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A DFT calculation on the Hydrogen Adsorption of Copper-Passivated Armchair Graphene Nanoribbon.

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Abstract: Graphene is a two dimensional carbon material that has caught the attention of the scientific community because of its unique properties. Graphene has many novel properties such as having a zero bandgap, however, this property has limited its application in specific fields. Methods of doping graphene to tune its band gap are being studied to overcome its limitations. These methods include introducing an edge to the graphene which is normally periodic in two directions; this structure is called a graphene nanoribbon. The armchair graphene nanoribbon is a quasi-one-dimensional material that shares similar properties with graphene, but the presence of an edge parallel to the periodic direction strongly affects its properties. In order to observe the effects of edge doping to surface adsorption, DFT calculations were conducted where the armchair graphene nanoribbon was doped along the edges with hydrogen, and copper. H-atoms were then adsorbed on its surface. Calculations were carried out to solve for the binding energy to quantify the strength of adsorption of the H-atom to the surface of the nanoribbon. The results show that the copper doped system exhibited higher adsorption energies for each H-atom.

Key Words: Armchair-graphene-nanoribbon; surface adsorption; DFT

1. INTRODUCTION

Carbon-based 2D materials such as graphene have been useful in the field of energy storage (Hussain et al., 2019). Given its high conductivity, surface area per mass, and tensile strength, graphene has caught the attention of the scientific community for its potential applications. Armchair graphene nanoribbons (AGNR) are derived from graphene and share some of its properties, but the termination along one of graphene's periodic directions introduced new ways to dope it, this process is called passivation (Johnson et al., 2020).

It was shown that passivation affects the conductivity of the AGNR system. In the study conducted by Narin et al. in 2019, AGNR became conducting when passivated with Zinc, while it remained semiconducting when bonded to Cadmium, and Mercury. Needless to say, these systems exhibited different band structures and band gap energies. AGNR when passivated with copper remained semiconducting. The copper passivated system exhibited greater values near the fermi level in its electronic density of states, consequently, the quantum capacitance and surface charge values were also increased (Paz et al., 2023). These studies show that the passivating elements for the AGNR are crucial to the properties the system will exhibit. Different studies also show that doping or passivating the ribbon also affects the adsorption

energies of the system (Kumar & Singh, 2022; Salih & Ayesh, 2021). In this study, we will see how the termination of AGNR with Hydrogen, and Copper affects the adsorption energies of H atoms. An illustration of the passivated AGNR is shown in Figure 1,

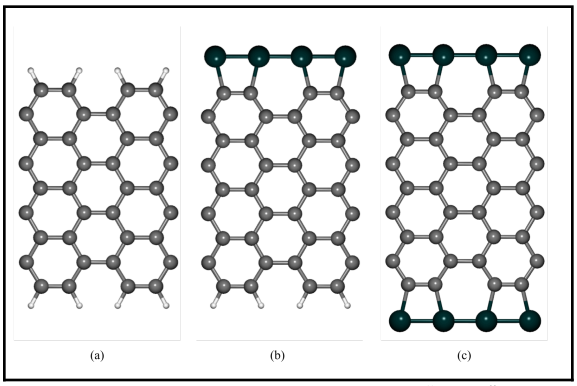

Fig. 1. Captions should be 9 pt. Century, "Tight" Text Wrapping

The surface adsorption will be quantified by the binding energy. By definition, the binding energy would be the energy required to bind an atom to a surface. A negative value for binding energy means that the surface would likely bond with the atom, while positive binding energy means that it would require external energy for the atom to be bonded to the surface. The magnitude of the binding energy would determine how strongly the aforementioned phenomena would be. The binding energy is given by the formula (Kumar & Singh, 2022; Narin et al., 2019; Paz et al., 2023; Salih & Ayesh, 2021).

$$E_b = E_{total} - E_{Cu/H-AGNR} - E_{H-atom} \quad \text{(Eq. 1)}$$

where:

E_b = Binding energy

E_{total} = Total energy of the copper or hydrogen passivated AGNR and the adsorbate

$E_{Cu/H-AGNR}$ = The energy of the isolated energy of the copper or hydrogen passivated AGNR

E_{H-atom} = The energy of the isolated H -Atom

2. METHODOLOGY

The atomic simulation environment (ASE) was used to manipulate atomic positions for geometric optimization and add the H-atoms on the surface of the AGNRs (Hjorth Larsen et al., 2017). Initial atomic position of the adsorbate H-atoms were identified using the adsorption site finder (ASF) function of PYMATGEN, its algorithm uses select sites on top of the atoms and creates a Delaunay triangulation to identify the rest of the adsorption sites, specifically hollow and bridge. (Ong et al., 2013). The PW-DFT calculator via Quantum Espresso was used in the code integrated within the ASE module (Giannozzi et al., 2020). LDA pseudopotential (PP) by Perdew and Wang was chosen for this study (Wang et al., 2011). Generally, the LDA-PZ PP exhibits good accuracy when calculating elastic moduli, and its overall efficiency when optimizing structures (Irifune & Tsuchiya, 2015). K-point sampling was selected to be 1x6x1, and the cut-off energy for the wave function was set to 25 Ry. The width of the nanoribbon was set to 9 carbon atoms.

The AGNR structure passivated with Hydrogen, and Copper was optimized to determine the vacuum size and the optimal periodic dimension cell size. The vacuum sizes for the two systems were determined to be 23.4 Å parallel to the surface, and 10.0 Å across perpendicular to the surface. The periodic cell dimension of the Hydrogen, and Copper passivated AGNR is 4.10 Å, and 4.21 Å, respectively. The passivated systems are shown on Figure 2. The carbon atoms are gray, the hydrogen atoms are white, and the copper atoms are orange. The ASE module was then used to add the H adsorbate on the surface using the coordinates identified by ASF, relaxed calculations were then performed. This was repeated for every adsorption site for the two systems.

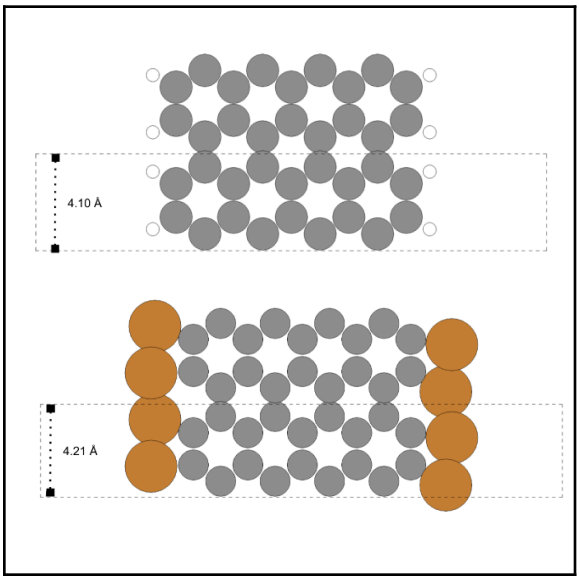

Fig. 2. H-Passivated (top), and Cu-passivated (bottom) AGNR after optimization, the box with dashed lines represents the unit cell.

3. RESULTS AND DISCUSSION

Figure 3 shows the binding energies in eV of the H-atom on the H-passivated AGNR. The colored dots represent different atoms. The gray atoms are carbon, the white atoms are hydrogen, and the atoms colored with a gradient are hydrogen adsorbates. For emphasis, only one hydrogen atom is adsorbed on the surface at a time. Figure 3 shows the highest binding energies are found on top of the edge carbon atoms. The H-adsorbates in the middle have varying values ranging from -0.4 eV to -0.8 eV. Figure 3 also presents the adsorption distance of the adsorbed H-atoms from the surface. The lowest binding energy also has a shorter distance from the surface of the ribbon. This is an expected outcome since the H-atom with the most negative binding energy should be closer to the surface.

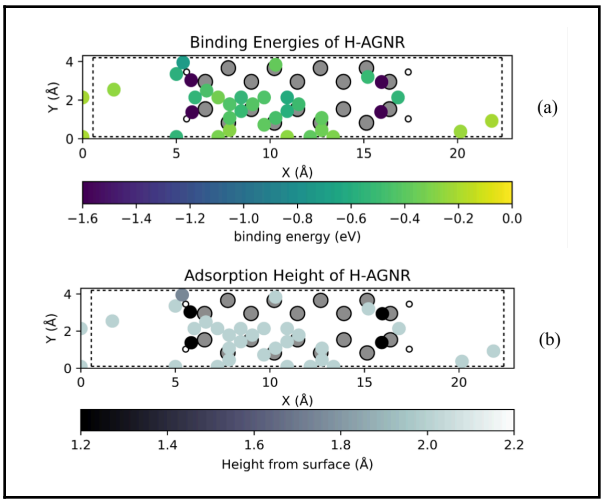

Fig. 3. Binding energies (a) and adsorption height (b) of the H-atom on H-passivated AGNR.

Figure 4 shows the binding energies of each H-atom on the surface of Cu-AGNR, where the bronze atoms are copper, and the rest is the same in Figure 3. When comparing Figures 3 and 4, one can see that more adsorption sites are identified for the Cu-AGNR system. This could be due to the copper atom having higher tendencies to bond with hydrogen atoms, and/or the increase in the Y cell dimension. Regardless, both effects are caused by the passivation of copper atoms. Based on the binding energies shown in Figure 4, the hydrogen atoms are more likely to bond well to the surface near the copper atoms. Although the binding energies of H-atoms situated at the center of the Cu-AGNR surface and H-AGNR surface have similar values, one can easily see that Figure 4 has a more structured pattern for the final position of each hydrogen atom. Whereas in Figure 3, the H atoms are clustered in the center and near the edge carbon atoms, Figure 4 shows that the H-atoms on the Cu-AGNR system are well distributed. Figure 4 also shows the adsorption height of every adsorbed H-atom from the Cu-AGNR surface.

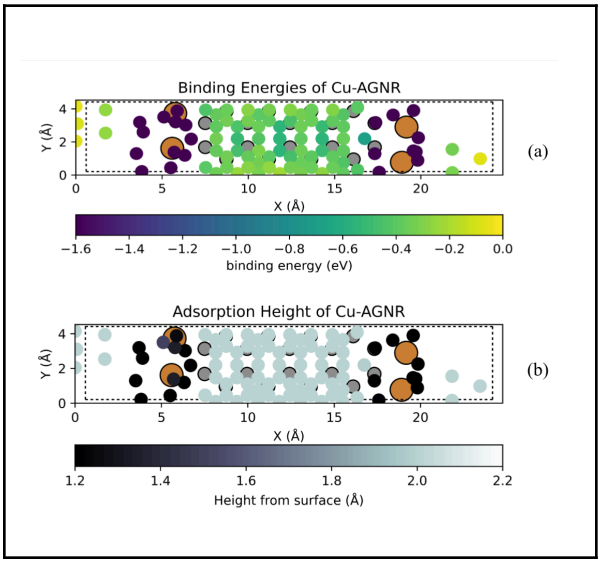

Fig. 4. Binding energies (a) and adsorption height (b) of the H-atom on Cu-passivated AGNR.

Similar to the H-AGNR system, the H-atoms with the lowest binding energy also have a closer distance to the surface.

4. CONCLUSIONS

This study aims to show the effects of passivation towards adsorption on the AGNR surface. This was accomplished by identifying the adsorption sites and their corresponding binding energies on the H-AGNR, and Cu-AGNR surfaces. More adsorption sites are identified in the Cu-AGNR system, and the highest binding energy values are located near the copper atom. However, the binding energy values at the center of the AGNR have no significant changes. This result could mean that the effects of passivation to surface adsorption are only evident along the edges, while the changes at the middle of the ribbon are insignificant.

5. ACKNOWLEDGMENTS

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