Spatially-resolved EEL studies of plasmons in silver filled carbon nanotubes using a dedicated STEM

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Abstract. Using a dedicated FEG STEM, we present highly spatially-resolved electron energy-loss (EEL) studies of individual multi-walled carbon nanotubes (MWCNTs), each with the inner cavity possessing regions completely filled with silver. The transmission and attenuation of graphite π-collective mode E-fields through the MWCNT walls are established. Noticeable changes in the graphite π-surface mode are witnessed, concomitant with coupling of the silver Mie mode and the graphite π-surface mode. The resulting collective mode is significantly red-shifted to below 5 eV, with considerable intensity in the visible frequency regime. It appears that silver retains its ability to enhance E-fields when surrounded by a MWCNT. Present observations lead to the possibility of collective modes propagating on graphene monolayers being tuned in frequency by the presence of a metal.

1. Introduction
MWCNTs are well known to possess exceptional electronic properties [1,2]. Similarly, silver nanoparticles have attracted much attention owing to their surface plasmon enhancement capability [3]. Plasmons consist of a large number of electrons oscillating coherently, and are termed collective modes. Optical processes dominate for small momentum transfer associated with collective excitation [5]. By convention, the lowest order surface mode of a cylindrically shaped object is denoted as the Mie mode [4]. A MWNCT and a silver sample with nanometric dimensions, can be combined by using the nanotube inner cavity as a mould, subject to the temperature of the silver not being too great [6]. The resulting nano-composite could conceivably serve as a transmitting and modulating medium for MWCNT collective modes. The nano-composite could then present one of the most interesting solutions to developing efficient photonic [7] and electronic devices based on collective modes. In the present contribution, the dielectric response of three separate MWCNT-silver nano-systems are probed at the optical limit, in order to deduce the effect of the silver filling on the frequency, intensity and transmission of silver and MWCNT π-collective modes.

2. Experimental
The dielectric response of the MWCNT-silver nano-systems were probed using EEL spectroscopy performed within a STEM. For high spatial resolution EEL measurements, the STEM is unrivalled as a tool [8]. Combined with effective deconvolution of the zero-loss peak (ZLP), transitions within the optical frequency regime can be routinely measured above confidence level [9]. The instrumentation consisted of a dedicated cold field emission VG601 STEM equipped with a UHV Enfina system,
located at the University of Liverpool, UK. At 100 kV, the STEM provides an energy resolution of 0.3 eV. Silver filling of MWCNTs was facilitated using the hydrogen arc discharge method. Details are provided elsewhere [6].

3. Results and discussion
3.1. Frequency modification

Figure 1 illustrates a MWCNT possessing a partially silver filled cavity. Diffraction contrast demonstrates the high crystallinity of the MWCNT, which has evidently been preserved during the filling process. Crucially, the interface between the filled and unfilled region of the cavity is localised to a small region. This allows any variation in parameter of collective modes, to be unambiguously ascribed to the presence of the cavity filling, whilst avoiding drifting conditions typical of large spectrum images [9,10]. Spectra were acquired in the aloof mode, representing an effective technique for isolating surface mode contributions, which are unimpinged by volume mode contributions [9].

The graphite $\pi$-surface mode is seen to experience a red-shift in the vicinity of the silver filling. Such eigenfrequency modification is characteristic of collective mode coupling [11-13], i.e. coupling of the graphite $\pi$-surface and silver Mie modes. Quantum size effects can be neglected due to the size of the MWCNT, and optical anisotropy can be neglected due to preservation of graphitization of the MWCNT (ascertained by HRTEM, images not shown). In aloof conditions, the volume mode cross section is small, but when the beam is relatively close to the sample, a volume mode can nevertheless be excited. Care was thus taken to ensure the distance between the aloof probe and outermost MWCNT wall was invariant, thus avoiding the influence of a non-uniform $\pi$-volume mode cross section. Were the $\pi$-volume mode intensity to vary, the close energy of the $\pi$-volume and $\pi$-surface modes could easily be mistaken for eigenfrequency modification of the $\pi$-surface mode.

![Figure 1](image.png)

The observed red-shifting may be a consequence of image dipoles induced by the silver Mie mode in the MWCNT wall. Such a phenomenon can arise owing to the silver Mie mode and graphite $\pi$-surface mode being similar enough in energy, to reduce the charge density participating in the $\pi$-surface mode oscillation. This effect can be interpreted as an intrinsically separate effect to that of conventional
hybridization, owing to the weak coupling of the MWCNT $\pi$-surface mode and silver Mie mode measured above [3].

3.2. Intensity modification

Figure 2(a) illustrates a MWCNT with the internal cavity entirely filled with silver. The associated spectrum images detail intensity distributions of the silver Mie, graphite $\pi$-surface and graphite $\pi$-bulk modes. The dotted line in figure 2(b) represents an EEL spectrum of an unfilled MWCNT with the $\pi$-bulk plasmon extracted; the solid line represents an EEL spectrum of a silver filled MWCNT. In each case, spectra were extracted from respective spectrum images at pixels corresponding to the location of the MWCNT outer wall, with ZLP extraction performed using a power law function applied to an energy window of identical parameters. Furthermore, each MWCNT was of similar dimensions and aspect ratio. The red-shift of the graphite collective $\pi$-surface mode by ~0.3 eV is again consistent with coupling of the graphite $\pi$-surface and silver Mie modes. However, in this case, significant intensity in the 2-4 eV regime is clearly witnessed, concomitant with transmission of the silver Mie mode $E$-field across the MWCNT walls. This is seen in figure 2(a) where significant intensity of the silver Mie mode at 3.7 eV is witnessed at the outer MWCNT wall. In graphite, whilst various optical processes associated with the $E_{\|}$ and $E_{\perp}$ polarizations are well characterised [14,15], as a process, intra-layer collective mode transmission is poorly understood. Intuitively, one would believe that propagation of collective modes, perpendicular to the basal planes, would be critically damped. Nevertheless, present results indicate that the $E$-field of such an oscillation can be transmitted.

3.3. $E$-field transmission

The HAADF image in figure 3 details a silver filled MWCNT with silver particles included within the wall (grey arrows), which is further contaminated at the outer surface with silver particles (white arrows) as a result of heating (‘lamping’ within the airlock of the STEM). Overlaid are EEL intensity maps of the silver Mie mode, obtained from spectrum images acquired at positions 1 and 2. The silver Mie mode (of frequency ~3.7 eV) is witnessed to have a maximal intensity at the outermost surface. A local intensity enhancement of the silver Mie mode at the silver particle (long white arrow) is also

![Figure 2](image-url)

**Figure 2.** (a) Inverted STEM DF image of a MWCNT completely filled with silver. Spectrum images showing the absolute EEL intensity at various energies are also detailed. The acquisition region is identified in the DF image. Black (white) pixels represent the least (greatest) intensity. (b) Experimentally acquired EEL spectra; (dotted line) EEL spectrum of an unfilled MWCNT with the $\pi$-bulk plasmon extracted, (solid line) the EEL spectrum of a silver filled MWCNT. Spectra were not normalised, in order to illustrate intensity variations.
witnessed. The silver plasmon transmission through the MWCNT walls is delocalised, which is apparent at position 1 where transmission remote from the silver filling occurs. Studies of optical biosensors demonstrate that it is the decay of the average induced $E$-field, which dictates the sensing range [3]. The present transmission provides an indication that the MWCNT does not therefore completely attenuate, but rather dampens the sensing range of the silver filling. The silver Mie-mode has previously been seen to be strongest in cavities within MWCNT silver fillings [3]. The inherent 3D variations intrinsic to graphene sheets could conceivably act as local mechanism for excitation of surface modes.

![Figure 3. STEM DF image of a silver filled MWCNT exhibiting contamination with silver particles. EEL spectrum images detailing the intensity of the silver Mie mode at 3.7 eV are overlaid. Black (white) pixels represent the least (greatest) intensity. The maximal intensity of this mode at the outermost MWCNT wall and remote transmission are clearly evident.](image)

4. Summary
Within various silver filled MWCNTs, hybridization of the silver Mie mode and graphitic $\pi$-surface mode could not detected, nor did the two modes appear to be separated. Nevertheless, noticeable changes in frequency and intensity of the plasmons were witnessed, apparent in a prominent tail at frequencies down to below 4 eV. The silver Mie mode at 3.7 eV was seen to have significant transmission through the MWCNT walls, with the strongest signal measured along the outer surface of the MWCNT wall, paralleled by the MWCNT $\pi$-surface plasmon at 5.3 eV. These localisations are contrasted by that of the MWCNT $\pi$-bulk plasmon, which is seen to be strongest inside the MWCNT. Present work paves the way for applying established dielectric theory to recently isolated graphene monolayers.

5. References
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