

Enhancing Liquid Crystals with Metal Oxide Nanoparticles: A Comprehensive Review

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ABSTRACT

Liquid Crystals (LCs) are versatile soft materials that exist uniquely between solids and liquids. Their remarkable properties have led to widespread success in display and non-display technologies. Metal oxide nanoparticles (MO -NPs) have attracted a great deal of interest on the grounds of their various properties in recent times. Recently, merging nanoscale particles into liquid crystals has attracted significant interest, leading to notable improvements in their properties and broader applications. This brief review explores the effects of incorporating metal oxides into liquid crystals, highlighting their contribution to enhancing performance and functionality. This review examines the impact of different nanoparticles such as Cobalt oxide, Magnesium oxide, Zinc oxide, Titanium oxide, Nickel oxide, and Ferric oxide doping on various liquid crystals.

Moreover, the impact of nanoparticle doping on many aspects of liquid crystals, including phase transitions, molecular alignment, electrical characteristics, optical properties, dielectric properties, and impedance, was also studied. A better understanding of these changes can help to more applications for liquid crystal. They can be useful in making sensors, improving displays, advancing optoelectronics, and developing photovoltaics.

KEYWORDS- Liquid crystal, Nematic Liquid Crystal, Nanoparticles, Metal Oxide nanoparticles, Doping MO-NPs in LC

I.INTRODUCTION

An Austrian botanist, Friedrich Reinitzer, studied liquid crystals in 1888. He noticed that a material called cholesteryl benzoate had two different melting points. First, when heated, the solid turned into a cloudy liquid. Then, as the temperature increased more, it became a clear, transparent liquid. When the temperature of a solid state is raised to 145.5 °C, it changes into a cloudy liquid state, whereas at 178.5 °C, the substance transforms into a translucent liquid as the temperature rises. The colour differences were also observed in the turbid liquid, which changed from red to bright blue-violet to pale blue. Otto Lehmann named liquid crystals (LC) in 1900. Earlier referred to them as "flowing crystals" in 1889 and "crystalline solids" in 1890. For his discovery, Reinitzer is credited with knowing a new state of matter called the

liquid crystal phase. They have stable properties but do not form a solid crystal structure. They exist between the solid and liquid phases and are called the mesophase, as shown in Figure 1.

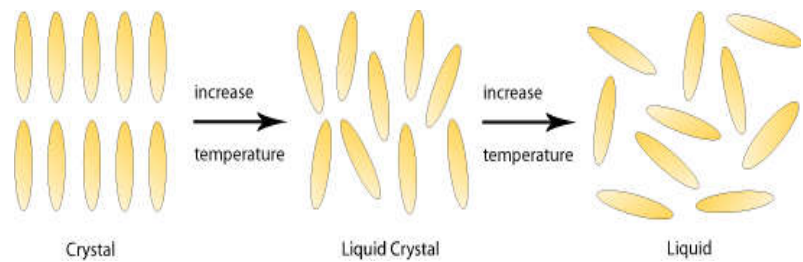


Fig. 1: Synthesis of Liquid Crystals

Liquid crystal is so termed because it has features common to solids and liquids. It has dielectric, electrical, and optical anisotropy, like crystalline solids, and fluidity and molecular mobility, like isotropic liquids. [1,2,3]

Classification of Liquid crystal-

Despite the availability of various classifications in literature, the most popular classification is based on how the liquid crystalline phases have been achieved and also depends upon the physico -chemical parameters responsible for the phase transitions as shown in fig 2.

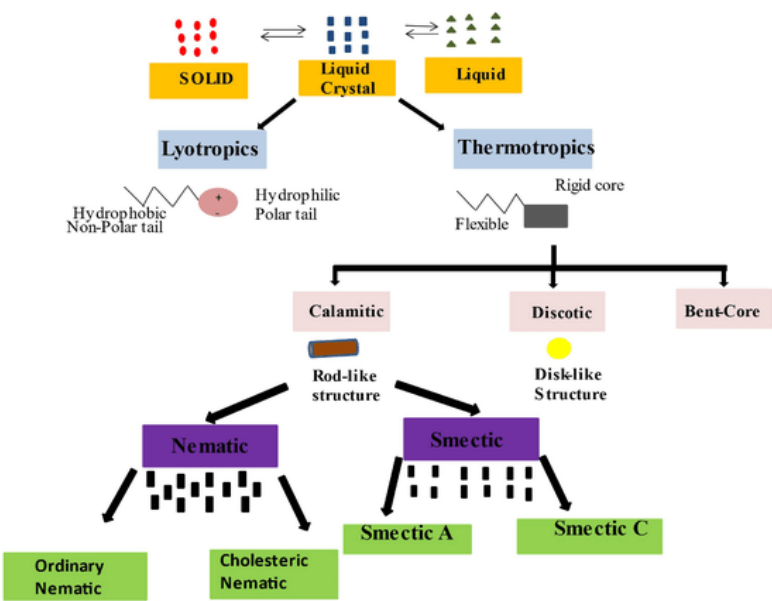


Fig. 2: Classification of Liquid Crystal.

They play a crucial role across diverse scientific and technological fields, including physics, chemistry, biology, material science, and telecommunications. Liquid crystals are used in displays, attenuators, tunable polarisers, spatial light modulators, and photonic sensors.[1] Researchers are combining liquid crystals with nanotechnology to develop a new technology based on these findings. Due to their unique scientific properties and numerous applications, liquid crystals doped with nanoscale particles have garnered attention in recent decades. As

research progresses and new technologies emerge, liquid crystals will play a growing role in modern advancements. Recent research shows that mixing nanomaterials with liquid crystals has led to new advantages and applications beyond what each can achieve independently. This exciting discovery has enhanced modern optoelectronic devices, products, and technologies.[4]

Metal Oxide nanoparticles have been capturing a great degree of interest due to their unique physical, chemical, electro -optical and magnetic properties resulting from their limited size, large surface area -to -volume ratio, cations with valance states, anions with deficiencies, depletion of carriers and a high density of corner or edge surface sites [5],[6]. Types of MO-NPs as shown in fig. 3.

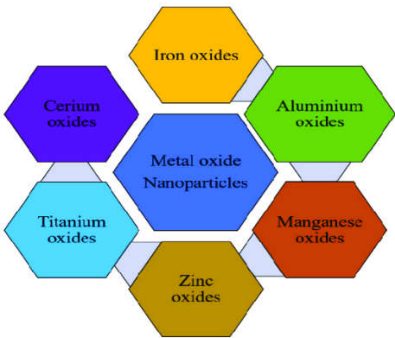


Fig.3: Types of MO-NPs

MO-NPs have notable applications in various fields, including medicine, information technology, indicators, bio-imaging detection, data security, missile plume detection, catalysis, energy storage, sensing, and defines applications. They are useful in many technological applications also such as microelectronic circuits, thermal conductivity enhancers, thermal stability, chemical resistance, optical devices, energy storage/conversion devices, sensors, piezoelectric devices, fuel cells, coatings for the passivation of surfaces against corrosion, and catalysts [7] as shown in Fig. 4.

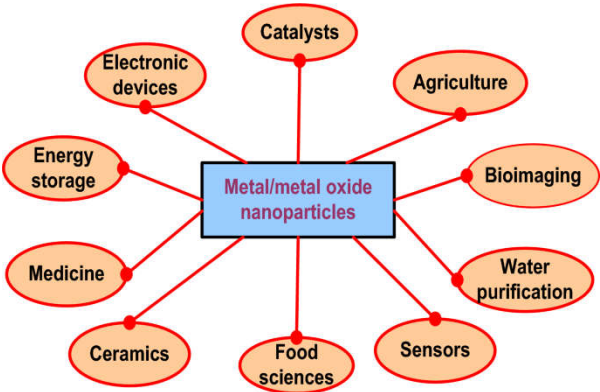


Fig. 4. Applications of MO-NPs.

Metal oxide nanoparticles (MO-NPs) have recently garnered significant consideration due to their multiple and valuable properties. Researchers have successfully incorporated appropriate MO-NPs into liquid crystals (LCs), enhancing their beneficial properties and distinctive characteristics, leading to outstanding and influential outcomes. This study investigates the impact that doping liquid crystals with metal oxide nanoparticles has on their properties.

Doping of Metal-Oxides nanoparticles in liquid crystals:

Adding metal oxide nanoparticles to liquid crystals has attracted great research interest because of their many improvements. The conductivity of these nano particle's changes based on their oxidation states and the defects in their crystal structure. The doping of the metal oxide -NPs (MO - NPs) in LC materials is a major research thrust area as it enhances the electro -optical, structural, magnetic and physical -chemical properties of LC materials. The reason for selecting MO -NPs lies in their capability to take up a stupendous number of structural forms and display metallic, semiconducting or insulating character [5]

Doping of Zinc Oxide nanoparticles (ZnO NPs):

ZnO nanoparticles have both piezoelectric and semiconducting properties. They are also non-toxic and act as strong oxidisers. These materials are widely used in nanogenerators, optoelectronics, electronics, and various sensors, including gas, chemical, and biological sensors. These materials are also used in cancer-detecting biosensors, ultrasensitive DNA sequence detectors, drug delivery systems, biomedical imaging, high-efficiency solar cells, field emitters, and UV photo detectors [8],[9].

T. Joshi observed low operating voltage and improved optical contrast when FLC was doped with ZnO nanoparticles. The fall in operating voltage and improved optical contrast have been attributed to the larger dipole moment of ZnO-NPs, which enhances the anchoring of FLC molecules around ZnO-NPs.[10]

WT. Chen observed that the minor transient current found in the doped cells shows that doping insulating nanoparticles into the LC cell can decrease the moving-ion density, and thus suppresses the undesired field-screening effect, contributing to a reduction of the V_{th} . [11]

The dielectric behaviour of pure nematic liquid crystals and those with added ZnO nanoparticles (NPs) has been investigated by Amit Sharma. It is found that POM results confirm a minor increase in phase transition temperature from nematic to isotropic phase by 2-3°C after adding ZnO NPs. A slight increase in permittivity with increasing temperature

(30°C to 60°C) was observed. When ZnO nanoparticles added, permittivity in the nematic phase decreased noticeably.[12]

Khushboo reported in the study of ZnO NPs with NLC (8CB) with the increase of the temperature and ZnO concentration, density and sound velocity decrease and intermolecular mean free length increases. The rise in intermolecular free length and adiabatic compressibility with temperature and ZnO concentration suggests a weak molecular interaction.[13]

Eskalen H, Ozgan studied the doping of ZnO NPs in NLC had decreased V_{th} considerably and increased the dielectric constant.[14]

Doping of Cobalt oxide nanoparticles (Co_3O_4 NPs):

Cobalt oxide nanoparticles, often called Co_3O_4 , are materials with unique properties due to their nanometre size, including semi conductivity, piezoelectricity, and optical properties. These nanoparticles are being studied for various applications, including energy storage, catalysis, and biomedical uses.

Depanshu Varshney found that the doping of CoO NPs does not affect the alignment of nematogens. Due to the attraction of ionic impurities on the surface of CoO NPs, the dielectric permittivity of 5CB is reduced. It also observed that a decrease in ionic impurities results in a decrease in dielectric absorbance of 5 CB. Also analysed the moderation of relaxation frequency. In addition to these evolutions, CoO NPs improve the thickness-dependent changes in dielectric permittivity.[15]

Sarah Khalil has investigated, that polymer's viscosity increased the polysiloxane's properties; however, the temperature of the transfer of glass decreased due to the addition of nanoparticles. The order parameter calculated in this research using infrared spectroscopy, which is used to determine the threshold voltage to test the theory, as well as studying the effect of Cobalt Oxide nanoparticles (Co_3O_4) on the Eastern orientation order parameter (\bar{S}), voltage and response time.[16]

It has been observed that by Hyung-Koo Chung, higher doping concentrations in LC cells result in a lower threshold voltage and quicker response time and can control the performance and low energy consumption of LC devices without capacitance hysteresis.[17]

Doping of Titanium oxide nanoparticles (TiO_2 NPs):

One of the excellent properties of TiO_2 NPs is the ability to improve the electro-optical performance of LC systems due to capturing ions impurities in an LC cell. It is known that ions reduce the overall performance of LC devices and are responsible for many adverse

effects, such as image sticking and flickering, slow response times, etc. TiO_2 NPs were also used to increase the birefringence of the LC system without increasing viscosity. [19-23]

Habib Ayeb observed dielectric and viscoelastic properties in the study of 5CB (4-pentyl-4-biphenylcarbonitrile) nematic liquid crystal doped with TiO_2 and Cu- TiO_2 NPs. Optical microscopy showed that copper-incorporated TiO_2 nanoparticles spread evenly in the nematic 5CB. However, pure TiO_2 nanoparticles formed clusters. Also, for all doped samples except pure TiO_2 , the nematic isotropic transition temperature increased slightly by 1.4–2.4°C compared to pure 5CB which indicates increased in order parameter. It has been also observed that there is decrease in the dielectric anisotropy, response time, splay elastic constant and threshold voltage. It was found that rotational viscosity shows a slight increase with respect to pure 5CB for copper-incorporated TiO_2 and a clear decreasing for pure TiO_2 nanoparticles.[18]

Geeta Yadav observed that, due to doping concentration, the ionic contribution to dielectric loss in the low-frequency region has decreased, and a shift in relaxation frequency toward the higher frequency side has also been detected. As the concentration of nanoparticles increases, both electrical conductivity and threshold voltage decrease. At the same time, there is a continuous increase in dielectric anisotropy and an enhancement in UV absorbance. In doped systems, a continuous increase in photoluminescence (PL) intensity has been noted, with no shift in the emission peak. [24]

The influence TiO_2 NPs on E204 NLC has been extensively studied by Bhupendra Singh. DC conductivity and dielectric anisotropy for nematic LC with the suspension of TiO_2 NPs for application in display and photonic devices, has been thoroughly investigated. With the dispersion of TiO_2 nanoparticles the threshold voltage reduces and the absorption band of pure NLC has been slightly blue shifted. Due to the increase in adsorption of ionic impurities by TiO_2 it is found that the rotational viscosity has been significantly decreased and thereby a two-fold time faster response time of nematic LC is achieved. It was reported that increasing concentration of TiO_2 nanoparticles; the change in the UV–visible absorbance and photoluminescence intensity of NLC composites is found.[25]

Rohit Katiyar measured the dielectric, electro-optical, and optical parameters of NLC (NLC 1823A) with the dispersion of TiO_2 NPs. It has been observed that after dispersion of TiO_2 NPs on NLC, relative permittivity is increased, dielectric anisotropy decreased, the rise time as well as the fall time have been decreased and photoluminescence has been enhanced.[26]

Doping of Ferric Oxide nanoparticles (Fe₃O₄ NPs):

The magnetic properties of Fe₃O₄ NPs have been utilised in a broad range of applications such as magnetic seals and inks, magnetic recording media, in data storage applications, catalysts, ferro fluids, for biomedical applications - in magnetic resonance imaging (MRI), targeted drug delivery vehicles, as well as in magnetic hyperthermia and therapeutic agents for cancer treatment. These are also employed in environment and food analysis, organic and biochemical synthesis, industrial water treatment and biosciences.[27]

A. Maleki found that the dielectric properties of NLC N-(4-methoxy benzylidene)-4-butylaniline (MBBA) added with Fe₃O₄ nanoparticles. By doping Fe₃O₄ NPs mass percentages, it was observed that the dielectric permittivity was significantly increased. The characterization of the synthesised NPs with 14-18 nm studied by X-ray diffraction and field emission scanning electron microscopy. It is examined that when Fe₃O₄ NPs doped NLCs the measured dielectric anisotropy and mean dielectric values have significantly increased at 1% and 10% weight concentrations. [28]

Baeckkyoung Sung, H. Yan and C. Kim researched the way a thermotropic liquid crystal changes from a nematic to an isotropic phase when mixed with iron oxide nanoparticles. The experiment used a type of liquid crystal called 4-cyano-4'-pentylbiphenyl, along with iron oxide nanoparticles that are 6 nanometre's wide. They noticed small granules when looking through polarized light microscopy in the mixture with the nanoparticles, but these granules were not seen in the pure liquid crystal. They studied how the transition between the nematic and isotropic phases happens and suggested that the heterogeneity textures in the liquid crystal, as seen through polarized microscopy, are caused by clusters of the iron oxide nanoparticles.[29]

Pankaj Kumar Tripathi has studied dielectric and electro-optical properties of ferric oxide nanoparticles doped 4-octyloxy-4' cyanobiphenyl liquid crystal-based nanocomposites. They investigated several observations such as dielectric spectroscopy, switching time (τ_{on} and τ_{off}), dielectric permittivity (ϵ'), dielectric loss (ϵ''), relaxation frequency and optical texture of pure 8OCB and 8OCB-Fe₂O₃ nanocomposite. Due to the proper and homogenous dispersion of Fe₂O₃ NPs into 8OCB LC; molecular ordering of Fe₂O₃ nanocomposites was found to be improved. With increasing the doping of Fe₂O₃ NPs within the 8OCB dielectric anisotropy ($\Delta\epsilon$) reduced while the threshold voltage is increased. [30]

Doping of Magnesium Oxide nanoparticles (MgO NPs):

Nano-sized magnesium oxide (MgO; magnesia or periclase), an oxide of alkaline earth metal, has many advantages due to the presence of oxygen vacancies on surfaces and edges

which have the potentiality of charge transfer between substrate and adsorbate enhancing its catalytic activity [32]. It is useful as a destructive adsorbent in the hazardous waste water treatment, because of the capability to adsorb molecules by a bond-breaking process combined with its nanocrystalline variety. The additional characteristics are its bactericidal effects and optically transparency [31, 33-36]. Owing to these properties, it was chosen as a suitable dopant in LCs to yield a composite with better applications.

Kobayashi et al. had observed a reduction of the V_{th} and the operating voltage after doping of MgO nanoparticles into TN -LCD cells and electrically controlled birefringence (ECB) LC cells, and the reason behind this was reported to be the reduction in order parameter [37].

MgO nanoparticles dispersion effects in electro optical parameters of 5CB nematic liquid crystal investigated by R. Vafaei. It was found that by increasing MgO NPs concentration, elastic splay constant (K_{II}) dielectric permittivity ($\epsilon_{||}$ and ϵ_{\perp}) and dielectric anisotropy ($\Delta\epsilon$) continuously decrease as well as reduces conductivity at low concentration. For pure and nano doped systems dielectric permittivity decreases for low frequency range ($<200\text{Hz}$) but for the range $200 < f < 500\text{ Hz}$ it remains constant. Phase delay (δ) between $I_{||}$ and I_{\perp} was also measured.[38]

Zahra Seidalilir and Sura Abbas Taher studied enhanced electrochemical characteristics and superior electro-optical switching performance of E7-NLC doped with MgO NPs. The double-layer capacitance of the NLC shows a substantial increase as the concentration of nanoparticles (NPs) rises to 0.5 wt%. Dielectric results indicate that the molecular order in the NLC system is improved in the presence of the NPs. The addition of MgO NPs to the E7 NLC it has been observed that an increase in $\epsilon_{||}$ and a reduction in ϵ_{\perp} , a significant rise in the dielectric anisotropy as well as lowering of relaxation time and threshold voltage reduced mixture rotational viscosity. They also examined that the field-off switching time of NLC doped with 0.5 wt% NPs decreases by 31% relative to the pure E7 sample. [39]

Doping of Nickel oxide nanoparticles (NiO NPs):

Nickel oxide (NiO; transition metal oxide; referred to as bunsenite in its mineralogical form) NPs can be used in electrochemical capacitors, supercapacitors, batteries, gas sensors, humidity sensors, memory devices, high energy density devices, antibacterial materials, etc. They are highly suitable for energy conversion and storage devices and are favoured as anode materials because of their high theoretical specific capacitance. NiO NPs have superior functionality, non-volatile memory characteristics, and desirable optical, electrochemical, and magnetic properties.

The improvement of dielectric and optical parameters by doping NiO nanoparticles in the NLC (5CB) investigated by Gaurav Jamwal. With the addition of NiO nanoparticles dielectric permittivity and dielectric loss values decreases as well as decreases the value of $\tan\delta$ which shows the low relaxation frequency of the ions. They investigated that after doping NiO on NLC; optical contrast has been improved.[40]

H. M. Lee and H. K. Chung investigated those superior electro-optical properties for Nickel oxide nanoparticles doped liquid crystal system. They confirmed the electro-optical characteristics of twisted nematic (TN) cells doping NiO nanoparticles on rubbed polymer surface, had faster response times and lower threshold voltage characteristics without capacitance hysteresis.[41]

CONCLUSION

This review focuses on a detailed and organized study of how metal oxide nanoparticles (MO-NPs) interact with liquid crystals (LCs). It also explores the potential of MO-NPs/LC composites for technological improvements. Combining nanotechnology and liquid crystals (LCs) through metal oxide nanoparticle (MO-NP) doping has been essential in advancing research. It has also helped raise awareness of the potential benefits of MO-NP-doped LCs for modern display technology and innovative new applications. This innovative method has improved the electro-optical, thermal, physical, and rheological properties of MO-NP-doped liquid crystals, making them highly useful for abundant applications across several fields. Today, many researchers are exploring various metal oxide nanoparticles (MO-NPs) to dope into liquid crystals (LCs). Their goal is to broaden the scope of research and discover new advancements in the field. In the future, more valuable metal oxide nanoparticles (MO-NPs) can be identified and effectively used with advanced techniques and strategies in liquid crystals (LCs) to achieve better results. As research progresses, significant advancements are expected in this field.

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