Radiative collective modes in ion-implanted multiwalled carbon nanotubes

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Abstract. Surface mode fields are strongly confined to a MWCNT surface, representing a conceivable solution for realization of quasi-2D optics. In the present Contribution, MWCNTs are ion implanted with guest ions. Implantation enables engineering of the local dielectric tensor $\varepsilon(k,\omega)$, allowing specific selection of the $\gamma$ emission eigenfrequency. Cs-corrected STEM is used to acquire EEL spectra with atomic resolution. Lines are subsequently characterized using EEL spectra simulated using first-principles DFT calculations, utilising the full-potential linearised augmented plane wave formalism. In addition to presenting virtual collective modes, implanted guest ions are seen to introduce waveguide eigensolutions which provide a possible mechanism for light transmission in MWCNTs.

1. Introduction

With the metallic or semiconducting character of MWCNTs (multi-walled carbon nanotubes) dictated by chirality, MWCNTs present a potentially versatile component for use in plasmonic circuits. Doping modifies the dielectric response. The intra-layer $sp^2$-hybridization, combined with the $p_z$ orbitals orthogonal to the basal planes, results in MWCNTs being particularly receptive to introduction of foreign species, in typically substitutional or intercalated configurations. In the present Contribution, doping is performed using ion implantation, offering an intrinsically clean nature and precise dose control. EEL (electron energy-loss) spectroscopy, in combination with scanning transmission electron microscopy (STEM), represents an ideal characterization technique capable of providing information concerning chemical bonding and electronic structure of dopants in the nanometre and sub-nanometre regimes, from volumes not merely restricted to the surface. Lines and features arising in low energy loss EEL spectra are then characterised using optical loss spectra and dielectric functions calculated within the DFT (density functional theory) framework.

Graphite possesses a characteristic band structure near $E_F$, manifesting in a distinctive optical anisotropy, and polarization-dependent semimetallic behaviour. Using a simple ridged band filling model, one can view the graphite $\pi$-collective modes as originating from the $\pi\rightarrow\pi^*$ electric dipole transition. Whilst a zero DOS exists at $E_F$, crucially, degeneracy of the $\pi$ and $\pi^*$ bands allows excitations at small $k$ close to the $\Gamma$ point, presenting the possibility of collective modes in the UV to IR frequency regimes. Whilst few studies exist concerning radiative modes and waveguide modes propagating on graphitic materials [8], the radiative or waveguided nature of certain graphite
collective eigensolutions is utilised in the present study to suggest a possible mechanism for $\gamma$ emission from MWCNTs. Literature details electrically induced radiation from a single s-SWCNT FET [1]; light emission through electroluminescence and photoluminescence in InP nanowires [2] and field-emission-induced luminescence [3]. However, the ion implantation method for modifying eigenfrequency is particularly suitable for mass production methods, which avoids the need for device structures or field emission.

2. Experimental

EEL spectra were acquired using a C$_3$-aberration-corrected STEM operated at 100 kV at the SuperSTEM Laboratory, UK. The 0.1 nm probe enables EEL spectra of projected features the size of individual atomic columns to be obtained. In nano-structured specimens consisting of only a few atoms, the probability of single impurity atom detection amongst matrix atoms is thereby dramatically improved. The EEL spectrometer consists of a CCD detector-based Gatan UHV Enfina instrument. The energy resolution of the entire system, at high dispersion (0.02 eV/channel), is $\sim$0.3 eV. All spectra presented herein represent raw data, from which a power-law fitted background was subtracted. The acquisition time per spectrum was 1 s. Commercially available pristine MWCNTs, from the same manufactured batch, were dispersed using an identical method for each sample, onto standard, lacy carbon film-coated TEM copper grids. The MWCNTs were of high purity and graphitisation, and possessed few (<10) walls. All glassware were vigorously washed in ethanol in order to prevent silicon contamination. Ion implantation was carried out into the TEM-ready specimens; the Salford University low energy implanter was used to deliver ion beams at the following energies and doses: B – 100 eV / $1 \times 10^{14}$ cm$^{-2}$; BF$_2$ – 200 eV / $2.5 \times 10^{15}$ cm$^{-2}$; Ag – 200 eV / $20 \times 10^{14}$ cm$^{-2}$.

3. Discussion

The linear response of a medium to an external field is characterized by its complex dielectric function. Consider an optically anisotropic medium (such as graphite); the complex dielectric constant assumes the form of a 3 x 3 tensor. The dielectric functions can be described by,

\[
\begin{align*}
\epsilon_{||} &= \epsilon_{1,||} + i\epsilon_{2,||} \\
\epsilon_{\perp} &= \epsilon_{1,\perp} + i\epsilon_{2,\perp}
\end{align*}
\] (1a)

\[
(\epsilon_{1,||} - \omega^2/c^2) \text{ defines the light line in the medium. The light line is of fundamental importance, since it defines regions in the (\omega,|\mathbf{k}|) space, where virtual, waveguide and surface modes exist [5], as detailed in figure 1(a). One can immediately see the effect of } \epsilon_{1,||} > 1 \text{ in a CW rotation the light line. For a given } |\mathbf{k}|, \epsilon_{1,||} > 1 \text{ enables a mode to be within the virtual domain, in comparison to } \epsilon_{1,||} = 1. \epsilon_{1,||} \text{ thus represents the term dictating transformation of surface mode characteristics to virtual mode characteristics. Should } 0 \leq \sqrt{\epsilon_{1,||}} < 1, \text{ then the medium will possess a smaller refractive index than vacuum, largely resulting in total internal reflection of } \gamma.
\]

![Figure 1.](image)

Figure 1. (a) Definition of the virtual mode and surface mode domains by the light line, for varying values of the dielectric constant. (b) DFT calculations of $\epsilon_{1,||,2,||}$ of pristine graphite and graphite doped with Ag adopting a substitutional configuration. (c) The calculated number of waveguide modes for various media.
Furthermore, when $\varepsilon_{2'||c,\perp}$ are small, the more pronounced an eigensolution (i.e. the narrower a peak), in a loss spectrum. Modification of the graphite dielectric function is detailed in figure 1(b), consisting of a calculation using the Wien2K DFT code [4], demonstrating Ag atoms adopting a simple substitutional configuration in planar graphite can result in $\varepsilon_{1'||c,\perp}$>>1. For DFT calculations detailed herein, the muffin-tin radii were set at R=1.34 atomic units, 250 k-points were utilized, and self-consistent iterations were performed until convergence (0.1 eV) on the total energy. An $R_{\text{max}}$ value of 5 was used. The number of waveguide modes [5] calculated [8] for various media is detailed in figure 1(c): when $\varepsilon_{1'||c,\perp}<$1, waveguide modes cannot be excited. EEL spectra acquired from various MWNCTs doped with various species are detailed in figure 2; crucially, the dimensions and number of walls were nearly identical for each MWCNT.

Figure 2(a) and 2(b) detail the change in eigenfrequency and linewidth of a single Gaussian peak fitted to the EEL spectra of doped MWCNTs. For each spectrum, the zero-loss peak was extracted using and identical model and energy window, and the Gaussian peak was fitted to an identical energy window between 3.0 eV – 8.4 eV. The pristine MWCNT exhibits the characteristic redshift and increase in linewidth from b=0 to grazing incidence. These trends are ascribed in to optical anisotropy and cylindrical anisotropy [5].

For the BF$_2$ and boron doped MWCNTs, the pristine MWCNT redshift trend from b=0 to grazing incidence is preserved. B is predisposed to assuming substitutional configurations in MWCNTs. The consistently lower energies of the BF$_2$ and boron doped MWCNTs, compared to those of the pristine MWCNT, is attributed to transitions lower in energy than the pristine graphite $\pi$-plasmon, as detailed in the Wien2K [4] DFT calculated spectra (figure 2(c)). The similarity between observed trends for the B and BF$_2$ doped MWCNTs can be ascribed to the dissociation of the BF$_2$ radical, solely resulting in B, and not F incorporation. Figure 2(c) details a lifting of degeneracy or near-degeneracy of the graphite $\pi$-plasmon with B doping, constituting another possible cause of the Gaussian peak redshift. Figure 2 details the introduction of a Drude plasmon for very high (>25% at. %) substitutional levels. For the Ag implanted MWCNT, the largely invariant eigenfrequency and clear increase in linewidth can be attributed to substitutional or intercalated configurations, which are predicted [5] to introduce (higher energy) states at around 8 eV. It is feasible that very low level Ag intercalation may also contribute to the observed trends, in such an instance, a Drude plasmon obscured by the ZLP fails to weight the fitted Gaussian peak. Individual spectra are detailed in figure 3, which reproduce the trend in eigenfrequency identified in figure 2: the uppermost spectra correspond to zero impact parameter, with the lowermost spectra representing grazing incidence. For equivalent impact parameter, the BF$_2$ doped MWCNT always has a lower plasmon frequency than that of the pristine MWCNT. Furthermore, for the BF$_2$ doped MWCNT, splitting of the graphite $\pi$-plasmon is evident, consistent with the simulations detailed in figure 2(c).

Figure 2. (a) Measured eigenfrequency, and (b) linewidth, of a single Gaussian peak fitted to an identical energy window for MWCNTs doped with various species. (c) DFT simulated dielectric functions of planar graphite doped with B.

BF and HAADF (high-angle-annular-dark-field) images (figure 4) confirm that structural integrity has been preserved following the ion implantation, but in the case of Ag, HAADF imaging (not...
shown) reveals the Ag has clustered on the outermost surface of the MWCNT, thus accounting for an unexpectedly low level of Ag doping observed during single atom EELS of present specimens [6].

![Figure 3](image1.png)

**Figure 3.** (a) Experimentally measured spectra from a BF$_2$ doped and, (b) pristine MWCNT. (c) Simulated dielectric functions of B or Ag atoms, adopting various configurations in planar graphite.

However, single atom EELS reveals the retention of B dopant atoms is much greater [6]. The strength of the present technique is now clearly evident: by performing first-principles DFT calculations, one can ascertain the effect of dopant atoms on modifying the dielectric response, with ion implantation parameters adjusted accordingly.

![Figure 4](image2.png)

**Figure 4.** BF and HAADF images of (a) a pristine MWCNT, and (b) a BF$_2$ implanted MWCNT. Visible in the HAADF image are bright spots corresponding to high scattering centres. Since B is of lower Z than C, we attribute this effect to the possible presence of B-O bonding.

### 4. Summary

Careful modification of the dielectric function can transform surface modes into virtual radiative modes or waveguide modes. Such modes would conceivably allow $\gamma$ emission, or $\gamma$ transmission over long distances, respectively. The relative cleanliness of ion implantation doping is of fundamental importance to the present technique, largely avoiding the inadvertent doping associated with other methods. Use of C$_s$-corrected STEM presents the unique possibility of deducing the bonding state of individual atoms within a matrix [6].

### 5. References

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