Adsorption of ammonia on ZrO x modified graphene nanoribbon: a first-principles investigation

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Adsorption of ammonia on ZrO$_x$ modified graphene nanoribbon: a first-principles investigation

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Abstract

Ammonia (NH$_3$) is a main environmental pollutant related to global warming, and reduction of its emission is the subject of multiple international agreements and regulations. Accordingly, the development of highly precise detectors to monitor its content in the environment is essential to track and limit its emission. This work examines the influence of modifying of armchair-graphene nanoribbon (AGNR) by zirconium (Zr) and its oxides on its adsorption for NH$_3$ gas. Density functional theory (DFT) computations are utilized to investigate the band structure, adsorption energy ($E_d$), adsorption length ($D$), charge transferred ($\Delta Q$), and density of states (DOS) of pristine and modified structures with ZrO$_x$ ($x = 0, 1, or 2$). ZrO$_x$ is presented to AGNR nanostructure by two pathways: substitution of carbon atoms (doping), and introduction on top of the AGNR surface (decoration). The findings of the investigation illustrate great improvement of NH$_3$ adsorption on AGNR due to its modification. Although the adsorption energy is enhanced in general upon modification, AGNR structures where ZrO$_x$ substitute carbon atoms exhibit greater adsorption energy as compared with the decoration scheme. The maximum energy of adsorption is for the AGNR structure doped with ZrO$_2$, followed by that doped with Zr. As compared to the pristine structure, the adsorption energy for NH$_3$ on AGNR doped with ZrO$_2$
increases 22.2 times. Therefore, AGNR nanostructure doped with ZrO$_x$ can be considered for practical sensors for the applications of detection and control of ammonia emission.

**Keywords:** graphene nanoribbon; ZrO$_x$; ammonia sensor; DFT

1. **Introduction**

Agricultural activities result 80-90% of the total global ammonia (NH$_3$) emission [1]. Its emission results mainly through volatilisation of livestock manure as well as a synthetic mineral for nitrogen based fertilizers [2, 3]. NH$_3$ emissions alongside with other greenhouse gases that result mainly from agricultural activities have negative effects on air quality [4]. It is associated with two main environmental hazards: acidification besides to eutrophication [5]. When ammonia interact with water, it increases the acidification of both soil and water [6]. Furthermore, the deposition of ammonia in soil and water can increase their nitrogen level that may increase the eutrophication of aquatic ecosystems [5]. Human exposure to ammonia concentrations of 25 ppm or higher may negatively influence the lung functions and respiratory track, and it may result injuries and risking burns for high exposure concentrations [7]. Accordingly, precise environmental monitoring of ammonia level and control of its emission (especially at the industrial production plants such as production plants of plastics, fabrics, explosives, ..etc.) are essential [8].

Conductometric chemical sensors are electronic devices that detect the presence of selected chemicals and their concentrations at their surroundings through the change in the electrical conductance [9-13]. The chemical sensors are important for domestic safety in addition to
environmental assessment because they identify hazardous gas concentrations, and send their values to safety as well as control systems.

Graphene is known as a two dimensional material of a mono layer of carbon atoms in a lattice structure of honeycomb [14, 15]. Graphene exhibits two main structures following the arrangement of its atoms: zigzag (ZGNR) and armchair (AGNR). The two structures have different energy band structures where ZGNR is categorized as a conductor whereas AGNR can be either conductor or semiconductor [16-18]. Graphene is considered a material with extraordinary characteristics that include excellent thermal conduction, optical transparency, alongside its high density that inhibits its penetration by gases [19]. Experimentally, the band gap of AGNR can be controlled through decreasing its dimensions to one or quasi one dimensional [20]. AGNR may be classified into three categories depending on the quantity of dimers through a nanoribbon line \( N_d \), with \( N_d = 3n, 3n + 1, \) or \( 3n + 2 \), with \( n \) is an integer. The first two categories are semiconductor, whereas the last one is metallic [21]. The semiconductor AGNR is more attractive for device applications such as optical devices, biodevices, chemical sensors, …etc. [12, 22, 23]. Additionally, it is investigated heavily for gas sensor applications due to its ability to adsorb various gases [18, 24-26]. The sensitivity as well as the selectivity may be promoted by modification of AGNR surface, i.e. by i) doping that involves replacement of selected carbon atom(s) by dopant atom(s), and ii) decoration that involves precise addition of atom(s) on its surface [23, 27, 28]. The effect of modifying graphene nanoribbon has investigated intensively recently for gas sensing utilization [29], since its impact on enhancing AGNR adsorption features was illustrated experimentally [12, 19]. M. Miao et al investigated the decomposition of ammonia on graphene
modified by metal clusters of $\text{Ni}_6$, $\text{Co}_6$, and $\text{Fe}_6$ using DFT computations [30]. They found that graphene modified with $\text{Ni}_6$ is more active for ammonia adsorption and dissociation. P. Barkov examined modifying graphene nanoribbons with carboxylic acid (COOH) group and its effect on ammonia adsorption using DFT calculations [31]. They found that wet nanoribbons interact further with ammonia. The carboxyl group attracts water molecule that is favorable in terms of energy that in turn promotes ammonia adsorption where COOH and water represent adsorption centers for $\text{NH}_3$. VE. C. Padilla et al examined ammonia adsorption on graphene doped with P and Si atoms by means of DFT computations [32]. Phosphorus modified graphene exhibits metallic behavior, while the silicon modified graphene is a semiconductor (band gap $\sim$ 0.25 eV). The phosphorus modified structure was found to be more favorable for ammonia adsorption than the silicon modified one.

Herein, the effect of modification of AGNR ($N_a = 3p$) by $\text{ZrO}_x$ ($x = 0, 1, \text{or} \ 2$) on its adsorption for ammonia gas is investigated using first principles and DFT computations [33]. The AGNR structures are modified by $\text{ZrO}_x$ species through either substitution of carbon atom(s) by $\text{ZrO}_x$ (doping), or addition of $\text{ZrO}_x$ on AGNR surface (decoration). The adsorption of ammonia on pristine and modified graphene structures is explored by detailed investigation of band structure, adsorption energy ($E_d$), adsorption length ($D$), charge transfered ($\Delta Q$), and density of states (DOS).

2. Simulation methods

Kohn-Sham (KS) DFT calculations were employed to explore the influence of $\text{ZrO}_x$ modification of AGNR structures on their adsorption of $\text{NH}_3$ [34]. The different structures were labeled as presented in Table 1. The computations utilized a framework that consists of a linear combination
of atomic orbitals (LCAO) along with pseudopotential perturbation. The electrons are modeled as a system of non-interacting gas that exhibits a density \( n \) within an effective potential \( V^{\text{eff}}(n) \) according to the equation [35]:

\[
V^{\text{eff}}(n) = V^H(n) + V^{xc}(n) + V^{\text{ext}}(n) \quad \ldots \quad (1)
\]

The electrostatic interaction amongst electrons is represented by the Hartree potential \( V^H \). The exchange-correlation (XC) potential is represented by \( V^{xc} \), whereas the electrostatic potential energy of electrons is indicated by \( V^{\text{ext}} \).

The Hamiltonian of KS \( \hat{H}^{KS} \) may be presented as [35]:

\[
\hat{H}^{KS} = -\frac{\hbar^2}{2m} \nabla^2 + V^{\text{eff}} \quad \ldots \quad (2)
\]

Where \( m \) is the mass of electron and \( \hbar = \frac{\hbar}{2\pi} \) (\( \hbar \) is Planck’s constant). The KS equation is represented by a DFT-LCAO process through numerical values to permit effective implementation of KS-DFT computations for all different structures. Two types of approximations were implemented within the KS-DFT formalism: local density (LDA) alongside with generalized gradient (GGA). Their implementation was according to Perdew–Burke–Ernzerhof (PBE) scheme combined with Grimme approximations (DFT-D2) that account for Van der Waals force [36, 37]. The above estimates were selected because of their reasonable consideration of both accuracy and efficiency of DFT computations as presented by various reports [38].

A simulation package from Synopsys: Quantum ATK associated with a virtual nanolab (VNL) was utilized to perform the DFT calculations. Single sheets of AGNR with the edge atoms terminated by hydrogen were used in this investigation [39]. Zr, ZrO, and ZrO\(_2\) (referred as ZrO\(_x\)) were used to modify the structures either by doping or by decoration. Prior to any computations, an LBFGS optimizer was employed to optimize the structures [40], and they were relaxed where the
residual force per atom and stress tolerance were under 0.05 eV/Å and 0.1 GPa, correspondingly. The \( k \)-point sampling mesh was \( 4 \times 2 \times 1 \), with a mesh density of 100 Hartree. The ammonia adsorption energy for a structure was evaluated using [17, 18]:

\[
E_d = E_{\text{structure}+\text{NH}_3} - (E_{\text{structure}} + E_{\text{NH}_3}) \quad \ldots \ldots (3)
\]

Herein, \( E_{\text{structure}+\text{NH}_3} \) is the total energy of AGNR structure with adsorbed NH\(_3\), \( E_{\text{structure}} \) is the total energy of an unexposed AGNR structure, and \( E_{\text{NH}_3} \) is the total energy for NH\(_3\) molecule. The value of \( E_d \) is an indication of the suitability of a structure to adsorb NH\(_3\): the further the negative \( E_d \), the more appropriate the structure for NH\(_3\) adsorption. The charge relocation among NH\(_3\) and a structure is another indicator of preference for its adsorption, and it was evaluated by the Mulliken method as [20, 23]:

\[
\Delta Q = q_f - q_0 \quad \ldots \ldots (4)
\]

Where \( q_f \) and \( q_0 \) denote the final and initial Mulliken charges of the gas, respectively. If electros were moved from NH\(_3\) to AGNR, \( \Delta Q \) will be negative.

3. Results and discussion

The effect on the adsorption capacity for ammonia gas of AGNR structures modified by ZrO\(_x\) is examined. The modification is established either by doping or decoration for AGNR structure. The detailed description of the different examined nanostructures is presented in Table 1. The table also reveals the band gap energy \( (E_g) \) of the different structures. The maximum value of \( E_g \) is for the pristine structure, while the modified structures exhibit lower values of \( E_g \). AGNR structures doped with ZrO and ZrO\(_2\) demonstrate the lowest \( E_g \) values. The optimized doped AGNR structures are presented in Figs. 1(a) - 1(d). The carbon atoms are rearranged as a result of energy optimization near the doping site. The edge atoms of AGNR structures are passivated.
using hydrogen atoms to avoid reconstruction of the structures as a result of satisfying dangling bonds for the edge atoms [39]. The modification cites of ZrO$_x$ are selected at the center of the structures to minimize edge effect, where many cites reveal similar results because of the high symmetry of nanoribbons. The C-C bond length of pristine AGNR is 1.42 – 1.43 Å. The doped structures exhibit the following bond lengths. i) Zr+AGNR structure: the Zr-C bond length is 1.89 – 1.90 Å. ii) ZrO+AGNR structure: the Zr-C bond length is 1.86 – 1.87 Å, the Zr-O bond length is 1.90 Å, and the O-C bond length is 1.42 – 1.44 Å. iii) ZrO$_2$+AGNR structure: the Zr-C bond length is 1.83 Å, the Zr-O bond length is 1.89 Å, and the O-C bond length is 1.42 – 1.44 Å. The bond lengths are as follows for the decorated structures. i) Zr on AGNR structure, the Zr-C bond length is 2.30 Å. ii) ZrO on AGNR structure, the Zr-C and Zr-O bond lengths are 2.41 – 2.44 Å and 1.78 Å, respectively. iii) ZrO$_2$ on AGNR structure, the Zr-C and Zr-O bond lengths are 2.75 – 2.95 Å and 1.82 Å, correspondingly. Doping an AGNR structure with ZrO$_x$ by substitution of carbon atoms produces a stress on the structure that results modifications of the bond lengths for C-Zr, Zr-O, and C-O to relief the stress [41]. The optimized decorated structures are presented in Figs. 2(a) – 2(c). Both Zr and ZrO are bonded to interstitial locations with the structures that minimize their overall energy. Nevertheless, ZrO$_2$ remains on top of the structure unbounded due to its high stability as compared with both Zr and ZrO [42].

The effect of AGNR structure modification on the band structure is presented in Figs. 3(b) – 3(d) for doped structures, and Figs. 4(b) – 4(d) for decorated structures. The band structure of the pristine AGNR is presented in Figs. 3(a) and 4(a). The figures demonstrate that all the band structures have a parabolic form near the Γ point. The evaluated density of states within the band structures within both valance and conduction bands increases as a result of modification (for
both modified structures, doped and decorated) as compared with the unmodified structure. The modification leads to the introduction of new bands near the Fermi level, and shift of the valance band close to the Fermi level in agreement with the results presented in Table 1.

Figures 1(e) – 1(h) reveal the doped AGNR structures post to adsorption of NH$_3$ gas. The figures illustrate that NH$_3$ molecule is unbonded to the pristine structure, however, it is bonded to all other ZrO$_x$ doped AGNR structures. Upon introduction of an NH$_3$ gas molecule to an AGNR structures, where the molecule orientation is set during the optimization stage to exhibit the minimum energy leading to the maximum stable configuration. The chemisorption of NH$_3$ gas on the ZrO$_x$ doped AGNR structures indicates that they are favorable for NH$_3$ adsorption unlike the pristine structure. The decorated AGNR structures post to adsorption of NH$_3$ gas are presented in Figs. 2(d) – 2(f). The figures reveal that NH$_3$ molecule is not chemisorbed on any decorated AGNR structure, i.e no bond can be observed between NH$_3$ gas and the structures.

The effect of ammonia adsorption on AGNR structures on the band structure is demonstrated in Figs. 3(a) and 4(a) for pristine structure, Figs. 3(e) – 3(h) for doped structures, and Figs. 4(e) – 4(h) for decorated structures. Further bands appear as a result of NH$_3$ gas adsorption and, in general, the band gap increases after adsorption as presented in Table 2. The modifications in the band structure post to NH$_3$ adsorption and the introduced bands are indicators of the generation of extra electronic states as a result of adsorption [32]. The developments appear within the band structure specify that the ZrO$_x$ modification of AGNR is an effective approach for adsorption of NH$_3$ molecule.

The effect of AGNR doping on band structure is examined using DOS as presented in Fig. 5(a). The figure illustrates that DOS decreases generally due to doping, and new bands appear within
both conduction and valance bands. For example, the following bands appear as a result of
doping at: 1.06, 3.52, -0.65, and -4.00 eV for the Zr doped AGNR; and 0.726, 3.48, and -1.43 eV
for the ZrO doped AGNR; and 0.726, 2.85, 3.33, -3.63, and -4.26 eV for the ZrO$_2$ doped AGNR.
Decoration of AGNR modifies the DOS as illustrated in Fig. 5(b). Although the intensity of DOS is
lower for the decorated structures as compared with the pristine structure, it is higher than the
equivalent for the case of doping. New bands appear within both conduction and valance bands
of decorated AGNR such as at: 0.67, 0.93, 1.37, 1.85, and -0.19 eV for the Zr doped AGNR; 0.36,
0.61, 1.96, and -0.24 eV for the ZrO doped AGNR; and 0.22, 1.69, and -1.52 eV for the ZrO$_2$ doped
AGNR. 
Figure 5 reveals that the DOS of both doped and decorated structures increases near the
Fermi level, in agreement with the results of Figs. 3 and 4. In addition, the conduction band
exhibits lower DOS than the valence band for all AGNR structures. Figure 6 shows the effect of
NH$_3$ adsorption on DOS for the different ZrO$_x$ modified AGNR sheets. The DOS preserves its
overall features prior to adsorption of NH$_3$ gas. The DOS near the Fermi level is higher for the
decorated structures as compared with the doped structures. Adsorption of NH$_3$ decreases the
intensity of DOS of many bands for the doped AGNR structures, such as at: 1.28, -1.34, -2.69, and
-4.42 eV. Nevertheless, lower decrease in the DOS is observed for the decorated AGNR
structures. The results of DOS designate that many electronic states are available within the
AGNR structures post to NH$_3$ adsorption [43]. Accordingly, the ZrO$_x$ modified AGNR structures
can be considered as effective systems for NH$_3$ gas adsorption.

The adsorption capacity for NH$_3$ of AGNR modified by ZrO$_x$ is explored using adsorption energy,
charge transferred to the NH$_3$ molecule, along with the adsorption length as shown in Table 2.
The table demonstrates that the modified AGNR structures have greater adsorption energies in
comparison with the unmodified AGNR, indicating that ZrO\textsubscript{x} modification of AGNR structures enhances their NH\textsubscript{3} adsorption. The adsorption energy of the doped structures is higher than its equivalent of the decorated structures. In fact, all doped structure are suitable for NH\textsubscript{3} adsorption. Herein, ammonia molecule bonds to the ZrO\textsubscript{x} dopant which is already bonded to AGNR structure. Nevertheless, the highest adsorption energy for NH\textsubscript{3} is for the ZrO\textsubscript{2}+AGNR doped structure, where it is 22.2 times greater than that of the unmodified AGNR structure. Furthermore, the adsorption length results are in agreement with those of the adsorption energy. Here, all doped structures exhibit low adsorption length of \textasciitilde2.4 Å indicating strong bonds among NH\textsubscript{3} and the structures. The adsorption length is higher for the decorated structures, in comparison with the doped structures, which is in agreement with the observation (Fig. 2), i.e. no chemisorption is established for those structures. The charge transferred from/to ammonia molecule for the doped structures is \textasciitilde-0.2e which is almost similar for the three structures, and it is higher than that of decorated structures (except that for the Zr decoration case). The negative sign indicates that the charge is transferred from NH\textsubscript{3} to AGNR structures. The considerable amount of transferred charge from NH\textsubscript{3} molecule to the doped structures specifies the formation of chemical bonds between them. The charge transfer observation indicates that adsorption of NH\textsubscript{3} molecule on doped AGNR structures modify their electronic features notably (in agreement with DOS in Fig. 6) to generate strong interactions among NH\textsubscript{3} and the AGNR structures resulting high energy of adsorption [44]. The charge transferred among NH\textsubscript{3} and the ZrO\textsubscript{x} modified AGNR structures are extracted within AGNR [12]. On the other hand, the low magnitude of charge transferred among NH\textsubscript{3} and the decorated AGNR structures is allocated to the fact that NH\textsubscript{3} is not chemisorbed on either of them.
The adsorption energy towards ammonia of the doped AGNR structure is boosted due to ZrO$_2$ modification, for instance, it is ~ 41 times greater than that presented for zigzag graphene nanoribbon modified with OH [20]. The illustrated results indicate that the ZrO$_x$ doped structures are more favorable for NH$_3$ adsorption than the decorated ones [45-47]. Accordingly, one can conclude that although the small differences in the adsorption energy for the doped structures, their values are close, signifying that doping AGNR with Zr metal and its oxides is a suitable approach for adsorption of NH$_3$. Additionally, if decoration is considered for AGNR adsorption of NH$_3$, the ZrO decorated structure is the suitable one due to its relatively high adsorption energy.

The improved NH$_3$ adsorption on doped AGNR structures can be allocated to the high affinity of ZrO$_x$ to the gas upon doping [48]. Here, the reaction of both Zr$^{1+}$ and Zr$^{2+}$ with nitrogen and oxygen atoms is favorable [49]. Doping AGNR structures with ZrO$_x$ improves their reactivity by supplying additional negative charges for the delocalized π bond due to the low electronegativity of ZrO$_x$ in comparison with carbon atoms [41]. The low ammonia adsorption energy of decorated AGNR structures in comparison with the doped ones may be allocated to the weak hybridization among their overlapped orbitals: 3p for nitrogen, and 3d and 4s for zirconium [50]. On the other hand, the 3p orbital of nitrogen, 3d orbital of zirconium, and 2p orbital of oxygen exhibit strong hybridization for the doping case [50]. The influence of zirconium and its oxides on enhancing ammonia adsorption is examined and presented experimentally [51]. This is assigned to trapping of electrons within the conduction band that generates electron depletion region. NH$_3$ molecule reacts with the adsorbed ions of oxygen, causing the release of the trapped electrons and narrowing the space charge [51]. The adsorption of NH$_3$ is enhanced by the transfer of charge due to the presence of oxygen ions on the AGNR surface which may be presented as [52]:
\[ 4NH_3 + 3O^{2-}_{\text{ads}} \rightarrow 2N_2 + 6H_2O + 6e^- \]

The equation reveals that NH\textsubscript{3} adsorption generates additional charges as demonstrated by the charge transferred (Table 2). In all doped structures, NH\textsubscript{3} is bonded to the Zr atom. The reaction of NH\textsubscript{3} with zirconium can be presented as below [53]:

\[ NH_3 + Zr \rightarrow ZrNH_3 \]

However, for decorated structures, the bond of Zr atom are established with carbon rather than the ammonia. The present value of adsorption energy for ZrO\textsubscript{2}+ZGNR structure towards NH\textsubscript{3} is compared with latest results for NH\textsubscript{3} adsorption of graphene based structures, as presented in Table 3. The table demonstrates the major improvement of the present work for ammonia adsorption due to ZrO\textsubscript{2} doping.

4. Conclusion

First principles computations of density functional theory (DFT) were employed to explore the effect of modification of nanoribbon with armchair-graphene structure (AGNR) by ZrO\textsubscript{x} (\(x = 0, 1, or 2\)) on its adsorption of ammonia (NH\textsubscript{3}) gas. The modification of AGNR structures was established either by doping (i.e. substitution of carbon atom(s)), and decoration on the surface. Ammonia adsorption was examined by thorough investigation of the adsorption energy (\(E_d\)), band structure, charge transferred (\(\Delta Q\)), adsorption length (\(D\)), as well as density of states (DOS). The findings reveal that NH\textsubscript{3} adsorption was greatly enhanced upon modification with ZrO\textsubscript{x}, nevertheless, decoration was less effective than doping. The highest adsorption energy of NH\textsubscript{3} was found for the structure doped by ZrO\textsubscript{2}, followed by that doped by Zr. The energy of adsorption for the AGNR structure doped with ZrO\textsubscript{2} for NH\textsubscript{3} gas was 22.2 times greater than that
of the undoped structure. Moreover, AGNR structures doped with Zr and ZrO have also exhibited high adsorption energy for NH₃. The results of this investigation demonstrate that doping of AGNR with ZrOₓ is a high potential approach towards production of sensitive NH₃ sensors.

Declarations

Ethical Approval
No human or animal parts were included in this study.

Competing interests
No financial or personal conflicts.

Authors' contributions
Ahmad I. Ayesh: Visualization, Investigation, Writing- Original draft preparation, Conceptualization, Methodology, Software, Supervision, Writing- Reviewing and Editing
Maitha D. Al-Muraikhi: Conceptualization, Writing- Reviewing and Editing

Funding
No funding received.

Availability of data and materials
The raw data required to reproduce these findings are available on request from the author.

References

[34] A.I. Ayesh, DFT investigation of H2S and SO2 adsorption on Zn modified MoSe2, Superlattices and Microstructures, 162 (2022) 107098.
Table captions

Table 1. AGNR structures and their descriptions alongside with the band gap energy ($E_g$) prior to NH$_3$ adsorption.

Table 2. Band gap energy, adsorption energy, ammonia adsorption length, and charge transferred among the gas and the structures post to adsorption of NH$_3$.

Table 3. Recent reported values for the adsorption energy of NH$_3$ on graphene based structures.

Figure captions

Figure 1. Optimized AGNR structures (top and side views) prior (a) – (d) and post (e) – (h) to NH$_3$ adsorption: (a) & (e) AGNR, (b) & (f) doped Zr+AGNR, (c) & (g) doped ZrO+AGNR, and (d) & (h) doped ZrO$_2$+AGNR.

Figure 2. Optimized AGNR structures (top and side views) prior (a) – (c) and post (d) – (f) to NH$_3$ adsorption: (a) & (d) decorated Zr on AGNR, (b) & (e) decorated ZrO on AGNR, and (c) & (f) decorated ZrO$_2$ on AGNR.

Figure 3. Band structures for the optimized AGNR structures prior (a) – (d) and post (e) – (h) to NH$_3$ adsorption: (a) & (e) AGNR, (b) & (f) doped Zr+AGNR, (c) & (g) doped ZrO+AGNR, and (d) & (h) doped ZrO$_2$+AGNR.

Figure 4. Band structures for the optimized AGNR structures prior (a) – (c) and post (d) – (f) to NH$_3$ adsorption: (a) & (d) decorated Zr on AGNR, (b) & (e) decorated ZrO on AGNR, and (c) & (f) decorated ZrO$_2$ on AGNR.

Figure 5. Electronic density of states of both (a) doped, and (b) decorated AGNR structures before adsorption of NH$_3$ gas.
Figure 6. Electronic density of states of both (a) doped, and (b) decorated AGNR structures after adsorption of NH$_3$ gas.
Table 1

<table>
<thead>
<tr>
<th>Structure</th>
<th>Description</th>
<th>$E_g$ (eV)</th>
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<tbody>
<tr>
<td>AGNR</td>
<td>Pristine AGNR structure</td>
<td>0.7122</td>
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<tr>
<td>Zr on AGNR</td>
<td>AGNR structure decorated with Zr</td>
<td>0.2516</td>
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<tr>
<td>ZrO on AGNR</td>
<td>AGNR structure decorated with ZrO</td>
<td>0.4404</td>
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<td>ZrO$_2$ on AGNR</td>
<td>AGNR structure decorated with ZrO$_2$</td>
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## Table 2

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<th>Structure</th>
<th>$E_s$ (eV)</th>
<th>$E_d$ (eV)</th>
<th>$D$ (Å)</th>
<th>$\Delta Q$ (e)</th>
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<tr>
<td>NH$_3$+AGNR</td>
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<tr>
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## Table 3

<table>
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<th>Structure</th>
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<td>ZrO$_2$+AGNR</td>
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<td>Co-AGNR</td>
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<td>Pt-AGNR</td>
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<td>N-AGNR</td>
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<td>[20]</td>
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<tr>
<td>Ce modified graphene</td>
<td>-0.8</td>
<td>[57]</td>
</tr>
</tbody>
</table>
Fig. 5

(a) and (b) show the density of states (DOS) per electron (DOS/eV) as a function of energy (eV) for different configurations:

- AGNR
- AGNR+Zr
- AGNR+ZrO
- AGNR+ZrO2
- Zr on AGNR
- ZrO on AGNR
- ZrO2 on AGNR

Energy levels range from -5.0 to 5.0 eV.