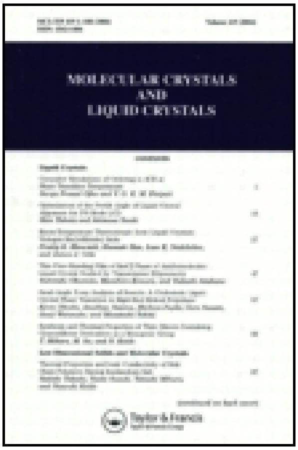

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Electrochemical Doping of Bundles of Unopened Single Wall Carbon Nanotubes

Gamini Sumanasekera [a] , Jan Allen [b] & Peter Eklund [a]

[a] Department of Physics and Astronomy, University of Kentucky, Lexington, Kentucky, 40506, USA

[b] Gillete Research Institute, 401 Professional Drive, Gaithersburg, Maryland, 20879, USA

Version of record first published: 24 Sep 2006

To cite this article: Gamini Sumanasekera, Jan Allen & Peter Eklund (2000): Electrochemical Doping of Bundles of Unopened Single Wall Carbon Nanotubes, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 340:1, 535-540

To link to this article: http://dx.doi.org/10.1080/10587250008025521

Mol. Cryst. and Liq. Cryst., 2000, Vol. 340, pp. 535-540
Reprints available directly from the publisher
Photocopying permitted by license only

Electrochemical Doping of Bundles of Unopened Single Wall Carbon Nanotubes

GAMINI SUMANASEKERA[a], JAN ALLEN[b] and PETER EKLUND[a]

[a]*Department of Physics and Astronomy, University of Kentucky, Lexington; Kentucky 40506, USA and* [b]*Gillete Research Institute, 401 Professional Drive, Gaithersburg, Maryland 20879, USA*

(Received May 30, 1999; In final form June 30, 1999)

Electrochemical doping of bundles of unopened nanotubes with bisulfate ions (acceptor) and Lithium ions (donor) has been studied using coulometry and Raman spectroscopy. The interstitial channels between the tubes in the "rope lattice" or bundles provide a new graphitic environment for intercalation. Using concentrated (18 M) sulfuric acid, a spontaneous charge-transfer reaction is observed prior to the application of the electrochemical driving force, in sharp contrast to previous studies in graphite-H_2SO_4 system. Using Raman scattering, we were able to separate the spontaneous and electrochemical contributions to the overall charge transfer between the intercalant and the rope lattice.

Keywords: Electrochemical doping; Raman scattering; Charge transfer

INTRODUCTION

Graphite's lamellar structure with weak van der Waals bonding between the graphene sheets, and its amphoteric nature, have allowed the synthesis of a large number of donor and acceptor graphite intercalation compounds (GICs) in which sheets of intercalated atoms and/or molecules are inserted between the host graphene sheets which retain their structural form. Intercalating ions into the interstitial channels between carbon SWNTs grouped in a bundle is the cylindrical analog to the GIC. It is of interest to learn if this new geometry and the curvature of the nanotube wall will produce any surprises. One such surprise was the intercalation of I_3^- and I_5^- into SWNT bundles when Iodine was not found to react with graphite at all [1].

A single wall carbon nanotube (SWNT) can be envisioned as a long, rolled up graphene sheet with a seamless joint [2]. The SWNT exhibits a well-defined, periodic structure defined by the integers (n,m) in the "roll-up" vector $C(n,m) = n\mathbf{a} + m\mathbf{b}$, where **a** and **b** are primitive translation vectors of the graphene sheet. SWNTs prepared by pulsed laser vaporization (PLV) and arc discharge (AD) methods have been shown to self-organize into bundles containing tens to hundreds of tubes held in a triangular "rope" lattice by the van der Waals force. Thus, by analogy to GICs, it was expected that bundles of SWNTs could be oxidatively (reductively) intercalated, where the guest anions (cations) occupy sites in the interstitial channels in the rope lattice. Evidence for the existence of such SWNT compounds has been demonstrated recently [3,4]. In particular, using vapor phase intercalation on mats of tangled SWNT bundles, we have demonstrated using Raman scattering and thermopower that p-type doping of SWNTs is initiated with acceptors such as Br_2 and I_2 and n-type doping is initiated with donors such as K, Rb, and Cs. Large decreases in the electrical resistivity of the mats confirmed the significant increase in the number of conduction electrons created by this chemical doping [3]. Here, we present a study of the electrochemical anodic oxidation of SWNTs in sulfuric acid (p-type doping). As the tubes have not been opened via a post-synthesis treatment in HNO_3 acid, etc., the dopant is expected to reside as ionic species inside the interstitial channels between the nanotubes and is blocked (by the naturally closed tube ends) from entering the tube interior.

EXPERIMENTAL

Electrochemical reactions were carried out in a closed quartz cell with the standard three-electrode configuration. The quartz cell allowed *in situ* Raman spectroscopy of the SWNTs during anodic oxidation. A mat of SWNTs was pressed onto a platinum (Pt) plate and used as the working electrode. A Pt wire served as the counter electrode and the cell potential was measured between a reference electrode (SCE) and the working electrode. A potentiostat/galvanostat (EG & G model 273) provided electrochemical control during the experiment. *In situ* Raman spectra of the SWNT rope lattice were recorded in the backscattering geometry using radiation from an argon ion laser. In an independent experiment, the mass uptake of the SWNT electrode was obtained during anodic oxidation in sulfuric acid using an analytical balance.

RESULTS & DISCUSSION

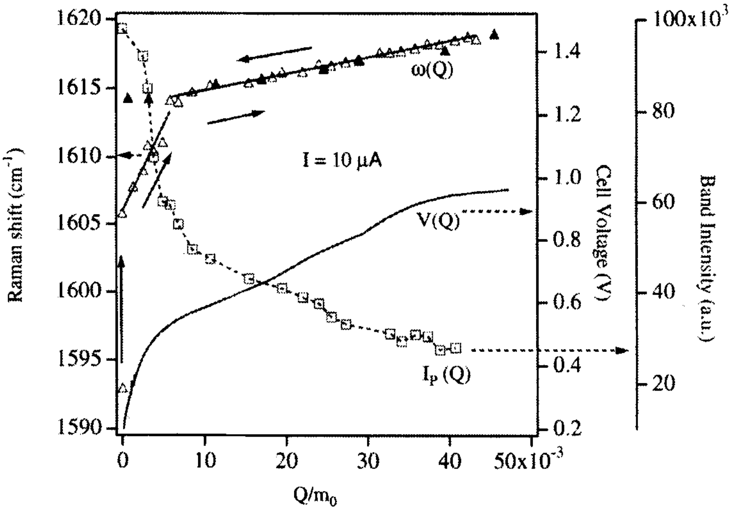

FIGURE 1 SWNT tangential band frequency ω, intensity I_p, and cell potential V as a function of Q/m_0

In Fig. 1, we plot both the SWNT tangential band frequency ω_T and the cell potential V versus the electrochemical charge Q per unit initial mass m_0 of the SWNT electrode based on wt % yield estimates. The data were collected for a constant cell current of 10 μA using 18 M H_2SO_4. The initial sudden jump $\Delta\omega_T$ ~ 12 cm^{-1} of the Raman frequency is due to a spontaneous reaction between acid and carbon structure which was not observed in the case of the graphite- H_2SO_4 system [5]. In the GIC, it was observed [5] that the Raman frequency of the ~ 1600 cm^{-1} modes changed only with applied cell potential and increased linearly with the electrochemical charge as electrons were removed from the graphene sheets creating positive holes to neutralize the negative charge on the HSO_4^- ions. The reason for the upshift in ω_T is that the loss of electrons from the graphene sheet contracts the in-plane C-C bonds [5]. We expect the same response from the SWNT.

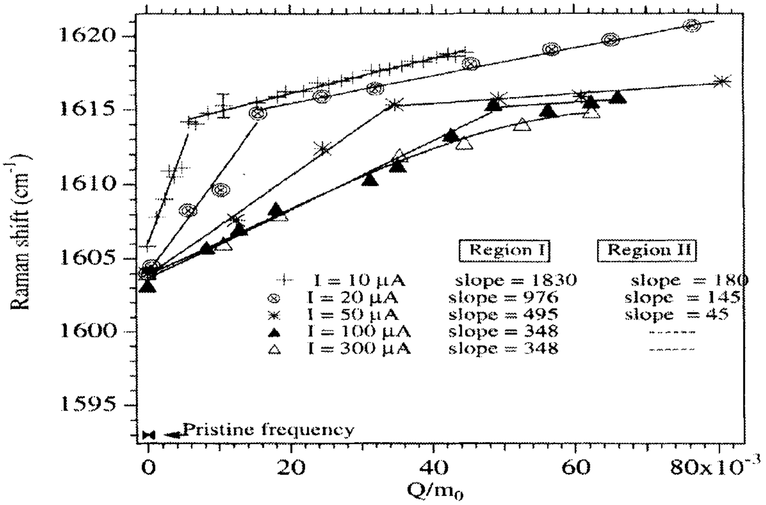

FIGURE 2 Raman shift w vs Q/m_0 with 18 M H_2SO_4 at constant currents

Returning to the anodic oxidation of SWNT in H_2SO_4, after the spontaneous charge transfer reaction and during the subsequent electrochemical intercalation, two nearly linear regimes for ω_T versus (Q/m_0) are observed (Fig. 1). Thus electrochemical charge transfer is active during this period. Once the cell potential exceeds ~0.5 V, a kink is observed in the data at ω_T~1614 cm^{-1}, and above this frequency, they exhibit a shallower slope. If the current was reversed at ω_T~1618 cm^{-1}, the data retraced along the same curve until ω reached 1614 cm^{-1}. Continuing the reverse current was observed to have no further effect on ω_T which remained constant at 1614 cm^{-1}. We identify the kink in the Raman data at 1614 cm^{-1}, and the decrease in the growth of the cell potential with the onset of an "overoxidation" region for SWNT bundles during which time C-O bonds form irreversibly on the walls of the SWNTs. If the cell current was reversed before ω_T reached 1614 cm^{-1}, the charge transfer reaction could be reversed, and ω_T could be returned to 1604 cm^{-1}. Also, we interpret the linear charge transfer region (Fig. 1) from 1604-1614 cm^{-1} to a mechanism similar to "overcharging" observed in graphite-H_2SO_4. During this interval, neutral H_2SO_4 molecules (previously co-intercalated with HSO_4^- ions) are converted to HSO_4^- ions by releasing H_2. Therefore, this conversion further removes electrons from the graphene sheet or in this case, from the walls of the SWNT. In Fig. 2, we show the evolution of ω_T vs the normalized electrochemical charge (Q/m_0) for several values of the cell current I. As can be seen, for I in the range 10-300 μA the data always exhibit the characteristic kink at ω_T ~ 1614 cm^{-1} identified with the onset of "overoxidation". However, the slope of the initial linear regime between 1604 and 1614 cm^{-1} is seen to be a function of I. The slope of this line saturates at

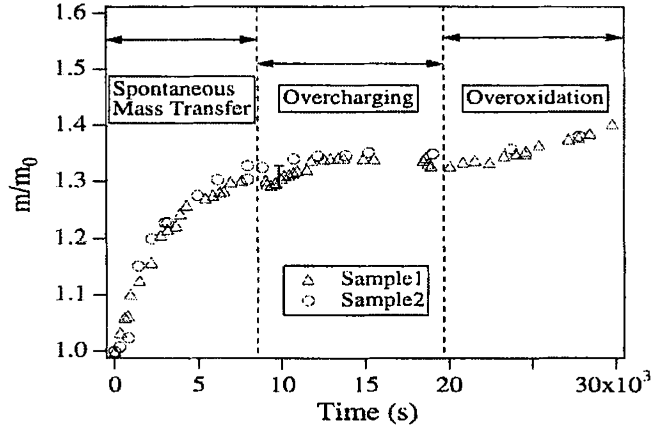

FIGURE 3 The evolution of The SWNT electrode mass for two samples.

high currents to $d\omega/df \sim 348\ cm^{-1}$, where f is the charge transferred per C-atom under the assumption that each electron passed in the external circuit is compensated by a loss of one electron from the wall of the SWNTs. This current-dependent behavior in ω_T vs (Q/m_0) signals a simultaneous contribution to charge transfer from (1) a spontaneous side reaction not requiring electrochemical assistance and, (2) from an electrochemical overcharging reaction. Since our "overcharging" hypothesis should involve a very small mass change (i.e., only H_2 is evolved), we were interested to confirm this by making *in situ* mass measurements. In Fig. 3, we show the results of the time evolution of the SWNT electrode mass (m_0= 50 mg). During the initial spontaneous reaction, before the cell current was activated, the electrode mass was observed to increase significantly and saturate at $1.3m_0$. The cell current was then initiated ($I = 1$ mA) and the cell potential and the electrode mass were recorded vs time. During the "overcharging" region, as determined by the cell potential, the mass was observed to be nearly constant, consistent with the evolution of H_2 by internal conversion of H_2SO_4, and in agreement with the proposed electrochemical model.

Acknowledgments

The authors gratefully acknowledge funding from the NSF (NSPOSR9452895, DMR-9809686).

References

[1] L. Grigorian, K. A. Williams, S. Fang, G. U. Sumanasekera, A. L. Loper, E. C. Dickey, S. J. Pennycook, & P. C. Eklund, Phys. Rev. Lett., **80,** 5560.

[2] For a review of single wall carbon nanotubes, see M. S. Dresselhaus, G. Dresselhaus, and P. C. Eklund, Science of Fullerenes and Carbon Nanotubes, Academic Press, New York, 1996.

[3] R. S. Lee, H. J. Kim, J. E. Fischer, A. Thess, & R. E. Smalley, Nature, **388,** 255 (1997).

[4] A. M. Rao, P. C. Eklund, S. Badow, A. Thess, & R. E. Smalley, Nature, **388,** 257 (1997).

[5] P. C. Eklund, C. H. Olk, E. T. Arakawa, J. Mater. Res., **1(2),** 361 (1986).