Electromagnetic response of the composites containing chemically modified carbon nanotubes

A M Nemilentsau, M V Shuba, P N D’yachkov, G Ya Slepyan, P P Kuzhir and S A Maksimenko

1 Institute for Nuclear Problems, Belarus State University, Bobruiskaya 11, 220030 Minsk, Belarus
2 Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, Leninskii Prospekt 31, 119991 Moscow, Russia

E-mail: andrei.nemilentsau@gmail.com

Abstract. We demonstrate theoretically that the chemical modification of the bundles and composites containing mixture of semiconducting and metallic single-wall carbon nanotubes (SWNTs) leads to the substantial enhancement of the characteristics of their electromagnetic response in the terahertz (THz) frequency range. Boron and nitrogen doping is used to illustrate the effect. In particular, frequencies of antenna resonances in the bundles containing doped SWNTs are shifted to the blue in comparison to the ones in the bundles containing the same number of pristine SWNTs. Moreover, doping increases the resonant values of the bundles polarizability. Enhancement of the conductivity of the composite containing doped SWNTs is also demonstrated. The origin of the behavior is the metallization of the chemically modified semiconducting SWNTs in the bundles and composites due to the injection of the additional charge carriers.

1. Introduction

It is known that chemical modification of carbon nanotubes can lead to substantial improvement of their electric transport characteristics due to the enrichment by charge carriers [1]. Particularly, appreciable decrease of the dc resistivity has been reported [2] for the boron-doped multi-walled nanotubes. Moreover, increase of the dc electrical conductivity and the metallic to semiconductor nanotubes ratio has been experimentally demonstrated in case of the nitrogen substitutional doping of the composites containing mixture of metallic and semiconductor single-wall carbon nanotubes (SWNTs) [3]. Note that the metallization of semiconducting SWNTs due to nitrogen doping could serve as a tool for percolation threshold reducing in SWNT-based composites; normally this threshold is attained at the pristine SWNT weight concentration of about 1 % [4].

By analogy with the quasi-static regime one can expect that the high-frequency electromagnetic response of carbon nanotubes can also be controlled by the chemical modification. The enhancement of the terahertz electromagnetic response of SWNT bundles and composites is of particular interest due to the rapid progress in the field of the terahertz imaging and sensing [5]. The SWNT-based terahertz detectors have already been demonstrated experimentally [6, 7]. Metallic SWNT antennas [8, 9, 10, 11] can be utilized for the terahertz radiation manipulation as they are predicted to possess antenna resonances in the frequency rage.
from 1 to 30 THz [9]. In contrast, semiconducting SWNTs weakly interact with electromagnetic radiation in this frequency range and therefore are not suitable for terahertz applications. Unfortunately, fabrication of uniform composites containing only metallic SWNTs is still a challenging task [12] and typical SWNT bundles and composites consist of mixtures of metallic and semiconducting SWNTs.

In this work we demonstrate theoretically that SWNTs doping by either boron (B) or nitrogen (N) atoms improve electromagnetic response of bundles and composites comprising mixture of metallic and semiconducting SWNTs. Substitution of carbon atoms in the SWNT crystalline lattice by the third and fifth valence group atoms injects additional charge carriers to the SWNT. Weakly affecting the metallic SWNT conductivity this leads to the semiconductor SWNTs metalization. In its turn, this leads to the enhancement of the antenna efficiency of the bundles and conductivity of the composites comprising chemically modified SWNTs in comparison with the pristine SWNT based bundles and composites.

The paper is organized as follows. The band structures of both pristine and chemically modified SWNTs are presented in section 2. In section 3 we present results of calculations of electromagnetic response of chemically modified SWNT based bundles and composites. Brief conclusions are presented in section 4.

2. Band structure

In order to demonstrate the SWNT doping influence on the SWNT electromagnetic response we restrict our consideration to the case when only a single carbon atom in each unit cell of a SWNT is replaced by the dopant atom (yellow color). (b)-(d) Band structure of (13,0) SWNT in the vicinity of the Fermi level (red line): (b) pristine, (c) N doped, (d) B doped. $c = 3b$ is the SWNT translational vector length, where $b = 1.42$ Å is the interatomic distance in the SWNT.

![Figure 1](image-url)
the augmented cylindrical waves that obtained by matching the solutions of the Schrödinger equation within each muffin-tin sphere with cylindrical-wave solutions in the interstitial region [14]. The Bloch functions expansion coefficients and electron dispersion law are defined by the variational method. We construct augmented cylindrical waves assuming that the electron motion is restricted to the cylindrical layer by two infinitely high cylindrical potential barriers of radii $R_l - 1.38$ Å and $R_l + 1.27$ Å, where $R_l$ is the radius of the SWNT of type $l$. The LACW method has been already successfully implemented to calculate band structure of the pristine SWNTs [15]. Results of calculations of band structures of both pristine and chemically modified (13,0) SWNTs are presented on Fig. 1. As one can see, carbon atoms replacement by N (B) atoms leads to the Fermi energy increasing (decreasing) due to the additional electron (holes) incorporation. As the Fermi level crosses either the conductivity (1c) or the valence band (1d) one can make a conclusion that chemical modification by N and B atoms leads to the metalization of semiconducting SWNT.

3. Electromagnetic response of chemically modified SWNTs

To study electromagnetic wave scattering by SWNT-based bundles and composites we use the integral-equation technique presented earlier for single [9] SWNTs and for bundles [10] of SWNTs. To apply integral equations formalism [9], the linear axial surface conductivity of a SWNT should be calculated first. In the terahertz frequency range the dominant contribution to the SWNT conductivity is provided by the electron intraband motion [16]. Thus, the conductivity of pristine semiconducting SWNTs is negligibly small in comparison with the conductivity of metallic ones and is assumed to be zero in further calculations. To evaluate the axial conductivity of metallic SWNTs and chemically modified semiconducting SWNTs (revealing metallic behavior accordingly to Fig. 1), we use the Drude model of the conductivity[16]. The electron relaxation time for both pristine and doped SWNTs is assumed to be the same since the electron mean-free path corresponding to the scattering on the optical phonons is much less than the mean-free path corresponding to the scattering on impurities [17]. This assumption is in a good agreement with the experimental results [18] on the electromagnetic waves absorption by SWNT-based composites in the THz range: The THz absorption peak width is only slightly affected by the SWNT doping. Further we assume the relaxation time to be equal to $3.3 \times 10^{-14}$ s [19].

As an example, let us consider the electromagnetic response of an approximately cylindrical bundle with the diameter 3.8 nm, containing three (13,0), two (12,0) and two (11,0) SWNTs (further we refer to it as M-bundle). The polarizability spectra of both pristine and N-doped M-bundles of two different lengths $L$ are depicted in Figs. 2a,b. The electromagnetic response of B-doped SWNTs is similar to that of N-doped SWNTs and is not discussed further. As one can see, polarizability spectra of both pristine and doped SWNT bundles contain resonance peaks, the resonance frequency of the doped SWNT bundles being blue-shifted in comparison with the pristine ones. These resonances are the antenna resonances of surface waves in the SWNT bundle. The angular resonance frequency $\omega$ is defined by the condition [9]

$$L\omega = \pi c(2s - 1)\text{Re} \beta,$$

where $s$ is an integer and $c$ is the speed of light in the vacuum. In single SWNT the slow-wave coefficient $\text{Re} \beta$ can be as small as [16] $\text{Re} \beta \approx 0.01$. However, in the bundle the slow-wave coefficient is increased due to the electromagnetic interaction of the metallic SWNTs [10] resulting in the resonance frequency blue shift in comparison to the single SWNT resonance frequency. In its turn, the doping-caused metallization of semiconducting SWNTs in the M-bundle increases the number of metallic SWNTs in the bundle in comparison to the pristine SWNT bundle and thus leads to the additional resonance frequency blue-shift.
Figure 2. Frequency dependence of the imaginary part of polarizability of SWNT bundle comprising three (13,0), two (12,0) and two (11,0) SWNTs before (solid line) and after (dashed line) the SWNTs chemical modification by the nitrogen atoms (Fig. 1). SWNTs length in the bundle is equal to (a) $L = 1000$ nm and (b) $L = 200$ nm. Doped SWNTs contain approximately 2 percent of nitrogen impurities.

Let us now consider a dilute composite material comprising different types of randomly dispersed and oriented SWNTs in the matrix with dielectric permeability close to 1. The distribution function $N_\ell(L)$ describes the number of SWNTs of type $\ell$ and length $L$ per unit volume. All orientations are equiprobable, and $f$ denotes the volume fraction occupied by the SWNTs (conceived as cylinders of volume $\pi R^2 L$). To calculate the effective conductivity $\sigma_{eff}(\omega)$ of the composite material in case when $L \ll \lambda$, where $\lambda = 2\pi/k$ is the free-space wavelength, we use the simple Waterman-Truell formula \[ \sigma_{eff}(\omega) \approx \frac{\omega}{4i\pi} \left[ 1 + \frac{4\pi f}{3} \sum_\ell \int_0^\infty \alpha_\ell(\omega, L) N_\ell(L) dL \right], \] \[ (2) \]

where $\alpha_\ell(\omega, L)$ is the polarizability of an isolated SWNT calculated using the integral-equation technique [9].

We calculate the conductivity of the composite containing SWNTs of length $L = 1000$ nm of three different chiralities (with chiral vectors (11,0), (12,0), (13,0)). For simplicity we assume that the number of SWNTs of different types in the composite is the same. Terahertz peak in the conductivity spectrum of undoped SWNT composite depicted on Fig. 3(a) is due to the antenna resonance in the metallic (12,0) SWNTs. The nitrogen doping leads to the substantial enhancement of the conductivity of semiconducting (11,0) and (13,0) SWNTs while the conductivity of the (12,0) metallic SWNT changes only slightly. As a result, the antenna resonances emerge also in semiconducting SWNTs and the effective composite conductivity is increased over the whole low-frequency range, as shown in Fig. 3(a). It should be noted, that doping of the composite containing isolated SWNTs leads to the increase of the resonant peak amplitude and width while the resonance frequency remains practically unchanged. Similar behavior of the terahertz conductivity peak for SWNT-based composite doped by the tetrafluorotetracyanoquinodimethane is observed experimentally in Ref. [18].
Figure 3. Frequency dependence of conductivity $\text{Re}(\sigma_{eff})$ of the SWNT-based composite, containing (a) (11,0), (12,0), (13,0) SWNTs and (b) M-bundles (Fig. 2) before (solid line) and after (dashed line) doping. $L = 1000$ nm. Doped SWNTs contain approximately 2 percent of nitrogen impurities. $f = 0.005$.

Conductivity frequency dependence of the composite containing identical M-bundles (Fig. 3) is presented on Fig. 3(b). In this case doping not only increases the resonant peak amplitude but also shifts to the blue the low-frequency resonance in correspondence with the blue-shift of the resonance frequency of the single bundle polarizability (Fig. 2(a)).

4. Conclusions
Concluding, we demonstrate theoretically that the chemical modification of the bundles and composites containing mixture of the semiconducting and metallic SWNTs is an efficient way of the control of their electromagnetic response in the terahertz frequency range. In particular, in CNT bundles we predict the doping-caused increase of the antenna resonance frequency and amplitude. The enhancement of the conductivity of the doped SWNT composites resulting in the improvement of the absorbance and reflectance of the SWNT-based samples has also been demonstrated. Extrapolating these results to the microwave range, we can propose doping as a tool for the enhancement of the electromagnetic shielding of composite materials with embedded SWNTs and nanotube bundles.

Acknowledgments
This research was partially supported by the IB BMBF (Germany) under project BLR 08/001, EU FP7 CACOMEL project FP7-247007, ISTC project B-1708, and NATO Collaborative Linkage Grant (Reference No. CBP. EAP.CLG983910). The work of A. M. N. was supported by the BRFFR (Belarus) young scientists grant F09M-071. The work of P. N. D. was supported by the RBRF (Russia) grant 08-03-00262.

References
[1] Lee R S, Kim H J, Fisher J E, Lefebvre J, Radosavljevic M, Hone J and Johnson A T 2000 Phys. Rev. B 61 4526
[2] Ishii S, Watanabe T, Ueda S, Tsuda S, Yamaguchi T and Takano Y 2008 Appl. Phys. Lett. 92 202116
[3] Villalpando-Paez F et al 2006 Chem. Phys. Lett. 424 345
[4] Liu L, Matitsine S, Gan Y B, Chen L F, Kong L B and Rozanov K N 2007 Appl. Phys. Lett. 101 094106
[5] Chan W L, Deibel J and Mittleman D M 2007 Rep. Prog. Phys. 70 1325
[6] Fu K, Zannoni R, Chan C, Adams S H, Nicholson J, Polizzi E and Yngvesson K S 2008 Appl. Phys. Lett. 92 033105
[7] Kawano Y, Uchida T and Ishibashi K 2009 Appl. Phys. Lett. 95 083123
[8] Hanson G W 2005 IEEE Trans. Antennas Propag. 53 3426
[9] Slepyan G Ya, Shuba M V, Maksimenko S A and Lakhtakia A 2006 Phys. Rev. B 73 195416
[10] Shuba M V, Maksimenko S A and Lakhtakia A 2007 Phys. Rev. B 76 155407
[11] Rutherglen C and Burke P 2009 Small 5 884
[12] Hersam M C 2008 Nat. Nanotech. 3 387
[13] Ashcroft N W and Mermin N D 1976 Solid State Physics (New York: Holt-Saunders)
[14] D’yachkov P N 2003 Encyclopedia of Nanoscience and Nanotechnology vol 1, ed H.S. Halwa (New York: Am. Sci. Publ.) p 191
[15] D’yachkov P N and Hermann H 2004 J. Appl. Phys. 95 399
[16] Slepyan G Ya, Maksimenko S A, Lakhtakia A, Yevtushenko O and Gusakov A V 1999 Phys. Rev. B 60 17136
[17] Yao Z, Kane C L and Dekker C 2000 Phys. Rev. Lett. 84 2941
[18] Akima N et al 2006 Adv. Mater. 18 1166
[19] Slepyan G Ya, Shuba M V, Maksimenko S A, Thomsen C and Lakhtakia A 2010 Phys. Rev. B 81 205423
[20] Waterman P C and Truell R 1961 J. Math. Phys. 2 512