Terahertz time-domain spectroscopy characterization of carbon nanostructures embedded in polymer

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Abstract. This work presents results of terahertz time-domain spectroscopy (THz-TDS) investigations of two types of polymer-based nanocomposites, consisting of bulk samples of graphene nanoflakes embedded in a polymer matrix and thin films where single-walled carbon nanotubes (SWCNTs) with a chiral index (7,5) were wrapped in single strains of a polymer. Our THz-TDS setup is a room-temperature system with a frequency range of 0.1 to 3.5 THz, based on photoconductive switches as both the emitter and detector, excited by 100-fs-wide optical pulses. We have studied THz spectra of both types of samples and compared them to the ones obtained for the pure polymer reference specimens and fitted the experimental complex conductivity data to the Drude–Smith model. The Drude–Smith model fits our data well, demonstrating that graphene nanoflakes and SWCNTs, exhibit highly localized intra grain/tube electron backscattering with a femtosecond relaxation time.

1. Introduction
The terahertz (THz) region of the electromagnetic spectrum has been receiving increasing interest in many areas of science, such as physics, materials science, chemistry, and biology, and has found many applications as a nondestructive and noncontact technique applicable in research laboratories, industrial production lines, security systems, and even ultrafast communications [1]. Specific spectral signatures [2] of a number of polar and crystalline materials [3], organic molecules, and solid and liquid composites [4] that are present in the far-infrared radiation region can be observed by means of transmission THz time-domain spectroscopy (THz-TDS). Since this technique simultaneously provides information on both the amplitude and phase of the THz transient, it can reveal extremely small changes in the complex index of refraction, or equivalently the conductivity, of various, e.g., composite materials [4]. Finally, because of the extremely high sensitivity of THz radiation to water, the THz-TDS method can detect even very minute amounts of water in, e.g., biological specimens [5].

The THz-TDS technique is also uniquely suitable for broadband, THz-range frequency characterization of semiconducting and dielectric materials and recently has been widely implemented in studies of carbon nanocomposites containing graphene and carbon nanotubes [6–9]. While it is well known that the presence of graphene nanoflakes improves the mechanical strength [10] and/or
biological sensing properties [11] of a polymer, it is also known that they affect dielectric properties of polymer matrices, resulting in a modified, THz-frequency dielectric function [7] or, equivalently, complex conductivity. A single-walled carbon nanotube (SWCNT) is a two-dimensional (2-D) graphene sheet rolled up into a hollow cylinder. The diameter and helicity of a defect-free SWCNT are characterized by the chiral vector connecting equivalent crystalline sites on a 2-D graphene sheet [6] and represented by chiral indexes, i.e., a pair of integers \((n, m)\) that define how a graphene sheet can be rolled up into an individual SWCNT. Knowing the indices of a given SWCNT, one can determine its electronic band structure and electric conductivity [12], i.e., whether a given tube is a metal or a semiconductor. Therefore, SWCNTs in their different crystallographic forms have been considered attractive candidates for a number of diverse electronic applications such as molecular electronics, photovoltaic devices, field-effect transistors, etc.

2. Sample preparation and THz-TDS measurement setup

We have tested two types of polymer-based carbon nanocomposites: bulk samples of the graphene nanoflakes embedded in a poly(ethylene terephthalate)-based copolymer matrix (graphene+PET) [13] and thin films of SWCNTs wrapped with poly(9,9-di-n-octylfluorenyl-2,7-diyl) (PFO) strains, deposited by spin coating onto 1-mm-thick fused-silica substrates (SWCNTs+PFO). The bulk samples were prepared by intermixing a commercial, exfoliated graphene during a melt polymerization process and a subsequent hot-press technique. The resulting samples were polymer foils with a thickness ranging from 0.15 to 1.0 mm with 1% graphene content by weight. In the case of thin-film samples, they were ~400-nm-thick films and contained more than 90% of SWCNTs of chirality (7,5) with a tube diameter of 0.83 nm [14]. Consequently, they were expected to exhibit semiconducting electronic properties. Pure bulk PET polymer and thin PFO film samples of corresponding thicknesses were also fabricated and used as references.

Our THz-TDS setup is based on low-temperature--grown GaAs photoconductive switches implemented as both the THz transient emitter and detector. As an optical excitation, we use 800-nm-wavelength, 100-fs-wide optical pulses generated at a 76-MHz repetition rate by a commercial mode-locked Ti:sapphire laser. The emitter and detector were equipped with Si lenses, separated by 24 cm, and placed inside a dry nitrogen gas enclosure. The THz pulse spectrum routinely obtained in an empty setup (no sample between the emitter and detector) extended to 3.5 THz (see figure 1a; black curve).

![Figure 1](image-url)

**Figure 1.** Semi-log plots of the transmitted THz signal spectra through (a) a 0.9-mm-thick foil of graphene+PET material (red line) and a reference (light blue line), and (b) a 0.4-mm-thick film of (7,5) SWCNT+PFO (red line) and a pure PFO reference spectrum (blue line). The inset in (a) shows experimental time-domain transients used to compute the spectra presented in the main panel. The inset in (b) shows the same data as the main panel, but the FFT amplitude is in a linear scale. In (a) we also present the spectrum of an empty setup (nitrogen gas, black line).
3. Measurement results and discussion

Figures 1a and 1b present spectra for both the graphene+PET and SWCNTs+PFO samples, as well as the spectra of corresponding, pure polymer references, obtained by means of a fast Fourier transform (FFT) from corresponding experimental time-domain transients (see examples in the inset in figure 1a). For both samples, the spectra are rather similar, i.e., the FFT amplitude of the THz signal decreases with increasing frequency, reaching the system noise floor level. However, we observe that for the selected 0.9-mm-thick graphene+PET sample, over the entire frequency range, the absorption is significantly larger than that for the pure PET sample. Conversely, for the SWCNTs+PFO film, its absorption spectrum almost overlaps with that of the pure PFO. There are, in this case, two noticeable exceptions: namely, an extra absorption at low frequencies with the peak around 0.4 THz (see inset in figure 1b) and a measurable absorption decrease for >2 THz. The latter effect could be related to an increased THz transmittance of SWCNTs at high frequencies [15].

Subsequently, we extracted the THz-frequency–range index of refraction \( n(\omega) \) for both sample types using the relationship [16]

\[
n(\omega) = 1 + \frac{c(\phi_{\text{sample}} - \phi_{\text{ref}})}{\omega d},
\]

where \( c \) and \( d \) are the speed of light and sample thickness, respectively, \( \omega \) is the angular frequency, and \( \phi_{\text{ref}} \) and \( \phi_{\text{sample}} \) are the phases of the reference and sample signals, respectively. In the case of the graphene+PET sample, the \( n \) spectrum is flat in the entire tested frequency range, but the presence of graphene flakes in the polymer increases its value from 1.75 to 1.85. The presence of nanotubes in a SWCNTs+PFO sample was more visible since the value of \( n \) roughly doubled, reaching ~20 at high frequencies.

Next, complex conductivity spectra for both sample types were calculated and are presented in figure 2 together with numerical fits (solid black lines) based on the Drude–Smith model [17], i.e.; the Drude conductivity with the Smith correction (second expression in parenthesis):

\[
\sigma(\omega) = \frac{ne^2\tau/m}{1 + \omega^2\tau^2} \left[ 1 + \frac{c(1 - \omega^2\tau^2)}{1 + \omega^2\tau^2} \right],
\]

where \( n, m, \) and \( \tau \) are the effective density, mass, and relaxation time of electrons, respectively, and \( c \) is the fitting parameter expressing a fraction of the electrons’ original velocity that is retained after electron-scattering events.

![Figure 2](image-url)

**Figure 2.** Real \( \sigma' \) and imaginary \( \sigma'' \) parts of the complex conductivity for (a) graphene+PET and (b) SWCNTs+PFO thin films. Black lines represent the Drude–Smith model fits [see Eq. (2)].
We note that for both carbon nanostructures, $\sigma''$ are negative and best fits shown in figures 2a and 2b correspond to $c \approx -1$, which indicates virtually complete elastic backscattering of electrons with relaxation times $\tau$ equal to 21 fs and 11 fs, for graphene and SWCNTs, respectively. A likely explanation is that carriers are fully localized within a given nanostructure and can freely move only inside the nano-carbon material.

4. Conclusions
Our results demonstrate that THz-frequency dielectric properties of nanocarbon-embedded polymer nanocomposites are sensitive to their nanocarbon forms, i.e., graphene nanoflakes or SWCNTs. In both tested samples, we have observed an enhanced index of refraction, as compared to pure polymer references; the effect was particularly large in the SWCNT+PFO sample. Complex conductivity spectra of both sample types exhibited the negative imaginary part and the $\sigma(\omega)$ experimental results could be very well fitted with a simple Drude–Smith model, indicating a total confinement of electrons inside localized carbon nanostructures with the femtosecond-range backscattering of carriers. A direct comparison of transmitted THz spectra of the test and reference samples enabled us to analyze frequency-dependent complex conductivity without resorting to Kramers–Kronig relations.

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