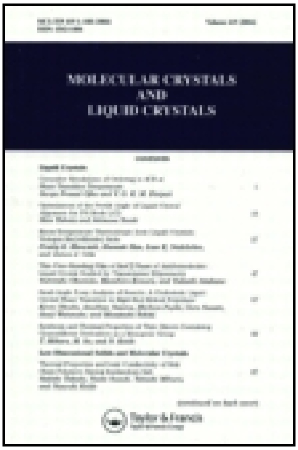

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Novel Carbon Nanotubes Based on Disk-Rod Assemblies of Lyotropic Liquid Crystals

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We have fabricated carbon nanofibers and nanotubes using disk-rod assemblies of lyotropic liquid crystals in which the orientation of graphene layers can be manipulated using surface anchoring techniques common to liquid crystal displays. The bulk material properties of the carbon can be engineered by the spatial arrangement of the graphene layers due to their anisotropic nature. We have also demonstrated a method to pattern arrays of nanotubes using an automated printing technique.

Keywords: liquid crystal; lyotropic; nanotubes

1. INTRODUCTION

Since their discovery in 1991 [1], there has been significant academic and industrial interest in carbon nanotube (CNT) processes and materials. Due to their unique chemical and physical properties, CNTs have been

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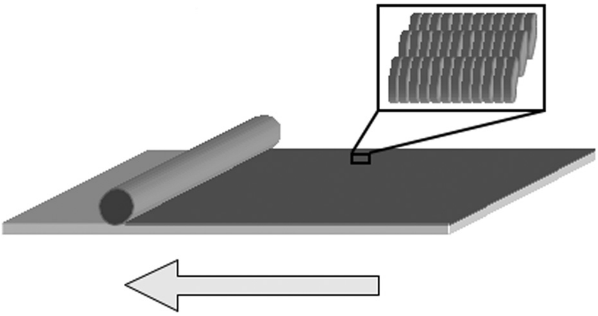

FIGURE 1 A schematic diagram of the coating process in which a glass substrate is coated with a thin film polarizer using a Meyer rod. The molecules align along the rub direction (denoted by the arrow).

looked at for use in various types of applications including nanoprobes [2], chemical sensors [3], energy storage [4], field effect transistors [5], composite materials [6,7], and field emitters [8]. A wide variety of methods to fabricate nanotubes have been looked at. These include arc evaporation of carbon [1], catalytic decomposition of hydrocarbons on metal particles [9–11], and templating methods using nanochannel membranes [12–14].

In this contribution, we employ solutions of indanthrone disulfonate, a discotic liquid crystal that possesses a lyotropic phase in water. These materials have been developed by *Optiva, Inc* for extraordinary-type polarizers useful in liquid crystal display applications [15]. For this application, the materials are typically coated onto a substrate with a Meyer bar in order to create a uniform, submicron film as shown in Figure 1. The shear force applied during the coating process provides enough energy to align the lyotropic molecules in the coating direction shown in the boxed area of Figure 1. As water evaporates, a highly oriented, submicron-thick crystal film forms. During this phase transition from liquid crystal to solid crystal, further self-alignment also occurs [16].

We report on a new method for achieving systematic molecular control over the graphene layer orientation of a CNT using this particular lyotropic liquid crystal. The orientation of the graphene planes is extremely important in controlling the properties of the resulting carbon nanostructures. By controlling the orientation of the graphene planes, the electrical, mechanical, and thermal properties of the CNTs can be tailored. In order to achieve control over the graphene layer orientation, interactions between polyaromatic liquid crystal molecules and confining surfaces are exploited during the fabrication of these carbon structures in order to achieve control over the graphene layer orientation.

The use of a polyaromatic liquid crystalline precursor that already possesses the basic graphite kernel provides a degree of systematic molecular control over graphene layer arrangement not obtainable with discotic mesophase pitch materials [17]. These naturally occurring mesophases must be melt processed. Heating to 300°C prior to processing softens the pitch material; at this softening point, the material becomes extremely viscous and difficult to manipulate [17].

Nanotubes can also be fabricated using discotic, thermotropic LC phases, but strong intermolecular π-π forces lead to high temperature melting solid phases or limitations on solvent processing. By using a soluble lyotropic liquid crystal carbon precursor to fabricate nanotubes, these difficulties can be avoided. When in an aqueous solution, the disk-like lyotropic molecules form rod-like aggregates. These aggregates can then be easily manipulated in solution, where mobility is achieved without the need to overcome π-π forces [18]. The use of solvent rather than melt processing allows hollow forms to be assembled and the wall thickness to be tailored through selection of the initial concentration of the precursor.

In most mesophase materials, true mesogenic order is lost after heating past the isotroptic transition temperature. However, in some systems including those using discotic mesophase pitch materials [17], polycyclic aromatic hydrocarbon materials [19], and the indanthrone materials [18] described in this paper, the mesogenic order can be covalently captured during and remains present after heating cycles above the nematic-isotropic transition.

2. EXPERIMENTAL PROCEDURE

2.1. Materials

The nanotubes described in this paper were fabricated using indanthrone disulfonate solutions. Indandtrhrone disulfonate, a commercial dye provided to us by *Optiva, Inc.*, is a planar, polyaromatic molecule with a lyotropic liquid crystal-phase when in an aqueous solution. A current commercial application of this lyotropic material is in the fabrication of e-mode polarizers that are thin enough (500 nm) to be integrated inside of a liquid crystal display [15].

Ionic groups can be introduced to the periphery of planar polyaromatic precursors [20,21] making the disk edges hydrophilic, while the polyaromatic faces remain hydrophobic. In order to provide favorable local environments for both face and edge groups, the molecules stack face-to-face in aqueous solution. In indanthrone disulfonate solutions, extensive face-to-face stacking leads to the formation of rod-like aggregates of ~1.5 nm in diameter and 300 nm in length (~200:1 aspect ratio) [22]. These rod-like aggregates, shown in the boxed region of Figure 1, are highly anisotropic. Their molecular order parameter (S) of the rods increases rapidly from 0.65 for the deposited coating up to 0.90 for the completely dried film [20]. The order parameter of the completely dried film can be tuned by controlling the drying time of the material and can range from 0.85 to 0.90 [20]. At high concentrations, these solutions form lyotropic liquid crystalline phases in which the rod-like aggregates align by self-exclusion and electrostatic repulsion [22].

2.2. Nanotube Fabrication

In order to fabricate a highly ordered and homogeneous carbon nanomaterials [23], cylindrical nano-channel alumina templates [24], shown in Figure 2, with radii of 100 nm are filled by capillary

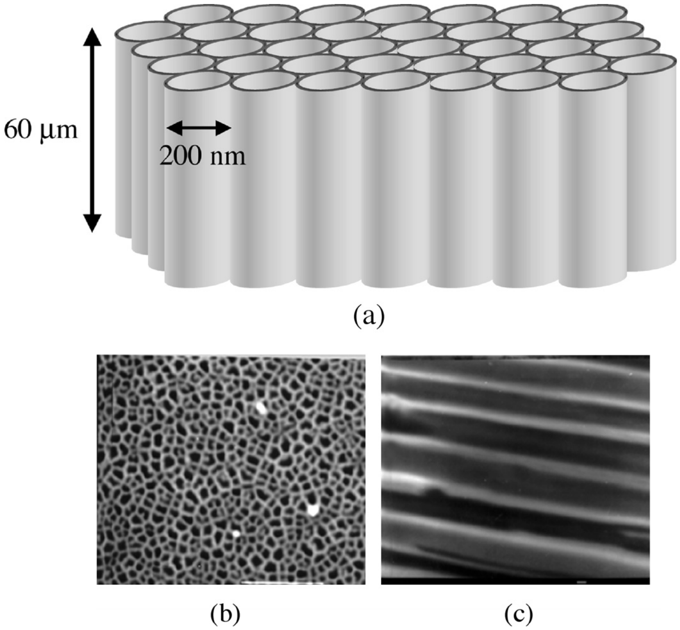

FIGURE 2 A schematic illustration of the Al_2O_3 template (a). The substrates are on average 40% porous, with pore sizes on the average of 200 nm in diameter and 60 μm deep. Scanning electron microscope (SEM) images of the top surface (b) and a cross section (c) of the Al_2O_3 template.

action with indanthrone disulfonate solutions [25]. In the past, these alumina membranes have been used to study finite size effects on liquid crystals [26–28] and to create polymer microstructures [29,30].

After filling the templates with the discotic lyotropic material, the templates are dried overnight leaving a thin film on the inner surfaces of the channels. The dried templates are placed in a tube furnace, slowly heated at a rate of 4°C per minute to 700°C, and held there for one hour in order to carbonize the organic nanotubes and form carbon tubes while ultra high purity nitrogen is continuously passed through the furnace. Once fully carbonized, the templates can be mounted to graphite stubs using carbon paste or silver paint, and the template can be etched away using by placing the sample in a 0.4 molar NaOH solution for 24 hours.

A benefit to fabricating nanotubes using a water soluble carbon precursor and room temperature processing and a template is that an automated fluid dispensing system can be used to apply pattern the precursor while infiltrating the template. A syringe with a narrow tip diameter is filled with the lyotropic carbon precursor. The syringe is part of a computer controlled, automated fluid dispensing system. This system, made by *Asymtek*, was originally designed for the automated dispensing of solder, glue seals, and other fluids used in electronics manufacturing. Using a software interface, the writing conditions (writing speed, desired pattern, fluid pressure) used for the application of the carbon precursor can be precisely controlled. A wide array of shapes from simple dots to complex linear and arc patterns as well as text patterns can be dispensed using this method. Currently, the smallest tip size available for the fluid dispensing system is 130 μm. Using this tip, we estimate a line width of 150 μm; however, by creating smaller tips and optimizing the writing procedure, we hope to improve on this. We also hope to further develop this patterning technique in order to take advantage of existing commercial inkjet printing technology.

In order to automatically dispense the carbon precursor into linear patterns, the writing syringe was filled with a 7.5 wt% solution of indanthrone disulfonate in water. The syringe tip used for the application of this solution had a diameter of 130 μm. A back pressure of 5 psi was applied to the liquid crystalline carbon precursor in the syringe barrel during the patterning process. The writing speed used to dispense linear arrays of nanotubes was 7.5 mm/s. When using slower speeds excessive material was deposited on to the template resulting tube in non uniform linear arrays. Optical microscope images of the resulting patterned lines can be seen in Figures 3(a) and (b).

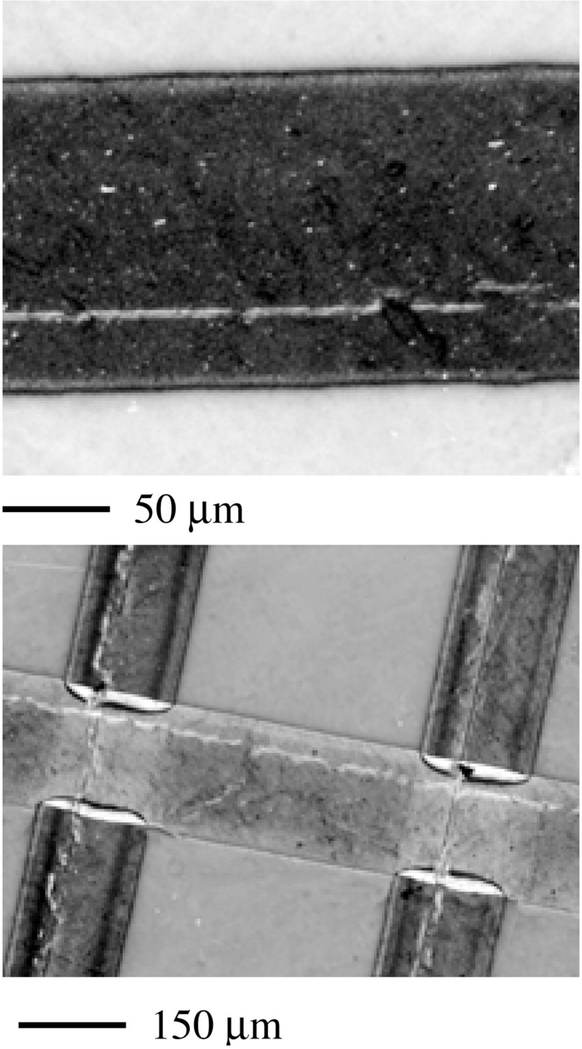

FIGURE 3 Optical microscope images of patterned nanotubes lines. A variety of patterns – continuous and intersecting can be formed. These patterns could form the basis of patterning circuits with nanotubes.

Using this system, ordered arrays of carbon nanotubes can easily be mass-produced. The automated fluid dispensing system allows for the simple creation of complex patterns of arrayed nanotubes. The quantity of material deposited on the substrate can be accurately controlled and easily adjusted via a software interface in order to insure that the patterns of the tubes produced are identical. This flexibility and reproducibility is if carbon nanotube arrays are to be successfully introduced in any of a variety of commercial applications.

3. RESULTS

Using the technique described above, we were able to successfully fabricate arrays of nanotubes 150 μm wide and 50 mm long. The length was only limited by the size of the alumina templates used during the printing process. Patterned nanotubes have also been fabricated by Cao *et al.* [31]. Unlike with our simple, automated printing process; their nanotube arrays are fabricated by growing nanotubes by chemical vapor deposition on SiO_2 growth templates that have been masked with a patterned Au layer.

The resulting nanotubes were examined using SEM techniques. Figure 4 shows a SEM image of the resulting nanotubes. In order to minimize the amount charging in the SEM, the samples were sputter coated with a thin layer of gold. The SEM images reveal hollow tubes. By controlling the amount of precursor used, the wall thickness of the tubes can be controlled.

High-resolution transmission electron microscope (TEM) images indicate that the graphene layers orient perpendicularly to the long axis of the nanotube. This structure is shown in the inset of Figure 4. We believe this unique structure is formed by orientational ordering of the rod-like aggregates, which is driven by the configurational entropy as the rods concentrate in the highly curved thin liquid films that coat the inner nanochannel walls. Due to the template's small confining area, this order propagates throughout the entire thickness of nanotube wall. Upon carbonization, this unique molecular arrangement is thermally polymerized, and the resulting graphene layers retain the molecular order of the carbon precursor. The success of this covalent capture scheme could not be predicted prior to examining the resulting structure since many thermal carbonization processes destroy supramolecular order in the organic precursor or alter the overall form of the carbon body though re-softening and volatile product release [22].

These inverted nanotubes show promise in sensing and energy storage applications because of the highly active, all edge surfaces and easy access to interlayer spaces. Preliminary electrical testing reveals that the nanotubes with this crystal structure are poor conductors on the order of hundreds of nA/mm^2. This is expected because due to the small size of the graphene planes and the defects resulting from the low carbonization temperature [32]. In Figure 5, current density

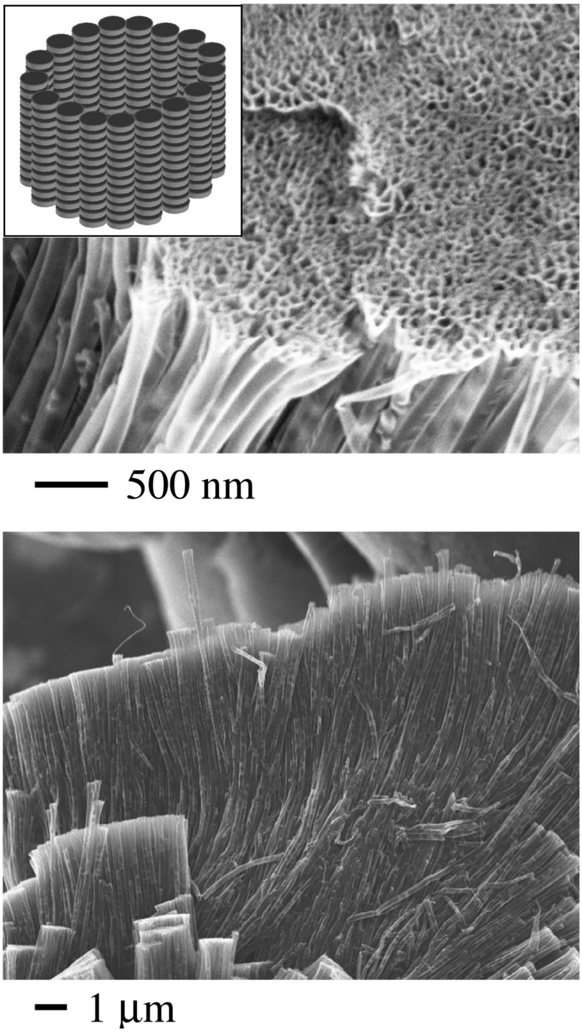

FIGURE 4 Carbon nanotube arrays formed by capillary infiltration of indanthrone disulfonate solutions into nanochannel alumina followed by thermal covalent capture at 700°C and template removal. The inset of Figure 4(a) schematically represents the inverted crystal structure of the resulting nanotubes. The graphene planes are oriented perpendicularly to the long axis of the nanotubes.

versus applied voltage is plotted for an array of nanotubes fabricated using the method described above. We are currently working on methods of coating the template walls with other precursors in order to

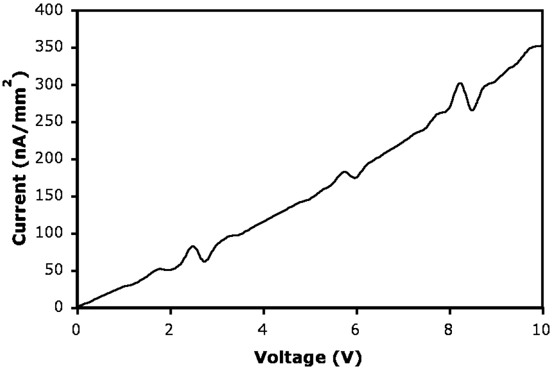

FIGURE 5 A plot of current density versus applied voltage for a nanotube array fabricated using a 7.5 wt.% solution of indanthrone disulfonate.

fabricate tubes with a more traditional structure in which the graphene planes are aligned parallel to the long axis of the nanotube. This structure should produce nanotubes with higher conductivity as well as an increased tensile strength after thermal annealing.

4. SUMMARY

This technique for fabricating CNTs in a single step is relatively simple, yet still allows precise control over the orientation of the graphene layers and thus, the overall material properties of the resulting CNTs. By using a liquid crystalline carbon precursor we can also use a printing method to deposit ordered arrays of nanotubes, which is not possible with conventional nanotube fabrication methods. This allows for rapid production of identical nanotube arrays, which will be essential in order to use them on a mass reproducible scale required for commercial production.

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