Lab-in-Silico
https://lab-in-silico.com
eISSN: 2717-1922

ORIGINAL RESEARCH

Lab-in-Silico. 2021;2(1):38-43. DOI: 10.22034/labinsilico21021038

DFT Approach on SiC Nanotube for NO_2 Gas Pollutant Removal

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Received: 18 February 2021 / *Accepted*: 24 February 2021 / *Published Online*: 30 June 2021

ABSTRACT. This work was performed to investigate removal process of nitrogen dioxide (NO_2) gas pollutant by its adsorption at the surface of a representative silicon carbide (SiC) nanotube through density functional theory (DFT) calculations. Singular models were optimized first and bimolecular models were optimized again to achieve complex formations. Two models of N@SiC and O@SiC were obtained regarding the initial starting position of NO2 from N site or O site towards the tubular surface. The results indicate that the strength of O@SiC complex could be more favorable than N@SiC complex in terms of energy and distance. Further analyses of frontier molecular orbitals showed the effects of such complex formations on the original energy levels in addition to values of their gap and average. The obtained values of atomic scale quadrupole coupling constants (Qcc) showed the effects of such complex formation on the atoms of NO2 gas providing information about the reason of Si-N and Si-O interacting configuration. As a consequence, the results of this work showed very well the benefit of using such bimolecular complex formation for removal of NO_2 gas pollutant by means of its adsorption at the SiC nanotube surface.

KEYWORDS. Silicon carbide; Nanotube; NO_2; DFT; Adsorption; Pollutant; Gas removal.

INTRODUCTION. Technological improvements of current world provided several benefits to human life but also harmful effects such as exhausting gaseous pollutants.[1] In those industrial cities, existence of air pollutants is almost a serious problem without real solution up to now.[2] Therefore, the researchers have put considerable attempts these years to arise some types of gas adsorbents to remove or reduce such pollutants from the air as much as possible.[3] Such works have been actually initiated by the innovation of nanostructures as proper surfaces for such adsorption function of gas pollutants removal from environment.[4] Indeed, nanostructures have been always seen interesting to be investigated in order to evaluate characteristic features for their further recognition and application aspects.[5-10] To this time, advantages of nanostructures for adsorption of gaseous pollutants have been extensively studied especially employing computational methods.[11-15] Indeed, it is a benefit of computer-based works to investigate chemical structures and processes in the lowest atomic and molecular scales to provide insightful information for

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the specified purposes.[16-20] Very much recently, adsorption of hazardous monoxide carbon by nanostructures has been reported based on computations.[21] Since the experimental media of gaseous pollutants adsorption would be supposed to work in gas phase, performing such pure molecular calculations could help to make sense the idea through such computer-based obtained results.[22] To this aim, adsorption process of nitrogen dioxide (NO_2) gas at the surface of a representative silicon carbide (SiC) nanotube was investigated in the current work employing the computational molecular approach (Fig. 1). After introduction of carbon nanotube (CNT) to the science world, several other types of tubular structures were recognized such as SiC nanotubes.[23-26] In contrast with the pure carbon surface of CNT, such hetero Si-C surface could help to provide more reactivity for SiC nanotube.[27] Therefore, exploring the advantage of SiC nanotube application for adsorption of NO_2 gas pollutant was targeted in this work.

Chemical and petrochemical industries mainly produce different types of pollutant gases, in which NO_2 is one of the most important ones with serious harmful effects.[28] The gas could easily react with the available humid of air to make some types of acids for acidic rains in addition to its oxidative reactivity for destroying nature.[29] Such activities of NO_2 exposure are very much deathful for the human life and its removal should be considered regarding the environmental safety aspects.[30] Several attempts have been reported up to now to produce some novel materials for gas removal, but the story has not been completed yet and further works are required.[31] Hence, this work was set up as a complementary work to yield some more insightful information about details of such NO_2 gas pollutant removal by its adsorption process at the SiC nanotube surface (Fig. 1) through computer-based methodologies. All model structures were optimized and the corresponding descriptors were obtained to reach to the aim of this work.

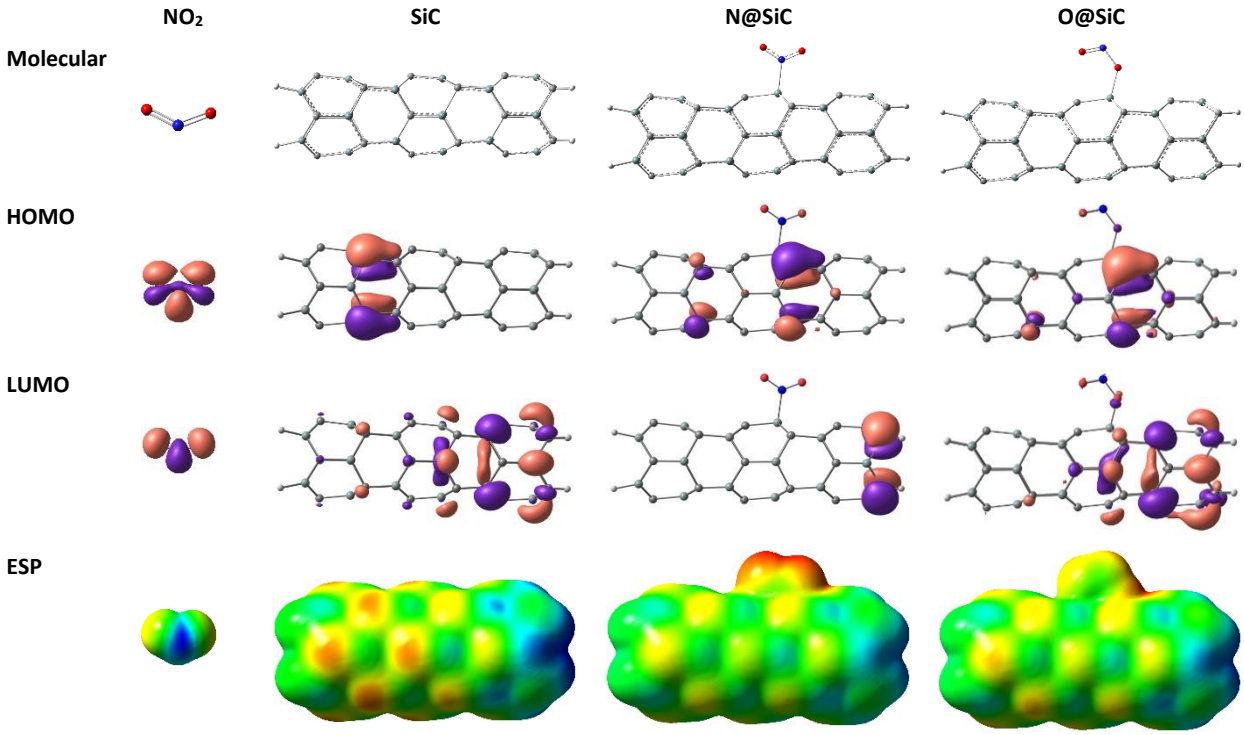

Fig. 1: Models representations in structural and molecular orbital forms.

METHODOLOGY. Within this work, quantum chemical density functional theory (DFT) calculations were performed to achieve the specified goals of NO_2 gas adsorption at the surface of SiC nanotube. The B3LYP exchange-correlation functional and the 6-31G* standard basis set were employed for DFT calculations using the Gaussian program.[32] Showing in Fig. 1, singular molecules of NO_2 and the representative $Si_{24}C_{24}H_8$ nanotube were first optimized to achieve the minimum energy structures in addition to optimized molecular descriptors. Next, possible complex formations of NO_2 and SiC nanotube were investigated by the initial locating of NO_2 from its N or O atomic sides towards the tubular surface producing N@SiC

and O@SiC complexes respectively. The complex models were re-optimized using the optimized singular molecules in addition to including dispersion correction in the calculations.[33] As a result, the optimized complex systems were ready to be involved in further calculations to yield electronic properties for the molecular scale systems. All the results including energy levels of the highest occupied and the lowest unoccupied molecular orbitals (EHOMO and ELUMO), energy gap (EG), Fermi energy (FE), dipole moment (DM), total energy (TE), adsorption energy (AE), and interacting distance (ID) were summarized in Table 1. Moreover, the HOMO and LUMO distribution patterns and electrostatic potential (ESP) surfaces were also represented for the models (Fig. 1). The atomic quadrupole coupling constant (Qcc) for each of N and O atoms were also obtained for singular and complex models (Table 2) to show the effects of such adsorption process on the properties of the gas molecule. Such Qcc properties are useful elements for describing the electronic properties of matters at the atomic scales especially for interacting systems.[34-46]

Table 1: Molecular descriptors.*

Descriptor	NO_2	SiC	N@SiC	O@SiC
EHOMO eV	-7.832	-5.416	-5.634	-5.507
ELUMO eV	-3.897	-4.307	-4.253	-4.169
EG eV	3.935	1.109	1.381	1.338
FE eV	5.864	-4.862	-4.944	-4.838
DM Debye	0.322	9.971	8.395	7.593
TE eV	-5580.425	-214066.203	-219647.936	-219648.532
AE eV	N/A	N/A	-1.308	-1.904
ID Å	N/A	N/A	1.903 Si-N	1.746 Si-O

*See Fig. 1 for models. EG = ELUMO – EHOMO; FE = ½(EHOMO + ELUMO); AE = ($TE_{Complex}$ - TE_{SiC} - TE_{NO_2})

RESULTS & DISCUSSION. Regarding the importance of gaseous pollutants sensing and removal from the environment, this work was performed to investigate such goal about NO_2 gas pollutant removal by its adsorption at the surface of SiC nanotube (Fig. 1). To achieve this purpose, singular molecules of NO_2 and SiC nanotube were optimized first to reach the minimum energy structures and their complex formations were optimized again to explore such adsorption processes. In this case, the minimum energy structures were obtained for both of singular and complex models for further investigating their electronic and structural features. It is important to remember here that, two models of complexes including N@SiC and O@SiC were achieved regarding their initial starting position for the optimization processes as the N site of NO_2 was located towards the tubular surface or the O site was located in this direction. Hence, two models of adsorbed gas at the surface were obtained as the result of optimization processes. The obtained molecular and atomic scale features were included in Tables 1 and 2 and the visual representation of the investigated models and their properties were exhibited in Fig. 1.

Carefully examining the results of obtained molecular descriptors of Table 1 could show insightful information about the investigated system structures. The first point could be explained about the energy levels of HOMO and LUMO frontier molecular orbitals, in which the results indicated that such features of complex models were able to be recognized in comparison with singular models. Both of HOMO and LUMO levels detected the effects of complex formations in addition to values of their EG and FE features, which were both showing significant recognition capabilities. Additionally, such frontier molecule orbitals deviations were very well recognized by the distribution patterns and ESP of Fig. 1. The obtained values of DM showed also such electric charge deviations for the models. It was obvious that the small singular molecular of NO_2 gas could significantly influence on the features of SiC nanotube surface as indicated by both of quantitative and qualitative parameters. To explore more about such deviations, values of total energies were obtained and the results showed better stability for O@SiC complex model in comparison with N@SiC complex. Careful examining the values of AE could better explain such

achievement, in which the adsorption strength was higher for O@SiC model with Si-O ID of 1.746 Å in comparison with N@SiC model with Si-N ID of 1.903 Å. It should be noted that formations of both complex systems were favorably achievable regarding meaningful values of their AE in addition to appropriate values of ID for such complex formation systems. Additionally, possible configurations of NO_2 adsorption at the surface of SiC nanotube were successfully achieved by such calculations to take account any possibility for such bimolecular adsorption process.

Table 2: Quadrupole coupling constants (Qcc /MHz).*

Atom	NO_2	N@SiC	O@SiC
N	3.515	2.783	5.772
O	8.968	12.848	12.486
O	8.955	12.742	9.998

*See Fig. 1 for models. Method of calculation was described in a reference work.[40]

To show the effects of complex formations on the atomic features of NO_2, values of Qcc were obtained for singular and complex models (Table 2). The results showed that two O atoms detected different environments in the singular model and deviations were also detected for the complex models. Very much interestingly, the obtained values of Qcc showed the effects of adsorption processes at the atomic sites of NO_2, in which such effects were shown by means of the amount of changes of values from singular to complex forms. F such atomic parameters, electronegativity is very much important and it could lead the electron gaining of an atom from bond interaction systems with another atom. Values of electronegativity for both of N and O atoms were larger than both of Si and C atoms and the changes of Qcc values could show such electronic gaming for the atoms of NO_2. Moreover, the tendency of interaction formation with Si atom could be also related to such achievement, in which the value of electronegativity for Si atom was smaller than C atom for contributing to the interaction.

CONCLUSION. This work was performed using DFT calculations to investigate electronic and structural features of NO_2 gas adsorption at the surface of SiC nanotube for removal purposes of this pollutant from environment. Based on the obtained results, some remarkable achievements were summarized. First, the optimized complex formations were achieved in two models based on initial starting position of NO_2 gas at the tubular surface yielding N@SiC and O@SiC complex models. Second, both obtained complex models were favorable regarding the strength of adsorption in cases of energy and distance. Third, HOMO and LUMO showed significant changes of systems regarding the values in addition to their gap and average energies. Fourth, atomic scale features of Qcc showed changes of atomic sites of NO_2 of complex models in comparison with singular model. Fifth, the tendency of contribution of Si atom of SiC nanotube to interactions with NO_2 gas molecule was described by the values of atomic electronegativity. Finally, such examined molecular model systems of this work could be proposed for NO_2 gas pollutant sensing and removal by means of adsorption at the SiC nanotube surface.

DISCLOSURE STATEMENT. The author(s) did not report any potential conflict of interest. Wd

ACKNOWLEDGEMENTS. This work was evaluated from a part of master thesis of A. Iranimanesh granted by the research council of Tehran Medical Sciences, Islamic Azad University, which is acknowledged.

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How to Cite: Iranimanesh A, Yousefi M, Mirzaei M. DFT Approach on SiC Nanotube for NO_2 Gas Pollutant Removal. Lab-in-Silico. 2021;2(1):38-43.
DOI: https://doi.org/10.22034/labinsilico21021038
URL: https://sciengpub.com/lab-in-silico/article/view/labinsilico21021038