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Comparative Computational Study on the Adsorption Properties of SO_4^{-2} on Al-doped single-walled BN and CNT nanotubes

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ABSTRACT

The behavior of the sulfate anions SO_4^{-2}adsorbed on the external surface of H-Capped (8, 0) AlN and BN zigzag Single-walled nanotubes was studied by using density functional calculations. Geometry optimizations were carried out at the B3LYP/6-31G level of theory using the Gaussian 03 suite of programs. We present the nature of the SO_4^{-2} interaction in selected sites of the nanotubes. Our results show the BN nanotubes cannot significantly detect SO_4^{-2}. The calculated binding energy of the AlN (8, 0) single-walled AlN nanotubes indicated that SO_4^{-2}can be adsorbed significantly on the Al sites and these nanotubes can therefore be used for SO_4^{-2}storage. Binding energies corresponding to adsorption of SO_4^{-2}on the Al site in the (8,0) single-walled AlN nanotubes was calculated as (-299.04hartree or -187650.11k.cal/mol or -8137.46ev).The calculated was binding energies for SO_4^{-2} in o-down orientation on surface Al N nanotubes higher than that adsorption on surface BN nanotubes. We also report the effects of SO_4^{-2} adsorption on electronics properties of the nanotubes.*

Keywords: AlN, BN, DFT, Binding Energy, Adsorption

INTRODUCTION

Since the discovery of the carbon nanotube (CNT) by, Iijima [1], numerous studies have been devoted investigate the electronic and structural properties of this attractive novel material [2.]The stable tubular structure of boron nitride (BN) was initially predicated by calculations and was than successfully synthesized [3]. The BNNTs are very similar to CNTs and they are basically regarded as isomorphic of the CNTs. Among them, Aluminum nitride nanotubes (AlNNTs) are inorganic analogs of carbon nanotubes (CNTs) and always behave as semiconductors [4]. AlNNTs because of its high temperature stability, largest band gap, thermal conductivity, and low thermal expansion are widely used in technological applications, mainly in micro and optoelectronics, such as laser diodes and solar-blind ultraviolet photo detectors and semiconductors[5]. Aluminum nitride nanotubes (AlNNTs) are inorganic analogs carbon nanotubes (CNNTs). The understanding is of the physisorption of SO_4^{-2}AlNNTs and BNNTs at different states. Sensitivity of AlNNTs and BNNTs to the sulfate anion (SO_4^{-2} has been indicated by quantum mechanics calculations. The determination of the structure of adsorbed SO_4^{-2} on AlN and BN nanotubes surfaces is important for understanding its bonding and reactivity in catalysis and other surface phenomena. The study of the chemical reactions of the sulfate anion on AlN and BN nanotubes surface is of scientific interest because SO_4^{-2} is important in the oil industrial and environmental issue[6]. The understanding of the physisorption of SO_4^{-2}on AlN and BN nanotubes surfaces is important for SO_4^{-2}storage. In this study, we report the results of density functional model calculations on the physisorption of SO_4^{-2}on (8, 0) AlN and BN (8, 0) zigzag SWNTs, with one molecular orientations o-down.

MATERIALS AND METHODS

Computational Method

In the first step, zigzag (8, 0) AlN& BN (Al30N30&B30N30) have been selected. The structure was allowed to relax by all atomic geometrical parameters in the optimization at the DFT level of B3LYP exchange functional and 6-31G* standard basis set. The BE (Binding Energy) of SO_4^{-2}on the optimized nanotubes model is calculated as follows:

$$BE=Eso_4^{-2}\text{-}AlNNT - [EAlNNTs+Eso_4^{-2}]$$
$$BE=Eso_4^{-2}\text{-}BNNT - [EBNNTs+Eso_4^{-2}]$$

Where Eso_4^{-2}AlNNTs was obtained from optimization of the adsorption SO_4^{-2}on surfaces AlN models, AlNNTs is the energy of the optimized AlNNTs structure and BNNTs energy of the optimized BNNTs structure and $Eso_4^{-2}$the energy of the optimized sulfate anion[7].

RESULTS AND DISCUSSION

SO_4^{-2}can approach the nanotubes walls from outside (out), which is the most common case. Zigzag configurations of (8, 0) BN and (8,0) AlN SWNTs. For the adsorption of SO_4^{-2}(O-down) on the AlNNT and BNNT, we considered two possible sites [the Al site and B site] as described in Fig1a and b.

Table 1.structural properties of representative models of the (8, 0) zigzag AlNNT and BNNT adsorbed sulfate anion on surface these.

Bond length	AlN pristine	AlN-SO_4^{-2}	Bond length	BN pristine	BNSO_4^{-2}
Al1-N1	1.815	1.808	B1-N1	1.450	1.441
Al2-N1	1.815	1.818	B2-N1	1.450	1.462
Al3-N3	1.815	1.797	B3-N3	1.450	1.420
Al4-N4	1.815	1.814	B4-N4	1.450	1.437
Al5-N4	1.815	1.801	B5-N4	1.450	1.423
Al10-N10	1.810	1.817	B10-N10	1.452	1.470
Al11-N12	1.808	1.769	B11-N12	1.452	1.381
Al12-N12	1.809	1.769	B12-N12	1.452	1.503
Al17-N9	1.810	1.815	B17-N9	1.449	1.447
Al18-N10	1.811	1.816	B18-N10	1.449	1.448
Al19-N11	1.810	1.831	B19-N11	1.449	1.452
Al21-N13	1.810	1.875	B21-N13	1.449	1.436
Al17-N17	1.814	1.806	B17-N17	1.454	1.449
Al18-N17	1.813	1.824	B18-N17	1.454	1.469
Al19-N19	1.813	1.788	B19-N19	1.454	1.434
Al20-N20	1.813	1.829	B20-N20	1.454	1.563
Al21-N20	1.813	1.829	B21-N20	1.454	1.433
Al25-N17	1.810	1.809	B25-N17	1.499	1.443
Al26-N18	1.809	1.808	B26-N18	1.450	1.439
Al27-N19	1.810	1.810	B27-N19	1.450	1.423
Al25-N25	1.811	1.820	B25-N25	1.453	1.463
Al26-N27	1.811	1.795	B26-N27	1.453	1.444
Al27-N28	1.810	1.794	B27-N28	1.453	1.465
Al28-N29	1.811	1.866	B28-N29	1.453	1.473
Al33-N25	1.805	1.803	B33-N25	1.452	1.446
Al34-N33	1.810	1.823	B34-N33	1.448	1.459
Al35-N34	1.810	1.831	B35-N34	1.448	1.444
Al35-N35	1.810	1.805	B35-N35	1.448	1.447
Al36-N35	1.810	1.833	B36-N35	1.448	1.462
Al37-N36	1.809	1.818	B37-N36	1.448	1.450
Average Al-N			Average B-N		
Al-H	1.581	1.592	B-H	1.192	1.199
N-H	1.018	1.017	N-H	1.014	1.015
Bond angles			Bond angles		
N1-Al9-N10	119.74	120.05	N1-B9-N10	120.34	120.50
N2-Al10-N11	119.82	120.53	N2-B10-N11	120.04	120.92
N9-Al17-N17	119.57	119.75	N9-B17-N17	119.94	120.21
N10-Al18-N18	119.51	121.07	N10-B18-N18	119.97	120.99
Al18-N18-Al26	118.53	118.65	B18-N18-B26	118.79	119.28

The notation O-down denotes an SO_4^{-2} perpendicular to the surface via o. respectively. For the optimized AlNNT and BNNT models, the quantum molecular descriptors including electronic chemical potential(μ), global hardness(ŋ), electrophilicity index(w) energy gap, global softness(S) and electro negativity (x) of the nanotubes were calculated as follows:

μ=-x=-(I+A)/2], [ŋ= (I-A)/2], [W=μ2/2ŋ] and [s=1/2ŋ]

Where I (-EHOMO) is the first vertical ionization energy and A(-ELUMO) the electron affinity of the molecule. The electrophilicity index is a measure of electrophilic power of a molecule[8]. When two molecules react with each other one molecule behaves as a nucleophile while the other acts as an electrophile. Higher electrophilicity index shows higher electrophilic of a molecule. The quantum molecular descriptors were compared for the pristine and the adsorption SO_4^{-2}on surfaces AlN and BN models. The structural properties of representative (8, 0) zigzag AlNNT and BNNT models are summarized in Table1.

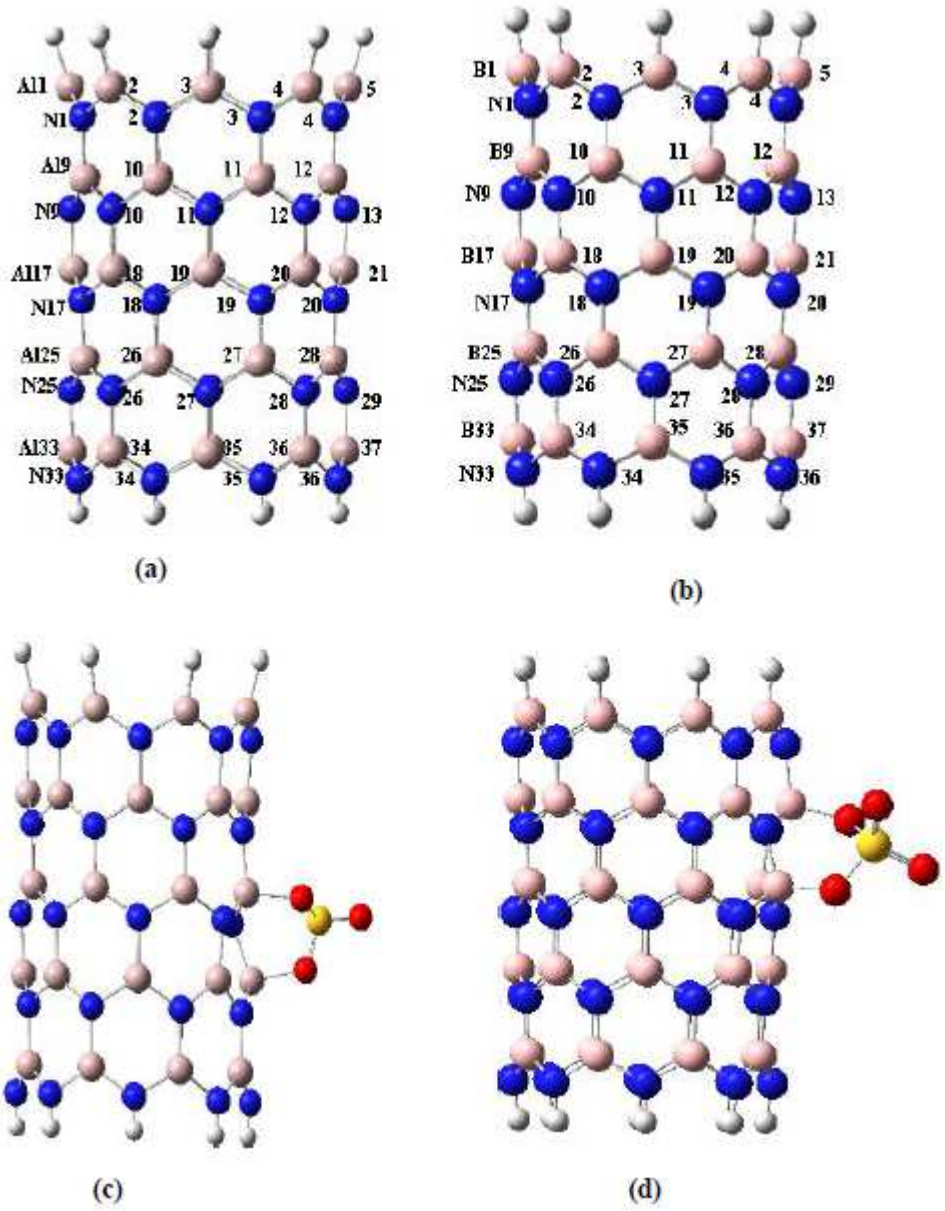

Fig. 1 a) and (b) Two dimensional (2D) views of pristine (8,0) zigzag AlNNTs and BNNTs models and 2D views of the adsorption SO_4^{-2} on surface (c) AlNT and (d) BNNT models

Electronic properties adsorption SO_4^{-2} on surface (8,0) AlNNT and BNNT

We studied the influence of SO_4^{-2}adsorption on the electronic properties of the AlNNTs and BNNTs. The total densities of state (TDOS) of these tubes are shown in Fig.3. As is 5 evident from Fig.3, the calculated band gaps of the clean prefect (8,0) AlNNTs and BNNTs are -0.1305 and-0.1195ev. The effects of SO_4^{-2}on Adsorption energies in the AlN and BN relate to their electronic structure. When $SO_4^{-2}$is adsorbed on the NTs, the interaction, between them being weak, the electronic properties of these tubes are changed obviously and the band gaps are calculated as about 0.0225, 0.0605ev. The DOS of these tubes show some significant changes due to SO_4^{-2}adsorptions in the gap regions of the TDOS plots. Therefore, the adsorption of SO_4^{-2}2on BNNTs slightly decreases the energy gap of the pristine BNNT and increases their electrical conductance. But for the AlN(8,0) zigzag SWNTs, the interaction between $SO_4^{-2}$and AlN is much further from the interaction of between $SO_4^{-2}$and the BNNTs.

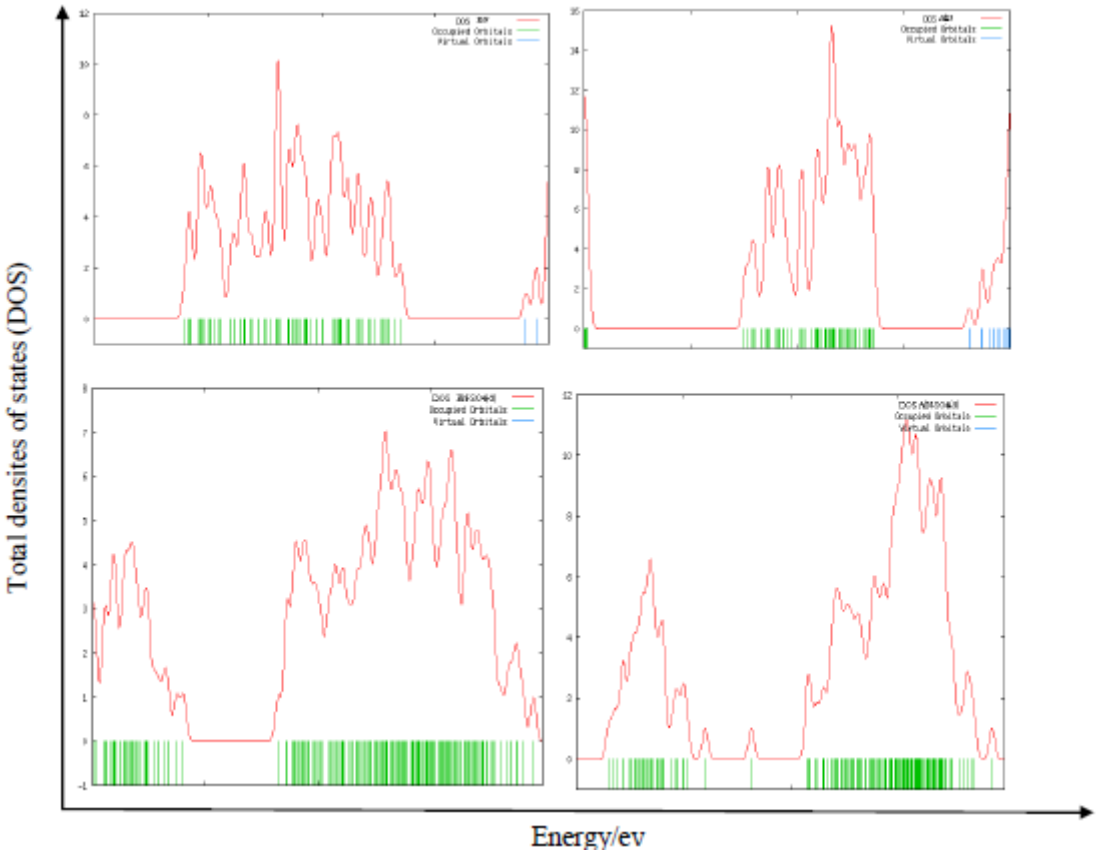

Fig. 2 Total densities states (TDOS) for different models of the AlNNT and BNNT

Therefore, the adsorption of SO_4^{-2} on the AlNNTs significantly increases the energy gap of the BNNTs, and reduces their electrical conductance.

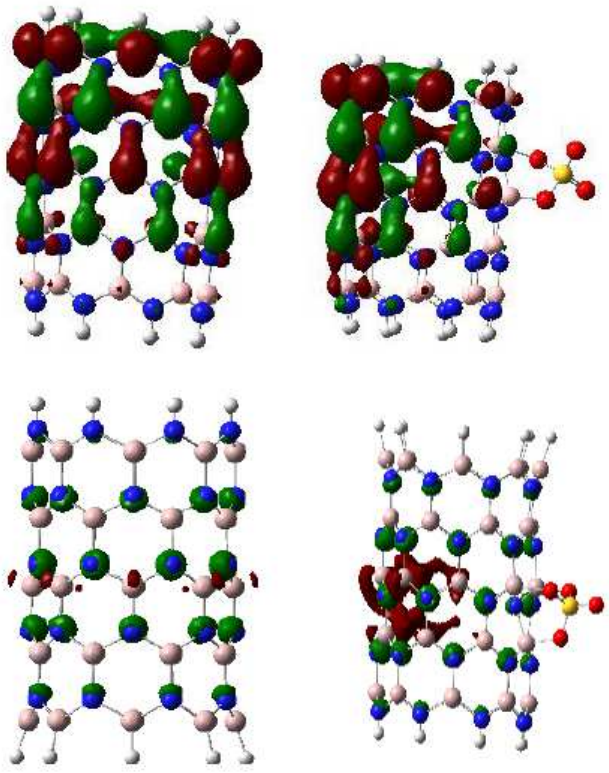

Fig. 3 HOMO and LUMO for different models SO_4^{-2}adsorption of the AlNNTs and BNNTs

Quantum molecular descriptors of the (8,0) zigzag AlNNT and BNNT and SO_4^{-2}adsorption on AlNNT and BNNT models are summarized in Table2. We observe that in the SO_4^{-2}adsorption on AlN and BNNT models, the energy gap (ELUMO-EHOMO) depressed. This lowering of energy gap in the SO_4^{-2}adsorption on BNNTs processes may be able to increase the reactivity of the models. The global hardness and ionization potential of the SO_4^{-2}adsorption on Al NNT models decreases with a decrease in energy gaps of the models. Decrease in global hardness, energy gap, and ionization potential because of the SO_4^{-2}on BN process lowers the stability and increases the reactivity of the models.

Table 2.quantum molecular descriptors in representative models of the (8,0) AlNNTs and BNNTs, I=ionization potential, A=electron affinity, ŋ=Global hardness, μ=chemical potential and w=electrophilicity

Property	AlN pristine	BN pristine	SO_4^{-2}on AlN	SO_4^{-2}on BN
EHOMO/ev	-0.225	-0.238	-0.058	-0.041
ELUMO/ev	-0.036	-0.001	0.103	0.162
[ELUMO-EHOMO]/ev	0.189	0.237	0.161	0.203
[I=-EHOMO]/ev	0.225	0.238	0.058	0.041
[A=-ELUMO]/ev	0.036	-0.237	-0.103	-0.162
[ŋ=(I-A)/2]/ev	0.094	0.237	0.080	0.101
[μ=-(I+A)/2]/ev	-0.130	0.00	0.022	0.060
[s=1/2ŋ]/ev-1	0.047	0.118	0.04	0.050
[w=μ2/2ŋ]ev	0.359	0.00	0.001	0.72

The electrophilicity index is a measure of electrophilicity power of a molecule. The electrophilicity of the SO_4^{-2} adsorption on AlNNTs models are much further from the electrophilicity of the pristine model. The value of hardness, softness, electrophilicity and chemical potential for the SO_4^{-2} adsorption on AlNNTs models differ from that of the individual tube. In the SO_4^{-2}adsorption process, the capacity of the AlNNTs models to attract electrons was diminished and the hardness of the SO_4^{-2}adsorption AlNNTs models was decreased, which means decreased stability of the system.

CONCLUSION

We studied the electronic structure properties including bond lengths, bond angles, dipole moments, band gap, the quantum molecular descriptors parameters of the pristine and SO_4^{-2}adsorption AlNNT and BNNT models by means of DFT calculations. The calculated results showed that the effects adsorption SO_4^{-2}on AlN than adsorption on BN.

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