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Interaction of hydrogen molecules with perfect, defective and scandium doped polycyclic aromatic hydrocarbon structures

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ABSTRACT

In the present work the interaction of hydrogen molecules with perfect, defective and scandium doped polycyclic aromatic hydrocarbon (PAH) has been evaluated. At first the potential barrier for the penetration of hydrogen molecules through PAH structures has been investigated and then the adsorption of hydrogen molecules over PAH structures has been studied. To model the graphene surface for barrier calculations, it is shown that coronene can successfully estimate the graphene monolayer. The barrier height is calculated for perfect and two different defective PAH structures including Stone–Wales (SW) and 585. It is found that PAH even with small defects is impermeable to hydrogen molecules. In the adsorption section, it is revealed that adsorption of hydrogen molecules over defective PAH structures is as weak as perfect graphene (less than 0.1 eV). To enhance the hydrogen storage capacity, scandium (Sc) has been used as the dopant and it is shown that Sc binds more strongly to 585 defective structure with higher number of hydrogen molecules in comparison with SW structure.

1. Introduction

Increasing energy demand with the growth of world population, depletion of fossil fuel reserves and global climate changes have motivated research on alternative renewable and more environment-friendly energy sources and technologies. Hydrogen has the potential to serve as a promising energy carrier in the near future. It can reduce dependence on fossil fuel and simultaneously decrease the environmental damage. The main advantages of hydrogen include high specific energy, abundant reserves and pollution-free nature [1,2]. However for hydrogen technology to become a practical reality, hydrogen must be stored efficiently and reliably. This is especially important for onboard hydrogen storage, since in this case efficient storage of hydrogen in low-weight storage systems is very essential. At present, hydrogen is mainly stored in following forms: compressed gas, cryogenic liquid and solid state storage in the form of metal hydrides and physisorption on high surface area materials. But none of these technologies has met the US DOE target for hydrogen storage capacity which was revised in 2009 to 5.5 wt% and 7.5 wt% as 2015 and ultimate target [3–8]. It should be noted that all these targets are based on the system basis, i.e. the complete storage system including the weight of tank, material and media and other hardware.

Hydrogen is the lightest element in the world. It can escape through many elements and compounds. That means hydrogen has a very high permeability rate through different materials. Hydrogen permeation leads to very serious problems like hydrogen embrittlement, ductility reduction and hydrogen-induced cracking in many high strength steels [9,10]. Although for preventing hydrogen embrittlement, use of materials such as high strength composites has been suggested instead of metals and steels, these compounds alone cannot solve hydrogen permeation problem. Therefore additional liners are needed, leading to further increase in the weight of hydrogen vessels. As a result the ideal storage tanks should have a very low diffusivity to hydrogen while having a variety of other characteristics such as low density, nonreactivity with hydrogen and high tensile strength. Finding a suitable novel material for hydrogen storage tanks, with mentioned criteria is still an open-ended problem.

Successful isolation of free-standing sheet of graphene in 2004 [11], opened a new branch of research in science. This isolation of carbon atoms arranged in hexagonal lattice has allowed researchers to study a truly two dimensional system with thickness of just one layer of atoms. Superior properties of graphene such as excellent thermal and electrical conductivity, chemical stability, high carrier mobility and great mechanical strength make this nanomaterial attractive for many different potential applications ranging from future electronics to very sensitive gas sensors [12,13]. Taking into account unique properties of graphene including very low density, inertness and very high strength [14], it

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seems that graphene has all essential properties needed for use as an ideal material for hydrogen storage tanks. The only required property which has not been proved yet is the non-diffusivity of graphene to hydrogen molecules. Indeed the impermeability of perfect graphene to some gases such as helium was first demonstrated experimentally by Bunch et al. [15]. After that Leenaerts et al. used density functional theory to indicate that graphene is impermeable to helium atoms [16]. In another study single and double-layer graphene sheets were proposed as ultrabarriers in fluorescent polymer films for protecting a device from chemical degradation under ambient conditions [17]. Also there are a number of other research works that have used porous graphene as an ideal membrane for separating different molecules [18–23]. However to the authors' knowledge the permeation of hydrogen molecules through graphene has not been investigated yet.

On the other hand, due to enormous surface area of graphene ($\sim$2600 $m^2 g^{-1}$) [24], this nanomaterial has been studied as the storage media for hydrogen storage. But pristine graphene alone does not provide sufficient binding energy for hydrogen adsorption at ambient conditions. To overcome this obstacle, one strategy is to dope graphene with transition-metal (TM) atoms. It has been proved that Kubas interaction (hybridization of d states of TM atom with σ states of H_2 molecule) is responsible for enhanced hydrogen storage [25]. This topic has been the subject of some recent research works [26–31]. Among transition metals, scandium has drawn significant interest due to its lighter weight and higher H_2 storage capacity. Furthermore, in comparison with other TMs, Sc atom occupies lower number of electrons in d level and as a result the excessive hydrogen binding energy which is common for TMs, is lower for Sc atom. Kim et al. indicated that in comparison with early transition metals (Ti and V), graphene with vacancy doped by Sc can adsorb more hydrogen molecules [32]. In a similar work, it was revealed that pyridine-like nitrogen-doped graphene with dispersed Sc is a better option for hydrogen storage compared to structures dispersed with Ti or V [33]. In another study Wu et al. found that Sc doped edge-decorated graphene nanoribbons can be a viable hydrogen storage media by adsorption of hydrogen molecules in a quasi-molecular fashion [34]. Chen et al. proved that divacancy BN graphene doped by Sc has better hydrogen adsorption performance in comparison with 11 transition metals, since only in Sc/DV-BN all H_2 molecules remained molecular [35]. Moreover promising effect of Sc on enhancing hydrogen storage in other structures such as phthalocyanines, metal organic frameworks and hydrides has been revealed previously [36–38]. However for practical applications of Sc-doped graphene, the main issue is that TM atoms dispersed on pristine graphene have a tendency to form clusters due to larger cohesive energy of TMs in comparison to the binding energy of TMs with graphene. To avoid clustering, it is needed to enhance the binding energy between metal atom and graphene. One solution is to introduce defect sites in graphene in which reactive carbon atoms provide trapping site for adsorption [39].

The main aim of the present work is to study two different applications of graphene for hydrogen storage including impermeable barrier against hydrogen permeation and adsorption media made from Sc doped graphene structure. The work is organized as follows: at first the appropriate size of polycyclic aromatic hydrocarbon molecule for modeling graphene monolayer in barrier calculations is found for He atom and results are compared with previously published data. Also the energy barrier for penetration of hydrogen molecules through perfect defect-free PAH is evaluated. Parallel and perpendicular orientations of hydrogen molecule in hollow and bridge sites of the PAH layer are examined. Then, the permeability of hydrogen molecules through two different structures of defective PAH is calculated. Afterward, the interaction of pristine and defective PAH with hydrogen molecules will be evaluated. Finally hydrogen adsorption capacity of Sc doped defective PAH will be investigated. It should be noted that evaluation of interaction between hydrogen molecules and the edges of PAH structure is out of scope of this work.

2. Computational details

To model the graphene sheet, polycyclic aromatic hydrocarbon (PAH) molecules were used. To identify the appropriate PAH size for predicting the barrier height and also to compare the results of this work with previously published data, the barrier heights of helium atom approaching towards PAH molecules were calculated. The size of PAHs started from six carbon atoms (benzene) to forty atoms (circumanthracene). In all calculations planar structures of PAH molecules with initial C–C distance of 1.42 Å and an H–H distance of 0.74 Å were used. Note that in barrier calculations; PAH structure was kept fixed, since Leenaerts et al. showed that relaxation of graphene has no significant influence on the barrier height [16]. On the other hand for adsorption calculations, the structures were fully relaxed. Møller–Plesset second-order perturbation method (MP2) with 6-311G basis set was used in barrier calculation, while in adsorption calculations, density functional theory (B3PW91) was used due to suitability of DFT methods for systems with TMs. All calculations were performed by using GAUSSIAN 03 package [40].

The energy barrier (E_b) for helium atom approaching toward the PAH structure was evaluated by:

$$E_b = E_{P\text{-}He} - E_P - E_{He} \quad (1)$$

where $E_{P\text{-}He}$ is the total energy of PAH–helium system, and E_P and E_{He} are energies of PAH and helium atom, respectively.

After choosing the appropriate size of PAH for representing the graphene sheet, barrier heights for penetration of hydrogen molecules in parallel and perpendicular orientations were examined. The energy barrier for hydrogen molecule approaching PAH, E_b, was evaluated by:

$$E_b = E_{P\text{-}H_2} - E_P - E_{H_2} \quad (2)$$

where $E_{P\text{-}H_2}$, is the total energy of PAH–H_2 system, and E_P and E_{H_2} are energies of PAH structure and hydrogen molecule, respectively.

In the adsorption calculations, the binding energy of hydrogen molecules over PAH structure was calculated according to the similar equation:

$$E = E_{P\text{-}H_2} - E_P - E_{H_2} \quad (3)$$

while the binding energy for the adsorption of scandium over PAH structure was found by:

$$E = E_{P\text{-}Sc} - E_P - E_{Sc} \quad (4)$$

And the binding energy for the adsorption of ith hydrogen molecule over scandium doped PAH was evaluated from:

$$E = [E_{P\text{-}Sc\text{-}iH_2} - (E_{P\text{-}Sc+iE_{H_2}})]/i \quad (5)$$

where $E_{P\text{-}Sc\text{-}iH_2}$ is the total energy of Sc-doped PAH containing i hydrogen molecules and $E_{P\text{-}Sc}$ and E_{H_2} are energies of Sc-doped PAH and hydrogen molecules, respectively.

3. Results and discussion

3.1. Barrier calculation

3.1.1. Validation with helium atom

As it is represented in Fig. 1, five PAH molecules including benzene, naphthalene, anthracene, coronene and circumanthracene were used for representing graphene sheet. To find the barrier