
EFFECT OF COPPER OXIDE DECORATED CARBON NANOTUBES ON THE RESPONSE TIME OF FERROELECTRIC LIQUID CRYSTALS

In this chapter, fast electro-optic response in copper oxide (CuO) decorated multi walled carbon nanotubes (MWCNTs) doped ferroelectric liquid crystal (FLC) has been discussed. The electro-optical measurements confirmed the fastening of response in doped FLC material. Doping of CuO decorated MWCNTs into FLC also reduced the unwanted ionic impurities present in the studied FLC material which can be confirmed by the dielectric measurements followed by the electrical measurements. The underlying mechanism would certainly help to understand the basic mechanism of interaction of CNTs with FLC molecules and to fabricate ionic defect free faster display devices.

5.1 INTRODUCTION

In previous chapter, we have discussed that a minute addition of graphene oxide (GO) into FLC material improved the alignment without any surface treatment and enhanced the material parameters. GO formerly called graphite oxide or graphitic acid, is a compound of carbon, oxygen, and hydrogen in variable ratios and can be obtained by treating graphite with strong oxidizers. In the present study, we are using metal oxide [*i.e.*, copper oxide (CuO)] decorated MWCNTs to observe the effect on the material parameters of FLC material. CNT is itself an important member of carbon family whose configuration is totally different from GO, as GO shows the layered morphology while CNTs are cylindrical fullerenes and a fullerene is any molecule composed entirely of carbon, in the form of hollow sphere, ellipsoid or cylindrical tubes. The field of CNTs has drawn a great deal of interest in fundamental and applied research since their discovery by Iijima in 1991 [1]. CNTs because of

their unique molecular structure results in extraordinary macroscopic properties, including high tensile strength, high flexibility, high electrical conductivity, and chemical stability [2, 3]. The morphology, size (aspect ratio) and electrical properties of CNTs have proven their importance in employing the devices, such as, field effect transistors [4], memory storage devices [5], sensors and actuators [6, 7], field emission sources [8] and many more.

In the demand of fast operation of the display devices, the response time plays the most important role for addressing the liquid crystal (LC) based display devices. LCs turn out to be excellent hosts for CNTs. Having molecular structure similar to CNTs, LCs perfectly incorporate CNTs into their own structure. The doping of CNTs [either single walled (SW) or multi walled (MW)] into LCs have been pursued by various groups around the world for improving their electro-optical properties [9-12], dynamic response [13] and other physical parameters [14, 15].

But much of the reported work has been focused on nematic liquid crystals (NLCs) and twisted nematic liquid crystals (TNLCs). Lee *et al.* demonstrated the effect of CNTs on TNLC to improve the switching behavior [9]. Faster electro-optical response characteristics of CNTs-nematic suspension have been studied by Chen *et al.* [10]. The CNTs doped LC optically compensated birefringent (OCB) cells was studied by Lu *et al.* [12] for improvement in response time where the change in anchoring energy was taken into account. The doping of CNTs into FLCs, which are special members of LC family and well known for their good optical contrast, low threshold voltage, memory effect, fast response etc., is rarely reported in literature. However, some researcher observed the effect of MWCNTs on the response time of FLC material and predicted faster display devices based on them [16].

Till now, researchers around the world have doped only CNTs into LCs/FLCs to improve the material parameters. In recent time, there has been great interest to tap the potential of CNTs in the area of catalysis. Recently, many scientists and nanotechnologists attempted to decorate metals or metal oxide compounds onto the CNT surfaces which are easy to synthesize, having large production rate and low cost and could be used in many applications, such as, electrochemical sensor, and solar energy converter etc.[17-20]. The basic method to achieve the decorated CNT would be to melt the element on the tube surface. In 1996, Ebbesen *et al.* shows that only

liquids with low surface tensions will wet the surface on CNTs [21] but these results may not apply below a critical nanotube diameter. After these findings a chemical method has been developed in which CNT surface is tailored by oxidation in order to deposit metal or metal compounds of interest on the CNT surface [22, 23]. We have initiated to dope CuO decorated MWCNTs in host FLC medium in order to improve the material/physical parameters of the latter.

In this chapter, we present our results based on CuO decorated MWCNTs doped FLC material namely KCFLC 7S. We observed that CuO decorated MWCNTs fasten the response of the FLC material and reduce the ionic impurities of the same [24]. These impurities enter within LCs either through the atmosphere or alignment layer or during their synthesis and can be the cause of degradation of the display devices based on these materials [25-27]. The fastening of the response in CuO decorated MWCNTs doped FLC has been attributed to decrease in rotational viscosity whereas the reduction in ionic impurities of the FLC material has been attributed to the adsorbance/trapping of ions by CuO decorated MWCNTs. The experimental results have been confirmed and analyzed by observing the various dielectric and electro-optical measurements.

5.2 EXPERIMENTAL DETAILS

The CuO decorated MWCNTs were synthesized by chemical reduction method [17]. There are two main steps to achieve CuO decorated MWCNTs. In the first step, preparation of functionalized MWCNTs takes place while in second step, decoration of MWCNTs with CuO was taken into account. MWCNT was functionalized in order to disperse well in water. In this we take about 2g of MWCNT, 2g of sodium nitrate (NaNO_3) and 60ml sulphuric acid (H_2SO_4) stirred together in an ice bath. This is followed by slow addition of 12g of potassium permanganate (KMnO_4). All chemicals were purchased from MERCK and were used as received. Once mixed, the solution was transferred to a water bath having temperature around 35°C and stirred for about 1 hour resulting in the formation of a thick paste. Now we mixed 100 ml of distilled water into the thick paste and stir it for 2 hours with the temperature maintained at 90°C . Finally, 200 ml of water was added, followed by the slow

addition of 10 ml of H₂O₂. The warm solution was then filtered and washed with 200ml of 10% HCl and later by 200 ml water. The filtered material was then dispersed in water by mechanical agitation and stirred overnight. The final product (functionalised MWCNT) was filtered and can be easily dispersed in water.

In the synthesis of CuO decorated MWCNTs, we used Cu salts namely copper sulphate penta-hydrate (CuSO₄.5H₂O). The salt was dissolved in half litre distilled water and heated upto 50-80°C on magnetic hot plate stirrer. Potassium sodium tartrate (0.0031g) was used as a complexing agent. Functionalized MWCNTs prepared as above, were added with salts hydrazine hydrate as reducing agent (around 10 ml). The pH of the solution (10-12) was maintained by sodium hydroxide (NaOH) at temperature 50-80°C. Stirring was continued for 2 hours and then solution was filtered and washed with distilled water two or three times.

To make the dispersion with FLC material, a small amount (0.5 wt %) of CuO decorated MWCNTs was added into FLC material and sonicated the mixture at higher frequencies for two hours. The prepared mixture of CuO decorated CNTs doped FLC material and pure FLC material were introduced into the LC sample cells by means of capillary action at temperatures just above the isotropic transition temperature of the FLC material used.

The sample cells for the present study were prepared by using photolithographic technique and the homogeneous (HMG) alignment on the patterned glass plates was obtained by using rubbed polyimide technique. The phase sequence of the FLC (KCFLC 7S) material used in this study, is as follows:



The dielectric and resistivity/conductivity studies of the pure and doped cells have been measured using an impedance analyzer 6540 A (Wayne Kerr, U. K) in the frequency range 20 Hz –1 MHz. The tilt angle measurement was carried out by observing the texture under polarizing microscope (Ax- 40, Carl Zeiss, Germany) on the application of bias field. Microstructures of the samples were analyzed by using scanning electron microscope (SEM, LEO 440), coupled with energy dispersive spectroscopy (Oxford, Link ISIS 300). The material parameters such as spontaneous

polarization (P_s), rotational viscosity (η), and response time (τ) were measured by automatic liquid crystal tester (ALCT, Instec, U. S. A.).

5.3 RESULTS AND DISCUSSION

The size of CuO decorated MWCNTs, which were doped in FLC material, play a critical role for electro optic response of these materials. Figure 5.1 shows the scanning electron microscopic (SEM) images of CuO decorated MWCNTs with different magnification.

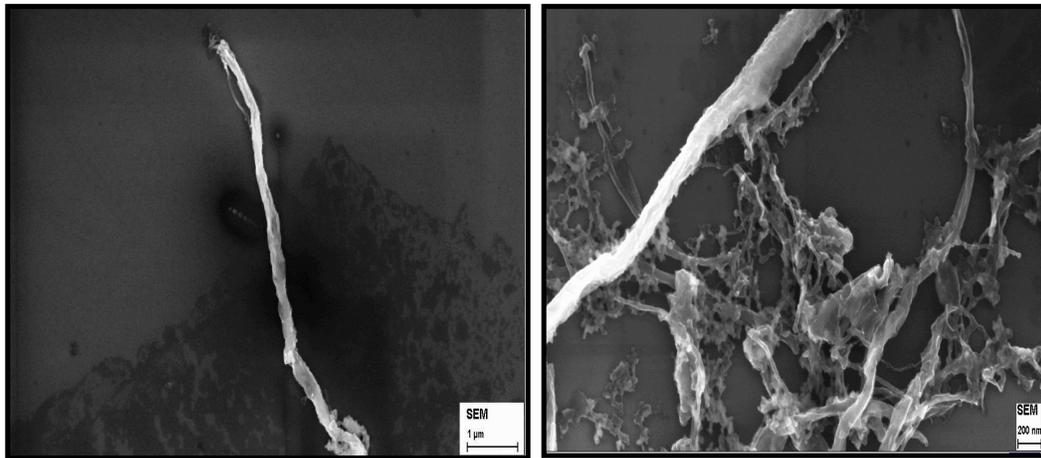


Figure 5.1: Scanning electron microscopic images of CuO decorated MWCNTs at scale bar: 1 μ m and 200 nm.

The diameter of synthesized MWCNTs ranged 5-20 nm whereas the typical length was from 0.3 to 8 μ m. SEM microstructures allow us to study the surface of the sample and are not suitable for investigating bulk LC-CNT dispersions. SEM images have been found the most informative when CNT dispersion is to be tested for particle size, concentration, agglomeration, bundling and alignment in an external electric field.

The doping of CuO decorated MWCNTs into host FLC medium, can improve the material parameters. Among all intrinsic physical parameters of FLC materials, the response time (τ) plays the most important role in order to design fast display devices.

So, we measured the electro-optical response of pure and CuO decorated MWCNTs doped FLC material at different voltages. Figure 5.2 shows the behavior of response time (τ) with different applied voltages for pure and CuO decorated MWCNTs doped FLC material in 4 μm sample cells while inset of the figure shows the behavior of response time (τ) for both pure and doped FLC material in thick sample cells ($\sim 10 \mu\text{m}$), with different applied voltages.

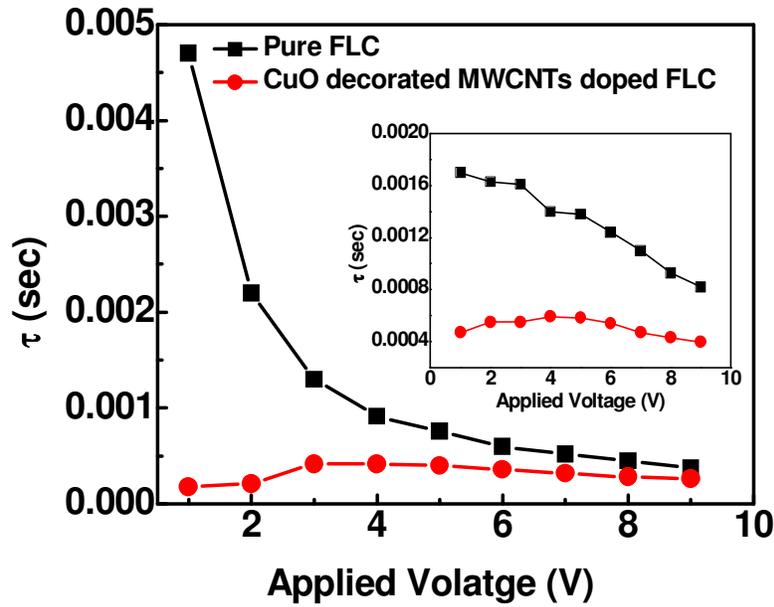


Figure 5.2: Behavior of response time with different applied voltages for pure and CuO decorated MWCNTs doped FLC at room temperature for thin sample (4 μm) cells. The behavior of the same for thick sample (10 μm) cells has shown in the inset.

It is clearly reflected from Fig. 5.2 that after doping CuO decorated MWCNTs, the response time (τ) of FLC material has been improved and this improvement was independent of thicknesses of the sample cells and this change is more significant particularly at lower voltages. The improvement in response time (τ) in case of the CuO decorated MWCNTs doped FLC has been attributed to the decrease in rotational viscosity (η). The doping of CuO decorated CNTs looses the packing of FLC molecules so they respond faster as compared to the pure FLC material and this loosening of molecules is also one of the reasons behind the fastening of the response.

The rotational viscosity (η) of LC material affects the response time (τ) of the same because it is directly related with the response time (τ) through the following relation:

$$\tau = \frac{\eta}{P_s E} \quad (5.1)$$

where, P_s is the spontaneous polarization and E is the applied field, respectively.

Figure 5.3 shows the behavior of rotational viscosity (η) as a function of applied voltage for pure and CuO decorated MWCNTs doped FLC sample cells, respectively, while inset of the figure shows the behavior of rotational viscosity (η) for both pure and doped FLC material in thick sample cells ($\sim 10 \mu\text{m}$), with different applied voltages.

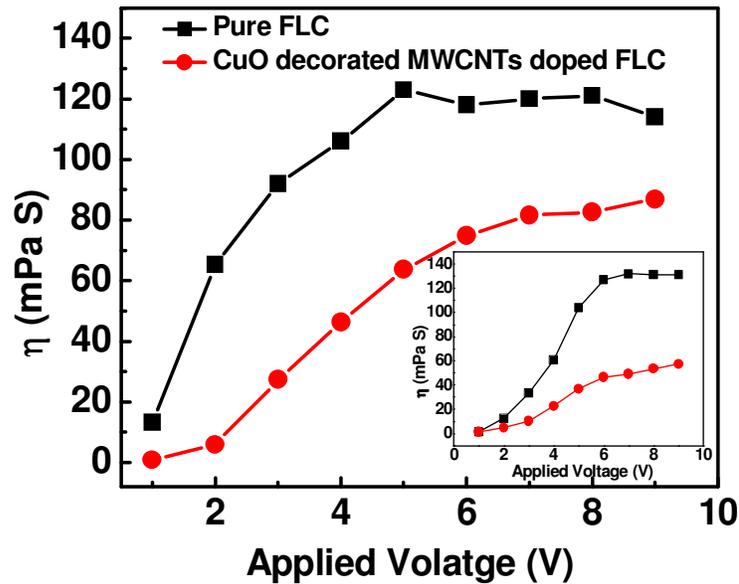


Figure 5.3: Behavior of rotational viscosity (η) with different applied voltages for pure and CuO decorated MWCNTs doped FLC material at room temperature for thin sample ($4 \mu\text{m}$) cells. The behavior of the same for thick sample ($10 \mu\text{m}$) cells has shown in the inset.

As shown in the figure, the rotational viscosity (η) in the doped FLC material has been lowered almost half to that of the pure FLC material in both thick and thin sample cells, and such decrement in rotational viscosity (η) is twofold [16, 28]. First, it has been observed that both CNTs and FLC molecules experience a torque due to

their non-trivial dielectric anisotropies on the application of electric field. The distinct dielectric anisotropies and aspect ratios imply that the dynamic response is not the same in the pure and doped FLC sample cells. Hence, we observed the change in viscosities of pure and doped FLC material. Secondly, the doping of CuO decorated MWCNTs in FLC perturbs the order parameters such as tilt angle (θ) and spontaneous polarization (P_s), which are primary and secondary order parameters in case of FLC materials, respectively, and these parameters can alter the value of rotational viscosity (η) of the material. Figures 5.4(a) and (b) show the behavior of optical tilt angle (θ) and spontaneous polarization (P_s) as a function of applied voltage for both pure and CuO decorated MWCNTs doped FLC material, respectively, in thin sample cells. As reflected from the Fig. 5.4(a), the saturation value of the tilt angle (θ) in both pure and doped samples is almost the same while Fig. 5.4(b) shows a little change in the values of the spontaneous polarization (P_s) of pure and CuO decorated MWCNTs doped FLC samples.

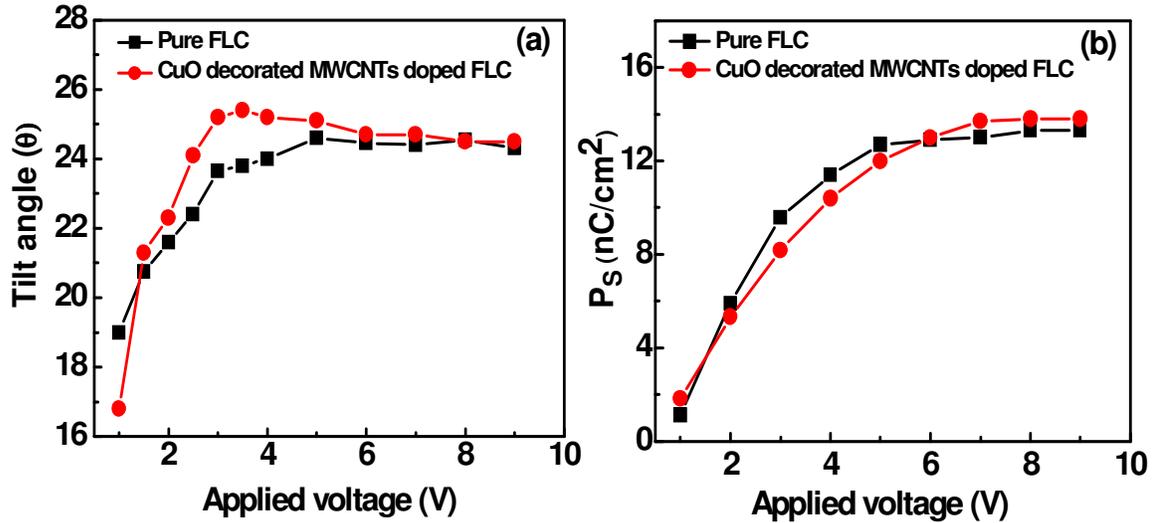


Figure 5.4: Behavior of (a) the optical tilt (θ) and, (b) spontaneous polarization (P_s) with different applied voltages for pure and CuO decorated MWCNTs doped FLC samples at room temperature.

The decrease in rotational viscosity (η) lowers the response time (τ), *i.e.*, fastens the response of material in accordance with the Eq. (5.1). For the estimation of rotational

viscosity (η), we have to calculate response time (τ) and spontaneous polarization (\mathbf{P}_S) of the sample as we know ($\eta = \tau \mathbf{P}_S E$) from Eq. (5.1).

Response time (τ) is calculated by square wave method. These square wave signals are applied to FLC sample and the current response associated with switching process is monitored as voltage across a series resistance in storage oscilloscope. The spontaneous polarization (\mathbf{P}_S) is calculated by using triangular wave method in which a triangular wave pulse of desired amplitude and frequency was applied across the sample cell and the response of output current was recorded using oscilloscope. Details of response time (τ) measurement by square wave method and spontaneous polarization (\mathbf{P}_S) measurement by triangular wave method have been discussed in **Chapter II** of the thesis. The existence of CNTs in LC does not alter the dielectric permittivity (ϵ') appreciably [11, 15]. Figure 5.5 shows the behavior of dielectric permittivity (ϵ') as a function of frequency in doped FLC sample.

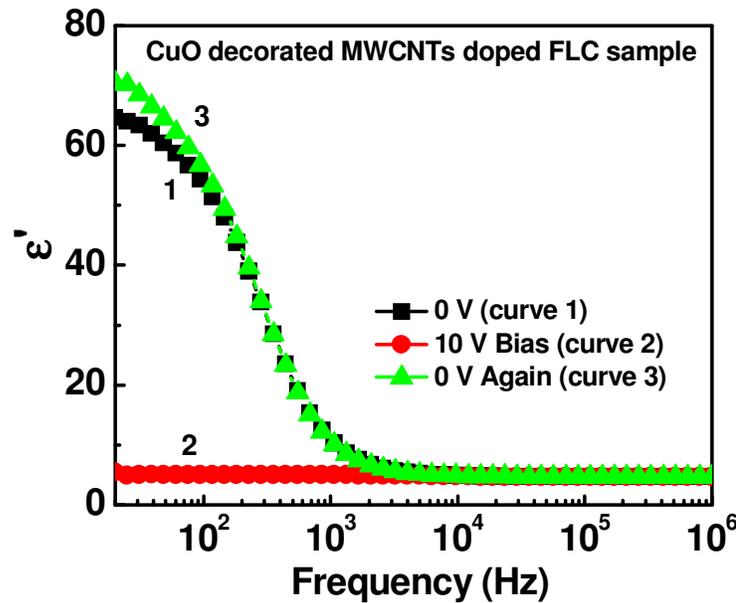


Figure 5.5: Dielectric permittivity as a function of frequency at room temperature at 0 V (curve 1), 10 V (curve 2), and again 0 V (curve 3) of CuO decorated MWCNTs doped FLC cell.

One can clearly see from the figure that the change in bias voltage of measuring field from 0 to 10 V, the value of dielectric permittivity (ϵ') decreases to the minimum that is due to suppression of Goldstone mode. Again applying 0 V bias, the value of dielectric permittivity (ϵ') appears same as it was before applying the bias. This confirms that the cell does not remain in stable state and hence no memory effect. The reasons behind observing no memory in doped FLC are its decrease in rotational viscosity (η) and loosening of molecular packing. When the molecules are loosely packed, they do not remain in stable state otherwise doped FLC would have shown the memory effect.

The ionic impurities, which enter within LCs either through the atmosphere or alignment layer or during their synthesis, generate electric field which leads to polar surface interactions or affect the anchoring energy and driving voltage of the LC material [29, 30]. These ions may cause grey-level shift, image sticking and slow response of the LC devices [31]. So, it is important to minimize/reduce these undesired ionic impurities in order to get better electro-optic devices based on LCs/FLCs. Recently, some remarkable efforts have been made in the direction of minimization of ionic impurities of LC materials by doping nanomaterials, such as insulating nanoparticles (NPs), ZnO NPs, TiO₂ NPs, Si₃N₄ NPs, inorganic montmorillonite nano-platelets, and CNTs into the LC material [32-36]. More recently, our group tried to suppress the undesired ionic effect in FLCs by doping of alumina NPs and observed the reduction of the former up to some extent [37].

The FLC material used in the present studies also possesses ionic impurities which may cause the degradation of the display devices based on it. Figure 5.6 shows the behavior of dielectric loss factor ($\tan \delta$) of pure and CuO decorated MWCNTs doped FLC material with frequency at room temperature in a homogeneously aligned cell having thickness of 4 μm . As can be seen from Fig. 5.6, there are two relaxation peaks in pure FLC material and the peak at high frequency side corresponds to the Goldstone mode whereas the low frequency peak is related with the low frequency relaxation of the material. This low frequency mode can not be assigned either as Goldstone mode or the mode purely due to space charge accumulation near the substrate surface [38].

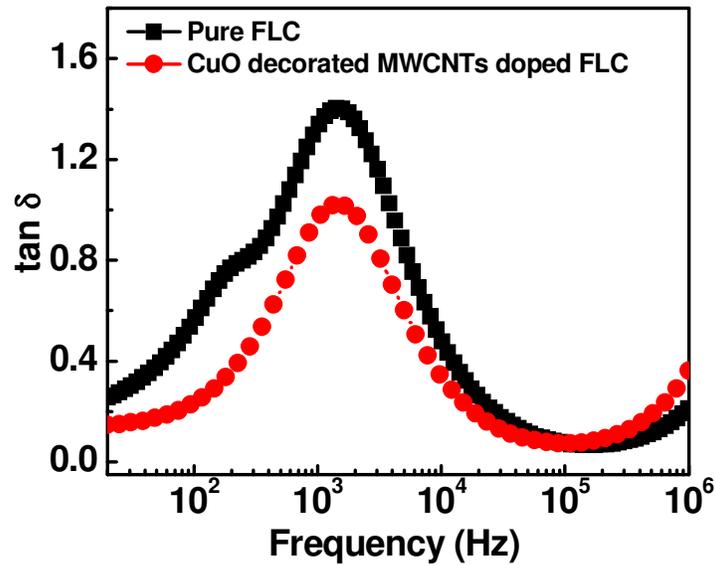


Figure 5.6: Behavior of dielectric loss factor ($\tan \delta$) with frequency for pure and CuO decorated MWCNTs doped FLC sample cells at room temperature.

The occurrence of such mode was related to the relaxations of the ionic impurities present in the material and was attributed to the ionization–recombination assisted diffusion of slow ions in HMG alignment configuration. It is clear from Fig. 5.6, that the low frequency mode has been completely disappeared in CuO decorated MWCNTs doped FLC material. The disappearance of low frequency mode suggests that CuO decorated MWCNTs adsorb/trap the ions those are responsible for the generation of low frequency relaxation. The suppression of ionic contributions of studied FLC material has further been confirmed by observing the behavior of electrical resistance (R) with frequency.

Figure 5.7 shows the behavior of electrical resistance (R) with frequency for pure and CuO decorated MWCNTs doped FLC sample cells.

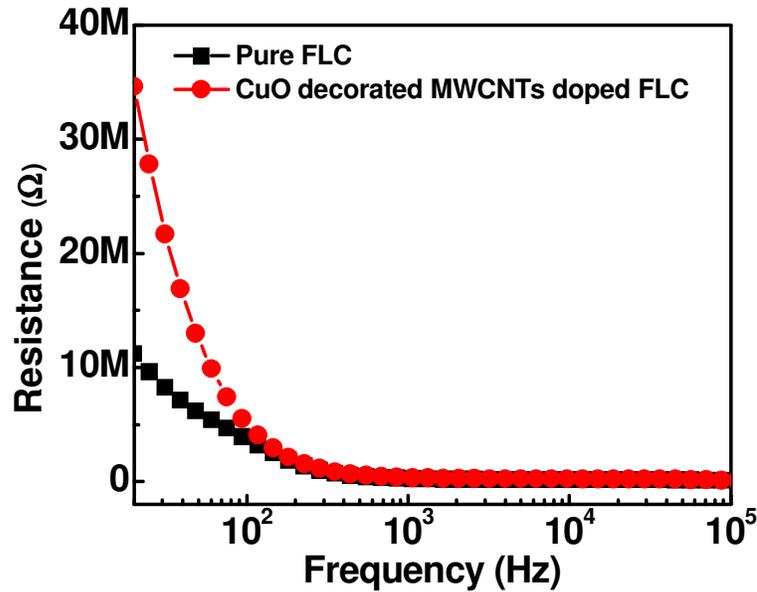


Figure 5.7: Behavior of electrical resistance (R) with frequency for pure and CuO decorated MWCNTs doped FLC sample cells at room temperature.

The value of resistance (R) for doped FLC material is around 35MΩ while the value of resistance (R) for pure FLC material is around 10MΩ, at frequency 20 Hz at room temperature, which is higher than that of pure one, suggesting the reduction of ions.

The possible mechanism behind the reduction in ionic impurities of the studied FLC material is the trapping of ions by MWCNTs and adsorption of the same by CuO with which the MWCNTs were decorated. It has been observed earlier that MWCNTs trap the ions whereas oxides of metal and non-metals are known to be useful for removing constituents from a gas or liquid stream by adsorbent mechanisms [36, 38-40]. So, the collective effect of CuO and MWCNTs doping into FLC material helps to reduce the ionic impurities by the adsorption/trapping of the ions present in pure FLC material.

5.4 CONCLUSIONS

The results based on CuO decorated MWCNTs doped FLC material have been demonstrated. It has been observed that CuO decorated MWCNTs fasten the response of the FLC material and reduce the ionic impurities of the same. The fastening of the response in CuO decorated MWCNTs doped FLC has been attributed to the decrease in rotational viscosity (η) whereas the suppression of ionic impurities of the host FLC

medium has been attributed to the adsorbance/trapping of ions by the guest CuO decorated MWCNTs. The experimental results not only clarify the fastening of the response but also provide the fundamental concept enabling one to develop electro-optic applications of LC device by incorporation of nano scale material. The results presented here also suggest that the CNTs doped FLCs are superior to any other types of sample and such superior advantages would suggest promising alternative to conventional LC material for LC photonic devices and the underlying mechanism would certainly help to fabricate ionic defect free faster electro-optic devices.

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