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Carbon Nanotube Film Sensors**

By Zhiling Li, Prasad Dharap, Satish Nagarajiah,*
Enrique V. Barrera, and Jong Dae Kim

Since their discovery,^[1] carbon nanotubes have been investigated extensively. Several experiments^[2–4] have demonstrated the potential of single-walled carbon nanotubes (SWCNTs) as strain/stress sensors by relating the strain/stress of the nanotube to the Raman band shift. The electronic bandgap changes have been computed as a function of axial compression, tension stretch, torsion, and bending strain.^[5–7] It has been possible to develop nanoelectromechanical sensors because of the strong dependence of the SWCNTs' band structure on the mechanical deformation. SWCNTs exhibit excellent mechanical and electrical properties. Most of the studies to date relate the mechanical deformation with the change in electrical properties at the nanoscale. The main objective of this study is to use the strain-sensing capability at the nanoscale to develop macroscale strain sensors. We propose the use of carbon nanotube films that possess isotropic properties due to the random orientation of SWCNTs; such films could be applied to structural surfaces, e.g., the skin of an aircraft wing, to measure strain at the macroscale.

It is difficult to use Raman spectroscopy for strain measurements at the macroscale in the field. The use of conventional electrical resistance strain gauges is limited to discrete points and fixed directional strain sensing. We propose the use of external probes to measure strain by contact with carbon nanotube films; the probes can easily be moved to different directions or locations, imparting the ability to sense multidirectional and multiple-location strain at the macroscale. Additionally, the strain gauges are separate from the material, not embedded. Carbon nanotube films can be integrated into the material, for example in composites, and hence can function both as sensors and as the structural material. We demonstrate here that carbon nanotube films can be used to measure strain at the macroscale.

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[**] The authors wish to acknowledge the support of the Texas Institute for Intelligent Bio-Nano Materials and Structure for Aerospace Vehicles, funded by NASA Cooperative Agreement No. NCC-1-02038.

Several experiments have demonstrated the potential of SWCNTs in composites as nanoscale sensors.^[2-4] The Raman band of SWCNTs in a polymer matrix at about 2630 cm⁻¹ has been studied as a function of tensile strain^[3] and the Raman band of SWCNTs in composites at about 1590 cm⁻¹ has also been studied.^[2] Both these studies have shown that the shift in the Raman modes is a function of the strain applied to the SWCNTs. As a first step, we demonstrate that carbon nanotube films are Raman-active and can be used to sense strain.

In order to produce the carbon nanotube films, unpurified SWCNTs from Carbon Nanotechnologies Incorporated (CNI) were mixed with 0.25 mg/mL *N,N*-dimethylformamide (DMF) and the mixture was filtered through a 0.2 mm Teflon membrane. After rinsing and drying of the remaining material, freestanding carbon nanotube films (buckypapers) were peeled from the filter. Then, the films were dried for 24 h under vacuum. Figures 1a,b show scanning electron microscopy (SEM) pictures of a carbon nanotube film with 30 μm thick-

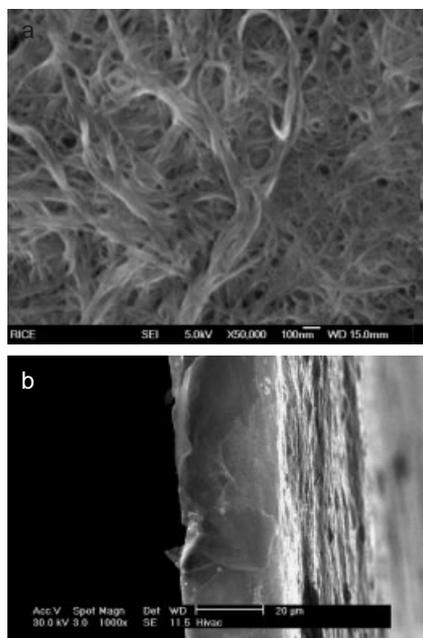


Figure 1. SEM images of a carbon nanotube film: a) plan view showing randomly distributed bundles of SWCNTs in a carbon nanotube film (scale 100 nm); b) cross-section of the carbon nanotube film (scale 20 μm).

ness. It can be seen that the film is made up of randomly oriented bundles of SWCNTs. To study the effectiveness of the film in measuring strain, it was attached to a rubber strip, using high strength epoxy to ensure perfect bonding. The rubber strip was loaded with tensile forces in order to induce axial tensile strains in the film, and the corresponding Raman spectra were recorded. A conventional strain gauge was attached to the other side of the rubber specimen to measure the strain transferred to the nanotube film.

Polarized Raman measurements were performed at room temperature using a Renishaw Raman microscope. Ar⁺

(514.5 nm, 2.41 eV) laser light was used and the readings were recorded in the back-scattering configuration. As concluded by Frogley et al.,^[3] when using polarized light, randomly oriented nanotubes can be used as strain sensors so that no fixed nanotube alignment is necessary and strains can be measured in all directions in a single sample. The exciting laser spot was kept at the same position throughout the experiment and the polarized laser was kept parallel to the direction in which the axial tension was applied.

It can be seen from Figure 2a that the Radial Breathing (RB) modes^[2,8] are not affected by the strains in the film. The peaks remain unchanged as the axial tensile strains are increased from 0.03 % to 0.094 %. However, for the correspond-

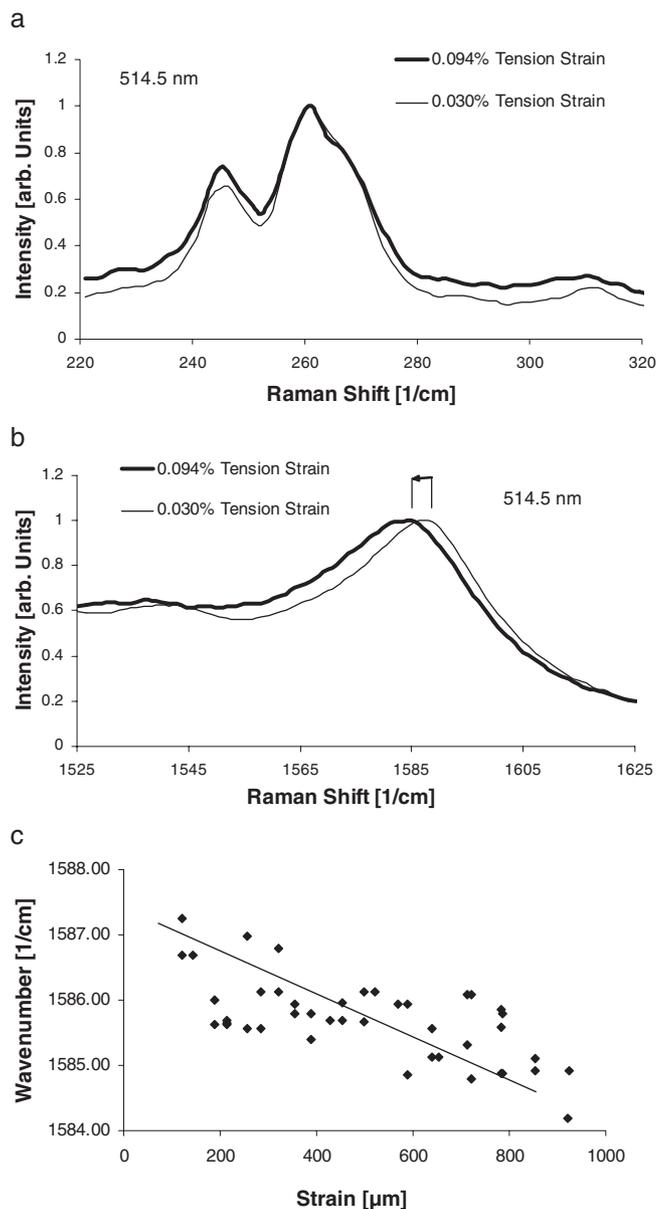


Figure 2. Raman spectra of the carbon nanotube film: a) RB modes; b) shift in G-band modes; c) the G-band peak position for SWCNTs in the carbon nanotube film, as a function of tensile strain.

ing change in strains, the peak of the G band (C–C stretching tangential modes) shifts downwards by about 2 cm^{-1} , as shown in Figure 2b. The D band, at 2654 cm^{-1} , is rather complicated to interpret^[2,9] because of the mode dispersion involved in the scattering process, and is therefore not considered in this study.

The Raman wavenumber shift of the G band of carbon nanotube films as a function of tensile strain is shown in Figure 2c. From this figure it can be seen that the Raman wavenumber of the G modes shifts downward when the tensile strain in the film increases. Although the data are scattered, the downward trend is clear—the solid line is the linear regression of the data. It can be concluded that there is a relationship between the tensile strains applied to the carbon nanotube films and the G band mode peak from the Raman spectroscopy study.

The Raman shift confirms that nanotubes are strained due to axial tensile strain on the carbon nanotube film. The strain in the nanotubes alters its electrical properties,^[5–7] hence carbon nanotube films can be used as strain sensors.

The elaborate setup needed for Raman spectroscopy makes it less practical for field applications such as measuring the strain in an aircraft wing. Therefore, a movable four-point probe was proposed to measure the change in voltage across the carbon nanotube film due to tensile strain. A carbon nanotube film was attached to a 12 in. \times 1.5 in. \times 0.065 in. (1 in. = 2.54 cm) brass specimen, with poly(vinyl chloride) (PVC) between the brass specimen and film for insulation. The Young's modulus of the brass specimen is 96 GPa. High-strength epoxy and a vacuum-bonding method were applied to ensure perfect strain transfer between the brass, PVC, and film. A conventional electrical resistance strain gauge was attached to the other side of the specimen to measure the strain. The specimen was subjected to tensile force using a servohydraulic machine and the corresponding change in voltage was measured using a four-point probe measurement.^[10] Four colinear copper probes spaced at 0.3 in. center to center were used for the four-point-probe measurement. The input current across the two outer probes was kept constant during the measurement and the change in voltage across the two inner probes was measured.

Figure 3 shows the voltage changes in the carbon nanotube film as a function of the measured tensile strain from the conventional gauge. As the tensile strain measured by the conventional gauge increases from 0–1000 $\mu\text{m}/\text{m}$ the voltage changes measured across the two inner probes increase by nearly 350 μV . There is a linear relationship between the change in voltage and the strain, although the data are scattered and further investigation is needed. The change in voltage was measured by moving the four-point probe to several parallel locations, in line with the axial forces on a single carbon nanotube film; this also yielded a linear trend.

The change in voltage between the inner two probes comes from two sources: 1) the change of resistivity in the nanotube film, and 2) dimension changes of the nanotube film. Since in this experiment the strains of the brass specimen are of the order of 0.1 %, the changes in the dimensions of the film will be

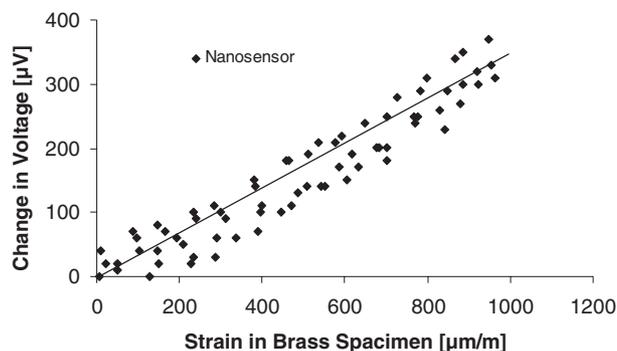


Figure 3. Brass specimen, with a carbon nanotube film attached to it, subjected to tension: strain as a function of change in voltage in the carbon nanotube film.

small, and therefore their contributions to the change in voltage will also be small, as demonstrated below. The film resistivity ρ is given by^[10]

$$\rho = \frac{V}{I} C \left(\frac{a}{d} \cdot \frac{d}{s} \right) \quad (1)$$

where V is the voltage across the inner two probes, I is the constant input current across the outer two probes, and C is a factor dependent on the length (a), width (d), and distance (s) between the probes. If the resistivity of the nanotube film is assumed to be constant, the change in voltage due to the dimension change can be obtained by

$$\Delta V = \rho I \left(\frac{1}{C_2} - \frac{1}{C_1} \right) = 32 \text{ } (\mu\text{V}) \quad (2)$$

where C_1 (1.94645) and C_2 (1.94586) are the factors^[10] depending on the change of dimensions of the nanotube film due to tensile strain, and the input current is constant at 107.5 mA. From the above equations the change in voltage corresponding to the change in tensile strain from 0 to 0.1 % is 32 μV . From Figure 3 the measured change in voltage across the inner two probes is 350 μV for 0.1 % tensile strain. From the above analysis it is clear that the change in voltage due to the dimension change of the nanotube film is small (9 %) and hence the change in voltage is mainly related to the change in resistivity (91 %).

In conclusion, a carbon nanotube film can be used as a strain sensor at the macroscale, due to the dependence of the electrical properties of SWCNTs on mechanical deformation at the nanoscale. In addition, carbon nanotube films are made up of randomly oriented SWCNTs, so their electronic properties are independent of direction. Hence, taking measurements along different directions will provide the corresponding strains.^[11] Carbon nanotube films made up of aligned SWCNTs can be expected to be more sensitive to tensile strains than carbon nanotube films made up of randomly oriented SWCNTs, although further research is needed. The results presented in this paper demonstrate the potential of carbon nanotube films in measuring strain at the macroscale.

Experimental

Nanotube films made of unpurified SWCNTs from CNI were attached to a rubber specimen. The G-band and RB mode shift in the carbon nanotube films were measured on a Renishaw Raman microscope as the rubber specimen was subjected to a tensile force. The corresponding strain in the carbon nanotube film was measured by conventional strain gauges attached to the other side of the rubber specimen.

Carbon nanotube films were attached to the brass specimen using high-strength epoxy combined with a vacuum bonding method. Conventional strain gauges were attached to the opposite side of the brass specimen. A four-point-probe method was used to measure the voltage across the inner two probes with a constant current passing through the outer two probes. The brass specimen was subjected to tensile forces on an Instron 5586 servo hydraulic test frame.

Received: October 12, 2003
Final version: December 25, 2003

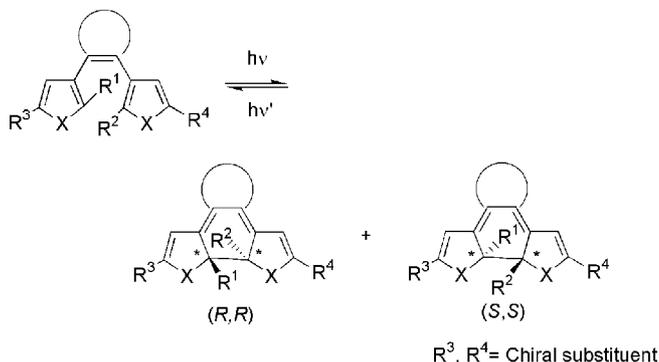
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Reversible Diastereoselective Photocyclization of Diarylethenes in a Bulk Amorphous State

By Tadatsugu Yamaguchi,* Kazuko Nomiyama, Munetoshi Isayama, and Masahiro Irie

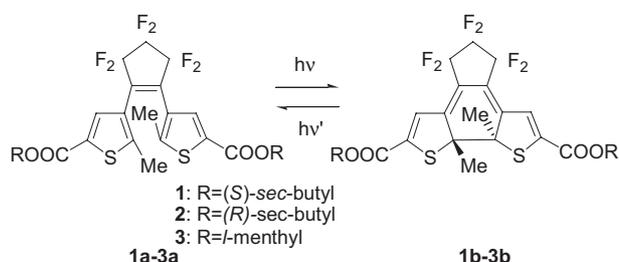
Diarylethene derivatives are very promising photochromic compounds for application as optoelectronic devices because of their fatigue resistant and thermally irreversible perfor-

mance.^[1,2] One of the characteristic properties of the diarylethenes is that the colored closed-ring isomers have chiral carbon atoms. Upon irradiation with ultraviolet light, colorless open-ring isomers are converted to enantiomers (*R,R* and *S,S*) of the closed-ring isomers.



Various attempts have been carried out to enrich one of the enantiomers (or diastereomers),^[3-7] because optical rotation changes by photoirradiation are potentially useful for non-destructive readout in optical memories.

For practical applications, photochromic reactions should take place in solid matrices. Although successful enrichment of one of the diastereomers was observed in crystals of a diarylethene with a chiral substituent,^[4] the crystalline state is hard to process. A bulk amorphous state is favorable for processing and has various advantageous characteristics for practical usage, such as high dye density and high optical transparency.^[8-10] In this communication we report on an asymmetric induction in the photochromic reactions of diarylethene derivatives **1a**, **2a**, and **3a** in the amorphous state.



Diarylethenes **1a–3a**, which have two chiral units, were synthesized by carboxylation of the 1,2-bis(2-methyl-5-bromo-thiophen-3-yl)perfluorocyclopentene **4**,^[11] which is prepared by bromination of 1,2-bis(2-methyl-thiophen-3-yl)perfluorocyclopentene in tetrahydrofuran (THF),^[12] and successive esterification of the carboxylic acid with (*S*)-2-butanol, (*R*)-2-butanol, *l*-menthol.^[13-15]

Upon irradiation with UV light in hexane solution, compounds **1a–3a** underwent photocyclization reactions to give two diastereomers. These diastereomers were isolated by high performance liquid chromatography (HPLC) performed with a silica gel column (Wakosil 5SIL), using hexane/ethyl acetate as an eluent, and the electronic absorption spectra of the two diastereomers were measured.^[13-15] Because the two closed-ring diastereomers showed the same absorption maximum

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