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Imaging of liquid crystals confined in carbon nanopipes

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This letter investigates the unexplored phenomenon of the wetting of liquid crystals inside carbon nanopipes. Carbon nanopipes are similar to carbon nanotubes but are open ended with straight walls. Using environmental scanning electron microscopy, the authors have observed liquid crystal menisci inside the nanopipes. Raman spectroscopy was used to confirm the presence of liquid crystals confined in the nanopipes and verify the physical interaction between the two materials. In addition, observations from reflection polarized optical microscopy experiments suggest the use of liquid crystals inside carbon nanotubes to develop electro-optic switches. © 2006 American Institute of Physics. [DOI: 10.1063/1.2240739]

The use of fluids at the nanoscale has sparked great interest in the scientific community, as fluid manipulation offers unprecedented possibilities in technological advancement. Microfluidic devices with controlled fluid delivery using nanochannels are currently being developed for applications ranging from chemical analysis and drug screening to computation.¹ Carbon nanopipes (CNPs) and carbon nanotubes (CNTs) are nanoconfinement materials that show tremendous promise for developing applications in fields including drug delivery, electronics, and energy storage. These materials are of particular interest for fundamental fluidic studies due to their unique mechanical, physical, and electrical properties.²

In order to observe different fluids in real time at high magnification, we have synthesized CNPs that are open-ended large-diameter nanotubes with walls of disordered carbon, making it possible to observe fluids flowing through them using environmental scanning electron microscopy (ESEM).³ The CNPs have been filled with water,³ fluorescent,⁴ and magnetic nanoparticles,⁵ demonstrating their ability to imbibe both aqueous and particulate fluids. However, there are very few experimental studies on the filling of CNTs and CNPs with complex fluids.

Liquid crystals (LCs) are materials used in a variety of applications from displays to imaging of biological cells due to their electrical and thermal properties. Their confinement has been a topic of great interest for fundamental studies and for developing electro-optic devices.⁶ Efforts in creating functional materials combining LC and CNTs/CNPs have been limited to the orientation and alignment of CNTs in the presence of LC.⁷ Some work on filling cylindrical channels with LC has been reported in literature.⁸ However, as the size of confinement shrinks to the nanoscale, it becomes difficult to image the molecular ordering within the channels. Filling of CNT with naphthalene polymer, which displays discotic LC properties,⁹ led to alignment of liquid crystal inside multiwall nanotubes. However, microscopic studies were only

performed on the carbonized polymer. While these results show great promise in creating materials with improved electrical and optical properties, the interactions between carbon nanostructures and LC are yet to be defined. In an effort to understand the behavior of LC in confined spaces, characterize the behavior of complex fluids inside freestanding CNPs, and define the wetting of CNPs with LC, we have performed wetting and filling experiments of LC and CNPs.

CNPs were synthesized with a noncatalytic chemical-vapor deposition (CVD) method using a commercial alumina membrane as a porous template (Whatman Anodisc®, nominal pore diameter: 200 nm±10%, thickness: 60 μm). Freestanding nanopipes were obtained after dissolution of the alumina template in a boiling 1M solution of sodium hydroxide. The diameter of the resulting nanopipes corresponds to the diameter of the original membrane, and length, after sonication, generally ranges from 5 to 10 μm. After synthesis, the CNPs have a disordered wall structure.¹⁰ The liquid crystal used was K15 (T_{NI} −34.5 °C), also known as 4-pentyl-4-cyanobiphenyl (5CB), purchased from EM Industries (Hawthorne, NY).

A suspension of CNPs and ethanol was placed on a glass microslide. After the ethanol evaporated, a droplet of 5CB was deposited over the CNPs and a glass cover slip was used to cover the sample and spread the LC into a uniform film. Shown in Fig. 1 are reflection polarized microscopy images of the LC-CNP dispersion. It can be seen that the light reflected along the length of the CNPs varies at different angles of the analyzer. The light variation is due to the presence of a birefringent material either inside or on the surface of CNPs, which are insensitive to light polarization. Since all the CNPs were submerged in the LC, only the tubes filled with the LC should exhibit this behavior.

An FEI XL30 ESEM was employed to observe the LC menisci inside the CNPs. The experiments were performed by maintaining the ESEM chamber at 3–5 Torr and using a gaseous secondary electron detector at voltages ranging from 10–30 kV. A LC-CNP suspension was prepared, and a droplet of this suspension was placed on the sample holder and washed with methanol to remove excess LC. As a result,

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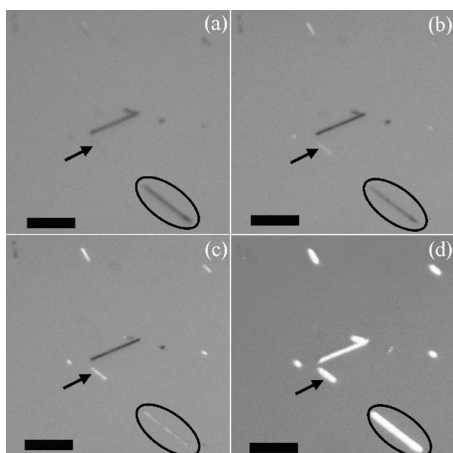


FIG. 1. Reflection polarized optical microscopy images of CNPs dispersed in LC. Images (a)–(d) correspond to analyzer angles of 0° , 60° , 75° , and 90° , respectively. The scale bar is $10\ \mu\text{m}$. The arrow points to a tube, which is not observed in (a) but appears in (b)–(d), reflecting varying intensities. The circled tube also exhibits variations in reflected intensity depending on the analyzer angle.

while much of the LC on the surface of the sample holder was washed away, some of the LC remained trapped within the CNPs and could be observed in the ESEM. All of the methanol has evaporated by the time the ESEM chamber achieves low pressure. In order to image liquids inside the CNPs, generally, a voltage of 10 kV or higher is necessary so that the beam can penetrate through the CNP walls. Liquid inclusions inside the CNPs tend to block the electron beam, causing these regions to appear lighter in color than the parts of the CNP that are empty. In Fig. 2, therefore, the lighter phase represents the LC residue within the CNPs forming a low contact angle meniscus, while the darker phase is the part of the CNP that is not filled with LC.

Raman spectroscopy was used to confirm the presence of LC inside CNPs and to identify the nature of interaction between LC and CNPs. A droplet of the LC-CNP suspension was placed on a polished silicon wafer and analyzed. Subsequently, the excess liquid crystals were removed by washing with methanol, and a single nanpipe, not surrounded by liquid crystals, was analyzed. A LC signal was observed only in the center of the nanpipe and not at the two ends, as shown in the schematic in Fig. 3, thus verifying the hypothesis that LC remained inside the nanpipe after the ethanol wash. The Raman spectra shown in Fig. 3 were recorded using a Raman spectrometer (Renishaw) with an Ar ion laser (514 nm excitation wavelength). LC is characterized by a distinctive peak for $\text{C}\equiv\text{N}$ stretching at $2226\ \text{cm}^{-1}$ and by peaks at 1180 and $1605\ \text{cm}^{-1}$ corresponding to in-plane C–H

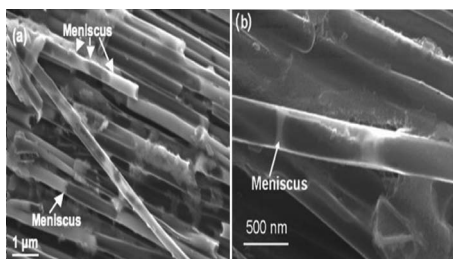


FIG. 2. (a) ESEM image of LCs inside an agglomerate of CNPs. (b) ESEM image of menisci inside an individual CNP. The lighter phase is the LC plug, while the darker phase is the empty part of the CNP.

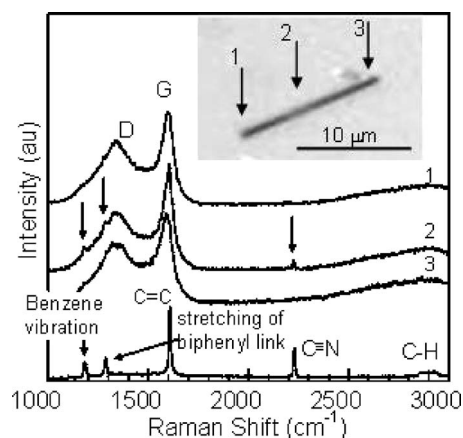


FIG. 3. Raman spectra for pure 5CB liquid crystal (below) and from the ends (1) and (3) and the middle (2) of a CNT filled with LC. In (2) LC peaks for $\text{C}\equiv\text{N}$, benzene vibrations and stretching of the biphenyl link (indicated with arrows) are superimposed to the CNT spectra, being absent from the CNT's ends. After being filled with LCs the tube has been washed with methanol at 40°C to remove excess LC. A small part remained after the process only inside the CNT. Inset shows an optical image of actual CNT analyzed. CNT is $\sim 200\ \text{nm}$ in diameter.

bending and $\text{C}=\text{C}$ stretching in the ring structure of the 5CB, respectively.¹¹ The peak at $1285\ \text{cm}^{-1}$ is attributed to the stretching of the biphenyl link, and the broadband in the region of $2900\text{--}3100\ \text{cm}^{-1}$ corresponds to C–H vibration in the linear hydrocarbon chains of the molecule. The Raman spectrum of carbon nanpipes consists of a broadband around $1350\ \text{cm}^{-1}$, which is a double resonance band common for carbon materials (*D* band) and a slightly narrower one around $1600\ \text{cm}^{-1}$ related to in-plane vibrations of graphite (*G* band). The spectrum collected from the suspension of carbon nanpipes in LC shows an overlapping of the spectra for the single phases. No additional Raman bands or changes in the CNP or LC peak positions have been observed. Thus, there is no chemical change in either material, implying that the primary interaction between the materials is physical.

Due to the physical interaction between the two materials, we can model them as a solute-solvent interaction considering the LC as the solvent and the CNPs as the solute. The interfacial energy is given by¹²

$$\gamma_{\text{LC-CNP}} = \gamma_{\text{LC}} + \gamma_{\text{CNP}} - 2\sqrt{\gamma_{\text{LC}}\gamma_{\text{CNP}}} = (\sqrt{\gamma_{\text{LC}}} - \sqrt{\gamma_{\text{CNP}}})^2,$$

where $\gamma_{\text{LC-CNP}}$ is the interfacial energy, and γ_{LC} and γ_{CNP} are the surface energies for LC and CNPs, respectively. The surface tension for the CNPs, γ_{CNP} , is $\sim 41\ \text{mN/m}$ (Ref. 10) and that of 5CB, γ_{LC} , ranges from 30 to 40 mN/m.¹³ Thus, the net interfacial energy can be calculated to give an upper value of $0.857\ \text{mN/m}$ ($\gamma_{\text{LC}}=30\ \text{mN/m}$) and a lower value of $0.006\ \text{mN/m}$ ($\gamma_{\text{LC}}=40\ \text{mN/m}$). These low values of interfacial energies explain the free flow of the LC within the CNPs and indicate complete wetting. Using the Sessile drop method, complete wetting of LC droplets on CNP films was observed within 20 s, as shown in Fig. 4. For this experiment, a CVD carbon film was deposited on a polished silicon wafer and treated with NaOH. This treatment ensures that the film is chemically and structurally identical to the wall structure of the CNPs used in this study.¹⁰

From an application viewpoint, CNPs filled with LCs could be used to realize nanoscale optical switches based on polarized light reflection from CNPs filled with LCs. For this

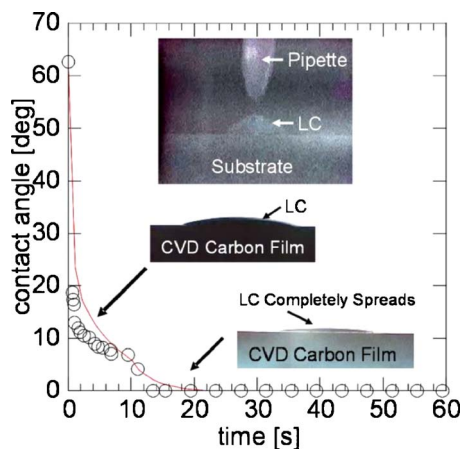


FIG. 4. Contact angle measurements of LC on a film of CVD carbon that is identical in surface chemistry and structure to the carbon of which the CNPs are composed. The graph depicts the reduction in contact angle with respect to time as the droplet of LC begins to spread on the film.

device, the LC alignment state is responsible for the polarization rotation of the reflected light to generate off (dark) or on (bright) states. Transitions between the on and off states would be regulated by suitable electromagnetic fields.

In conclusion, we report on the filling and observation of liquid crystals inside carbon nanopipes using the ESEM. Due to low interfacial energies between the materials, LC is able to flow freely within the nanopipes. As verified by Raman spectroscopy, primary interaction between these two materials is physical in nature.

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