Int. J. Bio-Inorg. Hybr. Nanomater., 5(4): 245-255, Winter 2016

TiO_2/Graphene oxide nanocomposite as an ideal NO gas sensor: A density functional theory study

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Received: 16 August 2016; Accepted: 19 October 2016

ABSTRACT: We performed a density functional theory investigation on the structural and electronic properties of pristine and nitrogen-doped TiO_2/Graphene oxide nanocomposites as the adsorbents for the removal of toxic NO molecules in the environment. We presented the most stable adsorption configurations and examined the interaction of NO molecule with these doped and undoped nanocomposites. It turns out that the NO molecule is preferentially adsorbed on the active oxygen and nitrogen atom sites of nanocomposite. The insights of the computations include the structural and electronic analyses such as bond lengths/ angles, adsorption energies, density of states (DOSs) and molecular orbitals. It was found that the adsorption of NO on the N-doped nanocomposite is energetically more favorable than the adsorption on the undoped one, representing the higher reactivity of N-doped nanocomposites with NO molecule. It means that the adsorption on the N-doped nanocomposite provides the most stable configurations and consequently the most efficient adsorption processes. Nevertheless, our computational study on TiO_2/Graphene oxide nanocomposites suggests that the N-doped nanocomposites are more sensitive than the undoped ones when utilized as detectors or sensors for NO detection.

Keywords: *Adsorption; Density Functional Theory; Density of states; Nanocomposite; NO molecule; TiO_2/Graphene oxide*

INTRODUCTION

Titanium dioxide has been characterized as one of the most important metal oxide semiconductors because of its unique properties such as chemical stability, non-toxicity and low-cost (Satterfield, 1991, Ando, *et al.*, 1997, Fujishima and Honda, 1972). TiO_2 can be observed in a various range of applications both in scientific research and industrial applications such as gas sensor devices, semiconductor materials, heterogeneous catalysis, photocatalysis and so on (Dutta, *et al.*, 1999, Garfunkel, *et al.*, 1998, Banfied and Veblen, 2015, Erdogan, *et al.*, 2010). In the past few years, it has aroused many scientific considerations (Zarei, *et al.*, 2013, Liu, *et al.*, 2012, Landman, *et al.*, 2012, Topalian, *et al.*, 2012) on the ex-

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(*) Corresponding Author - e-mail: a_abbasi@azaruniv.edu perimental and theoretical research in order to develop TiO_2 associated science and industry. The electronic structure of TiO_2 gives it some exceptional properties and applications, such as its wide band gap (3-3.2eV) and its photocatalytic activity (Wang and Doren, 2005, Wei, *et al.*, 2010). Doping of titanium dioxide with different nonmetal elements, especially nitrogen, improves its photocatalytic activity to the visible region and greatly increases the optical sensitivity of TiO_2 (Liu, *et al.*, 2013, Zhao, *et al.*, 2011, Ebrahimzadeh, *et al.*, 2015). N-doped TiO_2 anatase nanoparticles have attracted many scientific and industrial interests over the last decades. Nitrogen-doping can introduce a hole inside the band-gap of titanium dioxide, impurity states in the band-gap can increase the photocatalysis rate of titanium dioxide and oxidize nitric oxide (NO) molecule. The adsorption of air pollutants on N-doped TiO_2 nanoparticles has not been widely studied. In this research, we investigated the adsorption of NO molecule on N-doped TiO_2 anatase nanoparticles using the DFT calculations. The adsorption configurations of NO molecule between TiO_2 nanoparticle and two dimensional graphene oxide nanostructures were examined in detail. Meanwhile, N-doping in titanium dioxide increases the adsorption energies for doped structures. Furthermore, more NO molecules can be adsorbed on the N-doped nanoparticles in comparison with pristine ones. The doping of nitrogen into TiO_2 anatase has a considerable influence on the adsorption energies for the studied nanocomposites, acting as an efficient method to remove the air pollutants from the environment. NO is a toxic material, which can cause a severe damages in the human body. Thus, monitoring its concentration is a significant topic to public health (Liu, *et al.*, 2012). The main strategy towards attaining extensive usefulness of TiO_2/Graphene oxide nanocomposites is to perform important studies on the electronic properties such as density of states (DOS), molecular orbitals and structural properties such as bond lengths and adsorption energies. In industrial processes, metal oxides especially TiO_2, are commonly employed as detectors or adsorbents to eliminate the NO molecules from the atmosphere (Liu, *et al.*, 2012). In this study, we performed DFT calculations in order to understand NO adsorption on N-doped TiO_2/Graphene oxide nanostructures. As well as, some electronic and structural properties including the total density of states (TDOS), bond lengths, bond angles, adsorption energies and Mulliken population analysis for studied systems were examined. The results show that the NO molecule is more effectively adsorbed on N-doped nanocomposites, compared to the undoped ones. The main aim of this work is to supply an overall understanding on the adsorption configurations of NO molecule on the TiO_2/Graphene oxide nanocomposites.

CALCULATION METHODS

Calculation details

We have carried out all of the calculations based on density functional theory (Hohenberg and Kohn, 1964, Kohn and Sham, 1965) as implemented in the OpenMX3.8 code (Ozaki, 2013), to study the structural and electronic properties of perfect and N-doped TiO_2/Graphene oxide nanocomposites with adsorbed NO molecule. OPENMX is an effective software package for nano-scale material simulations based on DFT, norm-conserving pseudopotentials, and numerical pseudo-atomic localized basis functions (Ozaki, 2003, Ozaki and Kino, 2004). Pseudo atomic orbitals (PAO's) adjusted on atomic sites were employed as basis sets in order to expand the wave functions in a Kohn-Sham schema. The local density approximation (LDA) parameterized by Ceperly-Alder (CA) and generalized gradient approximation (GGA) in the Perdew–Burke–Ernzerhof form (PBE) were employed to define the exchange-correlation energy functional (Perdew and Zunger, 1981, Perdew, *et al.*, 1997). The energy cutoff was set at 150 Ry during the calculations. For PAO functions, the database version of 2013 was utilized. The cutoff radii of basis functions were considered to be 7 for Ti, 5 for O, N and C and 5.5 for H (all in Bohrs). Two s-state radial functions and two p-state radial functions were used for N, O and C atom, while three s-state, three p-state and two d-state radial functions were defined for Ti atom. For s-state of H atom, one radial function was assumed. In the calculations related to the electronic properties, 21 k-points along each high symmetry lines were considered. The charge transfer between NO molecule and

TiO_2/Graphene oxide nanocomposite was evaluated based on the Mulliken charge analysis. For visualizing data such as isosurfaces of molecular orbitals, the open-source program XCrysDen (Koklj, 2003) was utilized. The size of the box considered in these computations is 20×20×35 $Å^3$, which contains undoped or N-doped TiO_2 nanoparticle and graphene oxide nanosheet. The computations were carried out by use of a cluster of Ubuntu systems installed on the core-i7 processors with at least 8 GB memory per each computational core. The adsorption energy, Eads, of each configuration was determined by,

$$E_{ads}=E_{nanoparticle+adsorbate}-(E_{nanoparticle}+E_{adsorbate}) \quad (1)$$

where $E_{adsorbate}$ represents the energy of an isolated NO molecule, $E_{nanoparticle+adsorbate}$ and $E_{nanoparticle}$ are the total energies of the nanocomposite with and without NO molecule respectively.

Structural models

The chosen TiO_2 anatase nanoparticles encompassing 72 atoms were constructed by putting 3×2×1 numbers of TiO_2 unit cells along x, y and z axis, respectively. A distance of 12.4 A° was set between neighboring particles to reduce the interaction between neighbor particles. The unit cell of TiO_2 was obtained from "American Mineralogists Database" webpage and introduced by Wyckoff (Wyckoff, 1963). A 4×4 supercell of graphene oxide nanosheet was chosen in the calculations. The considered TiO_2 anatase nanoparticle was shown in Fig. 1.

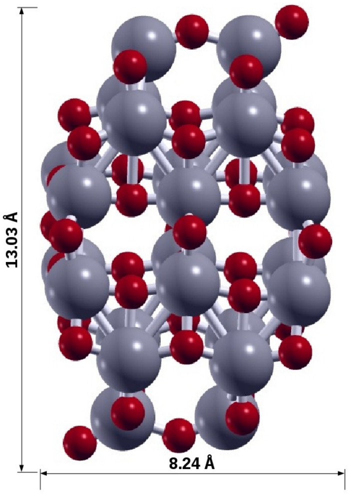


Fig. 1. Optimized structure of a pristine TiO_2 anatase nanoparticle constructed from the 3×2×1 unit cells; O_C: central oxygen; O_T: twofold coordinated oxygen; O_D: dangling oxygen.

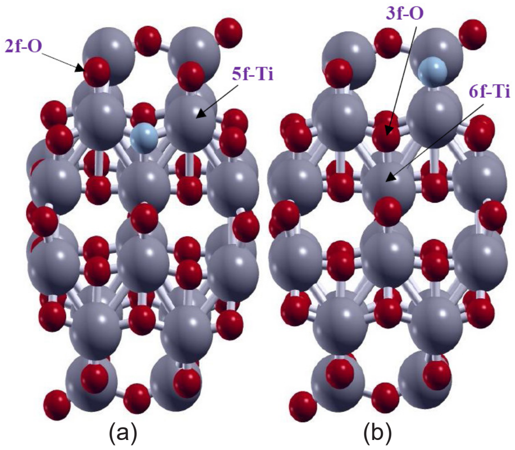


Fig. 2. Optimized N-doped TiO_2 anatase nanoparticles constructed using the 3×2×1 unit cells; (a) O_C-substituted nanoparticle. (b) O_T-substituted one.

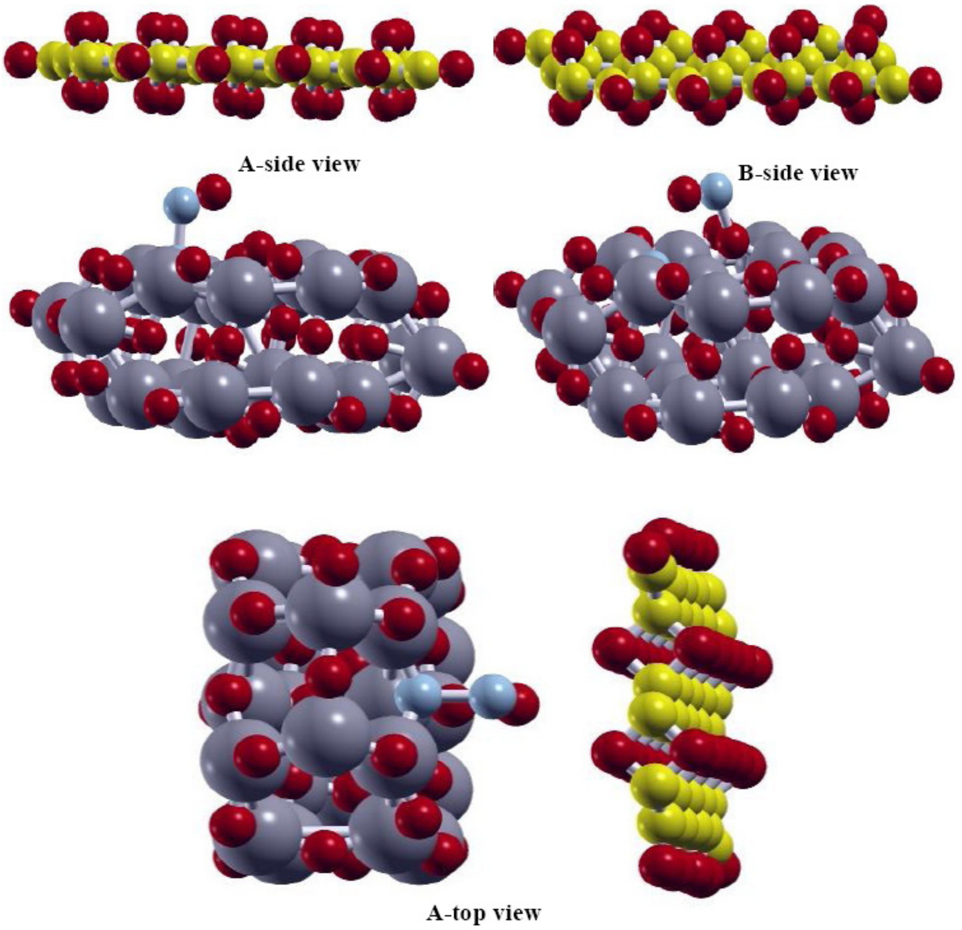
N-doped anatase nanoparticles were built via replacement of two appropriate active surface oxygen atoms by nitrogen atoms. In one doping configuration, a nitrogen atom substitute an oxygen atom in the middle of the particle and the other is a nitrogen atom substitute an oxygen atom at O_T position. The substituted oxygen atoms are the so-called "central oxygen" and "twofold coordinated oxygen" atoms, which specified by O_C and O_T in Fig. 1, respectively. The optimized structures for two kinds of N-doped nanoparticles were illustrated in Fig. 2.

We have geometrically optimized the obtained N-doped nanocomposites and constructed complex systems consisting of the NO molecule positioned towards the optimized nanocomposites. In this study, we have mainly investigated the adsorption on the doped nitrogen atom site of the considered nanocomposites due to the relatively high activity of this site in adsorption process, compared to the other surface oxygens (Liu, *et al.*, 2012).

RESULTS AND DISCUSSION

Bond lengths and bond angles

The NO adsorption on the undoped and N-doped TiO_2/Graphene oxide nanocomposites has been modelled as five adsorption configurations. The simulated TiO_2/



A-side view

B-side view

A-top view

Fig. 3. Optimized geometry configurations of NO molecules adsorbed on the N-doped TiO_2 anatase/Graphene oxide nanocomposites. Colors represent atoms accordingly, Ti in grey, O in red, N in blue and C in yellow

Graphene oxide +NO complexes after the adsorption process were presented in Figs. 3 and 4.

Each complex is different in substituted oxygen of TiO_2 and / or NO position towards the nanocomposite from the others. For instance, complex A was constructed from the substitution of central oxygen atom (O_C) of TiO_2 in TiO_2/Graphene oxide nanocomposite by nitrogen atom and NO molecule with upward oxygen. In configurations A and C, the NO's oxygen atom was positioned downward (position 1) after relaxation, while in configurations B and D, the NO molecule was put horizontally towards the nanocomposite with NO's oxygen atom located upward (position 2). The adsorption of NO on undoped nanocomposite was presented only with position 1. Therefore, only one configuration for the NO adsorption on undoped nanocomposite was considered. In all adsorption configurations, the nitrogen atom of NO molecule is preferentially placed towards the nanocomposite surface. Table 1 lists the optimized values of some important bond lengths before and after adsorption process.

After the adsorption process, the N-O bond of the NO molecule was elongated due to the transfer of electronic density from the nanocomposite and N-O bond of the adsorbed NO molecule to the newly formed bonds between the NO molecule and the nanocomposite. The results of this table were using both of LDA and GGA functionals. The smaller bond formed between the nitrogen atom of NO molecule and the nitrogen atom of nanocomposite (N-N), is stronger than the interaction of NO molecule with TiO_2/Graphene oxide nanocomposite.

Adsorption energies

Adsorption energy values for NO adsorption on the TiO_2/Graphene oxide nanocomposites were listed in Table 1. These values were obtained using both of

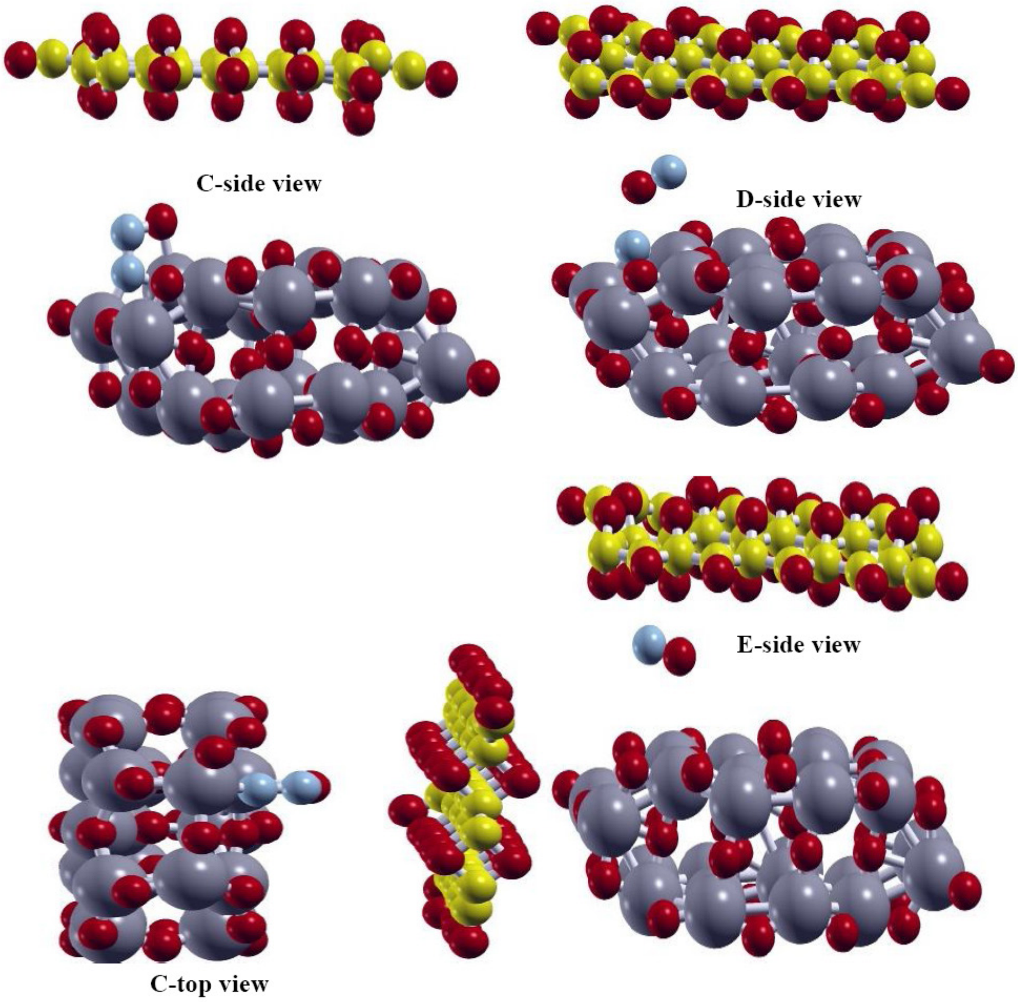


Fig. 4. Optimized geometry configurations of NO molecules adsorbed on the undoped TiO_2 anatase/Graphene oxide nanocomposites. Colors represent atoms accordingly, Ti in grey, O in red, N in blue and C in yellow

LDA and GGA integral approximations. The doped nitrogen site is expected to be an energy favorable adsorption site because of its high activity in the adsorption process. For this type of adsorption, for example configuration A, the average adsorption energies are calculated to be -3.15 eV and -2.72 eV based on LDA and GGA methods, respectively, which are much lower than the adsorption on the undoped system (-2.17 eV and -1.90 eV, respectively). It implies that the adsorption of NO molecule on the N-doped nanocomposite is more energetically favorable than the adsorption on the pristine one. In addition, the adsorption energy for configuration B is lower than that of configuration A, it means a less strong configuration in

Table 1. Bond length (Å), adsorption energies (eV) and Mulliken charge values for NO molecule adsorbed on the TiO_2/Graphene oxide nanocomposites

Type of nanocomposite	**N-O bond length**	E_{ads}		ΔC_i
		LDA	**GGA**	
A	1.20	-3.15	-2.72	-0.149
B	1.22	-3.02	-2.50	-0.144
C	1.25	-3.25	-2.85	-0.154
D	1.19	-2.19	-1.95	-0.112
E	1.18	-2.17	-1.90	-0.087

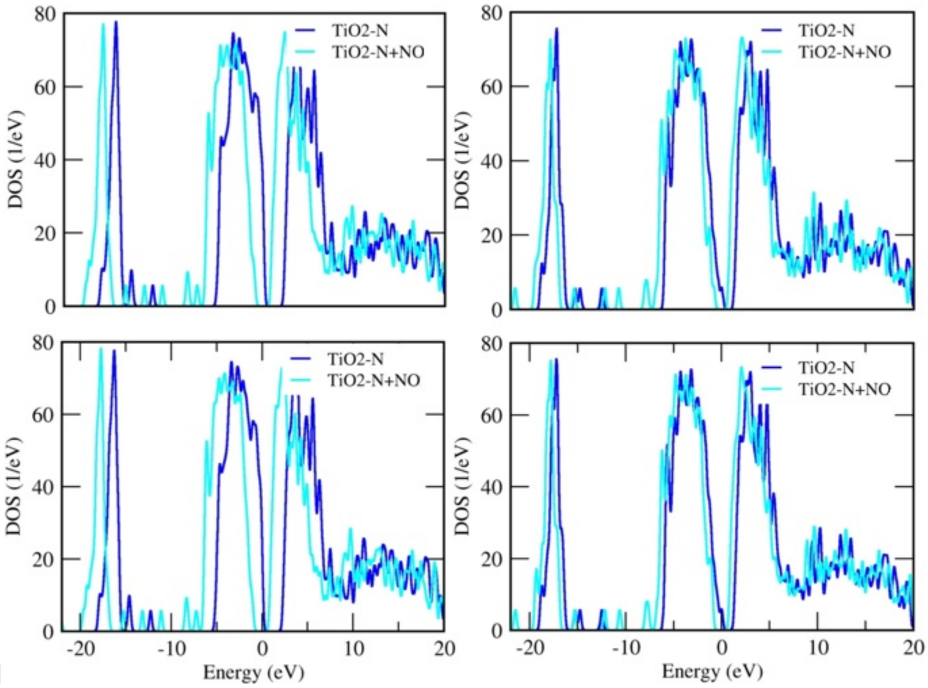


Fig. 5. The total density of states (TDOS) of the NO molecule adsorbed on the TiO$_2$/Graphene oxide nanocomposite (the structures are shown in Fig. 3). (a) Complex A; (b) Complex B; (c) Complex C; (d) Complex D

comparison with the configuration A. Configuration C provides two contacting point between the NO molecule and the nanocomposite with nitrogen and oxygen atoms of NO molecule binding to nitrogen and titanium atoms of nanocomposite. The adsorption energy of this configuration is higher (more negative) than the adsorption energies of the other configurations, suggesting that the adsorption in this configuration is the strongest in comparison with the others. It means a more stable configuration in comparison with the undoped system adsorption and other N-doped particles adsorption. Therefore, the adsorption configuration in which the NO molecule with upward nitrogen is adsorbed on the nanocomposite with two interaction point is the most stable (energy favorable) configuration. For all adsorption configurations, the adsorption energies by LDA method are more negative than those calculated by GGA, because the LDA overestimates the adsorption energy values. This results from the common feature in the DFT calculations. The more negative the adsorption energy, the higher tendency for adsorption, and consequently more stable adsorption. This makes the interaction of NO on the anatase nanoparticle very strong. The improvements of both adsorption energy and structural properties (like bond lengths and angles) of the adsorption of NO on TiO$_2$/Graphene oxide nanocomposite induced by N-doping hint us that the N-doped nanocomposite can be effectively used for removing or sensing of NO in the environment. Thus, the pristine TiO$_2$/Graphene oxide nanocomposite would not be an ideal NO gas sensor.

Electronic structures

The total density of states for the considered nanocomposites with adsorbed NO molecules were displayed in Fig. 5. This Figure shows that the differences between DOS of N-doped and undoped nanocomposite are increased by adsorption of NO molecule. These differences are included both growing shift of energies of peaks and creation of some new peaks in the DOS of nanocomposite.

So, the adsorption process does not change the DOS of considered systems considerably. The major effects included shifting in energies of the states to the lower energy values and appearance of some small peaks at the energy levels ranging from -12 eV to -8 eV. A closer consequence of this statement would be the fact that the electronic transport properties of the nanocomposites were affected by energy gap of DOS, being an effectual feature for sensing of nitro-

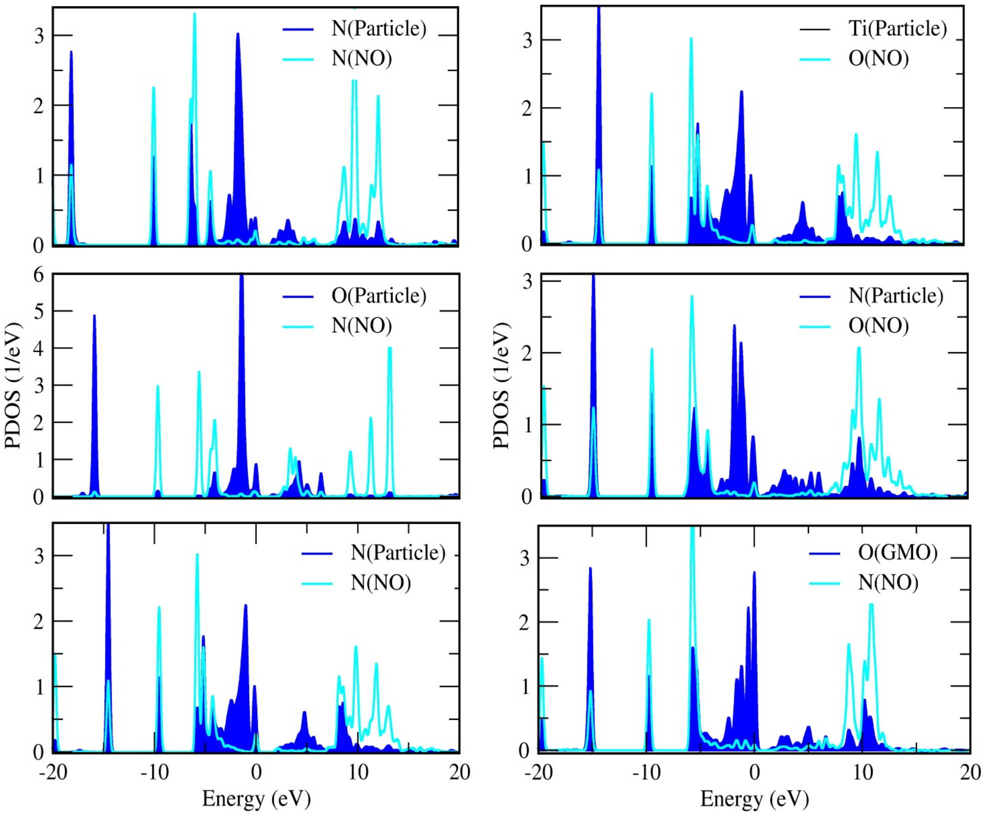


Fig. 6. PDOS for the adsorption of NO molecule on the undoped and N-doped TiO_2 anatase/Graphene oxide nanocomposites, (a) Complex A; (b) Complex B; (c) Complex C; (d) Complex C; (e) Complex D; (f) Complex E

gen oxides by TiO_2/Graphene oxide nanocomposites. In order to further analyze the electronic variations of the considered nanocomposites, we have calculated oxygen projected and the nitrogen projected DOSs (O-PDOS and N-PDOS) for the studied nanocomposites to indicate the electron transport between the contacting atom of nanocomposite and NO molecule. Fig. 6 includes six panels for the adsorption of NO molecule on TiO_2/Graphene oxide nanocomposites. Panel (a) in this Figure represents the PDOSs of the nitrogen atom of nanocomposite and nitrogen atom of NO molecule for complex A, while the PDOSs of the oxygen atom of nanocomposite and nitrogen atom of NO molecule were displayed as panels (b) for complex B. The large overlaps between the PDOSs of nitrogen atoms of nanocomposite and NO molecule represent that these two atoms form a chemical bond after the adsorption. The significant overlap of the DOSs of nitrogen and oxygen atoms in panel (b) shows that the nitrogen atom of NO molecule is chemisorbed on the surface oxygen atom of the nanocomposite. In panels (c, d), we can see the large PDOS overlap for two nitrogen atoms, suggesting the formation of new N-N bond between nanocomposite and adsorbed NO molecule. Also, such overlap between the titanium atom of nanocomposite and oxygen atom of NO molecule reveals that a chemical Ti-O bond was formed between the adsorbent and adsorbed molecule.

These overlaps of the DOSs are in reasonable accordance with the formation of two interaction points between the nanocomposite and NO molecule for complex C. Panels (e and f) represent the corresponding PDOSs for complexes D and E, respectively. The PDOSs of the oxygen atom of NO molecule and different d orbitals of titanium atom were also presented in Fig. 7, suggesting a higher overlap between the PDOSs of the oxygen atom of NO molecule and d^1 orbital of titanium.

Besides, the isosurfaces of molecular orbitals for isolated gas phase NO molecule were displayed in Fig. 8, which indicate a positive and negative charge areas on the nitrogen and oxygen atoms of NO molecule. The isosurfaces of HOMO and LUMO molecular orbitals of the adsorption systems were shown as

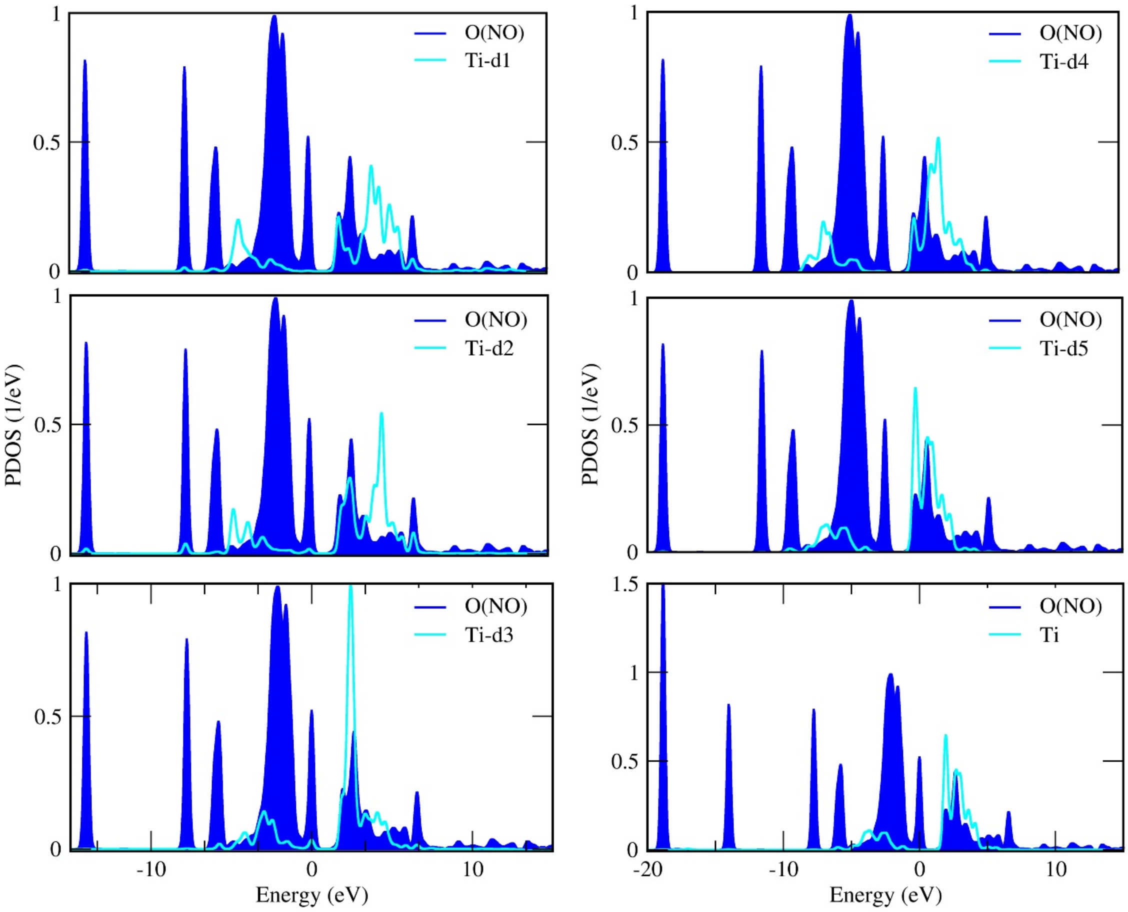


Fig. 7. PDOS of oxygen atom and different "d" orbitals of titanium atom for Complex C

Fig. 9. As it can be seen from this Figure, in each case, the HOMOs are strongly localized on the graphene oxide nanosheet, whereas for all studied systems, the LUMOs are strongly localized on the NO molecules.

Charge transfer analysis

In order to further investigate the adsorption of NO molecules on the considered nanocomposites, the charge analysis based on Mulliken charges was also provided in this work. The charge difference for the composite i after and before adsorption, was computed via the following equation:

$$\Delta C_i = C_{i(\text{in complex})} - C_{i(\text{in vacuum})} \tag{2}$$

where C_i is the value of Mulliken charge of the i. Subscript "I" is referred to nanocomposite or NO molecule. The charge difference, ΔC, is a measure of the

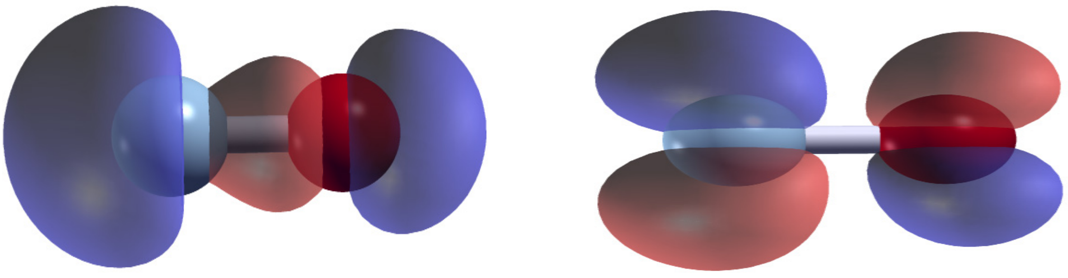

HOMO (NO)
LUMO (NO)

Fig. 8. The isosurfaces of HOMO and LUMO molecular orbitals for NO molecule before the adsorption process. The orange color is the positive area while the blue color represents the negative value area

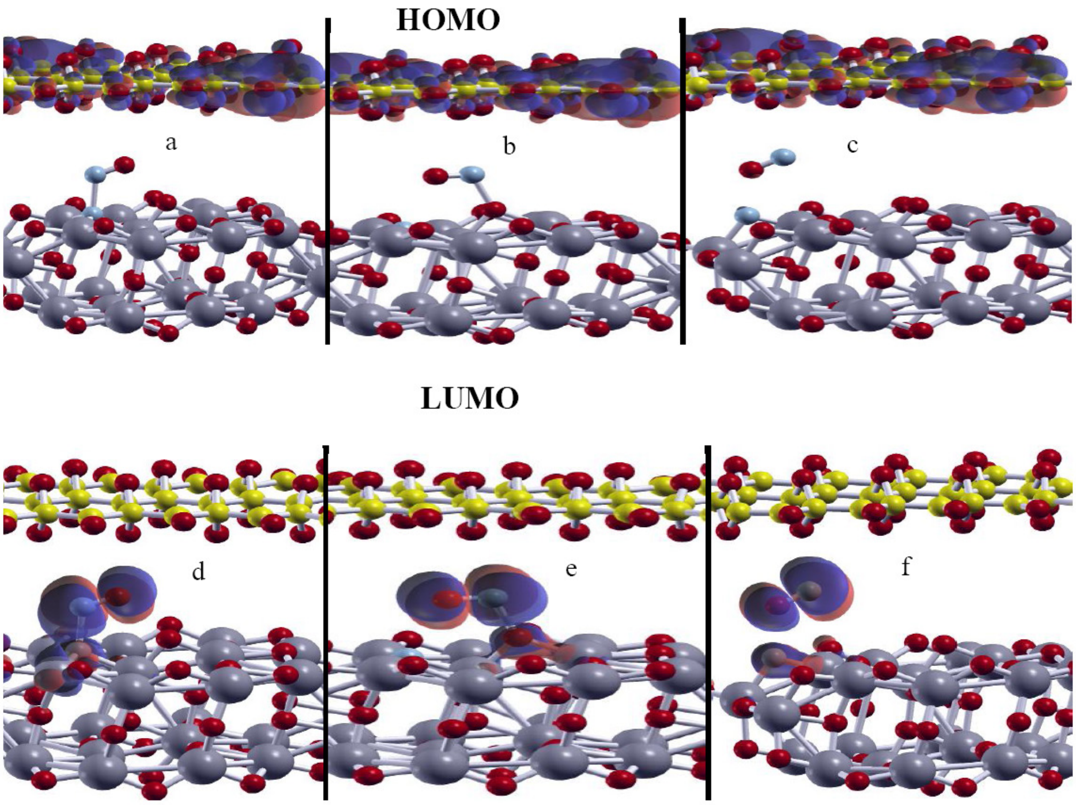


Fig. 9. The isosurfaces of HOMO and LUMO molecular orbitals for NO molecule adsorbed on the N-doped TiO_2 anatase/Graphene oxide nanocomposites, (a) Complex A; (b) Complex B; (c) Complex D; (d) Complex A; (e) Complex B; (f) Complex D. After the adsorption, the electronic density increases at the middle of the newly formed bond.

amount of charge transferred to, or, from the studied nanocomposites from, or, to the adsorbate. The calculated Mulliken charge values for different adsorption configurations were presented as Table 1. The values of ΔC for different complexes have negligible differences with each other. For example, the calculated Mulliken charge value for the nanocomposite in configuration A is -0.149 |e| (e, the electron charge) and that of NO molecule is +0.149 e. These values indicate that TiO_2/Graphene oxide nanocomposite behaves as a charge acceptor from the NO molecule. This suggests that the N-doped TiO_2/Graphene oxide nanocomposite would be an ideal NO gas sensor.

CONCLUSIONS

In this letter, we have carried out density functional theory calculations on structural and adsorption mechanisms of NO molecule on the intrinsic and nitrogen doped TiO_2/Graphene oxide nanocomposites. Our theoretical insights reveal that the N-doped nanocomposites are more energetic than the undoped ones and can react with NO molecules more efficiently. Structural analysis of the studied systems represents that, after the adsorption, the N-O bond of the adsorbed NO was elongated because of the transference of the electronic density from the nanocomposite and N-O bond of the adsorbed NO molecule to the newly-formed bond between the nanocomposite and the molecule. We have also commented on the electronic properties of the studied systems including the DOS and molecular orbital plots in order to understand the electron transport phenomena. The obtained results indicate that the N-doped nanocomposites are more active than the undoped ones. The N doping yields an increased affinity for TiO_2/Graphene oxide nanocomposites to interact with NO molecules in the environment, being an efficient property to be utilized in sensing and removing applications. Our calculated results thus suggest a theoretical basis for N-doped TiO_2/Graphene oxide nanocomposites to be effectively employed in sensing and removing applications and imply that the N-doped TiO_2/Graphene oxide nanocomposite would be an ideal NO gas sensor.

ACKNOWLEDGEMENT

This work was supported by the Azarbaijan Shahid Madani University.

REFERENCES

Satterfield, C.N., (1991). Heterogeneous catalysis in industrial practice. 2nd ed., McGraw-Hill, New York.

Ando, M.; Kobayashi, T.; Haruta, M., (1997). Combined effects of small gold particles on the optical gas sensing by transition metal oxide films. J. Catal. Today, 36: 135-141.

Fujishima, A.; Honda, K., (1972). Electrochemical photolysis of water at a semiconductor electrode. Nature, 37: 238-242.

Dutta, P.K.; Ginwalla, A.; Hogg, B.; Patton, B.R.; Chwieroth, B.; Liang, Z.; Gouma, P.; Mills, M.; Akbar, S., (1999). Interaction of carbon monoxide with anatase surfaces at high temperatures: optimization of a carbon monoxide sensor. J. Phys. Chem. B., 103: 4412-4422.

Garfunkel, E.; Gusev, E.; Vul, (Eds.) A., (1998). Fundamental aspects of ultrathin dielectrics on Si-based devices, NATO Science Series, Kluwer Academic Publishers, Dordrecht.

Banfied, J.F.; Veblen, D.R., (1992). Conversion of Perovskite to Anatase and TiO_2 (B): A TEM Study and the Use of Fundamental Building-Blocks for Understanding Relationship among the TiO_2 Minerals. Am. Mineral., 77: 545-557.

Erdogan, R.; Ozbek, O.; Onal, I., (2010). A periodic DFT study of water and ammonia adsorption on anatase TiO_2 (001) slab. Surf. Sci., 604: 1029-1033.

Zarei, H.; Zeinali, M.; Ghourchian, H.; Eskandari, Kh., (2013). Gold nano-particles as electrochemical signal amplifier for immune-reaction monitoring. Int. J. Nano. Dimens, 4(1): 69-76.

Liu, H.; Zhao, M.; Lei, Y.; Pan, C.; Xiao, W., (2012). Formaldehyde on TiO_2 anatase (1 0 1): A DFT study. Comput. Mater. Sci., 15: 389-395.

Landman, M.; Rauls, E.; Schmidt, W.G., (2012). The electronic structure and optical response of rutile, anatase and brookite TiO_2. J. Phys.: Condens. Matter., 24: 195503.

Topalian, Z.; Niklasson, G.A.; Granqvist, C.G.; Österlund, L., (2012). Spectroscopic Study of the Photofixation of SO2 on Anatase TiO_2 Thin Films and Their Oleophobic Properties, ACS Appl. Mater. Interfaces, 4 (2): 672–679.

Wang, Y.; Doren, D.J., (2005). First-principles calculations on TiO_2 doped by N, Nd, and vacancy. Solid State Commun., 136: 186-189.

Wei, Z.; Mei, W.; Xiyu, S.; Yachao, W.; Zhenyong, L., (2010). Electronic and optical properties of the doped TiO_2 system. J. Semicond.. 31: 072001.

Liu, J.; Dong, L.; Guo, W.; Liang, T.; Lai, W., (2013). CO adsorption and oxidation on N-doped TiO_2 nanoparticles. J. Phys. Chem. C., 117: 13037-44.

Zhao, D.; Huang, X.; Tian, B.; Zhou, S.; Li, Y.; Du, Z., (2011). The effect of electronegative difference on the electronic structure and visible light photocatalytic activity of N-doped anatase TiO_2 by first-principles calculations. Appl. Phys. Lett., 98: 162107.

Ebrahimzadeh, A.R.; Abbasi, M.; Sardroodi, J.J.; Afshari, S., (2015). Theoretical computation of the quantum transport of zigzag mono-layer Graphenes with various z-direction widths. Int. J. Nano. Dimens., 6(1): 105-109.

Liu, J.; Liu, Q.; Fang, P.; Pan, C.; Xiao, W., (2012). First principles study of the adsorption of a NO molecule on N-doped anatase nanoparticles. J. Appl. Surf. Sci., 258: 8312-8318.

Hohenberg, P.; Kohn, W., (1964). Inhomogeneous electron gas. J. Phys. Rev., 136: B864-B871.

Kohn, W.; Sham, L., (1965). Self-Consistent equations including exchange and correlation effects. J. Phys. Rev., 140: A1133-A1138.

Ozaki, T., (2013). The code, OPENMX, pseudoatomic basis functions, and pseudopotentials are available on a web site 'http://www.openmxsquare.org'.

Ozaki, T., (2003). Variationally optimized atomic orbitals for large-scale electronic structures. Phys.

Rev. B, 67: 155108.

Ozaki, T.; Kino, H., (2004). Numerical atomic basis orbitals from H to Kr, J. Phys. Rev. B, 69: 195113.

Perdew, J.P.; Zunger, A., (1981). Self-interaction correction to density-functional approximations for many-electron systems, J. Phys. Rev. B., 23: 5048–5079.

Perdew, J.P.; Burke, K.; Ernzerhof, M, (1997). Generalized gradient approximation made simple, J. Phys. Rev. Lett., 78: 1396.

Koklj, A., (2003). Computer graphics and graphical user interfaces as tools in simulations of matter at the atomic scale, J. Comput. Mater. Sci., 28: 155-168.

Wyckoff, R.W.G., (1963). Crystal structures, Second edition. Interscience Publishers, USA, New York.

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