Dispersion of Nanoparticles in Liquid Crystals by Sputtering and Its Effect on the Electrooptic Properties

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SUMMARY The authors describe a method to produce gold nanoparticle-dispersed liquid crystals by means of sputtering, and discuss how the presence of gold nanoparticles affect the electro-optic response of the host liquid crystal. The method exploits the fact that liquid crystals possess low vapor pressures which allow them to undergo the sputtering process, and the target material is sputtered directly on the liquid crystal in a reduced air pressure environment. The sample attained a red-brownish color after sputtering, but no aggregations were observed in the samples kept in the liquid crystal phase. Polarization optical microscopy of the sample placed in a conventional sandwich cell revealed that the phase transition behaviour is affected by the presence of the nanoparticles and that the onset of the nematic phase is observed in the form of bubble-like domains whereas in the pure sample the nematic phase appears after the passing of a phase transition front. Transmission electron microscopy confirmed the presence of single nano-sized particles that were dispersed without forming aggregates in the material. The electro-optic properties of the nanoparticle-dispersed liquid crystal was investigated by measuring the threshold voltage for a twisted-nematic cell. The threshold voltage was found to depend on the frequency of the applied rectangular voltage, and at frequencies higher than 200 Hz, the threshold became lower than the pure samples.

key words: liquid crystals, nanoparticles, sputtering

1. Introduction

Liquid crystals (LCs) are materials possessing properties of both liquids and crystals, i.e. fluidity and anisotropy [1]. The manifestation of both these properties has resulted in the application of these materials in various electronic devices, such as displays and spatial light modulators. While liquid-crystal-display technology has seen enormous growth in the past decade with commercial displays larger than 40 in. reaching viewing angles of nearly 180° and response times of a few ms, the demand for LC materials with smaller driving voltages and shorter response speeds is still high, in view of developing field-segmental color mode displays. Among the several candidates for next-generation LCs such as polymer-stabilized cholesteric blue phases [2], nanoparticle (NP)-dispersed LCs have recently gained much scientific and industrial interest, pushed by the appearance of novel or improved properties, not observed in the pure material. Lowering of the Fredericks threshold and improved response speeds have been demonstrated in nematic LCs doped either with metal, ferroelectric or dielectric nanoparticles, [3] while on the other hand, novel optical properties, such as tunable refraction including negative and zero refractive index have been predicted in core-shell semiconductor NP-dispersed LCs [4].

Dispersion of dielectric materials and particles larger than several 10 nms have been achieved by simply mixing the NPs with the host and sonicating the mixture; however, because of the high tendency of metallic NPs to aggregate, they are usually treated chemically with capping agents to attain sufficient solubility in the host [3], [5]. Since this requires the NPs to be prepared beforehand, treated with tedious chemical reactions for functionalization, and then treated again for the removal of unwanted byproducts, the purity and throughput becomes limited and the production process is not efficient.

In order to provide a simple solution to the complex fabricating procedure of NP-dispersed LCs, we previously proposed a physical process to disperse metallic NPs in LCs [6]. We employed the sputter deposition process and fabricated stable metal NP-LC suspensions by causing the sputtered atoms to self-organize into nano-sized particles inside the host LC. It has long been known that liquid substrates used in place of conventional solid substrates are capable of holding nanoparticles of materials deposited by vacuum evaporation. However, because deposition techniques require a reduced-pressure environment, only a limited number of liquids such as oils or ionic liquids had been used so far [7]–[9]. Certain LC materials also possess low vapor pressures of ≤ 1 Pa at room temperature, [10] which is sufficient for them to undergo the sputter deposition process (which is generally performed at a pressure of a few to several tens Pa). Our proposal was the first demonstration to use LCs as substrates in the sputtering process.

In this invited paper, we will first describe the fabrication procedure of NP-dispersed LCs by sputtering, and then characterize the NP-dispersed LC through measuring the optical extinction spectra and performing transmission electron microscope (TEM) and polarizing optical microscope (POM) observations. We will then discuss our recent results on the electro-optic properties of these materials with various gold NP concentrations.

2. Experimental

2.1 Preparation of the NP-Dispersed LC

In the proposed method, NP-dispersed LCs are fabricated
by sputtering a target material on a LC specimen positioned at a certain distance from the target. Although the complete mechanism of the formation of NPs in the LC has yet to be clarified, a possible scenario is described below. Since the atoms sputtered from the target material are smaller compared to the LC molecules, they penetrate deep into the bulk of the host LC. As more and more atoms enter the LC, the concentration of the atoms becomes sufficient to coalesce and form nano-sized particles, but the particles do not aggregate further because the solubility of the NPs is compensated by the LC molecules adsorbed on the particle surface.

It has been reported that when ionic liquids are utilized as hosts to suspend NPs either through a chemical reduction process or a vacuum deposition process, the degree of coalescence (i.e. size) of the sputtered species is controlled by the adsorption of the constituents of the ionic liquid on the particles and the electrostatic repulsion of the resultant particles [7]. However, in the case of LC molecules which are not necessarily charged, the degree of coalescence could be limited by other physical properties of the host, such as the elastic constants, wettability and viscosity. For example, if particles with diameters large enough that the macroscopic ordering of the LC is distorted by their presence exist, they will be segregated from the host LC to minimize the elastic energy of the system, and aggregate into even larger particles. However, for the sputtered species to grow that large, the particles must first collide with each other, distorting the LC orientation: this would be energetically unfavorable and the system will prevent this from occurring. As a result, the maximum diameter to which the nanoparticles grow is limited to a certain value determined by the physical properties of the host.

The nematic LC used in this study was 4-pentyl-4′cyanobiphenyl (5CB), which shows the nematic phase between 24°C and 35°C. The vapor pressure of 5CB is reported to be less than 0.23 Pa at room temperature, [10] which allows gold to be sputtered on the LC without significant evaporation of the host.

Approximately 0.3 g of 5CB was placed in a cylindrical glass container (base radius 15 mm and height 7 mm) and placed in a sputter deposition apparatus (Ulvac Kiko: VPS-20), opposite to the target material, gold (distance to target: ≈ 50 mm). The LC was sputter deposited with gold for various lengths of time (30 seconds–20 minutes) using air plasma at approximately 20 Pa and an applied DC voltage of 1 kV between the electrodes. After the deposition process, the sample was collected and used as is in the measurements followed. The content of the nanoparticles in all the fabricated suspensions are believed to be less than 1 wt%, but the precise concentrations could not be determined since the exact weight of gold deposited on the samples was too small to be measured.

2.2 Optical Characterization of the NP-Dispersed LC

The NP-dispersed LCs were characterized optically by measuring the extinction spectra and observing the sample by POM in conventional LC device geometries. The extinction spectra were measured using a UV-Vis spectrophotometer (Shimadzu, UV-3150) for samples placed in a 350 μm-thick sandwich cell assembled from cleansed glass substrates. No alignment treatment was performed on the substrates to prevent unwanted light absorption from the alignment layers. To cancel the effects of light scattering from the unaligned LC material, the measurements were made above the clearing point (40°C). For the POM observations, the samples were infiltrated in 5 μm-thick sandwich cell assembled from glass substrates coated with planar alignment layers (JSR, AL1254) rubbed uniaxially. The cells were then heated to 40°C, which is above the clearing point and gradually cooled at a rate of 0.5°C/min to 30°C at which the samples were observed.

2.3 Observation of the NPs Dispersed in the LC

TEM observations were performed on the sample in order to determine the morphology and size of the NPs. The TEM images were acquired on a transmission electron microscope (HITACHI, H-7650), using an acceleration voltage of 100 kV. A small amount (≈10 μl) of the sample was placed on a carbon supported grid and diluted with acetone to obtain a thin layer of the sample on the grid. The presence of gold atoms in the specimen was detected by energy-dispersive X-ray spectroscopy (EDX), and the particle size distribution was obtained by measuring the size of more than 50 NPs.

2.4 Measurement of the Electro-Optic Properties

In order to investigate the electro-optic response of the NP-dispersed LC, twist nematic cells were assembled using two ITO-coated glass substrates spin-coated with planar alignment layers (JSR, AL1254) and rubbed uniaxially. The cell-gap was approximately 9.8 μm and the twist angle was set at 90°. The threshold driving voltages of the twist nematic cells were obtained by measuring the light transmittance upon applying a rectangular voltage with various frequencies and amplitudes in the thickness direction of the cell. A HeNe laser (λ=633 nm) was used as the probe light source, and the voltage at 50% transmittance was taken as the threshold voltage. The sample temperature was kept at 30°C on a hot-stage during the measurements.

The dielectric properties of the sample was measured using an impedance analyzer (Agilent, 4294A). The frequency dependence of the complex dielectric constant in directions both parallel and perpendicular to the LC director were measured by applying a sinusoidal alternating voltage with root-mean-square amplitude of 350 volts. The sample was infiltrated in 6μm-thick sandwich cells assembled from ITO-coated glass substrates which were treated either with planar (JSR, AL-1254) and homeotropic (JSR, JALS-2021-R2) alignment layers. Measurements were performed at 30°C on a temperature controlled stage.
3. Results and Discussions

3.1 Optical Characterization of Gold NP-Dispersed 5CB

Shown in Fig. 1 are photographs of 5CB before and after sputter deposition of gold (at room temperature). An obvious change in the color from white to dark-brown was observed after sputter deposition. The color was darker in the samples that was sputtered with gold for longer times.

The extinction spectra of the material shown in Fig. 2 reveals that the color of the LC is attributed to an increase in the extinction covering the complete visible wavelength range. A slight shoulder is also observed at approximately 520 nm, possibly attributed to the local surface plasmon resonance of gold. The extinction coefficient is seen to increase linearly with the deposition time, indicating a linear relationship between the deposition time and the concentration of the NPs in the sample (inset Fig. 2). No aggregations were observed in the samples kept in the LC phase for at least 3 months.

3.2 Optical Texture of the NP-Dispersed LC in a Planar Cell

POM images acquired upon cooling both the pure and NP-dispersed (deposition time: 20 minutes) samples from the isotropic phase are shown in Fig. 3. The phase transition behavior was clearly different when the NPs were present. In the pure sample, the onset of the nematic phase was observed as a phase transition front passed from right to left in the viewing area (Fig. 3(a)). On the other hand, in the sample dispersed with gold NPs, circular nematic domains approximately 10 μm wide were observed at the transition temperature and gradually grew to fill the entire sample (Fig. 3(b)). However, when the transition was complete, a defect-free, uniform texture was observed for both cells. Considering that NPs in LCs act as impurities which lower the ordering of the molecules, it is plausible that the nematic droplets nucleate with the passing of the phase transition front, reflecting the local distribution in the NP concentrations. The transition behavior was similar in all samples deposited with gold, except that the phase transition temperature decreased depending on the deposition time of gold, attributed to the decrease in the liquid crystallinity of the samples: the decrease in the phase transition temperatures were approximately 0.3°C, 1.2°C and 2.4°C for 3, 10 and 20 minutes of deposition, respectively.

3.3 Morphology and Size Distribution of the Gold Nanoparticles

Figure 4(a) shows the TEM micrograph of the sample deposited with gold for 20 minutes, showing spherical nanoparticles approximately 3 nm in size. Statistical analysis of the micrograph revealed that the size of the nanoparticles are in fact narrowly distributed with a mean diameter of 2.9 nm and standard deviation of 0.6 nm (the size distribution and fit are shown in Fig. 4(b)). Shown in Fig. 4(c) is the EDX spectrum of the sample. The peaks at 9.7 keV and 11.43 keV correspond to the characteristic X-ray radiation of gold at L-α and L-β transitions and thus support the existence of gold in the suspension (the other peaks are attributed to the carbon-coated TEM grid used to support the NPs). Considering the fact that gold nanoparticles with small diameters of few nm do not exhibit a pronounced surface plasmon resonance peak, [11] the spherical particles observed in the TEM images can be attributed to the gold deposited on the host LC.

3.4 Electrooptic Properties of the NP-Dispersed LC

Figure 5 shows the frequency dependence of the threshold voltages of twist nematic cells fabricated from 5CB. In contrast to the pure sample which has a constant threshold voltage almost throughout the whole frequency domain, the NP-dispersed LCs exhibits a strongly frequency-dependent response. For both samples prepared by 10 and 20 minutes of sputtering, the threshold voltage increases steeply at frequencies lower than 200 Hz, but is lower than that of the
Fig. 4 (a) TEM micrograph of 5CB after sputter deposition of gold for 20 minutes, (b) size distribution of the spherical nanoparticles and (c) EDX spectrum of the sample showing the presence of gold.

Fig. 5 Frequency dependence of the threshold voltage of pure and NP-dispersed 5CB in the twist nematic cell configuration.

Fig. 6 (a) TEM micrograph of 5CB after sputter deposition of gold for 20 minutes, (b) size distribution of the spherical nanoparticles and (c) EDX spectrum of the sample showing the presence of gold.
causes an increase in the voltage required to reorient the LC molecules, but since the samples with higher NP concentrations exhibit dielectric relaxation at higher frequencies, the increase in the threshold voltage also occurs at a higher frequency for samples with higher NP concentrations. However, at frequencies high enough where there is no effect of dielectric relaxation, the threshold voltage decreases due to a decrease in the order parameter of the LC. A decrease in the dielectric anisotropy observed for NP-dispersed LCs ($\Delta \varepsilon = \varepsilon_\parallel - \varepsilon_\perp$ decreases as can be seen in inset of Fig. 6), is also qualitatively consistent with the discussion presented.

4. Concluding Remarks

We have described a method to produce metal NP-dispersed LCs utilizing the sputtering process and presented results on the changes induced in the optical and electrical properties of the host LC. This method is advantageous over other methods of preparing NP-dispersed LCs, since our method allows easier, faster, and purer production. The method is easier and faster since the NPs are fabricated through self-organization in the LC and the concentration is controlled simply by varying the deposition time, and purer because our method is a physical process which only utilizes raw materials of the constituents. The reduced-pressure environment in which sputtering is performed also helps to degas the LC of unwanted gases that may have dissolved in the sample.

Concerning the properties of the resultant LCs, the changes induced in the optical texture and the decrease in the clearing point do not seem to be so significant in terms of device applications, since uniform molecular alignment can be achieved by the conventional rubbing technique, and the drop in the clearing temperature is not substantial, added to the fact that many LC materials are available that possess much larger temperature ranges than 5CB. However, while we suggested possible mechanisms which cause a reduction in the threshold voltage and the appearance of a frequency-dependent electro-optic response, the complete physical picture is by no means clear. In order to fully understand the NP-LC molecule interactions and the interaction of the heterogeneous system with external electric fields, a systematic and quantitative study investigating various physical properties of LCs, such as the calorimetric properties, viscoelastic properties and temperature-dependent order parameter and optical/dielectric anisotropies should be performed.

We wish to conclude this article by stating some future prospects of the sputtering method to fabricate NP-dispersed LCs: since the proposed method is purely a physical process, the material to be dispersed in the LC is not limited to metals, but can be selected from a wide range of materials, from dielectrics, semiconductors, ferroelectrics to magnetic materials. The combination possibilities of the LC molecules and the NP materials is almost infinite and thus provides a wide avenue to develop next generation electro-optic materials. The material-property relationships of various NP-dispersed LCs is not only an interesting topic of investigation but the potential of these materials makes it equally technologically important. Secondly, NP-dispersed LCs are not only attractive from the viewpoint of display materials but as platforms to build nano to micro-scale NP assemblies that can be manipulated dynamically. It has been reported that NPs and polymers introduced in structured LC phases such as the cholesteric phase [14] or the cholesteric blue phase [15] segregate into less ordered regions and mimics the structure of the host. Thus, by doping nanoparticles on such structured LC phases, periodic assemblies of NPs can be fabricated, and dynamically controlled through external field-induced molecular reorientation. Such “active” NP assemblies should be useful in next-generation electronic, optical and biological applications.

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References


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