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Selective Sensing Characteristics of Ca Doped BeO Nano-sized Tube toward H₂O and NH₃

Maziar Noei*, Vali Zare-Shahabadib, Seyyedeh Najmeh Razic

a. Department of Chemistry, Mahshahr Branch, Islamic Azad University, Mahshahr, Iran
b. Young and Elite Researchers Club, Mahshahr Branch, Islamic Azad University, Mahshahr, Iran

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By means of density functional calculations, the structural and electronic properties of chemical modification of pristine and Ca-doped BeO nanotubes were investigated with NH₃ and H₂O molecules. It was found that the NH₃ and H₂O molecules can be adsorbed on the Be atom of the tube sidewall with the adsorption energies of about 36.1 and 39.0 kcal/mol, respectively. Density of states analysis shows that the electronic properties of the BeONT are slightly changed after the adsorption processes. Substitution of a Be atom in the tube surface with a Ca atom increases the adsorption energies by about 7.4 and 14.7 kcal/mol for NH₃ and H₂O, respectively. Unlike the pristine tube, the electronic properties of Ca-doped BeONT are sensitive to NH₃ and H₂O molecules. Also, the Ca-doped tube is much more sensitive to H₂O molecule than NH₃ one.

Key words: Doping, Density functional theory, Sensor, B3LYP

I. INTRODUCTION

Single-walled carbon nanotubes (CNT) with outstanding mechanical, chemical, electrical and one-dimensional structural properties have aroused great interest since their discovery by Iijima in 1991 [1]. These characteristic properties exhibited by CNTs had made them suitable for application in nanoelectronics, catalysis, sensors, energy capacitors, and as hydrogen storage devices [2–5]. The vast majority of studies have also recognized that the structures of non-carbon based nanotubes could also be stable. More recently, models of pristine single-walled beryllium oxide nanotubes (BeONTs) were proposed and their structural, cohesive and electronic properties were predicted [6, 7]. BeO compound often has different properties from the counterpart of C and BN nanotube (BNNT) because of the large ionicity of Be−O bond. For example, wurtzite BeO is an insulator with a wide band gap, high melting point, high thermal conductivity and large elastic constants [8]. In addition, compared with CNTs and BNNTs, it was found that the BeONTs have larger band gap which is less dependent on the chirality and diameter of tubes [9, 10]. Moreover, the BeONTs adopt interesting mechanical properties, namely their Young’s moduli are comparable to those for CNTs [10]. These advantages give the BeONTs considerable potential for applications in nanoelectronic devices.

Increasing demands for ever more sensitive vapor sensors for environmental monitoring and control, healthcare, defense and security, and other applications have led to an upsurge of interest in one-dimensional (1D) nanostructures (e.g., nanotubes, nanowires, nanorods, and nanofibers). Recently, 1D nanostructured semiconductor metal oxides based vapor sensors have been demonstrated excellent sensitivity, fast response and recovery [11–14]. A detailed understanding of surface structure is of great importance in surface science, heterogeneous catalysis, nanoscience, and such other technologies. Bonding of simple atoms and molecules such as NH₃, H₂O, CO, and alkali metals to metal oxides is one of the serious challenges in theoretical studies [15–19]. In this work, the interaction of a single H₂O and NH₃ with BeONT will be theoretically investigated within density functional theory (DFT) based on analyses of structure, energies, electronic properties, etc. The main purpose of this work is to gain fundamental insights into the influence of adsorbed molecules on the electronic properties of the nanotube, and how these effects could be used to design more sensitive gas sensing devices. The fundamental sensing mechanism in these materials relies on the change in electrical conductivity as a result of charge transfer with adsorbates [20]. However, a group of molecules cannot be detected by pristine nanostructured materials because the electrical conductivity during the adsorption process cannot be changed. In order to overcome this drawback, considerable experimental and theoretical studies have been focused on improving the sensing performance of several nanostructures by manipulating the structure [21, 22]. Among many possible strategies to tailor the sensitivity of nanostructures, generating new active sites on
their surface is classically the premier method to overcome the drawback of the intrinsically inert character. Embedding of foreign atoms or doping in these structures may enable them to detect a wide range of gases [21, 22]. To this end, we have studied the reactivity of H$_2$O and NH$_3$ molecule toward the pristine BeONT and B-doped ones, using DFT calculations.

II. COMPUTATIONAL METHODS

We selected a (4, 4) armchair BeONT consisting of 56 Be and 56 O atoms, in which the end atoms have been saturated with hydrogen atoms to reduce the boundary effects. Geometry optimizations, energy calculations, natural bond analysis (NBO) and density of states (DOS) analysis were performed on the BeONT and different H$_2$O/BeONT complexes using B3LYP functional augmented with an empirical dispersion term (B3LYP-D) with 6-31G(d) basis set as implemented in GAMESS suite of program [23]. The B3LYP has been demonstrated to be a reliable and commonly used level of theory in the study of different nanostructures [24–27]. GaussSum program has been used to obtain the DOS results [28]. We have defined adsorption energy in the usual way as $E_{\text{ad}} = E_{\text{BeONT}} + E_{\text{molecule}} - E_{\text{molecule/BeONT}} + E_{\text{BSSE}}$, where $E_{\text{molecule/BeONT}}$ corresponds to the energy of the BeONT in which H$_2$O or NH$_3$ molecules have been adsorbed on the tube, $E_{\text{BeONT}}$ is the energy of the isolated tube, $E_{\text{molecule}}$ is the energy of a single H$_2$O(NH$_3$), and $E_{\text{BSSE}}$ is the energy of the basis set superposition error.

III. RESULTS AND DISCUSSION

A. Geometry and adsorption energy

In Fig.1(a), we have shown partial structure of the side view of the optimized BeONT. In comparison with earlier findings and the adsorption systems we studied later, we first briefly investigate the relaxation structures and electronic properties of pure armchair BeONT. There are two types of Be–O bonds in BeONT, one is perpendicular to the tube axis and another one that is not parallel with the tube axis (diagonal). The calculated Be–O bond length and the average diameter of the optimized BeONT were found to be about 1.56 and 5.94 Å, respectively, in accordance with previously reported values [29]. We also obtained a rippled surface: the cations (Be atoms) move inward toward the tube axis, while the anions (O atoms) move outward, and this reduces the total energy of the system since the electron-electron repulsion is lowered, which also agrees reasonably with the previously calculated results [29]. The charge analysis using the Mulliken method indicates that about 0.502 e charges are transferred from the boron atom to its adjacent nitrogen atoms within the sidewall, indicating partially ionic character of the Be–O bonds in the sidewall.

In order to identify the minimum energy adsorption configurations of the H$_2$O and NH$_3$ molecules on the BeONT, we examined a number of potential conformations. For NH$_3$, the nitrogen atom located on the top of the center of square ring or near to a Be atom of the tube surface; hydrogen atoms located on the top of O and Be atoms of the tube. For H$_2$O, O and H atoms of H$_2$O molecule are close to either beryllium atom (Be site) or oxygen atom (O site) of the tube, the molecular axis being vertical to the surface of the tube. However, preliminary optimizations show that only stable adsorption configuration was obtained for both molecules in which the oxygen of H$_2$O or nitrogen atom of NH$_3$ is close to Be site and other configurations re-oriented to this site after relax optimization (Fig.2).

The adsorption of the N(O) atom of NH$_3$(H$_2$O) preferably on the Be atom of the tube surface rather...
TABLE I Adsorption energy ($E_{ad}$, kcal/mol), HOMO energies ($E_{HOMO}$), LUMO energies ($E_{LUMO}$) and HOMO-LUMO energy gap ($E_g$) of systems (Fig.1 and Fig.2) in eV.

<table>
<thead>
<tr>
<th>Configuration</th>
<th>$E_{ad}$</th>
<th>$Q_T$ [e]</th>
<th>$E_{HOMO}$</th>
<th>$E_{LUMO}$</th>
<th>$E_g$</th>
<th>$\Delta E_g$ [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>BeONT</td>
<td></td>
<td></td>
<td>-7.47</td>
<td>-0.43</td>
<td>7.04</td>
<td></td>
</tr>
<tr>
<td>H$_2$O/BeONT</td>
<td>39.0</td>
<td>0.203</td>
<td>-7.39</td>
<td>-0.41</td>
<td>6.98</td>
<td>0.8</td>
</tr>
<tr>
<td>NH$_3$/BeONT</td>
<td>36.1</td>
<td>0.186</td>
<td>-7.38</td>
<td>-0.33</td>
<td>7.05</td>
<td>0.1</td>
</tr>
<tr>
<td>Ca-BeONT</td>
<td></td>
<td></td>
<td>-7.37</td>
<td>-2.28</td>
<td>5.09</td>
<td></td>
</tr>
<tr>
<td>H$_2$O/Ca-BeONT</td>
<td>53.7</td>
<td>0.054</td>
<td>-7.36</td>
<td>-1.50</td>
<td>5.86</td>
<td>15.1</td>
</tr>
<tr>
<td>NH$_3$/Ca-BeONT</td>
<td>43.5</td>
<td>0.173</td>
<td>-7.30</td>
<td>-1.90</td>
<td>5.40</td>
<td>6.1</td>
</tr>
</tbody>
</table>

$^a$ $Q_T$ is defined as the total NBO charge on the molecule.
$^b$ Change of $E_g$ of tube after H$_2$O and NH$_3$ adsorption.

than the O site can be attributed to low ionization potential of Be. However, in the bare tube, some charges are transferred from the Be atoms to the O atoms; when an N(O) atom is placed in the vicinity of an Be atom of the tube surface, it competes with the O atoms of surface for receiving the electron from the Be atom. The $E_{ad}$ value corresponding to the adsorption of H$_2$O is about 39.0 kcal/mol (Table I), indicating strong adsorption in which O atom of H$_2$O is close to Be atom of the tube with distance of 1.71 Å (Fig.2(a)). The NBO charge analysis shows a net charge transfer of 0.203 e from the molecule to the tube.

As shown in Table I, the minimum energy configuration is obtained when the distance between NH$_3$ and BeONT surface is about 1.80 Å. In optimum structure, the calculated $E_{ad}$ is about 36.1 kcal/mol. The equilibrium distance of adsorbed NH$_3$ from the tube surface and the high positive $E_{ad}$ indicate a strong interaction. Moreover, NH$_3$ adsorption induces a structural deformation to both NH$_3$ molecule and BeONT. The NH$_3$ adsorbed Be–O bond is pulled outward from the tube wall with the bond length increasing from 1.56 Å of pristine tube to 1.63 and 1.65 Å (Fig.2(b)). Lu et al. recently have theoretically investigated NH$_3$ adsorption on CNTs [30]. They found that NH$_3$ can be physisorbed on CNT with $E_{ad}$ of 3.9 kcal/mol which is much smaller than BeONT. However, Leszczynski et al. have shown that NH$_3$ molecule can be chemisorbed on the Stone-Wales defects of CNTs through dissociation into H and NH$_2$ radicals [31]. They have demonstrated that this process is mostly endothermic except the adsorption at very few defect sites.

The sensing mechanism is to detect the conductance change of BeONT induced by charge transfer from gas molecules to the nanotube. Thus, we studied the influence of the H$_2$O and NH$_3$ adsorption on the electronic properties of the tube, respectively (Table I). For the bare BeONT in Fig.1, it can be concluded that it is an insulator material with a wide HOMO (the highest occupied molecular orbital)/LUMO (the lowest unoc-
occupied molecular orbital) energy gap ($E_g$) of 7.04 eV. Calculated DOS plots of adsorbed tube show that during H$_2$O and NH$_3$ adsorption through stable configurations neither valence nor conduction levels of the BeONT are significantly changed, so the large $E_g$ of BeONT is completely preserved. The $E_g$ of the tube has slightly changed from 7.04 eV to 6.98 and 7.05 eV for H$_2$O/BeONT and NH$_3$/BeONT complexes, respectively, which has no sensible effects on the electronic properties of the tube. Thus, we conjecture that the electronic properties of pure BeONT are insensitive to the H$_2$O and NH$_3$ molecule.

B. Calcium doping

We have tried to investigate the effects of replacing a Be atom by one Ca atom (in the adsorbing site of the tube) on the geometrical structure and electronic properties of the BeONT, and also on the adsorption behaviors. As shown in Fig.1(b), in the optimized Ca-doped tube, the impurity of the Ca is protruded out of the tube wall to relieve stress arising from the larger size of Ca compared with Be. The calculated bond lengths are 2.19 and 2.22 Å for the Ca–O bonds in the Ca-doped BeONT (Fig.3), being longer than the corresponding distances for the Be–O bonds in the pristine tube. Also, the O–Be–O angles in the Be-doped tube are 93.9 and 98.7 Å which are smaller than O–Be–O in the pristine tube (120.6 and 118.3 Å). DOS plot of the Ca-doped BeONT (Fig.3) reveals that after replacing one Be atom by an Ca atom, one new electron state appeared at the electron forbidden area compared with the DOS of the pristine tube. In other words, LUMO of the tube shifts dramatically from −0.43 eV to −2.28 eV which narrows the $E_g$. However, $E_g$ of the BeONT is dramatically decreased from 7.04 eV to 5.09 eV (27.7% change) after Ca-doping. All above-mentioned suggest that the BeONT is transformed from a semi-insulator to a p-type semiconductor after Ca-doping process.

Subsequently, we have explored the adsorption of NH$_3$ and H$_2$O molecules on the doped tube, so that they were attached to the Ca atom via their more electronegative atoms. Optimized structures of the adsorbate/doped-tube complexes are shown in Fig.3. As shown in Table I, the $E_{ad}$ values for both of the H$_2$O and NH$_3$ on the doped tube are slightly less negative compared with that obtained in the case of pristine tube. The $E_{ad}$ values were calculated to be 53.7 and 43.5 kcal/mol, and the adsorption distances are 2.26 and 2.52 Å for H$_2$O and NH$_3$ adsorptions, respectively. Interestingly, in the case of H$_2$O adsorption, an additional H-bonding was formed between one of the hydrogen atoms of molecule and the tube with distance of 1.48 Å. More favorability of adsorption of the H$_2$O and NH$_3$ in Ca-doped BeONT can be explained by the fact that in doped tube the LUMO is mainly located on the Ca atom of the doped site (Fig.4). As a result, the HOMO of H$_2$O(NH$_3$), locating on O(N) atom, donates electrons preferentially to the LUMO centered on Ca sites.

The nature of the tube’s DOS near the Fermi level is critical to the understanding of electrical transport through this material. Calculated DOS plot of NH$_3$/Ca-BeONT complex (Fig.3) shows that the NH$_3$ adsorption through stable configuration has no sensible effect on the electronic properties of the tube, so the $E_g$ of the Ca-BeONT has a slight increase from 5.09 eV to 5.40 eV. Calculated DOS plot of NH$_3$/Ca-BeONT (Fig.4) reveals that after replacing one Be atom by an Ca atom, one new electron state appeared at the electron forbidden area compared with the DOS of the pristine tube. In other words, LUMO of the tube. The electronic properties of the tube shifts dramatically from −0.43 eV to −2.28 eV which narrows the $E_g$. However, $E_g$ of the BeONT is dramatically decreased from 7.04 eV to 5.09 eV (27.7% change) after Ca-doping. All above-mentioned suggest that the BeONT is transformed from a semi-insulator to a p-type semiconductor after Ca-doping process.

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FIG. 3 Models for stable adsorption configuration of (a) H$_2$O/Ca-BeONT and (b) NH$_3$/Ca-BeONT and their DOS plot.
eV. Whereas, DOS plot of the H$_2$O/Ca-BeONT complex shows a considerable change, indicating that the electronic properties of the Ca-BeONT are sensitive to the H$_2$O adsorption (Table I). It is revealed from DOS plot of this configuration that its conduction and valence levels shift to lower energies significantly. As can be seen in Fig.4, the $E_g$ value of the Ca-BeONT is obviously increased from 5.09 eV to 5.86 eV (by about 15.1% change) in the adsorbed form, which would result in an electrical conductivity change of the defective sheet according to $\sigma=\exp(\frac{-E_g}{2k_B T})$, where $\sigma$ is the electric conductivity, and $k_B$ is the Boltzmann constant [32]. According to the equation, smaller values of $E_g$ at a given temperature lead to larger electric conductivity. Therefore, the predicted substantial increase of $E_g$ in Ca-BeONT after the H$_2$O adsorption process induces a change in the electrical conductance of the doped tube. Compared with bare BeONT, the Ca-BeONT network would have selective H$_2$O detection ability (in the presence of NH$_3$) due to its suitable adsorption energy and conductivity. Thus, we believe that Ca doping process may be a good strategy for improving the sensitivity and selectivity of BeONT to humidity (H$_2$O), which cannot be trapped and detected by the pristine tube.

IV. CONCLUSION

A DFT study was performed on the adsorption of H$_2$O and NH$_3$ molecules on the pristine and Ca-doped BeONTs. It was found that the most stable adsorption configurations are those in which the N and O atoms of the NH$_3$ and H$_2$O prefer to attach to the Be atom of the BeONT with $E_{ad}$ of 36.1 and 39.0 kcal/mol, respectively. Finally, it was revealed that by replacing a Be atom of the tube surface by an Ca atom, the insulator BeONT is converted to a p-type semiconductor. The doping process also increases the adsorption energies and the electronic properties of Ca-doped BeONT, revealing that it is significantly more sensitive to H$_2$O molecule compared with the pristine tube.