Evaporative deposition of SiO$_2$ nanoparticles multilayer on ITO substrates and application for vertical alignment of liquid crystals - Effect of dichroic dye

Ankit Rai Dogra, Vandna Sharma, Partha Khanra and Pankaj Kumar*

Centre for Liquid Crystal Research, Chitkara University Institute of Engineering and Technology, Chitkara University, Punjab, India

*Corresponding author’s e-mail ID: pankaj.kumar@chitkara.edu.in

Abstract. In this work the SiO$_2$ nanoparticles layer was deposited by solvent evaporation on ITO substrates and used for vertical alignment of pure and dye doped liquid crystal (LC) in confined cells. The pure nematic liquid crystal (NLC) material was filled into SiO$_2$ layer coated cell by the capillary injection method. The 0.5 wt.% of dichroic dye added into the LC mixture and studied its effect on electro-optic behaviour of display cell. The FESEM study reveals the multilayered deposition of the SiO$_2$ on Indium tin oxide (ITO) substrates. conoscopic and polarised optical microscopy (POM) study show good dark black and bright textures at OFF and ON state under the cross polarizers and confirm vertical alignment (VA) of LC molecules. The electro-optical (E-O) study shows the lower threshold and operating voltage with higher contrast ratio in dye doped vertically aligned LC (VALC) cell as compare to the pure SiO$_2$ coated VALC cell.

1. Introduction

Liquid crystals (LCs) constitute a state of matter intermediate between crystalline solids, which are defined by a orderly periodic arrangement of atoms or molecules, and isotropic liquids. They exhibit varying degree of orientational or translational order in specific spatial directions. LC materials have been widely used for several applications because of their controllable and optical properties, fast response to potential and low power consumption [1]. Now, a days various method has been developed for controlling the vertical alignment (VA) of the LC for flexible display applications. Such as photo-alignment method [2-3], nanoparticles doping such as POSS [4-5], carbon nanotubes [6-7], Ag [8], Au [9], ZnO [10-11], TiO$_2$[12-13], MgO [14], graphene oxide [15-16] and quantum dots [17-18] etc. In this work, the vertically aligned LC (VALC) cell was fabricated for display devices using silica (SiO$_2$) NPs coated ITO glass substrates prepared by capillary convective self assembly method. The SiO$_2$ NPs coating will generate the roughness and support the director of LC molecules to orient perpendicular to the substrates and attain VA on the substrates. Figure 1 (a) represents the schematic of pure SiO$_2$ coated VA of the LC molecules inside the confined cell at during zero voltage (OFF state) which will block the incident light to transmit through the VALC cell under crossed polarizers and obtain the darker textures on viewing under POM. In figure 1 (b) the bright texture was obtained during voltage increase due to the planar orientation switching of the LC molecules in the confined cell under cross polarizers. On the other hand in figure 1 (c) represents the dye doped VA in the
confined cell at zero voltage (OFF state), due to this black texture is appeared under the cross polarizers. When the sufficiently required voltage is applied, the orientation director of the LC molecules switch from vertical direction to planar state as shown in figure 1 (d) and transmit the incident light which showed the bright textures on viewing under POM. The morphological and electro-optical (E-O) characteristics have been observed for the pure SiO$_2$ NPs coated and dye doped VALC cells for display devices.

**Figure 1.** The schematic illustration of the pure and dye doped VALC cell. (a) shows the VA of LC in pure SiO$_2$ coated cell in OFF state, (b) ON state planar orientation of LC with respect to the ITO substrate, (c) the dye doped VALC cell with vertical orientation of dye-LC molecules inside the cell at OFF state and (d) the planar orientation of dye-LC molecules inside the cell in ON state under applied potential.
2. Materials and method

2.1 Materials used

Nematic liquid crystal (MJ98468, Merck, UK) with its negative dielectric anisotropy ($\Delta\varepsilon = -4$), having ordinary and extraordinary refractive index $n_o = 1.47$, $n_e = 1.55$ respectively and nematic to isotropic transition temperature $T_{(N-I)} = 75$ °C, was used in the experimental work. The SiO$_2$ with average diameter of 15 nm (polydisperse, Nanostructured & Amorphous Materials, Inc., USA) was used as received. Azo orange 3 dichroic dye (Sigma Aldrich) was used as a dopant with LC mixture. Further, the optical and conoscopic textures were observed using a polarized optical microscope (POM, Nikon Eclipse LV100POL, Japan) connected with CCD camera (Q28378), to confirm the alignment of LC molecules at the surfaces. The E-O properties of the cells positioned between crossed polarizers, with a direction of 45° were measured using a laser beam of wavelength 632.8 nm and square wave field at a frequency of 100 Hz using function generator.

2.2 Preparation of SiO$_2$ coated ITO cell

Initially, 0.3 wt.% of SiO$_2$ NPs were dispersed in deionized (DI) water. The homogeneous dispersion of was obtained by stirring the mixture for 24 hours with magnetic stirrer and then placed in ultrasonication bath at 40 kHz frequency for next several hours. On the other hand, Indium Tin Oxide (ITO) glass substrates were cleaned properly with DI water, acetone and isopropyl alcohol for several times. Clean ITO substrates dried in hot air vacuum oven for 2 hours at 120 °C and then further used for LC cells fabrication. For fabrication, the cell gap was maintained 10 µm with Mylar spacer. For deposition of SiO$_2$ NPs layer on ITO substrates, the homogeneous mixture of SiO$_2$ and DI water was filled into empty cell by capillary action. The filled cell further placed on hot plate at 50 °C for evaporation of the solvent. After completion of the evaporation of solvent the SiO$_2$ layer was deposited on the ITO surface in confined cell. Now the confined SiO$_2$ coated cells were filled with pure and 0.5 wt.% azo dye doped nematic LC mixture by capillary action. Here, the 0.5 wt.% azo dye doped LC mixture was prepared in a vial by continuously stirring using magnetic stirrer at isotropic temperature for overnight. The prepared cells were used to study the alignment of LC molecules and electro-optic study.

3. FESEM study of deposited SiO$_2$ layer on ITO substrates

The SiO$_2$ coated ITO substrates were analysed using the (FESEM, Hitachi, SU8010 Series, Japan). From results it has been analysed that the coating of the SiO$_2$ NPs shows the closely packed multilayer deposition on ITO substrate. Further, the E-O results show that at 0.3 wt.% concentrations of NPs, multilayered deposition provided the sufficient roughness on the ITO substrates to support the self assembly of LC molecules in the vertical direction.
4. **POM and morphological study of VALC cells**

Morphological study of pure and dye doped cells were observed by POM under the crossed polarizers at the magnification of 20x. The results show quite dark black texture in off state of both pure and dye doped cell without any light leakage. The conoscopic images as shown in inset in figure 3 (a and b) also show the perfect VA of LCs molecules. Further on increasing the potential, VA of the LCs twist towards the planar direction. As the potential starts to increase, near to the threshold value the POM textures exhibited fluctuation in the VA of LCs and can be seen in figure 3 (a and b). The perfect bright textures at 2.27V and 2.26V are observed in pure LC cell and dye doped LC cell respectively, as the applied potential increases the orientation of LC molecules changes from VA to planar alignment with respect to the substrate. On comparing the textures of both sample cell, the dye doped cell have lower switching and operating voltages and fast switching.
5. **Electro-optic study of VALC cells**

Voltage-Transmittance (V-T) study of pure and dye doped sample cells was conducted using E-O setup and has shown in figure 4. From results it has been found that the both pure and dye doped cell shows the almost similar value of threshold voltage ~ 2.10 V at beginning of the potential, while a significant reduction in operating voltage was obtained in dye doped VALC cell. The contrast ratio (CR) was also found much improved in dye doped cell as compare to the pure cell as given in table 1. The number of oscillations (i.e., the number of maxima during a complete reorientation of the director) in the V-T curve of figure 4 is approximately \((d\Delta n/\lambda)\) [15]. By adding the value \(\Delta n = 0.077\) for MJ98468, \(\lambda = 632.8\) nm for the He-Ne laser, and the LC cell gap, \(d = 10\ \mu m\), the calculated \((d\Delta n/\lambda)\) = 1.21. This indicates that the transmittance curve should exhibit one full maxima.
**Figure 4.** V-T characteristics of SiO$_2$ NPs coated pure and azo dye doped VALC cells.

| Sample                  | Threshold Voltage | Operating Voltage | Contrast Ratio |
|-------------------------|-------------------|-------------------|----------------|
| Pure LC cell            | 2.10              | 2.29              | 80.18          |
| azo dye doped LC cell   | 2.08              | 2.20              | 82.88          |

**6. Conclusion**

Results conclude that the SiO$_2$ coated ITO cells give the vertical alignment of the LC molecules on substrate surface and improved characteristics of the LC device. The FESEM results exhibit the closely packed multilayer deposition on ITO substrate that helps LC molecules to orient in the vertical direction. Further, the morphological study of POM results shows improve transmittance in azo dye doped LC cell as compare to pure LC cell. The E-O results exhibit comparatively lower threshold voltage and higher contrast ratio value for dye doped LC cell. Thus, with augmented E-O characteristics , the proposed study is much useful for flexible electronic display devices.

**References**

[1] Yuan S and Ingo D 2019 *Appl. Sci.* 9 47.
[2] Kumar P, Oh S Y, Baliyan V K, Kundu S, Lee S H and Kang S W 2018 *Opt. Express* 26 8385.
[3] Chinky, Dogra A R, Sharma V, Gahrotra R Malik P and Kumar P 2020 *AIP Conf. Pro.* 2220 3.
[4] Chen S H, Chou T R, Chiang Y T and Chao C Y 2017 *Mol. Cryst. and Liq. Cryst.* 646 15.
[5] Hwang S J, Jeng S C, Yang C Y, Kuo C W and Liao C C 2009 *J. Phys. D Appl Phys.* 42 1098.
Acknowledgment

The author (Pankaj Kumar) gratefully acknowledges the financial support by SERB, Department of Science and Technology (New Delhi), Government of India, under the research project number EMR/2017/005282.