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Scanning Transmission X-ray Microscopy of multi-walled carbon nanotubes

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Abstract. We have used the recently completed soft X-ray spectromicroscopy facility at the Canadian Light Source (CLS) to study individual multi-walled carbon nanotubes (MWCNTs) with scanning transmission X-ray microscopy (STXM). Specifically, spatially resolved C 1s X-ray absorption linear dichroism signals were used to map structural defects. The STXM on CLS 10ID1 beamline is particularly powerful for such studies since its elliptically polarized undulator provides fully linearly polarized X-rays with their E-vector orientation continuously tunable from -90 to +90°. We correlate the magnitude of linear dichroism of the C 1s $\rightarrow\pi^*$ transition with the quality of the crystalline structure, in particular presence of sp^2 defects. We show that the dichroic magnitude along a MWCNT can be used to map local defect density.

1. Introduction

Carbon nanotubes (CNTs) have great potential for a wide range of applications such as channels in electronic devices, emitters in field emission displays, and reinforcements for polymer composites. Such applications often require the CNTs to be essentially perfect structures, often of well-defined chirality, or to have precisely controlled amount and types of defects or dopants to tailor their electronic and/or mechanical properties. A major challenge to technological applications of CNTs is that actual materials are far from perfect [1] and are often quite impure. Methods to characterize the quality of CNTs are thus desirable. A number of techniques have been developed that provide characterization of defect type and/or spatial distributions in carbon nanotubes. High resolution transmission electron microscopy can visualize defects directly [1]. Bockrath et al have developed a scanning probe electrical transport method (scanning gate microscopy) to visualize defects in metallic single walled nanotubes [2]. Selective electrochemical deposition followed by high resolution TEM [3] can detect and categorize defects over a wide range of concentrations. Methods to intentionally introduce structural defects at specific points in a carbon nanotubes have also been developed [4]. A method to rapidly survey a nanotube structure and evaluate its defect density at high resolution would be useful. Resonant Raman microscopy is very powerful since it can identify defect type as well as density [5], but in conventional implementations, its spatial resolution is limited to ~300 nm.

Recently we have shown [6,7] that scanning transmission X-ray microscopy (STXM) is a useful tool to characterize carbon nanotubes. The C 1s near edge X-ray absorption spectrum (NEXAFS) can be used to differentiate carbon nanotube materials from other types of graphitic-like carbon. In addition there is a very strong linear dichroism [7], first predicted by Banerjee et al. [8], which can be quantified and related to the local density of sp^2 defects. Here we report on the dichroic phenomena, show that the spectra without the dichroic response can be measured using circularly polarized light, and explore the use of maps of the dichroic amplitude as a means of mapping defect density in multi-walled carbon nanotubes (MWCNT).

2. Experimental

STXM spatial resolution is determined by the Fresnel zone plate (ZP) properties, specifically $1.22\delta_r$ where δ_r is the width of the outermost zone. The ZP used for this experiment had an outermost width of 25 nm, corresponding to a spatial resolution of 31 nm. This resolution has been verified using high contrast test structures. The source of CLS beamline 10ID1 is an elliptically polarizing undulator (EPU) in which all 4 quadrants can be scanned along the beam direction, thus allowing tuned X-rays with >99% linear polarization to be produced with arbitrary inclination of the E-vector orientation, from -90° to +90° relative the plane of the ring [9]. This is particularly convenient for STXM as a careful, complete and quantitative study of the dichroism can be performed without having to move the sample. Here we report the linear dichroism of individual MWCNTs of two different types– arc discharge (AD) and chemical vapour deposition (CVD).

3. Results

Figure 1 plots C 1*s* spectra extracted from image sequences recorded on an individual carbon nanotube using EPU phasing such that the E-vector is either circularly polarized (black) or linearly polarized with E parallel to the nanotube (red), or with E perpendicular to the nanotube (green). There is a very dramatic change in the intensity of the C 1s → π* transition at 285.2 eV, as well as smaller changes elsewhere in the spectrum. As expected, the spectrum measured with circularly polarized light gives a π* signal about half way between those for the parallel and perpendicular light, consistent with the linear dichroism effect being 'turned off' when the EPU is tuned to this mode. Adjacent carbon onion material or the holey carbon support did not show significant changes with changes in nature (circular/linear) or orientation (parallel, perpendicular) of the polarization of the light. **Figure 2** plots the intensity of the C 1s → π* transition of straight regions of an AD-MWCNT and a CVD MWCNT.

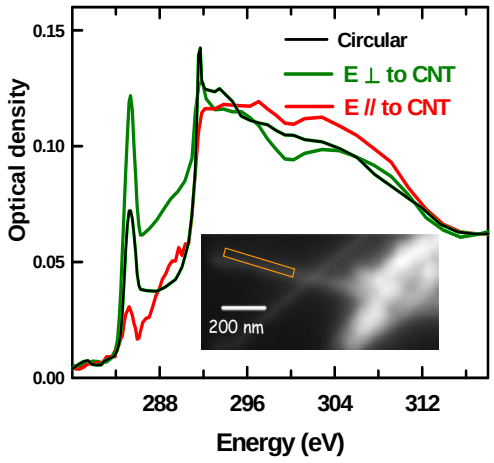

Figure 1. C 1*s* spectra, recorded with the indicated polarization, of a multi-walled carbon nanotube prepared by arc discharge.

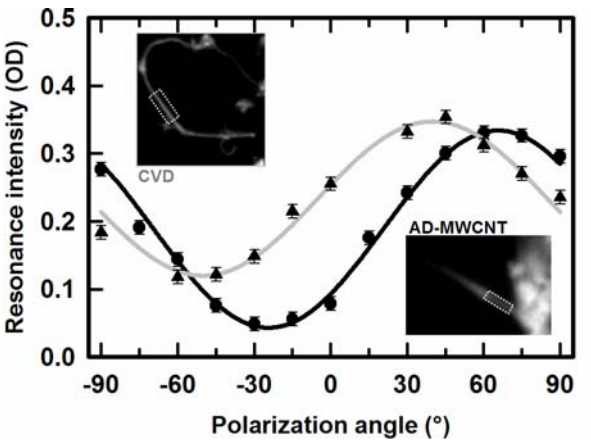

Figure 2 Fit of the intensity of the C 1s → π* transition of higher quality regions of an AD-MWCNT and a CVD-MWCNT.

Each curve is an excellent fit to the expected polarization dependence, $\{C + A\cos^2(\theta-\theta_{ref})\}$, where C represents the non-dichroic component of the signal, A is the amplitude of the dichroic component and θ_{ref} is the angle between the long axis of the MWCNT and horizontal. The position of the maximum agrees with the sample geometry and the fact that the intensity is maximum when the E-vector of the light is orthogonal to the tube axis. One sees that the amplitude of the dichroic signal is much larger for the AD-MWCNT than for the CVD-MWCNT, consistent with the expected relative quality and sp^2 defect density, since CVD-MWCNTs are known to be much more defective than AD-MWCNTs.

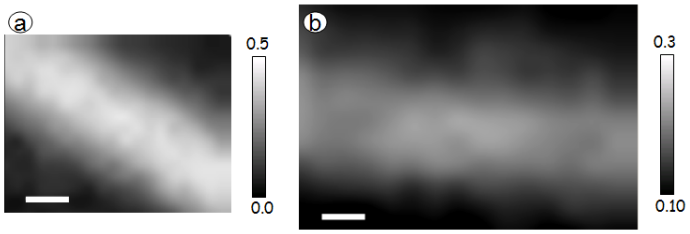

Figure 3. Map of the amplitude of the dichroic signal in a small region of (a) AD-MWCNT, and (b) CVD-MWCNT. Note different amplitude scales. Scale bar = 20 nm

In order to look in more detail at the spatial distribution of sp^2 type defects along individual nanotubes, we have fit the dichroic signal at each pixel (5 nm x 5 nm) to the dichroic equation, $\{C + A\cos^2(\theta-\theta_{ref})$, and then assembled the dichroic amplitude coefficients from those fits into pseudo-images. Figure 3a plots this signal for the AD-MWCNT, while figure 3b plots that for the CVD-MWCNT on the same spatial scale, but different dichroic amplitude scales. It is clear that the dichroic amplitude from the AD-MWCNT is larger and more uniform than that for the CVD-MWCNT, indicating in a more detailed fashion the higher quality of the AD-MWCNT.

4. Summary

We have shown that the C 1s→π* transition measured by STXM for individual multi-walled carbon nanotubes exhibits a strong linear dichroism with maximum intensity when the E-vector is perpendicular to the carbon nanotube axis. Using a STXM with an EPU capable of inclining the E-vector over a full 180^o greatly facilitates quantitative mapping of the dichroic signal. Comparison of AD- and CVD-MWCNTs showed that the π* dichroic magnitude correlates with the quality of the carbon nanotube. We have extended this approach to a full pixel-by-pixel fit of dichroic data in order to show how the amplitude of the dichroic effect could be used to map sp^3 defects along individual nanotubes. This method could be useful to help optimize preparation and purification procedures as well as the development of sensors or electronic devices based on single carbon nanotubes.

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