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First-principle density functional study on Al decorated and pristine boron nitride nano-cones for sensing of dopamine by/through WBI, NBO and work function analyses

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Abstract. In the current study, dopamine (DA) drug interaction with the Al-decorated and the pristine boron nitride nano-cones (BNNCs) was investigated at the molecular level with 240° disclination angles by employing first-principles density functional theory. Wiberg bond index (WBI), natural bond orbital (NBO) and work function analyses were carried out to describe the nature of intermolecular interactions between DA and the nano-cones. The DA adsorption energy onto the Al-decorated and pristine BNNCs was computed to be about –23.02 and –5.79 kcal mol^{-1}, respectively. Moreover, the E_g value associated with Al-decorated BNNCs reduced to a great extent by about 41.18% after the adsorption of DA, which correlates with increasing electrical conductivity. However, the E_g value associated with pristine BNNCs was decreased to a small degree. This shows that, unlike pristine BNNCs, the Al-decorated BNNCs could be used to detect DA and are ideal to be employed in electronic sensors. WBI and NBO analyses confirmed the result obtained here. In addition, the DA adsorption impacts on the work function associated with Al-decorated BNNCs, and the pristine and decorated BNNCs work function was decreased by about 21.71 and 10.61%, respectively. Besides, molecular and electrostatic interactions as well as the formation of Al–N bond are considered to have a critical role in the adsorption of DA in the Al-decorated BNNCs. According to WBI and NBO results, the nature of interactions between DA and BNNCs is noncovalent. Also, the short recovery time associated with the Al-decorated BNNCs, 16.43 ms, is considered to be an advantage for the DA desorption at room temperature.

Keywords. Boron nitride; nano-cones; NBO; sensor; dopamine.

1. Introduction

Dopamine (3,4-dihydroxyphenyl ethylamine, DA) is an important neurotransmitter and hormone, which has an important role in the brain and body [1]. However, high dosage of DA in the body can result in serious illnesses, including autism, Huntington's disease, senile dementia and other neurological diseases [2]. Thus, after its identification in the late 1950s, simple but precise methods were established by various researchers [3] to detect DA, such as spectroscopic, colorimetric methods, distinguished among all other methods used to analyse DA [4–10]. All the above-mentioned methods require extraction processes before detection. Also, owing to the higher sensitivity and selectivity of these methods, their widespread application is restricted by the complicated operation and high costs. Nanomaterials are considered ideal to be used to detect chemical species, as they have exceptional physical and chemical properties, including extremely small size, high stability, flexible lifetime, etc. [11–13]. Moreover, numerous studies have focused on their applications owing to their versatile properties [14]. Thereafter, as they are highly sensitive, less costly and due to the fact that they have quicker response and the real-time ability of direct detection of DA, nanomaterial-based detectors have aroused considerable interest.

Nano-cones have enjoyed the attention of scientists owing to their specific characteristics among all other nanomaterials. Boron nitride nano-cones (BNNCs) are hopeful sources of electron field emission owing to their dependency on the topological defect in terms of geometry near the apex [15,16]. The angle of disclination (D_θ) is a parameter used to distinguish the conical configuration of the BNNCs, known as the angle of the sector detached from the flat sheet to form a cone [17]. Only five D_θ are conceivable for carbon nano-cones derived from graphite to satisfy the cohesion condition at the junction of the flat graphite layer [17,18]. Unlike carbon nanostructures, which only have C–C bonds, isoelectronic BNNCs are mostly comprised of B–, B–B and N–N bonds, which represent various physical, chemical and electronic properties in carbon and boron nitride nanostructures [18–20]. However,

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undesirable formation of B–B and N–N bonds can result in the emergence of frustration energy [21]. Thus far, BN nano-cones have been synthesized with 120°, 240° and 300° disclination angles by various research teams [22]. The nano-cones located at the tip will result in further energy states close to Fermi level via homonuclear bonds, which might result in the reduction in the ionization potential of these BNNCs. However, it improves the emission current [23]. In the current study, the primary aim is to investigate the nature of adsorption behaviours and the electronic response of Al-decorated and pristine BNNCs to the DA drug by employing the first-principles density functional theory (DFT). Also, for the first time, work function, natural bond orbital (NBO), wiberg bond index (WBI) and evaluation of recovery time were used to scrutinize the mechanism of electronic response.

2. Computational methods

All of the calculations associated with the BNNCs, particularly the optimizations of energy and full geometry, were made by the B3LYP functional and the 6-31G(d) as implemented in the GAMESS code [24]. For the sake precision in the calculations, B3LYP-D, an experimental dispersion term, is introduced to the basis set [25,26]. Also, this functional enjoys the advantage of providing exact and consistent results in the computation of III–V semiconductors [27]. GaussSum program was used in or to evaluate [28]. Generally, the following equation is used to measure the adsorption energy (E_{ad}):

$$E_{ad} = E(\text{DA/BNNCs}) - E(\text{BNNCs}) - E(\text{DA}) + E(\text{BSSE}), \quad (1)$$

where E(BNNCs) represents the total energy of BNNCs, and E(DA/BNNCs) represents the total energy of the DA adsorption of the BNNCs surface. E(BSSE) designates the basis set superposition error calculated by the counterpoise method. Energy gap (E_g) is defined as the variance of HOMO (highest occupied molecular orbital) – LUMO (lowest unoccupied molecular orbital).

3. Results and discussion

3.1 *Pristine BNNCs reopens to DA drug*

According to the optimization results associated with BNNCs, the bond length and bond angle on the top of the nano-cone were different from the others. The BNB and NBN bond angles were about 104–109° on the top of the nano-cones. However, as can be seen in figure 1a, the bond angle was increased to 118–120° in the bottom layers for BNB and NBN, respectively. This considerable change in bond angles corresponds to different hybridization of N atoms on the top and the bottom based on the NBO analysis. It seems that the hybridization of N atoms on the top of the nano-cone is more similar to $sp^{3.08}$, but for N in the bottom layer, the hybridization is much closer to $sp^{2.18}$. However, the hybridization of B atom was closer to $sp^{2.42}$ and $sp^{2.04}$ on the top and the bottom layers, respectively. The B–N bond length on the top of BNNCs is around 1.29 Å. However, the B–N bond length is around 1.44–1.47 Å in the middle layers of the nano-cone. Based on the variation of the HOMO–LUMO levels of energy, the E_g value of BNNCs was calculated to be about 4.60 eV. This range of the bandgap correlates with the bandgap of semiconductive materials in comparison with the results cited in the literature [19]. In other words, the BNNCs have the properties of semiconductive materials. Also, the electron density was distributed on the top of the nano-cone based on the total density profile (figure 1b). The B atomic charge on the top of BNNCs is more positive (0.552 e) compared to other B sites (0.245 e) in the BNNCs. Hence, we can assume that more reaction sites exist on the top of the nano-cone with other molecules in these regions.

Different orientations and configurations for DA were taken into account to investigate the DA adsorption of BNNCs. As can be seen in figure 2a, the O atom of the DA drug is closer to BNNCs, which is named complex **I**. The O–B binding distance between DA and BNNCs is 1.96 Å and, also, the adsorption energy was calculated to be about -3.27 kcal mol^{-1}. The interaction between BNNCs and DA in the above-mentioned complex is weak according to the adsorption energy. In the complex **II**, the interaction of the N atom belongs to DA drug and BNNCs was investigated. The corresponding structure of this complex in the position mentioned is shown in figure 2b. The energy of the DA adsorption onto the BNNCs in complex **II**, with the N atom anchored at B atom, was computed to be -5.79 kcal mol^{-1}. The minimum distance between N atom of DA and B in BNNCs, the N–B bond length, is 1.93 Å. This shows that the interaction of DA in this configuration is stronger compared to complex **I** according to the adsorption energy. Also, in comparison with complex **I**, the charge transfer of complex **II**, and DA that is adsorbed onto BNNCs from N side, 0.17 e, is less.

The electronic properties, the HOMO, the LUMO and the E_g, of DA–BNNCs complex with different configurations are summarized in table 1. As can be seen in table 1, in pristine BNNCs, the LUMO level shifts from -2.29 to -2.19 eV in the more stable complex form, which is insignificant. Likewise, there was a slight decrease in the E_g and Fermi level of BNNCs after the adsorption of DA. The E_g variable is considered to be employed as an effective variable for an adsorbent's sensitivity towards an adsorbate. As equation (2) shows, it is associated with the electronic conductivity (σ) and E_g [29].

$$\sigma \propto \exp(-E_g/2kT), \quad (2)$$

where k represents the Boltzmann's constant and T represents the absolute temperature. The results of this approach

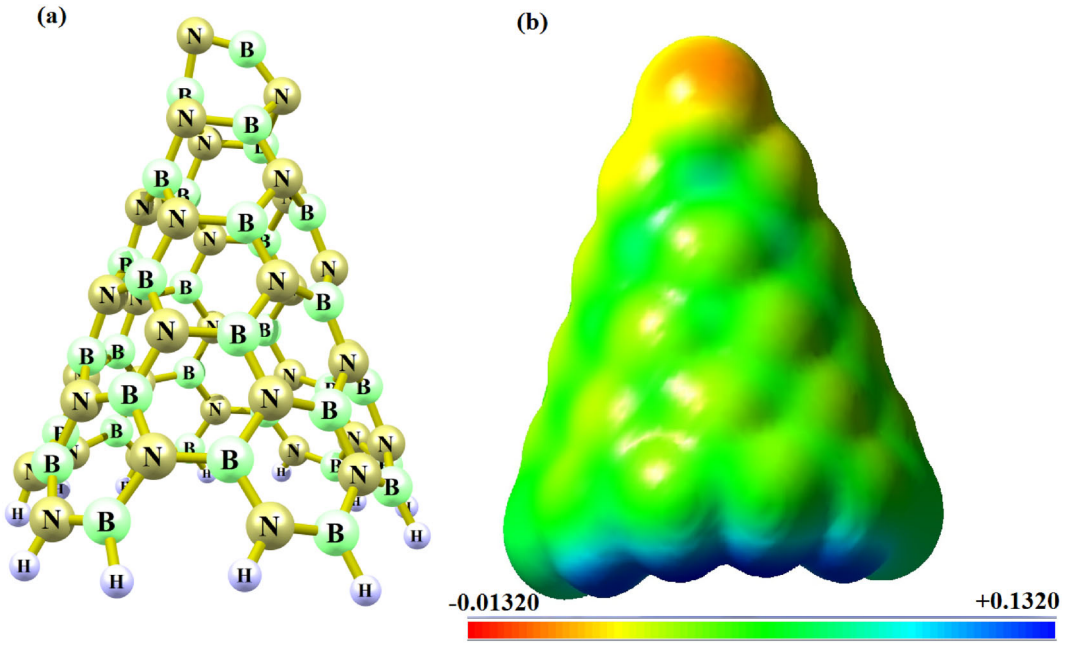

Figure 1. (**a**) Optimized structure and (**b**) total electrons density profile of BNNCs molecules.

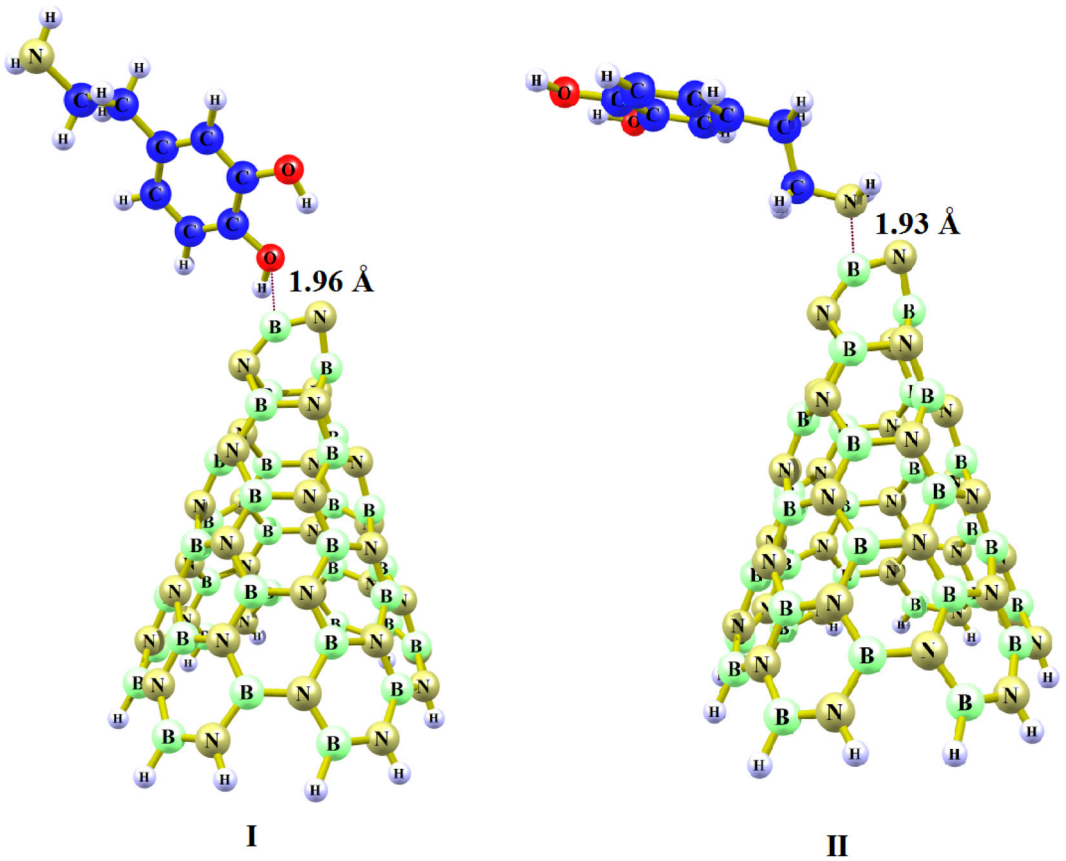

Figure 2. Adsorption configurations for DA drug optimized configurations (**a**) **I** and (**b**) **II** of DA–BNNCs. Distance is in Å.

Table 1. E_{ad} indicates the adsorption energy of DA molecules on the BNNCs in kcal mol^{-1}. HOMO energies (E_{HOMO}), LUMO energies (E_{LUMO}), HOMO–LUMO energy gap (E_g), Fermi level energy (E_F), and work function (Φ) of BNNCs and its complexes with different configurations are in eV. $\%\Delta E_g$ and $\%\Delta\Phi$ indicate the change of E_g and Φ after adsorption process, respectively.

Structure	E_{ad}	E_{HOMO}	E_F	E_{LUMO}	E_g	$\Delta\sigma$	Φ	$\%\Delta\Phi$
BNNCs	—	−6.88	−4.58	−2.28	4.60	—	4.58	—
DA	—	−5.32	−2.50	0.31	5.63	—	2.50	—
I	−3.27	−6.05	−4.10	−2.16	3.89	−15.32	4.10	−10.60
II	−5.79	−6.04	−4.11	−2.19	3.84	−16.28	4.11	−10.38

are in good agreement with those of the experiments [24]. According to equation (2), electrical conductivity increases exponentially as the E_g decreases. The change in the conductivity can be computed by using the following formula and the coefficient can be eliminated as well:

$$\Delta\sigma = \sigma_0 - \sigma/\sigma_0. \tag{3}$$

The σ and σ_0 represent electrical conductivity following and prior to the DA drug adsorption. The DA concentration is claimed to determine the magnitude of this electrical conductivity or signal. Also, the electrical conductivity can be used to estimate the detection (LOD) and the quantification (LOQ) limit. Based on equation (3), the change in the conductivity value was computed to be about 12.60% for pristine BNNCs for DA adsorption. As a result, the performance of pristine BNNCs for DA detection is low.

3.2 *Al-decorated BNNCs response to DA drug*

The decoration of Al on BNNCs was inspected by bonding single Al atom on BNNCs by scanning vertical intermolecular distances between BNNCs and Al atom from 1.0 to 5 Å on the top of BNNCs. On the other hand, the Al atom was adsorbed onto the BNNCs surface in the decorated BNNCs. Also, the energy of Al decoration is as follows:

$$E_{dec} = E(\text{Al}-\text{BNCs}) - E(\text{Al}) + E(\text{BNNCs}), \tag{4}$$

where E(Al–BNCs), E(Al) and E(BNNCs) represent the total energy of Al decoration, the total energy of BNCs and Al atom, respectively. Here, a different distance was taken into account to decorate Al, which is shown in figure 3. The most stable Al–BNCs complex with the lowest energy for Al decoration is about –20.17 kcal mol^{-1}. Also, the bonding distance with Al and BNNCs was optimized by about 2.05 Å. In addition, the value of E_g in Al–BNCs was calculated at around 3.38 eV, being smaller than the pristine BNNCs. Al atom can act as an affinity centre towards the chemisorption of the DA drug in the decorated site (table 2).

Afterwards, as can be seen in figure 4, the interaction between DA and Al–BNNCs was investigated by putting the species mentioned on the top of the Al atom with N atom of DA by scanning the distance between Al atoms and DA. During the interaction, the distance of the Al atom of the Al–BNNCs from the N atom of DA was obtained to be about 1.74 Å, as can be seen in figure 4. The optimized adsorption energy of Al–BNNCs and DA was calculated to be about –23.02 kcal mol^{-1}, as shown in figure 4b. The more adsorption energy in comparison with pristine BNNCs can be considered as a criterion for increasing the sensitivity of a sensor. The higher charge transfer value (0.64 e) and the more negative adsorption energy between Al–BNNCs and N atom of DA demonstrated that Al decoration in BNNCs will result in an improvement in the activity of the nano-cone in comparison with the pristine BNNCs counterpart. Contrary to Al, the electrostatic potential around the N atom is more negative, and the particles with positive charge have a strong interaction with this atom and they interact easily when they are close to this atom. Also, the electrostatic potential around the Al-decorated atom in BNNCs is positive. In other words, the nitrogen atom bonds at the exposed Al atom, as an area of low electron density can receive electrons from the electron-rich areas, which mainly include oxygen.

Thus, the adsorption of DA molecules considerably changes the electronic properties of DA complex with Al–BNNCs. As was foreseeable, the adsorption process brings about the stabilization of the LUMO of Al–BNNCs level from the N atom of the DA. The t change in the electronic properties can be ascribed to the interaction of DA with the LUMO level of the Al–BNNCs via its lone pair of electrons of nitrogen. Also, the variation of HOMO energy level and Fermi level show that there is a shift from the Al–BNNCs on the DA surface. The decrease in the E_g of Al–BNNCs after the DA adsorption will increase its electrical conductivity. The calculated variation in electrical conductivity was about 41.18%. These signal values were comparable with those reported by other techniques for the detection of DA on physical and chemical surfaces [30–32]. Therefore, it can be implied that Al–BNNCs can be utilized as a promising electronic sensor for the detection of the DA drug in comparison with pristine BNNCs. In the current study, the electrostatic and non-covalent interaction played an important role in the interaction of DA with pristine BNNCs. However, in the Al–BNNCs, in addition to the electrostatic, the formation of the Al–N bond plays a critical role in the adsorption of DA. In other words, in the pristine

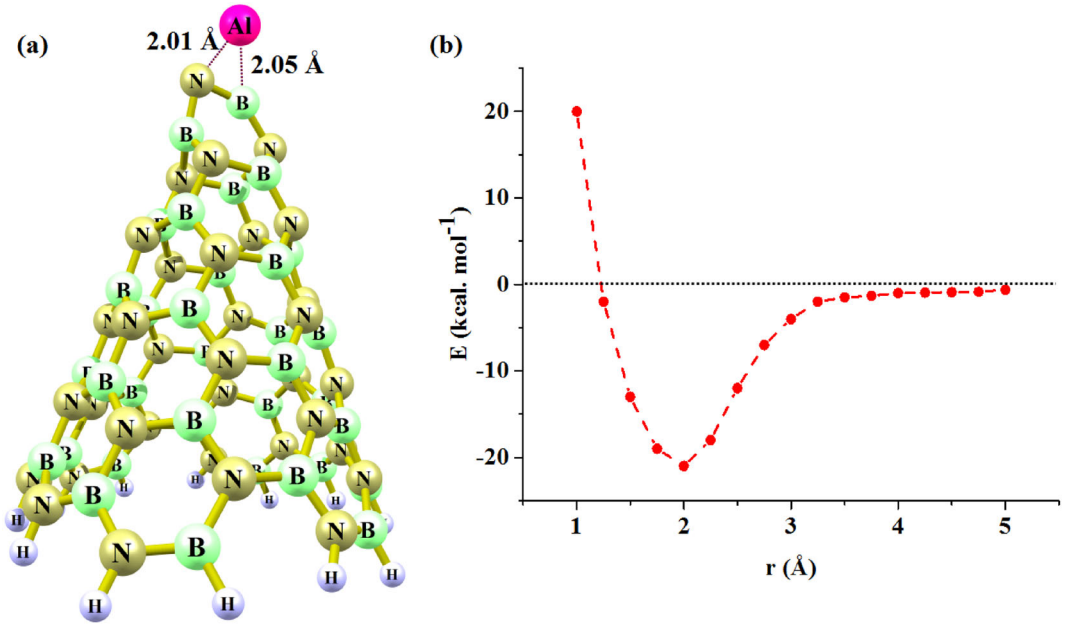

Figure 3. (**a**) Optimized structure Al-decorated BNNCs and (**b**) energy of Al decoration curves obtained by vertical scanning of intermolecular distances (1.0–5 Å) between Al atom and BNNCs.

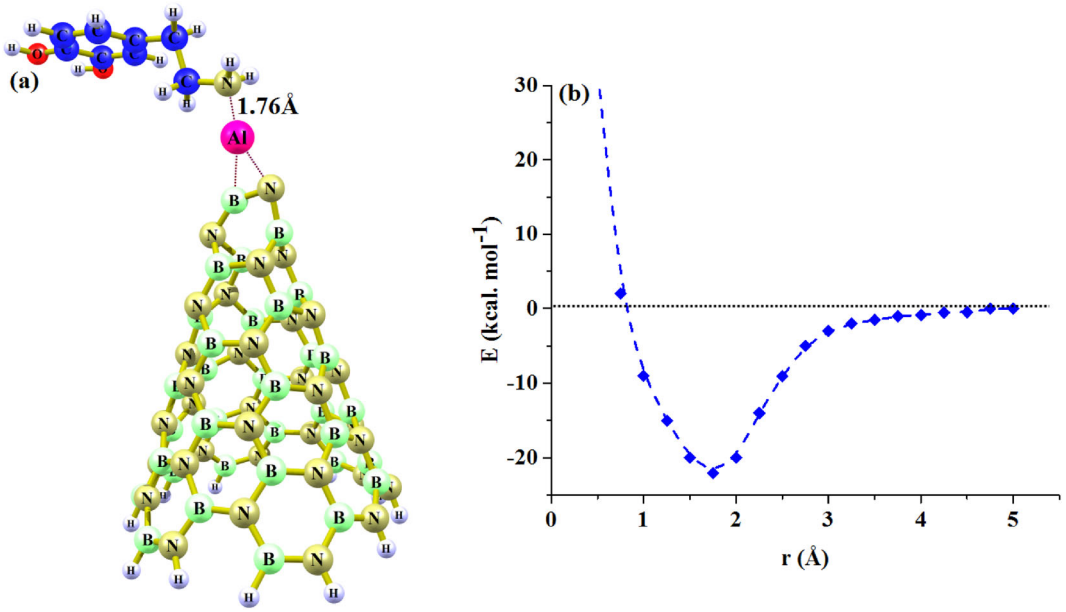

Figure 4. (**a**) Optimized structure DA and Al–BNNCs complex and (**b**) adsorption energy curves obtained by vertical scanning of intermolecular distances (0.5–5 Å) between DA and Al–BNNCs.

Table 2. E_{ad} indicates the adsorption energy of DA molecules on the Al–BNNCs in kcal mol^{-1}. HOMO energies (E_{HOMO}), LUMO energies (E_{LUMO}), HOMO–LUMO energy gap (E_g), Fermi level energy (E_F) and work function (Φ) of Al–BNNCs and its complexes in eV. $\%\Delta E_g$ and $\%\Delta\Phi$ indicate the change of E_g and Φ after adsorption process, respectively.

Structure	E_{ad}	E_{HOMO}	E_F	E_{LUMO}	E_g	$\Delta\sigma$	Φ	$\%\Delta\Phi$
Al–BNNCs	—	−5.51	−3.82	−2.12	3.38	—	3.82	—
Al–BNNCs + DA	−23.05	−3.93	−2.95	−1.97	1.96	−41.18	2.95	−22.70

BNNCs, there are three nitrogen atoms around the B atoms. When the N atom of the DA drug is close to the BNNCs, the repulsion force is applied to it by the nitrogen atoms of BNNCs and the interactions are non-covalent. But in the Al–BNNCs, due to the presence of Al atoms, Al–N covalent bonds are formed between the DA drug and Al–BNNCs.

3.3 *Evaluation of drug sensing mechanism*

3.3a *Work function analysis:* The work function variation of Al-decorated and pristine BNNCs was investigated to evaluate the DA sensing mechanism in a better way. Experimentally, the mechanism of the Φ-type gas sensors involves the Kelvin process in which a Kelvin oscillator device is utilized to evaluate Φ of the sample prior to and following the adsorption of DA onto BNNCs. When the Φ of the adsorbent is substantially affected by the DA adsorption, the gate voltage shifts afterwards, which produces an electrical noise conducive to the identification of DA [33]. As reported in studies on sensors, the minimum energy which is required to extract one electron from the Fermi level of a material to an infinite distance is often represented by Φ:

$$\Phi = V_{\mathrm{el}}(+\infty) - E_{\mathrm{F}}. \tag{5}$$

Equation (5) shows the electron electrostatic potential energy as $V_{\mathrm{el}}(+\infty)$, which is rather far from the material surface, and it is supposed to be negative, and E_{F} is the Fermi level energy. By assuming $V_{\mathrm{el}}(+\infty) = 0$, according to equation (5), $\Phi = -E_{\mathrm{F}}$, the Fermi level energy is computed as:

$$E_{\mathrm{F}} = E_{\mathrm{HOMO}} + (E_{\mathrm{LUMO}} - E_{\mathrm{HOMO}})/2. \tag{6}$$

There exist a correspondence between the Φ value and the current densities of the electron based on the Richardson Dushman equation (equation (7)). Hence, the Fermi level changes as a function of Φ variation, which is related to the changes in the field emission [34]:

$$j = AT^2 \exp(-\Phi/kT), \tag{7}$$

where A is the constant of Richardson (A m^{-2}), and T the absolute temperature (K). Correspondingly, the electron current density released from the BNNCs surface changes significantly, and the nano-cones can be considered as a DA adsorption Φ-type sensor. The work function of DA drug adsorbed onto the Al-decorated and pristine BNNCs decreases from 4.58 to 4.10 eV and 3.81 to 2.95 eV. In comparison with pristine BNNCs, the reduction of the work function value of Al–BNNCs after the DA drug adsorption is more by about 22.71%. Accordingly, the Al–BNNCs are both electronic and Φ-type sensors for the DA detection, while the pristine BNNCs is only an electronic sensor.

3.3b *Wiberg bond index analysis:* The strength of the intermolecular interaction between the drug and BNNCs can be analysed by employing the wiberg bond index (WBI) parameter as follows [35]:

$$\mathrm{WBI} = \sum_k p_{jk}^2 = 2p_{jj} - p_{jj}^2. \tag{8}$$

Here, the p_{jj} represents the elements of charge density and p_{jk} represents the elements of density matrices. WBI is profoundly identified with the bond order character of the BNNCs and the DA drug. Simply put, the higher values of WBI in this complex relate to stronger intermolecular interactions or covalent properties. The WBI value of DA drug on the Al-decorated and pristine BNNCs surface was calculated at B3LYPD/6-31(d) level. Based on the obtained results, the value of WBI for DA on the BNNCs and Al–BNNCs was calculated to be about 0.04 and 0.31, respectively. Moreover, the Al...N interaction in Al–BNNCs is stronger compared to B....N interaction in pristine BNNCs, which shows the covalent properties of Al...N intermolecular interactions. However, based on the values obtained for WBI for DA on the Al–BNNCs and pristine BNNCs system is more corresponding to weak van der Waals (vdW) interactions and the drug adsorption on the Al–BNNCs and pristine BNNCs is corresponding to physisorption process.

3.3c *Natural bond orbital analysis:* Delocalization of electrons from $\sigma \rightarrow \sigma^*$ in NBO, where σ and σ^* are Lewis-type donor and non-Lewis-type acceptors and they can

Table 3. Delocalization of electrons from electrons transfer in Al decorated and pristine with DA drug system based on the B3LYPD/6-31(d) level calculations.

System	Donor (*i*)	Acceptor (*j*)	E^2 (kcal mol^{-1})
BNNCs	LP (N)	LP* (B)	0.12
	LP (N)	RY* (B)	0.08
	LP (N)	LP* (Al)	15.65
	LP (N)	DB* (Al–N)	10.37
Al–BNNCs	CR (N)	DB* (Al–N)	3.73
	CR (N)	LP* (Al)	2.19

LP = 1-centre valence lone pair; DB* = 2-centre anti-bond; CR = 1-centre core pair; RY = 1-centre Rydberg.

produce donor–acceptor interactions. Also, these interactions can be calculated based on second-order perturbative NBO methods [36]:

$$\Delta E^2_{i\to j^*} = -2\frac{\left\langle \sigma_i \middle| \hat{F} \middle| \sigma_{j^*} \right\rangle^2}{\varepsilon_{j^*} - \varepsilon_i}, \tag{9}$$

where F is the effective orbital Hamiltonian (Fock or Kohn-Sham operator) and the diagonal elements of Fock matrix can be defined as $\varepsilon_i = \langle \sigma_i | F | \sigma_i \rangle$ and $\varepsilon_{j^*} = \langle \sigma_{j^*} | F | \sigma_{j^*} \rangle$ and also, ΔE^2 is the energetic stabilization. The most important donor–acceptor interactions based on the highest values of E^2 are summarized in table 3. The most important donor–acceptor interactions observed from one-centre lone pair (LP) valence of N atom belong to DA drug as a donor to one-centre anti-valence lone pair (LP*) of Al and two-centre anti-bond (BD*) of Al–N bond belong to Al–BNNCs as acceptors based on table 3. In addition, the energy of electron transfer in pristine BNNCs and the DA drug is lower in comparison with Al–BNNCs, which is in agreement with other analyses.

3.4 *Evaluation of recovery time*

Owing to the fact that a suitable sensor requires fast desorption, chemical interactions that too strong are considered perfect for sensors. In other words, intense adsorption often result in long recovery periods that are not perfect for sensor utilizations. As indicated by the current transition state theory, longer recovery time is required in strong adsorption as follows [37]:

$$\tau = \nu_0^{-1} \exp(-E_{\text{ad}}/kT), \tag{10}$$

where ν_0 is the attempt frequency. Earlier, the attempt frequency of ($\nu_0 \sim 10^{12}$ s^{-1}) was applied to the DA drug attached to Al–BNNCs, and the recovery time at ambient temperature was close to 16.43 ms. It is important to note that in higher temperatures, this period can be diminished. BNNCs have a generally fast recovery period and are perfect to sense DA species.

4. Conclusion

In order to evaluate the interaction of decorated and pristine BNNCs with the DA drug at the molecular level, DFT calculations were performed using the B3LYP-D functional in combination with a 6-31G(d) basis set. The interpretation of the interaction between the nano-cone and the DA drug at the molecular level was delineated by using NBO analysis. The results demonstrated that the DA drug was strongly adsorbed onto the Al–BNNCs surface. However, the adsorption of DA in the pristine BNNCs was weak, in agreement with the higher value of electrostatic potential surface on the Al and N atoms. Based on the NBO results, the electron transfer from LP* natural state of N atom from DA as a donor to LP* of Al atom and two-centre BD* of Al–N as an acceptor play an important role in the interaction between the donor and acceptor. Also, based on the electronic properties, the adsorption energy, and the charge transfer results, it could be concluded that the DA drug can be adsorbed onto Al site of BNNCs by forming the Al–N bond. Furthermore, the Al–BNNCs reinforce the tendency of this substrate towards the DA drug and can be utilized as a Φ-type sensor. Ultimately, vacuum ultra-violet light was employed to compute the recovery time, being approximately 16.43 ms at room temperature.

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