Controlling Terahertz Conductivity in SWNT/Polymer Composite

D. Polley¹, A. Barman¹, and R. K. Mitra²

¹Department of Condensed Matter Physics and Material Sciences
²Department of Chemical, Biological and Macromolecular Sciences
S. N. Bose National Centre for Basic Sciences, Block-JD, Sector-III, Saltlake, Kolkata 700098, INDIA

Abstract— Terahertz (THz) conductivity of single walled carbon nanotube (SWNT)/poly-vinyl alcohol (PVA) composites has been studied in the frequency window of 0.3-2.0 THz. It is found that conductivity of these samples can be efficiently tuned by changing the length of the SWNTs and also the SWNT weight fraction. For the highest weight fraction at a frequency of 1 THz, longer SWNT sample (average length ~ 15 µm) showed ~90% increased conductivity than its shorter counterpart (average length ~ 2 µm) having the same diameter. A modified Universal Dielectric Response (UDR) model is applied to analyze the conductivity spectra.

I. INTRODUCTION

With the rapid advancement of THz technology in the last decade high quality single walled carbon nanotubes (SWNTs) have received major attention as a building block in THz electro-magnetic interference shielding devices [1], THz attenuator [1], THz polarizer [2] due to their fascinating optoelectronic response in THz frequency range. As THz conductivity of those devices plays a crucial role in determining their performance, the study of THz conductivity of different SWNT compounds is of immense importance. In this respect, several groups have tried to modulate THz conductivity of SWNT via alignment, doping or functionalization. It was also demonstrated that dimensions of CNTs, in particular their length play an effective role in modifying frequency dependent (near d.c. to GHz) conductivity of such composites. In the present report we have attempted to regulate the conductivity of SWNT/PVA films within the frequency range of 0.3-2.0 THz in a controlled way by changing the SWNT length.

II. MATERIALS & EXPERIMENTAL PROCEDURE

SWNTs (dia ~ 1-2 nm) of two different lengths were purchased from NanoAmor, USA at highest available purity and processed without further purification. Poly-vinyl alcohol (PVA)(Sigma Aldrich), Ethanol (Merck) and Millipore de-ionized (DI) water are used for sample preparation. No special care has been taken for CNT isolation procedure. PVA is dissolved in DI water by continuous magnetic stirring at a temperature of 80°C. SWNT solution is mixed with clear PVA solution and ultrasonicated for 15 minutes before pouring it in a petridish for slow drying at room temperature under ambient condition for 10 days. SWNT/PVA composite films of thickness 300 ± 20 µm are prepared for measurements using a commercial THz time domain spectrometer (TERA K8, Menlo Systems) in transmission geometry at room temperature under N₂ atmosphere. Two different types of SWNT samples namely S_L (average length ~ 15 µm) and S_S (average length ~ 2 µm) were dispersed in PVA matrix at three different weight fractions (0.1%, 0.8% and 1.6%) and named as S_L1, S_S1, S_L8, S_S8, S_L16, S_S16 respectively. Complex optical constants of the samples are derived by numerically solving Fresnel’s transmittance equations and special care has been taken to consider thickness variation in the samples. Conductivity of the samples were extracted from complex refractive index in the probed frequency window and analyzed using a modified UDR model [3].

III. RESULTS & ANALYSIS

Transmitted THz amplitude through the SWNT/PVA composite materials is shown in Fig. 1a for the lowest SWNT concentration in the polymer matrix for both long and short SWNT and the corresponding frequency domain amplitude is shown in Fig. 1b. Transmitted THz amplitude is larger for shorter SWNT/PVA composites than their longer counterpart and this is more clearly visible in the frequency domain spectra. Larger THz amplitude means smaller THz absorption and hence smaller THz conductivity for shorter SWNT/PVA composites [4].

Fig.1. (a) THz pulses passing through S-L1 and S-S1 samples in time domain and (b) corresponding amplitude in frequency domain. (c) THz conductivity of all the samples and fitted with modified UDR model.

THz conductivity can be derived from complex optical constants using the following relation [4]. \( \tilde{\sigma}(\omega) = \tilde{n}^2(\omega) \cdot \tilde{\varepsilon}(\omega) = \varepsilon_{\infty} + \frac{i \omega \varepsilon_0}{\omega_0^2} \), where, \( \tilde{n}(\omega) \) is the complex refractive index, \( \tilde{\varepsilon}(\omega) \) is the complex dielectric constant of the system, \( \varepsilon_{\infty} \) is the dielectric constant at infinite frequency, \( \varepsilon_0 \) is the permittivity of free space, \( \omega \) is the angular frequency of radiation and \( \tilde{\sigma}(\omega) \) is the complex conductivity. THz conductivity spectra for all the samples are shown in Fig. 1c and fitted with the modified UDR model which has been
discussed later. It is clearly visible that THz conductivity is significantly larger for longer SWNT/PVA composites for all SWNT concentrations and this conductivity change is more prominent in higher SWNT concentrations. It is also found that THz conductivity increases with the frequency of incident radiation irrespective of the lengths of SWNT in the SWNT/PVA composites and it is due to appearance of THz conductivity tail of the well-known THz conductivity peak which arises in the broad frequency range of 4.5-30 THz depending on the dimensions of SWNT in the composite [5-6].

Real THz conductivities at 1.0 THz of long and short SWNT/PVA composites have been plotted as a function of SWNT weight fractions in Fig. 2a. It is found that, THz conductivity of SWNT/PVA composites at 1.0 THz increases linearly with increasing SWNT weight fraction in the polymer inclusion. Good linear fits are obtained with the slope being higher for longer SWNT films. THz conductivity at 1.0 THz can be calculated for any given SWNT weight fraction within the range of the present measurement window using the relation \[ \frac{\sigma_{SWNT-long} - \sigma_{SWNT-short}}{\sigma_{SWNT-short}} \times 100 \] plotted in Fig. 2b at the probing frequency of 1.0 THz. It is evident from the figure that THz conductivity can be increased up to as high as 90% for the highest SWNT weight fraction and the increment can be modulated by simply varying the SWNT weight fraction in the PVA matrix. Such an easy conductivity tuning is important in different high frequency device applications such as EMIS and storage devices.

The real conductivity spectra of a disordered composite material like CNT/polymer film obey a power law behaviour described by the following formulae [4]:

\[ \sigma_{\text{real}}(\omega) = \sigma_{\text{DC}} + A\omega^s \]

where \( \sigma_{\text{DC}} \) is the D.C. plateau at low frequency regime, \( A \) is a parameter which depends on the temperature, \( s \) is the frequency exponent depending on the conductive properties of the sample and temperature. Hopping or tunnelling type of conduction of carriers is described by a sub-linear frequency dependence \( 0 < s < 1 \) and in case of \( 1 < s < 2 \), motion of carriers gets disturbed by cumblic traps and there movement is limited only in the local environment.

<table>
<thead>
<tr>
<th>Property</th>
<th>Type</th>
<th>Long_SWNT</th>
<th>Short_SWNT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exponent ( s' )</td>
<td></td>
<td>1mg SWNT</td>
<td>1.22</td>
</tr>
<tr>
<td></td>
<td></td>
<td>8mg SWNT</td>
<td>0.82</td>
</tr>
<tr>
<td></td>
<td></td>
<td>16 mg SWNT</td>
<td>0.76</td>
</tr>
</tbody>
</table>

THz conductivity spectra for all the samples are fitted using UDR model and the fitted values of the frequency exponent \( s' \) are tabulated in table 1. For \( S_{L1} \) and \( S_{S1} \), \( s \) value is greater than 1 \((1.22 \text{ and } 1.61 \text{ respectively})\) with \( S_{S1} \) offering a higher value of \( s' \) than \( S_{L1} \), indicating more semiconducting nature of that sample. Due to very small SWNT weight fraction, hopping conduction is not favoured \((s > 1)\) even in long SWNT sample. With increasing SWNT weight fraction, number of possible percolation pathways increases hence the conductivity also increases which is also reflected in the decreasing \( s' \) value in all the samples with increasing SWNT inclusion. The values of \( s' \) are 0.82 and 0.75 in \( S_{L8} \) and \( S_{L16} \), respectively indicating hopping conduction and increased conducting pathways with increasing SWNT weight fraction. The value of \( s' \) is greater than 1 for \( S_{S8} \) and \( S_{S16} \) films and the conductivity is less than the corresponding long SWNT samples. The confined local motion of carriers in \( S_{S} \) samples is due to their short length, increased tube-tube junction in the vicinity of traps have the character of purely dipolar interactions. Despite the simplicity of the model, all the conductivity spectra could be well described and correlated with physical explanation.

IV. SUMMARY

SWNT/Polymer composite film are prepared with varying the average length of SWNT inside the polymer matrix and THz conductivity spectra of those composites were measured in the frequency window of 0.3-2.0 THz. THz conductivity was found to increase by ~90% at the highest SWNT weight fraction at 1 THz by changing the length of SWNT inside the composite.

REFERENCES


