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Density Functional Study on the Functionalization
of BN Nanotubes with Nitramide¹

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Abstract—Chemical functionalization of a boron nitride nanotube (BNNT) with nitramide molecule (H_2NNO_2) has been investigated using density functional theory. It was found that the molecule prefers to be adsorbed and dissociated on a diagonal B–N bond of the tube surface so that the $-\text{NH}_2$ and $-\text{NO}_2$ groups are attached on B and N atoms, releasing energy of 0.50 eV. The results show that the functionalized BNNT is more soluble than the pristine one which may render the chemical modification process to be an effective way for purification of the BNNTs. Depending on the cleavage behavior of nitramide on the tube, HOMO/LUMO gap of the system can be either decreased or increased while the chemically modified BNNT is still a semiconductor. Furthermore, the chemical functionalization results in hindered field emission in the tube by raising the potential barrier of the electron emission.

Keywords: boron nitride nanotube, density functional theory, adsorption.

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INTRODUCTION

The discovery of carbon nanotubes (CNTs) has been followed by extensive efforts to introduce and prepare similar non-carbon-based nanostructures [1]. CNTs have a wide range of applications from nano-electronics to nano-biotechnology, e.g., they can be used as either electron field emitters or artificial muscles [2–4]. Numerous studies have been devoted to investigating the stable structures of the non-carbon nanotubes, among which the III–V analogues of CNTs such as boron-nitride nanotubes (BNNTs) and aluminum-nitride nanotubes (AlNNTs) are of great importance [5, 6]. The BNNTs are wide band gap semiconductors which are characterized by high temperature stability, considerable thermal conductivity, low thermal expansion, resistance to chemicals and gases used in semiconductor processing, and reliable dielectric properties [7]. However, the relatively large band gap of the BNNTs has imposed great limitations to their applications [7]. The application of these nanotubes has been further hampered by their poor solubility and difficulties in purifying and processing [8].

Chemically modified (i.e., functionalized) nanotubes are being extensively promoted as one of strategies to overcome the above mentioned problems. Recent advances in linking specific groups or molecules to the nanotubes clearly testify the strong potential of chemical functionalization not only for tuning the electronic properties of the tubes, but also for

enabling their assembly into more complex architectures required for integrated device operation [9]. Furthermore, chemical functionalization imparts increased solubility to the nanotubes, thus opening new perspectives for solution-based chemical transformations and spectroscopy. Although there are plenty number of reports on functionalization of CNTs [9, 10], the BNNTs functionalization has remained largely unexplored. It has been previously reported that covalent functionalization using adatoms, organic molecules, and functional groups can effectively change the electronic structure, magnetic properties, and solubility of the nanotubes [9].

Very recently, Zettl et al. [11] have reported a convenient, highly efficient, radical-based chemical approach to functionalize the BNNTs with amine functional groups via an aggressive non-equilibrium ammonia glow plasma treatment. This renders the BNNTs highly dispersible in the common organic solvent chloroform. The NH_2 groups are covalently bonded to the surface of the BNNTs, which is different from the functionalizations with pristine NH_3 and related amino functional groups [12]. Altering the surface chemistry of BNNTs is still in its early stages, and effective surface functionalization is a challenging task. The functionalization of the BNNTs with some groups such as H [13], F [14], CCl_2 [15], and NH_3 [12] have been investigated in previous theoretical works, finding that these functional groups modify the electronic properties of the tubes in different ways.

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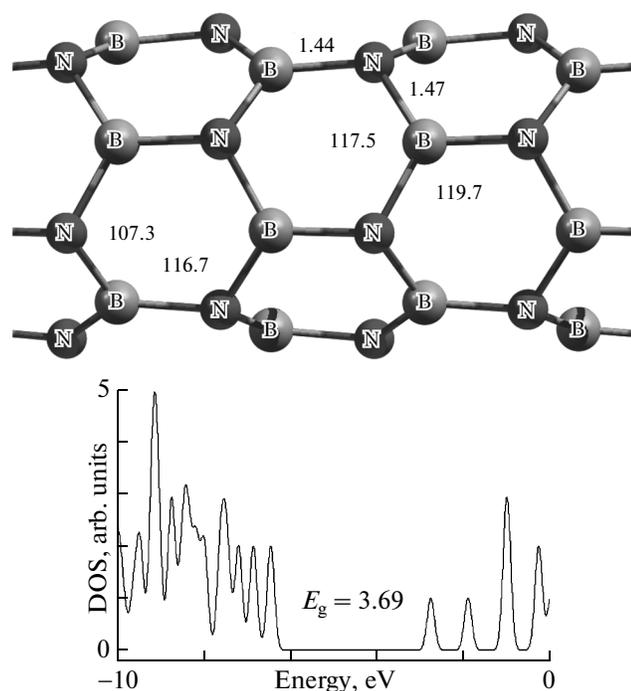


Fig. 1. Geometrical parameters of the optimized BNNT and its DOS plot. Distances are in Å and the angles in deg.

In the present work, we have investigated the functionalization of BNNTs by nitramide (H_2NNO_2) using density functional theory (DFT). Nitramine energetic materials are widely applied in military explosive, propellant and fuel. They have been intensively studied both theoretically and experimentally over the past decades [16]. The present study is an attempt to find out (1) where the nitramide group is placed upon the functionalization, (2) how the geometric and electronic properties of the tubes are modified by nitramide, and (3) how the solvation properties of the BNNT in water are influenced by functionalization.

COMPUTATIONAL METHODS

Geometry optimizations, natural bond orbital (NBO), and density of states (DOS) analyses were performed on a zigzag (5,0) BNNT, and different $\text{H}_2\text{NNO}_2/\text{BNNT}$ complexes at B3LYP/6-31G(d) level of theory as implemented in GAMESS software [17]. Harmonic vibrational frequencies have been calculated at the same level of theory, which enable us to confirm real minima. It has been previously demonstrated by Tomic et al. [18] that the B3LYP provides an efficient and robust basis for calculations of III–V semiconductors, capable of reliably predicting both the ground state energies and the electronic structure. This function has been commonly

used for nanotube structures [19–21]. The chemical functionalization energy (ΔE_{CF}) is defined as follows:

$$\Delta E_{\text{CF}} = E(\text{H}_2\text{NNO}_2/\text{BNNT}) - E(\text{BNNT}) - E(\text{H}_2\text{NNO}_2), \quad (1)$$

where $E(\text{H}_2\text{NNO}_2/\text{BNNT})$ is the total energy of the functionalized BNNT with nitramide, and $E(\text{BNNT})$ and $E(\text{H}_2\text{NNO}_2)$ are total energies of the pristine BNNT and the H_2NNO_2 molecule, respectively. The negative value of ΔE_{CF} indicates an exothermic process. Solvation effects have been included using the polarized continuum model (PCM). A dielectric constant of 78.4 was used corresponding to that for water as the solvent.

RESULTS AND DISCUSSION

Optimized structures and geometry parameters of the BNNT have been shown in Fig. 1. From a structural view of point, the B atoms move inward the tube, while the N atoms move in the opposite direction. Thus, the relaxed zigzag BNNT can be characterized by two coaxial cylindrical tubes, with an outer N cylinder and an inner B cylinder, resulting in a radial buckling. Structurally, there are two types of individual B–N bonds in the BNNT; one with the bond length of 1.44 Å and in parallel with the tube axis, and another with the bond length of 1.47 Å, diagonal to the tube axis. The length and diameter of the optimized pure BNNT have been computed to be about 13.70 and 4.23 Å, respectively. In order to avoid boundary effects, atoms at the open ends of the tube are saturated by hydrogen atoms. The difference in energies between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), E_g , has been calculated based on the results obtained from DOS (Fig. 1) analysis, indicating that it is a semi-conductive material with a wide E_g of 3.69 eV.

A H_2NNO_2 molecule has been considered to be adsorbed on the outside surface of the BNNT. There are two kinds of N atoms in the molecule; one is attached to two H atoms (N1) and the other one which is bonded to two oxygen atoms (N2). We have probed four different functionalization configurations on the tube surface including 1, 2 addition of N–N bond of the molecule to two types of B–N bonds. More detailed information including values of E_{CF} , Mulliken charge transfers (Q_{T}), and the E_g (the change of E_g of the tube upon the functionalization process) have been listed in Table 1. As shown in Table 1, ΔE_{CF} values are calculated to be in the range of -0.50 to $+0.91$ eV. The obtained values of ΔE_{CF} depend on the orientation and location of the molecule outside the BNNT.

Overall, configurations **A** and **B** (diagonal additions, Fig. 2) are more favorable than parallel additions (**C** and **D**). Since the BNNTs are obtained by rolling the BN graphene sheets, the diagonal bonds

have a larger local curvature in the zigzag BNNTs [15] and our NBO analysis shows their more double character than parallel ones. Among the four considered additions, only the configuration A is formed through an exothermic process. In this configuration, the N1 and N2 atoms of the nitramide are located on the B and N atoms of a diagonal B–N bond, respectively. A net charge about $0.31 e$ transfers from the tube to the molecule and calculated ΔE_{CF} value is about -0.50 eV. Why the reaction of H_2NNO_2 in orientation of A is more stable than other configurations? To answer this question we have investigated Mapped electrostatic potential (MEP) analysis of Molecule and BNNT. The charge distribution can be explained by MEP calculations. MEP is the potential generated by the charge distribution of the molecule, which at an atomic site is defined as follows:

$$V(r) = \sum_A \frac{Z_A}{|R_A - r|} - \int \frac{\rho(r') dr'}{|r' - r|}, \quad (2)$$

where Z_A is the charge on nucleus A, located at R_A . The sign of $V(r)$ depends on whether the effects of the nuclei or the electrons are dominant at any point. The MEP has frequently been used to explore the chemical properties of several materials [20–23]. As it has been

Table 1. Calculated energetic data (ΔE_{CF} , ΔH_{CF} , ΔG_{CF} , and E_{solv} , eV) and dipole moment (μ , D) of systems

System	ΔE_{CF}	ΔH_{CF}	ΔG_{CF}	E_{solv}	Q_T, e	μ
BNNT	–	–	–	–0.60	–	7.40
A	–0.50	–0.43	–0.36	–0.69	–0.31	10.25
B	+0.49	+0.54	+0.62	–0.67	–0.29	9.12
C	+0.63	+0.70	+0.78	–0.71	–0.30	11.34
D	+0.91	+0.95	+0.98	–0.69	–0.31	11.01

Q is defined as the average of total Mulliken charge on the nitramide molecule.

shown by mapped molecular electrostatic potential (MEP) of the BNNT in Fig. 3a, the B and N atoms are positively and negatively charged and are favorable sites for nucleophilic and electrophilic attacks, respectively. As it's well known $-NH_2$ and $-NO_2$ groups are electron-donating and withdrawing functional groups, respectively (Fig. 3b). Therefore, the $-NH_2$ strongly tends to locate on the electron deficient site of B atom while the $-NO_2$ prefers the electron-rich N atom. As shown in Fig. 3c, the charges of the

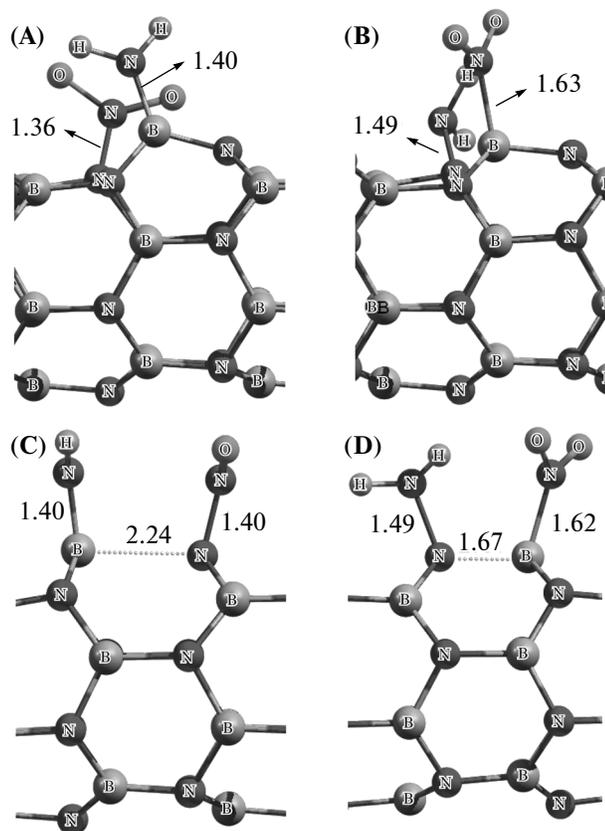


Fig. 2. Four configurations for functionalization of BNNT by H_2NNO_2 . Distances are in Å and the angles in deg.

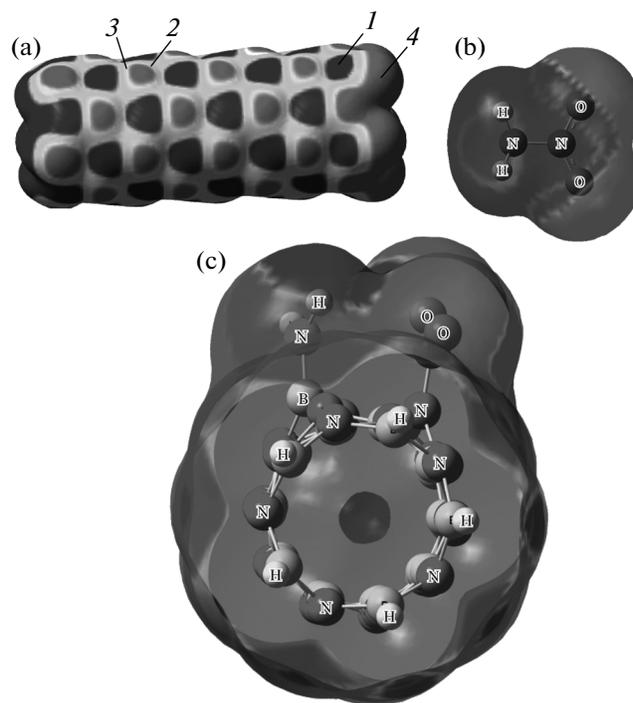


Fig. 3. Charge density of (a) BNNT, (b) H_2NNO_2 molecule and (c) H_2NNO_2 /BNNT in configuration A. The surfaces are defined by the 0.0004 electrons/b3 contour of the electronic density, ranges, in arb. units: (1) more positive than 0.010; (2) between 0.010 and 0; (3) between 0 and -0.015 ; (4) more negative than -0.015 .

Table 2. The HOMO, LUMO and gap (E_g) in between energies (eV) and Fermi level energy (E_{FL} , eV) for different systems

System	E_{HOMO}	E_{FL}	E_{LUMO}	E_g	$\Delta E_g, \%$
BNNT	-6.45	-4.44	-2.76	3.69	–
A	-6.57	-4.61	-2.65	3.92	+6.2
B	-6.62	-4.69	-2.77	3.85	+4.3
C	-6.32	-4.62	-2.93	3.39	-8.1
D	-6.24	-4.71	-3.19	3.05	-17.3

ΔE_g is the change of HOMO–LUMO gap of BNNT after adsorption.

H_2NNO_2 molecule BNNT are overlapped seriously, indicating the formation of chemical bonds.

The lengths of the newly formed B–N and N–N bonds in the configuration **A** are about 1.40 and 1.36 Å, respectively. In particular, the length of the B–N bond attached to H_2NNO_2 is increased from 1.47 to 2.78 Å, implying the bond cleavage and the formation of open structure on the sidewall of the BNNT. Based on the NBO analysis, such structural deformation is attributed to the hybridization change from sp^2 to approximately sp^3 on the adsorbed atoms. Isolated H_2NNO_2 molecule has partially planar geometry with O–N–N and H–N–N angles of 116.1° and 109.4°, respectively. When the nitramide is attached to the tube, significant out-of-plane displacement of H and O atoms is observed, where both the O–N–N and H–N–N angles are reduced to 89.4° and 77.8°, therefore the H_2NNO_2 molecule is bent due to the intramolecular steric repulsion.

The stretching vibrational frequency of the B–N bonds in the pristine BNNT is approximately concentrated at 1429 cm^{-1} . It shifts to 760 cm^{-1} for the functionalized B–N bonds (in the configuration **A**) due to increasing the lengths of these bonds in the presence of the H_2NNO_2 molecule. Also, the vibrational modes of the newly formed B–N and N–N bonds are about 1424 and 1366 cm^{-1} , indicating that these bonds are weaker than the corresponding ones in the tube surface. The stretching frequency of N–N bond in the adsorbed H_2NNO_2 is concentrated at 324 cm^{-1} , but the calculated frequency for N–N mode of the free molecule is about 174 cm^{-1} , indicating that the length of N–N bond should be broken upon the adsorption process. Our calculations show that the N–N bond length is increased from 1.39 to 2.86 Å after the adsorption process which is consistent with the frequency change.

In order to further examine the thermodynamic feasibility of the H_2NNO_2 adsorption on the BNNT at ambient temperature and pressure, we have calculated changes of free energies (ΔG) and enthalpies (ΔH) involved at 298.14 K and 1 atm. based on the obtained results from vibrational frequency calculations.

The value of the ΔH for the configuration **A** is about -0.43 eV and that of the ΔG equals to -0.36 eV, confirming the exothermicity of the process. However, lower value of the ΔG compared to that of the ΔH is due to the fact that the entropy is decreased upon the functionalization process. Other configurations have positive ΔG (0.62 to 0.98 eV) and ΔH (0.54 to 0.95 eV).

Solvation energies (E_{solv}) for the pristine and functionalized BNNT have been obtained by geometrically optimizing the structures in vacuum and water. The E_{solv} has been calculated with the aid of the ‘Conductor-like Screening Model’ for solvation [22]. The more negative values of the E_{solv} , the higher degrees of solubility are obtained. The calculated results show that the functionalized BNNT is more soluble than the pristine one. The values of E_{solv} for the functionalized–BNNT in water are ranged between -0.67 to -0.72 eV, indicating that it is more soluble in water than the pristine tube (with E_{solv} of -0.60 eV). We believe that the enhanced solubility renders the chemical modification of the BNNTs with nitramide to be an effective way for purification of these tubes. Electric dipole moment is of great importance for obtaining data of the electronic distribution in a molecule. It is one of the properties which has been used traditionally to discuss and rationalize the structure and reactivity of many chemical systems [23, 24]. When nitramide is adsorbed on the BNNT, dipole moment of the tube is significantly increased from 7.40 in the bare tube to 10.25 D in the most stable configuration, **A**. We think that the increased solubility is attributed to increment of the dipole moment.

Table 2 summarizes the HOMO, LUMO, and E_g of different functionalized BNNTs. To verify the effects of nitramide adsorption on the electronic properties of the BNNT, total electronic densities of states (DOS) of the nitramide–BNNT complexes have been calculated and the results have been shown in Fig. 4. It can be found that the E_g of the BNNT has slightly changed after chemisorption of the nitramide and its contribution is largely away from the Fermi level. Hence, the chemically modified BNNT can be still named as a semiconductor. Depending on the behavior of the nitramide cleavage on the tube, the E_g of the system is either decreased or increased. In the configurations **A** and **B** which the $-NH_2$ group is attached to a B atom of the tube, the E_g is increased. While, the E_g is decreased in the configurations **C** and **D** where the functional group is placed on the N atom. The largest change of E_g belongs to the configuration **D** in which the E_g of the tube is decreased from 3.69 eV in the pristine form to 3.05 eV in the nitramide/BNNT complex.

Calculated profiles of HOMO and LUMO for H_2NNO_2 /BNNT in configuration **A** (Fig. 5) demonstrate that the HOMO has shift to functionalized molecule but LUMO has yet remained on the BNNT surface. This change may significantly change the semiconductive character of the tube. However, more studies are needed to find other chemical modification

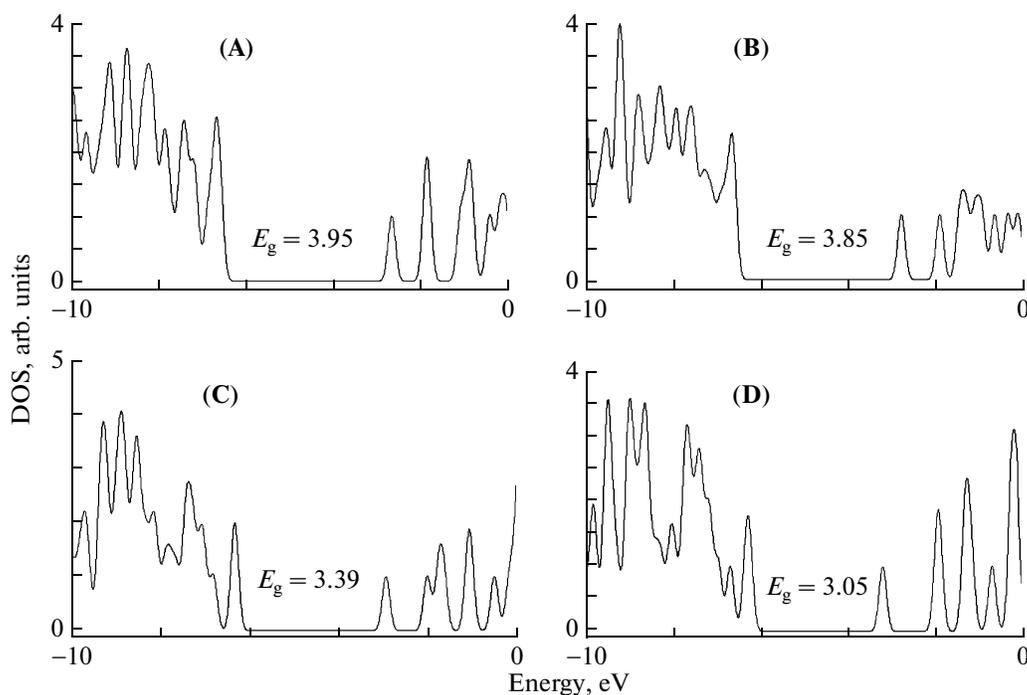


Fig. 4. Calculated DOS plots for different $\text{H}_2\text{NNO}_2/\text{BNNT}$ complexes.

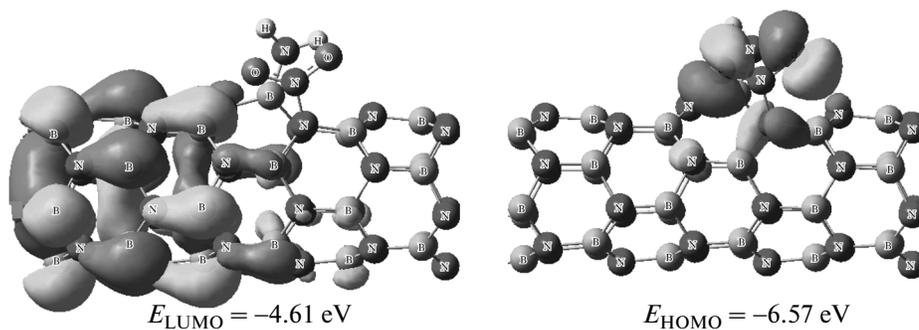


Fig. 5. LUMO and HOMO profiles for $\text{H}_2\text{NNO}_2/\text{BNNT}$ complex in configuration A.

strategies to modify the electronic properties of the BNNTs using molecular design. As can be seen from Table 1, the chemisorption process of the nitramide decreases the Fermi level energy of the BNNT. The canonical assumption for Fermi level is that in a molecule (at $T = 0$ K), it lies approximately in middle of the E_g . It is noteworthy to mention that, in fact, what does lie in the middle of the E_g is the chemical potential, and because the chemical potential of a free gas of electrons is equal to its Fermi level as traditionally defined, herein, the Fermi level of the considered systems is at the center of the E_g . However, the decrement of the Fermi level energy leads to an increased work function that is important in field emission applications. The work function can be found using the standard procedure by calculating the potential energy dif-

ference between the vacuum level and the Fermi level, which is the minimum energy required for one electron to be removed from the Fermi level to the vacuum. The increment in the work function indicates that the field emission properties of the tube are impeded upon the adsorption of the nitramide.

CONCLUSION

The chemical functionalization of BNNT with nitramide has been investigated using density functional calculations. The results has shown that the nitramide prefers to be adsorbed atop a diagonal B–N bond of the tube surface rather than the parallel one based on feasibility of the HOMO/LUMO interaction. Adsorption of the nitramide on the wall of the BNNT has not

significantly changed the E_g of the nanotubes. However, it can enhance solubility of the BNNT in water solution. Preservation of the electronic properties of the BNNTs coupled with the enhanced solubility suggests that the chemical modification of the BNNTs with nitramide may be an effective way for purification of these nanotubes.

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