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Hydrogen Adsorption on Chemically Functionalized Carbon Nanostructures: *Ab Initio* Calculations on Graphene Nanoribbons

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We have performed *ab initio* density functional theory calculations, incorporating van der Waals corrections, to study the adsorption of hydrogen on zigzag graphene nanoribbons whose edges have been functionalized by OH, NH₂, COOH, NO₂, or H₂PO₃. We find that hydrogen always preferentially binds at the edge of the graphene sheet. The largest enhancement in adsorption, to 86.5 meV per molecule, is found for H₂PO₃; this may be compared with a binding energy of 52.4 meV per molecule on bare graphene. The binding appears to be mainly electrostatic in origin, with an induced dipole on the hydrogen molecule interacting with the dipole moment on the functionalized edge. Our results suggest that edge functionalization can increase the uptake of hydrogen on graphene. They also have relevance for the storage of hydrogen in activated carbon materials.

PACS numbers:

I. INTRODUCTION

For economic, environmental and geopolitical reasons, it has become clear that our reliance on fossil fuels must come to an end, and we have to search for alternative sources of energy. For on-board vehicular applications, hydrogen presents an attractive possibility as a fuel, being the most abundant element in the universe, and producing only water vapor when combusted or used in a fuel cell. Being the lightest element, it also has excellent gravimetric energy density. One of the main problems facing the use of hydrogen as a fuel in automobiles is finding a suitable way of storing it. Onboard storage as a compressed gas or liquid requires heavy, large, and cumbersome tanks under potentially cryogenic conditions, and raises safety concerns due to the highly explosive nature of gaseous hydrogen. One would therefore prefer to store hydrogen in the solid state. From a thermodynamic perspective, the ideal scenario would be to have a gas binding strength with the absorptive medium that is intermediate between physisorption and chemisorption. This ensures that a significant amount of hydrogen can be stored at ambient temperature and readily achievable pressures yet released without difficulty under operating conditions.

Carbon-based materials are one class of materials that have been considered for the adsorptive storage of hydrogen. Several micro- and mesoporous systems, including activated carbon, as well as recently synthesized carbon nanostructures such as fullerenes, carbon nanotubes and graphene, have high theoretical capacities due to their large surface area. However, molecular hydrogen binding is generally too weak to realize these capacities at reasonable temperatures. There have been a number of suggestions for increasing the binding strength, including doping with alkali or transition metals, as well as the imposition of mechanical strain or curvature. Nevertheless,

none of these approaches has proven completely successful when used alone, making it clear that a combination of multiple strategies will be required if carbon-based systems are to achieve room-temperature storage targets.

The creation of edges in sp^2 carbon-based materials, and the proper chemical functionalization of those edges, represents an additional possible path for increasing the molecular hydrogen binding strength in graphene derivatives. A number of theoretical and experimental studies have shown a strong dependence of the properties of graphene nanoribbons on the presence of edges.[1, 2] For instance, edges significantly increase the chemical reactivity of graphene,[3, 4] with zigzag edges exhibiting particularly high reactivity.[6] It has also been shown that some small chemical functional groups such as carboxyl [5] and hydroxyl,[6] as well as some large molecules such as peptides,[7] tend to bind preferentially to the edges of graphene sheets. The presence of these functional groups affects the stability and electronic and magnetic properties of the system.[8–11]

Functional groups at edges also represent a promising avenue for tuning the hydrogen uptake of activated carbons. These materials have a cost advantage among candidate hydrogen-storage media, being inexpensively produced from agricultural waste such as corn husks and coconut fibers via pyrolysis, followed by treatment with a base or acid. The precise structure of activated carbons is not known, but model structures generally consist of fragments of sp^2 bonded graphitic sheets separated by slit pores, with a large proportion of exposed edges.[12] Activated carbons feature functional groups such as phenolic (OH), amine (NH₂), phosphonic (H₂PO₃), peroxide (OOH), pyran (-O-), and carboxyl (COOH); it is believed that these groups occur predominantly at graphitic edges.[14]

Here, we show that creating functionalized edges in sp^2 carbon-based materials can lead to significant additional

increases in molecular hydrogen binding strength, in excess of 60% for certain functional groups. This suggests it could be useful in tandem with other approaches for improving the ambient-temperature hydrogen capacity of graphene derivatives. The relevance of this study can be viewed in two ways: it can be seen as applying directly to graphene itself. At the same time, it can be viewed as having implications for the use of activated carbons and related materials as hydrogen storage media. These results are an extension of recent work in our group examining methane and carbon dioxide adsorption on functionalized graphene edges, in which we found that the presence of OH-containing moieties increased gas binding with respect to a H-passivated edge.[15]

II. COMPUTATIONAL DETAILS

Our calculations were performed using spin-polarized *ab initio* density functional theory (DFT), employing the PWscf code, which is part of the Quantum-ESPRESSO distribution.[16] The code uses a plane-wave basis and periodic boundary conditions. The interaction between ionic cores and valence electrons was described by ultrasoft pseudopotentials.[21] The plane-wave cutoffs used for the wave-functions and charge densities were 40 Ry and 480 Ry, respectively. Exchange-correlation interactions were treated within a generalized gradient approximation of the Perdew-Burke-Ernzerhof (PBE) form.[20] Calculations for adsorption on the extended graphene sheet were performed using a (4×4) unit cell and a Brillouin zone sampling of $(3 \times 3 \times 1)$ k-points in a Monkhorst-Pack grid. Calculations of adsorption on zigzag graphene nanoribbons were performed using a ribbon that was six carbon atoms wide, with a unit cell that was eight carbon atoms long (see Fig. 1); for these calculations, a $(3 \times 4 \times 1)$ k-point grid was used. Marzari-Vanderbilt cold smearing [22] with a width of 0.007 Ry was used for improving convergence. We note that our system sizes and calculation parameters generally match those used in a previous study on the adsorption of methane and carbon dioxide on edge-functionalized ZGNRs.[15]

It is expected that van der Waals interactions will play an important role in the binding of hydrogen to the systems we study here, and thus one should use one of the methods that have been developed in recent years to include dispersive interactions in DFT calculations.[17–19] We have chosen to use the “DFT-D2” treatment of Grimme, which gives a fairly accurate treatment of van der Waals interactions at relatively low computational cost.[17]

In the calculations involving edge-functionalized ZGNRs, one functional group is adsorbed on one of the zigzag edges of the unit cell considered (see Fig. 1, where OH adsorption is depicted as an example). This system is first relaxed, and the total energy of the system, E_{FZGNR} is computed. Next, a hydrogen molecule is adsorbed on this functionalized ZGNR system, the geometry is again

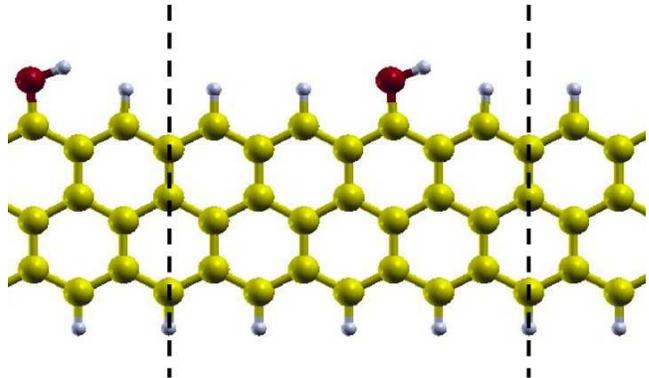


FIG. 1: The functionalized ZGNR used in the calculations. As an example, the optimized geometry for OH functionalization is shown. The black dashed lines demarcate the boundaries of the unit cell. Large yellow spheres are C atoms, small gray spheres are H atoms, and the large crimson spheres are O atoms.

optimized, and the total energy of the combined system, $E_{\text{FZGNR}+\text{H}_2}$ is computed. The force tolerance for geometry optimization is 10^{-3} Ry/bohr.

The adsorption energy is defined as:

$$E_{\text{ads}} = -(E_{\text{FZGNR}+\text{H}_2} - E_{\text{H}_2} - E_{\text{FZGNR}}), \quad (1)$$

where E_{H_2} is the energy of an isolated hydrogen molecule in the gas phase.

III. RESULTS

For adsorption of hydrogen on a bare graphene sheet, we find that the hydrogen molecule binds with an adsorption energy E_{ads} of 52.4 meV. (Of course, in computing this, the first and third terms on the right-hand-side of Eq. 1 are replaced by the corresponding values for an extended graphene sheet). This value is based on H_2 adsorption at a hollow site, with its molecular axis oriented perpendicular (\perp) to the plane of the graphene sheet; the bottom of the H_2 molecule sits at a distance of 2.5 Å above the graphene sheet. Adsorption in the parallel (\parallel) geometry is slightly less favorable, with a binding strength of 49.7 meV, and a molecule-graphene basal plane distance of 2.84 Å. Our values are in good agreement with experimental values of 43 meV and 2.87 Å for H_2 adsorption on graphite.[23] Many of the previous theoretical investigations on this system did not incorporate van der Waals interactions, rendering a comparison of our results with theirs problematic. In one case where the authors did include van der Waals interactions, they obtained a value for E_{ads} on graphene of 59.8 meV, and a separation of 2.92 Å, in the \parallel geometry.[24]

Next, we considered adsorption with five functional groups: OH, NH₂, COOH, NO₂, and H₂PO₃. We note that the first two groups are considered to be electron-donating groups, while the latter three are considered to be electron-withdrawing groups. The dangling bonds at the ribbon edges were all passivated with H atoms.

For adsorption at or near the edges of the ZGNRs, in order to span the space of possible geometries, we started with six kinds of initial geometries. Four of these had the hydrogen molecule placed outside the ribbon, these are referred to as “outer edge” configurations. These are further divided into “out of plane” (OP) and “in plane” (IP) configurations. In the IP configurations, the center of mass of the hydrogen molecule lies initially in the plane of the graphene nanoribbon, whereas in the OP configurations, it lies above this plane. Finally, each of these configurations can further be divided into either a “parallel” (||) or “perpendicular” (⊥) geometry, depending on whether the H₂ molecular axis is parallel or perpendicular, respectively, to the edge of the ZGNR. For adsorption on the inner edge of the ribbon, where the H₂ molecule is positioned above the ZGNR, but near the functional group, one can have OP || and ⊥ geometries. Thus, there are six possible initial geometries: (a) outer, OP, ⊥, (b) outer, OP, ||, (c) outer, IP, ⊥, (d) outer, IP, ||, (e) inner, OP, ⊥, and (f) inner, OP, ||. Moreover, for inner adsorption, the H₂ molecule was tested at both the hollow site or the atop site of the graphene nanoribbon.

Our results for the adsorption energies and equilibrium distances for the major classes of geometries are tabulated in Table 1 for the H-passivated ZGNR and the five functionalized ZGNRs. For conciseness, we do not list the results for all initial geometries and sites considered by us, but instead list only the highest-adsorption configurations for outer-edge adsorption (both IP and OP) and inner-edge adsorption (both || and ⊥). In each case, the identity of the corresponding site and/or geometry is also indicated. The boxed numbers correspond to the highest adsorption geometry among all configurations considered for that particular functional group.

An examination of our results produces the following findings: first, binding near the edge is always favored over binding in the center of the graphene sheet. For the case of the H-passivated edge, and the ZGNRs functionalized with NH₂ and NO₂, binding on the inner edge (where the hydrogen molecule can interact with both the π manifold of the graphene sheet and the atoms of the functional group) is stronger than binding to the outer edge or to an extended graphene sheet. In contrast, for the OH, COOH and H₂PO₃ cases, the most favored geometry is the outer edge one; the binding in this case is again stronger than to an extended graphene sheet or to the H-passivated edge. Note that this is quite different from what was observed in earlier calculations on the adsorption of CH₄ and CO₂ on these systems,[15] where edge functionalization increased the binding with respect to an H-passivated edge but not relative to an extended graphene sheet. This is very interesting, since it suggests

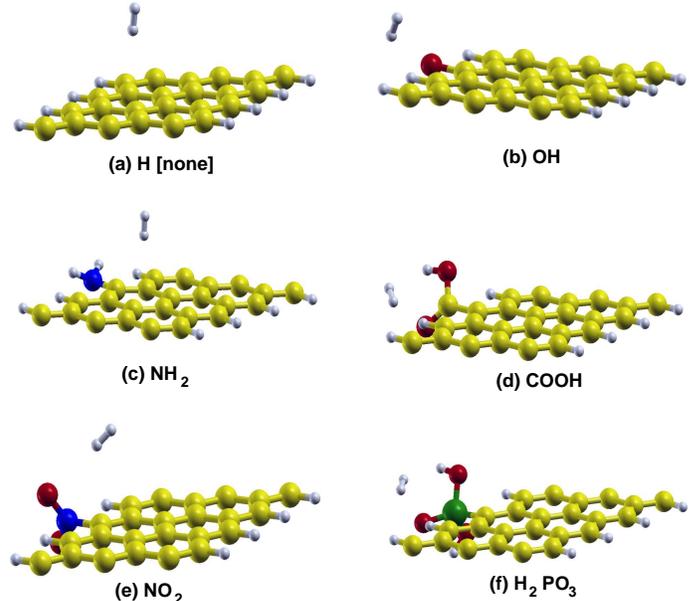


FIG. 2: Relaxed geometries for the most favored configuration of H₂ on (a) an unfunctionalized ZGNR; and on ZGNRs functionalized with (b) OH, (c) NH₂, (d) COOH, (e) NO₂, (f) H₂PO₃. Color scheme for atomic spheres: H (gray), C (yellow), O (crimson), N (blue), P (green)

that the presence of edges, and especially functionalized edges, will increase the binding of hydrogen.

In Fig. 2, we show the final relaxed configurations for the most favored geometry (corresponding to the boxed numbers in Table 1) for each functional group. From an examination of this figure, as well as Table 1, we see that there is no clear trend in the adsorption geometries, with all types of geometries, IP and OP, || and ⊥, being favored in various cases. However, outer edge adsorption is favored over inner edge adsorption, for the three functional groups containing the highly polar OH group. This suggests that there is an electrostatic interaction between the hydrogen molecule and the permanent dipole moment of the functionalized substrate. The highest enhancement is found for the COOH and H₂PO₃ groups, which have both the OH groups and a lone pair present. As has been pointed out earlier,[15] there is a charge transfer from the lone pairs of the doubly bonded O atom to the O-H bond of another O atom, resulting in a greater electrostatic interaction between the adsorbing molecule and the functionalized substrate.

The dipole moment on the functionalized substrate induces a redistribution of charge in the hydrogen molecule, inducing a dipole moment in the adsorbed molecule. The electrostatic interaction between the molecule and the substrate is then primarily responsible for the weak binding between the two. This can be clearly seen in Fig. 3, where, as an example, for the case of functionalization by H₂PO₃, we have plotted the redistribution of electronic charge upon adsorption. In other words, we have sub-

TABLE I: Final relaxed geometries and adsorption energies E_{ads} , for H_2 adsorbed on a graphene sheet, and bare and functionalized ZGNRs. The final orientation and position of the H_2 molecule is mentioned along with the adsorption energies (see text for description of acronyms). For outer edge adsorption, d_{min} is the distance from a H atom in the the H_2 molecule to the nearest functional group atom, whose identity is give in parentheses. For inner adsorption, the position of the H_2 molecule is given as hollow (h) or atop (a) site. d_z is the distance of the nearest H atom of the H_2 molecule to the ribbon basal plane. d_c is the distance of the nearest H atom of the H_2 molecule to the atop carbon atom of the ribbon. The adsorption energies E_{ads} are in meV and the distances in Å. The highest adsorption energies for each functional group have been boxed.

Group	Outer edge adsorption				Inner adsorption			
	OP		IP		\perp		\parallel	
Graphene	-	-	-	-	$E_{\text{ads}}(\text{h})$	52.4	$E_{\text{ads}}(\text{h})$	49.7
Sheet	-	-	-	-	d_z	2.50	d_z	2.84
Bare(H)	$E_{\text{ads}}(\perp)$	34.7	$E_{\text{ads}}(\parallel)$	19.4	$E_{\text{ads}}(\text{h})$	55.1	$E_{\text{ads}}(\text{h})$	49.1
	$d_{\text{min}}(\text{H})$	2.53	$d_{\text{min}}(\text{H})$	2.60	d_z	2.59	d_z	2.88
OH	$E_{\text{ads}}(\perp)$	60.8	$E_{\text{ads}}(\parallel)$	46.7	$E_{\text{ads}}(\text{h})$	57.1	$E_{\text{ads}}(\text{h})$	53.2
	$d_{\text{min}}(\text{H})$	2.14	$d_{\text{min}}(\text{H})$	2.57	d_z	2.56	d_z	2.86
NO_2	$E_{\text{ads}}(\perp)$	38.9	$E_{\text{ads}}(\perp)$	37.7	$E_{\text{ads}}(\text{a})$	63.2	$E_{\text{ads}}(\text{a})$	58.0
	$d_{\text{min}}(\text{N})$	3.22	$d_{\text{min}}(\text{N})$	3.22	d_c	2.86	d_c	2.92
NH_2	$E_{\text{ads}}(\perp)$	54.9	$E_{\text{ads}}(\parallel)$	45.8	$E_{\text{ads}}(\text{h})$	65.6	$E_{\text{ads}}(\text{h})$	58.7
	$d_{\text{min}}(\text{H})$	2.25	$d_{\text{min}}(\text{N})$	2.66	d_z	2.93	d_z	2.88
COOH	$E_{\text{ads}}(\perp)$	73.9	$E_{\text{ads}}(\parallel)$	76.1	$E_{\text{ads}}(\text{h})$	61.3	$E_{\text{ads}}(\text{h})$	58.3
	$d_{\text{min}}(\text{C})$	3.12	$d_{\text{min}}(\text{C})$	3.67	d_z	2.66	d_z	2.98
H_2PO_3	$E_{\text{ads}}(\perp)$	86.5	$E_{\text{ads}}(\perp)$	80.9	$E_{\text{ads}}(\text{h})$	57.0	$E_{\text{ads}}(\text{h})$	56.6
	$d_{\text{min}}(\text{P})$	3.10	$d_{\text{min}}(\text{P})$	3.01	d_z	2.55	d_z	2.86

tracted from the electronic charge density of the combined system, the separate electronic densities of the functionalized substrate and the hydrogen molecule in isolation:

$$\Delta\rho = \rho(\text{FZGNR} + \text{H}_2) - \rho(\text{FZGNR}) - \rho(\text{H}_2), \quad (2)$$

where the last two terms are evaluated at geometries corresponding to those in the combined system. This is the quantity plotted in Fig. 3, where red and blue lobes correspond to an accumulation and depletion of electronic charge, respectively. We see that while there is little change in the electronic distribution in the functionalized substrate, there is clearly a dipole moment induced in the hydrogen molecule, with one of the H atoms gaining electrons from the other.

In Fig. 4, we compare our results, for binding of hydrogen, with previous results on binding of methane.[15] We note that the results on methane binding, though they also incorporated van der Waals interactions, did so in a different way than has been done in the present study, viz., using the so-called vdW-DF formalism.[18] In all cases, the results for the most favored adsorption geometry for a given functional group have been plotted. We see that while, as expected, the binding of hydrogen is smaller than the binding of methane, by approximately a factor of two, the trends across functional groups are fairly similar, with the greatest binding being obtained

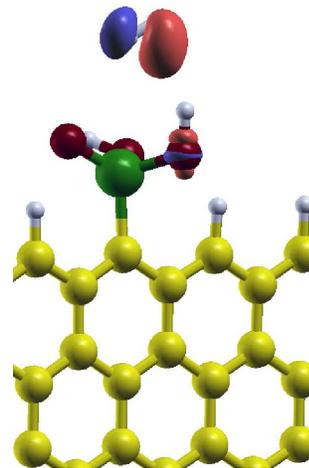


FIG. 3: Redistribution of electronic charge upon adsorption of hydrogen, on the ZGNR functionalized with H_2PO_3 . Red and blue lobes correspond to a gain and depletion of electronic charge, respectively. The isosurface corresponding to 0.001 electrons/bohr³ is plotted. Color scheme online for atomic spheres: H (gray), C (yellow), O (maroon), P (green)

for H_2PO_3 in both cases. We believe that this is because the origin of the binding is the same in both cases, being a weak electrostatic interaction which has its origin

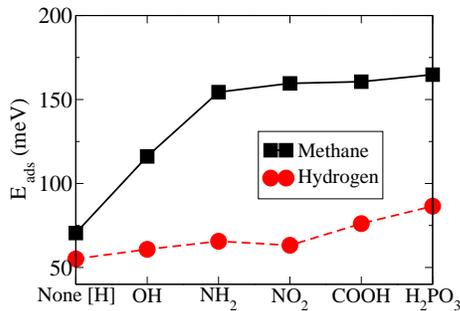


FIG. 4: Adsorption energy of hydrogen and methane on ZGNRs functionalized with various groups. The values for methane are taken from Ref. 15. The red dots are for hydrogen adsorption, and the black squares are for methane. In all cases, the values corresponding to the geometry that yields the highest E_{ads} are plotted. One sees that the trends are similar for both gases.

in the permanent dipole moment of the functionalized substrate.

IV. CONCLUSIONS

In this study, we have used density functional theory calculations, with van der Waals corrections incorporated within the semi-empirical DFT-D2 treatment, to study the binding of hydrogen to edge-functionalized zigzag graphene nanoribbons. Our most notable finding

is that hydrogen molecules always prefer to bind to the edge of the nanoribbons rather than to the clean infinite graphene sheet, and that the strength of the binding can be increased by functionalizing the edge by various groups. Of the groups considered by us, H_2PO_3 leads to the greatest enhancement in binding. Though the trends in binding across various functional groups are similar to those we previously found for methane and carbon dioxide,[15] there is the notable difference in the case of hydrogen that binding to the edge is favored over binding to the clean graphene sheet, whereas the reverse was true for methane and carbon dioxide. The maximum enhancement in binding we obtain is 65%, leading to an adsorption energy of 86.5 eV/molecule. However, while this enhancement in binding at the edge can be used to tailor graphene and/or activated carbon materials so as to increase the uptake of hydrogen, this value of adsorption energy should ideally be almost doubled before it reaches the optimum value[25] for on-board vehicular applications. Nevertheless, we suggest that edge functionalization could be useful when used in tandem with other strategies in order to achieve the required room-temperature storage capacity.

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