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Investigation of boron modified graphene nanostructures; optoelectronic properties of graphene nanoparticles and transport properties of graphene nanosheets

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ABSTRACT

In this work we investigated optoelectronic properties of graphene nanoparticles and transport properties of graphene nanosheets and the consequences on these properties after modifications with boron atoms. Within the framework of density functional theory (DFT) several important optoelectronic quantities have been calculated for graphene nanoparticles: oxidation and reduction potentials, hole and electron reorganization energies, while thermally activated delayed fluorescence was assessed by calculations of energy separation between the lowest excited singlet (S1) and triplet (T1) state, $\Delta E(S_1 - T_1)$. Obtained results show that optoelectronic properties of graphene nanoparticles are significantly improved by the modification with boron atoms and that investigated structures can be considered as a promising organic light emitting diode (OLED) materials. Influence of boron atoms to charge and heat transport properties of graphene nanosheets was investigated as well, employing the self-consistent non-equilibrium Green's functions with DFT. On the other side it is shown that charge transport of graphene nanosheets is not influenced by the introduction of boron atoms, while influence to the phonon subsystem is minimal.

1. Introduction

Graphene represents a one-atom-thick carbon sheet where carbon atoms are arranged in a two dimensional array, having the same structure as the carbons in the planes of graphite [1,2]. Thanks to its specific structure it possesses some outstanding properties because of which it is expected to be applied in many scientific fields. Thanks to many theoretical and experimental studies for graphene is expected to be the basis of modern nanoelectronic devices [1,3–6].

One of the most striking properties of graphene is the fact that its electrons behave like massless relativistic Fermions, because of which they can move through the lattice many times faster than in present day silicon devices [2,7]. This has led to the fabrication of single field effect transistors [8], while further efforts are made in order to determine the suitable procedures for their large scale and low cost production.

The search for effective organic light-emitting diodes (OLED) and light-emitting electrochemical cells (LEEC) have been significantly intensified during the past decades. As expected, important results have been accomplished, yet with the increasing use of OLED, production cost has become an important factor. Therefore, it is an imperative to find an alternative procedure for the development of efficient OLED and LEEC based on less expensive materials. In order to assess the potential of the certain molecular structure as an efficient OLED material it is very useful to quantify the crucial parameter that determines the effectiveness of the thermally activated delayed fluorescence (TADF) – the energy separation between the lowest excited singlet (S1) and triplet (T1) state, $\Delta E(S_1 - T_1)$. If $\Delta E(S_1 - T_1)$ has suitably low value, then the singlet state S1 can be populated thermally at ambient temperature from the energetically lower-lying triplet state. This process consequences in the, so called, TADF. If $\Delta E(S_1 - T_1)$ is larger than ca. 3×10^3 cm^{-1} (or 0.37 eV) a thermal population of the singlet state S1 is not effective [9,10].

High charge mobilities and efficient charge injection are the main prerequisites for the production of efficient electronic devices and materials [11]. At room temperatures, related to the charge transport, the most important mechanism is hopping mechanism. In this regard the main quantity that regulates the charge carrier mobility is charge hopping rate, k_{ET}. This quantity represents the rate constant or the hopping rate for charge transport

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between adjacent molecules and in the framework of Marcus theory it can be expressed as [12,13]:

$$k_{ET} = \frac{4\pi^2}{h}\frac{1}{\sqrt{4\pi\lambda k_B T}}t^2 exp\left[\frac{-\lambda}{4 k_B T}\right]. \quad (1)$$

Reorganization energy (λ) and charge transfer integral (or charge coupling, t) principally determine the k_{ET}. While t depends on the mutual orientation of molecules between charge hopping occurs, λ can be treated as one of the fundamental optoelectronic properties regulating the efficiency of electronic material. In order to obtain maximal values of k_{ET}, λ and t should be minimized and maximized, respectively.

Beside reorganization energies there are several important quantities that can be calculated: oxidation and reduction potentials (OP and RP respectively), hole and electron reorganization energies (HRE and ERE respectively), while TADF was assessed by calculations of energy gap between lowest three triplet states and the first excited singlet state. It should be noted that results of Marcus theory should be considered as a first approximation and the obtained values of charge mobilities should be treated only as qualitative trends, due to the simplicity of used models [14,15].

According to aforementioned facts, it is imperative to search for organic structures with suitable as low as possible values of $\Delta E(S_1 - T_1)$ and reorganization energies. In this work we investigated in details mentioned properties of three graphene nanoparticle model structures and consequences to optoelectronic properties after modification with two boron atoms. We were motivated to study the influence of boron atoms thanks to the many theoretical works where boron modified carbon nanostructures have been investigated [16–21]. For example Faccio et al. reported that boron atom fillings of single- and di-vacancies suppressed spin polarization of the charge density [22], while Panchakarla et al. successfully synthesized boron doped graphene by arc discharge of graphite and boron-stuffed graphite electrodes [23].

We decided to investigate three pristine types of graphene nanoparticles and their derivatives obtained when two carbon atoms of central ring are substituted with two boron atoms. Since production of graphene nanoparticles could be performed starting from graphene nanosheets we have also investigated charge and heat transport properties of graphene nanosheets. In this way we were able to fully summarize the effects of boron atoms to optoelectronic and transport properties of representative graphene nanostructures.

2. Computational details

All density functional theory (DFT) calculations related to optoelectronic properties of graphene nanoparticles were performed with Schrödinger Jaguar 8.8. program and its corresponding optoelectronics module, as implemented in Schrodinger Material Science 2015-2 suite of programs [24,25].

Optoelectronic properties, namely OP and RP, HRE and ERE, were obtained using the screening calculation method which is intended to produce high quality results using small basis set [26]. Detailed information on calculation of these quantities can be found in our previous publication [27]. $\Delta E(S_1 - T_1)$ parameter was calculated using the TDDFT approach with Tamm–Dancoff approximation, as implemented in screening method of Jaguar optoelectronics module [25].

In order to investigate the charge and heat transport properties of graphene nanosheets we considered a device system as presented in Fig. 5. Graphene nanosheet of 10 repetitions of cell is partitioned in three regions as following: the semi-infinite left electrode (denoted as L), the semi-infinite right electrode (denoted as R) and the central scattering region (denoted as C). We used 10 repetitions in order to make the central region long enough so that no direct tunneling occurs between the electrodes and that it can be approximated that introduced boron atoms have negligible influence to the electrodes during the transport study.

Simulations of transport properties were done by the QuantumWise Atomistix Toolkit 2014.3 (ATK) [28,29,53,54]. In this powerful software package quantum transport properties are investigated through employment of the self-consistent non-equilibrium Green's functions and the density functional theory. Prior to calculations of transport properties structures were optimized by the ATK until the atomic forces were less than 0.02 eV/Å, without constraints. GGA approximation and PBE functional were used with Double Zeta Polarized (DZP) basis set, although according to literature data Single Zeta Polarized (SZP) basis set would be enough as well [30–32]. Transport simulations with ATK were done employing the self-consistent extended Hückel method [55] with Cerda Hückel basis sets [33]. For both optimization and transport calculations mesh grid of the k space was set to $1 \times 1 \times 100$, while the electronic temperature was set to 300 K. Phonon subsystem of pristine graphene device has been investigated employing the Tersoff [34,35] potentials as optimized by Lindsay and Broido [36]. For modified graphene devices phonon subsystem has been investigated employing the Tersoff potentials [34,35] as optimized by Matsunaga et al. [37].

3. Results and discussion

3.1. Optoelectronic properties of graphene nanoparticles

3.1.1. Investigated systems

For the investigation of optoelectronic properties the three pristine model graphene nanostructures were obtained with

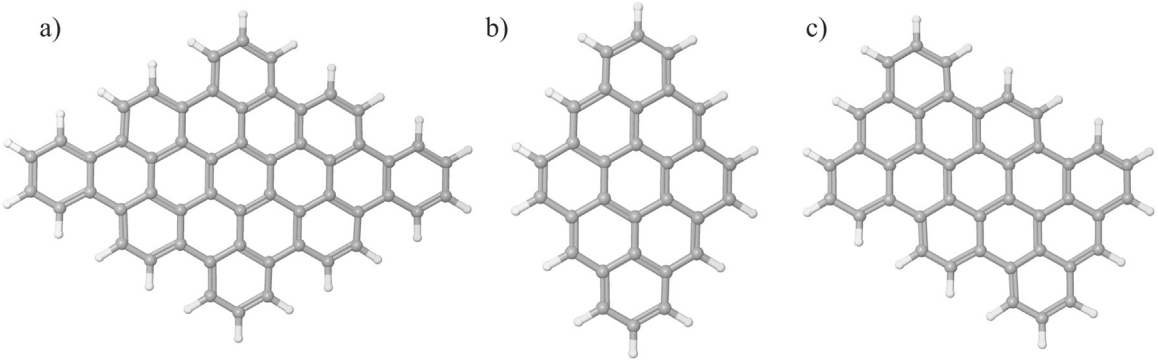

Fig. 1. Optimized geometries of a) AA, b) ZZ and c) AZ type of pristine graphene nanoparticles.