Red-Shift of Carbon Nanotube Surface Plasmon EEL Features Utilising a Dielectric Filling

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Abstract. Simulations of the dynamical polarisability of a MWCNT (multi-wall carbon nanotube) by primary STEM electrons were performed. The simulations demonstrated eigenenergy modification (red-shifting), ascribed to the presence of a MWCNT dielectric filling, of coupled $\pi$-surface plasmon EEL (electron energy-loss) features. Experimental EEL spectra of MWCNTs were acquired utilising a Gatan Enfina system attached to a dedicated STEM. These spectra confirmed the eigenenergy modification predicted by the model. In a filled MWCNT, an eigenenergy modification of a coupled $\pi$-surface plasmon feature, red-shifted from ~5.7 eV to ~4.4 eV, was experimentally validated. Red-shifting of this feature down to the visible frequency regime was not possible, owing to eigenenergy modification not occurring at the coupled limit. The eigenenergy modification phenomenon is remarkable since it is only one factor, namely whether or not a MWCNT is filled with a dielectric, that allows the plasmon energy to be red-shifted.

1. Introduction
As a primary electron passes close to an isotropic metal foil of thickness $D$, the electron polarises the foil. The dynamical polarisability consists of surface plasmons excited on each of the two foil surfaces [1]. As $D$ decreases, the degree of interaction (coupling) between the plasmons propagating on each foil surface increases. Splitting of the surface excitation into two discrete resonances $\omega_{\pm}$ occurs, associated with the higher-energy asymmetrical and lower-energy symmetrical surface plasmon field configurations, respectively [1].

In the cylindrical MWCNT geometry, the parameter $(r_2-r_1)$ is equivalent to that of $D$, where $r_1$ ($r_2$) represent the inner (outer) wall radii. As for a planar foil with decreasing $D$, as $(r_2-r_1)$ decreases, coupling between surface plasmons propagating on each of the inner and outer MWCNT walls increases [2-6]. In contrast to a dielectrically isotropic medium, the dielectric constant of graphite consists of a tensor, with components $\varepsilon_{II}$, $\varepsilon_{\perp}$ [3]. This results in the dynamical polarisability of the MWCNT being comprised of numerous coupled asymmetrical (symmetrical) peaks, which are associated with the dielectric tensor components $\varepsilon_{II}$ ($\varepsilon_{\perp}$). The eigenenergy of these peaks can be confirmed from experimental MWCNT EEL spectra of the plasmon-loss regime [3].

The goal of the present contribution is to excite a $\pi$-surface plasmon in the visible or UV frequency regimes. Therefore, solely MWCNT EEL features originating from $\pi$ surface plasmons are considered, since these are of a lower resonance energy than features originating from $\sigma$ and $\pi+\sigma$ surface plasmons.
2. Experimental details
The MWCNTs were formed within a water-cooled high isostatic pressure apparatus, with a carrier gas containing pure nitrogen at a pressure of 70 MPa. Details of the MWCNT production are presented elsewhere [7].

EEL spectra were acquired utilising a dedicated VG HB-601 STEM (scanning transmission electron microscope) equipped with a Gatan UHV Enfina system. The STEM possessed a 100 keV cold field emission source, providing a spatial resolution of down to 1 nm, and energy resolution of 0.34 eV, given by the FWHM of the ZLP, with a point spread function drop-off at ~2 eV. Separation of the ZLP from the signal was further aided by use of a high dispersion (0.01 eV/channel) for spectral acquisition [2]. Objective / collector aperture semi-angles of 5.9 / 3.4 mrad were utilised.

3. Dielectric model
The eigenenergy of coupled MWCNT EEL features have a dependency on \( r_1/r_2 \). Eigenenergy modification of these features occurs from the presence of a dielectric filling and / or dielectric surround of the MWCNT, possessing dielectric constants of \( \varepsilon_i, \varepsilon_e \), respectively. The modification arises from the depolarising effect [10] of the dielectrics. In order to demonstrate this, a dynamical polarisability model was utilised [6], providing simulated EEL spectra of coupled \( \pi \)-surface modes excited on a MWCNT, by aloof primary electrons. The model allowed a MWCNT to be approximated as an anisotropic spherical multi-wall nanoshell, owing to the surface plasmon propagating along the circumference of a cylinder being similar to the surface plasmon propagating along the circumference of a spherical shell [8]. Approximation of a MWCNT as a nanoshell had the advantage of being far more analytically simple [8]. In the spherical geometry, the transferred azimuthal momentum can be decomposed into \( \ell = 1, 2, 3, \ldots \) modes. The \( \ell = 0 \) mode has monopole character, the \( \ell = 1 \) mode dipole character, the \( \ell = 2 \) mode quadrupole character, etc. [9]. For the aloof mode, the \( \ell = 0 \) mode is silent [8].

Features appear in the simulated EEL spectra attributed to the maxima of \( \text{Im}[\varepsilon_{\perp i} (\omega)] \) [11,12] i.e. \( \omega_0 \) (plasma frequency of the in-plane excitations), and to the maxima of \( \text{Im}[-1/\varepsilon_{\| i} (\omega)] \) i.e. \( \omega_p \) (Langmuir frequency of out-of-plane excitations) [11,12]. This is true even when the small thickness limit \((r_1/r_2 \to 1)\) is not fully realised [11,12]. Owing to resonance energies of the graphite in-plane and out-of-plane loss functions being close, decomposition into features associated with each of \( \varepsilon_{\perp i}, \varepsilon_{\| i} \) in the simulated EEL spectra is difficult for thicker tubes [12]. In the simulations, features in the \( \pi \) EEL regime were approximated as a single Gaussian peak, as illustrated in figure 1(a). \( \omega_s \) represent the decoupled surface mode energy. Ref. [4] details the intensity of features attributed to the lower energy branch (\( \varepsilon_{\perp i} \)), always being greater than those attributed to the higher energy branch (\( \varepsilon_{\| i} \)).

![Diagram](image1.png)

Figure 1. (a) Simulated EEL spectra for a thick (thin) unfilled and unsurrounded MWCNT, at ~5.5 eV (4.5 eV). Dashed lines show fitted Gaussian peaks. (b) Eigenfrequency curves of the \( \ell = 1 \) mode lower energy branch, of a spherical anisotropic multi-wall carbon nanoshell.
This arises from the dipole length associated with the symmetrical field configuration, always being greater than that associated with the asymmetrical configuration. Therefore, the single Gaussian peak fitted to the simulated $\pi$ EEL spectra consists almost entirely of contributions from $\varepsilon_{\perp c}$. Ref. [2] details that the simulated spectra consist of numerous peaks. Fitting of a single Gaussian peak was justified owing to the multiple peaks associated with $\varepsilon_{\perp c}$, always being of such close energy (see figure 1(a)), they would remain unresolved in experimental measurements. Figure 1(a) further demonstrates that whilst the peak of the single Gaussian peak does not necessarily correspond precisely to the peak energy of the simulated spectra, it will nevertheless be very close. One can therefore gain an estimate of the change in eigenfrequency of experimentally measured $\varepsilon_{\perp c}$ features with $r_1/r_2$, and the effect of a dielectric filling, as illustrated in figure 1(b). A dielectric constant of $\varepsilon=7$ was selected as a typical value representative of a dielectric filling. Note for the $\ell=1$ mode, and higher order $\ell$-modes, $\omega_0$ and $\omega_s$ were calculated to be invariant, for all values of $\varepsilon_0$.

Figure 1(b) demonstrates when a nanoshell is filled but not surrounded, the thick limit asymptote energy (at $r_1/r_2 \to 0$) is the same as that for the unfilled and unsurrounded nanoshell. An unmodified thick limit asymptote energy is precisely the same behaviour as observed for the $\omega_0$ coupled surface mode of a metal foil embedded in vacuum [1]. In comparison to that of a nanoshell which is unfilled and unsurrounded, for the filled and unsurrounded nanoshell, one would expect a red-shifted thick limit asymptote energy, i.e. behaviour observed for the $\omega_0$ coupled surface mode of a metal foil coated only on one side with a dielectric [1]. Between the thick and thin limits, the lower-energy branch for the filled and unsurrounded nanoshell is red-shifted in energy, in comparison to that of the nanoshell which is both unfilled and unsurrounded. One can imagine that the filled and unsurrounded nanoshell responds as though it was unfilled, owing to the filling not being semi-infinite in extent. Similarly, one would expect an unfilled and surrounded nanoshell to respond as though it was filled, owing to the depolarising effect of the infinite surround, and the finite cavity size.

As can be seen from figure 1(b), between the thick and thin nanoshell limits, the filling of the carbon nanoshell dictates the degree of red-shifting of the lower-energy branch. By setting $\varepsilon_\parallel(\omega)=\varepsilon_{\perp c}(\omega)$ in the dynamical polarisability model, the nanoshell is modelled as an isotropic medium. Using this isotropic model, the thick limit asymptote energy for a carbon nanoshell which is both filled and surrounded, is red-shifted in comparison to the thick limit asymptote energy simulated using precisely the same model, for a carbon nanoshell which is both unfilled and unsurrounded. This explicitly confirms the depolarisation effect does not arise from the anisotropic properties of graphite.

4. Results and discussion

Aloof spectra were acquired from the MWCNTs illustrated in the STEM BF-images of figure 2, along the lines indicated. These MWCNTs represent a completely filled and a completely unfilled MWCNT, respectively, both of which provided a large $r_1/r_2$ parameter range. Spectra were acquired from these MWCNTs, in order to confirm the prediction of a MWCNT filling dictating the degree of red-shifting of the lower-energy branch. The ZLP was extracted using a power-law function. The filled MWCNT was filled with AgI. For the MWCNT illustrated in figure 2(a), the red-shifting arising from the changing weighting of various $\ell$-modes with decreasing $r_2$, has been shown to be vanishingly small [2].

The measured aloof spectra consisted entirely of contributions originating from the surface plasmon, and were approximated as a single Gaussian peak, for precisely the same reasons as detailed previously. The resonance energies of the fitted Gaussian peaks are detailed in figure 2(c). As the local thickness decreases, the Gaussian energy red-shifts, consistent with the model illustrated in figure 1. This red-shifting occurs for a decreasing local thickness in both the filled and unfilled MWCNTs. Of paramount importance, for identical or near-identical thickness, the filled MWCNT Gaussian peak always has a lower energy than that of the unfilled MWCNT. Whilst the unfilled data could equally well be fitted with a straight line, the most important result of figure 2(c) is that the filled data are of lower energy for an equivalent $r_1/r_2$ parameter. Furthermore, when the thickness is small ($r_2-r_1 \to 0$) or relatively large ($r_2-r_1 \sim 17$ nm), a convergence in energy seems to occur. This
appears to confirm the simulations of figure 1, demonstrating that a filling does not affect the decoupled and coupled limit eigenenergies.

Figure 2. (a) STEM BF-image of a completely unfilled MWCNT, (b) STEM BF-image of a completely AgI-filled MWCNT. (c) Resonance energies of the Gaussian peak fitted to the experimentally measured EEL spectra, acquired along the lines indicated in the BF-images. Unfilled (filled) symbols represent measurements from the unfilled (filled) MWCNT. Uncertainty in measured resonance energies was estimated at the energy resolution/2.

Summary
Simulations demonstrate that use of a dielectric filling does not modify the MWCNT lower energy branch eigenenergy at the coupled and decoupled limits. This appears to be supported by experimental results. The simulations therefore demonstrate that it is not necessary to have a very thin or very thick MWCNT in order to obtain a significant red-shifting of the lower energy branch; all that is required is a MWCNT possessing an intermediate thickness ($r_1/r_2 \approx 0.5$), and filled with a dielectric. In light of the difficulties presented in tailor-growing MWCNTs with specific dimensions, this fact offers much promise for practical applications.

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