1440 sub. Applied Physics Letters

Optical anisotropy of dispersed carbon nanotubes induced by an electric field

Karsten Bubke, Harald Gnewuch*, and Martin Hempstead

University of Southampton, Optoelectronics Research Centre, Southampton SO17 1BJ, United Kingdom

Jens Hammer and Malcom L.H. Green

Inorganic Chemistry Laboratory, University of Oxford, South Parks Road, Oxford OX1 3QR, United Kingdom

Abstract

Carbon nanotubes dispersed in ethanol are aligned by an electric field. Due to the orientation of these elongated particles, the dispersion exhibits anisotropic behaviour. Transmission experiments show rotation of the linear polarisation of an incident laser beam. Alignment and relaxation times and the influence of the magnitude of the electric field have been measured.

---

*corresponding author; Electronic mail: hwg@orc.soton.ac.uk

Since their discovery[1] and medium-scale synthesis[2], carbon nanotubes have captured strong attention. The tubes, all-carbon particles, consist of one or more cylindrical shells of graphitic sheets and are typically closed at each end. The diameters are usually on the order of tens of angstroms and the lengths of the order of microns[3]. Due to their nano-scale dimensions and high aspect ratios, carbon nanotubes constitute potentially interesting new structures for the optic community. However, separation and manipulation are still difficult tasks. Several techniques for nanotube alignment have been devised[4,5]. Recently Fishbine[6] suggested the use of electrostatic fields, and electric field orientation has already been demonstrated experimentally[7].

In this work we report on the optical effects induced by an electric field on a dispersion containing carbon nanotubes. Owing to the orientation of the particles, the dispersion exhibits anisotropic behaviour, similar to electrooptic effects in liquid crystals[8]. The induced anisotropy was measured by its effect on the state-of-polarisation (SOP) of a linearly polarized light beam incident on the dispersion. Through the change of the SOP, it is possible to measure the degree of orientation as well as alignment and relaxation times. Our aim has been first to demonstrate the optical detection of tube alignment in real time, and second to characterise it.

The possibilities for characterization are limited, due to the nature of the nanotube sample. The carbon nanotubes used in this study were synthesized in a conventional arc discharge[2] and dispersed in ethanol. They have not been purified, so that the carbon is only about 60% nanotubes, the remainder being made up of irregular particles of a range of sizes. Moreover, the tubes have a range of lengths and diameters. Fig. 1(a) shows an SEM picture of the deposit left by the drying of a freshly prepared dispersion. Another complicating effect is that the dispersion ages; the nanoparticles fall out of the dispersion and appear to clump together, over a period of days. The net gravitational force on the tubes is sufficiently high to make the particles fall out of the dispersion at room temperature, but at rates depending on the tube size. Thus we know neither the exact initial composition of the dispersion nor its change with time. The response to an electric field and the orientational relaxation times

depend on the tube size and shape; Fig. 1(b) is an SEM picture of nanotubes from the same dispersion as in 1(a) drawn to a cathode and apparently sorted by size-sensitive forces. Thus it is not possible to obtain more than an estimate of the tube properties.

A conducting or dielectric particle in an external field $\mathbf{E}$ develops a dipole moment $\mathbf{p}$; various calculations of the response of a conducting tube may be found in the literature[9,10], and predict a large form-anisotropy. In general, there is then a torque $\mathbf{p} \times \mathbf{E}$ on the object which tends to align it to the field. Theory predicts that carbon nanotubes are conducting or semiconducting, depending on their diameter and helicity[11]. Recently, measurements of individual tubes have suggested they are conducting[12]. In our theoretical calculations of orientation we assume that the nanotubes are conducting.

Ellipsometric measurements of the optical properties of aligned carbon nanotube films[5] show highly anisotropic response. This can be explained by the fact that light polarized along the tubes experiences a permittivity similar to that of in-plane graphite, whereas light polarized perpendicular to the tube axis should see a mixture between the dielectric functions parallel to and perpendicular to the graphitic sheets. Because of their form- and material anisotropy a dispersion of oriented carbon nanotubes should show optical anisotropy, in contrast to the isotropic behaviour of randomly distributed tubules.

The experimental arrangement for the optical measurements is shown in Fig.2. A 633 nm He-Ne laser beam with an output power of 10 mW is focussed on a gap d=200 μm wide and l_c=5 mm long between two electrodes in a cuvette containing the nanotube dispersion. The electrodes consist of two glass slides coated with aluminum and separated by a sheet of mica.

The incident laser beam is linearly polarized by polarizer PL1 at $\alpha = 135^0$ and therefore at 45^0 to the expected x- and y-axes of the anisotropic dielectric response. Another linear polarizer PL2 oriented at $\alpha = 45^0$ is positioned after the cuvette and the signal is detected with a Si-photodiode. For an isotropic medium between the crossed polarizers any signal on the output corresponds to background noise. Any change of SOP due to x-y anisotropy can be detected. First control experiments showed a slight, presumably stress-induced, bi-

refringence of the cuvette which was corrected by a Berek's compensator BC placed between cuvette and polarizer PL2 and adjusted for minimal output signal p_D with crossed polarizers before a voltage was applied to the electrodes.

Recent experiments on oriented nanotube films formed in a dc field show that the tubes drift to the cathode[7]. We reduce this complicating effect by use of an ac field and a high-pass filter to suppress any dc part of the voltage. Nevertheless, the measured anisotropic effect decreases over a period of minutes. Fig. 3(a) shows the evolution of loss from an initial value of 0.28 dB/mm in a dispersion with different applied fields. In these measurements, the laser beam was chopped, we applied a steady ac-voltage and the transmitted light power was measured with a conventional lock-in technique. After approximately 5 min no further change of loss occurred. We noticed that the induced polarization change had dropped off in proportion. Apparently, a proportion of the tubes move out of the light path until an equilibrium is approached. This may be a consequence of drift in the electric field gradients of the fringing fields of the electrodes, but definitive studies have yet to be carried out. In Ref. 7 the mobility of tubes in isopropyl alcohol under a dc field was estimated to be higher then $5 \cdot 10^{-5}$ $cm^2V^{-1}s^{-1}$. This is much higher than required to account for the effects seen here.

To further investigate the movement of the particles in the dispersion, a dc voltage of 50 V was applied for 30 s to a dispersion of excess loss of 1.4 dB/mm. Fig. 1(b) shows SEM-micrographs of the cathode after use. In comparison with the control evaporated deposit (Fig. 1(a)), the cathodic deposit shows a strong accumulation of longer tubes and fewer other particles. We thus conclude that it should be possible to purify as well as grade carbon nanotubes by electric fields, as well as by exploiting differential settling rates in dispersion, perhaps aided by controlled centrifugation. Conventional purification techniques[13] are mostly based on oxidation and a large fraction of material has to be burnt off. Purified samples contain mostly open tubes with a high degree of structural damage[14,15]. A technique based on the movement in an electric field could overcome these drawbacks. This is particularly attractive if damage or opening of tubes is undesirable.

Fig. 4 shows the result of our initial studies of field-induced SOP change. The detected signal p_D is due to the change of SOP caused by an ac-voltage of f_1=10 kHz and 45 V amplitude applied over a time interval of 0.75 s. For these measurements we used a nanotube dispersion with a 0.3dB/mm excess loss (in comparison with pure ethanol, at 633nm). The risetime τ_t, defined as the time required for the signal to rise from 10% to 90% of the final value, is about 10ms. The relaxation time τ_e has a 1/e value of about 80ms. For lower applied voltages the risetime increases, e.g. for 5 V amplitude we obtain $\tau_t \approx 250$ ms, whereas τ_e remains nearly constant.

Further measurements were undertaken by modulating the ac voltage with a lower frequency $f_2 = 300$ Hz and measuring the signal p_L with a lock-in-technique, see Fig. 2. In Fig. 3(b) the relationship between the induced polarisation change and the applied voltage is shown. No sign of saturation of p_L due to fully aligned nanotubes is seen. Fig. 3(c) shows as expected an induced polarisation change p_L proportional to the concentration of nanotubes in the dispersion.

To determine the nature of the induced change in polarisation state, the transmitted light power was measured as a function of the orientation of PL2. To prepare the sample for this lengthy measurement, we applied an ac voltage until the signal showed no change versus time. The signal was then measured by chopping the applied voltage as explained above. The field-induced rotation of the polarisation is clearly to be seen in Fig. 3(d). By curve-fitting we measured an induced difference of 5/m between the attenuation coefficients in the x- and y-directions. A phase change could not be detected.

We have attempted to compare our measured results with theoretical predictions. These predictions include the field required to saturate the orientational anisotropy and the alignment and relaxation times.

The saturation field depends on the dimensions of the nanotubes. For tubes of 10 nm diameter and a length of 2 microns, the formulae for the response of a tubular conductor[10] combined with Fishbine's analysis[6] predict saturation fields of 50V/mm and alignment times of the order of 0.1 ms. Our measurements give longer times, with the tail of the response

taking about 0.1s.

The relaxation times are related only to the tube mass and geometry, and the viscosity and temperature of the solvent[16]. We estimate that the relaxation time for a nanotube of 10nm radius and 2 microns length should be of the order of 0.1 ms. Again, this is much shorter than the observed 0.08 s.

Clearly, the theoretical predictions are far from the observed results. While the theory is admittedly uncertain and the tube properties are ill-defined, the differences seem too great to be accommodated by the allowed uncertainties. At present, we cannot account for the discrepancies.

In conclusion, optical anisotropy of a dispersion of carbon nanotubes due to orientation in an electric field was demonstrated. The effect of the drift of the particles in a dc-field was reduced by use of an ac field. Nevertheless it was found that the anisotropy as well as the absorption decreased on a time scale of minutes. The maximum electric field of 225 V/mm does not lead to a saturation of the effect. Investigation of the behaviour in higher fields and detailed characterization of the anisotropy are desirable, and require highly purified material. With purified material, it will become possible to make quantitative statements about the properties of individual nanotubes on the basis of the kind of measurements described here.

We thank Mrs. P. Hua for preparing the SEM-images and Mr. T. Austin for design of the electronics. J. Hammer thanks for his support by the Training and Mobility program of the European Union under the project ERB4001GT952175.

References

1. S.Iijima, Nature **354** , 56 (1991).

2. T. W. Ebbesen and P. M. Ajayan, Nature **358,** 220 (1992).

3. W. S. Bacsa, D. Ugarte, A. Chatelain and W. A. de Heer, Phys. Rev. B **20,** 15473 (1994).

4. P. M. Ajayan, O. Stephan, C. Colliex and D. Trauth, Science **265,** 1212 (1994).

5. W. A. de Heer, W. S. Bacsa, A. Chatelain, T. Gerfin, R. Humphrey-Baker, L. Forro and D. Ugarte, Science **268,** 845 (1995).

6. B. H. Fishbine, Fullerene Sci. Techn. **4,** 87 (1996).

7. K. Yamamoto, S. Akita and Y. Nakayama, Jpn. J. Appl. Phys. **35,** L917 (1996).

8. L. M. Blinov, *Electro-optical and magneto-optical properties of liquid crystals* (John Wiley & Sons, New York, 1983).

9. L. D. Landau, E. M. Lifshitz and L. P. Pitaevskii, *Electrodynamics of continuous media* (Pergamon Press, Oxford, 1981).

10. F. Behroozi, M. Orman, R. Reese, W. Stockton, J. Calvert, F. Rachford and P. Schoen, J. Appl. Phys. **68,** 3688 (1990).

11. N. Hamada, S. Sawada and A. Oshiyama, Phys. Rev. Lett. **66,** 1579 (1992).

12. H. Dai, E. W. Wong and C. M. Lieber, Science **272,** 523 (1996).

13. T. W. Ebbesen, P. M. Ajayan, M. Hiura and K. Tanigaki, Nature **367,** 519 (1994).

14. S. C. Tsang, P. J. F. Harris and M. L. H. Green, Nature **362,** 520–522 (1993).

15. P. M. Ajayan, T. W. Ebbesen, T. Ichihashi, S. Iijima, K. Tanigaki and H. Hiura, Nature **362,** 522 (1993).

16. J. McConnell, *Rotational brownian motion and dielectric theory* (Academic Press, London, 1980), pp. 6–9.

FIGURES

Fig. 1. SEM micrographs (a) of a sample prepared from a fresh dispersion and (b) of an area of the surface of the cathode after application of a dc field of 250 V/mm for 30 s.

Fig. 2. Experimental arrangement with polarizer (PL), cuvette (CV) containing electrodes and nanotube dispersion with the relevant parameters l_c and d, Berek's compensator (BC), detector (DT) and underlying coordinate system.

Fig. 3. (a) Evolution of loss in dispersion as a function of time with an applied ac field of ○ 225 V/mm, △ 150 V/mm, □ 75 V/mm, ▽ 25 V/mm; (b) detected signal p_L as a function of applied ac voltage U_E and (c) as a function of amount of material in the dispersion expressed by optical loss in comparison to ethanol; (d) signal p_L as a function of α (see Fig. 2), ○ without applied field, □ with applied ac voltage U_E=45 V.

Fig. 4. (a) Schematic diagram of applied ac voltage U_E of f_1=10 kHz and (b) resulting detected signal p_D.

Fig.1
Bubke et al.

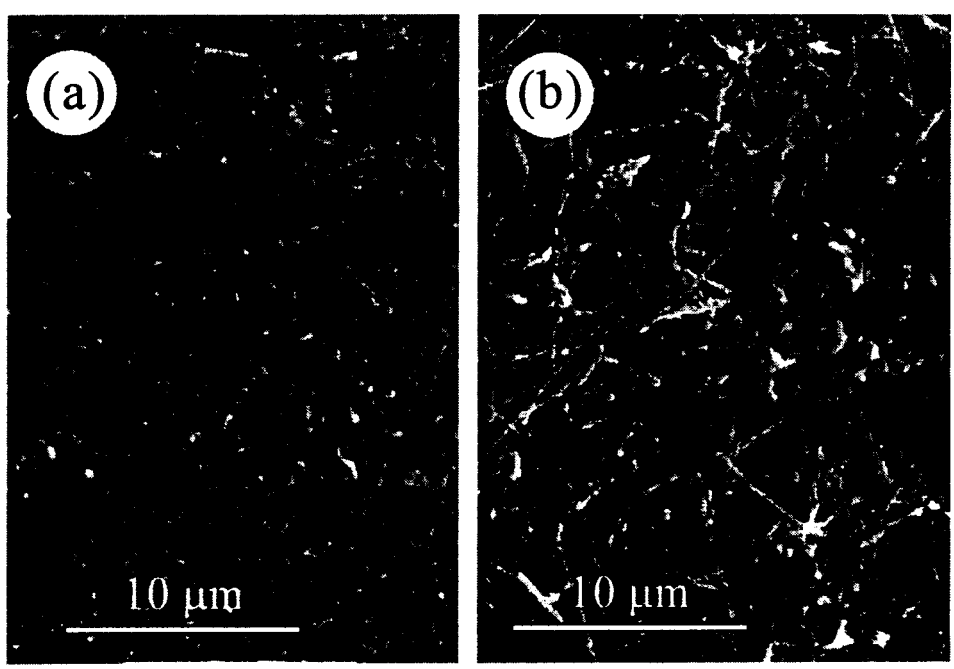

Fig. 2
Bubke et al.

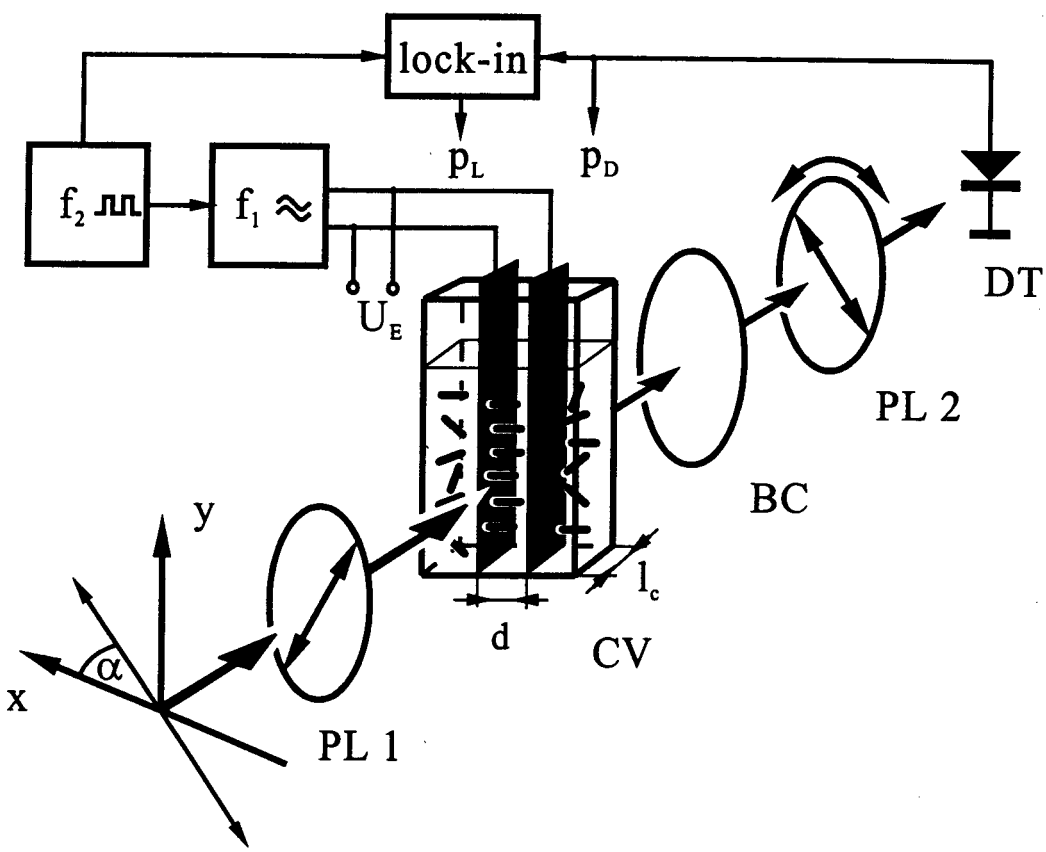

Fig. 3; Bubke et al.

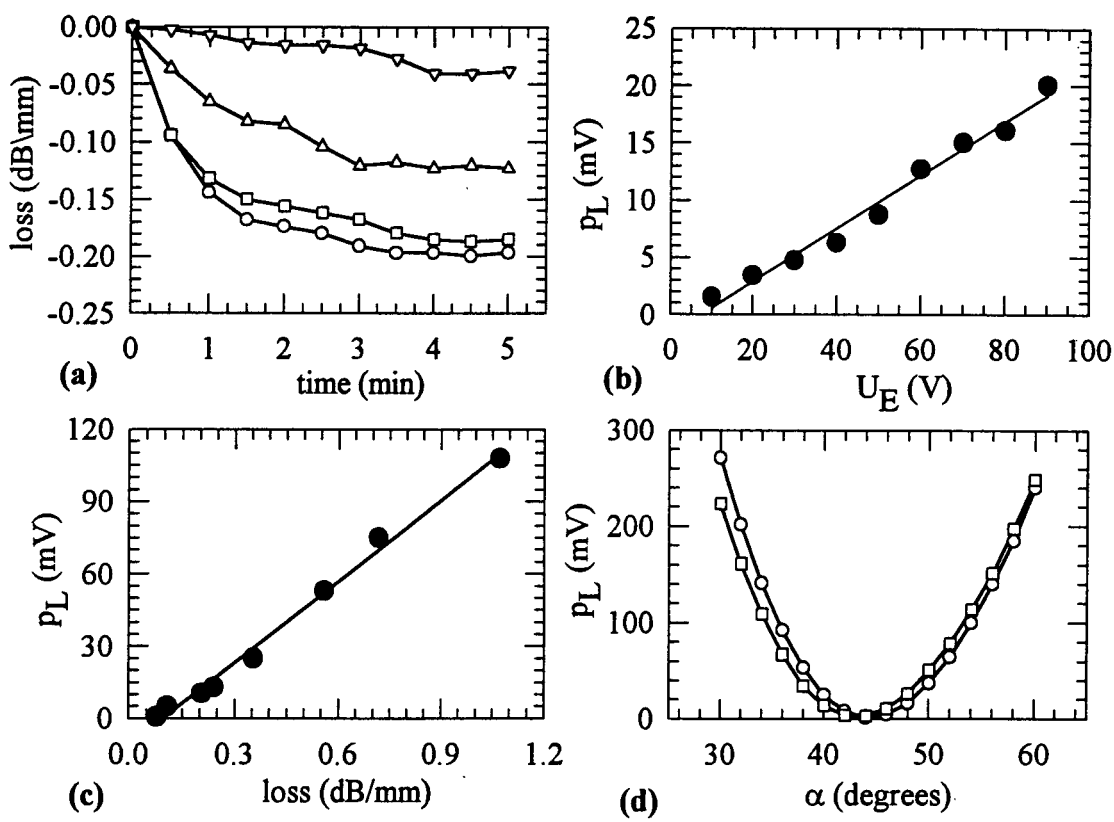

Fig. 4; Bubke et al.