Inelastic X-Ray Study of Plasmons in Oriented Single and Multi-Wall Carbon Nanotubes

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Introduction
Carbon nanotubes (CNT) have a wide variety of interesting properties and a large number of potential applications in electronic and optical devices[1]. In this study we concentrate on one important aspect of their electronic structure: the plasmon dispersions in both single- and multi-wall CNTs and their relation to those in graphite. For the first time inelastic X-ray scattering is used to study these collective electronic excitations in oriented CNT samples.

Methods and Materials
The experiments were performed on the IXS instrument at beamline 9ID CMC-XOR, APS, ANL. The incident energy was defined by a Si(333) monochromator, a spherically bent Ge(733) diced analyzer at the end of a 1-m arm focused the incident radiation onto a solid-state detector. The overall resolution was ~300 meV FWHM. The incident photons were linearly polarized perpendicular to the scattering plane. Energy loss scans were taken by varying the incident energy while keeping the exit energy fixed at 8.9805 keV. The momentum transfer was kept along the nanotubes’ axis. Spectra were taken at room temperature. The samples were oriented CNTs (both single- and multi-wall) grown on a Si substrate. The samples referred to as “single-wall” were in fact a few walls at most (1-5) while the multi-walled ones had ~12 walls.

Results
Fig. 1. shows the inelastic spectra for the single-, multi-wall, and highly oriented pyrolytic graphite (HOPG) from top to bottom. Momentum transfer was Q= 0.79 Å⁻¹ in all cases, its direction was along the tubes for the first two samples or parallel to the sheets for graphite. The peaks at ~10 and ~30 eV are known as the π and σ+π plasmons respectively[2]. Fig. 2. shows the complete dispersion curves for both plasmon modes as a function of momentum transfer for all three samples.

Discussion
The σ+π plasmons in both single- and multi-wall nanotubes exhibit a systematic shift in energy with respect to graphite and to each other. Specifically, they have a lower energy in multi-wall nanotubes than in graphite, and a still lower energy in single-wall nanotubes.

Since the plasma frequency is proportional to the square root of the electron density, we introduce a mechanism to account for the energy variations based on different effective electron densities.

Due to the increasing electron wave-function overlap for multiple graphene walls, the systematic variation in plasmon energy can be then explained by an effective lowering of the effective electron density in single- and multi-walled nanotubes.

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Fig. 1. IXS spectra for all three samples. Elastic lines were omitted for clarity. The π and σ+π plasmons are indicated. SWNT = single-wall CNT, MWNT = multi-wall CNT.

Fig. 2. Complete plasmon dispersion curves for both modes for all three samples. The lines are a guide to the eye.