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Review

Impact of Dispersion of Nanoscale Particles on the Properties of Nematic Liquid Crystals

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Abstract: This work reviews the recent progress made in last decade in understanding the role of dispersion of nanoparticles and quantum dots into host nematic liquid crystals. There are two important ingredients of this work: Even a minute concentration of these non-mesogenic materials in host matrix can have reflective impact on the dielectric, electro-optical, and spectroscopic properties of host nematics and the nematic-nanoparticles composite systems become suitable for the use in nematic based display and other devices.

Keywords: nematic liquid crystals; nanoparticles dispersion; quantum dots dispersion; dielectric permittivity; response time; threshold voltage

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1. Introduction

1.1. Scope of Paper

Liquid crystals (LCs)constitute a fascinating class of soft condensed matter characterized by the counter intuitive combination of fluidity and long-range order. They exhibit structural properties that are usually associated with solid crystalline state and isotropic liquid state. The study of liquid crystalline materials covers a wide area: Chemical structure and physical properties. They have been found suitable in various scientific, technological, and medicinal applications. In this area new science is being discovered and the possibilities of more applications are being explored. Despite the great advancements, the subject of liquid crystals continues to have a revolutionary technological impact and consistently poses new challenges of fundamental interest.

Liquid crystalline materials show interesting dielectric, electro-optical, and spectroscopic properties due to their large anisotropy coupled with the collective molecular reorientation. The required qualities for liquid crystal devices (LCDs), LC sensors, switches, and other devices are: Good contrast, low threshold voltage, ionic impurities free, defects free alignment, good luminescence, low power consumption, good brightness, high viewing angle, low response time, etc. However, often LC based devices suffer with the disadvantages: Black level is not proficient at producing black, contrast lower than Cathode Ray Tube (CRT), gray scale, high response time, low viewing angle, etc. For achieving the required qualities and removing disadvantages, in recent decades, the interest and emphasis on the science and technology of LC materials have shifted towards two main directions: (i) to synthesize new LC materials with specific characteristics and (ii) to make composite systems and tailor their properties by the dispersion/doping of non-mesogenic materials (dyes, polymers, or nanomaterials) into the host LC matrix so that the dispersed system becomes suitable for the applications.

The present article does not intend to present a comprehensive review covering all the developments of last few decades on the LC-nanoparticles (NPs) composite systems. We are selective and our discussion concentrates on the influence of dispersion of quantum dots (QDs) or NPs into host nematic liquid crystals on the dielectric and electro-optical parameters and some of the spectroscopic properties. It is important to mention here that the dispersion of QDs, NPs, or other kinds of nanoscale materials into LCs, in general, do not induce significant structural distortions of host LC phases. However, in case of hydrogen bonded liquid crystal nanocomposites, the influence of doping on the scalar order parameter has been shown [1]. Also the effect of aggregated NP on director orientation is sometimes mediated by the usually observed homeotropic alignment at the NP surfaces that tend to segregate into disclinations and interfaces.

1.2. Nanoscale Nonmesogenic Materials (Nanoparticles and Quantum Dots)

Nanoscale materials, NPs and QDs, constitute a major class of nanomaterials (NMs). The diameters of NPs vary between one to a few hundred nanometers. The QDs are semiconductor nanocrystals in which excitons are confined in three spatial dimensions and exhibit interesting phenomena, such as size dependent emission wavelength, narrow emission peak, and broad excitation range. NPs and QDs are of interest because at this scale unique properties are exhibited and these properties are both size and shape dependent. The main reason why materials at the nanoscale can have different properties is the increased surface area to volume ratio in comparison to their conventional forms. Usually, nanostructured materials are classified as zero-, one-, and two-dimensional nanostructures.

1.3. Citation of Work Done

In recent years, various kinds of nanoparticles [2–11] or quantum dots [12–17] have been dispersed/doped in the host nematic matrix and their properties have been investigated. Singh et al. [2] found that due to dispersion of silver nanoparticles (Ag NPs) (0.2 and 0.5 wt% concentrations) into nematic matrix 4-(trans-4-n-hexylcyclohexyl) isothio-cyanatobenzoate (6CHBT) the nematic-isotropic (NI) transition temperature (T_{NI}) and the conductivity anisotropy have increased whereas the threshold voltage (V_{th}) has decreased. The V_{th} is the minimum voltage required by the LC molecules to switch from homeotropic (dark) state to homogeneous (bright) state. Yadav et al. [3,4] have addressed the question how the dispersion of tin oxide (TiO_2) NPs in host nematic matrix 4-cyano-4′-n-pentylbiphenyl (5CB) influences the ionic behavior and the screening effect in nematic LC. These works have shown that the TiO_2 NPs serve the role of an effective absorber for ions. Pathak et al. [5] dispersed TiO_2 NPs in three nematic mixtures NLC2020 (consisting of 4′-alkyl-4-isothiocyanatotolanes and 4′-alkylphenyl-4-isothiocyanatotolanes) [6], NLC1823A (4-(4-trans,trans-cyclohexyl)-and 4-(trans,trans-bicyclofluoro benzenes and isothiocyanatobenzenes)) [7], and NLC1550C (4′-(trans, trans-4-alkylbicyclohexyl) carbonates and 4′-(trans,trans-alkyl)-4-alkenylbicyclohexane and 4′-(4-(trans, trans-4-propyl)-4-yanobicyclohexane)). They have found that the dispersion has led to increased values of birefringence in all the three dispersed systems which depend on the NPs concentration, temperature range, and the chemical nature of the mixtures. We noticed in a few other works [8–11] that the various properties of LC systems have been changed by the dispersion of NPs in LC matrix. Similarly, it has also been observed that due to the dispersion of specific quantum dots into nematic LCs the alignment of molecules, switching behavior, and dielectric and electro-optic parameters are influenced significantly showing the possibility of use of dispersed systems in nematic LC based devices [12–17].

The study of dielectric and electro-optical properties of dispersed systems obtained by the dispersion of magnetic NPs (MNPs) into nematic LCs has been found to be very interesting [18–20]. Godovinova et al. [18] measured the $T_{NI}$of nematic LC 6CHBT dispersed with spherical or calamitic MNPs and found that the ferronematics dispersed with rod-like MNPs have higher T_{NI} than the host nematic or ferronematics containing NPs of spherical shape. The iron oxide (Fe_2O_3) NPs coated with a monomolecular film of surfactant dodecyl-tromethyl ammonium bromide (DTAB) was synthesized by Malekiet al. [19] and dispersed in nematic LC N-(4-methoxy benzylidene)-4-butylaniline (MBBA). They studied the effect of NPs dispersion on the dielectric properties of pure and dispersed systems in planar and homeotropic alignments in the temperature interval of 298–322 K. The values of dielectric anisotropy and mean dielectric $(\overline{\epsilon})_{av}$ are considerablyhigher in the dispersed system and have shown exhibited strong dependence on the concentration of NPs. Large increase in the dielectric properties have been observed on increasing the NPs concentration from 1 to 10 wt%. Jamwalet al. [20] studied the effect of nickel oxide (NiO) NPs on the dielectric and electro-optical properties of nematic LC 5CB and observed that due to the presence of NiO NPs the values of dielectric permittivity (ε'), dielectric loss (ε'') and tan δ are decreased whereas the optical contrast has improved. The decrease of tan δ shows the low relaxation frequency of the ions. Interestingly, efforts have also been made [21–24] to analyze how the magnetic and electrical properties of a mixture of nematic LC and ferronematic can be modified under the magnetic field. The purpose of these studies is to increase the weak diamagnetic response of LCs that is related with a large magnetic threshold field (~1–10 KG). In the recent decade, transition metal ferrite NPs have attracted lot of attention due to their unique properties that make them suitable for the use in various fields like magnetic storage, ferrofluids, biomedicine, devices, catalysis, and magnetic refrigeration system [25–29]. Among these NPs, zinc ferrite ($ZnFe_2O_4$) both in micro- and nano-scales, has found wide applications in several areas. The $ZnFe_2O_4$NPs have high electric resistivity and low eddy current loss and very unique electrical, magnetic, thermal, optical, magneto-optical, magneto-resistive, and mechanical properties. These specific properties of $ZnFe_2O_4$ NPs suggest the very wide possibilities of their technological applications [25,26,30–32]. Therefore, in our understanding a composite material obtained by the dispersion of $ZnFe_2O_4$ MNPs in host LC matrix will be of wide interest in modifying the properties of host mesogen leading to its wide applications including LC based devices. As far as known to us, a comprehensive investigation on the $ZnFe_2O_4$ MNPs dispersed liquid crystal system has not been reported so far.

The understanding of interaction between QDs and LCs, in recent years, has emerged as the most challenging area leading to the controlled self-assembly of QDs and improved electro-optic characteristics of LCs [33]. The organization mechanism of QDs in an anisotropic LC medium has been studied by Hirstet al. [34]. They also considered the possibility of fabricating multifunctional switchable devices. The influence of QDs on the properties of nematic LC materials has been investigated by several groups [12–17,35–41]. Lee et al. [12] selectively controlled the orientation of LC molecules between the homogeneous and heterogeneous states without using the conventional alignment method and showed that QDs doped nematic LC 5CB exhibits superior electro-optic characteristics. For example, these authors [12] have observed a 37.1% reduction in threshold voltage and a 36.6% decrease in the response time for ECB-mode LCDs whereasa 47% reduction in threshold voltage and a 38.3% decrease in response time in VA-mode LCDs. Cho et al. [13] have shown that the dispersion of graphene QDs in nematicmesogen MAT-05-881 gives faster response time and reduced threshold voltage. Prodanov et al. [37] prepared a colloidal system using specially quoted QDs andcadmium selenide/zinc sulphide (CdSe)/ZnSQDs dispersed in the host nematic 5CB and showed that the luminescent nature of QDs provides an opportunity to visualize the degree to which aggregation of NPs occurs in the LC host. The CdSe QDs were dispersed in nematic4-pentylphenyl 4-octyloxybenzoate (4PP4OB) and studied the thermodynamic, dielectric, and electro-optical properties of composite. Tripathi et al. [16] dispersed the $Cd_{1-x}Zn_xS/ZnS$ QDs into nematic p-butoxybenzylidene-p-heptylaniline (BBHA) and studied the impact of QDs dispersion, applied bias, and QDs concentration on dielectric and electro-optical properties as a function of frequency and temperature for the planar alignment and have shown that these properties are influenced by the QDs dispersion. The same QDs were dispersed in nematic NLC2020 by Rastogi et al. [14] and the same properties of pristine and dispersed systems were investigated in planar as well as homeotropic alignments. They have found that the dispersed system gives results lead to the better performance of NLC based devices. In another paper [17] these authors have found a memory effect in the same dispersed system. Petrescu et al. [38] theoretically studied the dynamic behavior of CdSe/ZnS QDs dispersed in nematic 5CB under electric field and showed that due to dispersion of QDs the relaxation time is decreased as compared to pristine 5CB.

2. Dispersion of Nanoscale Materials in Nematic Liquid Crystals

First NPs of interest are dissolved in some suitable solvent (e.g., water, chloroform, and toluene) and stirred for some time to minimize agglomeration of NPs. Then a proper volume (0.1, 0.2, 0.5,

. . . , wt%) of solution of NPs is mixed with LC under investigation in a glass vessel. The resulting composite solution is stirred continuously and then sonicated for two hours. Proper dispersion of NPs in LC is confirmed by imaging it with apolarized optical microscope (POM). This uniform mixture usually shows no sign of flocculation over a period of several weeks. Flocculation is a process in which colloids come out of suspension in the form of flock or flake, either spontaneously or due to the addition of a clarifying agent. The glass vessel along with stirrer is placed in a fume hood, and the solvent is allowed to slowly evaporate at ~70 °C (say) and ambient pressure until the sample shows mass constancy. After the evaporation of solvent, the pure and NPs dispersed samples are filled in sample cells by capillary action at a temperature 5 °C above the isotropic temperature. Repeating this procedure NPs dispersed LC composites of several concentrations of NPs can be prepared. The filled sample cells are again heated to temperature slightly above the isotropic phase and the isothermal stage is maintained at this stage for a few minutes. The filled sample cells are gradually cooled up to room temperature with a very slow cooling rate. Now the pristine and NPs dispersed LC filled sample cells are ready for the characterization and measurement of different properties.

In case of QDs dispersion exactly similar procedure is adopted as discussed above except that in place of NPs now QDs are used.

3. Influence of Dispersion of Nanoscale Materials into Nematics on Their Properties

In this section, we are very selective in presenting the results on the NPs or QDs dispersed nematic LC. The results have been explained as far as possible. Only few selected papers in which some positive and noticeable contributions have been made will be discussed.

3.1. Dispersion of Nanoparticles in Nematics

The dielectric properties, voltage-assisted ion reduction, and nonlinear optical properties of pristine and diamond NPs [41], silica NPs [42], ZnO NPs [43], and Fe_3O_4 NPs [44] dispersed nematic mixture E7 systems have been studied in detail. Tomylko et al. [41] studied the frequency dependence of real ε' and imaginary ε'' parts of the complex dielectric constant, and the concentration (0, 0.25, 0.5, 1.0, 2.0 and 4.0 wt%) dependence of diamond NPs of dielectric constant and conductivity in pristine and NPs dispersed nematic E7.

Figure 1a,b show the dielectric spectra (ε' and ε'') for planar aligned layers of pristine and diamond NPs (DNPs) dispersed (2 wt% concentration) nematic E7. It is obvious that three parts of spectra can be distinguished. Part A refers to low-frequency (f < 10 Hz) relaxation, part B (f = $10 - 5 \times 10^3$ Hz) corresponds to the bulk properties of sample, e.g., the polarization and the charge transfer in the nematic phase and part C (f > 10^4 Hz) is due to the dipole relaxation associated with the rotations around the short molecular axis [45]. From a comparison of the pristine and DNPs dispersed nematic E7 systems it can be inferred that the curves of ε'(f) and ε''(f) shift to lower frequencies side indicating that the dispersion causes slowing down of relaxation processes. This means that the presence of DNPs impedes the rotation of nematic molecules and influences the ionic concentration. It can also be seen that an increase of ε' occurs in the entire frequency region. These authors [41] have also observed that the dielectric constant has strong dependence on the concentration of DNPs in nematic matrix. The ε' monotonically increase with the concentration of NPs in nematic sample. The NPs concentration dependence of conductivity σ of (a) pure nematic E7 and (b) impure nematic E7 is shown in Figure 2 at two temperatures 20 °C (curve 1) and 80 °C (curve 2) in planar-aligned samples. The conductivity has been determined, at f = 100 Hz, according to the relation,

$$\sigma = 2\pi f \epsilon_0 \epsilon''$$

where ε_0 is the electric constant. In curve 7(a) curve 2(a) monotonic growth is observed. At the initial stage growth is rapid which may be due to peculation process. With the homeotropic anchoring similar behavior is observed. Surprising results have been observed with impure E7 (Figure 2b) sample. In this case monotonic decrease of σ with NPs concentration is observed.

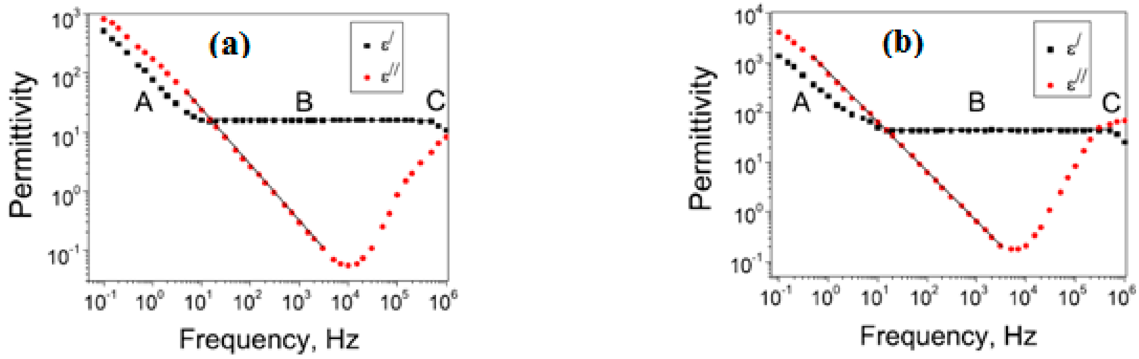

Figure 1. Variations of real (ε′) and imaginary (ε″) parts of complex dielectric constant at 20 °C for (**a**) pristine and (**b**) diamond nanoparticles (NPs) (2 wt%) dispersed nematic E7 [41].

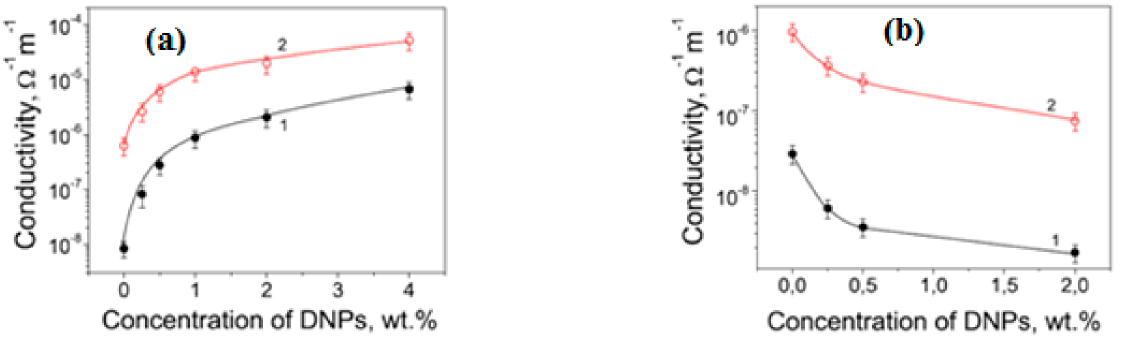

Figure 2. Variations of conductivity with concentration of diamond NPs dispersed (**a**) pure nematic E7 and (**b**) impure nematic E7. Curves 1 and 2 refer to the temperature 20 and 80 °C, respectively [41].

Liao [42] have analyzed the influence of silica NPs (SNPs) on the ionic properties of nematic E7 by employing an alternating-current high voltage pulse treatment (ACHVPT) method for reducing the amount of mobile ions in SNPs doped LC cells. It has been observed that after ACHVPT, the SNPs and mobile ions are absorbed onto the substrates, and thus the cell ion density is significantly decreased. The dielectric and optical properties of ZnO NPs dispersed nematic LC p-methoxybenzylidene p-ethylaniline (MBEA) have been studied by Tripathi et al. [43] and it has been shown that the ε′ in low frequency region is decreased, and also the amplitude of loss factor and activation energy are decreased due to NPs dispersion. This finding suggests that the dipole moment of NPs do not support the dipole moment of nematic molecules and interrupt the nematic ordering. The decrease in activation energy has been attributed to the asymmetrical potential barrier about to reorientational motion of nematic molecules. Iranizad et al. [44] synthesized the Fe_3O_4 NPs (average size ~ 20.7 nm) and characterized it with various techniques. The Fe_3O_4 NPs of various compositional percentages were dispersed in nematic E7. Nonlinearity of pristine and Fe_3O_4 NPs dispersed nematic E7 were investigated using close aperture and open aperture z-scan techniques. Figure 3 shows the results of close aperture (Figure 3a) and open aperture (Figure 3b) z-scane measurements. It has been observed that the close aperture (CA) z-scan is sensitive to both the nonlinear absorption and nonlinear refraction. The CA curve has been obtained after dividing the CA data by the open aperture (OA) data so that the contribution of nonlinear absorption can be eliminated (shown in Figure 3a). On choosing the focal plane as origin, it was observed that the beam is divergent corresponding to negative z values and convergent for positive z values. In case of OA z-scan (Figure 3b), the transmittance has been found to be insensitive to beam distortion and is only a function of nonlinear absorption.

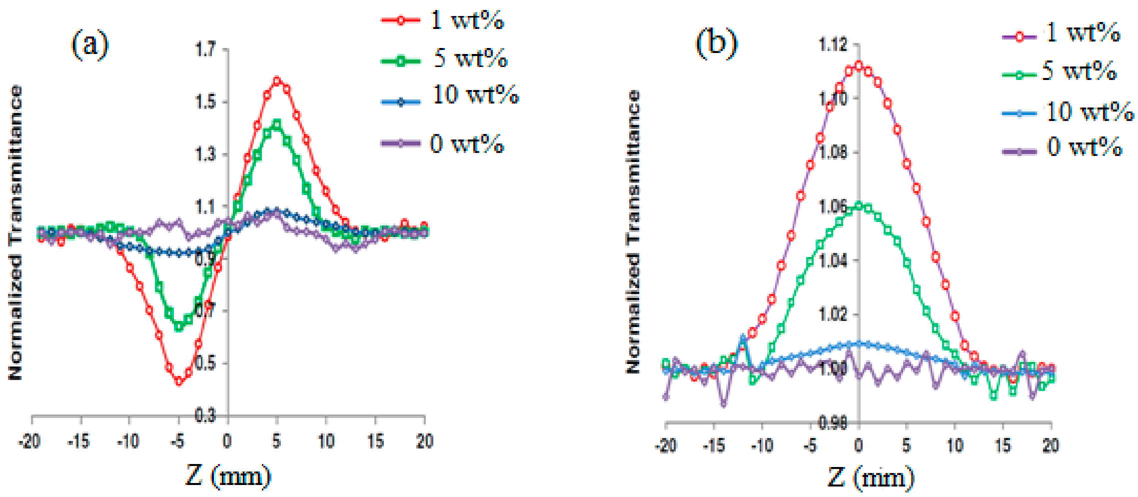

Figure 3. Curves of (**a**) close aperture and (**b**) open aperture of z-scan measurements of various concentrations of Fe_3O_4 NPs dispersed in nematic E7 at constant intensity [44].

Nematic LC 4-cyano-4′-pentylbiphenyl (5CB) is well studied mesogen. The effects of dispersion of TiO_2 NPs [3,4], CuS NPs [8], GNPs (gold) [46,47], and $BaTiO_3$ NPs [48] on the ionic behavior and screening effect, alignment and electro-optical properties, photoluminescence, and thermodynamic, optical and electrical properties have been studied extensively. In these works, different issues have been addressed. If same properties would have been investigated, questions regarding how various NPs influence the properties of a specific nematogen could have been answered. TiO_2 NP has shown potential application as an active component for different types of catalyst and photo-catalyst [49]. Yadav et al. [3] dispersed TiO_2 NPs of spherical size (<25 nm, with concentrations 0.1, 0.2, 0.5, 1.0 and 2.0 wt%) intonematic 5CB matrix and based on the Uemura model [50] explained the mechanism of ionic movement in the dispersed system. The optical texture was used to estimate the transition temperature. For the NPs concentration C_{NPs} < 2 wt% no change in the temperature range and transition temperature was found. At C_{NPs} = 2 wt% the transition temperature shifts towards lower temperature side by 1 °C. For the $C_{NPs} \geq 0.5$ wt% some small bright patches were observed and the entire region was captured by these bright patches at C_{NPs} = 2 wt%. So the 0.5 wt% dispersion of NPs was taken as the percolation threshold in nematic 5CB.

The variations of dielectric loss ε″, for the planar alignment geometry, with frequency for different concentrations of TiO_2 NPs dispersed in 5CB at a fixed temperature 30 °C are shown in Figure 4 in two frequency regions: (a) 100 Hz to 100 KHz and (b) 100KHz to 40 MHz. In the low frequency region, the ionic contribution to relaxation is obvious and the effect of space charge polarization is seen. In the frequency range 100 Hz to 10 MHz two relaxation phenomena in pristine and NPs dispersed nematic 5CB were easily observed which were attributed to the molecular reorientation process about short axis. It can also be seen that ε″ initially increases for 0.1 and 0.2 wt% dispersion of NPs and then decreases with further dispersion of NPs that point out towards the lower diffusion of ions. In this work [3] the ion concentration, diffusion constants, threshold voltage, activation energy and DC conductivity as a function of concentration of NPS have also been measured and following conclusions have been drawn: The ion density initially increases up to 0.2 wt% and then rapidly decreases and finally is saturated after 1 wt% loading of NPs. The threshold voltage and diffusion coefficient initially increases up to C_{NPs} = 0.2 wt% and then decreases with further dispersion of NPs. The initial increase of diffusion coefficient in suspension may be caused due to the lower value of activation energy in the composite sample. The activation energy decreases with the increasing concentration of NPs and interestingly it is lower in comparison to pristine nematic. This behavior may be due to lower value of activation energy which facilitates the easy movement of ions and so increases the conductivity and diffusion. The DC conductivity follows the trend of ion density. The lower DC conductivity for C_{NPs} > 0.5 wt% can be attributed to the restricted or hindered motion of ions. In another work [4], it has been seen that

AC conductivity initially increases up to C_{NPs} = 0.2 wt% and then decreases and finally is saturated for C_{NPs} > 1 wt% dispersion of NPs. The optical transmittance measurement shows that the relaxation processes are faster than in the host materials when the field is switched off. The faster relaxation in the NPs dispersed system has been attributed to the decrease in rotational viscosity and suppressed screening effect. The suppression of screening effect may be due to the trapping of the ion impurities on the surface of NPs. In Figure 5a,b these authors [4] have shown a schematic representation of ion impurities trapping mechanism. In the pristine sample some ions are attached to the alignment layer and some are free to move inside the host matrix. When NPs is dispersed these ions (free as well as bound) are get attached to the exposed NPs surface. Thus, NPs effectively play the role of reducing number density of ions and thereby the conductivity is further decreased and the screening effect is suppressed.

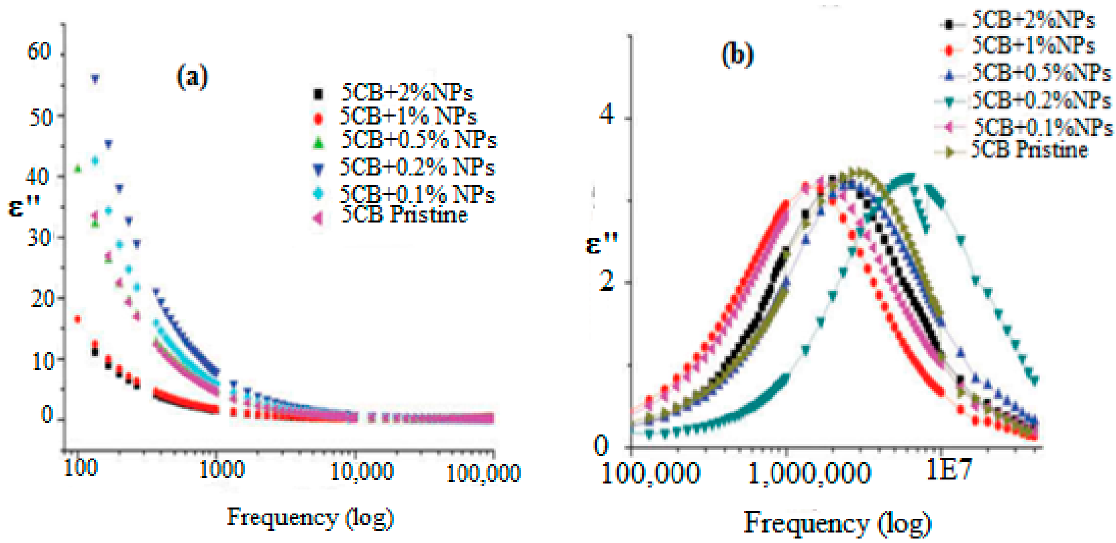

Figure 4. Dielectric losses ε″ as a function of frequency (in Hz) for various concentrations of NPs at 30 °C (**a**) frequency range 100 Hz–100 KHz and (**b**) frequency range 100 KHz–40 MHz [3].

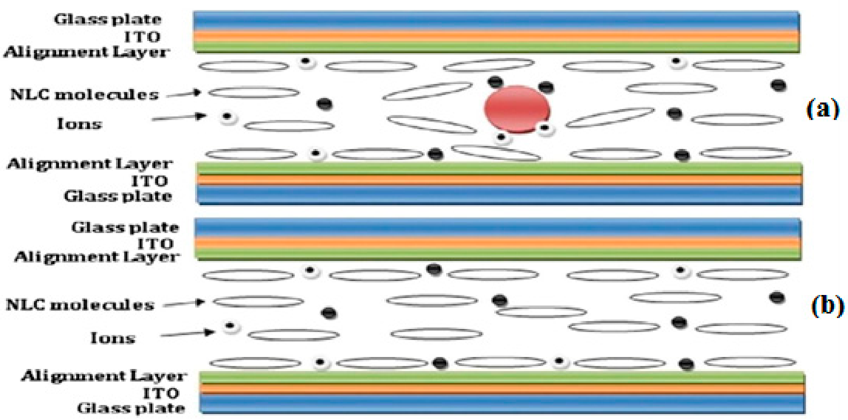

Figure 5. Schematic representations of ions impurities trapping mechanism, (**a**) in the presence and (**b**) in the absence of NPs. White circles with black spot represent the positive ions, black spots the negative ions and big red circle the NPs [4].

Copper sulphide (CuS) is a p-type semiconductor sulphide. It exhibits a bulk band gap of 1.2–2.0 ev in essence. CuS NPs is non-toxic and low-cost NMs and demonstrate remarkable morphology dependent electro-optical properties. These NPs have high conductivity and capacitance. Motivated from these properties of CuS NPs, Liu et al. [8] synthesized CuS NPs with flower-like and frame morphologies and dispersed these NPs (0.01, 0.03, 0.05, 0.07, and 0.1 wt% concentration) in nematic

5CB. The morphology and concentration dependent alignment and electro-optic effects of dispersed composite system were studied. It has been found that the orientational behavior and electro-optic properties of nematic 5CB are strongly dependent on morphology and concentration of CuS NPs. The presence of a small trace of flower-like NPs (0.05 wt%) has induced a uniform homeotropic orientation of nematic molecules and a remarkable improvement in the electro-optic properties has been found and thus CuS/5CB system will exhibit a better performance. The NPs dispersed in nematic host has trapped impurity ions, suppressed the shielding effect and strengthened the electric field leading to reduced V_{th} and saturation voltage (V_{sat}), an increased ratio of the maximum light transmittance to the minimum light transmittance (Con)and a faster response. This clearly indicates that CuS/5CB composite system is suitable for the applications in flexible nematic LC displays.

Zhang et al. [46] dispersed gold nanoparticles (GNPs) in nematic 5CB and showed the alignment, switching, and assembly of anisotropic calamitic and platelet shaped NPs. The composite NRs/5CB presents the first example of electrically switchable colloidal plasmonic color filters with negative scalar order parameter of NRs. The NRs can be organized at the nanoscale either as individual NPs or as chain-like self-assembled nanostructures. Chang et al. [47] investigated the photoluminescence (PL) in the GNPs dispersed homogeneous planar nematic 5CB. With a suitable amount of NPs dispersion around 64% increase in PL intensity was observed, which may be due to the increased surface area from GNPs. Further, it was found that the peak intensity of PL emission was stronger for the 13 nm gold particles at the same concentration of gold nanoparticles. This was attributed to the fact that smaller NPs have larger surface area, which causes multiple reflection and scattering of the excitons. Mishra et al. [48] dispersed ferroelectric $BaTiO_3$ NPs in nematic 5CB and studied the properties of pure nematic and dispersed systems using DSC, UV-Vis spectroscopy, polarized light microscopy, dielectric spectroscopy, and electro-optical techniques. It was observed that the effects of $BaTiO_3$ NPs dispersion in nematic host on the thermodynamic, optical, electrical, and electro-optical properties are highly dependent on the concentration of NPs in host matrix. The dispersion at low concentrations is uniform but at higher concentration demonstrates aggregation. A remarkable change in the values of V_{th}, K_{11}, $\Delta\varepsilon$ and σ_{ion} was observed at the low NPs concentration (<1 wt%) whereas for the higher NPs concentration (>1 wt%) the change is small.

3.2. Dispersion of Quantum Dots in Nematics

One of the most important technical challenges in fabricating the high quality LCDs is the uniform alignment of LC molecules in a preferred orientation. Commercially, mechanical rubbing of spin quoted polyimide layers is used to provide topographical microgrooves for achieving the uniaxial homogeneous or homeotropic alignment of LC molecules. This method suffers with some crucial drawbacks such as the introduction of dust particles and the creation of electrostatic charges that arise due to the friction between the rubbing roller and the substrate. A number of noncontact methods have been developed to remove the shortcomings of rubbing.

Prodanov et al. [37] addressed the question how the aggregation of NPs in LCs can be minimized. For this purpose, surfactants were used to coat the NPs surface. It is believed that the role of surfactant is to increase the excluded volume of the nanoparticles and to smooth out the disturbance of the local director of LC. However, how the surfactant structure influences the stability of colloids on LCs has not been studied extensively. These authors [37] have shown that it is critical to optimize the interaction between the molecules of LC matrix and surface coating of the NPs for avoiding aggregation of NPs and thus making truly stable colloidal systems. Such colloidal systems were achieved by dispersing coated CdSe/ZnS QDs in nematic 5CB. Two kinds of QDs were synthesized [39]: Green emitting quantum dots, QD_1, (minimum of photoluminescence at λ_{em} = 530 nm, quantum yield $\eta_{em} \cong 30\%$) and yellow emitting quantum dots, QD_2, (λ_{em} = 573 nm, $\eta_{em} \cong 17\%$). Next two types of alkyl phosphonic surfactants, 1-hexylphosphonic acid and 1-hexadecylphosphonic acid, were used to change the density of surfactants one and two on the surface of the NPs. Figure 6 shows the schematic representation of fabricated NPs where the first number in the abbreviation denotes the type of QD employed, and the second and third numbers denote the kind of ligand used. The results obtained from transmission electron microscopy, fluorescence and polarized optical microscopy, optical spectroscopy, and fluorescent correlation spectroscopy confirm that CdSe/ZnS QDs coated with specifically designed surfactants were dispersed in nematic 5CB and form stable colloids. Further, it was found [37] that coating of QDs with the mixture of long-length dendrite promesogenic surfactant and the short length aliphatic cosurfactant makes a true colloid of the QDs in a nematic 5CB.

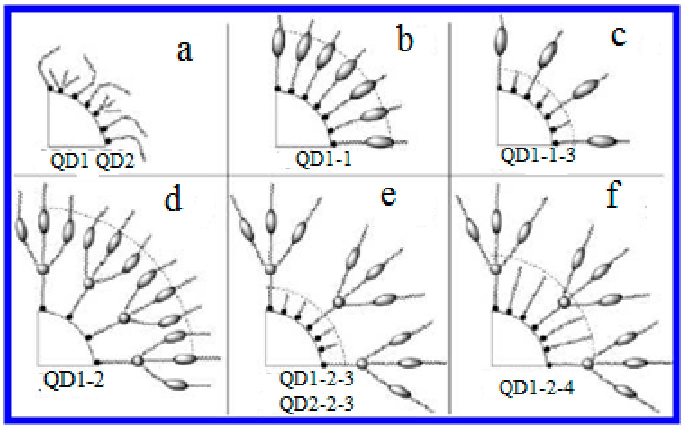

Figure 6. Schematic representation of the quantum dots (QDs) grafted with the surfactants; (**a**) native surfactant and (**b**–**f**) the new surfactants. The dotted lines indicate a possible depth of penetration of 4-cyano-4′-n-pentylbiphenyl (5CB) molecules into the QDs shell [37].

Graphene has been utilized in large number of applications because of its exceptional physical, chemical and mechanical properties. Cho et.al [13] explored the possibility of applying ZnO-graphene QDs in an LCD. It has been shown [13] that the doping of ZnO-graphene QDs into nematic MAT-05-881 gives improved electro-optic properties, e.g., faster response time and a decreased threshold voltage. The QDs were synthesized using the method discussed by Son et al. [40]. First, using powdered flake graphite combined with a mixture of sulfuric acid and nitric acid the graphite oxide (GO) was synthesized. Next, GO and zinc acetate dihydrate were mixed in dimethyl form amide (DMF). This solution was heated at 95 °C for 4 h and then was washed with ethanol and deionized water by centrifugation. For obtaining powder form of ZnO-grapheme QDs the solution was dried at 55 °C. The average diameter of QDs is ~30 nm. The ZnO-graphene QDs were dispersed in nematic LC (NLC) by employing usual method. The morphology of dispersed system obtained via TEM images clearly shows that the QDs are well dispersed in nematic medium [13]. The measured pretilt angle was found to be approximately the same for both the pristine and QDs dispersed nematic samples. Figure 7 shows the POM images of conventional nematic cell and the cell with the doped QD-NLC composite [13]. A comparison of Figure 7a–d show that the QDs doped nematic exhibits good alignment as that of pristine nematic. In this work, results of measurements of electro-optical characteristics, transmittance as a function of wavelength, time and voltage are also reported. It has been observed that the doping of QDs into the NLC leads to faster response time and a lower threshold voltage probably due to trapping of impurity ions. As a consequence, it is claimed that the field-screening effect that is caused by impurity ions can be reduced.

Singh et al. [15] dispersed CdSe-QDs (size ~ 3.5 nm) into NLC 4-pentylphenyl 4-octyloxybenzoate (4PP4OB) and studied the impact of QDs dispersion (0.01 wt%) on the thermodynamic, dielectric and electro-optical properties and display parameters. In a cooling cycle the nematic and dispersed samples exhibit the phase sequence:

$$\text{Pure 4PP4OB: IL}-65\ ^\circ\text{C}-\text{N}-55\ ^\circ\text{C}-\text{Sm A}-30\ ^\circ\text{C}-\text{Cr}$$

$$\text{4PP4OB + CdSe QDs: IL}-64.5\ ^\circ\text{C}-\text{N}-54.5^\circ\text{C}-\text{Sm A}-33.5\ ^\circ\text{C}-\text{Cr.}$$

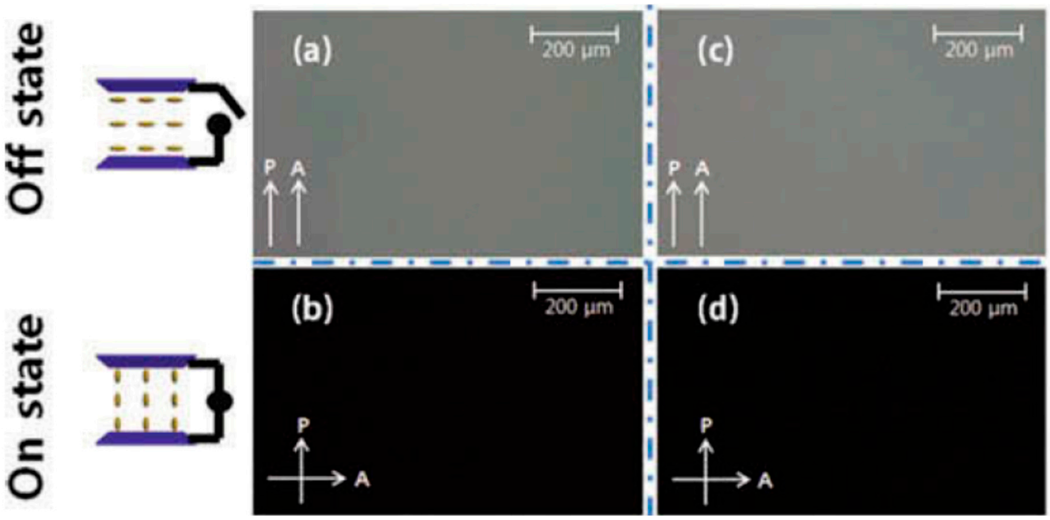

Figure 7. Polarized optical microscope (POM) images of a conventional nematic cell and a cell with the doped QD-nematic liquid crystal (NLC) composite. The images (**a**) off state and (**b**) on state correspond to pure nematic whereas (**c**) off state and (**d**) on state to the QDs doped nematic [13].

It can be seen that the IL−N and N−Sm A transition temperatures are lowered by ~ 5 °C due to dispersion of NPs. It has been found that due to dispersion of QDs in host nematic the values of ($\Delta\varepsilon$) and relaxation frequency (f_R) have increased whereas the values of switching V_{th}, splay elastic constant (K_{11}) have decreased. However, for the confirmation of these findings studies should be performed for the dispersion of few more concentration of QDs into host nematic matrix. The f_R is the frequency at which the dielectric loss factor of a dielectric material which has no static conductivity (DC) reaches a maximum value when it is subjected to an alternating electromagnetic field whereas the K_{11} characterizes the free-energy increase associated with the splay mode of deformation of the equilibrium configuration of nematic state. In other words, K_{11} measures the extra energy needed to create the splay distortion in equilibrium uniaxial nematic structure.

$Cd_{1-x}Zn_xS/ZnS$ QDs were dispersed into nematic LCs BBHA by Tripathi et al. [16] and NLC2020 by Rastogi et al. [14]. Tripathi et al. [16] measured the dielectric and electro-optical parameters as a function of QDs concentration (0.5 and 1 wt%), temperature and applied bias of pristine and QDs dispersed nematic BBHA in planar alignment whereas Rastogi et al. [14] studied these parameters as a function of same variables for the pure and QDs (0.1 and 0.25 wt% concentration) dispersed nematic NLC2020 in planar as well as homeotropic alignments. In another work, Rastogi et al. [17] addressed the question how the memory effect is influenced by the QDs dispersion in NLC2020. Figure 8 shows the variation of dielectric permittivity and dielectric loss at fixed temperature 70 °C as a function of frequency, applied bias and QDs concentration for both the pure and QDs dispersed nematic BBHA for the planar aligned cells. It is obvious from the Figure 8a,b that below the relaxation frequency, the values of ε' are higher in both cases without bias and with bias in comparison to dispersed systems. For the pristine nematic ε' does not depend upon frequency up to a critical value 8×10^5 Hz under no bias and 6×10^5 Hz under bias and then decreases rapidly with frequency. The impact of QDs concentration is apparent above the relaxation frequency. In case of dielectric loss ε'' it is seen that for pristine nematic the influence of applied bias up to 10 V is not noticeable. For both the cases without and with bias voltages the relaxation frequency of the dispersed system is increased for the QDs concentration 0.5 wt%. The relaxation frequency shifts towards higher frequency side as the QDs concentration in nematic increases. In the low frequency region, the application of voltage suppresses the ionic effect in both the pure and dispersed systems.

The temperature and QDs concentration dependence of rise time (τ_{on}) and fall time (τ_{off}) at fixed applied voltage can be seen in Figure 9. The rise time is the time required for the transmittance to rise from 10 to 90% whereas the fall time is the time required for the transmittance to fall from

90 to 10%. It can be seen from the Figure 4 that the τ_{on} decreases with temperature whereas τ_{off} increases. The decrease in τ_{on} with temperature is more rapid for higher QDs concentration (1.0 wt%) of dispersion in comparison to low concentration (0.5 wt%) dispersion. Similarly, under applied bias, at fixed temperature, τ_{on} decreases and τ_{off} increases rapidly with the increase of applied DC voltage for both the pristine and dispersed systems. These observations show that the dispersion of QDs in host nematic is of advantage from the point of view of applications in NLC based devices.

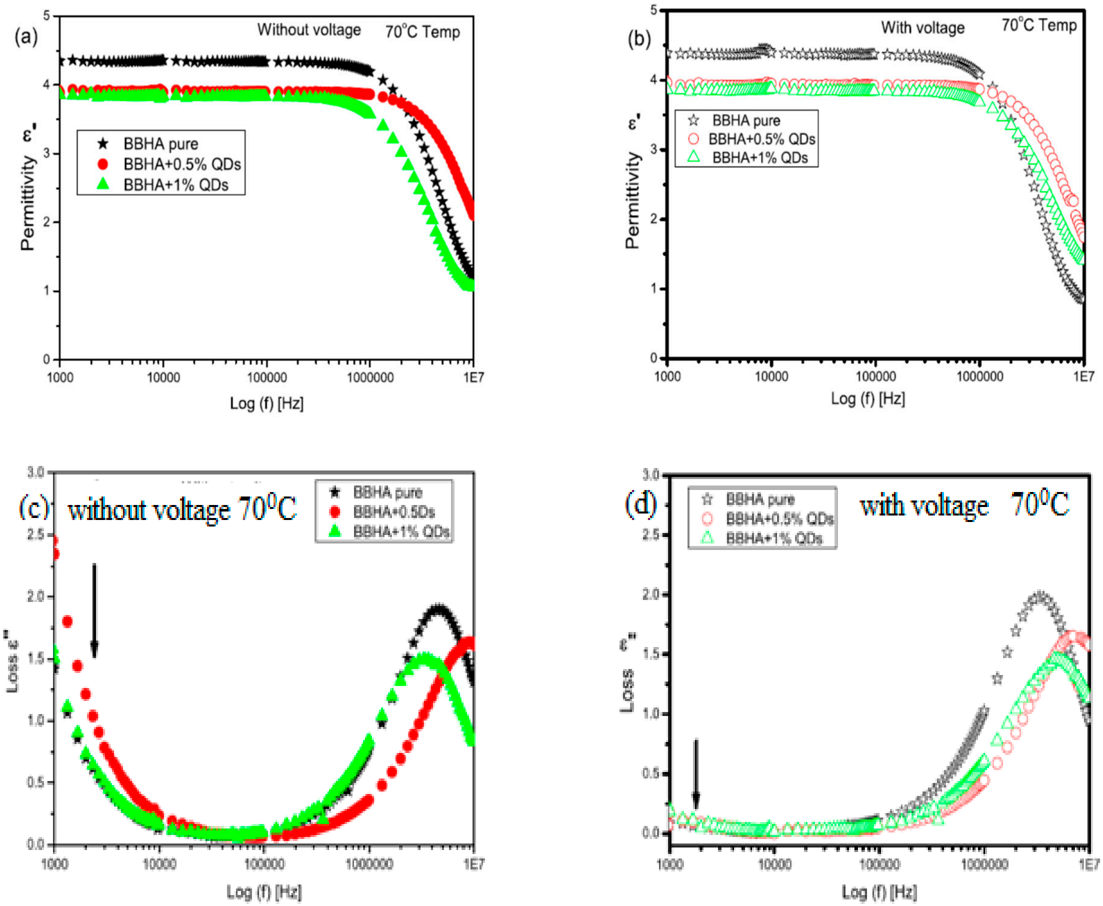

Figure 8. Variation of dielectric permittivity (**a**,**b**) and dielectric loss (**c**,**d**) of pristine and QDs (size 8.2 nm) dispersed nematic BBHA at fixed temperature 70 °C as a function of frequency, applied bias, and QDs concentrations for the planar aligned cells [16].

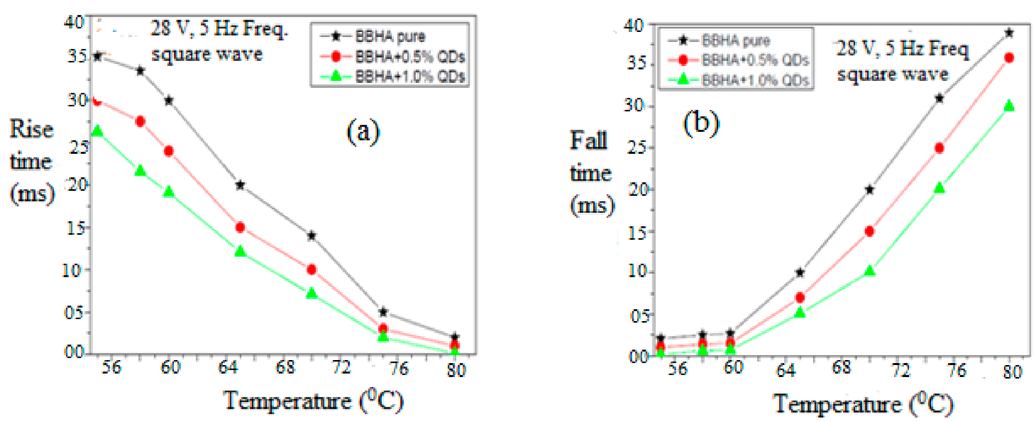

Figure 9. Variation of (**a**) rise time and (**b**) fall time of pristine and QDs (size 8.2 nm) dispersed nematic BBHA at fixed applied voltage with temperature and QDs concentration [16].

Rastogi et al. [14] measured the dielectric permittivity, dielectric anisotropy, dielectric loss, total power loss, specific power loss, rotational viscosity, response time, viscoelastic coefficient, birefringence and figure-of-merit of pristine and $Cd_{1-x}Zn_xS/ZnS$ core/shell QDs dispersed nematic NLC2020. In Figure 10 the variation of relative permittivity and dielectric loss of pristine and QDs dispersed nematic NLC2020 is shown. It can be seen (Figure 10a) that the value of relative permittivity is higher for 0.25 wt% QDs concentration while for 0.1 wt% concentration its value is lower as compared to pristine nematic. The value of parallel component of permittivity (ε_{II}) remains constant in the frequency region 300 Hz to 2.1×10^4 Hz and decreases rapidly above the frequency 6.0×10^4 Hz. Figure 10 b shows that the perpendicular component of permittivity ($\varepsilon_{\perp}$) decreases in low frequency regime, remains constant in the frequency region 1 kHz to 7.37×10^4 Hz, and decreases rapidly above the frequency 9×10^4 Hz. In low frequency regime the decrement is due to ionic polarization and in the high frequency is because of relaxation phenomenon. Under applied field pronounced increment is observed. It is obvious from Figure 10 c,d that pronounced influence of the electric field on the dielectric loss is found. This is due to suppression of ionic effect. Further, faster electro-optical response, total power loss, and specific power loss along with high figure-of-merit are the important results of this work [14]. The response time, rotational viscosity, and viscoelastic coefficient depends on the concentration of QDs. In another work, Rastogi et al. [17] have shown that the dispersion of $Cd_{1-x}Zn_xS/ZnS$ QDs in nematic NLC2020 plays an important role in enhancing the memory parameter by capturing and releasing the ionic charges in the presence of applied voltage. This has been confirmed from the capacitance-voltage curve.

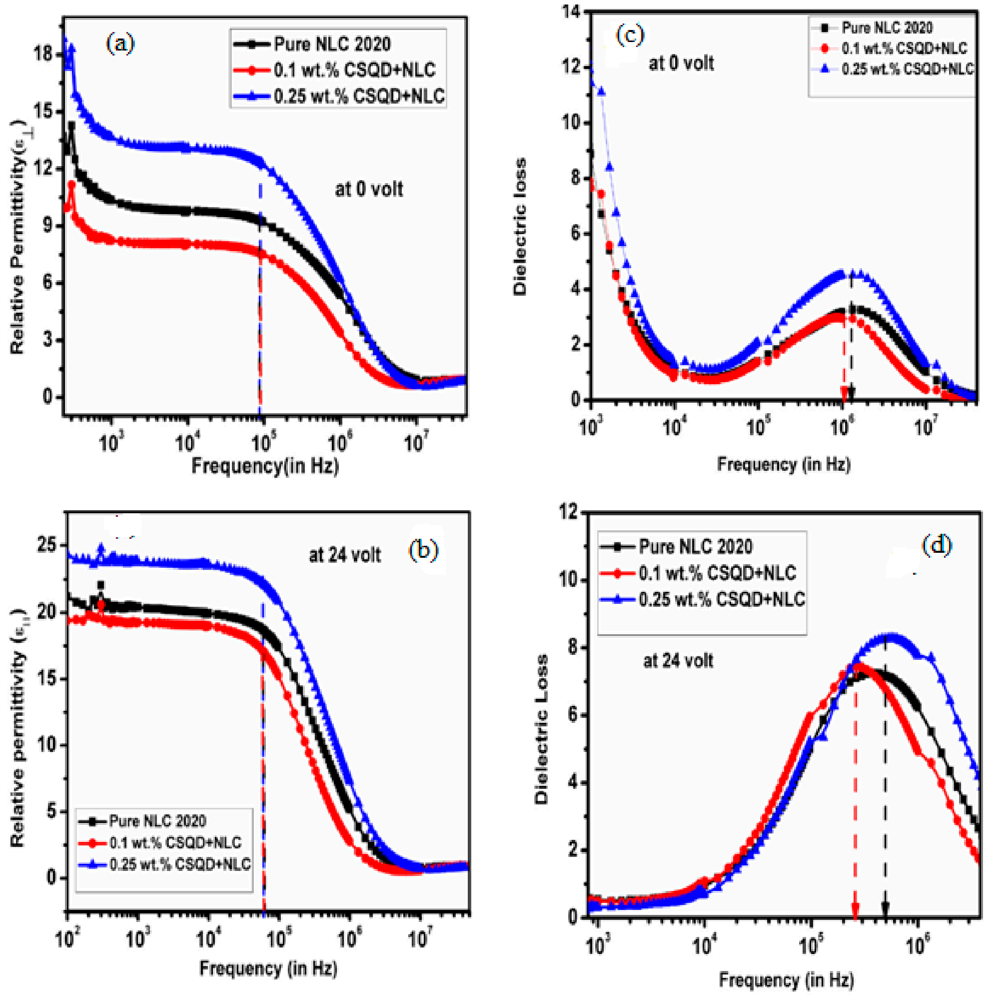

Figure 10. Variationof relative permittivity (**a**,**b**) and dielectric loss (**c**,**d**) at fixed temperature without bias (0 V) and with bias (24 V) of pristine and $Cd_{1-x}Zn_xS/ZnS$ QDs dispersed nematic NLC2020 [14].

4. Conclusion and Future Perspectives

During last few decades, it has been established that adding NMs (metallic and non-metallic) into nematic LCs has led to the increase in the dielectric, electro-optical and other parameters of NLCs, such as reduced threshold of operating voltage, variation in pretilt angle, and reduced switching time. The change in these and other parameters of NLCs by the addition of NMs has been attributed to the rearrangement of the NLC molecules around the NMs (QDs and NPs in this case). The present work is not intended to present a full overview of wide rich work on dispersion of QDs or NPs into NLCs as these may be found in nice reviews given elsewhere [51–55]. Based on the few recent and important works, we have made an attempt to address the question how the dispersion of quantum dots or nanoparticles in pristine nematic LC geometry influences the properties of NLC material to make the composite system suitable for various applications. It is important to mention that the basic understanding about the structure and properties of these systems is very poor. To the best of our knowledge there exist no microscopic theory and so option is to arrest the characteristic features of these properties by constructing Landau-de-Gennes type free-energy density expansion and understand the role of various degrees of freedom. The article is concluded with the list of a number of problems which are to be addressed and explored.

In recent years, from the point of view of applications emphasis has been given to modify the mesogenic materials with specific properties rather than to synthesize new materials. For developing more effective procedure for this purpose, the understanding at the basic level about the role of dispersed materials into LCs matrix is very essential. This requires sufficient experimental results under various conditions. So the main focus at present must be to generate experimental results on the thermal, morphological, dielectric, electro-optical, magnetic, and other properties of pure LCs and its dispersed/doped counterparts, that is, systems obtained by the dispersion/doping of dyes or polymers or nanomaterials of various sizes and shapes into achiral nematics, ferroelectric LCs, anti-ferroelectric LCs, and bent-core LCs geometries. However, it is important to emphasize that in many cases the measurements are very difficult to carry out.

Recently, the applications of modified liquid crystalline materials have been considered in the display industry for achieving better performance of devices. In this direction, in addition to nanomaterials or dyes dispersed LC materials, the polymer stabilized liquid crystal (PSLC) system has also shown potential of applications in the area of optoelectronics and photo-electronics. In the industrial applications the electro-optical response of the LC molecules, under the influence of electric field, is one of the major characteristics to be utilized. Few key aspects for the evaluation of LC display performance to the electric field are dielectric anisotropy, optical anisotropy, response time, threshold voltage, rotational viscosity, elastic constants, and birefringence. From the purpose of basic understanding and applications such measurements are required for a variety of PSLC systems.

Developing basic understanding about the role of dispersed materials into host LC matrix is very crucial for making better and better composite materials with desired properties and that is the real challenge of today.

Many aspects of QDs and NPs such as the formation, role of capping, uniform dispersion into LCs, tuning of NMs properties by LCs, and vice versa are moderately covered in this article. LCs are recognized as one of the best surrounding mediums for NMs, because the dielectric constant of LCs can be easily changed by the external electric field as compared to other dielectrics. The alignment of LC molecules around NMs also provides a good platform to understand the dynamics of interaction between NMs and LC molecules and hence the affected properties, finally leading to ordering of NMs and applications. Such interactions are found to be much more easily explained in NLCs due to their simple structural feature, unlike smectic liquid crystals. However, results in NMs-dispersed smectic liquid crystals are quite interesting but less understood and hence further crucial research is needed.

Even though the list of questions provided here are very limited, the investigations on the dispersion/doping of nanomaterials, polymers, and dyes in liquid crystalline materials are already an extremely active field. Instead of synthesizing new mesogens with specific properties, it is advisable to modify the properties of known mesogens by employing the route of above mentioned dispersions. One can be sure that incoming years, there is still much more to come. So it can be hoped that the field will grow very actively both in the direction of basic research and applications.

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