

Electronic sensor for sulfide dioxide based on AlN nanotubes: a computational study

Javad Beheshtian · Mohammad T. Baei ·
Ali Ahmadi Peyghan · Zargham Bagheri

Received: 22 February 2012 / Accepted: 21 May 2012 / Published online: 8 June 2012
© Springer-Verlag 2012

Abstract Single-walled aluminum nitride nanotubes (AlNNTs) are introduced as an electronic sensor for detection of sulfur dioxide (SO₂) molecules based on density functional theory calculations. The proposed sensor benefits from several advantages including *high sensitivity*: HOMO-LUMO energy gap of the AlNNT is appreciably sensitive toward the presence of SO₂ so that it decreases from 4.11 eV in the pristine tube to 1.01 eV in the SO₂-adsorbed form, *pristine application*: this nanotube can detect the SO₂ molecule in its *pristine type* without manipulating its structure through doping, chemical functionalization, making defect, etc., *short recovery time*: the adsorption energy of SO₂ molecule is not so large to hinder the recovery of AlNNTs and therefore the sensor will possess short recovery times, and *good selectivity*: the tube can selectively detect the SO₂ molecule in the presence of several molecules such as H₂O, CO, NH₃, HCOH, CO₂, N₂, and H₂.

Keywords AlNNTs · Electronic sensor · Nanostructured materials · SO₂ · Theoretical study

Introduction

Sulfur dioxide (SO₂), released in the process of fuel combustion, can result in a variety of breathing problems and also induce cardiovascular and lung diseases [1]. Additionally, it is a major precursor of acid rain, acidifying lakes, soils, and streams as well as accelerating corrosion of buildings. Thus, development of miniature and portable gas sensors with the ability of sensing SO₂ molecules is of great interest. Up to now, some kinds of SO₂ sensors have been presented by several research groups [2, 3]. Nanotubes, as quasi-one-dimensional structures, have attracted great interest of sensor industry because of their high surface to volume ratio, high sensitivity, and quick response time toward several molecules. It has also been shown that pristine carbon nanotubes (CNTs) can detect many molecules such as O₂, NH₃, NO₂, and CO [4–7].

Adsorption of chemical species affects the electrical properties of nanotubes and is of fundamental interest and importance in development of potential electronic sensors. Charge transfer between nanotubes and adsorbates can increase or decrease carrier density in semiconducting nanotubes, and thus significantly affects the electrical conductance of the nanotubes. Based on these observations, several groups have suggested the application of nanotube as promising gas sensors [8–10]. However, several pristine nanotubes usually are not able to adsorb the target molecules and cannot be used for detection of several toxic gaseous molecules. Therefore, considerable experimental and theoretical works have been focused on improving sensing

J. Beheshtian
Department of Chemistry,
Shahid Rajaei Teacher Training University,
P.O. Box: 16875-163, Tehran, Iran

M. T. Baei
Department of Chemistry, Azadshahr Branch,
Islamic Azad University,
Azadshahr, Golestan, Iran

A. A. Peyghan (✉)
Young Researchers Club, Islamic Azad University,
Islamshahr Branch,
Tehran, Iran
e-mail: ahmadi.iau@gmail.com

Z. Bagheri
Physics group, Science Department, Islamic Azad University,
Islamshahr Branch, P.O. Box: 33135-369, Islamshahr, Tehran, Iran

performance of the pristine tubes toward various desired molecules through doping or functionalization [11–13].

Since electronic properties of CNTs are mainly dependent on the tubular chirality and diameter [14], separation of the nanotubes with desired electronic properties from other kinds is a formidable task. Recently, several theoretical and experimental studies have been focused on non-carbon (inorganic) nanotubes such as BN, ZnO, SiC, AlN, InP, MgO, ect. [15–20]. Many of these nanotubes have attracted considerable research interest in gas sensor applications. In our previous report, for instance, it has been shown that MgO nanotubes selectively act against CO and NO gaseous molecules [21]. AlN nanotubes (AlNNTs) have been successfully synthesized by Tondare et al. and other research groups [22–24], and have been proposed as potential hydrogen storage media by Lim and Lin [25]. They are wide band gap semiconductors, exhibiting good dielectric properties, high thermal conductivity, and low thermal expansion coefficient [26]. In spite of several studies on CNTs and BN nanotubes, there are few reports on potential application of AlNNTs in gas sensors. So far, adsorptions of some gaseous molecules including NH₃, H₂, N₂, and CO₂ on the AlNNTs have been reported [27–29]. Recently, we have shown that the pristine type of these tubes is not sensitive toward NH₃ [28] and CO [30] molecules, while they may be used in formaldehyde detection [31]. Our previous study has suggested that O-doped AlNNT would be a potential candidate for NH₃ molecule detection [32]. Herein, the potential possibility of single-walled *pristine* AlNNT as a gas sensor for SO₂ molecule detection is investigated. To this end, we have studied the interaction between the SO₂ molecule and AlNNTs using density functional theory calculations.

Computational details

Geometry optimizations, natural bond orbital (NBO), and density of states (DOS) analyses were performed on a (5, 0) zigzag AlNNT (constructed of 30 Al and 30 N atoms), and different SO₂/AlNNT complex configurations at B3LYP/6-31 G* level of theory as implemented in GAMESS suite of program [33]. Vibration frequencies were also computed at the same level to confirm that all the stationary points correspond to true minima on the potential energy surface. All frequency calculations were performed using numerical second derivatives and verified that all of the structures are true minima by frequency analysis and obtained positive Hessian eigenvalues. This level of theory is a popular approach which has been commonly used for nanotube structures [34–38]. The length and the diameter of the optimized pure AlNNT are computed to be about 16.45 Å and 5.27 Å, respectively. In order to avoid boundary effects, atoms at the open ends of the tube are saturated by hydrogen atoms. The

adsorption energy (E_{ad}) of SO₂ molecule is defined as follows:

$$E_{ad} = E(SO_2/AlNNT) - E(AlNNT) - E(SO_2), \quad (1)$$

where $E(SO_2/AlNNT)$ is the total energy of the adsorbed SO₂ molecule on the AlNNT surface, and $E(AlNNT)$ and $E(SO_2)$ are total energies of the pristine AlNNT, and the SO₂ molecule, respectively.

Results and discussion

Partial structure and DOS of the optimized tube are shown in Fig. 1, indicating its semi-conductivity with HOMO/LUMO energy gap (E_g) of 4.11 eV. In order to obtain stable configurations of single SO₂ adsorbed on the AlNNT, various possible initial adsorption geometries including single (oxygen or sulfur), double (S–O or O–O) and triple O–S–O bonded atoms to Al and N atoms on different adsorption sites are considered. After geometry optimization, it was found that only three kinds of configurations are stable. Figure 2 shows the most and the second most stable configurations.

In the most stable configuration (A, Fig. 2), two S–O bonds of SO₂ molecule lie on two N1–Al6 and N1–Al2 (Fig. 1) bonds of the AlNNT, in which S and O atoms of the SO₂ molecule are located atop the N and Al atoms of AlNNT with

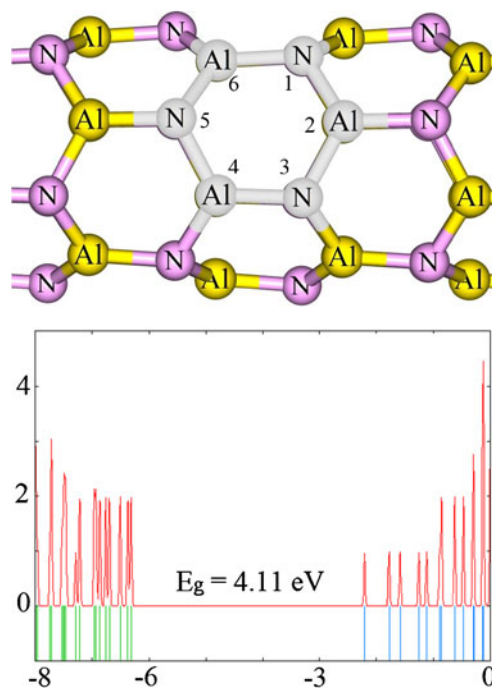
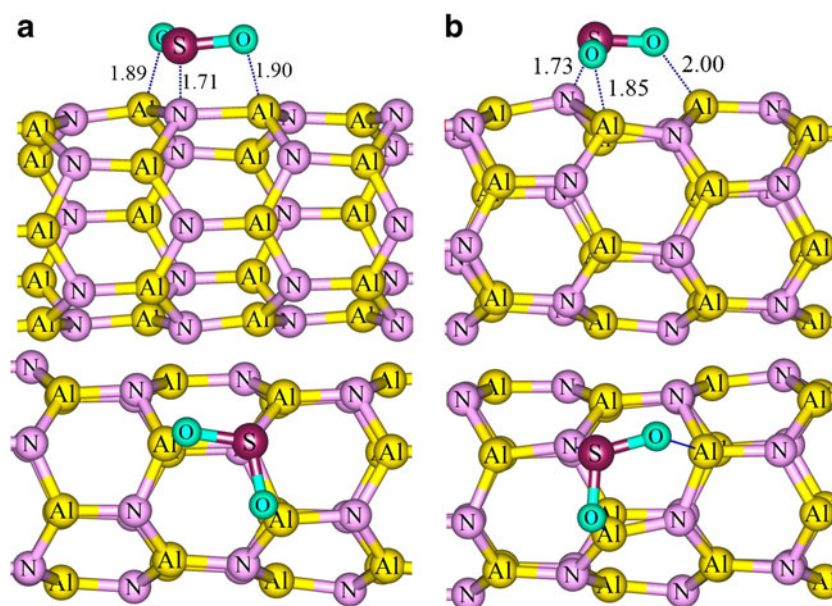


Fig. 1 Structural model and the electronic density of states (DOSs) of the (5,0) AlNNT

Fig. 2 Top and side views of the most (**A**) and second most (**B**) stable configurations of AlNNT/SO₂ complexes. Distances are in angstrom



bond lengths of 1.71 Å (S–N) and 1.89 (or 1.90) Å (O–Al), respectively. Moreover, the adsorption induces an apparent local structural deformation on both the SO₂ molecule and the AlNNT. The O–S–O bond angle of the SO₂ molecule is significantly decreased from 119.1° in free SO₂ to 109.9° in the adsorbed state. Further indication of the deformation degree in the geometry of SO₂ due to the adsorption process, is given by the bond reorganization energy (E_{br} , Table 1), calculated as the energy difference between the full relaxed SO₂ molecule and its adsorbed form. E_{br} of the SO₂ for the configuration **A** is about 16.6 kcal mol⁻¹ and the calculated E_{ad} is about -58.2 kcal mol⁻¹ (Table 1), indicating a strong interaction between the SO₂ molecule and the tube. Mulliken population analysis shows a net charge transferred (Table 1) from the tube to the adsorbate which can be rationalized by high electronegativity of the O atoms of SO₂. The Al and N atoms bonded to SO₂ molecule are both lifted up, which the NBO analysis suggests that it can be attributed to the change of their hybridization from sp^2 to nearly sp^3 . In addition, the lengths of N1–Al6 and N1–Al2 bonds are significantly increased from

1.81 and 1.82 Å in the pristine nanotube to 2.02 and 2.04 Å in configuration **A**, respectively.

For the second most stable configuration (**B**, Fig. 2) two S–O bonds of the SO₂ molecule lie on the N5–Al6 bond and N5...Al1 distance. It can be seen that the S and O atoms of the SO₂ molecule are bonded to the N and Al atoms of the AlNNT in both the most and the second most stable configurations. The major difference between the two configurations is the orientation of S atom of SO₂, which is toward N1 and N5 along the AlNNT for the most and the second most stable configurations, respectively. Adsorption process in the configuration **B** is somewhat weaker ($E_{ad} = -46.1$ kcal mol⁻¹) than configuration **A** (-58.2 kcal mol⁻¹). In addition, calculated E_{br} of the SO₂ molecule for the configuration **B** is about 15.4 kcal mol⁻¹ which is approximately 1.2 kcal mol⁻¹ smaller than that of configuration **A**.

As it was explained elsewhere [31], these strong types of interactions are not favorable in gas detection because of the following reasons: 1) Despite the thermodynamic feasibility of these interactions, an activation barrier for structure

Table 1 Adsorption energy of SO₂ on AlNNT (E_{ad} , kcal mol⁻¹), bond reorganization energy (E_{br} , kcal mol⁻¹, calculated as the energy difference between the geometry of SO₂ after adsorption on AlNNT and the

full relaxed molecule), Mulliken charge on the adsorbed SO₂, the HOMO, LUMO and gap (E_g) in between energies (eV) for different SO₂/AlNNT complexes

** ΔE_g (%)	E_g	E_{LUMO}	E_{HOMO}	Q_T (e)	E_{br}	E_{ad}	*Complex
–	4.11	–2.21	–6.32	–	–	–	AlNNT
1.6	4.04	–2.22	–6.26	–0.069	16.6	–58.2	A
5.4	3.89	–2.21	–6.10	–0.085	15.4	–46.1	B
75.5	1.01	–5.16	–6.17	–0.075	4.50	–15.2	C

*See Figs. 2 and 3

**Change of E_g of AlNNT upon adsorption of SO₂ molecule

deformation hinders their occurrence in the room temperature. 2) Recovery of the sensor device is one of the most important characteristics. Such strong interactions imply that the desorption of the adsorbate could be difficult and the device may suffer from long recovery times. If the E_{ad} is significantly increased, much longer recovery time is expected. Based on the conventional transition state theory, the recovery time can be expressed as:

$$\tau = \nu_0^{-1} \exp(-E_{ad}/kT), \quad (2)$$

where T is the temperature, k is the Boltzmann's constant, and ν_0 is the attempt frequency. According to this equation, more negative E_{ad} values will prolong the recovery time in an exponential manner.

The desired adsorption configuration is **C** (Fig. 4). In this configuration, two oxygen atoms of SO_2 molecule are close to Al12 and Al16 atoms so that its plane is perpendicular to the surface of AlNNT. The interaction distances of O...Al is about 2.02 and 2.03 Å (Fig. 3) and a net charge of 0.075 e is transferred from the tube to the SO_2 molecule. The E_{ad} for this configuration is about $-15 \text{ kcal mol}^{-1}$, which is significantly lower than those of the former configurations **A** and **B**. This phenomenon is an advantage in application of AlNNT as a gas sensor for SO_2 detection because it is not too large to prevent the sensor device recovery.

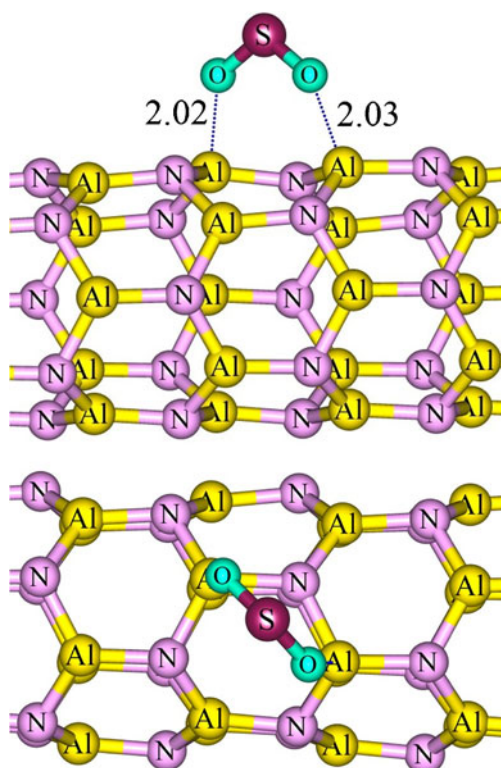


Fig. 3 Top and side views of the third most stable state (configuration **C**) of AlNNT/ SO_2 complex. Distances are in angstrom

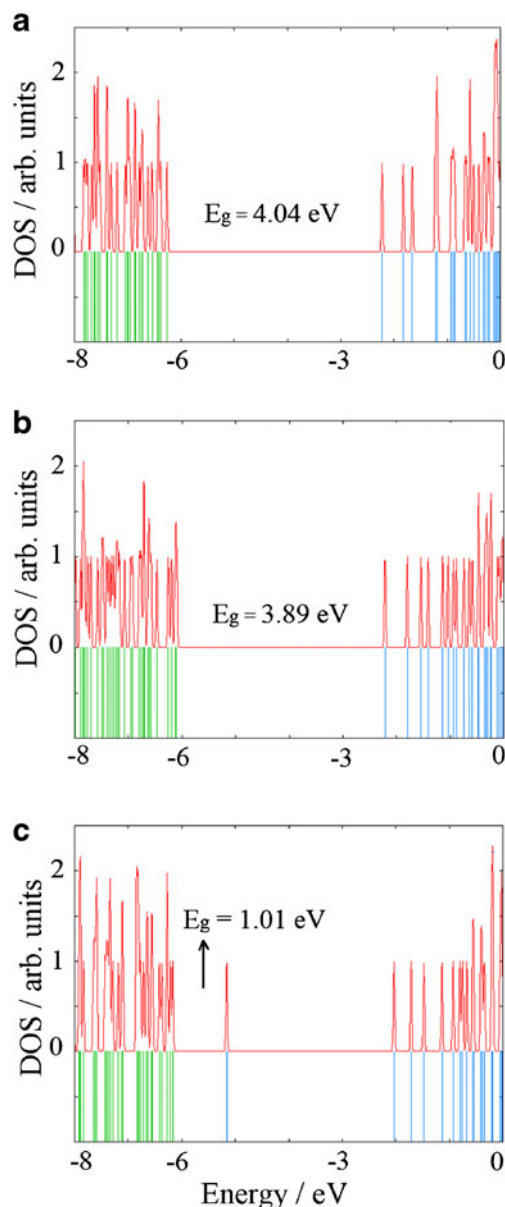


Fig. 4 Electronic density of states (DOSs) plots of the most (**A**), second (**B**) and third (**C**) most stable configurations of AlNNT/ SO_2 complexes

However, in order to investigate the potential possibility of pristine AlNNT as a chemical sensor for SO_2 molecule detection, it is necessary to explore the effect of SO_2 adsorption on the electronic properties of AlNNTs. To this end, DOS calculations were performed for pristine and all the SO_2 /AlNNT complexes. By referring to Fig. 4, it can be seen that the SO_2 /AlNNT complexes of configurations **A** and **B** attain E_g value of 4.04 and 3.89 eV, respectively, while the E_g of the pristine AlNNT is about 4.11 eV (Fig. 1). It is therefore concluded that the adsorption of SO_2 molecule can never essentially change the electrical conductance of AlNNT, suggesting that AlNNT has no capability of

generating an effective response to SO₂ molecule upon these adsorption states. From inspection of the DOS plots it is revealed that their valence levels in complexes **A** and **B** are similar to that of pristine AlNNT, while only the states of conduction levels slightly shift upward by about 0.06–0.22 eV which is negligible.

It should be noted that an impurity peak appears at -5.16 eV in DOS of configuration C, reducing the E_g of AlNNT from 4.11 to 1.01 eV. Appearance of this peak indicates that after adsorbing the SO₂ molecule, the complex **C** becomes more semiconductor-like, with a drop in the DOS near the Fermi level, and thus a significant increase in conductance is expected, compared to the pristine tube. The phenomenon can be explained by the following relation [30]:

$$\sigma \propto \exp\left(\frac{-E_g}{2kT}\right). \quad (3)$$

where σ is the conductance and k is the Boltzmann's constant. According to the equation, smaller E_g values lead to the higher conductance at a given temperature. The considerable change of about 75 % (Table 1) in the E_g value, demonstrates the high sensitivity of the electronic properties of AlNNT toward the SO₂ adsorption on its surface. It should be noted that the adsorption of SO₂ onto the AlNNT causes the major band features to move toward the higher energies; in other words, the Fermi level is shifted down. It can be deduced that AlNNT can transform the presence of the SO₂ directly into an electrical signal, and therefore could be potentially used in SO₂ sensors. Compared to the adsorptions of other molecules including H₂ [25], NH₃ [27], CO₂ [29], N₂ [29], CO [30, 38], H₂O [31], HCOH [31] on AlNNTs, it is revealed that the adsorbed SO₂ molecule causes much more change in the value of E_g of the tube, increasing its conductance. Therefore, the pristine AlNNT may be an ideal sensor for SO₂ molecules with high selectivity.

The advantages of AlNNT as a gas sensor for SO₂ detection can be briefly listed as follows: (i) conductance of the semi-conductive AlNNT is appreciably sensitive toward the presence of SO₂ molecule, (ii) AlNNT can detect the SO₂ molecule in its *pristine type* and there is no need to manipulate its structure through doping, chemical functionalization, etc., (iii) the adsorption energy of SO₂ is not so large to hinder the recovery of AlNNTs and the recovery time may be short according to the Eq. 2, (iv) as it was mentioned, AlNNT can detect the SO₂ molecule selectively in the presence of several interfering molecules.

Conclusions

We performed density functional theory study to investigate the adsorption of SO₂ molecule on AlNNTs to find the

potential possibility of single-walled pristine AlNNT as an electronic sensor for SO₂ detection. Results showed that the SO₂ molecule can be strongly adsorbed on the surface of the AlNNTs with significant changes in its electrical conductance. Thus, AlNNTs may be a promising candidate for detection of toxic SO₂ gaseous molecules and may cover some advantages including short recovery time, high sensitivity and selectivity, and also energetic favorability. Therefore, the present study is beneficial for detecting SO₂ gas and suggests the feasibility of experimental realizations.

References

- Lee WJ et al. (2002) Environ Health Perspect 110:991–995
- Wang L, Kumar R (2003) Ionics 9:357–364
- Randhawa J, Ambekar P, Bhoga S, Singh K (2004) Ionics 10:39–44
- Collins PG, Bradley K, Ishigami M, Zettl A (2000) Science 287:1801–1804
- Kong J, Franklin N, Zhou C, Chapline M, Peng S, Cho K, Dai H (2000) Science 287:622–625
- Li J, Lu YJ, Ye Q, Cinke M, Han J, Meyyappan M (2003) Nano Lett 3:929–933
- Goldoni A, Larciprete R, Petaccia L, Lizzit S (2003) J Am Chem Soc 125:11329–11333
- Wang R, Zhang D, Zhang Y, Liu C (2006) J Phys Chem B 110:18267–18271
- Wang X, Liew KM (2011) J Phys Chem C 115:10388–10393
- Field CR, Yeom J, Salehi-Khojin A, Masel RI (2010) Sensor Actua B-Chem 148:315–322
- Zhou X, Tian WQ, Wang X (2010) Sensor Actua B-Chem 151:56–64
- Wang R, Zhang D, Sun W, Han Z, Liu C (2007) Teochem 806:93–97
- Wang R, Zhu R, Zhang D (2008) Chem Phys Lett 467:131–135
- Zurek B, Autschbach J (2004) J Am Chem Soc 126:13079–13085
- Ahmadi A, Beheshtian J, Hadipour N (2011) Struct Chem 22:183–188
- Beheshtian J, Soleymnabadi H, Kamfiroozi M, Ahmadi A (2011) J Mol Model 18:2343–2348
- Politzer P, Lane P, Murray JS, Concha MC (2005) J Mol Model 11:1–7
- Chen L, Zhou G-Q, Xu C, Zhou T, Huo Y (2009) J Mol Struct THEOCHEM 900:33–36
- Bakkers EPAM, Verheijen MA (2003) J Am Chem Soc 125:3440–3441
- Guo H, Lin Z, Feng Z, Lin L, Zhou J (2009) J Am Chem Soc 131:12546–12550
- Beheshtian J, Kamfiroozi M, Bagheri Z, Ahmadi A (2011) Phys E 44:546–549
- Tondare VN, Balasubramanian C, Shende SV, Joag DS, Godbole VP, Bhoraskar SV, Bhadbhade M (2002) Appl Phys Lett 80:4813–4815
- Balasubramanian C, Bellucci S, Castrucci P, Crescenzi M, Bhoraskar SV (2004) Chem Phys Lett 383:188–191
- Stan G, Ciobanu C, Thayer T, Wang G, Creighton J, Purushotham K, Bendersky L, Cook R (2009) Nanotechnology 20:35706–357014
- Lim SH, Lin J (2008) Chem Phys Lett 466:197–204
- Wang Q, Sun Q, Jena P, Kawazoe Y (2009) ACS nano 3:621–626
- Ahmadi A, Beheshtian J, Hadipour NL (2011) Phys E 43:1717–1719

28. Ahmadi A, Kamfiroozi M, Beheshtian J, Hadipour N (2011) *Struct Chem* 22:1261–1265
29. Jiao Y, Du A, Zhu Z, Rudolph V, Smith SC (2010) *J Mater Chem* 20:10426–10430
30. Beheshtian J, Bagheri Z, Kamfiroozi M, Ahmadi A (2011) *Struct Chem* 23:653–657
31. Ahmadi A, Hadipour NL, Kamfiroozi M, Bagheri Z (2012) *Sens Actua B-Chem* 161:1025–1029
32. Ahmadi A, Omidvar A, Hadipour NL, Bagheri Z, Kamfiroozi M (2011) *Phys* 44:1357–1360
33. Schmidt M et al. (1993) *J Comput Chem* 14:1347–1363
34. Ruangpornvisuti V (2010) *J Mol Model* 16:1127–1138
35. Chelmecka E, Pasterny K, Kupka T, Stobiński L (2011) *J Mol Model*. doi:10.1007/s00894-011-1181-6
36. Ahmadi A, Beheshtian J, Kamfiroozi M (2011) *J Mol Model* 18:1729–1734
37. Chelmecka E, Pasterny K, Kupka T, Stobiński L (2011) *J Mol Model*. doi:10.1007/s00894-011-1242-x
38. Beheshtian J, Baei MT, Peyghan AA (2012) *Surf Sci* 606:981–985