Hydrogen molecule adsorption on a Ti-doped graphene+ semi-fullerene surface.

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Abstract. Density functional theory (DFT) was used to study the adsorption of a hydrogen molecule in the system formed by a graphene layer and a Ti doped semi-fullerene. We found that the semi-fullerene is bound to the graphene layer, with one of the hexagonal faces of the former being oriented into the latter, the adsorption energy is -14.97 eV. Afterwards, we found that the Ti atom is chemisorbed into the semi-fullerene, with an energy of -8.4 eV. Finally, we studied the interaction between the hydrogen molecule and the combined system, finding that the H2 is adsorbed by the system with an adsorption energy of -1.41 eV.

1. Introduction
The hydrogen storage describes one of the challenges in developing a clean-burning economy. It is not surprising that much effort has been focused on optimizing the hydrogen storage technologies. This gas is considered as one of the most promising energy sources in the future, due to its abundance, easy synthesis, and non-polluting nature. It is the optimal candidate as the energy carrier in an economy based on renewable resources. One possible way for hydrogen storage is an efficient and controllable adsorption/desorption system. Carbon nanostructures based materials appear promising for such a purpose, since they provide convenient materials for gas storage. This is because these nanostructures have high surface areas, and thermal stability along with unique mechanical properties. Furthermore, it is possible to improve their adsorption capacity by suitable modification. These properties are worthwhile analyzing in the case of the hydrogen storage [1-6].

We explore a possible novel system that could have application as a molecular hydrogen storage material. The carbon nanostructures, like graphene and fullerene are used as the principal elements of the mentioned novel system. Therefore, we expect that this hybrid material combining the unique characteristics of graphene and fullerene lead to an investigation of some novel many potential applications, including as a possible hydrogen storage material, solar cells or optical limiting devices [6-9].

In this work, the adsorption of H2 molecule in Ti doped graphene-semifullerene system was studied by DFT calculation. The semifullerene C30 (figure 1a), one-half of a C60 fullerene, was described in detail in [8]. The (5,6) and (6,6) bond lengths 1.425 Å and 1.360 Å are around 2.2% smaller than the experimental data. Moreover, we taked graphene layer containing six vacancies as shown in figure 1b, may create leading to formation of various sites in graphene which are susceptible to binding with semifullerene [10].
2. Computational methods

Self-consistent field calculations were used in the study based on the density functional theory (DFT) [11], using the pseudopotential formalism. The Quantum Espresso code was used [13]. This package considers a plane-wave expansion for the electronic wave functions, and periodic boundary conditions. Some computer details are previously given in reference [8]: We used Martin-Troulliers norm conserving pseudopotentials [14] for C and O atom and for Ti atom a Vanderbilt pseudopotential type was selected [15]. The exchange and correlation functional PBE-GGA, Perdew-Burke-Ernzerhof general gradient approximation was used [16]. The following valence electronic states were considered: Ti, \(4s^2\ 3d^2\); C, \(2s^2\ 2p^2\) and H, \(1s^1\).

The Monkhorst-Pack [17] scheme for k-point sampling was used for integration over the first Brillouin zone. The Kohn-Sham energy functional was directly minimized using the conjugate gradient method [14]. A 4x4x1 grid for k-point sampling and a cut-off energy for the plane-wave set used was 80 Ry (≈1100 eV) and the convergence threshold for the energy was \(1.2 \times 10^{-5}\) eV in the calculations. Previous calculations [8], give us confidence that non-relativistic calculations without polarized spin is enough to obtain reliable results for this type of carbon-based materials. We used for crystal structure visualization the XCrySDen package [18].

The lattice parameter values \(a = 2.863\ \text{Å}\) and \(c = 4.544\ \text{Å}\), obtained with the selected Ti pseudopotential, are around 3% smaller than the experimental values. In the same manner, for hydrogen, we optimized the \(H_2\) molecule, obtaining for the H-H length 0.7526 Å, with an angle between atoms of 179.99°. The experimental values are 0.7414 Å and 180°, respectively. The adsorption energies reported here are calculated using the equation

\[
E_b = E_{\text{system1 + system2}} - E_{\text{system1}} - E_{\text{system2}}
\]

3. Results and discussion

3.1 Adsorption of the semifullerene \(C_{30}\) on a graphene sheet

We studied the interaction of the semifullerene and the graphene sheet. We found that the semifullerene is strongly adsorbed on a graphene sheet, by one of its hexagonal faces as shown in Fig.2, with an adsorption energy of \(E_b = -14.97\) eV. We obtain a bonded highly asymmetric system. Four strong C-C bonds are formed with a bond distance \(d = 1.61\ \text{Å}\), for one pair and the other pair with a bond distance of \(d = 1.53\ \text{Å}\), that suggests stronger bonds between the carbons than in the
interaction of pristine graphene with a fullerene. Therefore, this system is very stable. However, a semifullerene bonding creates in some cases a system with a stronger set of C–C bonds than in the case of graphene without defects [4, 10].

Figure 2. a) Initial configuration of semifullerene C_{30} on a graphene sheet. b) Final configuration of semifullerene C_{30} on a graphene sheet.

3.2 Adsorption of a Ti atom on the system formed by graphene + semifullerene (C_{30})
We made the Ti atom interact with the surface formed by a graphene sheet and the semifullerene C_{30}. The distance from the Ti atom to the adsorbed semifullerene, in the initial configuration is 4 Å (see Fig 3a). We obtained that the Ti is chemisorbed onto the semifullerene (figure 3b) with an adsorption energy of -8.4 eV. We observe that the Ti atom bonds with five of the fullerene atoms, with an average bond distance of d_{C-Ti} = 2.1 Å. When we compare this adsorption energy with those obtained for the titanium atom interacting with the fullerene (E_b = - 6.76 eV) [8], and for the titanium atom interacting with graphene (E_b = -1.51 eV) [9], we can conclude that our system is the most energetically favorable one for the adsorption of Ti.

Figure 3. a) Initial configuration during the interaction between the Ti atom and the surface. b) Final configuration during the interaction between the Ti atom and the surface. The Ti atom bonds with five of the fullerene atoms.

3.3 Adsorption of a H_2 molecule on the system
Finally, we studied the interaction of the hydrogen molecule and the proposed system. We found that the hydrogen molecule is adsorbed with an energy -1.41 eV, with no dissociation, as shown in Figure 4. The bond distance H-H is d_{H-H} = 0.781 Å.
Figure 4. Structural relaxation of the hydrogen molecule with the Ti-doped graphene+ semifullerene surface. The final configuration shows no dissociation of the hydrogen molecule.

The adsorption of H$_2$ in the Ti doped graphene is stronger than in other systems ($E_b=-0.427$ eV) [7]. We observed that the hydrogen molecule approaches on a location that is adjacent to the titanium atom, with a distance $d_{H-Ti}=2.08$ Å as shown in figure 5.
4. Conclusions
We performed numerical simulations of the adsorption of the hydrogen molecule on the Ti doped graphene–semifullerene system using the density functional theory (DFT). It was found that the adsorption of H₂ occurs around the Ti atom which is bound to the semifullerene. These simulations attempt to provide model predictions for related experimental systems, which consider the use of metal-doped carbon systems for hydrogen storage. The Ti doped hybrid system could be a promising molecular hydrogen storage material because of the dominant interaction of H₂ and the Ti atom in the doped system.

References
[1] Geim AK and Novoselov KS 2007 The rise of graphene Nat. Mater. 6(3) 183–91
[2] Wudl F 2002 Fullerene materials J. Mater. Chem. 12(7)1959–63
[3] Kroto H W 1987 The stability of the fullerenes Cn, with n = 24, 28, 32, 36, 50, 60 and 70 Nature 329 529–31
[4] Zhang X, Huang Y, Wang Y, Ma Y, Liu Z and Chen Y 2009 Synthesis and characterization of a graphene–C 60 hybrid material Carbon 47 334-7
[5] Ulbricht H, Moos G and Hertel T 2003 Interaction of C60 with Carbon Nanotubes and Graphite, Phys. Rev. Lett. 90(9) 095501
[6] Xu WC, Takahashi K, Matsuo Y, Hattori Y, Kumagai M, Ishiyama S, et al. 2007 Investigation of hydrogen storage capacity of various carbon materials International Journal of Hydrogen Energy 32(13) 2504-12
[7] Rojas M I and Leiva E P M 2007 Density functional theory study of a graphene sheet modified with titanium in contact with different adsorbates Phys Rev B 76 155415
[8] M Canales M, Ramirez de Arellano Niño Rincon J, Magaña L F 2016 Interaction of a Ti-doped semi-fullerene (TiC30) with molecules of CO and CO2, Journal of Molecular Modeling 22 10.1007/s00894-016-3086-x.
[9] Yildirim T and Ciraci S 2005 Titanium-decorated carbon nanotubes as a potential high-capacity hydrogen storage medium. Phys. Rev. Lett. 94 175501e4
[10] Bartosz T, Ludwik A, Beck W, Muralidharan K and Deymier P A 2013 Impact of Local Curvature and Structural Defects on Graphene–C60 Fullerene Fusion Reaction Barriers, *J. Phys. Chem. C* 117(38) 19664-71

[11] Hohenberg P and Kohn W 1964 Inhomogeneous electron gas *Phys Rev* 136(3B) B864-B871

[12] Kohn W and Sham L J 1965 Self-consistent equations including exchange and correlation effects *Phys Rev* 140(4A) A1133-A1138

[13] Giannozzi P, Baroni S, Bonini N, Calandra M, Car R, Cavazzoni C et al. 2009 QUANTUM ESPRESSO: a modular and open-source software project for quantum simulations of materials *J Phys Condensed Matter* 21 395502

[14] Troullier N, Martins J L 1991 Efficient pseudopotentials for planewave calculations *Phys Rev B* 431 1993–2006

[15] Vanderbilt D 1990 Soft self-consistent pseudopotentials in a generalized eigenvalue formalism *Phys Rev B* 41 7892–5

[16] Perdew J P, Burke K and Ernzerhof M 1996 Generalized gradient approximation made simple. *Phys Rev Lett* 77 3865

[17] Monkhorst H J and Pack J D.1976 Special points for brillouin-zone integrations *Phys Rev B* 13(12) 5188-92

[18] Kokalj A 2003 Computer graphics and graphical user interfaces as tools in simulations of matter at the atomic scale *Comput Mater Sci* 28 155–68

[19] Ao Z M, Jiang Q, Zhang R Q, Tan T T and Li S 2009 Al doped graphene: A promising material for hydrogen storage at room temperature *Journal of Applied Physics* 105 074307

[20] Koh W, Moon H S, Lee S G, Choi J L and Jang S S 2015 A First-Principles Study of Lithium Adsorption on a Graphene – Fullerene Nanohybrid System *Chem Phys Chem* 16(4) 789-95

[21] Yürüm Y, Taralp A and Veziroglu T N 2009 Storage of hydrogen in nanostructured carbon materials *International Journal of Hydrogen Energy* 34(9) 3784-98

[22] Sigal A, Rojas M I and Leiva E P M 2011 Interferents for hydrogen storage on a graphene sheet decorated with nickel: A DFT study, *Int. J. Hydrog. Energy* 36(5) 3537-46

[23] van den Berg A W C and Areán C O 2008 Materials for hydrogen storage: current research trends and perspectives *Chem. Commun.* 6 668-81

[24] Park N, Hong S, Kim G, and Jhi S H 2007 Computational Study of Hydrogen Storage Characteristics of Covalent-Bonded Graphenes, *J. Am. Chem. Soc.* 129(29) 8999-9003