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Out-of-plane mosaic of single-wall carbon nanotube films

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Out-of-plane mosaic of single-wall carbon nanotube films

Abstract
For single-wall carbon nanotube (SWNT) films deposited from suspension onto filter membranes, or by drop casting or spin coating onto flat substrates, the tube axes lie preferentially in the film plane. Using x-ray scattering and a two-dimensional detector, we show that this out-of-plane mosaic spread can be easily and accurately quantified. It varies significantly with deposition conditions, and the aligning effects of deposition and external force in the film plane (e.g., magnetic field) are additive. Films from well-dispersed tubes show better alignment than from poor dispersions. The finite out-of-plane mosaic in C$_{60}$@SWNT films enables quantitative separation of one-dimensional diffraction (chains of C$_{60}$ peas) from the 2D rope lattice diffraction.

Comments

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For single-wall carbon nanotube (SWNT) films deposited from suspension onto filter membranes, or by drop casting or spin coating onto flat substrates, the tube axes lie preferentially in the film plane. Using x-ray scattering and a two-dimensional detector, we show that this out-of-plane mosaic spread can be easily and accurately quantified. It varies significantly with deposition conditions, and the aligning effects of deposition and external force in the film plane (e.g., magnetic field) are additive. For semicrystalline nanotube ropes (chains of C_{60} peas) from the 2D rope lattice diffraction, the SWNT mosaic can be easily and accurately obtained by summing pixel intensity integrated over appropriate radial (Q) sectors; the azimuthal angle χ is equivalent to the rocking curve θ.

X-ray fiber diagrams were measured on film samples consisting of several strips ~0.5 mm wide and ~10 mm long, stacked parallel to each other in 0.7 mm capillaries. To obtain the out-of-plane mosaic, the film plane was parallel to the incident beam as illustrated in Fig. 1(b). We studied eight films prepared by different methods. One was deposited from suspension in a 26-T magnetic field, resulting in partial in-plane alignment along the H axis. We expect this film to exhibit an out-of-plane mosaic narrower than the in-plane value due to the additional driving force associated with the filter deposition geometry. Conversely, films deposited with no field will have some out-of-plane alignment but random in-plane orientation. The effect of dispersion was studied by comparing films deposited from SWNT/H_2O/NaDDBS (sodium dodecylbenzene sulfonate), and from SWNT/methanol. Films deposited on smooth substrates from SWNT/oleum and SWNT/H_2O were also compared. Uniaxial high pressure applied to nanotube soot yields pellets with out-of-plane alignment. We prepared a 0.5-mm-thick pellet by pressing purified SWNT powder at 700 atm.

Figure 2(a) is the detector image from a 26-T-aligned film. The out-of-plane mosaic was obtained by summing pixels in 2.4° radial sectors 1° wide in χ, centered at 2θ = 6.3° [the (1 0) Bragg position]. The result is plotted in Fig. 2(b), where the solid curve is the fit to a Gaussian centered at χ = 180° plus a constant. The Gaussian FWHM is ~27°, significantly smaller than the in-plane FWHM (~34°). We summarize the thicknesses, densities, and mosaics of the eight films in Table I. The H-aligned film has the best out-of-plane alignment because the magnetic force aligns the tubes both in-plane and out-of-plane. The films from H_2O/NaDDBS suspensions have smaller out-of-plane mosaics (44°–49°) than the one from methanol suspension (77°), while the film deposited from oleum (44°) is better than the one from H_2O without surfactant (62°). SWNT in...
electrical, or shear fields. Suspension with the aid of outside forces such as magnetic, achieved by gentle deposition from well-dispersed SWNT gates remaining in poor dispersions will limit the out-of-plane alignment. Based on the above analysis, we expect the best gates. High pressure may dramatically decrease the volume mainly of randomly oriented and entangled SWNT aggregates. This is not unexpected since dry SWNT powders consist of macroscopic pores resulting in high density, but is unable substantially reduced after filling with buckyballs due to cancellation of amplitudes from pea and pod. This is used to calculate the filling fraction of SWNTs by C_{60} in this film, ~80%. From profile III, the first-order 1D diffraction peak out-of-plane mosaic allows us to detect both the 1D (pea) and 2D (pod) lattices simultaneously, and for the first time to separate these in a bulk sample using x-ray diffraction. In Fig. 3(a) we show the detector image. Diffraction peaks from the 1D peas and 2D pods are concentrated along the horizontal and vertical axes respectively, similar to selected area electron diffraction from a single peapod rope.\textsuperscript{17} No (hkl) diffraction was observed indicating the absence of chain-chain correlations.

Azimuthal integrations of the 2D data 10° wide in χ centered at 90°, 135°, and 180° give the equivalent of wide-angle x-ray profiles with different fractional 1D and 2D components. Knowing the out-of-plane mosaic (59°), we can quantitatively separate the 1D and 2D behavior. In Fig. 3(b) we show the pea (II) and pod (III) profiles. Previously reported x-ray results from randomly oriented peapods are superpositions of both.\textsuperscript{10} We also show the profile of the control sample (I). The intensity of the (1, 0) rope peak is substantially reduced after filling with buckyballs due to cancellation of amplitudes from pea and pod. This is used to calculate the filling fraction of SWNTs by C_{60} in this film, ~80%. From profile III, the first-order 1D diffraction peak

H₂O with added NaDDBS contains mainly isolated nanotubes,\textsuperscript{13} and oleum is also a good dispersant.\textsuperscript{14} On the contrary, stable SWNT suspensions cannot be obtained in methanol or H₂O without surfactant. Large SWNT aggregates remaining in poor dispersions will limit the out-of-plane alignment. Films 12, 17, and 29 μm thick from H₂O/NaDDBS all have similar FWHMs, whereas a thickness dependence was observed in H₂O/NaDDBS. Data are the symbols; fit to a Gaussian plus a constant is the smooth curve. The deduced out-of-plane FWHM is ~27°, significantly smaller than the in-plane mosaic (34°) due to the additional effect of the deposition of long 1D objects on a flat surface.

Out-of-plane alignment results in azimuth(χ)-dependent anisotropic scattering within the 2D detector plane.

$C_{60}$ SWNT (peapod) films\textsuperscript{16} have no in-plane preferred orientation. Using the geometry of Fig. 1(b), the nonzero out-of-plane mosaic allows us to detect both the 1D (pea) and 2D (pod) lattices simultaneously, and for the first time to separate these in a bulk sample using x-ray diffraction. In Fig. 3(a) we show the detector image. Diffraction peaks from the 1D peas and 2D pods are concentrated along the horizontal and vertical axes respectively, similar to selected area electron diffraction from a single peapod rope.\textsuperscript{17} No (hkl) diffraction was observed indicating the absence of chain-chain correlations.

FIG. 2. (a) Detector image from a 26-T-aligned SWNT film measured with its plane parallel to the incident x-ray beam. Anisotropic intensities directly reflect the out-of-plane alignment. (b) Background-subtracted x-ray counts, summed over intervals 5.1°<2θ<7.5° about the (1,0) 2D rope lattice reflection, every 1° in χ. Data are the symbols; fit to a Gaussian plus a constant is the smooth curve. The deduced out-of-plane FWHM is ~27°, significantly smaller than the in-plane mosaic (34°) due to the additional effect of the deposition of long 1D objects on a flat surface.
TABLE I. Summary of the thicknesses, densities, out-of-plane, and in-plane mosaics for eight films produced under various conditions. FWHM$_{\text{out}}$ and FWHM$_{\text{in}}$ are the out-of-plane and in-plane Gaussian distribution widths of SWNT axes with respect to the film plane and in-plane preferred axis respectively. The values listed represent the samples we measured; any of these parameters could vary with other factors such as deposition rate, SWNT concentration, thickness, membrane material, etc.

<table>
<thead>
<tr>
<th>Method</th>
<th>Filter deposition</th>
<th>Direct deposition</th>
<th>Uniaxial press</th>
</tr>
</thead>
<tbody>
<tr>
<td>Source</td>
<td>SWNT/H$_2$O with Triton X-100</td>
<td>SWNT/H$_2$O with NaDDBS</td>
<td>SWNT/Methanol</td>
</tr>
<tr>
<td>External field</td>
<td>26 T magnetic</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Thickness (µm)</td>
<td>7</td>
<td>12</td>
<td>17</td>
</tr>
<tr>
<td>(±5%)</td>
<td>0.9</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>Density (g/cm$^3$)</td>
<td>27°</td>
<td>46°</td>
<td>49°</td>
</tr>
<tr>
<td>(±5%)</td>
<td>34°</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

has a sawtooth line shape. The mean C$_{60}$ separation is 9.68 Å by fitting the peak to a broadened Gaussian modulated by a sawtooth function. This value agrees well with high resolution transmission electron microscope lattice images of isolated peapods (9.68 Å),$^{17}$ and is slightly smaller than the value calculated from the peak position (9.77 Å).$^{16}$ It is surprising that the 1D chains have a mean lattice constant significantly smaller than that of the 3D fcc crystal; if anything, the lower coordination would argue for larger peapea separation. Clearly the pod environment is playing an important role.$^{18}$

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$^{11}$http://www.lrsm.upenn.edu/lrsm/facMAXS.html (description of apparatus).

$^{12}$The film plane was ensured to be parallel to the incident beam with the aid of an x-ray imaging camera. Scattered intensity was corrected for absorption by the sample, and background scattering from the empty capillary, etc., was subtracted. The χ resolution is better than 2.6° (measurement of graphite with known FWHM). The real out-of-plane FWHM could be 0°–5° smaller than the measured values due to misalignment of several sandwiched films.


$^{15}$A better fit was achieved by adding a Lorentzian component while the area-weighted average FWHM (26°) is quite close to the value obtained with just the Gaussian, so we use pure Gaussian for comparison purposes.


$^{18}$M. Hodak, Ph.D. thesis, University of Pennsylvania, 2002, in which can be found an as yet unpublished LDA calculation which gives the experimental lattice constant to within 0.01 Å.