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Anisotropy in the X-ray absorption of vertically aligned single wall carbon nanotubes

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Carbon nanotubes are archetypical one dimensional systems, with peculiar anisotropic electronic properties. Only recently μm thick films of vertically aligned SWNT became available. The vertical alignment of the nanotube mats allows the realization of scattering geometries promoting specific dipole transitions parallel and normal to the axis of the SWNT. We find well expressed mosaic spreads for the π^* and σ^* resonances. Full three dimensional modelling of the dipole transitions as well as of the alignment demonstrate polarization dependent X-ray absorption to be an accurate, versatile non destructive and reliable tool to quantify the alignment of SWNT on a bulk scale.

1 Introduction

Carbon nanotubes are the forth allotrope of elemental carbon after diamond, graphite and fullerenes. In particular nanotubes with a single shell, single wall carbon nanotubes (SWNT) have a one dimensional structure featuring a strong one dimensional character giving rise to a range of phenomena such as van Hove singularities [1], the Peierls transition [2] and Tomanaga Luttinger liquid [3] behaviour. Besides acting as "test tubes" for fundamental aspects of theoretical one dimensional physics SWNT also offer a rich variety of potential applications. Applications rely mainly on their mechanical strength, their maximum current density and aspect ratio. The key challenge for any application employing such nano scale properties is incorporating them into the macroscopic world of existing technology. As an example alignment of SWNT is casting the local one dimensional electronic properties of individual nanotubes onto a bulk macroscopic piece of material. Thus the anisotropy of "one dimensional properties" is then incorporated in macroscopic SWNT material. Alignment is the key to addressing the fundamental anisotropic properties of nanotubes by any bulk characterization method. In plane alignment of filtrated sheets of SWNT has been achieved and demonstrated by Liu and coworkers [4]. Complementary, layers of vertically (viz. normal to the surface) aligned SWNT can be directly achieved via chemical vapour deposition from catalytic metal layers that nucleate nanotubes densely [5]. Here we report on angle and polarization dependant X-ray absorption studies on such vertically aligned mats of carbon nanotubes. We observe a clear anisotropy of the bulk X-ray absorption and can thus provide the means to confirm and quantify the alignment of such arrays of nanotubes in a sample preserving manner. This essential information is the basis for conducting and interpreting further investigations on these macroscopic strongly anisotropic systems.

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2 Experimental

Vertically aligned films of SWNT (VASWNT) were directly synthesized by the catalytic decomposition of ethanol and floated off the supporting Si wavers in hot water and subsequently put on either TEM grids or Pt plates [6] at the University of Tokyo. High resolution transmission electron microscopy (TEM) imaging of freestanding films was conducted on a Tecnai FE30 at the IFW-Dresden. X-ray absorption (XAS) was conducted at beamline UE52 PGM at Bessy II. The beamline has a resolving power $E/\Delta E$ of 4×10^4 and the absorption was measured in total yield via drain current. All XAS measurements were performed at ambient temperature and under a base pressure better than 5×10^{-10} mbar.

3 Results and discussion

We shall first discuss the TEM studies on freestanding VASWNT. Figure 1 shows a representative compilation of TEM micrographs. Apparently, the material is very pure and consists only of SWNT mostly packed in thin bundles of a few SWNT. The overall abundance of SWNT cross sections is remarkably high and indicative of nanotubes preferentially passing the focal plane perpendicularly. At the edges the freestanding film has collapsed. The SWNT are aligned in plane and pointing towards the edge of the film. Thus the edge regions are exposing the side view of aligned SWNT to the electron beam. From local TEM studies a preferentially vertical orientation in the bulk interior of the films is apparent. However TEM is bound to freely suspended substrates and can not deliver accurate information on the average overall alignment or even the full angular distribution. These limitations are niftily overcome by non destructive resonant XAS on further processable VASWNT.

In resonant XAS on nanotubes an incoming X-ray photon matches an electronic dipole transition from the C1s core level into the π or σ conduction band, respectively. In sp_2 carbon this is not only a matter of matching energies of roughly 285 eV and 291 eV but also of the mutual angle between the electric field vector of the polarized light and the basal plane of σ bonds or the axis of the π orbitals, respectively. The dipole transition probability scales as the square of the scalar product of these two vectors. If the beam of incidence is parallel to the axis of alignment then all linear polarizations have naturally the same cross

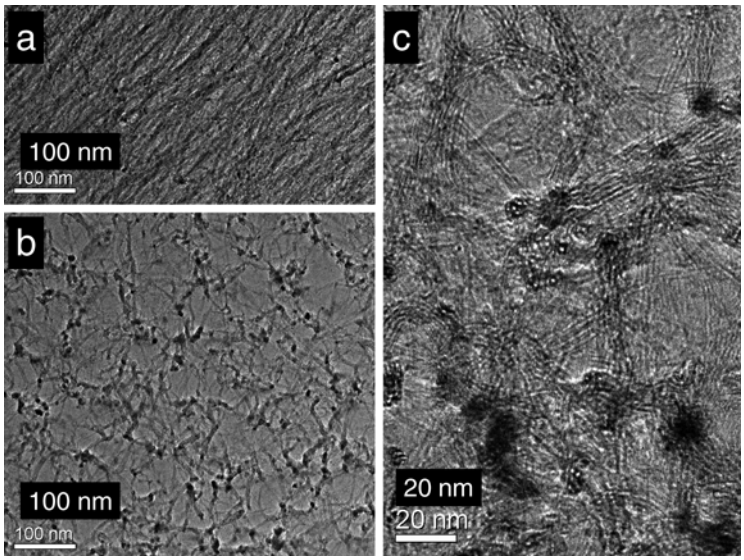

Fig. 1 TEM micrographs of freestanding films of VASWNT. (a) Side view of the collapsed edge of the film. The axis of alignment runs from the lower left to the upper right. (b) Top view of bulk vertically aligned nanotubes. All the black dots are cross sections of VASWNT. (c) Higher magnification top view resolving several cross sections of individual nanotubes passing the focal plane.

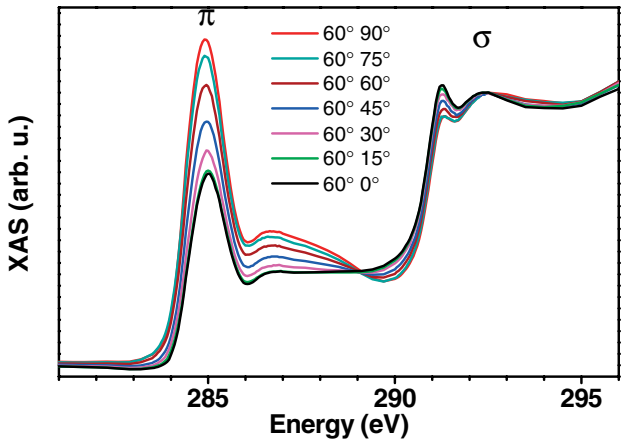

Fig. 2 (online colour at: www.pss-b.com) X-ray absorption response of vertically aligned SWNT. The angle between incident beam and axis of the alignment is 60° in the horizontal plane. The linear polarization of the light is turned from horizontal (0°) to vertical (90°). Spectra are scaled to σ absorption.

sections for σ^* and π^* absorption, respectively. At a finite angle of the beam to the axis of the alignment there are substantial changes in the relative cross sections of the π^* and σ^* resonance. This is illustrated in Fig. 2 where the angle to the beam was 60°. The polarization of the synchrotron light is rotated from 0° to 90°. At 0° the electric field vector lies in the horizontal plane and has the maximum projection on the VASWNT axis. Thus, the overlap to radial π states is minimal with this polarization.

The angular distribution of the SWNT axes is most conveniently described in spherical coordinates. The rotational symmetry of angular distribution is ensured by omitting the polar angle in the functional form. Thus the angular distribution is only a function of the azimuth angle. Further, every SWNT is at the same time pointing into the two opposite directions, thus the function is symmetric around the equator line. Once polar symmetry is given an equatorial mirror plane is sufficient to ensure inversion symmetry. We represent the azimuth angular distribution by two mirrored half sided Gaussians each at one pole. In this way a full three dimensional angular distribution within VASWNT is conveniently represented by one single parameter which is the standard deviation δ of the Gaussians. For any given angular distribution the relative cross sections for dipole transitions into unoccupied π^* and σ^* states are easily evaluated by decomposing the electric field vector into a radial (R) and axial (A) constituent for every solid angle. The π^* resonance scales as $R^2/2$ and the σ^* resonance as $A^2 + R^2/2$. The characteristic shapes of these cross sections are shown in the inset of Fig. 3. The factor one half in the radial component arises

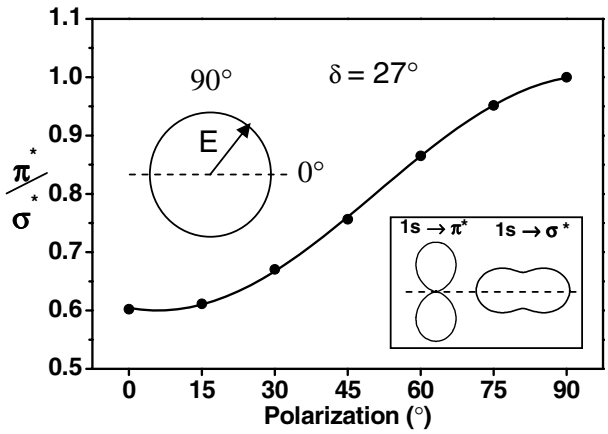

Fig. 3 Inset in the upper left illustrates the electrical field vector at different polarizations between 0° and 90°. Dots are the relative ratio of π to σ absorption measured at 60° horizontal angle to axis of alignment (see Fig. 2). The solid line is obtained from simulating a Gaussian diameter spread with a standard deviation δ of 27°. The inset in the lower right depicts the angular dependence of π and σ absorbance with respect to the nanotube axis (dashed horizontal line).

from averaging over the circumference of the SWNT. Now we can weight the local cross sections with the angular distribution and intergrate over the full sphere of solid angles. Comparing the relative change of the π^* to σ^* resonance to the experiment, we find a close match to the experiment with a calculation assuming an azimuth standard deviation δ of 27°. The match between the experimental data points and the calculated line is shown in Fig. 3. We want to point out, that this way of considering a fully three dimensional angular distribution for the alignment of VASWNT is an alternate approach to earlier reports on aligned MWNT [7].

4 Summary

Summarizing, we have investigated the alignment of directly grown vertically aligned SWNT by TEM imaging and resonant X-ray absorption. TEM micrographs reveal a high density of orthogonal nanotube cross sections and suggest a preferred axis. More quantitative spectroscopic information is obtained from XAS. We present a transparent and comprehensive way to obtain a fully three dimensional angular distribution from polarized absorption spectra. Thus we have now the means at hand to characterize and quantify the alignment of such vertical forests of carbon nanotubes in a sample preserving manner.

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