Physica E 83 (2016) 365–371

Contents lists available at ScienceDirect

Physica E

journal homepage: www.elsevier.com/locate/physe

Optical and electronic properties of SO_2 molecule adsorbed on Si-doped (8, 0) boron nitride nanotube

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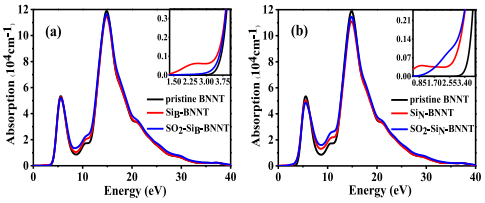
HIGHLIGHTS

- The optical properties of SO_2 adsorption on Si-doped BNNTs are investigated.
- Blue-shifts and red-shifts of main peaks are found in different constructions.
- The speculated optical band gaps are decreased after Si doping and SO_2 adsorption.
- The asymmetry impurity states are mainly contributed by the Si-3p states.

GRAPHICAL ABSTRACT

The absorption spectrums of the pristine BNNT, Si–BNNT and SO_2–Si–BNNT are calculated and plotted, and the absorption coefficient of the pristine BNNT, Si_B–BNNT, SO_2–Si_B–BNNT, Si_N–BNNT, and SO_2–Si_N–BNNT are showed in Figs. (a) and (b).



ARTICLE INFO

Article history:
Received 7 March 2016
Received in revised form
31 March 2016
Accepted 1 April 2016
Available online 2 April 2016

Keywords:
SO_2 adsorption
Boron nitride nanotubes (BNNTs)
Optical properties
Electronic properties
First-principles

ABSTRACT

The study of the optical properties of pristine BNNT, Si-doped BNNTs and SO_2 molecule adsorption on Si-doped BNNTs is that, to our knowledge, few relevant research have ever been found. In this paper, the adsorption behaviors of Sulfur dioxide (SO_2) molecule on Si-doped Boron nitride nanotubes (BNNTs) are investigated applying the first-principles calculations. The main contribution of this paper is that the foremost investigation for the optical properties of the pristine BNNT, Si-doped BNNTs and SO_2 adsorption on Si-doped BNNTs. Additionally, the electronic properties and the structural properties are also presented. In our calculations of optical properties, the dielectric constant, the refractive index and the absorption coefficient are obtained. Comparing the pristine BNNT, our results indicate that, the blue-shifts (in the main peaks of the dielectric constant of Si_B–BNNT and SO_2 –Si_B–BNNT), and the red-shifts (in the main peaks of the refractive index of Si_N–BNNT and SO_2 –Si_N–BNNT) are appeared. Under these conditions, Si-doped BNNT and Si-doped BNNT with SO_2 adsorption, the gaps are reduced both for the speculated optical band gaps and the electronic structure band gaps.

1. Introduction

One of the destructive pollutant gases which is known for its common environmental pollutant and serious toxicity is Sulfur dioxide (SO_2) [1]. It is one of the main components of air pollution and smog. Also, it has fatal effects on the human and the ecosystem of animals. Due to the inherent dangers, the detection of SO_2 is crucial. Consequently, exploring the reliable and low-cost SO_2 detection sensors with high sensitivity and selectivity at low energy consumption have been required for environmental safety and industrial control. Many sensors have been developed so far for different applications to monitor SO_2 [2].

Boron nitride nanotubes (BNNTs) have received considerable attention in the scientific community. They have been predicted by theoretical calculation [3,4] and synthesized experimentally [5,6].

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http://dx.doi.org/10.1016/j.physe.2016.04.002
1386-9477/

As a nanostructure representative, BNNTs possess the potential for nanoscale electronic devices owing to their uniform electronic properties regardless of their chirality, diameter and number of layers considered. The outstanding properties, such as thermal conductivity, oxidation resistance and mechanical elasticity [7,8], make BNNTs highly useful in wide range of applications. Moreover, many theoretical and experimental studies [9–13] have improved the physical and chemical properties of BNNT to enlarge and expedite BNNT practical application. Many interesting studies have demonstrated that the doping impurity atoms into BNNTs with transition metals could further improve the properties of BNNTs and increase their sensitivities toward gas molecules, which are undetectable by pristine BNNTs [14–21]. These works have shown that the ability of doped BNNTs to chemically adsorb the CO, NO, CO_2 and NH_3 molecules.

A few research for the adsorption of SO_2 molecule on pristine and doped BNNTs have been conducted. Recently, Deng et al. have firstly studied the electronic and magnetic properties of SO_2 molecule adsorption on Mn-doped BNNTs [22] and Si-doped BNNTs [23]. Since impurity states will give rise to new bound states in the band gap, which will change the optical response of the material, particular attention must be paid to the investigation of such optical properties of BNNTs. For example, the ultraviolet–visible absorption spectra of BNNT can be changed by surface chemical functionalization [24]. Another example can be found in Ref. [25], doping of ZnO nanotubes has a significant impact on the value of the dielectric constant and the results of the optical reflectivity, it shows that these nanotubes are transparent in a wide energy ranges which provide them for using in transparent coatings. In this paper, we concentrated on the optical and electronic properties for pristine, Si-doped BNNTs and Si-doped BNNTs with SO_2 molecule adsorption. Concerning the study of the optical properties, to the best of our knowledge, this paper is the first work which fully considers pristine BNNT, Si-doped BNNTs and SO_2 molecule adsorption on Si-doped BNNTs. What's more, their containing adsorption behaviors are investigated. We expect that our study can bring the understanding of these utilizable optical properties of BNNTs, doped BNNTs and doped BNNTs with gas molecule adsorption to enlarge and expedite the technical and industrial applications of BNNT-based materials for SO_2 detection sensors.

2. Calculation methods

We performed spin polarized density functional theory calculations with the Cambridge Sequential Total Energy Package Code (CASTEP) [26]. In this paper, the geometry optimization is carried out by using the Broydene Fletchere Goldfarbe Shanno (BFGS) method [27]. The electron–electron exchange correlation interaction is considered by the generalized gradient approximation (GGA) within the Perdew–Burke–Ernzerhof (PBE) formalism [28]. The convergence tests regarding the cut-off energy have been made before the calculations to the properties. The cut-off energy of the electronic wave function has been tested in the range between 300 eV and 600 eV. It has been found that the final enthalpy of the system nearly reached a constant at 450 eV. Hence, a plane wave set is used to describe the electronic wave functions with an energy cutoff of 450 eV, which is sufficient for total energy convergence. For the calculation of structural and electronic properties, $1 \times 1 \times 7$ Monkhorst–Pack mesh grid is employed, while for the optical properties, $1 \times 1 \times 21$ Monkhorst–Pack mesh grid is adopted [29]. All the atoms of the pristine BNNT, Si–BNNT and SO_2 –Si–BNNT are fully relaxed to their equilibrium positions with an energy convergence of 5×10^{-6} eV. The force applied on each atom is less than 0.01 eV/Å and the stress is less than 0.02 GPa. In addition, the atomic displacement is less than 5×10^{-4} Å and the self-consistentfield (SCF) tolerance is 5×10^{-7} eV. The atomic electronic configurations considered are B $2s^2 2p^1$, N $2s^2 2p^3$, Si $3s^2 3p^2$, S $3s^2 3p^4$ and O $2s^2 2p^4$. Ultrasoft pseudopotential is adopted in the reciprocal space. All optical calculations are performed using the light polarization parallel to the tube axis ($E//Z$).

3. Results and discussions

3.1. Structural properties

We choose a zigzag (8, 0) BNNT (pristine (8, 0) BNNT) as the simulated model, and the supercell contains 32 boron and 32 nitride atoms ($B_{32}N_{32}$). A single B atom (B site) or a single N atom (N site) in the middle of the supercell is substituted by an impurity Si atom to form Si-doped BNNT (Si–BNNT) system (they are marked as Si_B–BNNT and Si_N–BNNT, respectively). Then the impurity atom of each Si–BNNT is adsorbed by a SO_2 molecule to form SO_2–Si–BNNT system (SO_2 –Si_B–BNNT and SO_2 –Si_N–BNNT). Fig. 1 presents schematically the fully relaxed structures for Si–BNNT and SO_2–Si–BNNT as well as the pristine (8, 0) BNNT for comparison.

In Fig. 1(b) and (d), the geometric structure of Si–BNNT is obviously distorted near the doped site and the Si atom protrudes out of the corresponding tube for relieving compressive stress. That is because the radius of the impurity Si atom (1.46 Å) is greater than the B atom (1.17 Å) and the N atom (0.75 Å).

In order to determine the stability of the SO_2–Si–BNNT system in Fig. 1(c) and (e), the adsorption energy E_{ad} is calculated, defined as

$$E_{ad} = E(SO_2\text{–Si–BNNT}) - E(\text{Si–BNNT}) - E(SO_2) \quad (1)$$

where $E(SO_2$–Si–BNNT), E(Si–BNNT) and $E(SO_2)$ are the energies of Si–BNNT systems with an adsorbed SO_2 molecule, Si-doped (8, 0) BNNT and the SO_2 gas molecule, respectively. The calculated adsorption energies E_{ad} of the SO_2–Si–BNNT system are listed in Table 1. Apparently, SO_2 –Si_B–BNNT and SO_2 –Si_N–BNNT are exothermically adsorbed with negative adsorption energies and thus indicating the structures of SO_2 –Si_B–BNNT and SO_2 –Si_N–BNNT are stable.

3.2. Electronic properties

In order to gain deep insight into the impacts of the electronic structure for Si–BNNT before and after the adsorption of a SO_2 molecule, the spin polarized total density of states (DOS) of pristine BNNT, Si–BNNT and SO_2–Si–BNNT are presented. As shown in Fig. 2(a), the total DOS of the pristine BNNT are symmetric in both spin-up and spin-down channels. It indicates that the pristine BNNT is nonmagnetic semiconductor with a band gap of about 3.128 eV in accordance with the value of 3.324 eV reported earlier [23].

From Fig. 2(b–e), it can be found that the total DOS shift to the lower energy region and a few new asymmetry impurity states emerge in the proximity of the Fermi level for Si–BNNT and SO_2–Si–BNNT compared with that of the pristine BNNT. The asymmetry in both spin-up and spin-down channels of the Si–BNNT and SO_2–Si–BNNT leads to the generation of magnetic semiconductors. Additionally, the energy shift eventually results in a large reduction of the band gap (the band gap is listed in Table 1). In this case, the light absorption in the visible range might be improved.

For further exploration of the origin of the impurity states of Si–BNNT and SO_2–Si–BNNT, we depict the partial DOS (PDOS) of Si–BNNT projected onto Si-3p (red) and its neighboring B-2p (black)