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Mini-Review Article

Perspective on Transient THz Spectroscopy Characterisation of Carbon Nanotubes

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Abstract

Transient terahertz (THz) spectroscopy is a powerful non-contact, non-destructive technique for analysis of the photoinduced electronic properties of carbon nanotubes (CNTs). This technique allows measuring the photoinduced changes of the frequency-dependent conductivity (photoconductivity) with a picosecond timescale. Thus, it makes this technique suitable for ultrafast processes occuring in the nanotubes. Many important CNT parameters such as mobility, scattering rate, carrier concentration and a the lifetime can be measured accurately using transient THz spectroscopy. The strong many-body interactions inherent in CNT, result in bright, dark excitons, trions coexistence with free charges and can be revealed using this technique. Therefore, in this perspective, we discuss the recent THz photoconductivity studies of CNTs.

Keywords: Nanotubes; transient terahertz spectroscopy; pump-probe; photoconductivity

Introduction

Carbon nanotube (CNT) is a quasi-one-dimensional (1D) material that consists of rolled-up sheets of single-layer carbon atoms (graphene). The interest in this material comes from unique electrical, chemical, thermal, and optical properties due to the curvature and quantum confinement in comparison to two-dimensional (2D) and three-dimensional (3D) materials [1-4]. In addition, a unique band structure results in intraband, interband, intersubband transitions that lead to distinctive optical absorption within the broad range from ultraviolet (UV) to terahertz (THz) [5,6]. THz region (far infrared), on which we will focus, locates between the microwave and middle infrared regions, with a frequency range between 0.1 and 10 THz. Many physical processes such as free charge carrier collision frequency, plasmon resonance frequency, phonon frequencies, excitonic transition frequencies are in this region and correspond to picosecond timescale and can be seen in conductivity spectra and measured by terahertz time-domain spectroscopy (THz-TDS). Meanwhile, it was shown that in the visible and middle infrared regions, bound electron-hole pairs (excitons) are the primary photoproduct in single-walled carbon nanotubes (SWCNTs) even at room temperature. The selective excitation species in optical region result in the response in THz region in the form of photoconductivity and can be revealed by the extension of THz-TDS – transient optical pump - terahertz probe (OPTP) spectroscopy.

The unique properties of CNTs in the THz region compared to bulk materials come from their small size and charge carrier transport localization in the axial direction and percolation network. In addition to non-localized charge carrier response, the slow surface wave propagation (plasmons) along the nanotube axis sensitive to the length of the CNTs are observed [7,8]. Moreover, the conductivity of the films composed of CNTs strongly depends on the number of CNT interconnects and defects, which results in the localization of a charge carrier between two barriers created by these impurities [9]. The density of CNTs in a film becomes important due to the variation of the CNT interconnects and filling factor [9]. The CNT curvature, and therefore, a diameter is also expected to influence the conductivity properties [10]. In addition, the enhancement of the localized many-body interactions is observed in CNTs due to the reduced dielectric constant because of the low dimensionality [11]. The localization of charge carrier in one direction results in one of the most essential properties of 1D materials – anisotropic conductivity response [12].

OPTP is sensitive to many quasiparticles, such as electrons, phonons, and excitons, and suitable to measure their ultrafast dynamics quantitatively. Several OPTP independent investigations based on thin SWCNT films have come to opposite conclusions about the nature of the photoinduced conductivity. One of the first complete studies showed the photoconductivity of two films of pure metallic and semiconducting CNTs [13]. To evaluate the nature of photoinduced conductivity, a variety of wavelengths and photon fluence was used. Impotently, Beard *et al* found that the conductivity and its dynamics are independent of excitation fluence and excitation wavelengths for both films. The magnitude of the THz response was only found to be dependent on the total number of photons absorbed. This observation suggests the highly efficient generation of free charges from the exciton dissociation, which increased the photoinduced response. The influence of the small-gap CNT transitions (the density of states for zig zag metallic nanotubes appeared due to curvature and/or a pseudo-gap in bundles of identical (n, n) CNTs were ruled out due to the low content of metallic nanotubes in semiconducting films and bundles of identical CNTs. In contrast, Perfetti *et al* found an absence of free-carrier response and proposed that the photogenerated changes in THz transmission are caused by bleaching of optical transitions in small-gap CNTs [14]. It was explained as a luck of the negative real part of the dielectric function, which is a clear signature of the free charge carriers. The influence of bright excitons was ruled out as their binding energy exceed the THz probe energies. Moreover, the plasma frequency and Drude scattering rate response to the free-carrier response in the small-gap and metallic CNTs did not change upon excitation. The transient dichroism observed in the experiment proved the existence of spatially delocalised and localised carriers. It is also important to note that in the mentioned study the photoinduced response was investigated between 10 and 30 THz, which is different from the Beard *et al* study (Figure 1).

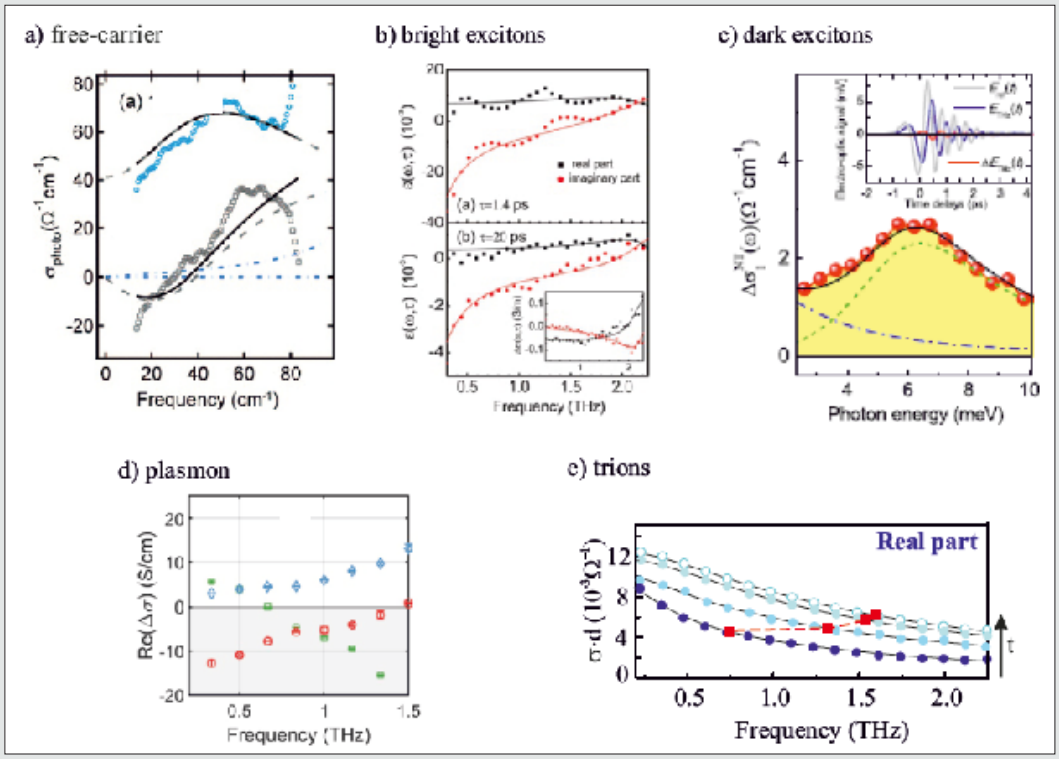

Figure 1: Summary of the THz photoconductivity studies. a) The photoinduced positive change of the THz conductivity 1 ps after the photoexcitation. Reprinted with permission from (13). Copyright (2008) American Chemical Society. Copyright 2008 American Chemical Society.

b) THz complex dielectric function of SWCNTs measured at 1.4 (top left) and 20 ps (bottom left) after excitation at a fluence of 158 μJ/cm^{-2}. Data for varioustime delays in units of picoseconds after excitation (right). Reprinted with permission from (15). Copyright (2009) American Chemical Society.

c) Ultrafast THz spectra of photocondutivity Δσ (left) and dielectric function Δε (right), measured at pump-probe delay 0.5 ps after 1.55 eV pumping. Reprinted with permission from (16). Copyright (2015) by the American Physical Society

d) Photo-induced conductivity due to 800 nm photoexcitation at pump-probe delay time of 1 ps for long (red), medium (green), and short (blue) length CNTs. Reprinted with permission from (20). Copyright (2018) by the American Physical Society.

e) Ultrafast THz spectra of photoconductivity Δσ measured at pump-probe delay 0.5ps after 1.55 eV pumping. Reprinted with permission from (17). Copyright (2015) by the American Physical Society.

To exclude CNT-to-CNT interactions, Xu *et al* investigated the isolated nanotubes in a gelatin matrix [15]. The selective excitation of isolated semiconducting SWCNTs led to transient changes in the THz transmission associated with the intrinsic properties of SWCNTs caused by the excitonic transitions. The results showed that the Auger recombination process occurs at several picoseconds and the excitonic-relaxation process happens in hundreds of picoseconds. In addition, two absorption maxima were clearly observed at about 0.6 and 1.4 THz (2.5 and 5.7 meV) and associated with the formation of exciton complexes such as biexcitons. Luo and co-workers presented another interpretation of the photoinduced conductivity of (6,5) SWCNTs in the THz region-dark excitons accompanied by the free charge formation [16]. Given the high stability of excitons in SWCNTs, such internal transitions located in the THz frequency range are very probable. These transitions are in the order of several to tens of meV depending on the diameter and chirality of nanotubes. This hypothesis was supported by pump photon energy and temperature dependence. They showed that the pump energies resonant to the exciton transition of (6,5) CNT results in the signal roughly three times larger than for signal under off-resonant excitation, which also supported the dark excitonic origins of the THz resonance. The detailed photoconductivity measurement of different length SWCNTs was performed by Karlsen *et al*. [9]. In this article, a novel effect of negative THz photoconductivity (the photoinduced transparency) was observed for long SWCNTs, while shorter nanotubes showed a typical for classical semiconductors positive photoconductivity. To interpret this result, an additional temperature-dependent measurement was performed. The similarity between temperature-dependent measurement and the photoinduced response was attributed to the thermal broadening of the conductivity due to the laser heating. The photoconductivity measurement of $HAuCl_4$-doped SWCNT films was performed by Burdanova *et al* [17]. The authors showed that the increase of the electrical conductivity due to the doping results in suppression of the relative change of the signal. They attributed the negative photoconductivity effect to lowering of the free charge density (or increased mass of free charges), which was ascribed to the formation of trions, and which simultaneously lowered the momentum scattering rate and resulted in narrowing of the conductivity. Kar *et al* reported the THz photoconductivity of SWCNTs and DWCNTs and interpreted the photoconductivity using Boltzmann transport theory for free charges only, ignoring the equilibrium plasmonic contribution [18]. Finally, the anisotropic process has been observed by changing the polarization of the pump (visible) and probe (THz) wave. The observed anisotropy was attributed to ultrafast exciton formation along the axial direction of CNTs.[19, 20].

As seen from the above discussion, numerous effects (that can be contradictory to each other) can be simultaneously observed in OPTP measurements of 1D nanomaterial SWCNTs. The difference in the observed effects is particularly due to the use of different CNT films of various CNT densities, consisting of nanotubes with different morphology, chiralities, lengths, and thus, making interpretation and comparison difficult. A systematic understanding of photoconductivity is required in future experiments. For a more conclusive origin of photoconductivity, the set of samples with the same diameter but different lengths or similar lengths and different diameter? of type-separated SWCNTs are required as well as the detailed temperature and wavelength-dependent measurement.

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