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A first principles study of hydrogen storage on lithium decorated two dimensional carbon allotropes

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ABSTRACT

Graphene has been intensively investigated as a possible hydrogen storage medium due to the spectacular properties granted by its two-dimensional nature. Since graphene's discovery, several new two-dimensional carbon allotropes have been theorized and synthesized. We investigated the hydrogen storage ability of six such allotropes: C_{65} , C_{64} , C_{63} , C_{62} , C_{31} and C_{41} . The ability to anchor lithium metal atoms over each allotrope and the hydrogen binding energies for each lithium decorated allotrope were studied with density functional theory using LDA, GGA and vdW-DF2 (for describing van der Waals interactions) functionals. All the allotropes were able to achieve double sided lithium decoration and hydrogen adsorption. Every allotrope other than C_{31} possessed lithium binding energies stronger than bulk lithium's cohesive energy which indicates that adsorbed lithium atoms will not cluster on the allotrope surface. Furthermore, every structure produced hydrogen binding energies stronger than that of lithium decorated graphene, suggesting the potential of use of these structures in practical hydrogen storage media. The C_{41} structure was able to adsorb far more hydrogen molecules than any other structure with a maximum hydrogen gravimetric density of 7.12 wt.% using the vdW-DF2 functional.

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Introduction

In recent years, the numerous environmental issues presented by fossil fuels have acted as a major driving force for the research community to place focus on greener and more sustainable alternatives. Among the many energy sources being investigated at the moment are hydrogen fuels as they do not create any carbon emissions when used to produce

energy [1]. One obstacle that researchers face with regards to hydrogen fuels is finding a method to effectively store hydrogen prior to fuel consumption. The US Department of Energy has set a target to achieve 5.5 wt% gravimetric density for hydrogen storage in light-duty vehicles by 2015 [2]. Conventional technologies have been unable to meet these targets in a safe and practical manner [3]. Hydrogen adsorption on substrates has been explored as a possible route towards meeting these storage goals [4], including the use of materials

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such as metal organic frameworks [5], carbon nanotubes [6] and boron nitride sheets [7] and fullerenes [8]. Among carbon based substrate materials, two-dimensional graphene has been found to be particularly promising [9]. Graphene's high specific surface area in addition to its unique mechanical and electronic properties allow it to be an ideal substrate which can be modified through metal decoration for increased hydrogen adsorption [10].

Since the discovery of graphene several other two dimensional carbon structures, such as graphyne [11,12] and graphdiyne [13], have been synthesized or theorized. These monolayer materials show promise for hydrogen storage applications. For example, in a study by Zhang et al. [14] lithium decorated graphyne was predicted to have a gravimetric density of 15.15 wt%, higher than that of graphene. In 2013, Lu et al. [15] theoretically predicted four new two-dimensional carbon structures which are mechanically stable at room temperature. These new carbon allotropes, along with graphyne and another proposed carbon allotrope called graphenylene [16], have different carbon bond hybridizations and electron density distributions than graphene. This may give them potential to better interact with and bind metal adatoms and hydrogen molecules, as graphyne has already been predicted to do [14].

The present study investigated the hydrogen storage ability with metal decoration of the six carbon allotropes discussed by Lu et al. [15], which according to the naming convention followed by them are: C_{65} , C_{64} (graphenylene), C_{63} , C_{62} (graphyne), C_{31} and C_{41} . The C_{6n} structures consist of hexagons connected by n -sided polygons, going from a pentagon for $n = 5$ to a triangle for $n = 3$ and a straight chain of two carbon atoms for $n = 2$. Similarly the C_{31} and C_{41} structures consist of triangles and squares connected by single carbon C_1 units. Three of the new structures (C_{65} , C_{63} and C_{41}) are considered more stable than graphyne and the fourth (C_{31}) is just barely less stable. The lithium binding ability for each of these structures was investigated, with lithium being selected for metal decoration as it is the lightest known metal and so would help increase relative hydrogen mass in the system. The maximum hydrogen gravimetric density was also investigated by adsorbing multiple hydrogen molecules on the lithium-decorated structures.

Another issue associated with most theoretical predictions of hydrogen adsorption on metal-decorated carbon-based structures is that they utilize density functional theory (DFT) with local density approximation (LDA) and generalized gradient approximation (GGA) functionals. For example, the previously mentioned study by Zhang et al. [14] of lithium decorated graphyne utilized LDA. However, the LDA functional can be quite inaccurate for such complex systems and will often overpredict adsorption strength. On the other hand, while the GGA functional models covalent type forces well, it poorly represents van der Waals (vdW) interactions. Such vdW interactions are significant in describing the weak physisorption type of bonding typical of molecular hydrogen adsorption on carbon substrates [17,18] and the interaction between neighboring metal atoms especially at higher coverages [18]. The more recently implemented vdW-DF2 [19] functional is said to better account for vdW forces [20] and so should provide more accurate adsorption energies. Hence,

this study compares theoretical predictions for lithium and hydrogen adsorption energies using the LDA, GGA and vdW-DF2 functionals for each simulation.

Computational details

The various carbon allotrope systems were studied using first principles calculations through density functional theory (DFT) as implemented using the plane-wave pseudopotential approach in Quantum Espresso [21]. In order to ascertain accuracy and the effect of different functionals, three electron exchange functional types were used. The local density approximation (LDA) functional was described using the Perdew-Wang method [22]. The generalized gradient approximation (GGA) functional was described using the Perdew-Burke-Ernzerhof (PBE) [23] method. The vdW-DF2 functional [19] was used to better describe van der Waals forces. This functional improves on the earlier vdW-DF [24] by replacing its revPBE semi-local exchange functional with PW86 and using an improved large- N expansion asymptotic gradient correction for the long-range nonlocal component of exchange-correlation energy. This results in increased accuracy in estimating equilibrium separations, H_2 bond strengths and van der Waals attraction at intermediate separations longer than equilibrium ones [19]. Ultrasoft pseudopotentials were used for GGA and vdW-DF2 calculations, while norm-conserving pseudopotentials were used for the LDA calculations. The kinetic energy cutoff value was set to 60 Ry (1 Ry \sim 13.606 eV) for the wave functions and to 600 Ry for the charge density. The Brillouin zone was sampled using a $8 \times 8 \times 1$ Monkhorst-Pack [25] k-point grid and Methfessel-Paxton [26] smearing of 0.01 Ry [27]. The supercell and atomic positions were optimized using the conjugate gradient (CG) algorithm. The total energy convergence was converged to within less than 5 meV/atom. Each of the structures were modeled using periodic supercells of 48 carbon atoms, except for the C_{65} supercell which had 40 carbon atoms. Each system had a vacuum layer thickness of more than 30 Å.

The average binding energy for a metal atom was calculated through the following equation:

$$E_b = -[E_{\text{carbon}+n\text{metal}} - (E_{\text{carbon}} + nE_{\text{metal}})]/n \quad (1)$$

where $E_{\text{carbon}+n\text{metal}}$ is the total energy of the metal decorated carbon allotrope system, E_{carbon} is the energy of the carbon allotrope sheet alone, E_{metal} is the total energy of the free metal adatom and n corresponds with the number of metal adatoms.

Consequently, the average binding energy for hydrogen adsorption on the lithium-decorated carbon allotropes can be calculated through the following equation:

$$E_b = -[E_{\text{metal-carbon}+iH_2} - (E_{\text{metal-carbon}} + iE_{H_2})]/i \quad (2)$$

where $E_{\text{metal-carbon}+iH_2}$ is the total energy of the metal decorated carbon allotrope system with hydrogen adsorbed, $E_{\text{metal-carbon}}$ is the total energy of the metal decorated carbon allotrope sheet, E_{H_2} is the total energy of the free H_2 molecule and i corresponds to the number of H_2 molecules. A positive binding energy in the previous two equations indicates a stable system configuration.

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