Ab initio investigation of optical properties in triangular graphene - boron nitride core-shell nanostructures

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Abstract

We calculate the optical properties of atomic-sized core-shell graphene - boron nitride nanoflakes with triangular shaped crosssection using the density functional theory. The optical properties can be tuned by using different sizes and proportions of the core-shell materials. Anisotropic effects manifested in the absorption of unpolarized light with different orientations of the optical vector are pointed out.

Keywords: density functional theory, core-shell nanostructures, absorption coefficient.

1 Introduction

A lot of effort has been dedicated recently, both theoretically and experimentally, for the study of core-shell nanostructures. Examples of this kind are core-shell nanowires and nanoparticles \cite{1,2} which are the building blocks of numerous promising applications. Tuning the optical properties by controlling the band gap is a great challenge since attention should also be directed to avoid the interfacial defects and stress which may occur due to lattice mismatches between the two materials \cite{3}.

Graphene is a remarkable material that has enjoyed numerous studies in the recent years, due to the special optical, electrical and mechanical properties. One way to control the band gap is to resort to lower dimensional systems or of finite size, such as quasi one-dimensional nanoribbons \cite{4} and nanoflakes \cite{5}. Another approach is to create heterostructures with graphene on top of a boron nitride substrate. Taking advantage of the similarity between the atomic
structure of graphene and of the hexagonal boron nitride (hBN), with a lattice mismatch of only 2%, hybrid graphene-hBN heterostructures have been synthesised using chemical vapor deposition [6].

In this paper we investigate the optical properties of core-shell graphene-hBN nanoflakes. Using density functional theory calculations we determine the complex dielectric function and the other optical quantities of interest such as the absorption coefficient and refraction index. Our goal is to characterize the gap opening and the optical properties by adjusting the core-shell ratios. In addition, we point out anisotropic properties of the system by modifying the orientation of the optical vector.

2 Model and Method

We consider triangular graphene-hBN structures of different sizes as depicted in Fig. 1. The graphene cores are surrounded by hBN shell layers, which are hydrogen passivated. We label this class of systems by G-BN. By exchanging the graphene with hBN we obtain similar, but complementary structures, which we call BN-G.

Figure 1: Graphene-hBN core-shell nanoflakes of different sizes: 54 (L4), 88 (L6), 130 (L8) and 180 (L10) atoms. The edges are hydrogen passivated. These nanoflakes are of G-BN type.

The ab initio calculations are performed using the SIESTA package [7] and the approach is based on the Khon-Sham self-consistent density functional theory in the local density approximation (LDA). The nanoflakes are placed in a cubic super-lattice of linear size 40\(a_0\), where \(a_0 = 1.42\text{Å}\) is the distance between two Carbon atoms in graphene, so that they do not interact for all the considered sizes. For the structural relaxations we considered a double zeta polarized (DZP) basis set and a real space grid cutoff of 100 Ry. The equilibrium configurations were obtained for residual forces less than 0.04 eV/Å.

The optical properties are calculated for unpolarized light for a given direction of the optical vector, chosen in-plane, in (100) and (010) directions, and
perpendicular to the plane (001). The complex dielectric function \( \epsilon(\omega) \) is calculated and the other optical quantities are extracted: absorption coefficient \( \alpha \), reflectance, refractive index \( \tilde{n} = n + ik \) and optical conductivity \( \sigma(\omega) \) using the relation \( \epsilon(\omega) = \epsilon_0 + \frac{i\sigma(\omega)}{\omega} \), where \( \epsilon_0 \) is the vacuum permittivity.

3 Results and Discussion

Despite being one atom thick the graphene monolayers absorb a rather large 2.3% intensity of the visible light. The investigated core-shell nanoflake systems are a mixture of graphene, which is a highly conductive material, and hexagonal boron nitride, which is a wide band gap semiconductor. Therefore mixed optical properties are expected. Figure 2 shows optical spectra of G-BN structures of different sizes for unpolarized light, with optical vector on the (100) direction. Although the systems have rather small sizes, the optical properties are rather similar to those of the constituent bulk systems. Several features can be identified, which originate in the pristine infinite graphene and hBN systems. If the optical vector is perpendicular to the pristine graphene plane one observes a narrow peak at \( \sim 4 \) eV, which corresponds to the \( \pi - \pi^* \) interband transition and a broader peak, with a prominent absorption at \( \sim 14 \) eV associated to the \( \sigma - \sigma^* \). For polarized light with the electric field perpendicular to the 2D plane, two peaks are observed in the high energy range at about 11 and 14 eV, corresponding to \( \pi - \sigma^* \) and \( \sigma - \pi^* \). Using unpolarized light with optical vector (100) we obtain contributions from both sets of transitions [8, 9, 10, 11].
By changing the core-shell ratios, the band gaps of the systems can be tuned. In Fig. 3 the absorption coefficient and the eigenvalue spectra are plotted for 6 structures, which gradually change from a pristine graphene nanoflake [Fig. 3(c)] to a hBN nanoflake [Fig. 3(d)]. As before, unpolarized light is considered, with the optical vector in the (100) direction. For the pure hBN system a gap in the eigenvalue spectrum of $\sim 5$ eV is obtained. By introducing core or shell graphene layers, this gap is reduced. In fact, in these systems the Fermi level crosses small groups of states separated by mini-gaps, which are responsible for the weak absorption in the low frequency range. The change is gradual and the features stemming from both materials are visible.

Figure 3: Absorption coefficient $\alpha$ and eigenvalue spectra for different core-shell ratios. The Fermi energy is marked by the horizontal dashed line.

Next, we performed calculations on the G-BN L4 system by changing the orientation of the optical vector of unpolarized light, in-plane and perpendicular on the 2D surface. In Fig. 4 the anisotropic effects can be pointed out by

Figure 4: Anisotropic effects introduced by unpolarized light with optical vectors with different orientations. The insets contain similar data for the infinite layers of graphene and hBN.
changing the orientation of the optical vectors. A larger absorption coefficient is obtained for the (001) optical vector, while the in-plane orientations are mostly equivalent. Although the core-shell system is rather small, a connection with the absorption spectra of graphene and hBN pristine systems can still be observed.

4 Conclusions

In summary, we have carried out ab initio calculation of optical properties for core-shell nanoflakes triangular cross-section in the framework of density functional theory using the SIESTA software [7]. Our results indicate the possibility of changing the optical properties with increasing the system size or composition. Moreover, the absorption coefficient can be changed by adjusting the proportions of the core-shell materials of different band gaps, i.e. graphene and hBN. Since graphene displays a zero band gap, by introducing BN either as core or shell material, the nanoflakes present a gradual increase of the gap. Anisotropic effects are pointed out in the case of unpolarized light, by changing the orientation of the optical vector for the core-shell system, in-plane and perpendicular.

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