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# Efficient and selective sensing of nitrogen-containing gases by Si<sub>2</sub>BN nanosheets under pristine and pre-oxidized conditions

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# ABSTRACT

Motivated by the promise of two-dimensional nanostructures in the field of gas sensing, we have employed van der Waals corrected density functional theory calculations to study the structural, electronic and gas sensing propensities of the recently designed  $Si_2BN$  monolayer. Our rigorous simulations reveal that the representative members of nitrogen-containing gases (NCGs) such as NO, NO<sub>2</sub> and NH<sub>3</sub> binds extremely strongly on pristine  $Si_2BN$  monolayer. However, a strong dissociative adsorption in case of NO and NO<sub>2</sub> would poison the  $Si_2BN$  and ultimately reversibility of the monolayer would be compromised. Exploring the sensing mechanism in more realistic pre-oxidized conditions, the binding characteristics of  $O_2@Si_2BN$  changed dramatically, resulting into much lower adsorption in associative manner for all NO, NO<sub>2</sub> and NH<sub>3</sub>. A visible change in work function indicates the variation in conductivity of  $O_2@Si_2BN$  upon the exposure of incident gases. Sustainable values of binding energies would also ensure a quick recovery time that makes  $O_2@Si_2BN$  an efficient nano sensor for pollutants like NCGs.

# 1. Introduction

Increasing amount of pollution coupled with the emission of toxic gases is a serious threat to the environment as well as to humans. Among many other air contaminants, nitrogen-containing gases (NCGs) like NO, NO2 and NH3, originated from several processes like unfinished combustion, cause grave hazards and therefore it is of outmost importance to sense/capture such gases efficiently [1-4]. The shortterm exposure limits of these NCGs are roughly 25 parts per millions (ppm) for just a few hours, which makes them noxious enough to be captured proficiently [5]. An ideal sensor capable of detecting and then capturing harmful NCGs should have excellent sensitivity and selectivity, prompt response, operation at feasible conditions of temperature/pressure, cost-effective, durable and detection limit of as low as ppm [6,7]. Although solid-state gas sensors have been in use for the detection of toxicants for many years, however, several of the abovementioned conditions for an ideal sensor requires a more proficient option.

Two-dimensional (2D) materials are a unique class of nanostructures that has captured unprecedented attention in the recent times due to their fascinating properties and the broad range of applications. Novel 2D materials have been the subject of studies in various fields like catalysis [8–12], hydrogen storage [13–19], battery applications [20–24], gas sensing [25–28] and many other scientific and technological fields. Particularly as gas sensors, large surface area and the detection of even the smallest change in the electronic properties upon the exposure of incident gases make 2D nanostructures like graphene (a pioneer of 2D materials) as a promising option [29]. However, the absence of band gap and relatively weaker binding of incident gases on graphene motivated researchers to explore other 2D avenues. Thus 2D materials like silicene, germanene, phosphorene, antimonene, graph-diyne (GDY), MoS<sub>2</sub> and many others have been synthesized and considered as efficient sensing devices particularly for NCGs [26,30–35].

In addition to others, a graphenelike Si<sub>2</sub>BN monolayer is the recent addition into the family of 2D nanostructures that has attracted great attention due to its exotic properties. By means of *ab initio* simulations, Andriotis et al. predicted the possibility of obtaining stable two-dimensional Si<sub>2</sub>BN monolayers [36]. It was reported that all of the atoms remained in the plane while making sp<sup>2</sup> bonding like graphene. It was claimed that the presence of Si in Si<sub>2</sub>BN monolayer would make the structure reactive, which could be beneficial for several applications like hydrogen storage. This statement turns out to be true recently when

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Fig. 1. Optimized structures of (A) Si<sub>2</sub>BN and (B) O<sub>2</sub>@Si<sub>2</sub>BN monolayers. Blue, green, gray and red balls represent Si, B, N and O atoms, respectively.

Singh et al. employed first-principles calculations based on DFT to study the hydrogen storage properties of palladium-doped Si<sub>2</sub>BN [37]. Formation energy analysis revealed the stability of Si<sub>2</sub>BN, which could anchor  $3H_2$  molecules after functionalizing with Pd dopants thus reaching a reasonably high H<sub>2</sub> storage capacity. Yuan et al. used timedependent DFT formulism to study the optical properties of Si<sub>2</sub>BN nanosheets and claimed their absorption range wider than that of graphene [38]. Another promising application of Si<sub>2</sub>BN has been explored by Shukla et al. through studying its energy storage properties as anode material for Li and Na-ion batteries [39]. An interesting transition from planar to buckled geometry was seen upon metal doping that resulted into a significantly high specific capacity of 1158.5 and 993.0 mA h/g for Li and Na respectively.

Apart from above-mentioned studies, there is hardly any work on exploring the potential of this intriguing monolayer of  $Si_2BN$ . The reactive nature of Si in  $Si_2BN$  nanosheets would make it an excellent gas sensing materials, however, to the best of our knowledge, no group has investigated this avenue. To bridge this void, we have performed a comprehensive study on the sensing of NCGs on pristine and pre-oxidized  $Si_2BN$  nanosheets. Our van der Waals induced DFT calculations revealed that pristine  $Si_2BN$  nanosheets dissociate both NO and NO<sub>2</sub> and bind NH<sub>3</sub> strongly in the absence of O<sub>2</sub>. But pre-oxidized  $Si_2BN$  nanosheets weakly bind NO and NO<sub>2</sub> in their molecular forms, however the binding of NH<sub>3</sub> remained between the ideal strong physisorption and weak chemisorption range thus making  $Si_2BN$  nanosheets a promising candidate for NH<sub>3</sub> sensing in O<sub>2</sub> rich environment.

# 2. Computational methodology

For geometry optimization and electronic characteristics throughout this study, we have used spin-polarized DFT calculations by means of the VASP code [40,41]. The electron-ion interaction and the exchange and correlation function have been described by plane wave based ultrasoft pseudo-potential and the Perdew-Burke-Ernzerhof generalized gradient approximation (GGA), respectively [42,43]. For the wave-function expansions, we have used an energy cut off value of 500 eV. In order to sample the Brillouin zone, Monkhorst-Pack scheme is used with a *k*-point mesh of  $5 \times 5 \times 1$  for structural optimization and  $9 \times 9 \times 1$  for density of states calculations [44]. We have used  $2 \times 2 \times 1$  supercells with 32 atoms (B = N = 8, Si = 16) in total. A vacuum space of 20 Å has been inserted along perpendicular direction to avoid the periodically repeating images. Well know underestimation in calculating the binding energies of GGA methods has been compensated by incorporating van der Waals corrections of Grimme (DFT-D2) as executed by VASP code [45]. The convergence benchmark for the atomic positions and lattice parameters has been set as  $10^{-5}$  eV whereas the forces criteria of 0.001-eV/Å are considered. Energies convergence criteria are set at  $10^{-3}$  eV/atom. The binding energies have been calculated by using the following relations:

$$E_{b}(X) = [E(Si_{2}BN:X) - E(Si_{2}BN) - E(X)]$$
(1)

$$E_{b}(O_{2}) = [E(Si_{2}BN: O_{2}) - E(Si_{2}BN) - E(O_{2})]$$
(2)

$$E_{b}(X_{@}O_{2}) = [E(Si_{2}BN: X_{@}O_{2}) - E(Si_{2}BN_{@}O_{2}) - E(X_{@}O_{2})]$$
(3)

where X = NO,  $NO_2$ ,  $NH_3$  and 1st, 2nd and 3rd terms in each of above equations represent total energies of the Si<sub>2</sub>BN nanosheets loaded with  $X/O_2/X@O_2$ , pristine/ $O_2$  adsorbed Si<sub>2</sub>BN and gases, respectively.

#### 3. Results and discussion

We will divide the results and discussion part into structural properties of Si<sub>2</sub>BN followed by the adsorption of NCGs on pristine nanosheets. Later on the oxidation process of Si<sub>2</sub>BN will be discussed and eventually the binding characteristics of NCGs on pre-oxidized Si<sub>2</sub>BN will be presented. On structural part the optimized B–N, Si–B, Si–N and Si–Si bond lengths are 1.47 Å, 1.95 Å, 1.76 Å and 2.24 Å, respectively. Lattice constants for  $2 \times 2$  supercell in the direction of *a* and *b* are 6.35 Å and 6.44 Å, respectively. The Si–B–Si and Si–N–Si bond angles are found to be 112.6° and 124.5°, respectively. These parameters agree well with the literature, which authenticates the level of theory being used in this study [37,39]. The top and side views of the optimized structure of Si<sub>2</sub>BN are shown in Fig. 1(A).

On electronic properties end,  $Si_2BN$  preserve a metallic behavior with the Si (p) and N (p) is found to be responsible for this metallicity. It is also clear that the valence band on the left of Fermi is dominated by B (p) and Si (p) whereas the conduction band by N (p) as shown in TDOS and PDOS plots in Fig. 2.

After attaining the lowest energy configurations, NCGs are exposed on Si<sub>2</sub>BN monolayer at 9 different available binding sites, which are Sitop, B-top, N-top, bridge (Si–B), bridge (Si–N), bridge (B–N), hollow (Si–B), hollow (Si–B), hollow (Si–N) and hollow (Si–B–N). The most stable configurations as shown in Fig. 3 reveals a dissociative adsorption with very high  $E_b$  of -5.27 and -4.97 eV for NO and NO<sub>2</sub>, respectively. These  $E_b$  values are much higher than that of graphene, antimonene, germanene, MoS<sub>2</sub>, aluminene and Ti<sub>2</sub>CO<sub>2</sub> [26,33,35,46,47]. The reason behind these high  $E_b$  lies in the fact that both NO and NO<sub>2</sub> undergo dissociative adsorption in contrast to their molecular adsorption on other 2D monolayers.

In case of NO adsorption on Si<sub>2</sub>BN, the N–O bond breaks, which are evident from calculated N–O distance of 3.30 Å, that is almost three times than the usual N–O bond length of 1.15 Å. After dissociation, both N and O atoms got attached to the neighboring Si atoms at Si–Si bridge site in Si<sub>2</sub>BN monolayer with binding distances of 1.61 Å and 1.71 Å for N and O atoms, respectively. Upon the binding of NO, the Si–Si bond length from 2.24 Å to 2.97 Å. The top and side views of the optimized structure of NO adsorbed Si<sub>2</sub>BN are shown in Fig. 3(A).

A strong Si $_2$ BN–NO binding could also be seen by their PDOS plots as given in Fig. 4.

In this plot, Si<sub>1</sub> and Si<sub>2</sub> represents Si atoms with which the



Fig. 2. Total (TDOS) and partial (PDOS) density of states of pristine Si<sub>2</sub>BN monolayer.

dissociated fragments of NO, N and O, got attached. N<sub>1</sub> and N<sub>2</sub> are the N atoms of Si<sub>2</sub>BN and incident NO molecules, respectively. One can clearly see a strong overlap between Si<sub>1</sub> (p) and N<sub>2</sub> (p) and also between Si<sub>2</sub> (p) and O (p) close to Fermi level on either side. The dissociative adsorption of NO does not change the metallic character of the Si<sub>2</sub>BN monolayer.

When it comes to NO2-Si2BN interaction, a similar dissociative adsorption takes place with one constituent of the incident NO2 molecule, the N atom, bonded to the Si-Si bridge site similar to that of NO adsorption. However, the other constituent NO optimizes itself in the hollow site of neighboring Si–B–N hexogen as shown in Fig. 3(B). This would elongate the Si-B, Si-N and Si-Si bond lengths of that particular hexogen to 2.0 Å, 1.80 Å and 2.36 Å, respectively. The Si-B-Si bond angle reduces from 112.6° to 104.7° whereas Si-N-Si angles elongate from 124.5° to 130.1°. The dissociation of both NO and  $NO_2$ could be caused by excessive charge transfer from Si<sub>2</sub>BN nanosheets to the incident molecules. Our Bader analysis shows that around 2.08 é and 2.09 é of the electronic charge have been transferred from Si<sub>2</sub>BN to the O atoms of NO and NO<sub>2</sub>, respectively, which causes first the elongation and then breaking of N–O bonds in both the molecules. Bulk of this transferred charge came from Si atoms of Si<sub>2</sub>BN, which has the least electronegativity among all the Si, B and N atoms.

Like NO binding to Si<sub>2</sub>BN, NO<sub>2</sub> shows similar electronic behavior as



Fig. 4. PDOS plots of dissociative NO binding on Si<sub>2</sub>BN monolayer.

given in Fig. 5. Here  $Si_1$  and  $Si_2$  are Si atoms with which the dissociated fragments of NO<sub>2</sub>, O and NO are bonded. Here  $N_1$  and  $N_2$  are N atoms of the  $Si_2BN$  monolayer and NO<sub>2</sub> molecules, respectively. In PDOS plot a



Fig. 3. Optimized structures of (A) Si<sub>2</sub>BN-NO, (B) Si<sub>2</sub>BN-NO<sub>2</sub> and (C) Si<sub>2</sub>BN-NH<sub>3</sub> monolayers. Blue, green, gray, pink and red balls represent Si, B, N, H and O atoms, respectively.



Fig. 5. PDOS plots of dissociative NO2 binding on Si2BN monolayer.

strong overlap between Si<sub>1</sub> (p) and O<sub>2</sub> (p) represent strong bonding mechanism between Si<sub>2</sub>BN and NO, whereas Si<sub>2</sub>(p) and O<sub>1</sub> (p) indicates Si<sub>2</sub>BN and O bonding. The metallic behavior of Si<sub>2</sub>BN remains intact upon the adsorption of NO<sub>2</sub> dissociative adsorption.

Significantly high E<sub>b</sub> associated with the dissociation of NO and NO<sub>2</sub> molecule would cause chemical poisoning, which restricts the use of Si2BN as an efficient sensor for both of these NCGs. In contrast to both NO and NO<sub>2</sub>, the binding of NH<sub>3</sub> takes place under associative adsorption manner with  $E_b$  value of  $-0.94\,eV$  at a binding distance of 2.0 Å. The calculated E<sub>b</sub> value is stronger than NH<sub>3</sub> adsorption on germanene selenide, graphdiyne, buckled antimonene and Ti<sub>2</sub>CO<sub>2</sub> [26,31,33,48]. However, a couple of previous studies on NH<sub>3</sub> sensing by co-doped graphene and fullerene also reported higher adsorption energies [49,50]. The reason for higher NH<sub>3</sub> binding is believed to be the existence of Au and Co dopants on both graphene and fullerene, respectively. The NH<sub>3</sub> molecule optimizes itself with its N atom sitting at the Si top of Si<sub>2</sub>BN as shown in Fig. 3(C). This would elongate the bond length of Si, on which NH<sub>3</sub> is sitting, with the neighboring Si and B to 2.33 Å and 2.0 Å, respectively. Similarly, the Si-B-Si and Si-N-Si bond angles also change a little to 113.74° and 122.91°, respectively. Unlike the other NCGs, a significantly lesser charge of 0.12 é is transferred from Si<sub>2</sub>BN to NH<sub>3</sub>. Thus an associative adsorption with feasible  $E_b$  would not cause any chemical poisoning for  $NH_3$ , that favors the application of Si<sub>2</sub>BN as a reversible NH<sub>3</sub> sensor.

The electronic properties given as PDOS plot in Fig. 6 for  $NH_3$  binding is different from NO and  $NO_2$ . Here  $NH_3$  bind with  $Si_2BN$  in an

associative manner, which is evident from relatively less pronounced overlapping of the N (p) of  $NH_3$  with Si (p) of  $Si_2BN$  monolayer. In Fig. 6,  $N_2$  is the N atom of  $NH_3$  attached to the  $Si_2$  of  $Si_2BN$  whereas  $Si_1$ , and  $N_1$  are the Si and N atoms of the monolayer.

From the above discussion, we conclude that in pristine form Si<sub>2</sub>BN could be used only for NH<sub>3</sub> sensing among the considered NCGs. The presence of abundant oxygen  $(O_2)$  in the atmosphere would affect the performance of a sensor, thus the sensitivity of any sensor should also be investigated under oxidized conditions. Considering this fact, we have studied the efficiency of Si2BN nanosheets towards NCGs under pre-oxidized conditions. For this purpose, an O<sub>2</sub> molecule is introduced both vertically (perpendicular to the sheet) and horizontally (parallel to the sheet) on the available binding sides on Si<sub>2</sub>BN monolayer. There are several binding sites available on Si<sub>2</sub>BN and O<sub>2</sub> can be introduced either parallel or perpendicular to the periodic sheet. The lowest energy configuration yields a structure with O2 molecule dissociated into two O atoms, which are bonded at the Si-Si bridge site as shown in Fig. 1(B). This trend  $O_2$  dissociation is similar to that of reported by Tawfik et al. on metal doped graphene nanoribbons [51]. The bond length and  $E_b$  are found to be 1.71 Å and around -10.0 eV, which is evident of the fact that Si2BN has an extremely strong tendency to get oxidized when exposed to O2. The dissociation mechanism of O2 on  $Si_2BN$  is caused by an excessive charge from the latter to the former and resembles to that of NO and NO2 dissociation. Bader analysis reveals that around 2 é of electronic charge is transferred to each O atoms from Si<sub>2</sub>BN, (majority of which has come from Si atoms), which has caused its dissociation of  $O_2$ . A strong overlap between Si (p) and O (p) in the PDOS plots as shown in Fig. 7 authenticates the strong O2-Si2BN binding mechanism. Here Si1 and Si2 are the Si atoms of Si2BN monolayer hosting the  $O_1$  and  $O_2$  atoms of dissociated  $O_2$ .

After attaining O<sub>2</sub> adsorbed Si<sub>2</sub>BN (O<sub>2</sub>@Si<sub>2</sub>BN), we expose NCGs in their different orientations at the several available binding sites. The value of E<sub>b</sub> for NO was reduced drastically to -0.155 eV, which is a tremendous decline as compared to its value on Si<sub>2</sub>BN in the absence of O<sub>2</sub>. The lower E<sub>b</sub> is believed resulted from a significantly lower amount of charge of 0.07 é being transferred from NO to O<sub>2</sub>@Si<sub>2</sub>BN. In the lowest energy configurations, NO prefers to sit horizontally at a binding distance of 2.50 Å as shown in Fig. 8. Furthermore, there is hardly any change in the bond length of NO on O<sub>2</sub>@Si<sub>2</sub>BN and the former retains its molecular character.

Considering the adsorption mechanism of NO<sub>2</sub> on O<sub>2</sub>@Si<sub>2</sub>BN, a similar trend of drop in  $E_b$  has been observed with the value of -0.201 eV at a binding distance of 3.20 Å, which is again a drastic reduction in  $E_b$  as compared to that of non-oxidized Si<sub>2</sub>BN. Bader analysis explains a relatively higher value of  $E_b$  for NO<sub>2</sub> than NO is resulted by the transfer of slightly more charge of -0.084 é from NO<sub>2</sub>



Fig. 6. PDOS plots of dissociative NH<sub>3</sub> binding on Si<sub>2</sub>BN monolayer.



Fig. 7. PDOS plots of dissociative O2 binding on Si2BN monolayer.



Fig. 8. TDOS plots of NO, NO2 and NH3 adsorption on O2@Si2BN monolayer.

to  $O_2@Si_2BN$ . However, in contrast to NO, there is little change in the structure of NO<sub>2</sub> with the elongation of N–O bonds to 1.217 Å from equilibrium value of 1.197 Å and the reduction of O–N–O angle to 131.85° from 134.3°. The lowest energy configuration of NO<sub>2</sub> on O<sub>2</sub>@Si<sub>2</sub>BN is shown in Fig. 9.

Drastic reduction in the  $E_b$  values of NO and NO<sub>2</sub> on pre-oxidized Si<sub>2</sub>BN could be attributed to the amount of charge transfer between NO/NO<sub>2</sub> and O<sub>2</sub>@Si<sub>2</sub>BN. In the case of pristine monolayer, a significantly large amount of charge is transferred between the NCGs and the Si<sub>2</sub>BN. Upon O<sub>2</sub> adsorption, most of the charge from Si<sub>2</sub>BN is captured by the O<sub>2</sub>, which would leave very small charges available to be exchanged with the NCGs. Moreover, the biding of both NO/NO<sub>2</sub> on pre-oxidized Si<sub>2</sub>BN monolayer takes place in a dissociative manner in contrast to the associative binding on O<sub>2</sub>@Si<sub>2</sub>BN.

Lastly, we discuss the binding mechanism of NH<sub>3</sub> on pre-oxidized Si<sub>2</sub>BN. Like other NCGs, NH<sub>3</sub> has exposed at various binding sites in different orientations and the resulted ground state configuration yields an E<sub>b</sub> value of -0.448 eV at the binding distance of 2.24 Å. Opposite to NH<sub>3</sub> adsorption on non-oxidized Si<sub>2</sub>BN, the former adjust itself with its H atoms points towards the O<sub>2</sub>@Si<sub>2</sub>BN as shown in Fig. 9. Although the E<sub>b</sub> is higher than other NCGs, however the structure of adsorbed NH<sub>3</sub> molecule remains the same with negligibly small variation in N–H bonds and H–N–H angle.

To operate reversibly the binding energy of the incident gas should lie between strong physisorption and weak chemisorption. Any value between -0.30 eV and -0.80 eV is considered as a suitable binding strength. For NH<sub>3</sub> both E<sub>b</sub> and binding distance are in ideal range as compared to the other NCGs considered in this study, which indicates the potential of O<sub>2</sub>@Si<sub>2</sub>BN as an efficient and selective sensor for NH<sub>3</sub>. Ground state configurations of  $O_2@Si_2BN$  with NO,  $NO_2$  and  $NH_3$  has been shown in Fig. 9.

To qualify as an ideal sensing device, a material should also show a variation in its conductivity upon the exposure of gases to be detected. In Fig. 8, TDOS plots for NO, NO<sub>2</sub> and NH<sub>3</sub> adsorption on O<sub>2</sub>@Si<sub>2</sub>BN is given. One can see a contribution at Fermi in case of NO, NO<sub>2</sub> and NH<sub>3</sub>, however the metallic character of O<sub>2</sub>@Si<sub>2</sub>BN is unperturbed even after the exposure of these gases. It is important to mention here that the surface sensitivity of 2D nanosheets (O<sub>2</sub>@Si<sub>2</sub>BN here) would be largely dependent on the surface potential, a parameter that could be approximated by calculating the variation in work function ( $\phi$ ). The measure of  $\phi$  is defined, as the energy required in dislodging an electron from a system to infinity. Moreover, it has been reported that the conductivity of a systems, especially 2D nanostructures is directly related to the change in work function [27,52]. Thus we have calculated work function for these systems by the following relation:

$$\phi = V_{\infty} - E_f \tag{4}$$

In the above relation  $\phi$ ,  $V_{\infty}$  and  $E_f$  represents work function, electrostatic potential at infinity and Fermi level, respectively (see Table 1).

A comparative analysis of calculated  $\varphi$  for different systems clearly shows a variation that could be coupled with the variation in conductivity upon the exposure of NCGs. In the case of NCGs adsorption on  $O_2@Si_2BN$ , the monolayers preserve their metallicity, which means the electrons would be moving through the system freely. Thus even a small change at the surface upon the exposure of gases would change  $\varphi$  and consequently conductivity. Calculated values of  $\varphi$ ,  $V_\infty$  and  $E_f$  for all the systems have been given in supplementary information, which clearly shows a change before and after the adsorption of NCGs.

In addition to sensitivity and selectivity, recovery time ( $\tau$ ) is equally important in designing an efficient nanosensor. Smaller value of  $\tau$ would validate the reversibility of a sensor. Here we briefly talk about  $\tau$ for O<sub>2</sub>@Si<sub>2</sub>BN, which determines its reversibility and could be calculated by transition state theory as given by the following relation:

$$\tau = v^{-1} \exp(-E_b/kT) \tag{5}$$

Here v,  $E_b$ , k and T represent attempted frequency, adsorption energy, Boltzmann's constant and operational temperature, respectively. A strong adsorption of NCGs on O<sub>2</sub>@Si<sub>2</sub>BN would result into enhancing  $\tau$  exponentially.

In the case of carbon-based materials, the values of  $\upsilon$  is taken as  $10^{-12}\,s$  [34]. Nevertheless, to attain a reasonable approximation of Si<sub>2</sub>BN monolayer, we have used the value of  $\upsilon$  similar to the one mentioned above. The main purpose of mentioning  $\tau$  here is to establish its relation with the  $E_b$  of incident NCGs rather than giving a quantitative analysis. However if we use the  $E_b$  values of NO, NO<sub>2</sub> and NH<sub>3</sub> on pre-oxidized Si<sub>2</sub>BN, and incorporate  $\upsilon$ , k and T (room temperature), the corresponding values of  $\tau$  are 0.99 and 59.6  $\mu$ s for NO and NO<sub>2</sub>, respectively. In case of NH<sub>3</sub>, a comparatively high  $E_b$  would result into a



Fig. 9. Optimized structures of (A) O<sub>2</sub>@Si<sub>2</sub>BN-NO, (B) O<sub>2</sub>@Si<sub>2</sub>BN-NO<sub>2</sub> and (C) O<sub>2</sub>@Si<sub>2</sub>BN-NH<sub>3</sub> monolayers. Dark blue, green, light blue, pink and red balls represent Si, B, N, H and O atoms, respectively.

Table 1Calculated work function of different systems.

| System                             | Work function (eV) |
|------------------------------------|--------------------|
| Si <sub>2</sub> BN                 | 4.352              |
| O <sub>2</sub> @Si <sub>2</sub> BN | 4.739              |
| O2@Si2BN-NO                        | 4.578              |
| O2@Si2BN-NO2                       | 4.870              |
| O2@Si2BN-NH3                       | 4.871              |

longer  $\tau$  of several minutes. Ideally, it is preferred to have as short value of  $\tau$  as possible.

# 4. Conclusion

Designing an efficient nanosensor is of utmost importance due to its usage in a variety of fields like toxic and explosive gas captures, industrial applications and environmental cleanliness. Advancement in technology has made it possible to explore the promise of 2D materials as sensing devices due to their advantages over the traditional semiconducting sensors. Motivated by this, we have performed comprehensive first-principles calculations based on density functional theory to study the structural, electronic and gas sensing characteristics of novel Si<sub>2</sub>BN monolayer towards NCGs like NO, NO<sub>2</sub> and NH<sub>3</sub>. Our vdW induced calculations to indicate that excessive charge transfer from Si<sub>2</sub>BN to both NO and NO<sub>2</sub> dissociates the gas molecules, which then bind to the monolayer strong enough to nullify the reversibility. However, NH<sub>3</sub> preserves it molecular geometry even on pristine Si<sub>2</sub>BN. Incorporating the presence of atmospheric oxygen while studying the adsorption mechanism of NCGs with Si2BN, a tremendous decrease in adsorption energies has been witnessed. The calculated adsorption energies of NCGs on the oxidized Si2BN (O2@Si2BN) fall in an ideal range to guarantee a prompt recovery time, which has direct connection to the efficiency and reversibility of the sensor. The variation in the work function of O2@Si2BN upon the exposure of NCGs indicates the change in conductivity, which is also vital for the sensing mechanism. Thus our study authenticates the potential of O2@Si2BN as an efficient nanosensor for hazardous NCGs.

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#### Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.apsusc.2018.11.020.

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