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Conductivity variations of multi-walled carbon nanotubes oriented in liquid crystal cells

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ABSTRACT:

The control of carbon nanotubes conductivity is generating interest in several fields since it may be relevant for a number of applications. The self-organizing properties of liquid crystals may be used to impose alignment on dispersed carbon nanotubes, thus controlling their conductivity and its anisotropy. This leads to a number of possible applications in photonic and electronic devices such as electrically controlled carbon nanotube switches and crossboards.

In this work, cells of liquid crystals doped with multi-walled nanotubes have been prepared in different configurations. Their conductivity variations upon switching have been investigated. It turns out that conductivity evolution depends on the initial configuration (either homogeneous, homeotropic or in-plane switching), the cell thickness and the switching record. The control of these manufacturing parameters allows the modulation of the electrical behavior of carbon nanotubes. .

Key words: liquid crystal, carbon nanotubes, conductivity, alignment, anisotropy,

1.- Introduction

Carbon nanotubes (CNTs) are perhaps one of the most interesting new materials emerged during the last decades. A nanotube is formed with one layer of graphene rolled up into a cylinder having a diameter in the nm range [1]. There are two main classes of CNTs. Single-walled carbon nanotubes (SWCNTs) consist of just one rolled up graphene layer. Multi-walled nanotubes (MWCNTs) are composed of several such concentric cylinders nested into one another (Fig. 1).

CNTs show peculiar electrical properties. As expected, the electrical conductivity is highly anisotropic; moreover, metallic or semiconductive is found along the tube axis. Because of the nearly one-dimensional electronic structure, electronic transport in metallic SWCNTs and MWCNTs occurs ballistically (i.e., without scattering) over long nanotube

lengths, enabling them to carry high currents with essentially no heating [2].

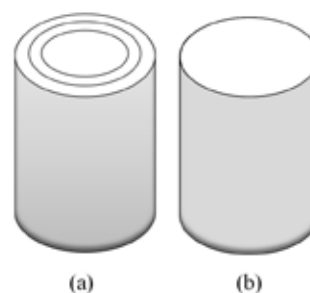


Fig. 1: Schematic illustration of a MWCNT (a) and a SWCNT (b) section.

Liquid crystals (LCs) are anisotropic fluids, thermodynamically located between the isotropic liquid and the three-dimensional ordered solid phase. From the technical point of view, the most interesting LCs are thermotropic calamitic materials, i.e., rod-like molecules that reach the LC state within a range

of temperatures between solid and liquid states. These LCs feature several more or less ordered phases. The nematic phase exhibits orientational order of the rod-like molecules, while their relative positions are randomly distributed. The average direction of the long molecular axes is called the LC director \mathbf{n} . LC cells can be oriented by preparing a thin (μm or $10^3 \mu\text{m}$) vessel whose inner surface is conditioned in advance to impose a certain orientation. It is customary to employ plates with a conductive coating in their inner surface. The LC director can be easily reoriented by application of electric fields above a certain threshold called Freedericksz transition [3]. For LCs with negative dielectric anisotropy ($\Delta\epsilon < 0$), application of an electric field will result in a reorientation of the LC from homeotropic (perpendicular to the electrode plates) to planar (parallel to the electrode plates) after threshold voltage is exceeded. When dielectric anisotropy is positive ($\Delta\epsilon > 0$), application of an electric field results in a reorientation from planar to homeotropic. In the in-plane switching (IPS) configuration, the homogeneously aligned LC rotates in plane.

The self-organizing properties of LCs may be used to impose alignment on dispersed CNTs and the Freedericksz transition to manipulate the alignment direction through elastic interactions with the LC director field, thus controlling the direction of currents carrying the CNTs.

This idea triggered proposals for applications in photonic and electronic devices [4] as well as electrically controlled CNT switches. Conductivity differences between SWCNTs doped and undoped cells have been demonstrated using LCs with positive and negative dielectric anisotropy [5]. Previous works suggest the existence of conductivity channels in MWCNTs supporting the planar LC alignment after turning the electric field off [6]. Furthermore CNT-doped LC cells driven by an in-plane field have been fabricated and their electrooptical characteristics have been investigated [7].

This work shows our preliminary results in this area. Our first goal has been to develop a reliable manufacturing method for CNT-

doped LC cells having very different thicknesses and several configurations. Once the fabrication protocol has been established, a characterization procedure for the detection of electrical conductivity variations has been designed. This includes follow-up of the conductivity evolution upon different switching cycles.

2.- Experimental

2.1.- Materials

The liquid crystal chosen for this study is the nematic mixture MLC-6290-000 (Merck). It is a standard material employed in the manufacturing of low and medium resolution liquid crystal displays. The LC features positive dielectric anisotropy, an optical birefringence (Δn) of $0.12 @ 588\text{nm}$, viscosity of $20 \text{ mm}^2\text{s}^{-1}$ at 20°C and an ample nematic phase temperature range including room temperature.

Multi-walled nanotubes (MWCNT) have been chosen for the first series of CNT-doped LC devices. These are in principle more easy to handle, and are relatively common commercially available materials (e.g. Sigma Aldrich) at reasonable cost. The specimens have a tube outer diameter of $6\text{-}9\text{nm}$ and a tube length of about $5\mu\text{m}$. It is worth mentioning the extremely high aspect ratio of CNTs, and their length, remarkably longer than the LC molecules long axis.

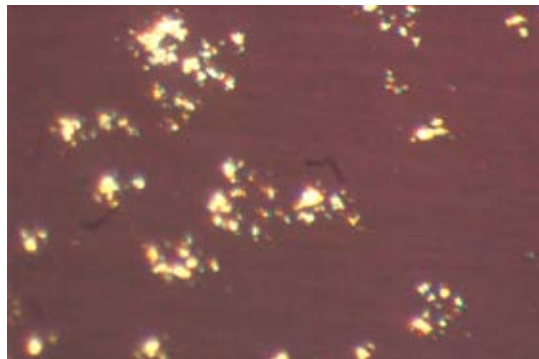


Fig. 2: A mixture of MWCNT- LC showing clusters.

2.2.- Preparation of nano doped LC mixtures

The CNTs were introduced in the LC matrix to obtain a nanoparticle dispersion. CNT concentrations in the LC-CNT mixtures were 0.01% , $0,001\%$ and $0,0001\%$. Given that a modest LC amount must be used in each batch, a number of successive dilutions [8]

was carried out. A 0.1% dispersion of MWCNTs in toluene was first prepared; the LC dispersions were obtained from this. It was previously checked that toluene did not affect the LC orientational properties. The samples were mixed for approximately 30 minutes [9] to achieve homogeneous dispersions.

Nevertheless, it was observed that dispersions were not stable upon aging (Fig.2). Whenever a mixture was to be used in cell manufacturing, a previous sonication for 30 minutes was performed to avoid clusters and recover homogeneity.

2.3.- Sample configuration

Two alignment configurations, corresponding to classical orientations for electrooptical uses have been utilized (Fig.3). Both configurations are homogeneous, i.e., the LC director is constant along the cell thickness and oriented parallel to the plane of the electrode plates (ITO-coated glass plates). The difference between those configurations is the switching strategy. The first configuration switches the director from parallel to perpendicular to the electrodes when a voltage is applied. These cells were constructed by conditioning the inner surfaces of the plates with buffed PIA 2000 polyimide.

The second configuration is called in-plane switching or IPS. Here the electrodes are located in the same plate, separated by a small (3 μm) gap. As a consequence, the homogeneously aligned LC director rotates from its original position to another orientation, perpendicular to the electrode gap. The director is always maintained in the plane of the glass plates, hence the name IPS.

In the IPS configuration only the top glass plate is coated with alignment layer (spin-coated Nylon 6, 14g/l in $\text{CCl}_3\text{CH}_2\text{OH}$). This contributes to promote the conductivity between the electrodes as enhanced by reoriented CNTs; otherwise the Nylon coating would hinder the current flow.

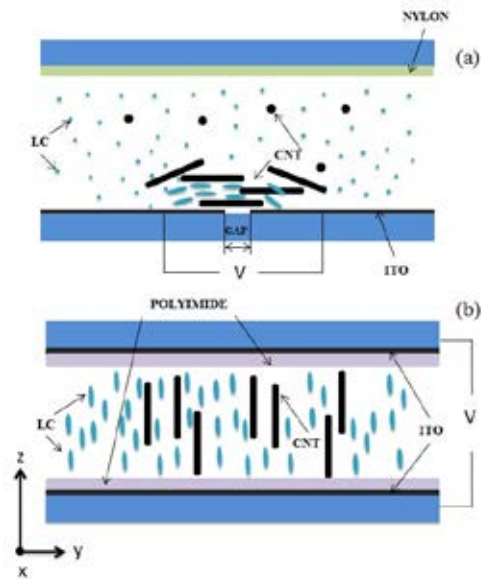


Fig. 3: Schematic structure of the CNT-doped LC cells in (a) IPS and (b) homogeneous alignment configurations.

The manufacturing protocol of standard LC cells for displays includes deposition of a SiO_2 barrier layer to avoid ionic contamination of the LC material from the electrodes upon driving. This step has had to be omitted in this case, since the barrier layer itself would interfere the conductive behavior of the samples.

3.- Results and Discussion

First results show conductivity differences between CNT-doped and un-doped cells with homogeneous alignment. CNT-doped cells show a conductivity variation as a function of the time elapsed between the electrical excitation of the cell and the actual measurement (Fig. 4).

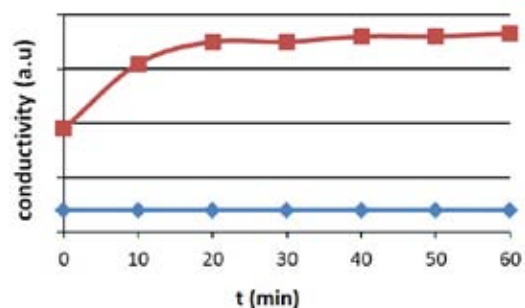


Fig. 4: Qualitative conductivity variation between un-doped (blue line) and CNT-doped (red line) cells.

Once the electrical excitation has been turned off, a memory effect is observed in the samples with homogeneous alignment, same as described in [6] where samples had homeotropic alignment (Fig.4).

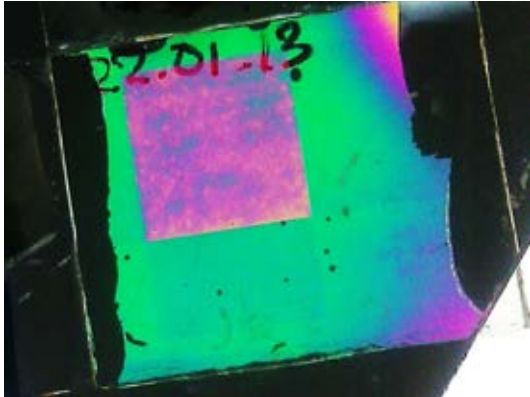


Fig. 4: Homogeneous alignment cell filled with LC MCL- 6290-000-CNTs($c=0.01\%$) between a pair of crossed polarizers. The pink area correspond to a pixel previously subjected to 5 minutes continuous switching cycle ($15.56V_{eff}$, $f=10kHz$)

LC cells have a circuitual equivalent formed for a capacitance value in parallel with a resistance. Depending of the frequency, the capacitance value translates into a characteristic impedance that may hinder the resistivity value. For this cause, it's necessary to design very carefully the procedure of conductivity measurements. In fact, a number of results published in literature could have overestimated their conductivity variations due to incorrect data capture.

The effect in IPS configuration is still under study.

4.- Conclusion

Preliminary results confirm changes in conductivity of CNT-doped cells as a function of the time elapsed from switching. Memory effect in homogeneous alignment CNT-doped cell has been demonstrated.

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