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Advances in gold nanoparticle-liquid crystal composites

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REVIEW

Advances in gold nanoparticle-liquid crystal composites

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We present the advancement in the research of gold nanoparticles (GNPs) dispersion in thermotropic calamitic liquid crystals. The formation/behavior of surface plasmon resonance (SPR) in GNPs is briefly described. The uniform dispersion of GNPs into liquid crystals along with two important aspects i.e. tuning of GNP properties by liquid crystal and vice-versa are widely discussed. Overall, the article highlights the advances in the research of GNP-liquid crystal composites in terms of their scientific and technological aspects.

A. Introduction

Over the past few decades, the research on nanomaterials has greatly influenced the emerging field of nanoscience and nanotechnology. The huge impact of nanomaterials in present day technology is solely based on their size-dependent electronic, optical, magnetic, and chemical properties. Under this framework, micro/nano scale colloids dispersed in liquid crystals (LCs) research[1,2,3] has facilitated enormous interest, due to their potential scientific and technological relevance. LCs are the best examples of anisotropic fluids and proven to be an appropriate medium to study the interaction among colloidal particles and LCs. Several theoretical and experimental investigations on colloidal particles dispersed in LCs are carried out; wherein shape/size of colloids and self-assembling nature of LCs are widely taken into considerations.[4-20] The topological defects (Saturn rings, hedgehog, and boojums) are produced due to the elastic deformation of LC by dispersed colloidal particles, which further mediate the long range anisotropic interaction among colloids leading to their controlled organization in LC matrix. Furthermore, the formation of topological defects also provides a platform to better understand the dynamics of alignment of LC molecules in the vicinity of colloidal particles.

More importantly, the multibillion dollar LC technology has recently tied up with nanotechnology to modify the physical properties of LCs through nanomaterials and vice-versa. For example, the use of metal nanoparticles (MNPs) to tailor LCs properties[21-30] and LCs to tune MNPs properties[31-37] has opened several avenues for these LC-MNP composites to be utilized into several opto-electronic devices. Among all MNPs, GNPs dispersed in LCs are widely studied and found pivotal for technological applications. In this article, we review (a) SPR formation/ behaviour in GNPs, and (b) GNP-LC nanocomposites: tuning physical features of GNPs by using LCs and vice-versa.

B. SPR in GNPs

GNPs show size-dependent electronic, optical and chemical properties due to the quantum confinement of free electrons, unlike bulk Au metal. The utmost absorption of visible light by GNP shows that there is a collective oscillation of free electrons, due to strong interactions of incident electromagnetic field with free electrons cloud at the surface of GNP (Fig.1). Such collective oscillation of free electrons is termed as surface plasmon resonance (SPR) and depends on the size, shape, and dielectric constant of GNP as well as surrounding medium such as water, alcohol, and etc.[38-43] In case of spherical GNPs, only pure dipolar resonance couples to the incident electromagnetic field, and depolarization factor (α) is 1/3. This value of α actually provides the well-known condition that a surface plasmon occurs at $\varepsilon(\lambda)=-2\varepsilon_m$,[44] where $\varepsilon(\lambda)$ is the dielectric constant of GNP at a wavelength λ and ε_m is the magnitude of dielectric constant of materials in which GNPs are embedded (i.e. surrounding medium).
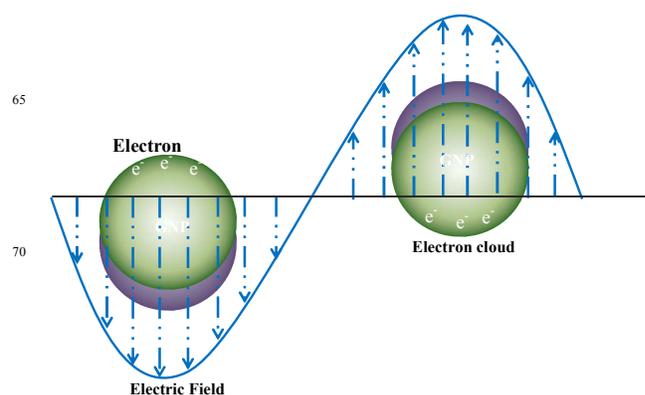
Fig. 1 Schematic representation of surface plasmon resonance where the free conduction electrons in GNP are driven into oscillation due to strong coupling with incident light.

The SPR peak also depends on interparticle spacing (i.e. centre to centre spacing) of GNPs.[45-47] The wavelength-dependent scattering intensity at various centre-centre spacing (Fig. 2a) and peak shift dependent spacing of variable shaped particles (Fig. 2b) show that after certain spacing, the coupling breaks and peak shift becomes independent of the effect of neighbouring nanoparticles.[48] In other words, the near field coupling becomes no longer effective after certain spacing value (Fig. 2b). However, the extinction coefficient mainly depends on particle shape rather than inter-particle spacing.[42,49] Moreover, the

resonance peak is also affected by the surface of the substrate on which they are placed[44,50]. Interestingly, theoretical and experimental studies reported the creation of holes on Si-substrate, wherein GNPs are placed, due to the presence of very intense near field around them. The shape of generated hole also depends on polarization of incident radiations.[50]
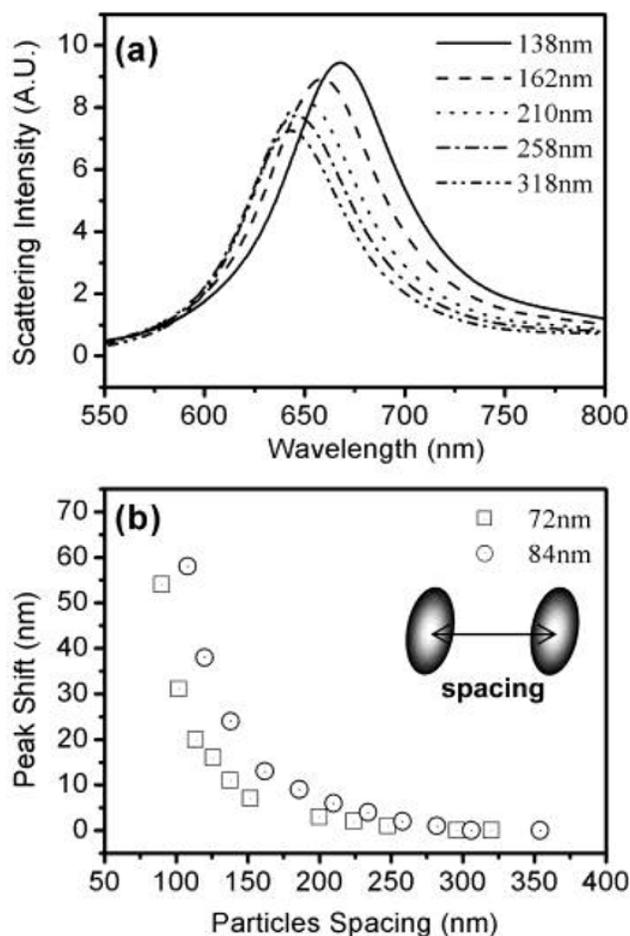
Overall, the SPR formation in GNPs leads to their numerous applications such as integrated optics, scanning near field optical microscopy, biological labelling, and biosensors.[51,52].

C. Gold nanoparticle-liquid crystal composites

The GNP-LC composites are usually prepared by dispersing capped GNPs into LC at isotropic temperature and followed by ultrasonication and evaporation. Wherein, the use of capped GNPs (Fig.3) is very significant as capping (non-mesogenic, mesogenic, or both): (i) controls the miscibility of GNPs into LC, (ii) prohibits GNPs' agglomeration into LC, and (iii) maintains long lasting stability of GNP-LC composites.[53-55] The detailed information about capping of GNPs can be readily obtained from very thoughtful reviews[56,57] and other references[58-66]. Despite numerous advantages of capping recipe, certain issues like (i) tedious chemical reactions for GNPs' functionalization, (ii) removal of unwanted by-products, (iii) limited purity and production, and (iv) prohibited direct interaction between GNP and LC, are still remained. In the view of these limitations, a novel method *'Sputter Deposition'* has been recently devised for uniform dispersion of GNPs into LC host.[67] It is reported that gold is sputter deposited uniformly in the form of nanoparticles into LC host having vapor pressure less than 1 Pa. It is speculated that certain parameters such as wettability and elastic constants of the LC would be responsible to control the size of GNPs. Such sputtered nanocomposites are found to be stable even more than three months. More importantly, this method is (i) completely physical and hence provides easier, faster, and more pure production as compared to other techniques and (ii) also applicable to the fabrication of dielectric, semiconductor, ferroelectric, and magnetic nanoparticles. However, the disadvantages of method are (i) only use of hosts (liquids, oils, and etc.) with low vapour pressure and (ii) size of nanoparticles depends upon physical properties of hosts.
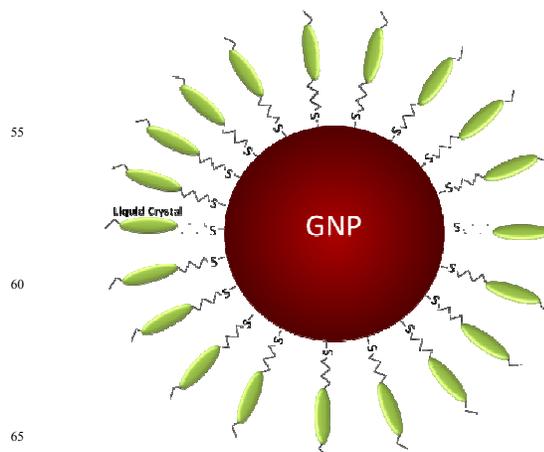
Fig. 3 The schematic shows mesogenic monolayer-capped GNP.

Last but not the least; it would be of worth to point out that the original dispersing medium (i.e. solvent) of GNPs should be chemically non-reactive with LC. Otherwise, this may affect the physical properties of LC, before its evaporation from the composite. Therefore, it is strongly advised to choose solvents, which are negligibly reactive with LCs and can be easily evaporated from GNP-LC composites.

Now we review both aspects of GNP-LC composites: (i) tuning of GNP's properties by LC (nematic, smectic, and their chiral analogues) and (ii) tuning of LC's properties by GNP.

C.1. Tuning of gold nanoparticles properties by liquid crystals

C.1.1 Nematic and chiral nematic (or cholesteric) liquid crystal

The nematic liquid crystals (NLCs) composed of rod-like mesogens are found to be the simplest anisotropic dielectric systems in terms of easier understanding of their molecular (i.e. director) alignment and related physical properties.[68] For example, the dielectric constant of NLC can be altered through variation in temperature and externally applied electric/magnetic

field and hence proved to be one of the best anisotropic dielectric media to tune the optical properties of GNPs in GNP-LC composites.
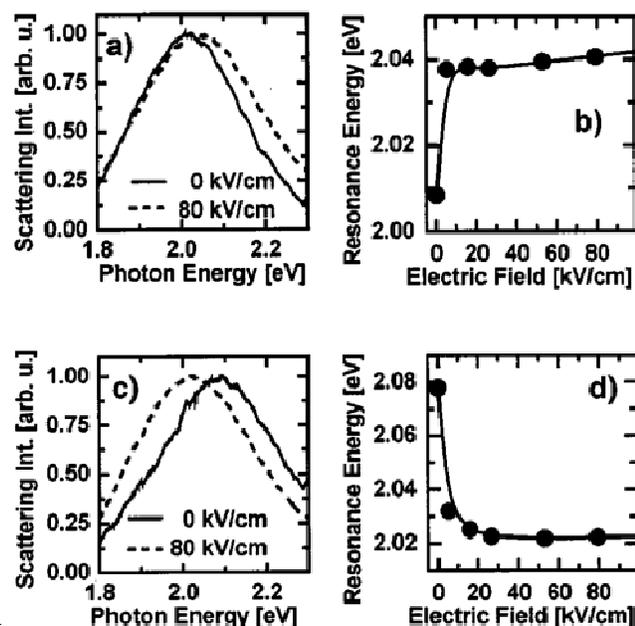
Fig. 4 (a), (c) Scattering spectra of a single gold nanoparticle in a LC cell with (dashed line) and without (solid line) an electric field applied. The analyzer is oriented parallel (a) or perpendicular (c) to the PI orientation; (b) and (d) show how the spectral shifts evolve with increasing field strength for parallel (b) and perpendicular (d) analyzer orientation. Reproduced with permission.[36] Copyright 2002, American Institute of Physics.

Based on light scattering experiments, Muller *et al.*[36] reported that GNPs optically behave as spherical (symmetric) and spheroids (asymmetric) before and after embedding them into NLC, respectively, due to anisotropic nature of NLC medium. In this composite, SPR (low/high-energetic) are widely spectrally tuned by external electric field. The low-energetic and high-energetic SPRs are associated with parallel and perpendicular alignment of LC's long molecular axis (i.e. director) with respect to rubbing direction, respectively. The low-energetic SPR (Fig. 4a & b) shows the electric field-dependent blue shift in scattering spectrum and related to the lowering of refractive index of LC molecules which are aligned parallel to the field direction. Similarly, the electric field-dependent red shift of high-energetic SPR in scattering spectrum (Fig. 4c & d) is also observed. The authors mentioned that the magnitude of spectral shifts of both SPRs varies from nanoparticle to nanoparticle and could be related to (i) local density of LC molecules after the application of external electric field and (ii) alignment/adhesion of LC molecules, on the periphery of GNPs. To explore more about low/high energetic SPRs in GNP-NLC composites, Park *et al.*[33] performed theoretical investigations in two concentration regimes
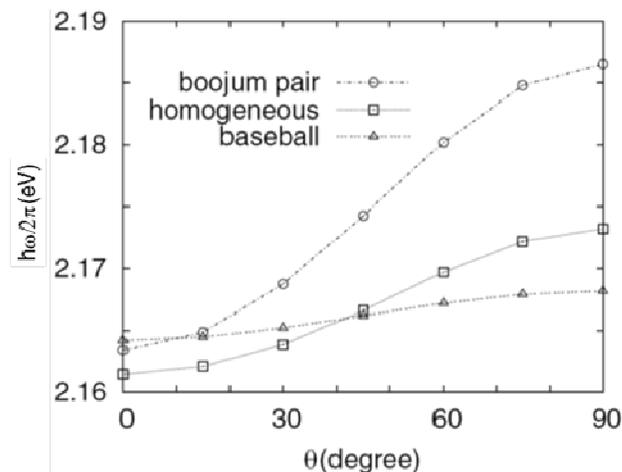
Fig. 5 Frequency of peak in scattering cross section for a liquid-crystal-coated gold nanoparticle (with the actual gold dielectric function with finite-particle-size correction) versus angle theta θ, for boojum pair, homogeneous, and baseball configurations. Reproduced with permission.[37] Copyright 2005, The American Physical Society (APS).

(i) lower: effective dielectric tensor, and (ii) higher (or single nanoparticle coated with NLC): generalized Maxwell-Garnett approximation (MGA) and discrete dipole approximation (DDA). The calculation is based upon the assumption that NLC is homogeneous around the nanoparticles and splitting is found roughly comparable to experimentally observed splitting.[36] Afterwards, Park *et al.*[37] included the possible perturbations of NLC director induced by nanoparticle's surface, into their calculations, in order to have precise comparison between theoretical and experimental data. Three plausible director configurations: (i) boojum pair (north-south pole), (ii) baseball (tetrahedral), and (iii) homogenous, are considered in zero electric field to calculate SPR splitting by using DDA. The calculated SPR splitting is found largest for boojum pair (Fig. 5) and also in agreement with experimental observations. The authors speculated that the observed enhanced SPR splitting is attributed to LC director deformation by the surface of nanoparticles. As mentioned above, Muller *et al.*[36] observed microscopic near-field spectral tuning from single GNPs, and which actually requires a very complex experimental setup and rigid substrates. However, Kossyrev *et al.*[69] recorded macroscopic far-field spectral tuning in gold nanodot array embedded in NLC matrix by using a very simple experimental setup and proposed that measurements could also be done on flexible substrates.
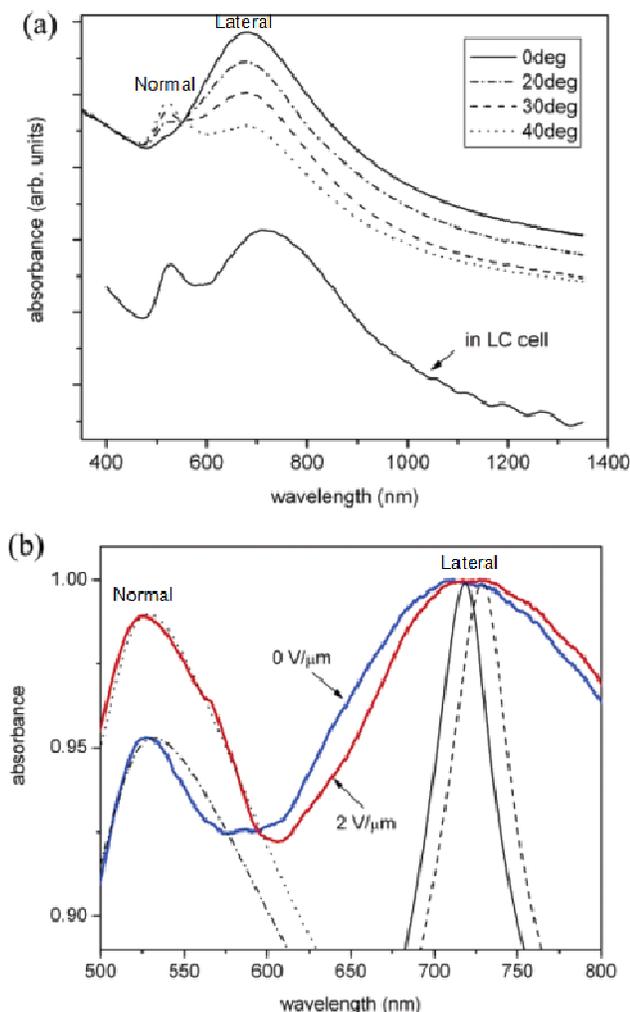
Fig. 6 (a) The absorption spectra of an array of gold nanodots on a glass substrate at various angles of light incidence. Normalization of all spectra to unity was performed at the wavelength of 200 nm. The lower spectrum
5 is the absorption of an array of nanodots in a liquid crystal cell under normal incidence. (b) The experimental absorption spectra at 0 and 2 V/μm electric fields. The spectra are normalized to unity at the lateral absorption peak wavelength. The fits (field-off and -on states) are shown by the black lines and are based on the effective medium model (solid and
10 dash lines, respectively) and the Mie theory (dash-dot and dot lines, respectively). Reproduced with permission.[69] Copyright 2005, American Chemical Society (ACS).

In this system, the normal and lateral SPR modes in the vicinity of nanoparticles' surface after infiltration into NLC can be tuned
15 by external electric field (Fig. 6).The observation of double peaks (short and long) and their relative shifting of shorter λ peak showing blue shift and longer λ showing red shift are interpreted by electric field-dependent refractive index of NLC. This further confirms that the refractive index of lateral mode increases and
20 decreases for normal mode, due to higher extraordinary refractive index of NLC. However, the complexity of NLC molecular configuration in nanodot array is difficult to figure out, but a voltage-controlled tuning of surface plasmon is clearly visible. Such tunable plasmonic nanocomposite materials are greatly
25 expected in the exploration of surface plasmonics based color tunable nanophotonic devices.
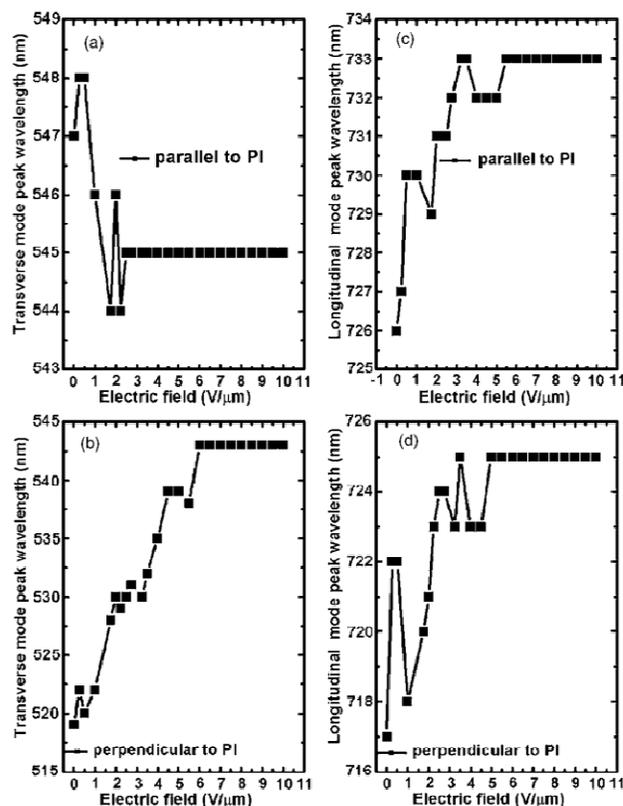
Fig. 7 Plot of varieties of plasmon peak position vs external electric field.
30 (a) and (b) exhibit the changes of the transverse mode when the analyzer is parallel or perpendicular to the PI direction. (c) and (d) show the changes of the longitudinal mode for parallel or perpendicular analyzer direction. Reproduced with permission.[71]Copyright 2006, American Institute of Physics.

35   Moreover, gold nanorods (GNRs)[70] intrinsically possess both transverse (i.e. normal) and longitudinal (i.e. lateral) modes of SPR and hence would be another promising system, very similar to the above-mentioned nanodot array[69], to obtain electrically tunable SPRs via electric field induced LC molecular
40 reorientation. In this context, Chu *et al.*[71] reported the electrically tunable plasmonic response (transverse/longitudinal mode) of absorption spectra of GNRs embedded into NLC along with their futuristic color tunable devices applications. They observed that (i) GNRs can be aligned along the rubbing direction of polyimide
45 coated substrate prior to external electric field application, (ii) the transverse mode shows blue shift or red shift with analyzer parallel or perpendicular to the rubbing direction, respectively, whereas longitudinal mode shows red shift independent of analyzer position (Fig. 7). The blue and red shift of transverse
50 mode in parallel and perpendicular analyzer configurations were explained by the reduction in effective refractive index and local density enhancement of LC molecules around GNRs due to the applied external electric field, respectively. However, red shift of longitudinal modes independent of analyzer positions was
55 explained on the basis of intrinsic characteristics (i.e. long axis senses more field-induced local density effect) and directionality of GNRs (i.e. alignment along the rubbing direction).
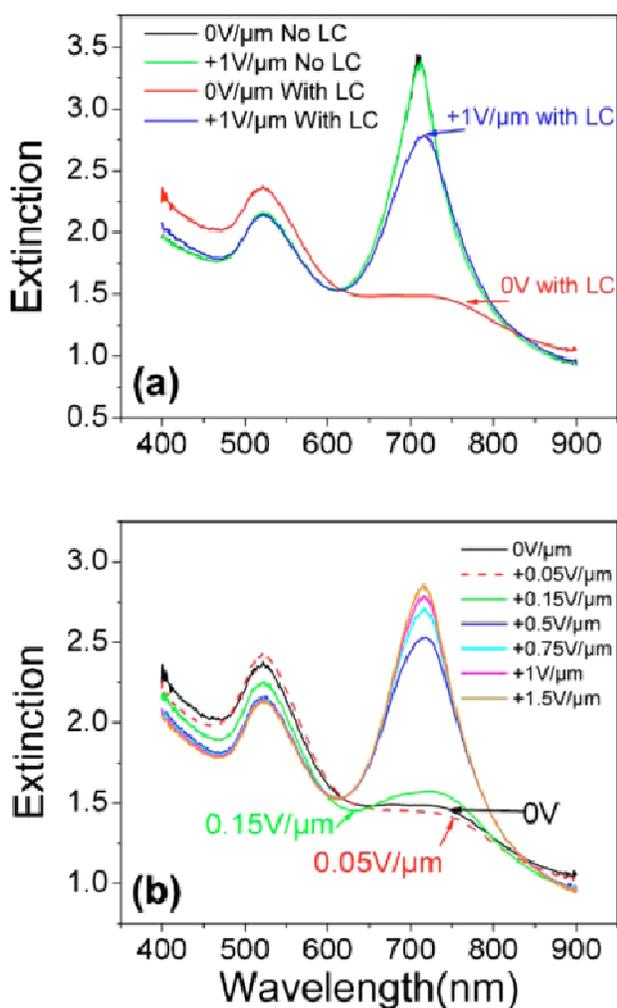
Fig. 8 (a) Extinction spectra of 20 nm diameter and 400 nm long gold nanorods embedded in alumina with and without liquid crystal and with and without a field of +1 V/m applied. (b) Variation of the extinction with applied field. The incident light was p polarized and the angle of incidence was 40°. Reproduced with permission.[72] Copyright 2006, American Institute of Physics.

Later on, Evans *et al.*[72] reported the electrically switchable nonreciprocal transmission of plasmonic GNRs with NLC, in a very different electro-optic device than Chu *et al.*[71]. It consists of (i) bottom gold coated glass substrate and on top of it, vertically aligned GNRs are grown through electrodeposition of gold on porous alumina thin film, (ii) top ITO coated glass substrate, (iii) no alignment layer, and (iv) NLC. Different plasmonic responses, depending upon whether light is incident from LC side or GNR side of device, are observed. For instance, when light is illuminated through LC side with no external electric field, the longitudinal resonance peak at 712 nm is completely quenched which was present in case of no LC, while transverse resonance extinction at 520 nm is slightly increased (Fig. 8a). However, application of small electric field of 1 V/μm recovered the longitudinal resonance peak and transverse resonance extinction as observed with no LC. The effect of varying electric field on the transverse and longitudinal resonance extinctions is also seen (Fig. 8b). When light is incident onto GNR side of device, the longitudinal resonance peak at 712 nm is not changed and applied electric field has very small effect on intensity measurements.

This is in agreement with previous study on gold nanodot array in LCs[69] and confirms that plasmonic resonances of the nanorod arrays are not really sensitive to the dielectric layer on top of the nanorods but mainly to the dielectric among them, due to electromagnetic configuration in the closely spaced nanorod assemblies. The observed electric field-dependent plasmonic responses were explained on the basis of polarization properties of LC and polarization sensitivity of GNR arrays, unlike previous reports.[69,71] Such electro-optic device has promising applications in making tunable polarization sensitive absorbers, reflectors, beam splitters, and spectral filters. The observed non-reciprocity could also be useful for unidirectional optical gates in micron scale very similar to Faraday isolators.

Muller *et al.*[36] and Chu *et al.*[71] used the polarized light to excite longitudinal/transverse SPR modes and depicted that observed red/blue spectral shifts are determined by the nature of incident light polarization. However, later on, Hsu *et al.*[73] studied GNPs doped in liquid crystals (ANDLC) by using unpolarized light and showed the electric field-dependent reversible/irreversible redshift of SPR. Interestingly, the spectral position of SPR peak is found electrically tuneable (Fig. 9a) and reversible (Fig. 9b), only if the applied electric field is lower than threshold field. Wherein, threshold field corresponds to the magnitude of electric field at which dielectrophoresis force occurs and overcomes the viscosity between GNP and LC and finally leads to the aggregation of nanoparticles. The magnitude of redshift is dependent upon the magnitude of applied external electric field to ANDLC. However, once applied electric field crosses the threshold then observed redshift becomes irreversible even after removal electric field (Fig. 9c). This study presents the issues related to external field-induced aggregation of GNPs in LC, affected optical properties and certainly performance of electro-optical devices based on them.
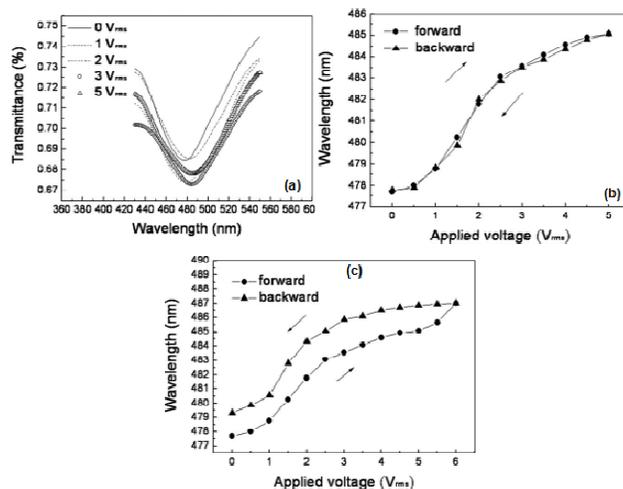
Fig. 9(a) The diagrams between the transmission spectra of the ANDLCs cell and applied voltages from 0 to 5 Vrms, (b) The corresponding absorption peak of the transmission spectra and its reverse, and (c) The absorption peak of the transmission spectra of the ANDLCs cell while the applied voltage increases from 0 to 6 Vrms and its reverse. Reproduced with permission.[73] Copyright 2008, American Institute of Physics (AIP)

There is consensus that the ordering (i.e. alignment) of LC molecules around GNPs could explain the observed tuneable SPR

features. However, the probing of such ordering at nanoscale is not straightforward and hence demands for rigorous simulation as well as experimental studies. In this direction, Koenig et al.[74] reported the coupling of the plasmon resonances of chemically functionalized GNPs (~10-40 nm) to local order in NLC (5CB). The absorption spectra of GNPs show small red shift in the localized surface plasmon resonance (LSPR) just after the chemical functionalization, whereas large red shift in case of NLC (Fig. 10). The surface induced ordering of NLC in the vicinity of chemically functionalized GNPs causes such large red shift in LSPR of GNPs i.e. surface chemistry dependent tuning of LSPR of GNPs. Temperature is also observed another factor to tune LSPR of chemically functionalized GNPs in 5CB. Moreover, by comparing the far field orientation of LC molecules and behavior of LSPR of GNPs, one can also get insights into the nanoscopic origins of the bulk ordering of LC molecules.
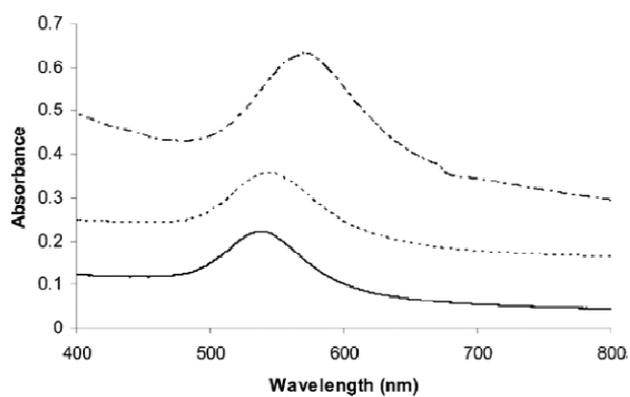
Fig. 10 UV-Visible absorbance spectra of gold nanoparticles (solid, bottom line) measured in air prior to functionalization with hexadecanethiol; (dotted, middle line) measured in air after functionalization with a monolayer of hexadecanethiol; (dashed, top line) measured in nematic 5CB after functionalization with a monolayer of hexadecanethiol. The spectra are offset for clarity. Reproduced with permission.[74] Copyright 2007, American Chemical Society.

The above-mentioned studies indicate that NLCs are mainly used to tune SPRs of GNPs through varying external electric field and temperature. However, very recently, Milette et al.[18] reported the formation of reversible and long range network (i.e. ordered assemblies) of GNPs in GNP-LC composites by LC phase transition (i.e. Isotropic-Nematic) (Fig.11). Authors mentioned that network formation in these composites is observed with GNPs concentration (≥1 wt%). Wherein, GNPs capped with mixed monolayer of hexanethiol and [CBO(CH$_2$)$_{12}$SH] (1:1) are used to have uniform and stable dispersion with GNP concentration up to 25 wt%.[55] The cooling rate, surface alignment, film thickness, GNP concentration, and ligand shell composition are the governing factors for observed network topology.
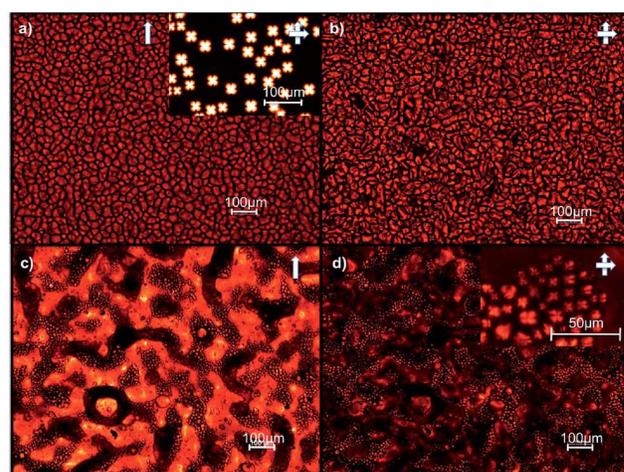
Fig. 11 POM images of 5 wt% Au of AuNPs dispersed in 5CB using thick cells. Untreated 20 μm thick glass cell results in a network of branches and no nodes with *Schlieren* texture mixed with homeotropically aligned LC (a–b). A cellular network is formed with stable radial director configuration (d, inset) when using untreated 70 μm thick cell (single arrow = parallel polars; crossed arrows = crossed polars; scale bars = 100mm; cooling rate = 1°/min). Reproduced with permission.[18] Copyright 2012, Royal Society of Chemistry.

Furthermore, besides NLCs, cholesteric liquid crystals (CLCs) have also been recently used to tune optical properties of GNPs. For instance, Sio et al.[35] reported electric field/temperature-dependent broad band tuning of plasmonic resonance of GNPs doped in CLC. The self-organization and LSPR properties of GNPs in CLC matrix are detailed by Bitar et al.[75], Ayeb et al.[76] and Pendery et al.[77]

C.1.2 Smectic liquid crystals

Because of layered structure in smectic liquid crystals, the understanding of the tunable features of GNPs doped into smectics would become more complex, unlike nematics. However, there are very few reports on GNPs doped smectics (SmA and SmC*), wherein efforts were employed to understand and explain the observed results.[78-80]

Pratibha et al.[78] studied experimentally the effect of surrounding anisotropic LC medium (SmA) on the SPR of GNPs with variable concentrations, and compared with theoretical results. The SPR wavelength shows red shift depending on (i) increasing concentration of GNPs in LC medium (Fig. 12), and (ii) incident light polarization (Fig. 13). The concentration-dependent SPR red shift is mainly attributed to the coupling between SPR from individual GNP in LC medium. The polarization-dependent SPR red shift is explainable with Mie scattering theory (Fig. 13a & b). The broader SPR peak shape in experimental results (Fig. 13a) as compared to theoretical (Fig. 13b) could be either due to polydispersity of GNPs in LC medium or alignment of LC molecules around GNP molecules. The comparison between SPR peak wavelengths as a function of volume concentration of GNPs, obtained from theory/simulation (Maxwell Garnett effective medium theory) and absorption experiments is also in good agreement i.e. increase in red shift with increase in volume fraction (Fig. 14). Furthermore, authors

extended their investigations on these nanocomposites by using AFM technique.[79] The stability of GNPs dispersed into SmA LC is found greater than NLC i.e. exclusion of agglomeration of GNPs in SmA. The experimental and simulated SPR spectra
5 show that the interparticle separations between isolated GNPs in the bulk of smectic layers remain large enough even for highly concentrated solutions. Moreover, GNPs in thin SmA films also do not show agglomeration but rather improve the free surface profile of film due to layer distortions around the inclusions in the
10 LC bulk. Authors predicted that such uniform dispersion of GNPs with high volume fraction in SmA LCs could produce nanoparticles-based tunable metamaterials. More importantly, such self-assembled technique to produce tunable metamaterials could be an excellent alternative to a very expensive and time
15 consuming nanolithographic technique.
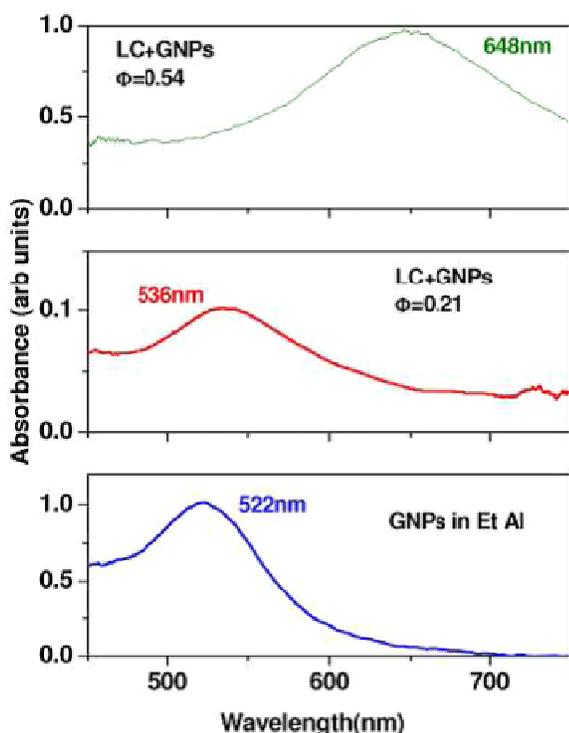
Fig. 12 Optical absorption spectra obtained with GNPs suspended in ethyl alcohol (Et Al) before addition of the liquid crystal and LC-GNP
20 dispersion with Φ=0.21 and Φ=0.54 concentrations. Reproduced with permission.[78] Copyright 2009, Optical Society of America (OSA).
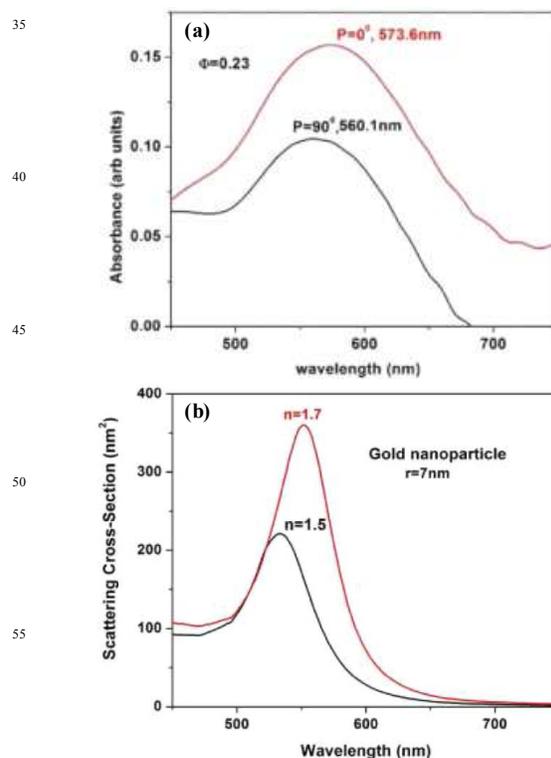
Fig. 13 (a) Optical spectra obtained with comparable volume fractions of GNPs (a) from experiment and (b) from calculations based on Mie scattering theory. Here, P=0°, and P=90° correspond to incident light polarized parallel and perpendicular to LC director, respectively.
65 Reproduced with permission.[78] Copyright 2009, Optical Society of America (OSA).
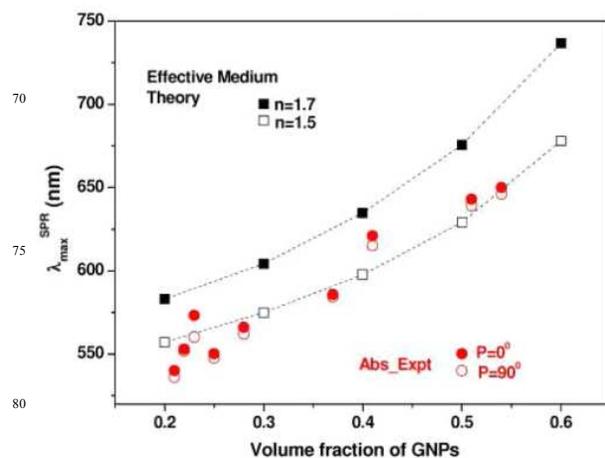
Fig. 14 Comparison of the surface plasmon resonance wavelength for
85 different volume fraction of GNPs from effective medium calculations (dotted line drawn as guide to the eye) and from experimental absorption spectra obtained with polarizer P=0° and P=90°. Reproduced with permission.[78] Copyright 2009, Optical Society of America (OSA).

90 Moreover, very recently, Milette *et al.*[80] reported the thermally reversible long-range patterning (micron-scale) of GNPs by homeotropically aligned SmA LC (Fig. 15). They have preferably

chosen mixed monolayer (mesogenic + alkylthiol) capped GNPs to dope into LC, in the view of their unprecedented solubility even at very high concentrations. The formation of periodic patterns starts at the N-SmA phase transition due to the phase separation of GNPs. Interestingly; the type of periodic patterns (i.e. linear or curved) depends upon the used cell geometry. Authors proposed that the accumulation of GNPs at edge dislocation defects of smectic phase could be attributed to the observed patterning. Authors pointed out that patterning of GNPs in SmA phase could be seen even at lower concentration such as 0.1 wt%, unlike N phase, wherein concentration of GNPs should be ≥1 wt%.[18]
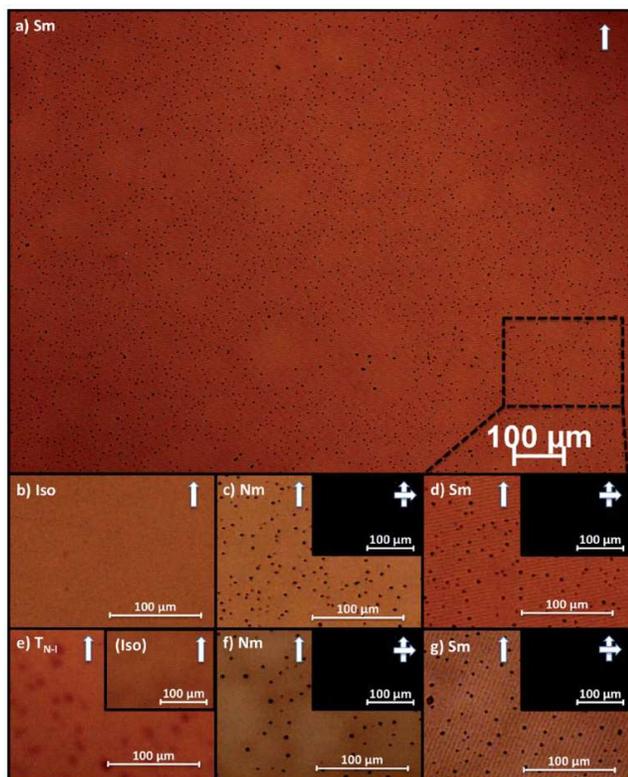
Fig. 15 1.0 wt% Au AuNPs dispersion between homeotropic glass slides (cooling rate: 1.0°/min). (a) A 964×1285 mm section of a single, uniform linear array of AuNP aggregates in the smectic phase viewed under parallel polars after the first cooling. Expanded area of the same sample in the (b) isotropic, (c) nematic, and (d) smectic phases. A second temperature cycle of the same sample shows (e) the complete redispersal of the AuNPs upon heating to the isotropic phase, (f) the reappearance of the circular aggregates in the nematic phase and (g) the linear arrays in the smectic upon cooling. (Insets: c–d, f–g = cross polars showing homeotropic alignment). Reproduced with permission.[80] Copyright 2012 Royal Society of Chemistry.

C.2. Tuning of liquid crystal properties by gold nanoparticles
C.2.1 Nematic and cholesteric blue phase liquid crystals
Prasad *et al.*[24] investigated the alkylthiol capped GNP (~15-20 nm, ≤5 wt%) doped NLC composites and observed that electrical conductivity and nematic to isotropic phase transition temperature (T_{N-Iso}) of NLC are dependent on the concentration of GNPs. The T_{N-Iso} of composite decreases almost linearly with increasing concentration of GNPs. The electrical conductivity

increases with doping concentration of GNPs, whereas conductivity anisotropy decreases very minutely. The authors believed that observed results could be due to the presence of GNPs and not their capping agent (i.e. alkylthiol). Sridevi *et al.*[81] also studied GNR doped NLC composites and observed enhanced anisotropic conductivity, elastic and dielectric constants, but no measurable changes in T_{N-Iso} of composite as compared to undoped sample, unlike Prasad *et al.*[24] The results were explained on the basis of shape anisotropy of GNR. On the other hand, Khatua *et al.*[54] reported an increase in T_{N-Iso} (Fig.16) and decrease
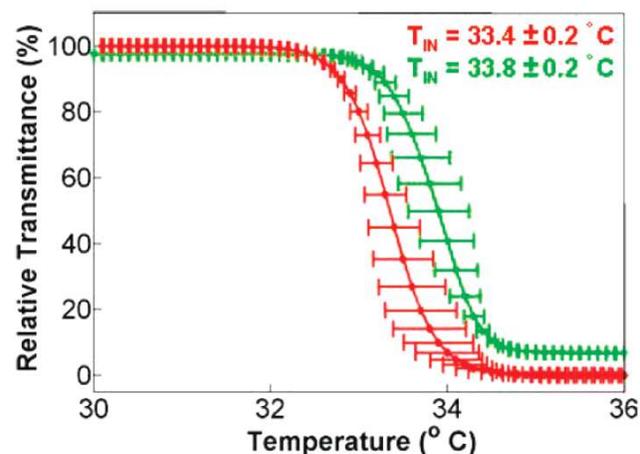
Fig.16 Nematic-to-isotropic phase transition of neat 5CB (red) and 5CB doped with SOPB-functionalized gold nanoparticles (green). The temperature dependence of the relative transmittance (data points) was fitted with a sigmoidal function (solid lines). Error bars were calculated from three independent measurements.[54] Reproduced with permission.[54] Copyright 2010 ACS publications
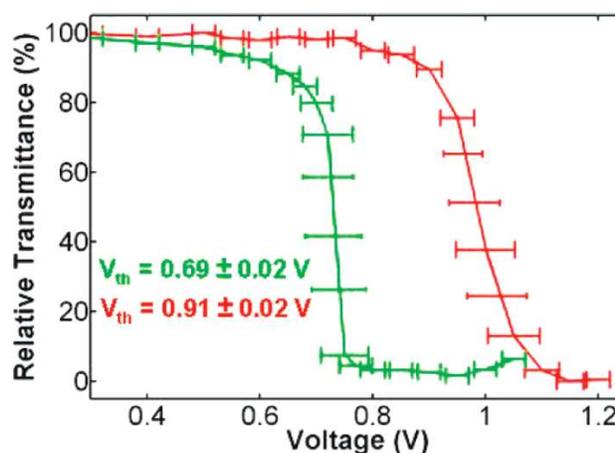
Fig.17 Freedericksz transition of nanoparticle-doped (green) and undoped (red) liquid crystal devices. The lines connect the experimental points and are included as guides for the eye only. Error bars were calculated from two independent measurements. Reproduced with permission.[54] Copyright 2010 ACS publications.

in threshold voltage for Freedericksz transition (Fig.17) of NLC doped with SOPB-capped GNP (~6 nm, ~0.2 wt%) composites. A point to be noted here is that capping agent (SOPB), structure very similar to NLC (5CB) is used in this study in order to

increase solubility of higher concentration of GNPs. The authors speculated that observed results could be due to the increase in order parameter as well as dielectric anisotropy of NLC, respectively. Later on, Pandey *et al.*[82] reported the significant increase in T_{N-Iso}, electrical conductivity and decrease in dielectric anisotropy and threshold voltage of NLC doped with functionalized GNPs (~2.4 nm, ~0.1 wt%). The results were explained by considering formation of anti-parallel dipoles and availability of extra space for ionic movement in the composite. Inam *et al.*[83] also reported the lowering of threshold voltage of NLC by doping of citrate ion capped GNPs (~10 nm). However, relaxation of short axis molecular reorientation shifted towards lower frequency in the composite, unlike Pandey *et al.*[82] The lowering of threshold voltage was explained by internal local electric field produced due to differences in dielectric constants of GNP and NLC.

More interestingly, Qi *et al.*[25] reported the formation of periodic stripe patterns (Fig. 18) in NLCs doped with functionalized (chiral/non-chiral alkyl thiolates) GNPs (≤5wt%). The stripe formation was explained by two ways (a) chiral alkylthiol capped GNPs transfer chirality to the non-chiral NLC host and (b) formation of topological defects by chiral/non-chiral GNPs. Later on, the confirmation of chirality transfer from the chiral GNPs to the non-chiral NLC was also done with induced circular dichroism (ICD), however in case of non-chiral GNPs, no relationship was found between stripe patterns and chirality.[84] An unprecedented dual alignment mode and electro-optical response in alkylthiol capped GNPs doped NLCs were also demonstrated.[85] Moreover, authors investigated the miscibility and alignment effects of mixed monolayer cyanobiphenyl LC capped GNPs in nematic cyanobiphenyl LC hosts in comparison with alkylthiol capped GNPs doped NLCs and found that cyanobiphenyl LC capped GNPs are not miscible in NLCs, unlike alkylthiol capped GNPs.[53]
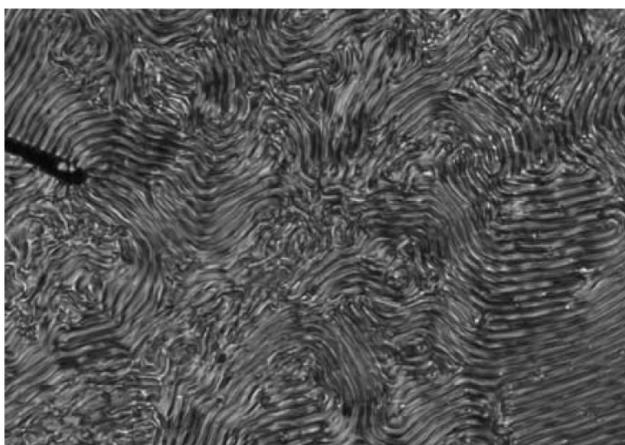
Fig. 18 POM micrographs (crossed polarizers) of the nematic phase of 5 wt% Au1 in LC1 taken on cooling from just below the Iso–N phase transition (cooling rate <1 °C min-1). Reproduced with permission.[25] Copyright 2009, Optical Society of America (OSA).

It is worth pointing out here that in the literature, LC-GNP composites with low concentration of GNPs are mostly investigated. However, very recently, Vardanyan *et al.*[86] extensively investigated the dispersion of GNPs with variable

concentration (lower to higher) into cyanobiphenyl homologues (nCB; n = 5, 6, 7, 8) LCs to study the affected material's parameters (i.e. display parameters) and mesophase stability. The uniform dispersion of GNPs into CB homologues was observed only for n = 5, 6, and 7, as 8CB does not disperse GNPs at all. Moreover, the GNP's concentration and the length of alkyl tail of CB molecules play important roles in affecting material's parameters. Authors tried to explain results by proposing formation of two different types of aggregates (LC/GNP and GNP/GNP) in these composites.

More importantly, GNPs are also used to tune the properties of cholesteric blue phase liquid crystals. Yoshida *et al.*[87] reported the increase of temperature range of blue phase from 0.5 to 5°C by doping of GNPs i.e. stabilization of blue phase. Authors believed that accumulation of GNPs in the lattice disclinations stabilizes the blue phase. Later on, Yabu *et al.*[88] demonstrated the tunable polarization-independent refractive index in these GNP stabilized blue phase system. Very recently, Yoshida *et al.*[89] studied the phase dependence of GNP dispersibility in blue as well as cholesteric liquid crystals and found that dispersibility depends upon the structure of LC phase. Moreover, Wong *et al.*[90] reported the enhanced blue phase temperature range as well as electro-optical performance in GNR-liquid crystal blue phase composites.

C.2.2. Smectic liquid crystals

The doping of citrate ion capped GNPs is mostly experimented with chiral Smectic C phase (SmC*) among all smectic liquid crystalline phases, due to technological importance of SmC* phase. Kaur *et al.*[26] reported the enhanced optical and electro-optical properties in GNP doped FLC composites. The fivefold increase in optical tilt, reduction of threshold voltage by one tenth, and enhanced memory effect (~half an hour) was monitored in doped FLC samples (Fig. 19). Authors predicted that (i) enhanced intrinsic electric field in the FLC sample due to the presence of GNPs and (ii) interaction of collective electron wave oscillations in GNPs with the electromagnetic wave from the photon of incident light traversing through FLC molecules, could be the plausible reasons. Later on, in the view of enhancing memory effect in FLCs, Prakash *et al.*[27] doped citrate ions capped GNPs into a special type of short pitch FLCs known as deformed helix ferroelectric liquid crystals (DHFLCs) and observed long lasting (~ hours to days) non-volatile memory effect (Fig. 20). Authors predicted that the electric field induced charge transfer from LC molecules to GNPs and stabilization of helix deformation of DHFLC material occurring beyond a critical electric field could be the reason for enhanced memory effect.
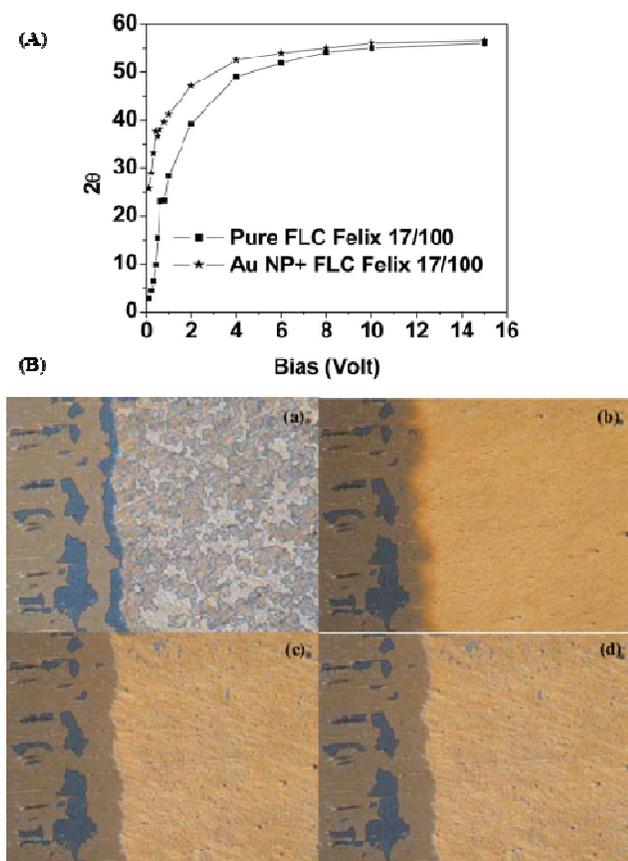
Fig. 19 (A) Behavior of optical tilt (×2) as a function of bias voltage in case of pure (square) FLC Felix 17/100 and Au NP doped FLC (star); (B) Optical micrograph of (a) scattering state before any bias application, (b) completely switched bright state on application of 10 V bias, (c) state after removal of bias, and (d) state after 30 min of bias removal in Au NP doped Felix 17/100 sample of 3 μm thickness. Reproduced with permission.[26] Copyright 2007, American Institute of Physics (AIP).
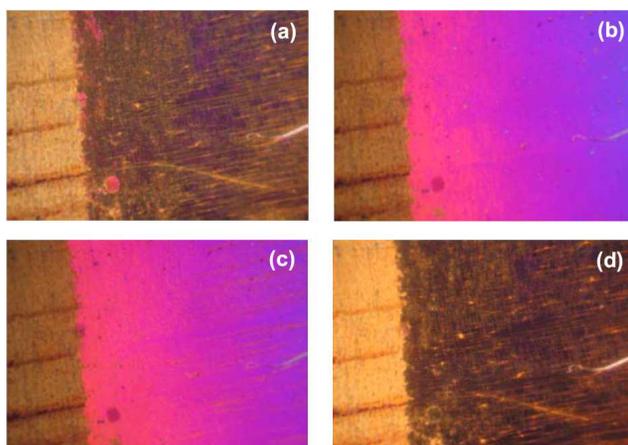
Fig. 20 Optical micrographs of 3 μm GNPs doped DHFLC memory cell at room temperature at (a) 0 V, (b) 15 V bias, (c) 6 hr after removal of bias, and (d) again 0 V. Reproduced with permission.[27] Copyright 2008, American Institute of Physics (AIP).

Besides above-mentioned enhanced electro-optic effects, Kumar *et al.*[91] also observed ninefold enhancement in photoluminescence (PL) intensity of a newly synthesized DHFLCs compound, after doping of GNPs (Fig. 21), useful in realizing PL-based LCDs. Authors believed that the constructive interaction between enhanced electromagnetic field generated near GNPs surfaces and molecular fluorophores (i.e. chiral terphenyl compound) present in DHFLCs could be the probable reason for enhanced PL intensity.
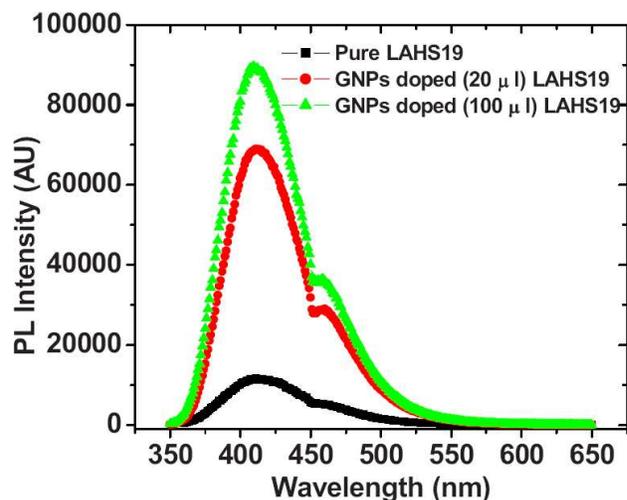
Fig. 21 Comparison of PL intensity of pure DHFLC material LAHS19 and GNPs doped DHFLC material, excited at 340 nm, emission wavelength is 411 nm. Reproduced with permission.[91] Copyright 2009, American Institute of Physics (AIP).

Joshi *et al.*[92] reported a new low frequency relaxation mode in SmC* phase of newly synthesized FLC (KCFLC 7S), independent of alignment (homogenous/homeotropic), and its clear resolution in GNP doped FLC composites. The temperature and bias-dependent dielectric characterizations performed on undoped and doped FLCs, revealed the characteristics of observed new relaxation mode. Authors interpreted their results by considering (i) ionization-recombination-assisted diffusion of slow ions present in FLC, and (ii) increased ionic conductivity because of dispersed GNPs, respectively.

Podgornov *et al.*[29] investigated the influence of size of GNRs on electro-optical and dielectric properties of FLCs. They observed significant decrease in spontaneous polarization, switching time and rotational viscosity, but no change in tilt angle of GNR-FLC composites, independent of diameter of GNR. This was attributed to the enhanced internal electric field (via shunting of electrical doubling layer) inside FLC, due to the presence of GNRs. On the contrary, the relaxation frequency and dielectric strength of Goldstone mode (GM) were found strongly dependent on diameter of GNRs and explained on the basis of charge transfer between GNRs and FLC molecules.

Lapanik *et al.*[93] reported in detail the influence of chain length and tethered liquid crystal functional groups of GNPs on electro-optical and dielectric properties of alkylthiol-capped GNP-FLC composites. The electro-optical properties such as spontaneous polarization, switching on time, and rotational viscosity of composites found to decrease with increasing concentration of GNPs. It is also observed that longer alkyl chain capped GNPs favored further decrement in these parameters, due to the elongation of the organic group in the system. However, there is no measurable effect of doping concentration and length of alkyl chain on the tilt angle (primary order parameter) of composites,

suggesting the similar order structure in both undoped and doped FLCs. The helical pitch, Goldstone mode relaxation frequency and its absorption strength are also increased by increasing the length of alkyl tails of the nanoparticles. Authors believed that such alkyl tail length dependence could be correlated to the reduced internal repulsion among nanoparticles by increasing tailing length and consequently the stronger interaction within FLC matrix. The thiolate alkyl capping layer around GNPs found as short-term stable, whereas thiolate capping layers with *p*-cynaobiphenyl end groups as long-term stable. The long-term stability could be attributed to additional dipole-dipole interactions among FLC molecular diploes and *p*-cyano-biphenyl end groups. However, the phase transitions in FLCs were not remarkably affected after doping of alkyl thiol capped nanoparticles. Lahiri *et al.*[94] recently developed a theory for nanoparticle doped FLC composites to explain the experimentally observed changes in electro-optical properties of FLC (spontaneous polarization, tilt angle, rotational viscosity, and response time). The possibility of shift in phase transition temperature of nanoparticles-FLC composites was also addressed by considering electrostatic interaction among nanoparticles and LC molecules. More importantly, theoretical results were found well in agreement with previously reported experimental results.

Conclusions and outlook

Every aspect of GNPs such as formation/behaviour of SPRs, role of capping, uniform dispersion into LCs, tuning of GNPs properties by LCs and vice-versa are widely covered in this article. The SPR peak of GNPs can be tuned by changing either the dielectric constant of surrounding medium or size of GNPs. LCs are recognized as one of the best surrounding medium for GNPs, because the dielectric constant of LCs can be easily changed by external electric field as compared to other dielectrics. The alignment of LC molecules around GNPs also provides a good platform to understand the dynamics of interaction between GNPs and LC molecules and hence affected SPR peak, finally leading to ordering of GNPs and sensing applications. Such interactions are found a lot easier to explain in NLCs due to their simple structural feature, unlike smectic liquid crystals. However, results in GNPs dispersed smectic liquid crystals are quite interesting but less understood and hence needs further crucial research.

The other important aspect of GNP-LC composites includes the tuning of LCs properties (optical, electro-optical, and dielectric) by GNPs. This aspect is closely related to futuristic display applications as GNPs dispersion into LCs has modified a lot its display parameters. However, display products based on LC-GNP nanocomposites are still far away from the reality because of some other practical issues. Researchers are continuously working on to fix these issues to realize the LCDs based on LC-GNP nanocomposites. We strongly believe that present review article will be really helpful for beginners in the area of LC-nanoscience/nanotechnology and nice update to experienced researchers.

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References

1　(a) M. C. W. van Boxtel, R. H. C. Janssen, D. J. Broer, H. T. A. Wilderbeek, and C. W. M. Bastiaansen, *Adv. Mater.* **2000**, 12, 753 and (b) M. C. W. van Boxtel, R. H. C. Janssen, C. W. M. Bastiaansen, and D. J. Broer, *J. Appl. Phys.* **2001**, 89, 838.

2　I. I. Smalyukh, S. Chernyshuk, B. I. Lev, A. B. Nych, U. Ognysta, V.G. Nazarenko, and O. D. Lavrentovich, *Phys. Rev. Lett.* **2004**, 93, 117801.

3　T. Albrecht, S. F. L. Mertens, and J. Ulstrup, J. Am. Chem. Soc. **2007**, 129, 9162.

4　(a) E. M. Terentjev, *Phys. Rev. E* **1995**, 51, 1330, (b) S. Ramaswamy, R. Nityananda, V. A. Rgahunathan, and J. Prost, *Mol. Cryst. Liq. Cryst.* **1996,** 288, 175, and (c) O. M. Monval, J. C. Dedieu, T. G. Krzywicki, and P. Poulin, *Eur. Phys. J. B* **1999**, 12, 167.

5　(a) R. W. Ruhwandl and E. M. Terentjev, *Phys. Rev. E* **1997**, 56, 5561 and (b) H. Stark, J. Stelzer, and R. Bernhard, *Eur. Phys. J. B* **1999**, 10, 515.

6　Y. Gu and N. L. Abbott, *Phys. Rev. Lett.* **2000**, 85, 4719.

7　(a) P. Poulin, H. Stark, T. C. Lubensky, and D. A. Weitz, *Science* **1997**, 275, 1770 (b) P. Poulin, V. Cabuil, and D. A. Weitz, *Phys. Rev. Lett.* **1997**, 79, 4862 and (c) P. Poulin and D. A. Weitz, *Phys. Rev. E* **1999**, 57, 626.

(a) T. C. Lubensky, D. Pettey, N. Currier, and H. Stark, *Phys. Rev. E* **1998**, 57, 610, (b) B. I. Lev and P. M. Tomchuket *Phys. Rev E* **1999**, 59, 591, (c) R. Yamamoto, *Phys. Rev. Lett.* **2001**, 87, 075502, (d) H. Stark, *Phys. Rev. E* **2002**, 66, 041705, (e) J. Fukuda, M. Yoneya, and H. Yokoyama, *Eur. Phys. J. E* **2004**, 13, 87, (f) J. Fukuda, H. Stark, M. Yoneya, and H. Yokoyama, *J. Phys.: Cond. Matter* **2004**, 16, S1957, (g) M. A. Bates, *Liq. Cryst.* **2005**, 32, 1525, and (h) J. C. Loudet, P. Barois, P. Auroy, P. Keller, H. Richard, and P. Poulin, *Langmuir* **2004**, 20, 11336.

8　I. I. Smalyukh, O. D. Lavrentovich, A. N. Kuzmin, A. V. Kachynski, and P. N. Prasad, *Phys. Rev. Lett.* **2005**, 95, 157801.

9　I. Musevic, M. Skarabot, U. Tkalec, M. Ravanik, and S. Zumer, *Science* **2006**, 313, 954.

10　N. Kanyama, O. Tsutsumi, A. Kanazawa, and T. Ikeda, *Chem. Commun.* **2001**, 2640.

11　(a) O. V. Kuksenok, R. W. Ruhwandl, S. V. Shiyanovski, and E. M. Terentjev, *Phys. Rev. E,* **1996**, 54, 5198, (b) T. C. Lubensky, D. Pettey, and N. Currier, *Phys Rev E* **1998**, 57, 610, and (c) H. Stark, *Eur. Phys. J. B.* **1999**, 10, 311.

12　H. Stark, *Phys Report*, **2001**, 351, 387.

13　C. E. R. Velazquez, C. Noguez, and I. L. Garzon, *J Phys. Chem. B* **2003**, 107, 12035.

14　H. K. Bisoyi and S. Kumar *Chem. Soc. Rev.* **2011**, 40, 306.

15　P. M. Phillips, N. Mei, E. R. Soule, L. Reven, and A. D. Rey, *Langmuir* **2011**, 27, 13335.

16　P. M. Phillips, N. Mei, L. Reven, and Alejandro, *Soft Matter* **2011**, 7, 8592.

17　J. Milette, S. J. Cowling, V. Toader, C. Lavigne, I. M. Saez, R. B. Lennox, J. W. Goodby, and L. Reven, *Soft Matter* **2012**, 8, 173.

18　E. R. Soule, J. Milette, L. Reven, and A. D. Rey, *Soft Matter* **2012**, 8, 2860.

19　J. Milette, V. Toader, E. R. Soule, R. B. Lennox, A. D. Rey, and L. Reven, *Langmuir* **2013**, 29, 1258.

20　H. Yoshikawa, K. Maeda, Y. Shiraishi, J. Xu, H. Shiraki, N. Toshima, and S. Kobayashi, *Jpn. J. Appl. Phys.* **2002**, 41, L1315.

21　(a) O. Buchnev, E. Osukova, Y. Reznikov, V. Reshetnyak, H. Kresse, and A. Grabar, *Mol. Cryst. Liq. Cryst.* **2004**, 422, 47, and (b) Y. Reznikov, O. Buchnev, O. Tereshchenko, V. Reshetnyak, A. Glushchenko, and J. West, *Appl. Phys. Lett.* **2003**, 82, 1917.

22　E. B. Barmatov, D. A. Pebalk, and M. V. Barmatova, *Langmuir* **2004**, 20, 10868.

23 S. K. Prasad, K. L. Sandhya, G. G. Nair, U. S. Hiremath, C. V. Yelamaggad, and S. Sampath, *Liq. Cryst.* **2006**, 33, 1121.

24 H. Qi and T. Hegmann, *J. Matter. Chem.* **2006**, 16, 4197.

25 S. Kaur, S. P. Singh, A. M. Biradar, A. Choudhary, and K. Sreenivas, *Appl. Phys. Lett.* **2007**, 91, 023120.

26 J. Prakash, A. Choudhary, A. Kumar, D. S. Mehta, and A. M. Biradar, *Appl. Phys. Lett.* **2008**, 93, 112904.

27 A. Hinojosa and S. C. Sharma, *Appl. Phys. Lett.* **2010**, 97, 081114.

28 F. V. Podgornov and A. V. Ryzhkova, and W. Haase, *Appl. Phys. Lett.* **2010**, 97, 212903.

29 A. Kumar, G. Singh, T. Joshi, G. K. Rao, A. K. Singh, and A. M. Biradar, *Appl. Phys. Lett.* **2012**, 100, 054102.

30 Y. Wang, *Appl. Phys. Lett.* **1995**, 67, 2759.

31 M. Mitov, C. Portet, C. Bourgerette, E. Snoeck, and M. Verelst, *Nat. Mater.* **2002**, 1, 229.

32 S. Y. Park and D. Stroud, *Appl. Phys. Lett.* **2004**, 85, 2920.

33 I. In, Y.-W Jun, Y. J. Kim, and S. Y. Kim, *Chem. Comm.* **2005**, 800.

34 L. D. Sio, R. Caputo, U. Cataldi, and C. Umeton, *J. Mater. Chem.* **2011**, 21, 18967.

35 J. Müller, C. Sönnichsen, H. von Poschinger, G. Von Plessen, T. A. Klar, and J. Feldmann, *Appl. Phys. Lett.* **2002**, 81, 171.

36 S. Y. Park and D. Stroud, *Phys. Rev. Lett.* **2005**, 94, 217401.

37 X. Zeng, G. Ungar, Y. Liu, V. Percec, A. E. Dulcey & J. K. Hobbs, *Nature* **1994**, 42, 157.

38 T. Jensen, L. Kelly, A. Lazarides, George C. Schatz, *J. Clust. Sci.* **1999**, 10, 295.

39 K. L. Kelly, E. Coronado, L. L. Zhao, G. C. Schatz, *J. Phys. Chem. B* **2003**, 107, 669.

40 B. Chen, X. Zeng, U. Baumeister, G. Ungar, C. Tschierske, *Science* **2005**, 307, 96.

41 B. B. Eran, C. Tschierske, S. Dielec and U. Baumeister, *J. Mat. Chem.* **2006**, 16, 1136.

     (a) P. Hanarp, M. Kall and D. S. Sutherland, *J. Phys. Chem.* **2003**, B 107, 5768, (b) J. J. Mack, D. R. Smith, and S. Schultz, *Nano Lett.* **2003**, **3**, 485, and (c) G. Raschke, S. Brogl, A. S. Susha, A. L. Rogach, T. A. Klar, J. Feldmann, B. Fieres, N. Petkov, T. Bein, A. Nichtl, and K. Kurzinger, *Nano Lett.* **2004**, 4, 1853.

42 (a) A. C. Templeton, J. J. Pietron, R. W. Muray, and P. Mulvaney, *J. Phys. Chem. B* **2000**, 104, 564, (b) Y. Sun and Y. N. Xia, *Analyst* **2003**, 128, 686 (2003), and (c) F. Tam, C. Moran, and N. Halas, *J. Phys. Chem. B* **2004**, 108, 17290.

43 U. Kreibig and M. Vollmer, *Optical properties of metal clusters* (Springer Series in Materials Science, **1995**).

44 T. R. Jensen, M. D. Malinsky, C. L. Haynes and R. P. Van Duyne, *J. Phys Chem. B* **2000**, 104, 10549.

45 M. D. Malinsky, K. L. Kelly, G. C. Schatz, and R. P. Van Duyne, *J. Am. Chem. Soc.* **2001**, 123, 1471.

46 N. G. Khlebtsov, *J. Quant. Spectrosc. Radiat. Trans.* **2003**, 89, 143.

47 K. H. Su, Q. H. Wei, X. Zhang, J. J. Mock, D. R. Smith, and S. Schultz, *Nano Lett.* **2003**, 3, 1087.

48 S. Link, M. B. Mohamed and M. A. El-Sayed, *J. Phys. Chem. B,* **1999**, 103 3073.

49 N. Nedyalkov, T. Sakai, T. Miyanishi, and M. Obara, *J. Phys. D: Appl. Phys.* **2006**, 39, 5037.

50 (a) C. J. Cogswell, D. K. Hamilton and C. J. R. Sheppard, *J. Microsc.* **1992**, 165, 103, (b) T. Kalkbrenner, M. Ramstein, J. Mlynek, and V. Sandoghdar, *J. Microsc.* **2001**, 202, 72, and (c) H. Ditlbacher, J. R. Krenn, N. Felidj, B. Lamprecht, G. Schider, M. Salerno, and A. Leitner, and F. R. Aussenegg, *Appl. Phys. Lett.* **2002**, 80, 404.

51 (a) A. A. Lazarides, K. L. Kelly, T. R. Jensen, and G. C. Schatz, *J. Mol. Struct. (Theochem)* **2000**, 529, 59, (b) N. Nath and A. Chilkoti, *Anal. Chem.* **2002**, 74, 504, (c) J. L. West and N. J Halas, *Annu. Rev. Biomed. Eng.* **2003**, 5, 285, and (d) A. J. Haes, W. P. Hall, L. Chang, W. L. Klein and R. P. V. Duyne, *Nano Lett.* **2004**, 4, 1029.

52 H. Qi, B. Kinkead, Vanessa M. Marx, Huai R. Zhang, and T. Hegmann, *Chem. Phys. Chem.* **2009**, 10, 1211.

53 S. Khatua, P. Manna, W. S. Chang, A. Tcherniak, E. Friedlander, E. R. Zubarev, and S. Link, *J. Phys. Chem. C* **2010**, 114, 7251.

54 J. Milette, V. Toader, L. Reven, and R. B. Lennox, *J. Mater. Chem.* **2011**, 21, 9043.

55 M. C. Daniel and D. Astruc, *Chem. Rev.* **2004**, 104, 293.

56 J. W. Goodby, I. M. Sacz, S. J. Cawling, V. Gortz, M. Draper, Alan W. Hall, S. Sia, G. Cosquer, S. E. Lee, and E. P. Raynes, *Angew. Chem. Int. Ed.* **2008**, 47, 2754 (2008).

57 (a) M. Brust, M. Walker, D. Bethell, D. J. Schiffrin, and R. Whyman, *J. Chem. Soc. Chem. Commun.*, **1994**, 801, (b) M. Brust, J. Fink, D. Bethell, D. J. Schiffrin, and C. Kiely, *J. Chem. Soc. Chem. Commun.*, **1995**, 1655.

58 R. S. Ingram, M. J. Hostetler, and R. W. Murray, *J. Am. Chem. Soc.* **1997**, 119, 9175.

59 P. A. Buining, B. M. Humbel, A. P. Philipse, and A. J. Verkleij, *Langmuir* **1997**, 13, 3921.

60 S. Chen and K. Kimura, *Langmuir* **1999**, 15, 1075.

61 N. Kanayama, O. Tsutsumi, A. Kanazawa, and T. Ikeda, *Chem. Commun.* **2001**, 2640.

62 I. Inn, S. –W. Jun, Y. J. Kim, and S. Y. Kim, *Chem. Commun.* **2005**, 800.

63 (a) L. Cseh and G. H. Mehl, *J. Am. Chem. Soc.* **2006**, 128, 13376, and (b) L. Cseh and G. H. Mehl, *J. Mater. Chem.* **2007**, 17, 311.

64 Z. Shen, M. Yamada, and M. Miyake, *J. Am. Chem. Soc.* **2007**, 129, 1427.

65 A. Dorris, S. Rucareanu, L. Reven, Christopher J. Barrett, and R. B. Lennox, *Langmuir* **2008**, 24, 2532.

66 H. Yoshida, K. Kawamoto, H. Kubo, T. Tsuda, A. Fujii, S. Kuwabata, and M. Ozaki, *Adv. Mater.* **2010**, 22, 622.

67 P. G. de Gennes, J. Prost, *The Physics of Liquid Crystals*, Clarendon, Oxford, **1993**.

68 P. A. Kossyrev, A. Yin, S. G. Cloutier, D. A. Cardimona, D. Huang, P. M. Alsing, and J. M. Xu, *Nano Lett.* **2005**, 5, 1978.

69 E. Hutter and J. H. Fendler, *Adv. Mater.* 16, 1685-1706 (2004).

70 K. C. Chu, C. Y. Chao, Y. F. Chen, Y. C. Wu, and C. C. Chen, *Appl. Phys. Lett.* **2006**, 89, 103107.

71 P. R. Evans, G. A. Wurtz, W. R. Hendren, R. Atkinson, W. Dickson, A. V. Zayats, and R. J. Pollard, *Appl. Phys. Lett.* **2007**, 91, 043101.

72 L. H. Hsu, K. Y. Lo, S. A. Huang, C. Y. Huang, and C. S. Yang, *Appl. Phys. Lett.* **2008**, 92, 181112.

73 G. M. K. Jr., M. V. Meli, J. S. Park, J. J. de Pablo and N. L. Abbott, *Chem. Mater.* **2007**, 19, 1053.

74 R. Bitar, G. Agez, and M. Mitov, *Soft Matter* **2011**, 7, 8198.

75 H. Ayeb, J. Grand, H. Sellame, S. Truong, J. Aubard, N. Felidj, A. Mlayah, and E. Lacaze, *J. Mat. Chem.* **2012**, 22, 7856.

76 J. S. Pendery, O. Merchiers, D. Coursault, J. Grand, H. Ayeb, R. Greget, B. Donnio, J. L. Gallani, C. Rosenblatt, N. Felidj, Y. Borensztein, and E. Lacaze, *Soft Matter* 2013, 9, 9366.

77 R. Pratibha, K. Park, I. I. Smalyukh, and W. Park, *Opt. Exp.* **2009**, 17, 19459.

78 R. Pratibha, W. Park, and I. I. Smalyukh, *J. App. Phys.* **2010**, 107, 063511.

79 J. Milette, S. Relaix, C. Lavigne, V. Toader, S. J. Cowling, I. M. Saez, R. B. Lennox, J. W. Goodby, and L. Reven, *Soft Matter* 2012, 8, 6593.

80 S. Sridevi, S. K. Prasad, Geetha G. Nair, V. D. Britto, and B. L. V. Prasad, *Appl. Phys. Lett.* **2010**, 97, 151913.

81 A. S. Pandey, R. Dhar, S. Kumar, and R. Dabrowski, *Liq. Cryst.* **2011**, 38, 115.

82 M. Inam, G. Singh, A. M. Biradar, and D. S. Mehta, *AIP Advances* **2011**, 1, 042162 (2011).

83 H. Qi, J. O. Neil, and T. Hegmann, *J. Mat. Chem.* **2008**, 18, 374.

84 H. Qi, B. Kinkead, and T. Hegmann, *Adv. Funct. Mater.* **2008**, 18, 212.

85 a) K. K. Vardanyan, E. D. Palazzo, and R. D. Walton, *Liq. Cryst.* **2011**, 38, 709, (b) K. K. Vardanyan, R. D. Walton, and D. M. Bubb, *Liq. Cryst.* **2011**, 38, 1279, (c) K. K. Vardanyan, R. D. Walton, D. M. Sita, I. S. Gurfinkiel, and W. M. Saidel, *Liq. Cryst.* **2012**, 39, 595, and (d) K. K. Vardanyan, D. M. Sita, R. D. Walton, W. M. Saidel, and K. M. Jones, *RSC Adv.* **2013**, 3, 259.

86 H. Yoshida, Y. Tanaka, K. Kawamoto, H. Kubo, T. Tsuda, A. Fujii, S. Kuwabata, H. Kikuchi, and M. Ozaki, *Appl. Phys. Exp.* 2009, 2, 121501.

87   S. Yabu, Y. Tanaka, K. Tagashira, H. Yoshida, A. Fujii, H. Kikuchi, and M. Ozaki, *Opt. Lett.* 2011, 36, 3578.

88   H. Yoshida, K. Inoue, H. Kubo, and M. Ozaki, *Opt. Mater. Exp.* 2013, 3, 842.

89   J. M. Wong, J. Y. Hwang, and L. C. Chien, *Soft Matter* 2011, 7, 7956.

90   A. Kumar, J. Prakash, D. S. Mehta, A. M. Biradar, and W. Haase, *Appl. Phys. Lett.* **2009**, 95, 023117.

91   T. Joshi, A. Kumar, J. Prakash, and A. M. Biradar, *Liq. Cryst.* **2010**, 37, 1433.

92   A. Lapanik, A. Rudzki, B. Kinkead, H. Qi, T. Hegmann, and W. Haase, *Soft Matter* **2012**, 8, 8722.

93   T. Lahiri, T. Pal Majumder, and N. K. Ghosh, *J. Appl. Phys.* **2013**, 113, 064308.

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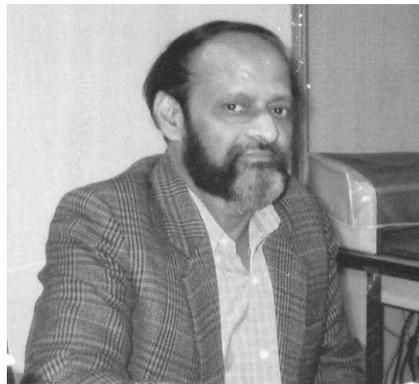
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