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Theoretical investigation of ethane and ethene monitoring using pristine and decorated aluminum nitride and silicon carbide nanotubes

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ABSTRACT

The adsorption of ethane and ethene molecules on pristine and Ni-doped armchair (4,4) single walled aluminum nitride (AlN) and silicon carbide (SiC) nanotubes are investigated employing density functional theory approach. Our results indicate that the ethane/ethene molecule physisorbed onto the outer surface of AlNNT and SiCNT through weak Van der Waals interaction. On the other hand, the encapsulation of ethane/ethene onto the inner surface of considered nanotubes is endothermic and difficult to realize with an appreciable energy barrier. Compared with weak adsorption of ethane/ethene onto the pristine AlNNT and SiCNT, Ni decorated AlN and SiC nanotubes exhibit strong affinity toward the ethane/ethene molecule with remarkable negative adsorption energies about −61/−179 kJ/mol for AlNNT/Ni and −96/−202 kJ/mol for SiCNT/Ni systems, respectively. Based on our results, it seems that ethene tends to be chemisorbed onto the Ni-doped nanotubes, whereas the ethane-adsorption process is through strongly physisorbed process and could serve as a signal of nanosensor due to affect the electronic conductance and structural properties. These observations show that functionalized AlN and SiC nanotubes are highly sensitive toward C_2H_4/C_2H_6 molecule. Moreover, these results may be useful for the design of new types of nanosensor devices that can detect the presence of small hydrocarbon molecules.

1. Introduction

The field of nanosensors has attracted considerable interest due to our current concern over environmental and health issues. [1]. In this regard, significant attempts have been made to investigate new nanomaterial-based sensors from both experimental and theoretical point of views, which some of these One-dimensional nanosensors such as carbon nanotubes (CNTs) [2], semiconductor nanowires [3], and graphene nanoribbons [4] can modify many of the draw-backs of traditional semiconductor-based gas sensors. In the context of sensor development work, CNTs have a set of unique and outstanding properties such as high sensitivity, fast response, small size and low operating temperature [5–8] that make them ideal candidates for nanosensors. So far, since the discovery [9], pure carbon nanotubes have been demonstrated to be promising nanoscale molecular sensors for detecting a few molecule gas such as O_2 [10], NH_3 [11], NO_2 [12] and H_2 [13] with fast response time and high sensitivity. This superior sensitivity has been theoretically explained in terms of change of the semiconducting single-wall carbon nanotube induced by charge transfer from gas molecules adsorbed on nanotube surfaces, which can dramatically influence the electrical conductivity of the latter by modifying the electronic structure of CNTs. To overcome this problem, functionalization of carbon nanotubes (CNTs) is a promising approach to increase their solubility and reactivity, since the adsorption capability of SWCNTs can be improved through exohedral or substitutional doping and forming active sites in tube walls.

Recently great advances have been made in demonstrating the viability of using inorganic semiconducting nanotubes such as aluminum nitride (AlN) and silicon carbide (SiC) nanotubes to detect the presence of chemical gases as well as organic chemical and biological substances and they have led to the design of a new type of sensor devices. AlNNT and SiCNT could provide very high sensitivity due to their large surface to volume ratios and their unique electronic properties.

The silicon nanotubes (SiNTs), which are analogous to carbon nanotubes in many respects such as electronical and structural characters, have been prepared by various experiments and

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theoretical studies in the recent years [14–20]. Unlike carbon nanotubes (CNTs), SiCNTs are semiconducting materials with a large band gap, which their stability is diameter-independent and weakly depended on the helicity [21]. Because of unusual mechanical properties, excellent chemical and thermal stabilities, the SiCNTs have been promising potential for applications in nanoelectronic devices operate at high temperatures, high frequency, and in harsh environment [22]. Theoretical studies show that O_2 [23], H_2 [24], CO and HCN [25], NO and N_2O [26] could be chemisorbed on the exterior surface of SiCNT with large binding energy, which indicate that SiCNT could act as sensor.

As an important member of semiconductor, 1-D III–V nanostructures of aluminum nitride nanotubes (AlNTs) have attached considerable attention due to unique properties such as direct wide band gap (~6.2 eV), high thermal conductivity [27], superior mechanical strength, highpiezoelectric response, small or even negative electron affinity, and so on [28]. Note that before first experimentally synthesized by Tondare et al. [29], the synthesis of AlNNTs have been a challenging task, but Zhang et al. have been testified the strain energy and stability of single-walled AlNNT using density functional theory and it have been found that AlNNTs are energetically favorable and arrange in a hexagonal network adopting an sp^2 hybridization [30]. Recently, a few theoretical studies also focus on the tips of AlNNTs with regard to defect properties, [31] and functionalization of the AlNNT's wall [32,33] to modify sensitivity of these nanotubes through different molecules. Furthermore, the interaction of AlNNTs with gases, excepting a few gas molecules such as H_2O, N_2 and O_2 [34], CH_4 [35], ammonia [36] and CO_2 [37] has seldom been investigated and remains largely an unexplored area.

Of particular interest in this paper are those studies related to interactions of small hydrocarbon molecule including ethane and ethene with AlN and SiC nanotubes in different kind including pristine and Ni-doped nanotubes. Here we propose to design a new type of nanoscale sensors using AlN and SiC nanotubes with modified electronical and chemical properties through doping impurity atom into them. We demonstrate that this type of nanosensors can overcome the weaknesses of existing intrinsic aluminum nitride and silicon carbide nanotubes. Hence, the results of this paper could provide the necessary tools for the molecular level manipulations that will satisfy some of the fabrication's needs of increasingly miniaturized devices that the microelectronic industry will demand within the next decades.

2. Computational details

The density functional theory are carried out using Gaussian03 [38] package to exploring the equilibrium geometries, stabilities, and electronic properties of nanotube/hydrocarbon and nanotube/nickel-hydrocarbon systems to search their potential usage as novel nanosensors. The spin-polarized generalized gradient approximation (GGA) with the modified Perdew-Wang91 exchange [39] plus the Perdew-Wang91 (MPW1PW91) [40] and the functional of Perdew-Burke-Ernzerhof (PBEPBE) corrections [41] are applied for describing the exchange-correlation term. An extra basis set formed by the CEP-121G [42] for Ni atom and the conventional 6-31G basis set for all other atoms were performed in this paper. We have selected two different nanotube models, which include finite single walled armchair (4,4) AlN and SiC nanotubes with comparable structural properties such as diameter, length and chirality. The length and diameter of both nanotubes is about 16 Å and 7.31 Å respectively and each of these nanotubes include totally 40 atoms. In addition, the two ends of AlNNT and SiCNT are terminated with hydrogen atoms, which this act can be a barrier for shutting of nanotube edges (see Fig. S1). The structural-optimization of these pristine nanotubes were performed using the PBEPBE/6-31G and MPW1PW91/6-31G level of theory.

Many attempts have been made during these years to use the quantitative chemical concepts in density-functional-based theory [43], namely chemical potential (μ) and hardness (η), in the understanding of molecular reactivity. For an N-electron system with total energy E and external potential ($\upsilon(r)$), chemical potential (μ) and hardness(η) are defined as the first- and second-order partial derivatives of the total electronic energy (E) with respect to the number of electrons (N) at a fixed external potential ($\upsilon(r)$) respectively [44]. Using a Janak's type of approximation [45], these descriptors could be approximated in terms of the obtained energies of highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) from density functional theory calculations (ε_H and ε_L), respectively.

$$\mu = \left(\frac{\partial E}{\partial N}\right)_{\substack{\rho \\ \upsilon(r),T}} \cong \frac{(\sim\varepsilon_L + \varepsilon_H)}{2} \tag{1}$$

$$\eta = \frac{1}{2}\left(\frac{\partial^2 E}{\partial N^2}\right)_{\substack{\rho \\ \upsilon(r),T}} \cong \frac{(\varepsilon_L - \varepsilon_H)}{2} \tag{2}$$

Parr et al. [46] have proposed electrophilicity index (ω) in terms of the chemical potential and chemical hardness as a measure of the electrophilic power of a molecule as:

$$\omega = \frac{\mu^2}{2\eta} \tag{3}$$

Using the Janak's approximations, this relation for electrophilicity has the simple forms of Eq. (3).

3. Result and discussion

3.1. Ethane/ethene adsorption on pristine AlN and SiC nanotubes

The structural optimization of pristine armchair (4,4) single walled AlNNT and SiCNT is performed in the framework of density functional theory using two MPW1PW91 and PBEPBE methods. Obtained results from relaxed geometries of these nanotubes indicate that SiC and AlN nanotubes are semiconductor with energy gap about 3.41 and 4.88 eV respectively, which these our results are in well agreement with other previous research works [27,47]. However, because difference in performed methods, there is slightly quantitative difference between obtained gap energy our research and other works. In addition, structural parameters of relaxed AlN and SiC were compared with several other research works [48–50], and it is found that the bond length of Al–N and Si–C, which are 1.818 and 1.813 Å respectively, are well reported. The natural bond orbital (NBO) calculations are also performed to obtain some electrical properties of these nanotubes such as partial atomic charge and bond order using MPW1PW91/3-21G* and PBEPBE/3-21G* level of theory (see Table S1). It is noteworthy that significant difference in electronegativity between Al/Si and N/C atoms in AlNNT and SiCNT causes the ionic character of Al–N and Si–C bonds (Table S1). Du to large ionicity of these bonds, the electronic structures of AlN and SiC nanotubes are almost independent of tube diameter and chirality, which mean of this phenomenon is that investigations on armchair nanotube could be transferred to zigzag one. Furthermore, the electronic properties of isolated components are collected in Table S2.

In order to investigate the adsorption of ethane (C_2H_6) and ethene (C_2H_4) molecules onto the pristine AlNNT and SiCNT, different possible adsorption sites including inside (C-position) and outside of nanotubes are selected. The considered hydrocarbon molecules horizontally (H-orientation) and vertically