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Effect of gold nano-particles on switch-on voltage and relaxation frequency of nematic liquid crystal cell

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We report the observation of large changes in the electro-optical properties of nematic liquid crystal (NLC) due to inclusion of small concentration of 10 nm diameter gold nanoparticles (GNPs). It is observed that GNPs lower switch-on voltage and also lower the relaxation frequency with applied voltage (AC field) to NLC cell. These studies of GNP doped NLC cell have been done using optical interferometry and capacity measurement by impedance analyzer. The change in threshold voltage and relaxation frequency by doping GNPs in NLC is explained theoretically. *Copyright 2011 Author(s). This article is distributed under a Creative Commons Attribution 3.0 Unported License.* [doi:10.1063/1.3668125]

I. INTRODUCTION

Liquid crystal display (LCD) devices are widely used for our day to day life. The electro-optical characteristics of LC material, such as, Guest-host effect, bi-stability and field induced director axes re-orientation and switch-on voltage are important factors^{1,2} for the display application. Recently, there has been enormous amount of research for the enhancement of electro-optical properties of LC materials by means of doping of metallic nano-particles (NPs),³⁻⁵ carbon nano-tubes (CNTs)^{6,7} and quantum dots⁸ into the LC cell. The effect of CNTs in the twisted nematic (TN)-LC device has been studied and found that the CNT doped cell reduces the switch-on voltage and improves the response time.⁷ Effect of gold nano-particles (GNPs) on the memory of ferroelectric LC material has been reported and it was found that the memory is enhanced remarkably due to electric field induced charge transfer from LC molecules to the GNPs and the stabilization of helix deformation of deformed helix FLC material, which occurs on the application of electric field beyond a critical value.⁹ The influence of gold nano-rods (GNRs) on the electro-optic and dielectric properties of the ferroelectric liquid crystals (FLCs) has also been investigated.¹⁰ It was reported that by dispersing GNRs in FLCs could lead to an increase of internal electric-field inside the liquid crystalline layer. This effect results in a significant decrease of the switching time and the rotational viscosity of the FLC/GNRs nano-dispersions independently on the GNRs diameter. Dielectric and electro-optic properties of FLC mixture doped with CNTs have also been investigated.¹¹ It was demonstrated that a small concentration of CNTs greatly affects the performance of the liquid crystal cell. The obtained experimental results are explained by the trapping of ions through the CNTs, which results in a significant modification of the internal electric field. More recently, the effects of GNRs on the nematic liquid crystal (NLC) matrixes have also been reported.¹² It was observed that GNRs form their own self assembling well ordered structures inside the LC matrix. A large change in the electro-optical properties of a polymer dispersed liquid crystal (PDLC) due to inclusion of 14 nm diameter GNPs has also been observed.¹³ It was found that GNPs lower switch-on electric field, increase optical transmission at certain voltages and influence the frequency response of the PDLC.

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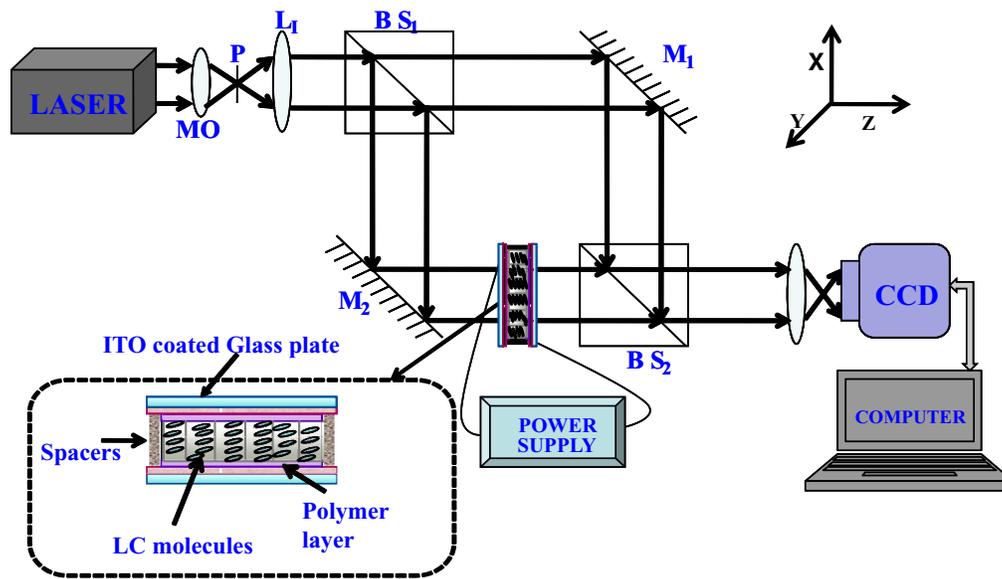


FIG. 1. Schematic of experimental set up of Mach-Zehnder interferometer.

However, the change in relaxation frequency of LC molecules in presence of GNPs with applied AC voltage has not been explained yet.

In this paper we report the effect of GNPs on threshold voltage of NLC cell of $3\mu\text{m}$ gap, and on relaxation frequency. We present evidence for relatively large changes in the electro-optical properties of NLC due to inclusion of small concentration of 10 nm diameter GNPs. It is observed that GNPs lower switch-on voltage and also lower relaxation frequency, with applied DC- and AC-voltage to NLC cell, respectively. All these studies have been done by optical interferometry and capacity measurement by impedance analyzer of a NLC cell. Theoretical explanation has also been given for change in threshold voltage and relaxation frequency.

II. EXPERIMENTAL DETAILS

For the study of NLC (E-7) material, a LC cell was prepared with spacing of $3\mu\text{m}$ between two parallel glass plates using Mylar spacer. Glass plates were coated with ITO (indium tin oxide; transparent and conducting material), and electrodes were formed by photolithography. After assembling the cell, NLC material was filled between the electrodes (formed by ITO coated pattern) by capillary action. GNPs were then mixed 1% of weight in NLC material and this mixture was filled in cell by capillary action. The interferometric and dielectric studies were done for both the cells filled with pure NLC material and GNP doped NLC material. For interferometric studies of the two cells, Mach-Zehnder Interferometer (MZI) was used. More details about the experimental set-up can be found in our previous paper,¹⁴ however the set-up is briefly described here. Figure 1 shows the schematic diagram of MZI set-up for the interferometric study of LC cell. Unpolarized light generated from He-Ne laser was expanded using microscope objective (MO) and spatially filtered by pinhole (P). The spatially filtered expanded beam was collimated by a collimating lens (L_1) of focal length 16 cm. The collimated beam was then divided into two beams by beam-splitter (BS_1). The two beams were then redirected by mirrors M_1 and M_2 and were re-combined at the BS_2 . Interference fringes were relayed by a relay lens and recorded by a CCD camera. The LC sample (pure NLC and GNP doped NLC filled cell) was placed in one arm of the interferometer, called object arm and the other arm acts as reference arm.

For dielectric studies of both the cells (pure NLC and GNP doped NLC), the capacitance was measured by impedance analyzer (Wayne Kerr, 6540A, UK) by varying the AC-voltages stepwise and frequency of applied AC voltage. The applied AC voltage to NLC cell was changed in steps

of 0.20 V, and the frequency was changed from 100 Hz to 1 MHz. Change in threshold voltage by inclusion of GNP also reported from capacity measurement graphs for both the cells. When voltage is changed the capacity associated with LC cell is changed due to change in relative permittivity of LC material along one direction (in z-direction shown in Fig. 1).

III. RESULTS AND DISCUSSION

A. Change in threshold voltage of NLC cell by doping GNPs

For interferometric study, the cell was placed in object arm of MZI and the voltage was applied to the liquid-crystal cell by DC-power supply in steps and the phase shifted interferograms were recorded. Shift in the interference fringes corresponding to the active area of the cell with applied voltage starts as soon as LC molecules starts rotating under the influence of applied field to LC cell. Light passes through the cell along z-direction as shown in Fig. 1. In the active area of the cell the LC-molecules rotate with applied-field and hence the refractive index along z-direction changes in the active area of the cell with respect to the rest of the area. Due to this change refractive index the fringe starts shifting at threshold voltage, i.e., NLC molecules starts rotating inside the cell. Figures 2(a) and 2(b) shows the recorded interferograms for pure NLC and GNP doped NLC cells at 0 V applied DC field, respectively. Figures 2(c) and 2(d) show the shift in interference fringes corresponding to the active area of the cell at threshold voltages for pure NLC and GNP doped NLC cell, respectively. The threshold voltages for pure NLC and GNP doped NLC cell are 7.4 V and 6.0 V, respectively. Since the refractive index of the LC material changes continuously with applied voltage, and hence the optical path length also changes in object arm of the MZI, corresponding to active area of the cell. So there will be a change in phase with voltage applied to the LC cell¹⁵

$$\Delta\phi(x, y; V) = \frac{2\pi}{\lambda_0} OPD = \frac{2\pi}{\lambda_0} \Delta n(x, y; V) \cdot d(x, y) \quad (1)$$

Where OPD is the optical path difference between the reference and object arms of MZI, $\Delta n(x, y; V)$ is the change in refractive index of LC material which is function of position (x, y) and voltage V, λ_0 is the wavelength of light and $d(x, y)$ is the geometrical thickness of the sample cell which is constant for an uniform gap cell. Hence the phase change (fringe shift) is a function of voltage. The threshold voltage at which the molecules starts rotating can be measured using initial fringe shift due phase change within the active area of the cell. We observed that in the presence of GNP doped NLC, the shift in fringes starts at lower voltages in comparison to pure NLC cell. Thus mixing GNPs in NLC, lowers the threshold voltage. A theoretical explanation of this effect is given below. Figure 3 shows the schematic diagram illustrating the interaction of LC molecules with GNPs. As we know that the relative permittivities of GNPs and NLC material are different. Due to this difference in relative permittivity a local internal electric field is generated which lowers the threshold voltage for GNP doped NLC cell and the expression for the lowering the threshold voltage is given by,¹⁶

$$E_{NLC} = \left(\frac{u}{u - m} \right) E_{GNP/NLC} \quad (2)$$

where E_{NLC} and $E_{GNP/NLC}$ are the electric fields required to rotate the LC molecules when pure NLC is filled in the cell and when GNP mixed NLC material is filled in the cell, respectively, $u = [1 - \frac{\epsilon_1}{\epsilon_2}]^{-1}$, where ϵ_1 is the relative permittivity of GNP at a particular frequency of the illuminating light and ϵ_2 is the relative permittivity (initial relative permittivity i.e. ϵ_{II} , which is parallel to LC director) of LC material, which is also the function of the frequency of illuminating light and depends on the direction of light passing through LC material and $m = 1/D$, where D is the dimensionality of mixed nano-particles and for spherical GNP the dimensionality is 2. Equation (1) can be rewritten in terms of threshold voltage as follows;

$$V_{th,NLC}/d = \left(\frac{u}{u - m} \right) V_{th,GNP/NLC}/d \quad (3)$$

where $V_{th,NLC}$, and $V_{th,GNP/NLC}$ are the threshold voltages corresponding to pure NLC, and GNP mixed LC material filled in the cell, respectively and “d” is the thickness of LC cell. Initially the

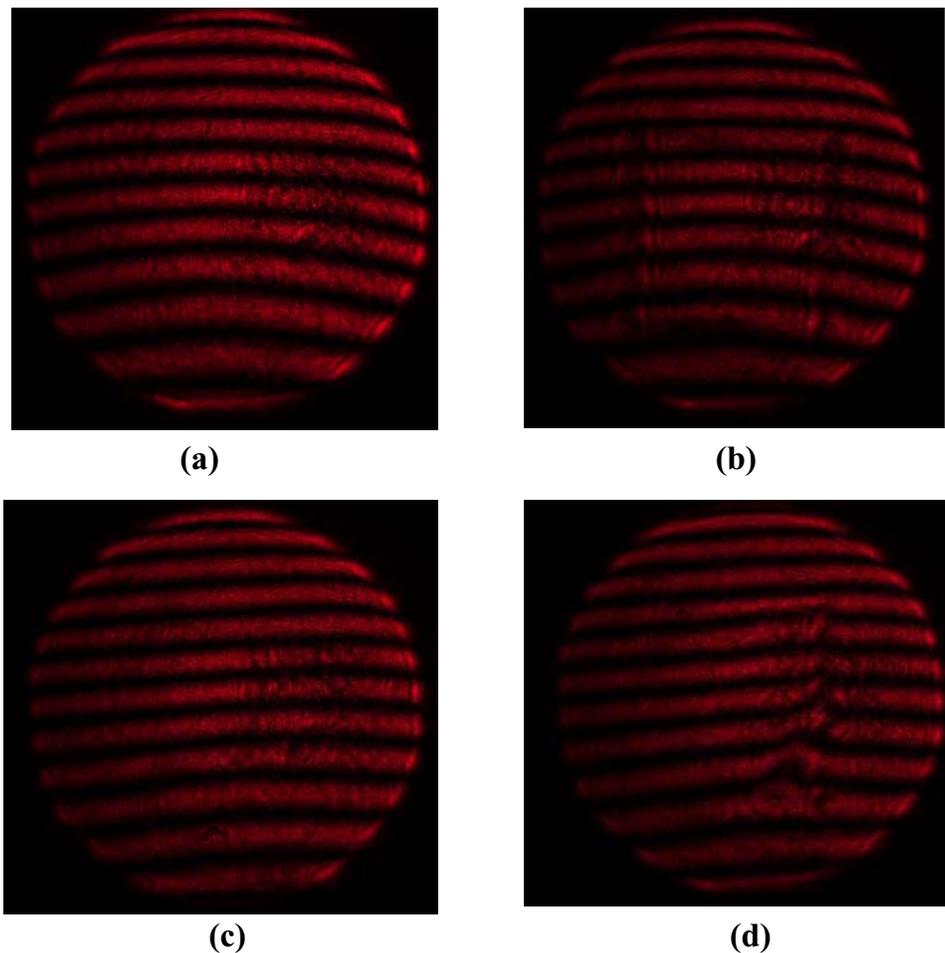


FIG. 2. (a), and (c) are the recorded interferograms at 0 V applied voltage to pure NLC filled cell and GNP doped NLC filled cell respectively, (b) is the recorded interferogram at 7.4 V applied voltage to pure NLC filled cell i.e. threshold voltage for pure NLC cell, and (d) is the recorded interferogram at 6 V for GNP doped NLC cell i.e. threshold voltage for GNP doped NLC cell.

molecules are parallel to the LC-cell glass surface due to the presence of grooves created by standard alignment method, therefore the director of LC molecules is initially in the x - y plane as shown in Fig. 1, and light passes in the z -direction across the LC cell. So initially, the extra-ordinary relative permittivity for NLC material (E-7) can be taken into account for the theoretical calculations. For used NLC material (E-7), the extra-ordinary relative permittivity (perpendicular to director) ϵ_2 is 16.87, and relative permittivity for GNP at wavelength 632.8nm is $\epsilon_1 (-10 + 2i)$ which is a complex number.¹⁷ So for relative permittivity of GNP, we can take magnitude of complex relative permittivity, i.e., approximately 10.19. Using these values of relative permittivities of NLC and GNP, the value of 'u' was calculated and which was found to be 2.53. Now from Fig. 2(a) the value of threshold voltage for pure NLC material filled cell was obtained which was 7.4 V for the cell thickness of 3 μm . By means of putting these values in Eq. (3), the calculated value of threshold voltage for GNP doped NLC cell was 5.94V. The calculated value of threshold voltage for GNP mixed NLC filled cell are matching with experimental results for threshold voltages as shown in Figs. 2(b) and 2(c), using optical interferometry i.e. 7.4 V and 6.0 V, respectively. This change in threshold voltage for pure NLC cell and GNP doped NLC cell were also observed by taking dielectric measurements of the same cells which also confirms our study that the threshold voltage of NLC cell can lowered by means of doing the GNPs.

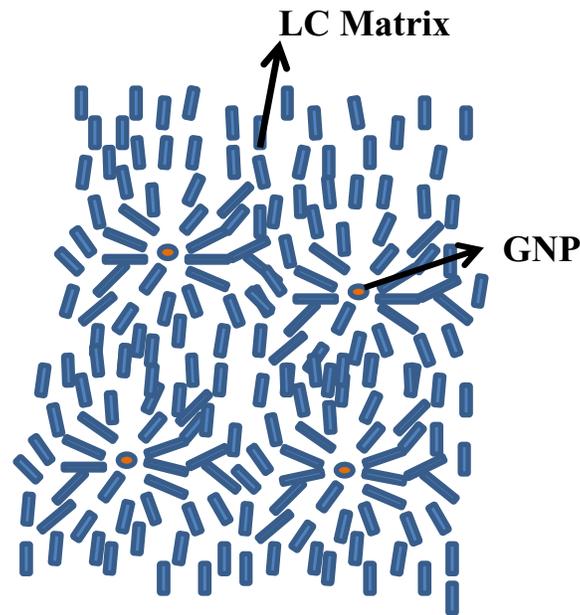


FIG. 3. Internal schematic diagram for GNPs doped NLC material.

B. Change in relaxation frequency of NLC cell by doping GNPs

Figure 4 shows the variation in relative dielectric permittivity with frequency, at different applied AC voltages. Similarly the variation in relative dielectric permittivity with frequency at different voltages for GNPs doped NLC filled cell is also shown in Fig. 5. As can be seen from Fig. 4 and 5 the relative dielectric permittivity measurement graphs, it is clear that the threshold voltages for pure NLC cell and for GNP doped NLC cell are different for the same cell gap, i. e., for GNP doped cell it is lowered by 1.4 V in comparison with pure NLC cell. From Figs. 4 and 5 it was also observed that the frequency at which the relative dielectric permittivity of NLC material starts decreasing is above 10^4 Hz for pure NLC filled cell, whereas in the case of GNP doped NLC filled cell, it is around 3×10^3 Hz which is an order of magnitude less. The physical reason for the change of frequency is given below.

If we apply AC field of higher frequency to LC cell, the liquid crystal molecules may not be able to align instantaneously with rapidly oscillating electric field due to their rotational viscosity, and hence the dielectric effect of LC material reduces at higher frequency of applied AC voltage.¹⁸ At higher frequency the dielectric effect of LC material is reduced, this term is called dielectric relaxation and the frequency at which dielectric relaxation occurs is termed as frequency relaxation. In presence of relaxation effect, the dielectric constant may conveniently be written as complex quantity¹⁹

$$\varepsilon^*(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega) = \varepsilon(\infty) + \frac{\varepsilon(0) - \varepsilon(\infty)}{1 + i\omega\tau} = \varepsilon(\infty) + \frac{\varepsilon(0) - \varepsilon(\infty)}{1 + (\omega\tau)^2} - i \frac{\varepsilon(0) - \varepsilon(\infty)}{1 + (\omega\tau)^2} \omega\tau \quad (4a)$$

where $\varepsilon'(\omega)$ and $\varepsilon''(\omega)$ are the real and imaginary parts of the dielectric constant, $\varepsilon(\infty)$ and $\varepsilon(0)$ are the dielectric constants at very high and zero frequency (D.C. voltage) of applied AC voltage respectively, ω is the frequency of applied AC field and τ is the relaxation time (the time interval characterizing the restoration of a disturbed system to its equilibrium configuration) of LC molecules. Eq. (4a) can be rewritten as at very high frequency of applied AC field ($\omega \gg \omega_c$)

$$\varepsilon^* = \varepsilon(\infty) + \frac{\varepsilon(0) - \varepsilon(\infty)}{\omega^2/\omega_c^2} - i \frac{\varepsilon(0) - \varepsilon(\infty)}{\omega/\omega_c} \quad (4b)$$

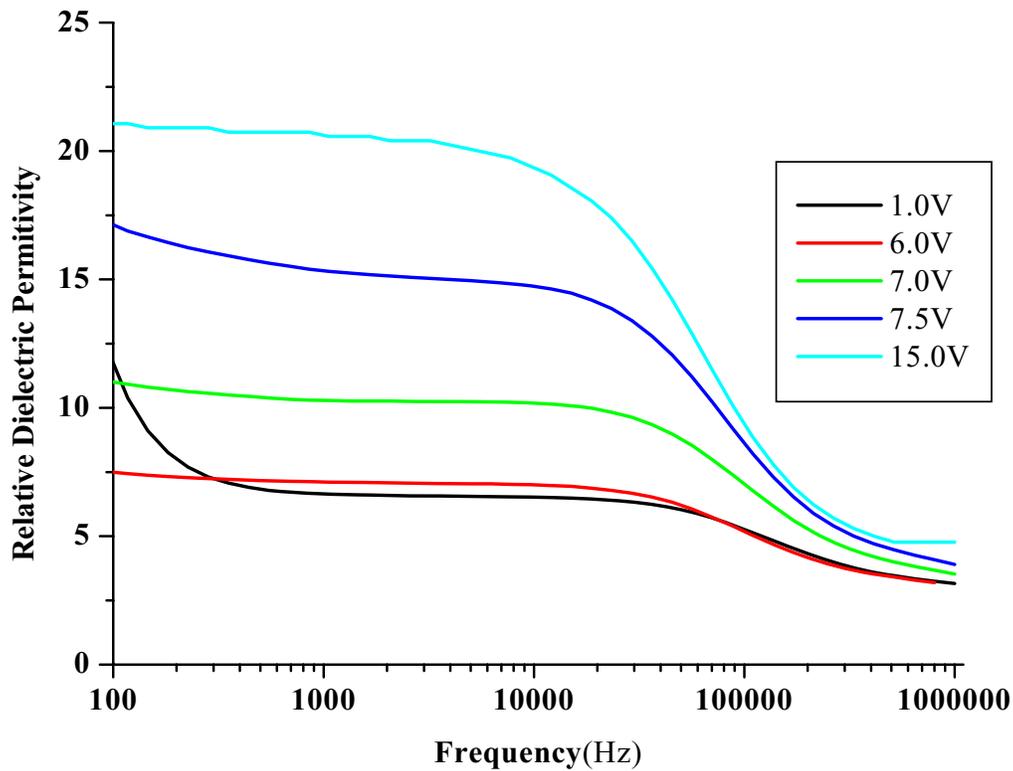


FIG. 4. Variation in relative dielectric permittivity with frequency at different voltages in pure NLC filled cell.

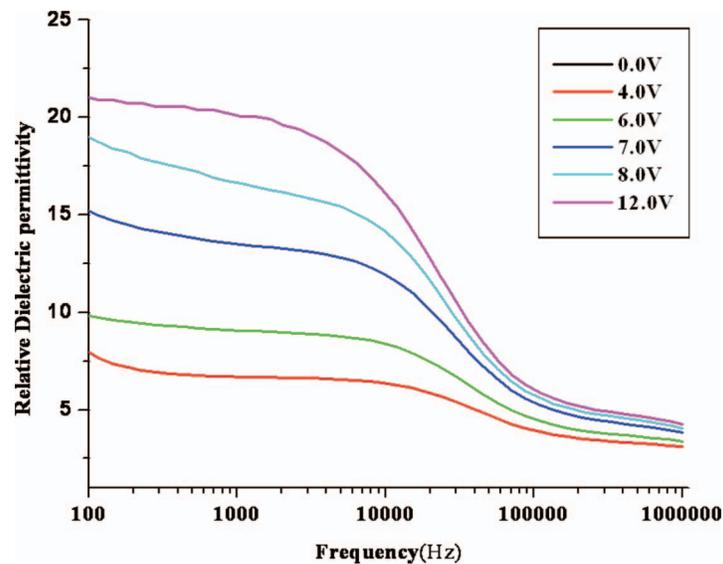


FIG. 5. Variation in relative dielectric permittivity with frequency at different voltages in GNP doped NLC filled cell.

Where $\omega_c = 1/\tau$ is the relaxation frequency for LC, which is the reciprocal of relaxation time.¹⁹ From Eq. (4b) it is clear that both real and imaginary parts of dielectric constant decreases rapidly at high frequency of applied AC field.

$$\tau = \frac{4\pi\eta V}{k_B T} \quad (5)$$

where ‘ η ’ is the viscosity of LC material, “ V ” is the molecular volume of LC material, k_B is the Boltzmann constant and T is absolute temperature. From Eq. (5) it is clear that relaxation time is proportional to viscosity, hence relaxation frequency is inversely proportional to viscosity of LC material. When GNPs are mixed with NLC material then the positive pole of NLC molecules are aligned toward the GNP (as shown in Fig. 3) due to local electric field generated because of the difference of relative permittivity’s of NLC material and GNPs. This tendency of LC molecules of aligning towards GNPs create resistance in rotation of LC molecules in presence of external applied electric field, which increases the rotational viscosity of LC molecules, and hence the relaxation frequency ω_c for LC molecules decreases. From Eq. (4b), it is clear that if ω_c is lesser then both real and imaginary parts of dielectric constant decreases at lower frequency (ω). This decrease in relaxation frequency has been observed experimentally as shown in Figs. 4 and 5. It is clear from Fig. 4 that, the relative dielectric permittivity of NLC starts to decrease at frequency more than 10^4 Hz of applied AC electric field for different value of applied voltage. In Fig. 5 the relative dielectric permittivity of GNPs doped NLC cell starts to decrease at frequency 3×10^3 Hz at different applied AC voltage.

IV. CONCLUSION

We have studied the effect of gold nano-particles on the switch-on voltage and relaxation frequency of NLC cell both experimentally and theoretically. It is concluded from above discussion that, if GNPs are induced in NLC material then it reduces the switch-on voltage of NLC cell, due to internal local electric field generated because of the relative permittivity differences of GNPs and NLC material. It was also found that the relaxation frequency of GNPs doped NLC is lower than that of pure NLC cell, and hence the relative dielectric permittivity starts decreasing at lower frequency of applied AC electric field. This means for GNPs doped NLC cell, the capacitor loses its charge storing capacity at lower frequency. Hence GNP doped NLC material filled cell can be used at lower voltages but cannot be used at higher frequency for using as capacitor (charge storing device).

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