Far-infrared absorption of undoped and Br-doped CMF powder in stacked cup cone configuration

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We carried out room-temperature far-infrared (40–650 cm\(^{-1}\)) transmission measurements on undoped and bromine-doped powder samples of carbon microfibers in stacked cup cone geometry. The transmission spectra of both doped and undoped samples were fit to a Drude-Lorentz model. A single Drude component and a small bandgap (around 8 meV) semiconducting Lorentzian component along with 3 other Lorentz components were essential to get a good fit in the entire measured frequency range. A decreased metallic conductivity along with a red-shift of the lowest semiconducting gap was found after bromine doping. Absorption spectra were derived from the transmission spectra under the assumption of non-dispersive reflectance. These spectra were compared to Drude-Lorentz model absorption spectra. The free-carrier density of the n-type powder and the electronic mean free path were estimated and compared with previously reported values for single-walled nanotubes and pyrolytic graphite.

I. INTRODUCTION

Their unique electronic and mechanical properties have caused carbon nanotubes (CNT) to attract much interest among researchers since their discovery\(^{11}\). CNTs constitute a new class of materials that could contribute to the development of novel nanoscale electronic devices\(^{12}\). Isolated single-wall nanotubes (SWNT) and bundled nanoropes have been studied extensively and are reported to have either metallic or semiconducting phases, based on their \((n,m)\) wrapping vector indices.\(^{13}\) The related materials, carbon nanofibers (CNF), also known as stacked cup carbon nanotubes (SCCNT), are bigger in diameter than carbon nanotubes. Despite losing the concentric structural integrity and the defect-free composition of CNTs, they are highly graphitic carbon nanomaterials\(^{14}\), with excellent mechanical properties, electrical conductivity, and thermal conductivity. These properties make them a suitable candidate for various applications such as radio frequency interference shields, electrostatic painting, or discharging electrostatic potentials in lightning strikes. CNF industries promise to offer solutions to many vexing problems in composite applications. Comparatively better net weight/strength ratio, low processing cost, improved tensile and bending strengths, high specific heat, high corrosion resistance and many such qualities make them an ideal alternative for reinforcing engineered composites\(^{15}\).

The doping process could alter the valence and conduction band statistics and also the electron dynamics in these systems; hence, doping serves as an effective tool for tuning of electronic and mechanical properties of such carbon nanomaterials.\(^{16}\) The study of doping behavior has always been tricky because of the mixed metallic and semiconducting phases existing in any CNT sample grown so far.\(^{17}\) Frequency-dependent optical studies of doped and undoped materials can provide a good deal of information about the electronic structure and the effect of doping in CNTs. In addition to showing low-frequency metallic behavior, the presence of a small bandgap semiconducting phase has also been reported in several optical studies. (The gap is around 8 meV and is rather sample-dependent.) However, there is an inconsistency regarding the interpretation of this gap. It is attributed either to a secondary gap which is caused by the curvature of certain semi metallic tubes or to symmetry-breaking due to neighboring tubes in metallic phase.\(^{18,19,20}\) Moreover, SWNT samples have been studied in the mid-infrared and higher frequency range after introducing p-type \((I, Br_2)\) and n-type \((K, Cs, organic\ radical-anions)\) doping. These studies have shown the disappearance and emergence of several new peaks, attributed to either electron depletion from or electron filling into specific bands in the semiconducting or metallic phase, thus modifying the conducting nature of CNT samples.\(^{14,17}\)

II. EXPERIMENTAL PROCEDURES AND RESULTS

Room-temperature far-infrared transmission measurements were conducted on hollow and cylindrical stacked-cup carbon microfiber powder samples. The microfibers had diameters of 60 nm to 150 nm and lengths ranging from tenths to tens of micrometers\(^{11}\). High quality samples (Pyrograf III, CNF PR-25-XT-PS) was prepared by Applied Sciences, Inc. A homogeneous layer of CMF powder of thickness 0.25 mm, 0.15 mm and 0.10 mm were uniformly spread between two polyethylene windows. The sample holder had a 6 mm aperture. Transmission spectra were acquired in the far infrared range \((40–650 \text{ cm}^{-1})\) using a Bruker 113v Fourier-transform interferometer. A helium-cooled silicon bolometer detector was used in this spectral range. Later, the transmission measurements were repeated under identical conditions immediately after exposing two additional powder samples to \(Br_2\) for 10 min and 100 min respectively to study the effect of p-type doping on the sample. The extent of bromine doping was estimated by observing the change in the density of the sample powder. The den-
sity of the undoped sample was estimated to be around 0.3 g/cm³. This density increases to 0.39 g/cm³ after 10 min. of bromination and 0.58 g/cm³ after 100 min. of bromination. Mass fraction of CMF to bromine is about 3.3:1 after 10 min. of bromination which decreases to about 1:1 after 100 min. of bromination. The polyethylene windows did introduce interference fringes in the transmission spectra. These were removed carefully using a Fourier-transform smoothening technique. The fringe removal process did not change the level of transmission.

Figure 1 shows the room temperature transmission spectra of the undoped CMF sample for different thicknesses as well as the spectra after bromination.

![Figure 1](image1.png)

**FIG. 1.** (Color online) Room temperature transmittance spectra of Br-doped and undoped CMF powder for different thicknesses.

We observed negligible transmission for the sample thickness of 0.25 mm. The transmission level increases slightly as the thickness decreases to 0.15 mm but is still below 1% in the entire far infrared range. However we observed notable increase in the transmission as thickness is decreased to 0.10 mm. The transmission decreases from about 5% to 1% as frequency decreases from 650 cm⁻¹ to 30 cm⁻¹. The transmission starts decreasing more quickly around 150 cm⁻¹; this behavior can also be seen in the spectra of the 0.15 mm thick sample. All further measurements and analysis were conducted with the 0.10 mm thick powder sample. The transmission measurements were repeated immediately after brominating two powder samples, one for 10 min and one for 100 min. The transmission for 10 min brominated powder sample is quite similar to the undoped sample except for a more obvious onset of increased transmission at low frequencies. In contrast, the transmission of the 100 min brominated sample is substantially increased over the entire range.

### III. ANALYSIS

#### A. Drude-Lorentz model fits

A Drude-Lorentz model was used to fit the transmission data of the CMF powder sample. Figure 2 shows the Drude-Lorentz fit to the transmission data. The Drude component characterizes the free carriers and their dynamics at zero frequency whereas the Lorentz contributions are also included to account for the electronic transitions due to both the low gap semiconducting phase of the sample and higher-energy transitions. The dielectric function is

\[
\varepsilon(\omega) = \varepsilon_{\infty} - \frac{\omega_{p0}^2}{\omega^2 + i\omega/\tau} + \sum_{j=1}^{4} \frac{\omega_{pj}^2}{\omega^2 - \omega_j^2 - i\omega\gamma_j} \tag{1}
\]

where the first term represents the core electron contribution (transitions above the measured range, the second term is free carrier contribution characterized by Drude plasma frequency $\omega_{p0}$ and free carrier relaxation time $\tau$ and the third term is the sum of four Lorentzian oscillators representing the electronic contributions to the dielectric function. The Lorentzian parameters are the $j$th oscillator plasma frequency $\omega_{pj}$, its central frequency $\omega_j$, and its linewidth $\gamma_j$. This dielectric function model is used in a least-squares fit to the transmittance data.

![Figure 2](image2.png)

**FIG. 2.** (Color online) Drude-Lorentz fit to the transmittance spectra of Br-doped and undoped CMF powder at room temperature.

Table 1 contains one Drude term along with 4 other electronic excitation terms. There were no obvious vibrational features observed in any of the samples. All three samples were identified as being in a mixed metallic phase of CMF bundles along with a low-gap semiconducting phase. In many previous studies, this semiconducting
gap around 8 meV has been attributed to a curvature-induced gap in CNT.

### TABLE I. Drude-Lorentz parameters for undoped and Br-doped CMF powder samples at room temperature (300 K).

| Modes                      | Symbol | No Br | 10 Min. | 100 Min. |
|----------------------------|--------|-------|---------|----------|
| Assignment                 |        | (cm\(^{-1}\)) | (cm\(^{-1}\)) | (cm\(^{-1}\)) |
| Drude component            | \(\omega_p\) | 71    | 65      | 45       |
| metallic phase             | \(1/\tau\) | 33    | 41      | 15       |
| Low-gap                    | \(\omega_{p1}\) | 30    | 24      | 25       |
| semiconducting phase       | \(\omega_{p2}\) | 69    | 67      | 43       |
| Electronic excitation      | \(\omega_1\) | 80    | 53      | 112      |
| 2                         | \(\gamma_1\) | 137   | 139     | 132      |
| Electronic excitation      | \(\omega_2\) | 838   | 829     | 850      |
| 3                         | \(\gamma_2\) | 616   | 613     | 613      |
| Electronic excitation      | \(\omega_{p3}\) | 110   | 104     | 103      |
| 3                         | \(\gamma_3\) | 696   | 672     | 709      |
| Electronic excitation      | \(\omega_{p4}\) | 202   | 220     | 186      |
| 4                         | \(\gamma_4\) | 1098  | 1098    | 1082     |

#### B. Far-infrared absorption

Next, the absorption coefficient was computed from the transmission data by inverting

\[
\Imag = \frac{(1 - \Re_{ab})^2 e^{-\alpha d}}{1 - \Re_{ab} e^{-2\alpha d}} \quad (2)
\]

where \(d\) is the thickness and \(\Re_{ab}\) is the single-bounce reflectance (the reflectance of a single surface). This equation is quadratic in \(e^{\alpha d}\) with one positive root

\[
e^{\alpha d} = \frac{(1 - \Re_{ab})^2}{\Imag} \left[1/2 + \sqrt{1/4 + \frac{\Re_{ab}^2 \Imag^2}{(1 - \Re_{ab})^4}}\right] \quad (3)
\]

The value for \(\Re_{ab}\) was estimated using

\[
\Re_{ab} \approx \left(\frac{n - 1}{n + 1}\right)^2 \quad (4)
\]

where \(n\) is the refractive index, here taken to be constant, with a value \(n = 4.1\).

Figure 3 shows the absorption coefficient \(\alpha\) found from the transmission spectra. The calculated absorption coefficients using the set of parameters used to fit the transmission (Figure 2) are also shown. That the agreement is good gives us confidence in the fitting procedure and the transmission based absorption coefficient estimation routine. Figure 3 also shows that the absorption coefficient decreases with Br-doping.

We interpret the rise in absorption below 150 cm\(^{-1}\) as due to free-carriers in the CMF samples. This is evident in the conductivity spectrum, calculated from the Drude-Lorentz fit and shown in Figure 4. The real part of the optical conductivity \(\sigma_1 = \omega \varepsilon_2/4\pi\) where \(\varepsilon_2\) is the imaginary part of the dielectric function in Eq (1). There is a free carrier absorption rise at the lowest measured frequency which rolls off as the frequency reaches the Drude relaxation rate \(1/\tau\). A small overlapping absorption shoulder around 50–80 cm\(^{-1}\) can also be observed; this feature is attributed to the low-gap semiconducting component seen in previous studies.

![Graph showing absorption coefficient vs. frequency](image_url)

**FIG. 3.** (Color online) A comparison between transmission based absorption coefficient with Drude-Lorentz parameter computed absorption coefficient for Br-doped and undoped sample at room temperature.

![Graph showing optical conductivity vs. frequency](image_url)

**FIG. 4.** (Color online) The Drude-Lorentz parameter computed optical conductivity for Br-doped and undoped sample at room temperature.
The optical conductivity, especially the Drude contribution, decreases with the extent of bromination. This effect can be seen in Table 1 where the Drude plasma frequency decreases with doping. Figures 4 and 5 illustrate this result. Figure 5 shows individually the two low-energy components of the conductivity.

![Drude conductivity and low gap excitation conductivity](image)

**FIG. 5.** (Color online) The effect of bromination of CMF on Drude conductivity and low gap excitation conductivity contribution at room temperature.

The semiconducting gap (around 8 meV for the undoped sample) shifts towards lower frequencies after 100 minute bromination. The oscillator strength of this doped sample shifts towards lower frequencies after bromination. We expect that bromine will remove electrons from the CMF. Assuming that \( n^* \approx n_c \), the Drude plasma frequency \( \omega_{p0} \) for the undoped sample implies a free charge carrier density \( n \approx 6 \times 10^{16} \text{ cm}^{-3} \) in the powder sample. We can allow for the low density of the CMF powder sample. The density of the powder is about 0.3 g/cm³, compared to the ideal SWNT density of 2 g/cm³. If we further assume 50% metallic phase CMF bundles in the sample, the adjusted free carrier density of metallic component of the sample is around \( n \approx 1 \times 10^{18} \text{ cm}^{-3} \), an order of magnitude smaller than in pyrolytic graphite at room temperature. Moreover it is reported in previous studies that only a fraction of the charge carriers contribute to the delocalized charge transport in CNT mat structure while the remaining localized fraction of charge carriers carry smaller contribution to the Drude conductivity leading to a reduced carrier density estimation. The mean free time of the charge carriers in the undoped sample is just the inverse of the scattering rate, leading to \( \tau \approx 1.6 \times 10^{-13} \text{ s}^{-1} \), comparable to the result found in previous study for CNT in mat structure. Using the Fermi velocity of graphite, \( v_F \approx 8 \times 10^5 \text{ m/s} \) we estimate the mean free path to be about \( \Lambda \approx 120 \text{ nm} \). The mean free path after 100 minutes of bromination is about twice this value. Some of the higher energy electronic excitations show very large linewidths. This behavior is expected; the linewidth of these interband transitions is due to the details of the electronic structure and not to lifetime effects. These parameters show very weak dependence on the extent of doping.

### IV. CONCLUSIONS

A reduction in the semiconducting gap and the optical conductivity after bromination suggests that undoped CMF powder has n-type carriers, which partially get neutralized after bromination. We expect that bromine will remove electrons from the CMF. Assuming that \( n^* \approx n_c \), the Drude plasma frequency \( \omega_{p0} \) for the undoped sample implies a free charge carrier density \( n \approx 6 \times 10^{16} \text{ cm}^{-3} \) in the powder sample. We can allow for the low density of the CMF powder sample. The density of the powder is about 0.3 g/cm³, compared to the ideal SWNT density of 2 g/cm³. If we further assume 50% metallic phase CMF bundles in the sample, the adjusted free carrier density of metallic component of the sample is around \( n \approx 1 \times 10^{18} \text{ cm}^{-3} \), an order of magnitude smaller than in pyrolytic graphite at room temperature. Moreover it is reported in previous studies that only a fraction of the charge carriers contribute to the delocalized charge transport in CNT mat structure while the remaining localized fraction of charge carriers carry smaller contribution to the Drude conductivity leading to a reduced carrier density estimation. The mean free time of the charge carriers in the undoped sample is just the inverse of the scattering rate, leading to \( \tau \approx 1.6 \times 10^{-13} \text{ s}^{-1} \), comparable to the result found in previous study for CNT in mat structure. Using the Fermi velocity of graphite, \( v_F \approx 8 \times 10^5 \text{ m/s} \) we estimate the mean free path to be about \( \Lambda \approx 120 \text{ nm} \). The mean free path after 100 minutes of bromination is about twice this value. Some of the higher energy electronic excitations show very large linewidths. This behavior is expected; the linewidth of these interband transitions is due to the details of the electronic structure and not to lifetime effects. These parameters show very weak dependence on the extent of doping.

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