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Optoelectronic and charge carrier hopping properties of ultra-thin boron nitride nanotubes

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Boron nitride nanotubes
DFT
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ABSTRACT

Optoelectronic properties of ultra-thin boron nitride nanotubes and charge carrier hopping properties between them were investigated within density functional theory. The study encompassed calculations of optoelectronic quantities, such as reorganization energies, oxidation and reduction potentials and charge carrier hopping rates between mentioned nanotubes. Charge coupling was calculated applying full quantum mechanical treatment, while Marcus theory was used for calculations of charge carrier hopping rates. Results indicate differences between investigated types of boron nitride nanotubes. With the increase in dimensions of boron nitride nanotubes optoelectronic properties are improving, while charge carrier hopping rates are the highest for (6,0) boron nitride nanotube.

1. Introduction

Ever since they have been firstly predicted in 1994 by Rubio et al. [1] and successfully synthesized in 1996 by Chopra et al. [2], boron nitride nanotubes (BNNTs) are considered as one of the most intriguing non-carbon nanotubes [3]. They are seen as adequate candidate structures for substitution

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of conventional carbon nanotubes (CNTs) [4]. Their structural similarity with CNTs is related with hexagonal structure in which boron and nitrogen atoms are placed instead of carbon atoms [2,5]. Regarding conductive properties, contrary to of CNTs, which can be semiconducting or metallic, BNNTs are always electrical insulators with relatively large band gap of around 5.8–6.0 eV and this property is nearly independent to both tube diameter and chirality [3,6,7].

The popularity of nanotube like structures based on non-carbon elements, such as BNNTs and boron-phosphide nanotubes (BPNTs), is constantly increasing and numerous theoretical and experimental studies have been performed so far [8]. With regard to carbon, boron and nitrogen atoms, their property related with small covalent radius (namely the generation of considerable strain energy) makes for them possible to form very stable low-dimensional structures with smaller coordination. Contrary to carbon, boron and nitrogen structures, low coordination structures based on Si atoms, are predicted to be unstable [8–11].

Beside conductive properties, reactivity properties are what mainly distinguish BNNTs over CNTs. Namely, exterior surfaces of BNNTs are more reactive, thanks to which functionalization through sidewall decoration, chemisorption and adsorption is more effective [12,13]. This is especially important for the practical applications of BNNTs, as this increased reactivity can be used for the production of efficient sensors for the detection of common atmospheric pollutants, otherwise hardly detected by CNTs [13–15].

In this study we decided to theoretically investigate the optoelectronic properties of (3,0), (4,0), (5,0) and (6,0) BNNTs within the DFT, for the first time. The aim of this work was the analysis of the effects of BNNTs dimensions to some of the crucial optoelectronic properties, important for practical application. We were encouraged with the fact that characterization experimental studies of optoelectronic properties of BNNTs have been performed [16,17] and also with the fact that biosensor for glucose [18] and light emitting device [7] based on BNNTs have been successfully manufactured.

Efficiency of electronic materials is related with high charge mobilities and efficient charge injection [19]. When it comes to the charge transport, at room temperatures the most important mechanism is hopping mechanism, which is used for study of charge mobilities in systems investigated in this work. Within this mechanism, charge hopping rate, k_{ET}, is the main quantity that regulates the charge carrier mobility and represents the rate constant or the hopping rate for charge transport between adjacent molecules. k_{ET} turned out to be useful quantity and in the framework of Marcus theory can be expressed as [20,21]:

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

The last equation is principally dictated by two key quantities, the reorganization energy, λ, and charge transfer integral (or charge coupling), t. It should be noted that we shall regard to the results of Marcus theory as a first approximation and the obtained values of charge mobilities shall be treated only as qualitative trends, due to the simplicity of used models [22,23].

2. Computational details

All DFT calculations were performed with Schrödinger Jaguar 8.4. program and its corresponding optoelectronics and electron coupling modules [24]. Optoelectronic properties, namely oxidation and reduction potential (OP and RP respectively), electron and hole reorganization energies (ERE and HRE respectively) were obtained using the screening calculation method which is intended to produce high quality results using small basis set [25]. Charge transfer integrals and hopping rates of electrons and holes were obtained employing full quantum mechanical treatment. Hopping rates were calculated according to the Marcus theory.

In this study we used the following computation procedure. Firstly, geometries of monomer systems of BNNTs were optimized with extensively checked B3LYP [26,27] functional with 6-31G + d,p basis set in order to obtain initial information on structures. Then, optoelectronic properties (OP, RP, HRE and ERE) were obtained within screening calculation method at B3LYP/MIDI! level of theory. The usage of this level of theory is explained later, in Section 3.2. Then, dimer BNNT structures were