DFT Investigation of the Hydrogen Adsorption on Graphene and Graphene Sheet Doped with Osmium and Tungsten

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KAUST Research Conference:
Hydrogen-Based Mobility and Power

Introduction

To make a promising solution for hydrogen storage materials, carbon materials are considered [1-3]. Graphene is one of the most important carbon materials was successfully made and demonstrated to be stable via structuring the carbon atoms by sp^2-bonding [4, 5]. Moreover, graphene sheets (GSs) attracted extensive interest from the researchers due to their low cost, lighter weight, special nano-surface structures, electrical properties, and wide industrial applications, gas storage as an example [2, 6, 7]. Hydrogen gas was more preferred due to its sustainability and low mass density for that the U.S. Department of Energy (DOE) has set a target value of 9wt.% hydrogen storage by 2015, which is far from today's possibly approaching value 6.5wt.% by 2020 [7, 8]. However, two main problems are found in the graphene as hydrogen gas storage that blocks the ability to apply it, and they are: (1) the low efficiency of pure graphene in the storage process, and (2) the weakness of the intermolecular interaction that affects the storage. Many studies show that doping a transition metal on the GS would significantly enhance the hydrogen storage binding energies with respect to the pure graphene sheet [1, 6]. What we are aiming to pursue in this work is to investigate another way of metal-doping graphene to improve the adsorption of the hydrogen. We nominated Osmium (Os) metal in order to be doped with graphene. Since, previous studies show that Os has the highest binding ability to GS [6], in which the Os metal was placed above the GS bonded to two carbon atoms. In this work, different configuration has been adopted, in which one of the carbon atoms was replaced by an Os atom. In addition, in another configuration, a Tungsten (W) atom was used in a similar way. For the best of the present author knowledge the two adopted configurations with the two metals has not been reported yet. We hope that this research could add a value point and a promising information in the field. The GS doped with TMs are abbreviated as Os-GS and W-GS, while the adsorbed systems of H_2 molecule on the GS and doped GS are abbreviated as H_2@GS, H_2@Os-GS, and H_2@W-GS. Our results show enhancement in the adsorption energies of systems of H2@Os-GS, and H2@W-GS H2 in comparison to undoped GS (H_2@GS).

Methodology

In order to obtain the optimized geometries, binding energies, and HOMO-LUMO orbitals of the adsorbed systems, the density functional theory (DFT) method was performed using Becke 3-Parameter (Exchange), Lee, Yang and Parr (B3LYP), functional with a the 6-31G(d) basis set a split-valence double zeta basis set enlarged with one polarized basis function; a d-type orbital was added to all atoms except the hydrogen atoms, and the Los Alamos National Laboratory 2– Double–Zeta (LanL2DZ) basis set for transition metals [6, 9, 10]. All calculations were carried out using Gaussian 09 [11] software package in conjunction with GaussView version 5.0 [12].

The adsorption energies (**Δ**E*ads*) of the hydrogen molecule adsorbed on the pure GS and TM-doped Gs can be obtained from equation (1) and (2), respectively.

$$\Delta E_{ads} = E_{H2@GS} - (E_{GS} + E_{H2}) \quad \text{Eq. 2.1}$$

$$\Delta E_{ads} = E_{H2@TM-G} - (E_{TM-G} + E_{H2}) \quad \text{Eq.2.2}$$

Where $E_{H2@GS}$ and $E_{H2@TM-GS}$ are total energies of the adsorption of hydrogen molecule on TM-doped to GS, respectively. E_{GS} and E_{TM-GS} are total energies of the GS and TM-doped to GS, respectively, and E_{H2} is the total energies of the isolated hydrogen molecule.

Summary

Significant interest has been focused on graphene materials for their unique properties as Hydrogen storage materials. The development of their abilities by modifying their configuration with doped or decorated transition metals was also of great interest. In this work using the DFT/B3LYP/6-31G/LanL2DZ level of theory, graphene sheet (GS) as one of the materials of interest was doped with two transition metals, Osmium (Os) and Tungsten (W). Two active sites on the GS were tested (C4 and C16) resulted into adsorbed systems, H2@C4-GS and H2@C16-GS. C16 position showed the largest adsorption energy compared to that at C4. Therefore, C4 was replaced by the two metals and two adsorbed systems were formed, H_2@Os-GS and H2@W-GS. The binding energy of H_2@Os-GS was found to be greater than that of H2@W-GS.

Results

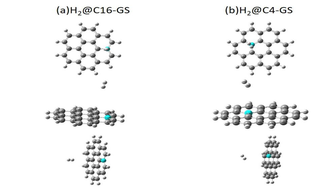

Figure.1: Hydrogen molecule attached to the graphene sheet (a) at C16 site, and (b) at C4 site.

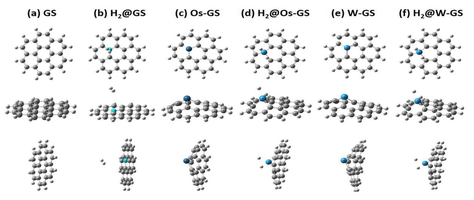

Figure.2: The optimized structures of (a) pure GS, (b) H_2@GS, (c) Os-GS, (d) H_2@Os-GS, (e) W-GS and (f) H_2@W-GS.

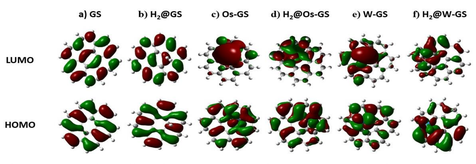

Figure.3: Visualized HOMO and LUMO orbitals of the pure GS and hydrogen molecule adsorbed on GS and Os–doped and W-doped as calculated at the B3LYP/6-31G(d)/ LanL2DZ level of theory.

	H_2@GS	H_2	GS	E_{ads}
H_2@C16-GS	-923.073	-1.175	-921.898	-0.0300
H_2@C4-GS	-923.073	-1.175	-921.898	-0.0306

Table.1: Adsorption energies (in kcal/mol) and their components (in Hartree) of hydrogen molecule adsorped at the two positions (C4 and C16) of graphene sheet.

System	Bond lengths		Bond angles		H–H distance	Binding distance
H_2@GS	C4-C2	1.421	C11-C4-C7	119.994		
	C7-C4	1.427	C4-C7-C14	120.005	H35-H37	H37-C4
	C4-C11	1.427	C2-C4-C7	120.009		
	C7-C14	1.427	C4-C11-C12	120.001	0.742	4.141
	C7-C6	1.421	C4-C2-C1	118.780		
H_2@Os-GS	Os-C13	1.930	C13-Os-C6	92.764		
	Os-C6	1.917	Os-C4-C2	120.146	H38-H37	H37-Os
	Os-C4	1.946	C4-Os-C13	90.476		
	C13-C15	1.426	Os-C13-C15	118.752	0.827	1.945
	C4-C10	1.432	C4-Os-C6	93.621		
H_2@W-GS	W-C13	1.937	C13- W-C6	99.009		
	W-C6	1.928	W-C4-C2	118.416	H36-H37	H36-W
	W-C4	2.122	C4- W-C13	81.525		
	C13-C15	1.425	W-C13-C15	102.114	2.016	1.781
	C4-C10	1.434	C4-W-C6	86.539		

Table.2: Selected geometrical parameters, H-H distance, and binding distance of H_2 adsorbed on pure GS, Os-doped and W-doped at GS with H–H distances of isolated hydrogen, calculated at B3LYP/6-31G(d)/LanL2DZ.

	adsorbed system	H_2	GS/W-GS/Os-GS	ΔE_{ads}
H_2@GS	-923.073	-1.175	-921.898	-0.030
H_2@Os-GS	-975.870	-1.175	-974.681	-8.369
H_2@W-GS	-952.611	-1.175	-951.379	-1.537

Table.3: Adsorption energies and their components (in kcal/mol) of H_2 molecule adsorbed on pure GS and TM–doped.

The B3LYP/6-31G(d)/LanL2DZ method/basis sets calculations were performed to obtain the geometrical parameters and adsorption energies of the adsorbed systems of bare GS and doped-GS (with Os and W) with molecular hydrogen. The results show that the adsorption energies of the doped systems are larger than that of the undoped system. In addition, the Os-doped system has the higher adsorption energy by 8.339 kcal/mol with respect to that of bare GS system, and by 6.832 kcal/mol with respect to that of W-GS system. Therefore, the GS doped with Os and W, specifically the Os, can be used as promising materials for hydrogen storage. Moreover, previous experimental studies performed electronic transport studies of graphene with a dilute coating of osmium adatoms, due to the potential for inducing a strong spin-orbit coupling, and the experimental results show that osmium is found to donate holes to graphene, otherwise, the graphene transport is impacted in similar fashion to other metallic anatomy, in that the scattering appears consistent with isolated coulomb impurities a small distance above the surface [13]. That could motivate us to plan for further studies on Os-GS at new position and compare it with other transition metals to explore the H2 adsorption possibility.