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Alignment of nematic liquid crystals using carbon nanotube films

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Abstract

Single-walled carbon nanotube bundles were deposited onto glass substrates with controlled nanotube orientation by two methods, self-assembly and dip-coating, generating dense and sparse carbon nanotube films, respectively. The carbon nanotube films were used to fabricate optical cells in which planar alignment of nematic liquid crystals is achieved. This configuration was amenable to electric-field-induced switching as verified by transmitted polarized light microscopy.

Keywords: Liquid crystal display; Liquid crystal alignment; Carbon nanotubes; Deposition

1. Introduction

Obtaining stable and uniform alignment of liquid crystals (LCs) on a macroscopic scale is essential to the fabrication of high-quality liquid crystal displays (LCDs). Typically, alignment involves modification of a solid substrate such that its interface with the LC has some anchoring action that results in either planar (tangential) or homeotropic (perpendicular) orientation of the LC director (symmetry axis) with respect to the interface. Such modification is carried out on a substrate having an electrically conductive layer (usually indium tin oxide or ITO-coated glass) for electric-field-induced reorientation of the director which, in turn, results in a variation in the transmitted light intensity. Currently, the preferred modification technique is rather primitive: the conductive substrate is coated with a polyimide layer that after thermal curing is mechanically rubbed [1,2]. The alignment mechanism associated with unidirectional rubbing has contributions from both the physical grooves caused by rubbing the polyimide substrate–the elastic energy costs of conformally wetting the irregular substrate topography [1]–and secondly, putative molecular interactions between exposed polyimide functionalities and the LC. However, the details of LC alignment are not well understood [1,3–5]. Thus, the search for more easily quantified alignment materials continues. Herein, we explore the potential of self-assembled carbon nanotube (CNT) bundles as an alignment substrate for LCs [6].

Carbon nanotubes are the focus of intense research due to their unique physical properties, namely their anisotropic mechanical, thermal and electronic behavior. Single-walled nanotubes (SWNTs) show high conductivity along the tube length and very low conductivity across the tube diameter [7,8]. SWNTs are also known to align parallel to each other in low concentration solutions while multi-walled nanotubes (MWNTs) show a propensity to spontaneously form lyotropic liquid crystalline phases above a critical CNT concentration [6,9,10]. The inherent conductivity and spontaneous self-alignment properties of CNTs make them an attractive alternative as an alignment layer. Deposition of CNT bundles onto solid substrates from a water solution with controlled nanotube orientation has been accomplished by a self-assembly method [6]. In this work CNT films were prepared by this self-assembly method as well as a dip-coating method to achieve dense and sparse deposition of CNTs, respectively. These CNT films were used to fabricate optical cells in which planar alignment of nematic LC is achieved and the director orientation can be manipulated with an electric field as verified by transmitted polarized light microscopy.

2. Experimental details

Graphite powder (natural, microcrystal grade, 99.9995%) used for the single-walled nanotube bundle synthesis was purchased from Alfa Aesar (cat. no. 14736). Nematic liquid

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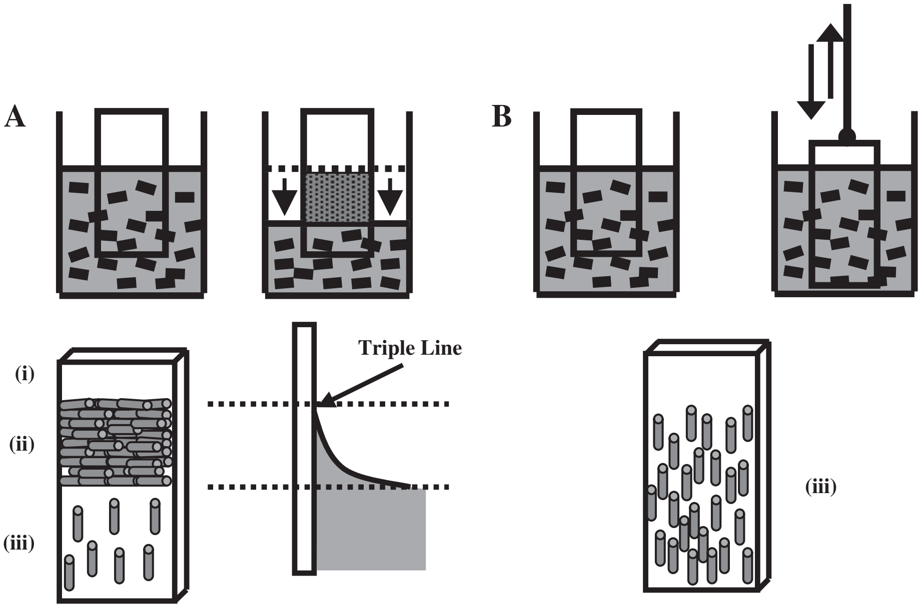

Fig. 1. Schematic representations of CNT deposition methods: (A) self-assembly of CNT bundles generated by gradual evaporation of CNT/water suspension onto ITO-coated glass slide, resulting in three distinct regions: region (i)—no CNT bundles, region (ii)—dense CNT bundle deposition and region (iii)—sparse CNT bundle deposition. (B) Sparse deposition of CNT bundles obtained by dipping of substrate into suspension at a controlled rate.

crystal Licristal K-15 (EM Industries IS-1143) was used without further purification. LC optical cells were fabricated using indium tin oxide (ITO)-coated glass (Delta-Technologies, Ltd., CG-81IN-S115) and sealed with epoxy marine (Power epoxy, 21601).

Birefringence measurements were made using the Nikon Microphot FX polarizing microscope equipped with a Sony CCD-IRIS camera. Images were obtained using video generation software by Roxio. AFM images were obtained in tapping mode using the Multimode IIIa Atomic Force Microscope (Veeco Metrology Group).

SWNT bundles were synthesized by laser ablation of a graphite target containing metal catalysts (0.3% NiCo), using a Nd:YAG laser operating at a wavelength of 532 nm (400 mJ/pulse) in an Ar-filled (200 standard cm^3/min and 93 kPa) furnace at 1150 °C. Samples were purified by reflux in hydrogen peroxide and filtration [11]. The purified SWNT bundles (typically >10 μm) were shortened to a length of approximately 2 μm and 0.5 μm by chemical etching using H_2SO_4/HNO_3 [12,13]. The morphology of the bundles was changed from that of highly entangled strands to rigid rods after etching [6]. The processed samples were rinsed with deionized water and annealed at 200 °C in 10^{-6} Torr dynamic vacuum before dispersion in deionized water (1.0 g/L).

For dense film deposition, a clean ITO-coated glass slide was immersed vertically into the SWNT/water suspension at room temperature (Fig. 1A). Upon gradual evaporation of the water over a period of days, the concentrated nanotubes were found to assemble and orient on the glass surface along the air/liquid/substrate triple line. The resulting film thickness for this dense film was ~0.5 μm [6]. For sparse film deposition, the clean ITO-coated glass slide was vertically dipped in the SWNT/water suspension (1.0 g/L or 0.5 g/L) at a controlled rate using a motorized dip-coating apparatus (Fig. 1B). These sparse films were considerably less than a monolayer; the individual bundle diameters were ~50 nm.

LC optical cells, used for observation of birefringent textures, were fabricated as follows: two CNT-coated substrates were sandwiched together with the CNT films facing each other at predetermined orientations separated by a spacer (6 or 40 μm) and sealed together using epoxy. The optical cells were filled with Licristal K-15 (in the isotropic or nematic state (room temperature) for comparison) by capillary action and examined for light intensity changes. For voltage switching experiments, electrodes were attached to both substrates by solder, allowing for the application of an electric field across the LC optical cell by means of a function generator.

3. Results and discussion

3.1. Birefringent textures of CNT films prepared by gradual evaporation

The substrates on which the self-assembled CNT films were deposited by gradual evaporation had three distinct regions (see Fig. 1A). Region (i) had no nanotube bundles; this portion of the glass substrate was not immersed in the SWNT/water suspension and served as a control surface. The remaining two regions resulted from immersion of the substrate, but differed in CNT deposition. Region (ii) consisted of SWNTs self-assembled by gradual solvent evaporation (region (ii) in Fig. 1A) with the nanotubes parallel to the short axis of the substrate (parallel to the triple line). Region (iii), a sparse deposition of CNTs, resulted from the rapid removal of the glass substrate from the suspension. These three distinct regions of varying nanotube densities showed different alignment properties in LC optical cells.

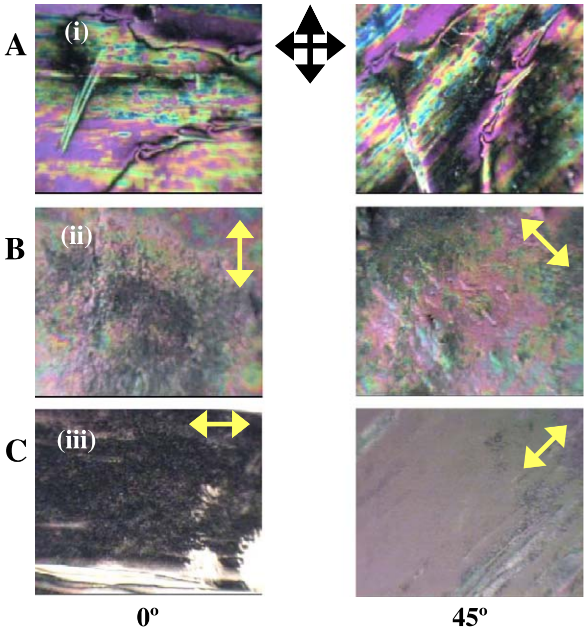

Fig. 2. Birefringent texture images for the three regions of alignment obtained from the self-assembly of CNTs (2.0 μm bundles). (A) Region (i): no CNT deposition. (B) Region (ii): dense CNT deposition. (C) Region (iii): thin CNT deposition. The orientation of the crossed polars is indicated by the crossed black arrows while the nanotube orientation is given by the double-headed yellow arrows. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

The birefringent textures of the nematic LC obtained from the macroscopic, long-range uniform alignment of K-15 were observed for substrates prepared by gradual evaporation using CNT suspensions of either 2.0 μm or 0.5 μm bundles in water. The textures observed with the substrate prepared by gradual evaporation of CNTs from a suspension of 2.0 μm bundles in water are given in Fig. 2. No LC alignment occurred in region (i) as expected for an untreated (control) substrate. However, uniform LC alignment was not evident in region (ii) (dense CNT coverage) either. Region (ii) exhibited domains of planar LC alignment. Only the very sparse deposition of nanotubes found in region (iii) exhibited macroscopic uniform planar alignment of the LC. Fig. 2A–C shows the birefringent textures observed in each region of the substrate at 0° and 45° rotation of the sample director (with respect to crossed polars). Fig. 2C shows uniform planar alignment of K-15, giving dark states at 0° and 90° rotation of the sample director (with respect to crossed polars) and bright states at 45° and 135° director orientations. The direction of this LC alignment reflects the mean nanotube orientation direction: parallel to the long axis of the substrate and to the dipping direction and perpendicular to the triple line.

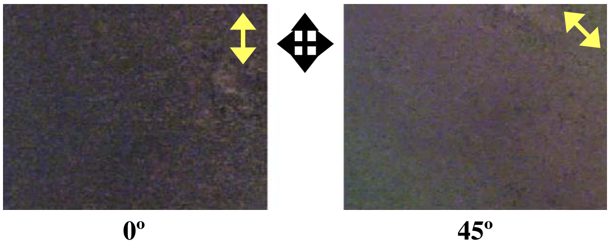

Fig. 3. Birefringent texture images for the alignment of liquid crystal by self-assembled CNTs (0.5 μm bundles). The CNT bundles are densely packed and uniform planar orientation of the LC is accomplished. The orientation of the crossed polars is indicated by the crossed black arrows while the nanotube orientation is given by the double-headed yellow arrows. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

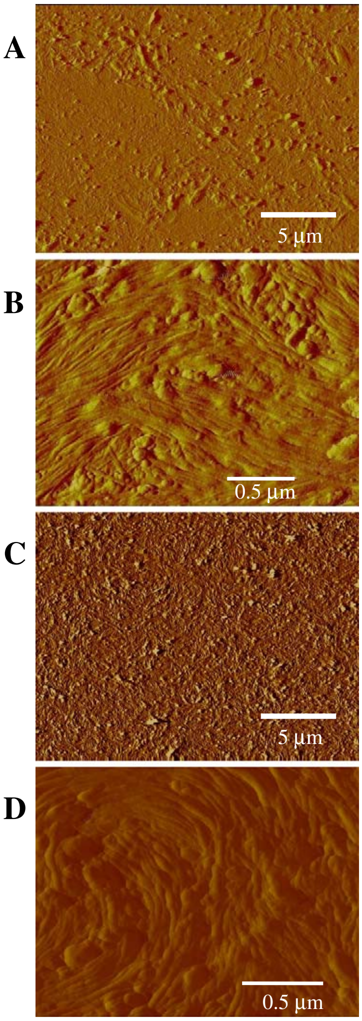

Fig. 4. Representative AFM images of dense CNT films (region (ii)). Images (B) and (D) are higher magnifications of a small area of images (A) and (C), respectively. Dense films composed of 2.0 μm bundles ((A) and (B)) are characterized by thick layers of bundles stacked on one another and random domains of orientation. Dense films composed of 0.5 μm bundles ((C) and (D)) have the rough topography seen in (A) and (B), but the tightly packed bundles have the same orientation on average.

Similar birefringent textures were observed for the substrate prepared by gradual evaporation of CNTs from a suspension of 0.5 μm bundles in water with one exception. As with films of 2.0 μm CNT bundles, region (i) exhibited no LC alignment while region (iii) exhibited macroscopic uniform planar alignment of K-15. However, unlike the films composed of 2.0 μm CNT bundles, region (ii) of the films composed of 0.5 μm CNT bundles, the region of densely packed CNTs, also

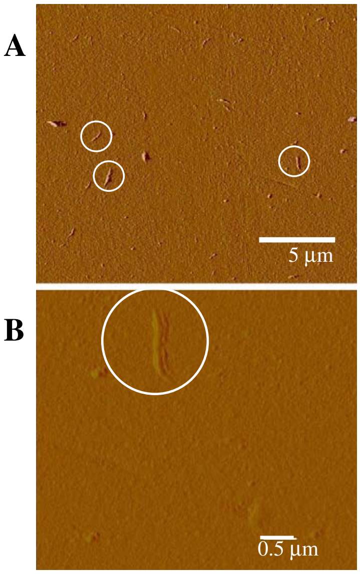

Fig. 5. Representative AFM images of sparse CNT films. Sparse CNT films composed of 2.0 µm bundles are characterized by sparse deposition of bundles aligned parallel (on average) with the dipping direction; (B) shows a high magnification image of a single CNT bundle.

exhibited macroscopic uniform planar alignment of the LC (Fig. 3). It is evident from Fig. 3 that a dark state is achieved at 0° orientation of the sample director (with respect to crossed polars) while a bright state is seen at a rotation angle of 45°. It is also apparent that the transmittance of light in this region is fairly low. This observation is not surprising given that the CNT bundles are densely packed, forming an opaque alignment layer. The associated reduction in transmitted light for the dense alignment layer suggests that sparse CNT films, such as those found in region (iii), are a more viable option for LCD applications. For this reason, the sparse deposition of CNTs achieved by dipping the substrate into a CNT suspension was further studied using a dipping apparatus having a variable dipping rate.

3.2. Deposition of carbon nanotubes by controlled dipping

CNT films with sparse bundle deposition were prepared by vertically dipping ITO-coated glass slides into an SWNT/water suspension at controlled rates ranging from 20.0 to 264.0 µm/s. Planar uniform alignment was achieved at rates of 80.0 µm/s and higher. The optimal dipping rate was ~ 143.0 µm/s.

3.3. AFM analysis of carbon nanotube orientation

The orientation of the individual SWNT bundles for both the dense and sparse CNT films was probed by AFM (in tapping mode) and it was found that the roughness of the surface is increased upon CNT deposition in all cases as can be seen in Figs. 4 and 5. Fig. 4A and B shows the dense packing of 2.0 µm SWNT bundles obtained by the evaporation method. It is obvious from the topology that multiple bundles are stacked on top of one another and that these bundles have domains of orientation that are randomly arranged on the substrate. Fig. 4C and D shows the dense packing of 0.5 µm SWNT bundles obtained by the evaporation method. Again, multiple bundles appear to be stacked on top of one another as in Fig. 4A and B, however there appears to be an average orientation of the bundles in one direction. These results may account for the domains of planar orientation observed in the dense 2.0 µm CNT films and the uniform planar orientation observed in the dense 0.5 µm CNT films. In contrast to the topologies of the dense CNT films, Fig. 5 shows that the SWNT bundles (2.0 µm) in the sparse films prepared by controlled dipping sparsely cover the substrate with an irregular spacing between bundles. Smaller SWNT bundles and possibly individual CNTs also appear to have been deposited on the substrate. However, on average the individual SWNT bundles are aligned parallel to the long axis of the glass and dipping direction as confirmed by analysis of the distribution of SWNT bundles with respect to their deviation from the long axis (Fig. 6).

3.4. LC alignment using carbon nanotubes

It has been shown that the phenomena of self-organization in LCs orients CNTs and that SWNTs dispersed in LC polymers can act as seeds for oriented domain growth [14–16]. Herein we show that the anisotropic nature of controlled nanotube orientation deposition can align nematic LCs. Sparse CNT films give a uniform planar alignment on the scale of centimeters. It is proposed that unidirectional roughness of the substrate surface induced by CNT deposition also contributes to alignment in a manner similar to that of a rubbed surface whereby microgrooves generate a preferred alignment direction [2].

3.5. Liquid crystal display pixel prototype

Liquid crystal optical cells were fabricated with ITO-coated glass substrates deposited with CNT films prepared by either gradual evaporation of 0.5 µm CNT bundles or controlled dipping of 2.0 µm bundles. Planar alignment was generated with both CNT films. Application of an electric field

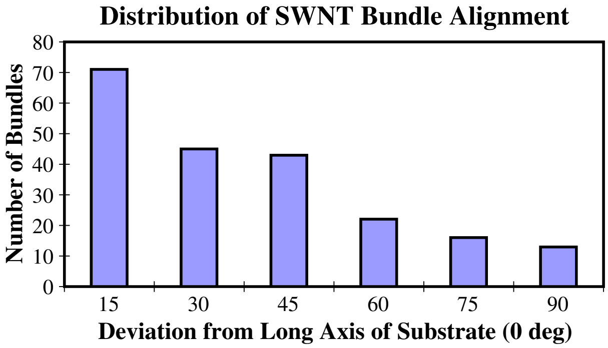

Fig. 6. Graph of the distribution of SWNT bundles on substrates dipped at 143.0 µm/s with respect to their deviation from the long axis of the substrate (designated as 0°).

perpendicular to the substrate for both cells resulted in homeotropic alignment with the director perpendicular to the substrate. Turning off the electric field caused the restoration of macroscopic uniform planar alignment. Thus LC anchoring by the CNT-coated substrate produces the essential characteristics of a light-valve optical cell, the critical component of LCDs.

4. Conclusion

Sparse CNT films composed of SWNT bundles deposited with controlled orientation onto ITO-coated glass substrates using a motorized dipping method are shown to induce uniform planar alignment of nematic LCs on a macroscopic scale. This alignment has the LC director oriented along the dipping direction. LC optical cells with CNT alignment layers exhibit switching on application of an electric field. CNT films constitute a novel alignment material that possesses intrinsic anisotropic conductivity which in time may facilitate the fabrication of liquid crystal displays.

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