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Optical Response of Ultrathin Periodically Aligned Single-Wall Carbon Nanotube Films

Chandra M. Adhikari and Igor V. Bondarev

Department of Mathematics & Physics, North Carolina Central University, Durham, NC 27707, U.S.A.

ABSTRACT

We present a semi-analytical expression for the dielectric response function of quasi-2D ultrathin films of periodically aligned single-walled carbon nanotubes. We derive the response function in terms of the individual nanotube conductivity, plasma frequency, and the volume fraction of carbon nanotubes in the film. The real part of the dielectric response function is negative for a sufficiently wide range of the incident photon energy, indicating that the film behaves as a hyperbolic metamaterial. Inhomogeneous broadening increases the effect.

INTRODUCTION

The study of the response functions of parallel aligned carbon nanotube (CNT) films is of great interest. Finite-thickness films of aligned single-wall CNTs (SWCNT) were recently shown experimentally to exhibit extraordinary optoplasmonic properties such as a tuneable negative dielectric response [1], which makes them a promising candidate for the development of a new family of highly anisotropic hyperbolic metamaterials (HMMs) [2]. To explain and help with the interpretation of these observations, we hereby present our theoretical study of the response functions for planar periodic quasi-2D arrays of identical SWCNTs.

We consider a homogeneous quasi-2D array of parallel aligned, identical SWCNTs immersed in a finite-thickness dielectric medium of static relative dielectric permittivity ϵ sandwiched between a substrate and a superstrate of relative permittivities ϵ_1 and ϵ_2 as shown in the inset of Fig.1 (a) below. The CNTs are aligned along the y-axis

with the intertube center-to-center distance Δ. The electron charge density is distributed uniformly all over the periodic cylindrical nanotube surfaces, whereby the pairwise electron Coulomb interaction in the system of CNTs embedded in a dielectric layer of thickness d, can be approximated by that of two uniformly charged rings of radius R of the respective n-th and l-th tubules [3]. An interesting thing occurs when $\epsilon_1 + \epsilon_2 << \epsilon$ and $d << \rho$, where ρ is the distance between the rings of the unit cells of the n-th and l-th nanotubes. Then the Coulomb interaction between the rings loses the dependence on the vertical coordinate component (for the geometry we choose this is the z-component) [4]. Thereby the vertical confinement leads to the reduction of the effective dimensionality from three to two while still retaining the thickness d as a parameter to represent the vertical size of the system [3-6].

Here, we start with the conductivity calculation for an individual SWCNT using the ($\boldsymbol{k}\cdot\boldsymbol{p}$)-method of band structure calculations [7]. Then we use the low-energy plasmonic response calculation technique proposed by one of us for finite-thickness metallic films with periodic cylindrical anisotropy [3], combined with the many-particle Green's function formalism as discussed in Ref. [8], to derive a semi-analytical expression for the dynamical dielectric response tensor of an ultrathin finite-thickness periodically aligned SWCNT array. We also study array inhomogeneity effects using the Maxwell-Garnett (MG) method [9] to obtain the optical response for an important practical case of inhomogeneous arrays with narrow CNT diameter distributions.

THEORY

Absorption of a photon excites an electron from the valence to conduction band of a CNT to create an exciton, thereby producing an induced polarization along the CNT axis. We here focus our study on the dielectric response due to the collective polarization resulting from the induced dipole-dipole coupling between individual CNTs in a periodic array. Following Ref. [8], we start with the total Hamiltonian of the system in the wave-vector space written as

$$H = H_0 + H_{\text{int}}, \tag{1}$$

where H_0 is the unperturbed Hamiltonian of the system of noninteracting CNTs,

$$H_0 = \sum_{E,\boldsymbol{k}} \hbar\omega_E b^{\dagger}_{E,\boldsymbol{k}} b_{E,\boldsymbol{k}} \ , \tag{2}$$

and H_{int} is the perturbation to the system that comes through the interaction between different excitations E and E' of the CNT array components, the nanotubes. Here, we assume that the CNTs can "talk to each other" through the induced dipole-dipole interaction, or in other words, an exciton in a CNT can excite the other exciton of a neighboring CNT due to the dipole-dipole interaction. In equation (2), $\hbar\omega_E$ is the excitation energy for an excitation E of the CNT array. The excitation creation and annihilation operators follow the Bose commutation relations

$$[b_{E,\boldsymbol{k}}, b^{\dagger}_{E'\boldsymbol{k}'}] = \delta_{EE'}\delta_{\boldsymbol{k}\boldsymbol{k}'}, \ [b_{E,\boldsymbol{k}}, b_{E',\boldsymbol{k}'}] = [b^{\dagger}_{E,\boldsymbol{k}}, b^{\dagger}_{E'\boldsymbol{k}'}] = 0 \tag{3}$$

Let $\boldsymbol{\rho}_n$ denote the position vector for the center of a unit cell ring of the n-th CNT; see the inset in Fig.1 (a). The Coulomb interaction between two such rings of the array is given by [3]

$$V(\boldsymbol{\rho}_n - \boldsymbol{\rho}'_\ell) = \frac{m^*}{LL_\perp N_{2D}} \sum_{\boldsymbol{k}}{}' \left(\frac{\omega_p(k)}{k} \right)^2 \exp\left[\mathrm{i}\boldsymbol{k} \cdot (\boldsymbol{\rho}_n - \boldsymbol{\rho}'_\ell) \right], \quad (4)$$

where N_{2D} is the electron surface density, m^* is the electron effective mass, L is the CNT length, and $L_\perp$ is the width of the film. The prime in the summation sign indicates that the $\boldsymbol{\rho}_n \neq \boldsymbol{\rho}'_\ell$ terms (self-interaction) and the $\boldsymbol{k} = 0$ term associated with electron displacement of the entire system, must be excluded. The wave vector $\boldsymbol{k}$ lays in the x-y plane and can be resolved into two components, $\boldsymbol{k} = \boldsymbol{q} + \boldsymbol{k}_\perp$ with $\boldsymbol{q}$ and $\boldsymbol{k}_\perp$ being, respectively, parallel and perpendicular to the CNT alignment direction. It is then evident that $k = (q^2 + k_\perp{}^2)^{1/2}$, where $k_\perp = 2\pi n_x / L_\perp$ with $n_x = 0, \pm 1, \pm 2, \ldots, \pm N_\perp / 2$ where $N_\perp$ stands for the total number of CNTs of radius R. In equation (4), $\omega_p(k)$ is the plasma frequency of the array which can be written in terms of the zeroth-order modified cylindrical Bessel functions $I_0(qR)$ and $K_0(qR)$ as follows [3]

$$\omega_p(k) = \omega_p(q, k_\perp) = \sqrt{\frac{4\pi e^2 N_{2D}}{\epsilon m^* d} \frac{2qRI_0(qR)K_0(qR)}{1 + (\epsilon_1 + \epsilon_2) \Big/ \epsilon d\sqrt{q^2 + k_\perp^2}}} \quad . \quad (5)$$

It is customary to assume that $\boldsymbol{r}_j = \boldsymbol{\rho}_j + \boldsymbol{x}_j$ is the new position of the unit cell of the j-th CNT due to the displacement $\boldsymbol{x}_j$ induced by an electronic excitation (exciton) created by the external radiation. Then, the Coulomb interaction in Eq. (4) generates the intertube polarization interaction due to the induced dipole-dipole coupling between the individual CNTs in the array. This comes from the series expansion in infinitesimally small displacements in the way identical to that presented in Ref. [8] for a 3D array of polarizable molecules. If $a = L/N$ and $\Delta = L_\perp / N_\perp$ are the translational period along the CNT axis and the intertube center-to-center distance, respectively, then in full analogy with the periodic polarizable molecule array the intertube interaction Hamiltonian in Eq.(1) take the following form

$$H_{\mathrm{int}} = \frac{1}{a\Delta} \sum_{q,E,E'} V_{EE'}(q) \left(b_{E,q} + b^\dagger_{E,-q} \right) \left(b_{E',q} + b^\dagger_{E',-q} \right) \quad (6)$$

Here

$$V_{EE'}(q) = \frac{m^* \omega_p^2(q,0)}{N_{2D}} X(E)\, T_{yy}(q,0)\, X(E') \,, \quad (7)$$

is the interaction matrix element, in which $\omega_p(q,0)$ stands for the plasmon frequency of Eq. (5) taken at $k_\perp = 0$. The second rank tensor $T_{yy}(q,0)$ represents the Fourier transform of the induced dipole-dipole interaction between the neighboring CNTs in the geometry sketched in the inset of Fig.1 (a). The quantity $X(E)$ is the transition dipole between the lower and upper states associated with an excitation E (exciton). In deriving Eqs. (6) and (7) we have used an obvious fact that a CNT is excited when any of its rings is displaced

to induce the longitudinal polarization (along the CNT axis) while the perpendicular polarization, if any, can be neglected due to the transverse depolarization effect [7].

To derive the dielectric response function of the CNT film, we follow the procedure similar to that presented in Ref. [8] for the array of polarizable molecules. The derivation begins with the calculation of the frequency-dependent correlation function of the polarization operator $P_{yy}(\mathrm{i}x)$ of the array of CNTs in the presence of the interaction H_{int}. Here we use x to denote the (dimensionless) energy expressed units of $2\gamma_0 = 5.4$ eV, the carbon nearest-neighbor overlap integral. The Dyson series summation can be done exactly in view of the fact that the higher order Green function expansion terms are just the multiples of the self-energy term $T_{yy}(q,0)/(a\Delta)$. Then the dielectric response functions are calculated using their relationship with the polarization obtained [10]. This gives the longitudinal component of the film dielectric response as follows

$$\frac{\varepsilon_{\|}(q,\mathrm{i}x)}{\epsilon} = 1 + \frac{4\pi}{a\Delta} P_{yy}(\mathrm{i}x) = 1 - \frac{8\pi f_{\mathrm{CN}}\,\overline{\sigma}_{yy}(\mathrm{i}x)}{f_{\mathrm{CN}}\,\overline{\sigma}_{yy}(\mathrm{i}x) + \epsilon\,\dfrac{2\gamma_0 R}{e^2}\left(\dfrac{\omega_p^{3D}}{\omega_p(q,0)}\right)^2 x}. \quad (8)$$

Here, $\overline{\sigma}_{yy}(\mathrm{i}x)$ is the individual CNT complex conductivity (dimensionless, in units of $e^2/2\pi\hbar$) as a function of the dimensionless energy, $f_{\mathrm{CN}} = N_{\perp} V_{\mathrm{CN}}/V = \pi R^2/d\Delta$ is the ratio of the volume occupied by the CNTs to the total volume V ($=LL_{\perp}d$) of the film, and $\omega_p^{3\mathrm{D}} = \lim_{d\to\infty} \omega_p^{3\mathrm{D}}(q,0)$. The thermal averaging of Eq. (8) over q can further be done as

$$\varepsilon_{\|}(T,\mathrm{i}x) = \sum_q f_{ex}(q,T)\ \varepsilon_{\|}(q,\mathrm{i}x) \quad (9)$$

with $f_{ex}(q,T)$ being the 1D normalized Boltzmann distribution of excitons [11], to obtain the room-temperature longitudinal response energy dependence for the CNT array. The perpendicular component of the dielectric response remains equal to the static dielectric permittivity ϵ of the embedding medium, making the CNT film a dielectric in the direction perpendicular to the CNT alignment.

DISCUSSION

A qualitative analysis can be helpful for a better understanding of the semi-analytical dielectric response expression in Eq.(8) presented in the previous section. One can see from Eq.(5) that $\omega_p(q,0)$, the key ingredient of Eq.(8), tends to zero due to the properties of the modified Bessel functions when the minimal possible q ($=2\pi/L$) approaches zero with increasing L, the length of the CNT array component. Thus, the longitudinal response of the film depends on L and decreases in absolute value as L increases. Being controlled by the induced longitudinal polarization through σ_{yy} in Eq.(8), the response of the film in the CNT alignment direction can be typical of the metallic or semiconducting SWCNT response depending on the nanotube type the array is composed of. No induced polarization and no plasma oscillations occur in the direction perpendicular to the CNT alignment within our theoretical model, making the film behave as a pure dielectric in this direction. Such a behavior is consistent both with that of a film of metallic cylinders discussed in Ref. [3] and with earlier experimental observations [12-14].

The intertube center-to-center distance Δ and the thickness of the film d also play crucial roles in defining the dielectric response properties of the CNT composite

film. For example, since $d,\Delta \geq 2R$, the parameter f_{CN} falls in the range $0 < f_{CN} \leq \pi/4$, i.e. always less than unity. Therefore, even for $d=2R=\Delta$ the screening effect of the dielectric background the array is embedded in will still be present. Increasing the thickness of the film or the intertube distance will increase the background screening effect. This will broaden both CNT exciton absorption peaks and plasmon modes, which are represented by Im $\varepsilon_{\|}$ and by $-\mathrm{Im}(1/\varepsilon_{\|})$, respectively, to make them overlap and thus provide the exciton-plasmon coupling effect. Earlier quasiclassical electromagnetic response theories have already demonstrated similar effects [15-17], though within the effective medium approach (known to be of limited validity at short intertube separations in closely packed CNT arrays) and for high-energy plasmonic bands ~6 eV (bulk graphite plasmon). The low-energy ~1−2 eV exciton-plasmon response and associated phenomena were studied for individual SWCNTs recently [18-22,11]. Our theory here is capable of doing such an analysis for closely packed SWCNT films, which we will present separately elsewhere.

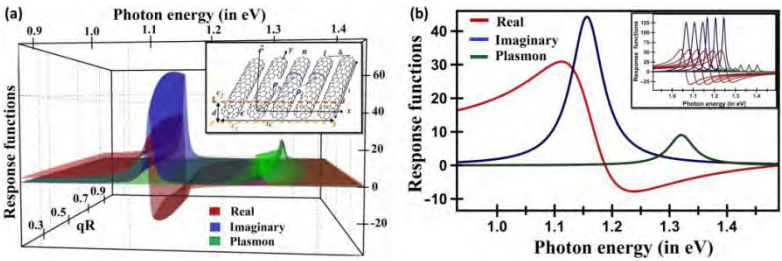

Figure 1. The longitudinal component of dielectric response functions of an ultrathin film of CNTs in air. The relative static permittivity of the medium, in which the CNTs are embedded, is taken to be ϵ =10. In panel (a), the first resonance peaks are shown for the exciton and interband plasmon resonances of quasi-2D array of the periodically aligned (11,0) CNTs. The inset sketches the geometry of the system under consideration and the notations for parameters used in our model. Panel (b) shows the thermal average of the response functions for an ultrathin film made up of a mixture of the (9,1), (10,0), (10,1), (11,0), (12,1), and (12,2) CNT arrays. The CNT arrays are mixed using the MG method by assigning different weights to each CNT array such that the total weight is equal to unity. The resonance peaks of the individual CNT arrays making the mixture are shown in the inset.

For an illustrative purpose, we now apply Eq.(8) to obtain the longitudinal dielectric response $\varepsilon_{\|}(q,ix)$ for an array of zigzag (11,0) CNTs standing in air. We take a nominal value of ϵ =10 for the screening background dielectric constant of the film. For comparison, a 100 nm thick film of titanium nitride standing in air has the background dielectric constant ≈7.8 and that deposited on a silicon substrate has the background dielectric constant ≈50 (see, e.g., Ref. [23]). Different background dielectric constant values reflect the differences in the Coulomb screening for the thin films immersed in different surroundings [5]. The radius of the (11,0) CNT is $R=11b/\pi$, where b=1.42 Å is the C-C nearest neighbor distance, to give the minimum thickness d_{min} ≈1 nm (=2R) of the (11,0) CNT film. The zigzag CNT translational period is $a=3b/2$ so that $a/R=3\pi/22$. The quantity γ_0/e^2=1.874 nm^{-1} and so the dimensionless parameter $\gamma_0 R/e^2$ in Eq.(8) is of the order of unity for the (11,0) CNT. We choose $d=20R$ for the thickness of the film. With this

choice, the thickness of the CNT (11,0) film is about 10 nm. Assuming the tight packing of the CNTs, we have $\Delta = 2R$ to give the fractional density parameter $f_{CN} = \pi/40$.

The graphs calculated from Eq. (8) with these parameters for the low-energy photon window are shown in Fig.1 (a). The inset sketches the geometry of the system. Presented in the figure are $\mathrm{Re}\,\varepsilon_{\|}$ (the first refraction band), the first exciton absorption resonance given by $\mathrm{Im}\,\varepsilon_{\|}$, and the first interband plasmon resonance given by $-\mathrm{Im}(1/\varepsilon_{\|})$. One can see how these response functions vary with the photon energy (expressed in eV) and wave vector q near the first exciton resonance of the semiconducting (11,0) CNT. The real part of the dielectric response function is negative for a sufficiently broad range of the photon energy. The plasmon resonance approaches the exciton absorption peak as q decreases. These features indicate that CNT films are good candidates for the development of a new family of advanced metamaterials.

Figure 1 (b) shows the response functions $\mathrm{Re}\,\varepsilon_{\|}$, $\mathrm{Im}\,\varepsilon_{\|}$, and $-\mathrm{Im}(1/\varepsilon_{\|})$ for the film made up of a mixture of (9,1), (10,0), (10,1), (11,0), (12,1) and (12,2) CNT arrays mixed at percentage 8%, 12%, 35%, 25%, 12%, 8%, respectively. The dielectric responses of these half-dozen CNT arrays with different chiralities and very close diameters of about 1 nm are first thermally averaged over q and then mixed using the MG method [9] to obtain the dielectric response of the room-temperature (300 K) mixed film. The inset in Fig.1 (b) shows the individual CNT responses. One can see a strong inhomogeneous broadening of the exciton and plasmon resonances in the mixture as compared to the individual CNT arrays. The broaden plasmon resonance overlaps with the broadened exciton resonance, thereby making the exciton-plasmon coupling possible. We believe that the CNT film dielectric response spectra reported in Ref. [1] come most likely from the inhomogeneous broadening similar to that shown Fig.1 (b).

CONCLUSIONS

In this paper, we use the low-energy plasmonic response calculation technique combined with the many-particle Green's function formalism to derive a semi-analytical expression for the dynamical dielectric response of an ultrathin finite-thickness CNT film made of a periodically aligned SWCNT array embedded in a dielectric layer sandwiched between a substrate and a superstrate. The expression we derive links the CNT film dielectric response tensor to the complex axial conductivity of an individual SWCNT and the plasma frequency of an aligned periodic SWCNT array. The SWCNT conductivity can be calculated using the ($\boldsymbol{k}\cdot\boldsymbol{p}$)-method of the band structure theory or by other means.

We show that the film dielectric response can be controlled by the volume fraction of CNTs, which can be done not only by varying the CNT content but also by simply varying the thickness of the dielectric layer. For homogeneous single-CNT films, the real part of the dielectric response function is negative for a sufficiently wide range of the incident photon energy (negative refraction band), indicating that the film behaves as a hyperbolic metamaterial.

We also study the array inhomogeneity effects using the MG mixing method to obtain the optical response for a practical case of inhomogeneous CNT films composed of homogeneous single-CNT arrays with a narrow CNT diameter distribution. We show that the inhomogeneous broadening of the exciton and plasmon resonances leads to their overlap, making the exciton-plasmon coupling and associated hybridization possible, which expands the negative refraction band of the composite CNT film as compared to that of the homogeneous CNT array.

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