

A DFT study on the interaction of doped carbon nanotubes with H₂S, SO₂ and thiophene

Hossein Tavakol^{*,a} and Hamed Haghshenas^b

*^a Department of Chemistry, Isfahan University of Technology, Isfahan, 84156-83111, Iran;
Tell(Fax): +98-3133913241; Email: h_tavakol@cc.iut.ac.ir*

^b Division of Biochemistry, Department of Biology, Faculty of Sciences, Shahrekord University, Shahrekord, Iran. Email: hamed.haghshenas@stu.sku.ac.ir

Corresponding Author

* Hossein Tavakol: Department of Chemistry, Isfahan University of Technology, Isfahan, 84156-83111, Iran; Tell(Fax): +98-3133913241; Email: h_tavakol@cc.iut.ac.ir

A DFT study on the interaction of doped carbon nanotubes with H₂S, SO₂ and thiophene

Abstract

The interactions of simple and Al, B, N, S, P and Si-doped carbon nanotubes with three sulfur-containing molecules (H₂S, SO₂ and thiophene) have been investigated to assess their adsorption potencies and sensor abilities. DFT calculations were used to calculate the adsorption energies and NBO parameters. Besides, Population analyses were performed to calculate the energy gaps and reactivity parameters and to obtain DOS plots. The results showed an exothermic interaction of H₂S, SO₂ and thiophene with simple and doped CNTs while the maximum negative adsorption energies were belonged to Al and B containing complexes. Furthermore, evaluation of second order perturbation energies (obtained from NBO calculations) confirmed that the highest energies were related to B and Al containing intramolecular interactions. The results revealed the favourability of adsorption of SO₂ by nanotubes (B and Al doped carbon nanotubes, in particular), in comparing with the other examined adsorbates.

Keywords:

Adsorption; Doped; Nanotube; Sulfur; Sensor.

Introduction

Based on the unique structural properties and wide range applications, Carbon nanotubes (CNTs) have attracted broad interests of various research groups [1-4] since their first report in 1991 [5]. The adsorption abilities of CNTs provide an excellent opportunity to solve environmental pollution problems and to prepare a new category of useful sensors. In recent years, several studies (experimental or theoretical) have been performed to evaluate the adsorption properties of CNTs and their doped derivatives [6-12]. In particular, the theoretical reports showed an increase in stability and hydrogen adsorption capacity of the CNTs in the presence of dopant atoms [13, 14].

Moreover, the analysis of the energy gaps for carbon nanotubes doped by various heteroatoms proved that different heteroatoms could have different effects on the conductivities of nanotubes [15]. Consequently, electrical conductivity and chemical reactivity of nanotubes could be improved by doping with heteroatoms [16], which make them proper candidates for application in chemical sensors [17-19]. Recently, the application of doped CNTs as a group of pollutant absorbents has been extensively studied. In this line, recent experimental works showed that simple and doped carbonaceous materials could be used to adsorb sulfur-based environmental pollutants, including H₂S, SO₂ and thiophene [20-23].

Despite all the reported studies related to the adsorption and sensor properties of doped carbon nanotubes, there are only a few reports considering the effect of various heteroatoms on these properties [24,25]. Therefore, a comprehensive study on the adsorption of desired molecules on the surface of carbon nanotubes is still needed. In this regard, the molecular properties, interaction energies and sensor properties of CNTs in the presence of sulfur-containing pollutants

should be investigated. For this purpose, hydrogen sulfide, sulfur dioxide, and thiophene have been selected as sample molecules for common sulfur-containing small molecules. The toxicities of sulfur-containing compounds, especially hydrogen sulfide, sulfur dioxide and thiophene have been studied extensively [26]. These compounds can be found in the crude oil and their combustion products can be released to the air and lead to several environmental issues such as acidic rain. Therefore, the detection and separation of these molecules are environmentally quite important.

Moreover, hydrogen sulfide inhibits the activity of some biological enzymes such as cytochrome oxidase and its high concentration quickly causes death [27]. Besides, several researchers have been reported regard to the effect of sulfur dioxide on asthma, bronchitis and mortality. Thiophene can also be the reason for the degeneration of neurons in the inferior colliculus and the cerebral cortex [28-30]. Therefore, in the course of our interest in the adsorption and sensor properties of doped carbon nanostructures [31-33], the adsorption of hydrogen sulfide, thiophene and sulfur dioxide on the surfaces of simple and N, P, S, Si, Al and B-doped CNTs have been studied. Consequently, in addition to the calculation of adsorption energies, molecular orbital properties and optimized parameters, density functional theory (DFT) has been employed to obtain the energy gaps (E_g) and density of states (DOS) plots to examine the sensor abilities of doped nanotubes versus desired molecules. Finally, the interaction parameters were investigated using NBO calculations. The adsorption of hydrogen sulfur, sulfur dioxide and thiophene on the surface of various doped CNTs was compared together and with simple CNTs to examine the effects of doping on them.

Methods

All the calculations were performed by Gaussian 09 program package [34] and using density

functional theory (DFT) at wb97xd/6-31+g* level of theory. DFT calculations were used because they could reproduce exact energy values, comparative with the most expensive MP2 methods [35,36]. wb97xd method is a DFT method based on long-range corrected hybrid density functions with consideration of empirical dispersion, which its result accuracy and reproducibility has been validated through the comparison with theoretical and experimental data [37]. This method is adequately modified for calculation of non-covalent interaction compared to standard DFT methods such as B3LYP, which made it desirable for calculation of CNTs and selected sulfur-based compounds interactions [37, 38]. The Optimization processes were carried out without any symmetric restriction. The integral equation formalism variant of Tomasi's polarized continuum (IEFPCM) model [39] was employed using the SCRF keyword to calculate the free energy of solvation. Natural bond orbitals (NBO) calculations for all structures was performed by employing NBO 5.0 [40], as implemented in Gaussian. The densities of state (DOS) diagrams were extracted using GaussSumm program [41]. The adsorption energies for all interactions were obtained from equation 1, by considering basis set superposition error (BSSE) and thermodynamics correction.

$$\Delta E_{\text{ads}} = E_{\text{complex}} - (E_{\text{adsorbent}} + E_{\text{adsorbate}}) \quad (\text{Eq. 1})$$

Koopman's theorem was employed to calculate reactivity parameters for all structures. Consequently, global softness (S), chemical hardness (η), chemical potential (μ) and electrophilicity index (ω) were obtained using the equations 2-5.

$$\mu = (E_{\text{LUMO}} + E_{\text{HOMO}}) / 2 \quad (\text{Eq. 2})$$

$$\eta = (E_{\text{LUMO}} - E_{\text{HOMO}}) / 2 \quad (\text{Eq. 3})$$

$$S = 1 / \eta \quad (\text{Eq. 4})$$

$$\omega = \mu^2/2 \eta$$

(Eq. 5)

Results and Discussions

Optimized parameters

In this work, the computations have been started from a simple (5,5)-carbon nanotube (simply named N), which its ends were saturated with 10 hydrogen atoms. This model has been used in the previous studies of this group, since it was decided to use the same model for CNTs in all works for the consistency and comparability of the results. Also, this model is a common model in many other reports because by using this model, the computational costs of the work will be reduced without employing important approximation, and one could use the higher theoretical model in an affordable time. Then, six doped structures containing one doped atom of aluminum (AN), boron (BN), sulfur (SN), nitrogen (NN), phosphorus (PN), and silicon (SiN) were made by the replacement of one carbon atom with the heteroatom. Optimizations of these structures (as adsorbents), were performed at ω B97XD/6-31+G* level of theory. The optimized structures were shown in Figure 1 and they were used to extract the molecular parameters, as listed in Table 1.

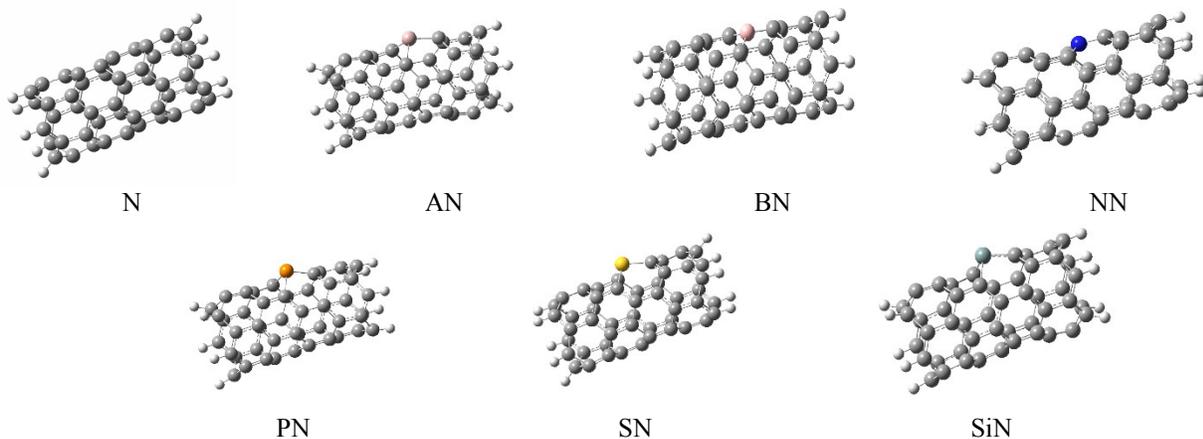


Figure 1. The optimized structures of simple and doped nanotubes, employed in this work

Table 1. The most important molecular parameters of simple and doped nanotubes, alone and in complex with H₂S, SO₂ and thiophene

	N alone	N-H ₂ S		N-SO ₂		N-thiophene	
	C-X (Av.) ^a	C-X (Av.) ^a	N-M ^b	C-X (Av.) ^a	N-M ^b	C-X (Av.) ^a	N-M ^b
N	1.439	1.442	2.391	1.444	2.974	1.444	3.243
AN	1.913	1.933	2.330	1.977	1.789	1.935	2.307
BN	1.526	1.590	2.163	1.594	1.448	1.538	2.804
NN	1.441	1.445	2.284	1.447	2.979	1.436	3.162
PN	1.870	1.871	2.567	1.867	3.300	1.869	3.255
SN	1.863	1.863	2.174	1.868	2.018	1.860	3.134
SiN	1.868	1.871	2.291	1.872	2.930	1.865	3.067

^aThis distance shows the average values of three C-X bond lengths

^bThis parameter is related to the minimum distance between nanotubes (N) and small molecules (M)

As shown in Figure 1, the doping of nanotubes deformed their structure due to the difference between the atomic radius of carbon and dopant atom, which lead to the differences in their bond's lengths. Next, three sulfur-containing molecules (H₂S, SO₂ and thiophene, generally named as M) were placed on the surface of each nanotube to obtain the complex structures. The next optimizations were performed on these complexes and their important parameters were also listed in Table 1. The optimized structures of these complexes were shown in Figure 2 that shows the relative position of the adsorbents and adsorbates.

In Table 1, C-X values are related to the average bond lengths of dopant atoms (X) and their surrounding carbons (C). Comparing C-X values of each single doped-CNTs with its sulfur-containing (H₂S, SO₂ and thiophene) complexes showed that C-X values are almost remained fixed regardless of the presence of adsorbate except in AN and BN doped-CNTs. In these two doped structures, C-X values were increased dramatically in the presence of adsorbates. The maximum variation in the C-X distances was observed in BN complexes where these values for BN, BN-H₂S, BN-SO₂ and BN-thiophene were 1.526, 1.590, 1.594 and 1.538 Å, respectively. It should be mentioned that in SO₂-containing systems, the C-X values were maximum, while thiophene-containing systems owned the minimum C-X values.

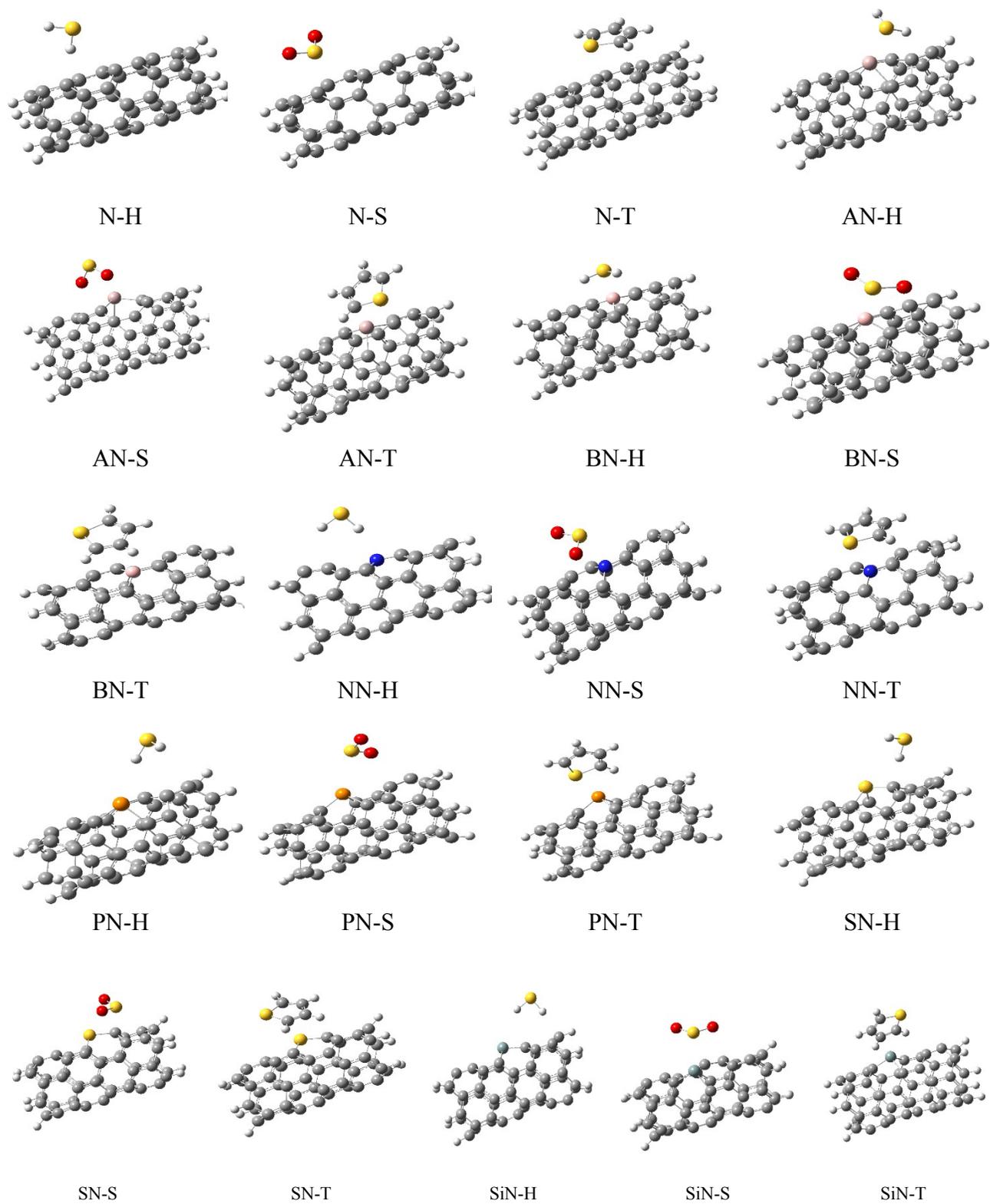


Figure 2. The optimized structures for all complexes of nanotubes with H_2S , SO_2 and thiophene

Averaging the N-M distances (between the nanotubes (N) and the small molecule (M)) among all studied complexes showed that the mean N-M distances for N-H₂S, N-SO₂ and N-thiophene are 2.314, 2.491, and 2.996 Å respectively. Moreover, average N-M distance for doped-CNTs was in this order: BN<AN<SN<SiN<NN<N<PN. Generally, the distance between adsorbent and adsorbate is affected by the strength of their interactions and the atomic sizes of adjacent atoms. The Al, P, Si and S atoms are in the third row of the periodic table and have larger atomic radii. Therefore, expecting larger N-M values for these doped-CNTs is quite reasonable. Moreover, Al and B have fewer electronegativity values than the other doped heteroatoms, which lead to the lower electron densities and stronger interactions with the electro-rich structures. Based on these arguments, it could be concluded that B and Al heteroatoms are the best candidates as dopant atoms for the adsorption of H₂S, SO₂ and thiophene, while PN and simple carbon nanotube are the worse adsorbents for these purposes.

Adsorption energies

The adsorption energies for all complexes were calculated in the gas phase and water to study the strength of interactions, as shown in Table 2. According to the data listed in this table, all of the adsorption energies in the solvent have negative values, which indicate exothermic interactions of H₂S, SO₂ and thiophene with the studied CNTs. Comparing the adsorption energies in the gas phase and water indicated that the interaction of H₂S and SO₂ with CNTs in the gas phase are more desirable than those in the solvent. In contrast, thiophene adsorption is quite better in the solvent rather than the gas phase. Besides, a comparison of all E_{ad} values indicated that SO₂-containing CNTs have the most negative E_{ad} values while H₂S-containing systems have the least negative ones. Besides, the averages adsorption abilities of nanotubes based on E_{ad} values are in this order: AN>BN>SiN>NN>PN>SN>N.

Table 2. Adsorption energies (ΔE_{ad}), thermal correction of adsorption energies, basis set superposition error (BSSE) values, enthalpies of adsorptions (ΔH_{ad}) and Gibbs free energy of adsorptions (ΔG_{ad}) of all nanostructures with H₂S, SO₂ and thiophene in the gas (G) and water as solvent (W). All energy values were reported in kcal/mol by considering BSSE and thermodynamics correction

	N-H ₂ S			N-SO ₂			N-thiophene		
	$\Delta E_{ad}(G)$	$\Delta E_{ad}(W)$	BSSE	$\Delta E_{ad}(G)$	$\Delta E_{ad}(W)$	BSSE	$\Delta E_{ad}(G)$	$\Delta E_{ad}(W)$	BSSE
N	-1.56	-1.49	0.91	-4.41	-4.11	2.20	-2.56	-2.67	2.20
AN	-5.15	-5.04	1.89	-7.08	-6.87	2.29	-5.69	-6.02	2.43
BN	-4.12	-4.05	2.01	-5.69	-5.44	2.08	-4.93	-5.18	2.38
NN	-3.21	-3.08	1.01	-3.67	-3.53	2.45	-3.51	-3.64	2.40
PN	-2.69	-2.57	0.98	-3.93	-3.78	1.91	-3.71	-3.76	1.75
SN	-2.99	-2.92	1.08	-4.14	-3.85	1.97	-2.72	-2.95	2.04
SiN	-2.46	-2.47	0.96	-5.17	-4.95	2.90	-3.60	-3.74	2.26
	$\Delta H_{ad}(G)$	$\Delta H_{ad}(W)$	Thermal correction	$\Delta H_{ad}(G)$	$\Delta H_{ad}(W)$	Thermal correction	$\Delta H_{ad}(G)$	$\Delta H_{ad}(W)$	Thermal correction
N	-1.24	-1.16	1.28	-3.92	-3.64	0.77	-2.01	-2.11	1.55
AN	-4.82	-4.71	1.66	-6.62	-6.41	0.98	-5.11	-5.44	1.84
BN	-3.75	-3.68	1.94	-5.18	-4.92	1.11	-4.37	-4.62	1.69
NN	-2.87	-2.73	0.60	-3.22	-3.08	0.96	-2.97	-3.09	1.76
PN	-2.33	-2.21	1.13	-3.41	-3.27	0.23	-3.12	-3.18	1.58
SN	-2.70	-2.62	1.35	-3.66	-3.38	0.85	-2.22	-2.46	1.42
SiN	-2.11	-2.13	1.47	-4.74	-4.51	0.81	-3.06	-3.21	1.55
	$\Delta G_{ad}(G)$	$\Delta G_{ad}(W)$	Thermal correction	$\Delta G_{ad}(G)$	$\Delta G_{ad}(W)$	Thermal correction	$\Delta G_{ad}(G)$	$\Delta G_{ad}(W)$	Thermal correction
N	-0.13	-0.06	2.39	-2.40	-2.13	2.99	-0.36	-0.47	3.20
AN	-3.62	-3.52	2.84	-5.06	-4.85	2.54	-3.41	-3.74	3.54
BN	-2.43	-2.35	3.26	-3.57	-3.32	2.72	-2.70	-2.94	3.36
NN	-0.46	-0.31	3.01	-1.71	-1.57	2.47	-1.35	-1.47	3.38
PN	-1.19	-1.08	2.27	-1.86	-1.71	1.78	-1.48	-1.55	3.22
SN	-1.42	-1.35	2.63	-2.06	-1.78	2.45	-0.61	-0.85	3.03
SiN	-0.92	-0.95	2.66	-3.16	-2.93	2.39	-1.40	-1.54	3.21

The order of adsorption energy values are strongly closed to the order obtained ones from the previous section, and analyzing the E_{ad} values confirmed that Al and B doped CNTs have the strongest interactions with sulfur-containing molecules. In contrast, CNTs and sulphur doped CNTs are the worse adsorbent for these adsorbates.

NBO calculations

In this study, NBO calculations were used to calculate the partial atomic charges and the second-order perturbation energies and they can provide more details about CNT and sulfur-containing compounds interactions. The NBO atomic charges were listed in Table 3. In this table, X refers to the partial atomic charges of doped heteroatoms, and partial charge of nearest carbon atom to the adsorbate for simple carbon nanotubes. C(Av) refers to the average values for the atomic charges of carbon atoms connected to the heteroatoms. Moreover, the S charges were used to report the atomic charges of the sulfur atom in H₂S, SO₂ and thiophene. Finally, the average charges of two adjacent hydrogen atoms in H₂S, two adjacent oxygen atoms in SO₂ and C1 and C5 in thiophene were labeled as Y charges.

Table 3. Selected NBO atomic charges (in atomic units) for all adsorbents, adsorbates and complexes

The charges of nanotube part of molecule	N alone		N-H ₂ S		N-SO ₂		N-thiophene	
	C (Av) ^a	X ^b	C (Av) ^a	X ^b	C (Av) ^a	X ^b	C (Av) ^a	X ^b
N	0.000	0.000	-0.022	-0.068	-0.017	-0.091	-0.003	-0.011
AN	-0.498	1.673	-0.493	1.568	-0.445	1.750	-0.536	1.747
BN	-0.310	0.639	-0.256	0.450	-0.178	0.222	-0.315	0.730
NN	0.219	-0.381	0.223	-0.414	0.205	-0.422	0.231	-0.381
PN	-0.271	0.928	-0.266	0.928	-0.275	0.894	-0.270	0.942
SN	-0.195	0.844	-0.223	0.851	-0.233	0.953	-0.194	0.856
SiN	-0.391	1.170	-0.391	1.146	-0.386	1.157	-0.398	1.203
The charges of adsorbate part of molecules	N-H ₂ S		N-SO ₂		N-thiophene			
	S	Y (Av) ^d	S	Y (Av) ^d	S	Y (Av) ^d		
small molecule ^c	-0.340	0.170	1.286	-0.643	0.358	-0.416		
N	-0.333	0.164	1.296	-0.673	0.360	-0.413		
AN	-0.242	0.235	0.967	-0.827	0.494	-0.507		
BN	-0.034	0.226	1.074	-0.724	0.372	-0.405		
NN	-0.356	0.172	1.262	-0.657	0.364	-0.415		
PN	-0.354	0.176	1.303	-0.660	0.352	-0.415		
SN	-0.361	0.169	1.289	-0.888	0.367	-0.416		
SiN	-0.340	0.165	1.216	-0.725	0.364	-0.415		

^aThis value is the average of atomic charges of three carbon atoms connected to the doped heteroatom

^bThis value is the charge of doped heteroatom in doped nanotubes. For N, this is the charge of carbon atom near to the adsorbate.

^cSmall molecule is implicated to H₂S, SO₂ and thiophene

^dY the average of atomic charges of two hydrogen atoms in H₂S, two oxygen atoms in SO₂ and C1 and C5 in thiophene

In all complexes, the charge transfer process could be easily traced by the measurement of charge alteration of adsorbent or adsorbate versus their initial charges. Regarding this, measurement of the charge transfers for H₂S complexes revealed that BN and AN complexes have the maximum charge transfer values and the obtained values were in this order: BN>AN>NN>SiN>SN>PN. Also, the maximum charge transfer for SO₂ complexes was related to BN and SN and charge transfer values were in this order: BN>SN>AN>NN>PN>SiN. Moreover, in the thiophene complex, the maximum charge transfer have belonged to BN and AN and they were in this order: BN>AN>SiN>PN>SN>NN. Therefore, it could be concluded that NBO charge values have strong agreement with the results of previous sections on the positive effect of B and Al as doped atoms on the improvement of the studied adsorption processes.

In addition to the atomic charges, NBO calculation was used to investigate the E2 values in all 21 complexes (Table 4). E2 is the second-order perturbation energies for donor-acceptor interactions and it shows the strength of the donor-acceptor interaction. The sum of these second-order perturbation energy values is reported in the last column. According to these values, the highest second-order perturbation energies have belonged to BN and AN complexes. The results of NBO calculations confirmed the results of previous sections and introduced BN and AN as the best adsorbents.

Population analyses and DOS plots

In the final part of this study, the molecular orbital population analyses were employed to obtain the HOMO-LUMO band gaps and reactivity parameters for all adsorbents and complexes. The results of these calculations were listed in Table 5 and the densities of state (DOS) plots for adsorbents were shown in Figures 3. The DOS plots for the complexes of the adsorbent and adsorbates were provided in the supporting information (Figures S1-S3).

Table 4. The strongest second order perturbation energies [E2] (in kcal/mol) for donor-acceptor transaction for all complexes

	donor	acceptor	E2	donor	acceptor	E2	donor	acceptor	E2	Sum ^a
N-H	LPC	σ^* S-H	0.55	σ S-H	LPC	0.36	σ C-C	σ^* S-H	0.17	1.08
N-S	LPC	Π^* S-O	1.65	Π^* c-c	σ^* S-O	0.83	LPC	σ^* S-O	0.61	3.09
N-T	Π^* c-c	Π^* c-c	0.60	Π^* c-c	Π^* c-c	0.40	Π^* c-c	Π^* c-c	0.17	1.17
AN-H	LPS	LP*AI	1.62	LPS	LP*AI	1.34	LPS	LP*AI	0.61	3.57
AN-S	LPO	LP*AI	3.09	LP*AI	σ^* S-O	1.39	LPO	LP*AI	1.09	5.57
AN-T	Π c-c	LP*AI	1.40	Π c-c	LP*AI	0.95	Π^* c-c	LP*AI	0.89	3.24
BN-H	LPS	LP*B	1.32	LPS	LP*B	0.95	CRS	LP*B	0.61	2.88
BN-S	LPO	σ^* C-C	1.75	LPO	σ^* C-C	1.36	LPO	RY*C	0.56	3.67
BN-T	Π^* C-C	LP*B	1.35	Π C-C	LP*B	1.32	Π^* C-C	LP*B	0.65	3.32
NN-H	LPN	σ^* S-H	0.71	Π C-C	σ^* S-H	0.64	σ S-H	RY*C	0.19	1.54
NN-S	LPN	LP*S	1.04	Π C-C	LP*S	0.58	σ S-O	RY*C	0.24	1.86
NN-T	Π^* C-C	Π^* C-C	0.70	Π C-C	Π^* C-C	0.57	Π^* C-C	Π^* C-C	0.42	1.69
PN-H	Π C-C	σ^* S-H	0.68	Π^* C-C	σ^* S-H	0.31	Π^* C-C	σ^* S-H	0.29	1.28
PN-S	LPP	LP*S	1.22	Π C-C	LP*S	0.92	LP*S	σ^* C-P	0.37	2.51
PN-T	Π^* C-C	Π^* C-C	1.13	LPS	σ^* C-P	0.67	Π C-C	Π^* C-C	0.45	2.25
SN-H	Π C-C	σ^* S-H	0.84	Π^* C-C	σ^* S-H	0.36	σ S-H	Π^* C-C	0.24	1.44
SN-S	LPO	σ^* C-S	1.56	LPO	σ^* C-S	1.06	LPO	σ^* C-C	0.32	2.94
SN-T	Π C-C	σ^* C-S	0.56	Π^* C-C	Π^* C-C	0.34	Π^* C-C	Π^* C-C	0.23	1.13
SiN-H	σ C-Si	σ^* S-H	0.57	Π C-C	σ^* S-H	0.38	Π^* C-C	σ^* S-H	0.20	1.15
SiN-S	LPS	σ^* C-Si	1.82	LPS	σ^* C-Si	1.02	LPS	LP*Si	0.81	3.65
SiN-T	Π^* C-C	Π^* C-C	1.19	Π^* C-C	Π^* C-C	0.42	Π^* C-C	LP*Si	0.28	1.89

^aThis is the sum of three E2 values listed in the same row

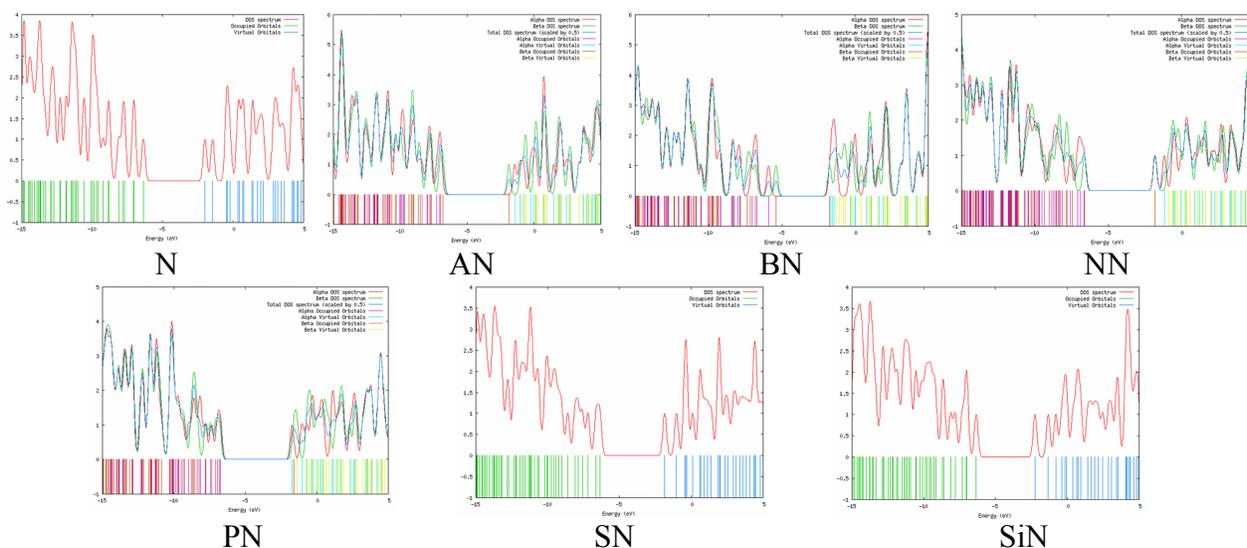


Figure 3. DOS plots of the employed nano models (CNTs and SCNTs), without the presence of adsorbates

According to these figures, any meaningful difference between the diagrams of the complexes with those of adsorbent could not be observed. However, the diagrams of CNTs with different dopant atoms are different from each other and each dopant atom meaningfully changes the DOS diagram.

Table 5. Energies of HOMO and LUMO levels, energy gaps (E_g), chemical potential (μ), chemical hardness (η), global softness (S) and electrophilicity index (ω) for all structures (all energy values in eV)

	E(HOMO)	E(LUMO)	E_g	μ	η	S	ω
N	-0.234	-0.073	0.161	-0.154	0.080	12.454	0.147
N-H	-0.237	-0.077	0.160	-0.157	0.080	12.508	0.155
N-S	-0.242	-0.093	0.149	-0.168	0.074	13.426	0.189
N-T	-0.233	-0.072	0.160	-0.152	0.080	12.467	0.145
AN	-0.252	-0.055	0.197	-0.154	0.099	10.149	0.120
AN-H	-0.245	-0.053	0.192	-0.149	0.096	10.440	0.116
AN-S	-0.249	-0.079	0.169	-0.164	0.085	11.801	0.159
AN-T	-0.240	-0.040	0.200	-0.140	0.100	9.994	0.097
BN	-0.217	-0.061	0.155	-0.139	0.078	12.870	0.125
BN-H	-0.240	-0.048	0.192	-0.144	0.096	10.440	0.108
BN-S	-0.237	-0.075	0.162	-0.156	0.081	12.318	0.149
BN-T	-0.232	-0.059	0.174	-0.145	0.087	11.527	0.122
NN	-0.244	-0.067	0.178	-0.155	0.089	11.268	0.136
NN-H	-0.251	-0.069	0.182	-0.160	0.091	10.984	0.140
NN-S	-0.250	-0.079	0.171	-0.165	0.086	11.667	0.158
NN-T	-0.242	-0.062	0.180	-0.152	0.090	11.083	0.128
PN	-0.248	-0.063	0.184	-0.156	0.092	10.854	0.131
PN-H	-0.248	-0.068	0.180	-0.158	0.090	11.131	0.139
PN-S	-0.252	-0.097	0.155	-0.174	0.078	12.902	0.196
PN-T	-0.245	-0.056	0.189	-0.150	0.094	10.590	0.120
SN	-0.234	-0.068	0.166	-0.151	0.083	12.056	0.138
SN-H	-0.239	-0.075	0.164	-0.157	0.082	12.192	0.150
SN-S	-0.250	-0.099	0.152	-0.174	0.076	13.165	0.200
SN-T	-0.232	-0.067	0.165	-0.149	0.083	12.104	0.135
SiN	-0.234	-0.083	0.150	-0.158	0.075	13.293	0.167
SiN-H	-0.241	-0.092	0.149	-0.166	0.075	13.405	0.185
SiN-S	-0.245	-0.100	0.145	-0.172	0.073	13.759	0.204
SiN-T	-0.232	-0.082	0.151	-0.157	0.075	13.280	0.164

The HOMO-LUMO energy gaps for various nanotubes were this order: AN (0.197 eV)>PN (0.184 eV)>NN (0.178 eV)>SN (0.166 eV)>N (0.161 eV)>BN (0.155 eV) >SiN (0.150 eV). It seems that the conductivity of carbon nanotubes was enhanced by doping with B and Si heteroatoms. In addition, according to the energy gap values for studied complexes, the intramolecular interactions between adsorbents and adsorbates changed the bandgap for each complex. Therefore, the HOMO-LUMO band gaps of CNTs could be changed in the presence of H₂S, SO₂ and thiophene. It should be mentioned that by adsorption of SO₂ the E_g values of CNTs were reduced more, compared to H₂S and thiophene, which can be interpreted as the stronger interactions of SO₂ with the studied carbon nanotube. The doping of Al, B, N and P atoms could affect E (HOMO) and E (LUMO) values while for S and Si-doped nanotubes, E(HOMO) values were exactly equal to the simple carbon nanotube. A comparison of chemical potential (μ) values indicated that the highest chemical potential was related to BN and the order of these values is: BN>SN>AN,N>NN>PN>SiN. Moreover, a slight decrease was observed in chemical potential (μ) values of complexes. Among all complexes, SO₂-Containing systems showed the most decline in chemical potential values versus their related simple and doped-CNTs. The global softness (S) values and the chemical hardnesses (η) is related to E_g values and no more explanation is needed. Finally, electrophilicity index (ω), for various nanotubes was in this order: SiN>N>SN>NN>PN>BN>AN. It could be concluded that electrophilicity indices were not meaningfully affected by doping nanotubes. Finally, a comparison of electrophilicity index in complexes indicated that in all complexes, SO₂ and H₂S could increase the electrophilicity indices while thiophene decreased them.

Conclusion

In this study, the sensor abilities and adsorption potentials of simple and Al, B, N, S, P and Si-

doped CNTs interacting with some sulfur-containing molecules (H_2S , SO_2 and thiophene) were investigated theoretically. In this line, DFT calculations were used to calculate the adsorption energies and their related parameters. The results showed an exothermic interaction of H_2S , SO_2 and thiophene with CNT and doped CNTs. The maximum negative adsorption energies have belonged to AN and BN. Besides, NBO calculations were used to calculate second-order perturbation energies related to the interactions between adsorbents and adsorbates. The highest perturbation energies were related to BN and AN. In the next step, Population analyses were performed to calculate the HOMO-LUMO energy gaps, reactivity parameters and to obtain DOS plots.

Comparing the results of this work with the previous studies showed similar findings in all of these works. For example, the theoretical studies of Sonawane et al. on the adsorption of SO_2 on silicon-doped CNTs showed that the presence of silicon has a meaningful effect on the adsorption energies [42]. Moreover, the work of Sun et al. showed the doping of carbon-based materials with nitrogen could enhance the effective surface area for the adsorption of SO_2 [43]. In this line, there are lots of work showing the enhancement effects of doping of carbon materials on their adsorption potencies for the studied molecules [44-47].

Briefly, the results demonstrated the favourability of adsorption of SO_2 by CNTs (BN and AN, in particular). Besides, the observed changes in the energy gap values of the BN and AN complexes (versus the CNTs alone) introduced Al and B doped CNTs as excellent candidates for employing in sensor devices.

Acknowledgment

We are thankful to the National High-Performance Computing Center (NHPCC) at Isfahan University of Technology (<http://nhpcc.iut.ac.ir>) for providing computational facilities (Raksh supercomputer) for this study.

References

- [1] Popov VN. Carbon nanotubes: properties and application. *Mat. Sci. Eng. R.* 2004;43(3):61-102.
- [2] Sun YP, Fu K, Lin Y, et al. Functionalized carbon nanotubes: properties and applications. *Acc. Chem. Res.* 2002;35(12):1096-104.
- [3] Odom TW, Huang JL, Kim P, et al. Atomic structure and electronic properties of single-walled carbon nanotubes. *Nature.* 1998;391(6662):62.
- [4] Chen J, Hamon MA, Hu H, et al. Solution properties of single-walled carbon nanotubes. *Science.* 1998;282(5386):95-8.
- [5]. Iuima S. Helical microtubules of graphitic carbon. *Nature.* 1991;354(7):56-8.
- [6] Zhao J, Buldum A, Han J, et al. Gas molecule adsorption in carbon nanotubes and nanotube bundles. *Nanotechnology.* 2002;13(2):195.
- [7] Ye Y, Ahn CC, Witham C, et al. Hydrogen adsorption and cohesive energy of single-walled carbon nanotubes. *Appl. Phys. Lett.* 1999;74(16):2307-9.
- [8] Striolo A, Chialvo AA, Gubbins KE, et al. Water in carbon nanotubes: Adsorption isotherms and thermodynamic properties from molecular simulation. *J. Chem. Phys.* 2005;122(23):234712.
- [9] Yang RT. Hydrogen storage by alkali-doped carbon nanotubes—revisited. *Carbon.* 2000;38(4):623-6.

- [10] Peng S, Cho K. Ab initio study of doped carbon nanotube sensors. *Nano lett.* 2003;3(4):513-7.
- [11] Hu X, Wu Y, Li H, et al. Adsorption and activation of O₂ on nitrogen-doped carbon nanotubes. *J. Phys. Chem. C.* 2010;114(21):9603-7.
- [12] Wang R, Zhang D, Sun W, et al. A novel aluminum-doped carbon nanotubes sensor for carbon monoxide. *J. Mol. Struct.* 2007;806(1-3):93-7.
- [13] Cruz-Silva E, Cullen DA, Gu L, et al. Heterodoped nanotubes: theory, synthesis, and characterization of phosphorus– nitrogen doped multiwalled carbon nanotubes. *ACS nano.* 2008;2(3):441-8.
- [14] Ganji MD, Ahmadian N, Goodarzi M, et al. Molecular hydrogen interacting with Si-, S-and P-doped C₆₀ fullerenes and carbon nanotube. *J. Comput. Theor. Nanosci.* 2011;8(8):1392-9.
- [15] Wang YL, Su KH, Zhang JP. Studying of B, N, S, Si and P Doped (5, 5) carbon nanotubes by the density functional theory. *Adv. Mater. Lett.* 2012;463:1488-1492.
- [16] Garcia AG, Baltazar SE, Castro AH, et al. Influence of S and P doping in a graphene sheet. *J. Comput. Theor. Nanosci.* 2008;5(11):2221-9.
- [17] Peyghan AA, Omidvar A, Hadipour NL, et al. Can aluminum nitride nanotubes detect the toxic NH₃ molecules?. *Physica E: Low-Dimens. Syst. Nanostruct.* 2012;44(7-8):1357-60.
- [18] Ahmadi A, Hadipour NL, Kamfiroozi M, et al. Theoretical study of aluminum nitride nanotubes for chemical sensing of formaldehyde. *Sens. Actuators B.* 2012;161(1):1025-9.
- [19] Beheshtian J, Baei MT, Bagheri Z, et al. Carbon nitride nanotube as a sensor for alkali and alkaline earth cations. *Appl. Surf. Sci.* 2013;264:699-706.

- [20] Nasresfahani S, Doroodmand MM, Sheikhi MH, Ghasemi AR. Specific H₂S gas sensor based on metal nanoparticles, sulfur and nitrogen/single-walled carbon nanotube-modified field effect transistor. *J. Nanoeng.* 2011;1:228-36.
- [21] Adib F, Bagreev A, Bandosz TJ. Adsorption/oxidation of hydrogen sulfide on nitrogen-containing activated carbons. *Langmuir.* 2000;16:1980-6.
- [22] Shimoyama I, Baba Y. Thiophene adsorption on phosphorus-and nitrogen-doped graphites: Control of desulfurization properties of carbon materials by heteroatom doping. *Carbon.* 2016;98:115-25.
- [23] Sun F, Gao J, Liu X, Yang Y, Wu S. Controllable nitrogen introduction into porous carbon with porosity retaining for investigating nitrogen doping effect on SO₂ adsorption. *Chem. Eng. J.* 2016;290:116-24.
- [24] Tavakol H, Shahabi D, Keshavarzipour F, et al. Theoretical calculation of simple and doped CNTs with the potential adsorption of various ions for water desalination technologies. *J. Struct. Chem.* 2019:1-1.
- [25] Tavakol H, Hashemi F, Molavian MR. Theoretical investigation on the performance of simple and doped graphenes for the surface adsorption of various ions and water desalination. *J. Struct. Chem.* 2017;28(6):1687-95.
- [26] Glasser M, Greenburg L. Air pollution, mortality, and weather. *Arch. Environ. Health.* 1971;22(3):334-43.
- [27] Khan AA, Schuler MM, Prior MG, et al. Effects of hydrogen sulfide exposure on lung mitochondrial respiratory chain enzymes in rats. *Toxicol. Appl. Pharmacol.* 1990;103(3):482-90.
- [28] Buechley RW, Riggan WB, Hasselblad V, et al. SO₂ levels and perturbations in mortality: A study in the New York-New Jersey metropolis. *Arch. Environ. Health.* 1973;27(3):134-7.

- [29] Cohen AA, Bromberg S, Buechley RW, et al. Asthma and air pollution from a coal-fueled power plant. *Am. J. Public Health.* 1972;62(9):1181-8.
- [30] Mori F, Tanji K, Wakabayashi K. Thiophene, a sulfur-containing heterocyclic hydrocarbon, causes widespread neuronal degeneration in rats. *Neuropathology.* 2000;20(4):283-8.
- [31] Saadat K, Tavakol H. An exceptional functionalization of doped fullerene observed via theoretical studies on the interactions of sulfur-doped fullerenes with halogens and halides. *RSC Adv.* 2015;5(68):55227-37.
- [32] Tavakol H, Shahabi D. DFT, QTAIM, and NBO study of adsorption of rare gases into and on the surface of sulfur-doped, single-wall carbon nanotubes. *J. Phys. Chem. C.* 2015;119(12):6502-10.
- [33] Tavakol H, Mollaei-Renani A. DFT, AIM, and NBO study of the interaction of simple and sulfur-doped graphenes with molecular halogens, CH₃OH, CH₃SH, H₂O, and H₂S. *J. Struct. Chem.* 2014;25(6):1659-67.
- [34] Frisch MJ, Trucks GW, Schlegel HB, et al. Gaussian 09 (Gaussian, Inc., Wallingford, CT). Revision D. 2009;1.
- [35] Jafari-Chermahini MT, Tavakol H. Adsorption of CO₂ on sodium iodide (NaI)_n (n ≤ 10) clusters: A density functional theory investigation. *Comp. Theor. Chem.* 2018;1145:37-43.
- [36] Shahabi D, Tavakol H. A DFT study on the catalytic ability of aluminum doped graphene for the initial steps of the conversion of methanol to gasoline. *Comp. Theor. Chem.* 2018;1127:8-15.
- [37] Chai JD, Head-Gordon M. Systematic optimization of long-range corrected hybrid density functionals. *J. Chem. Phys.* 2008;128:084106.

- [38] Chen Z, Li Y, He Z, Xu Y, Yu W. Theoretical investigations on charge transport properties of tetrabenzo [a, d, j, m] coronene derivatives using different density functional theory functionals (B3LYP, M06-2X, and wB97XD). *J. Chem. Res.* 2019;43:293-303.
- [39] Miertuš S, Scrocco E, Tomasi J. Electrostatic interaction of a solute with a continuum. A direct utilization of AB initio molecular potentials for the prevision of solvent effects. *J. Chem. Phys.* 1981;55(1):117-29.
- [40] Glendening ED, Reed AE, Carpenter JE, et al. NBO Version 3.1. There is no corresponding record for this reference. 1998.
- [41] O'boyle NM, Tenderholt AL, Langner KM. Cclib: a library for package-independent computational chemistry algorithms. *J. Comput. Chem.* 2008;29(5):839-45.
- [42] Sonawane MR, Habale D, Nagare BJ, Gharde R. Interaction of O₂, CO₂, NO₂ and SO₂ on Si-doped Carbon Nanotube. *Int. J. Appl. Phys. Math.* 2011;1(2):138.
- [43] Sun F, Gao J, Liu X, Yang Y, Wu S. Controllable nitrogen introduction into porous carbon with porosity retaining for investigating nitrogen doping effect on SO₂ adsorption. *Chem. Eng. J.* 2016;290:116-24.
- [44] Shimoyama I, Baba Y. Thiophene adsorption on phosphorus-and nitrogen-doped graphites: Control of desulfurization properties of carbon materials by heteroatom doping. *Carbon.* 2016;98:115-25.
- [45] Qu Z, Sun F, Liu X, Gao J, Qie Z, Zhao G. The effect of nitrogen-containing functional groups on SO₂ adsorption on carbon surface: enhanced physical adsorption interactions. *Surf. Sci.* 2018;677:78-82.

[46] Yoosefian M, Zahedi M, Mola A, Naserian S. A DFT comparative study of single and double SO₂ adsorption on Pt-doped and Au-doped single-walled carbon nanotube. *Appl. Surf. Sci.* 2015;349:864-9.

[47] Zhang HP, Luo XG, Song HT, Lin XY, Lu X, Tang Y. DFT study of adsorption and dissociation behavior of H₂S on Fe-doped graphene. *Appl. Surf. Sci.* 2014;317:511-6.

Graphical Abstract

