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Sparse Multiwall Carbon Nanotube Electrode Arrays for Liquid-Crystal Photonic Devices**

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Multiwall carbon nanotubes (MWCNTs) are normally grown as tangled masses by laser ablation[1] or arc discharge.[2] However, using plasma enhanced chemical vapor deposition (PECVD) techniques[3] it is possible to grow dense aligned mats of "grass-like" MWCNTs as well as individual nanotubes in sparse arrays through the use of e-beam patterning of the catalyst.[4] The fact that they exhibit very high conductivity and aspect ratio means that we can use them as electron source, as has been demonstrated in field emission displays,[5] and as microwave sources.[6] Conducting MWCNTs can also be used as electrode structures in optically anisotropic media such as liquid crystals, as potential alignment layers,[7] and making novel new micro-optical components possible. Their ability to appear as large (with respect to the size of the liquid-crystal molecules) structures within a liquid-crystal device means that there is a strong interaction between the nanotubes and the liquid-crystal material. This interaction can then be interpreted as an optical interaction through the optical anisotropy of the liquid crystal. Hence, nanostructures can be used to form defect centers in liquid-crystal materials, which can then be manipulated by applying an external electric field. On the other hand, considering the fact that the diameter of a MWNT is from tens of nanometers to a hundreds of nanometers, the interaction between the nanotubes and liquid crystal is restricted to the micrometer scale, which is much smaller compared with current liquid crystal devices. In this Communication, we demonstrate an electrically switchable micro-optical component based on a sparse array of MWCNTs grown on a silicon surface, which forms one of the electrodes in a liquid-crystal cell. The nanotubes act as individual electrode sites which spawn an electric field profile, dictating the refractive index profile with the liquid-crystal cell. The refractive index profile then acts as a series of graded index profiles which form a simple lens structure. By changing the electric field applied it is possible to tune the properties of this graded index structure and, hence, the optical structure.

When individual nanotubes are subjected to an applied electrical field, they form a field profile from the tube tip to the ground plane which is approximately Gaussian in shape,[8] as indicated by the dotted line in Figure 1a. If the nanotube electrodes are immersed in a planar aligned nematic liquid crystal material, as shown in Figure 1b, with no field applied, then the liquid crystal molecules will align parallel to the upper substrate surfaces owing to the planar alignment provided by rubbing a surface coating such as a thin film of polyimide. When an electric field is applied to the cell shown in Figure 1b, the molecules of the liquid crystal align to the electric field because of their dielectric anisotropy and freedom to flow. The electric field profile is approximately Gaussian in shape and the liquid crystal molecules will align to this field (assuming in this case a positive dielectric anisotropy), creating a torque about the long molecular axis which causes them to rotate. The final orientation of the liquid crystal is quite complex owing to the Gaussian field profile combined with the surface effects of the alignment layer applied to the upper substrate of the cell. The resulting combination of these two

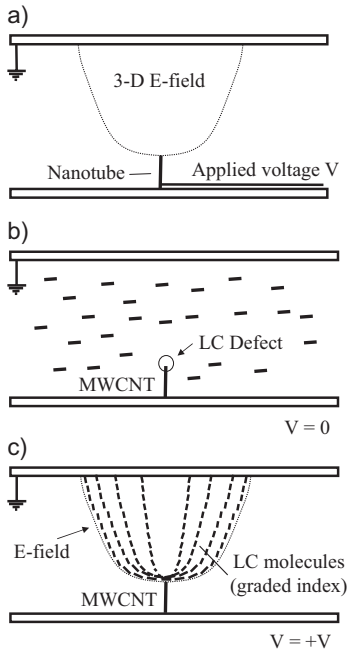

Figure 1. a) Electric field profile of a single nanotube electrode within a vacuum. b) A nanotube electrode in a liquid crystal cell with no external field applied. c) A nanotube electrode within a liquid crystal cell with an applied external voltage *V*.

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effects creates a varying (or graded) refractive-index profile across the cell. The profile formed is in effect a micro-optical element owing to the gradient index profile across the reoriented liquid crystal. If the graded index were Gaussian, then this would form a microlens capable of focusing an applied light wave. More importantly, the micro-optical elements can be tuned by varying the applied field and thereby reorienting the liquid crystal and varying the optical properties of the microlens. The optical element formed is similar to modal liquid crystal lenses formed with wire electrodes,[9,10] but with a much higher density and element resolution.

The device shown in Figure 1 depicts a nanotube attached to the lower electrode and an upper electrode acting as an earth plane for the electric field. The upper electrode is made of a transparent conducting material, indium tin oxide (ITO), on glass. A multiwalled carbon nanotube can be likened to a conductive metal rod of nanometer dimensions. When it is embedded between two plane electrodes in a sandwich structure, the nanotube changes the ideal plane electrostatic field profile. A theoretical study on the electrical field effects of carbon nanotubes has been carried out using the finite element method. A simulation of the electric field profile of the device structure in Figure 1a is shown in Figure 2. The simulation assumes a conducting MWCNT in a vacuum and a good ohmic contact with the substrate underneath.

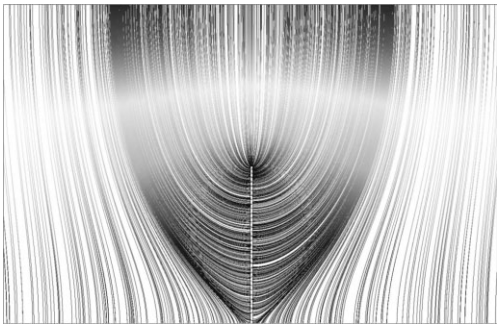

Figure 2. Simulated electrical field profile surrounding the single carbon nanotube (10 μm high) with an applied field of 1V m^{-1}.

The ideal electrical field of a pair of parallel conducting plates is modified by the nanotube. The confinement of the electric field from the nanotube was of the same order as its height. The 2D model of a single nanotube has also been extended into 3D to demonstrate that the field profile was circularly symmetric about the center of the nanotube. The curved electrical field profile in 3D can be used to control the behavior of the liquid crystal molecules as the field intensity is strong enough to reorient them with an applied field of only 1 V μm^{-1}. Varying the applied voltage changes the intensity of the field, the area over which the electric field extends, and hence the orientation of liquid crystal molecules within the area concerned.

Carbon nanotubes in the array were spaced at a distance twice their height to minimize electrostatic field shielding from the adjacent ones. Typical vertical multiwall carbon nanotubes in arrays are 2 to 5 micrometers in height, which implies that the distance between two carbon nanotubes has to be at least 10 micrometers to ensure there is no electrostatic interaction between one another. This means that the liquid-crystal microlens array in a 10 x 10 mm^2 chip would have a resolution of 1000 x 1000 lenslets for MWCNTs up to 5 μm high. For shorter MWCNTs, even greater density micro-optical arrays are possible.

One of the main limitations of the microlenses that could be formed with this structure was that they have a very tight aperture owing to the localization of the electric field around the nanotube electrodes. Further simulation showed that if small groups of 2, 3, or 4 nanotubes were grown within a micrometer of each other, then the field profiles overlap making a larger optical aperture for each lenslet. Figure 3 shows how two closely spaced nanotubes can be used to create an effective single electrode with a wider field profile than the single nanotube.

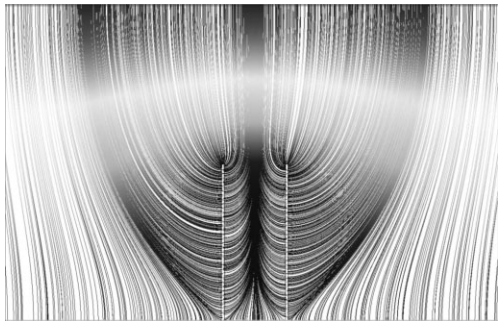

Figure 3. Electric field profile of a two-nanotube electrode, 1 μm apart at 1 V m^{-1}.

In conclusion, we have demonstrated a new device based on the combination of a sparse array of vertically grown multiwall carbon nanotubes and liquid crystals to form a electrically reconfigurable micro-optical array. The micro-optical effect comes from the variation of the refractive index of the liquid crystal layer placed above the electrode array. By applying a voltage to the nanotube electrode the focal properties of the micro-optical element can be adjusted. Such a device has many potential applications such as in adaptive optical systems, wavefront sensors and optical diffusers.

Experimental

Three different kinds of MWCNT electrode structure were grown on silicon substrates. Each nanotube array was grown directly on a silicon wafer by PECVD after employing e-beam lithography to pattern a 5 nm thick nickel catalyst layer into an array with each dot being 100 nm in diameter, to allow the growth of a single MWCNT of 50 nm diameter on each dot. The substrate was heated by dc current under vacuum of 10^{-2} mbar to 650 °C at a ramping rate of 100 °C per minute. A mild heating process was preferred to protect the catalyst dots from cracking. Ammonia gas was then introduced to etch the sur-

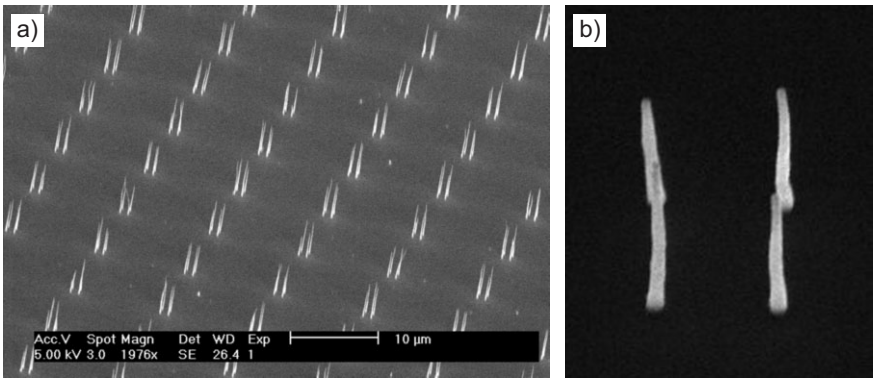

Figure 4. Sparse array of nanotubes in groups of four. a) Array view with group spacing of 10 µm. b) View of a single group with nanotube spacing of 1 µm.

face of the nickel catalyst islands. Acetylene was chosen to be the carbon source, and was imported into the deposition chamber after the temperature reached 690 °C, followed by a dc voltage of 640 V between the gas shower head and the heating stage to create plasma of 40 W in power. The growth process lasted for 10 to 15 min at 725 °C, which gives multiwall carbon nanotubes of nearly 2 µm in height.

A typical array of individual nanotubes is shown in the electron microscopy image of Figure 4a, with a higher magnification view in Figure 4(b). In this case the nanotubes were patterned in small groups of 4 with 1µm spacing between the nanotubes and 10 µm spacing between the groups.

The sparse array shown in Figure 4 was then fabricated into a liquid crystal device. In order to make the device both reflective and also to provide a common electrical connection to all the nanotubes, 400 nm of aluminum was cold-sputtered onto the array. The array was then assembled with a top electrode containing ITO on 0.5 mm thick borosilicate glass into a liquid crystal cell with a 20 µm cell gap set by spacer balls in UV glue. No alignment layer was applied to the nanotube array, but the top glass electrode was coated with AM4276 liquid crystal alignment (low pretilt polyimide from Merck) and rubbed in the horizontal direction to give planar alignment. The cell was then capillary filled with a positive dielectric anisotropy nematic liquid crystal mixture, BLO48 also from Merck.

The assembled device was then viewed under horizontally polarized light on an optical microscope. The arrays of nanotubes were clearly visible as black dots as each 50 nm nanotube tip was the site for a defect in the nematic liquid crystal. Individual nanotubes with their groups of 4 could be seen at a magnification of 40x. Figure 5a shows the sparse array at zero applied electric field. The array of CNT groups can be clearly seen as defects in the image. As the applied field was increased, the nanotube electrodes were seen to begin switching at 1.8 V μm^{-1}, which corresponds to the equivalent of a Freedrickzs transition. Figure 5b shows the nanotube array at 2.2 V μm^{-1} applied field and the nanotubes were all fully switched. The distortion in the liquid crystal director can be seen in this image as visible contrast, with an analyzer in the horizontal direction, centered on each nanotube group. The irregular structure seen in Figure 5b was not perfectly circularly symmetric as the liquid crystal was horizontally (planar) aligned on the top substrate. The liquid crystal reoriented to the field of the nanotube electrodes in a complex manner, forming a twisted structure centered on each nanotube group.

The distortion in the liquid crystal can also be seen without any polarizer or analyzer under the microscope, as shown in Figure 6. Each feature is based around a group of 4 CNTs (like the group shown in Fig. 4b) in the array and can be switched on and off with the applied electric field. Each feature resembles a roughly circular defect surrounding the CNT group. The difference in sizes of the defects was due to the different ohmic contacts made between the MWCNTs and the aluminum electrode layer.

The lensing properties of these micro-optical elements were verified under the same microscope at 40x magnification. Owing to the limited depth of focus of the high magnification it should be possible to switch the CNT tip in and out of focus with an applied electric field. Figure 7a shows the array with 0 V μm^{-1} applied field and the microscope adjusted to be out of focus. The image in Figure 7b is the same area with an applied field of 2.1 V μm^{-1} and no adjustment made to the microscope. The lensing function of the liquid crystal can be seen

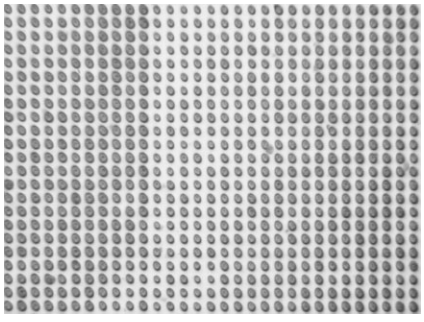

Figure 6. Image of the LC-CNT array at 2.2 V μm^{-1} taken at 20x with no polarizer or analyzer on the microscope.

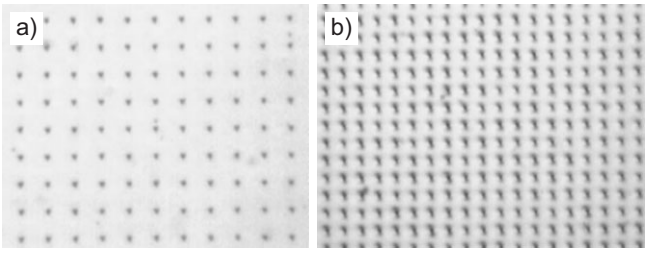

Figure 5. Sparse nanotube array (10 µm spacing) in a liquid crystal at 20x optical magnification under a polarizing microscope with the analyzer aligned parallel to the rubbing direction of the liquid crystal (horizontal). a) 0 V μm^{-1} applied field, and b) 2.2 V μm^{-1} applied field.

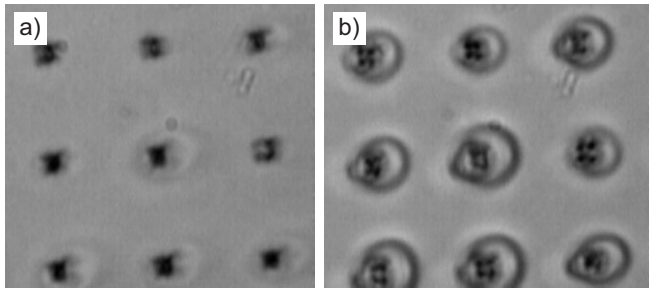

Figure 7. Defocus of the nanotube lenslet array at 40x. a) Defocused image of the array at 0 V μm^{-1} applied field. b) Array brought into focus with 2.1 V μm^{-1} applied field.

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as the liquid crystal defect state at the tip of the nanotubes now appear in focus and are visible as a cluster of black dots at the center of each lenslet.

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Sparse Multiwall Carbon Nanotube Electrode Arrays for Liquid-Crystal Photonic Devices

A new class of devices based on a hybrid combination of two different materials, nanotubes and liquid crystals, is presented. An array of individual vertically aligned multiwall carbon nanotubes creates a Gaussian electric field profile which reorients a nematic liquid crystal. The variation in refractive index acts like a graded index optical element which can be varied electrically. Results are presented from a device fabricated with 10 μm pitch micro-optical elements.