of LC molecules has an effective refractive index that is described with the isotropic Maxwell–Garnet model. Therefore, we have used the average refractive index of 1782B for the (LC-NP) layer [19]. The dielectric constant of the plasmonic NP is deduced from Johnson and Christy [20] and is corrected for the average NP size (~35 nm) [21]. The color map of the simulated squared electric field inside the cavity in the wavelength spectrum is shown in Fig. 2(a). Clearly, a standing wave pattern, characteristic of an FP resonance, is visible inside the cavity. The magnitude of the electric field is dramatically intensified in the reflection range around the LSPR. The FP mode resonance wavelength is defined with Eq. (1) [22]:

$$\frac{4\pi nd}{\lambda} + \Delta \varphi_D + \Delta \varphi_{plasmonic} = 2\pi m,$$

where \(m\) is the integer mode number; \(n\) and \(d\) denote refractive index and thickness of the cavity, respectively; and \(\Delta \varphi_D\) and \(\Delta \varphi_{plasmonic}\) are the reflection-induced phase change in the LC/polyamide/ITO and LC/(Au-NP)/ITO multilayer interfaces, respectively. According to the Fresnel theory, \(\Delta \varphi_D\) and \(\Delta \varphi_{plasmonic}\) are equal to the argument of the reflection coefficient.
According to the above-mentioned TMM method, the extinction spectrum of the device for two states is calculated, and the results with the parameters of calculation are shown in the Fig. 2(b). The extinction is equal to one minus reflection minus transmission. The simulated extinction spectrum of the LC-NP layer on the ITO substrate is considered as an extinction of bare NP covered with an LC molecule and, for two refractive indices of LC, is calculated and shown in Fig. 2(b). In the hybrid extinction spectra, the interplay of the FP modes and the localized plasmonics spectrum leads to narrow spectral bands. As clearly observable, the spectral modification of the HMs due to the change of refractive index is much larger than for the spectrum of bare NP. This validates that the cavity is enhanced by the plasmonic sensitivity [22]. Figure 2(c) shows the measured extinction spectrum of the bare NP and the prepared sample. By means of fast Fourier transform filtering (FFTF) analysis, a fast oscillating component (FP mode) of the HM is removed and gives a Lorentzian spectrum which reveals spectral properties of the LC-NP [8]. The corresponding FFTF spectrum of the HM is demonstrated in the same color in Fig. 2(c). Obviously, the HMs (FWHM ~ 20 nm) are narrower than the width of the extinction spectrum of the bare NP (FWHM ~ 130 nm) which makes it more sensitive to external stimuli. A remarkable result that is recognizable from Figs. 2(b) and 2(c) is the intensity of plasmonic extinction. Clearly, the amplitude of the HM for each peak, especially the ones close to the plasmonic peak wavelength, is larger in comparison to the amplitude of the LC-NP layer and FFTF spectrum [12] which is affected by the mutual coupling of the plasmonic NP and FP modes. The differences in the extinction amplitude (ΔE) between the HM and bare NP at peak wavelengths [according to the left inset of Fig. 2(d)] from experimental [Fig. 2(c)] and simulation [Fig. 2(b)] results are shown in Fig. 2(d). Clearly, this difference becomes more pronounced for modes closer to the peak wavelength [23]. Due to the multi-traveling of the photon, the cavity hinders the photon for a long time, and the photon could find more chance for photon-plasmon interaction. For the explanation of this phenomenon, the real and imaginary parts of the dielectric function of the (LC-NP) layer are calculated and shown in the inset of Fig. 2(d). As shown inside the dashed box, In spite of the higher absorption of NP, the anomalous dispersion in the real part of the dielectric function enhances the scattering cross section as a nano-mirror which is understandable from Fig. 2(a).

The polarization dependency of the HM—related to the parallel and perpendicular polarization with respect to the rubbing direction—is shown in Fig. 3(a). Based on Eq. (1), when the polarization changes from parallel to perpendicular, the incident light experiences a reduction of the refractive index and, consequently, the HMs shift to the blue side. By means of Eq. (1), and knowing the cavity thickness (2.7 μm), the calculated anisotropy for two orthogonal polarizations are found to be 1.73 and 1.53 (for more details, see the supplementary material in Ref. [12]). The effective values of the refractive indices for parallel and perpendicular to rubbing directions, by considering the weight ratio of each material contributed in the PDLC mixture, are 1.77 and 1.53, respectively [24]. Although the maximum birefringence decreased by ~0.04 in sample preparation, the macroscopic order induced by the rubbing was retained in the PDLC sample. The FFTF spectra of the sample for orthogonal polarizations are also calculated and are shown in Fig. 3(a). According to this figure, both spectra are located at the same position, which implicitly demonstrates the random orientation of LC molecule surrounding the NP.

The tunability was verified by applying an electric field. Figure 3(b) shows a voltage-dependent HM before and during the application of 7 and 15 V/μm DC electric fields. The FFTF spectrum of the HMs corresponding to 0 and 15 V/μm has only a 5 nm shift compared with the 16 nm shift of the HM. A 5 nm blueshift of the FFTF spectrum according to the Mie theory is related to the reduction of the refractive index due to reorientation of the LC molecule from random orientation to the perpendicular state. As clearly seen, we obtain HMs without the disappearance of FP modes, which have a blueshift when a voltage is applied, which serves as further evidence of the scattering-free nature of the nanocomposite PDLC. As discussed above, by utilizing mesogenic monomers in the PDLC, the film will be transparent, and the modes will only shift while maintaining transparency. An important feature of active systems is the reversibility under driven external

![Fig. 2](image1.png)

**Fig. 2.** (a) Color map of the electric field inside the cavity in the presence of the NP layer refractive index of the BLC and LC-NP which are 1.77 and 1.65, respectively. The thickness of the cavity is 3 μm. (b) Simulated extinction spectrum for the HM and bare NP layer using different refractive indices for the layer. (c) Measured extinction spectra of the bare NP layer and HM. The red line corresponds to the FFTF of the HM. The inset shows the slope of the bare NP and HM spectra (nm⁻¹). (d) Extinction difference (ΔE) for the simulation and experimental results. The left inset shows the meaning of the ΔE value. The right inset shows the real (n) and imaginary (k) parts of the dielectric constant of NP.

![Fig. 3](image2.png)

**Fig. 3.** (a) Measured polarization dependence of the HM extinction spectrum: polarization parallel (blue curve) and perpendicular (red curve) to the rubbing direction. The corresponding FFTF spectra of each hybrid spectrum are shown in the same color. (b) Measured electric field-induced blueshift of the HMs. The inset shows the blueshift of the FFTF spectrum corresponding to 0 and 15 V/μm.
stimuli. The experimental results on the alternating turn on/off of electric field demonstrate a completely reversible action (data are not shown). The anchoring of the polymeric network draws LC molecules back to its first aligned direction.

The spectral sensitivity of the system is directly related to the slope of the spectrum. The fast rising and falling of the spectrum, therefore, is indicative of high sensitivity. The slopes related to the bare NP and HM are presented in the inset of Fig. 2(c). A comparison reveals that the HM is more than three times steeper than the bare NP. The degree of spectral deformation in response to the external stimulus represents its applicability. For this reason, we define the FoM parameter as follows [13]:

$$\text{FoM} = \frac{1}{\lambda_{sp}} \frac{d\lambda_{sp}}{dn} = \frac{2d}{\Delta\lambda_{sp}, m}, \quad (2)$$

where $\lambda_{sp}$ and $n$ are the resonance wavelength and the refractive index of material inside the FP cavity, respectively, and $\frac{d\lambda}{dn}$ and $\Delta\lambda$ are the refractive index sensitivity and the resonance line width. The calculated FoM of the HM from Fig. 2(c) is about 14. In the previous study, the FoM for a bare NP layer obtained from measuring the sensitivity of the refractive index for changes in the refractive index of the surrounding organic solvents was about 0.3. A comparison of the two FoMs demonstrates a boost of a factor of 45 in the FoM. This result is understandable from spectral modulation of the HMs and of the bare NP layer in the Figs. 2(b) and 3(b).

For the demonstration of fast response of PDLC, the sample is examined in an electro-optic setup. In this experiment, the sample is placed between crossed polarizers and the transmission for a He–Ne laser beam (after passing through a polarizer-sample-analyzer) is detected with a photodiode. Figure 4(a) shows the transient response of the sample under a square wave electric field. The rise and decay times related to 10–90% transmittance extracted from this figure are 340 and 580 μs, respectively, which demonstrates that the reorientation time of LC is in the micro-second range. Actually, the response time decreases further with higher polymer concentration. However, it needs a higher driving voltage. In another electro-optic experiment, a sine wave with a frequency and amplitude of 10 kHz and 15 V/μm is applied to the samples. The response of the samples with and without a monomer is shown in Fig. 4(b). Because of the high modulation frequency, the sample without a monomer is not able to follow the alternating electric field and, therefore, the electro-optic response is a straight line [straight line in Fig. 4(b)]. However, the PDLC sample can follow the electric field, although there is some delay [red line in Fig. 4(b)]. As can be seen, the period of the driven electric field and the electro-optic response time differ by a factor of two. This is because the LC is not sensitive to the polarity of the voltage, only to the amplitude. Therefore, the modulated signal has a frequency of 20 kHz [25]. The small size of the droplet increases the anchoring between the LC and the polymeric network and, consequently, the rotation of LC molecules requires a higher driving electric field. However, the speed of rotation to the ground state dramatically increases, leading to a switching time in the range of microseconds.

In this Letter, by means of hybridization of the extinction spectrum of the NP layer with the FP mode excited in a PDLC cavity, we achieved effective and high-speed modulation of the extinction spectrum. The HMs offer the opportunity to activate the extinction spectrum of plasmonic NPs in selective narrow wavelength ranges. The appearance of the FP mode is due to the scattering-free nature of the PDLC cavity. Mixing LC with an LC line monomer realizes an active plasmonic device in the microsecond range. The simulation of coupling leads to a good agreement with the experimental results. The FoM related to sensitivity demonstrates a 45 times enhancement compared to bare NP. In the application view, this result is usable for externally controlling the scattering of a single NP and tunable single-mode lasers [8], and many optoelectronic devices.

REFERENCES