Physica E 66 (2015) 40–47

Contents lists available at ScienceDirect

Physica E

journal homepage: www.elsevier.com/locate/physe

Hydrogen adsorption and storage on palladium-decorated graphene with boron dopants and vacancy defects: A first-principles study

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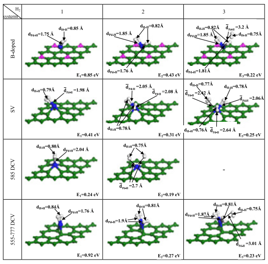
HIGHLIGHTS

- Pd atom can be stabilized on graphene with SV and 585 DCV defects.
- Pd-decorated B-doped, SV and 555-777 DCV defect graphene can bind three H_2 molecules.
- Pd-decorated 585 DCV defect graphene can bind two H_2 molecules.
- Pd-decorated SV defect graphene is the best for hydrogen storage.

GRAPHICAL ABSTRACT

Optimized atomic geometries for Pd-decorated B-doped, SV, 585 DCV and 555-777 DCV defective graphenes with one to three H_2 molecules. Green, pink, blue and white balls represent C, B, Pd and H atoms, respectively.



ARTICLE INFO

Article history:
Received 23 July 2014
Received in revised form
27 September 2014
Accepted 29 September 2014
Available online 6 October 2014

Keywords:
Hydrogen adsorption and storage
B-doped graphene
Vacancy defect
Density functional theory

ABSTRACT

The geometric stability and hydrogen capacity of Pd-decorated graphene with experimentally realizable boron dopants and various vacancy defects including single carbon vacancy (SV), "585"-type double carbon vacancy (585 DCV) and "555-777"-type double carbon vacancy (555-777 DCV) are investigated using the first-principles calculations based on density functional theory (DFT). It is found that among the four types of defective structures, Pd′s binding energies on SV and 585 DCV defect graphene sheets exceed the cohesive energy of the Pd metal bulk, thus Pd atoms are well dispersed above defective graphene sheets and effectively prevent Pd clustering. Up to three H_2 molecules can bind to Pd atom on graphene with B dopants, SV and 555-777 DCV defects. For the cases of Pd-decorated graphene with B dopants and 555-777 DCV defect, a single H_2 or two H_2 are molecularly chemisorbed to Pd atom in the form of Pd–H_2 Kubas complex, where the stretched H–H bond is relaxed but not dissociated. Out of two adsorbed H_2, the third H_2 binds to Pd atom by small van der Waals (vdW) forces and the nature of bonding is very weak physisorption. Different from above two cases, three H_2 are all molecularly chemisorbed to Pd atom with stretched H–H bond for Pd-decorated SV defect graphene, the hybridization of the Pd-4*d* orbitals with the H_2-σ orbitals and the electrostatic interaction between the Pd cation and the induced H_2 dipole both contribute to the H_2 molecules binding, and the binding energies of 0.25–0.41 eV/H_2 is in the range that can permit H_2 molecules recycling at ambient conditions.

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http://dx.doi.org/10.1016/j.physe.2014.09.022
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1. Introduction

In recent years, hydrogen as a recyclable, environment friendly source and carrier of energy has drawn significant interest and stimulated the search for better hydrogen storage and transport media [1–4]. Commonly, low weight materials with a large surface area are used to improve the capacity of hydrogen storage. So the carbon based nanostructures, such as carbon nanotubes (CNTs) [5,6], fullerene [7] and graphene [8], have been suggested as promising systems. Unfortunately, for carbon in any form, they cannot provide sufficient binding for hydrogen, namely less than 0.1 eV/H_2 compared with the ideal binding range 0.16–0.4 eV at ambient conditions [9–11]. To overcome it, one strategy is to functionalize the surface of carbon based nanostructures with alkali, alkali earth [12–16] or transition metal (TM) [17–23] atoms to improve hydrogen binding energy.

Theoretical studies have proposed two binding mechanisms contribute to the H_2 molecules adsorbed to metal atom decorated carbon based nanostructures. One is the induced polarization of the H_2 molecules under the electric field produced by metal-support dipole [12–15]. Another one is the hybridization of the *d* orbitals of TM atom with the σ orbitals of H_2 [17–19] (so-called Kubas interaction [24]). Initially, the TM (Sc, Ti and V) decorated carbon nanostructures adsorb multiple H_2 molecules with a binding energy of 0.2–0.6 eV and may satisfy the U.S. Department of Energy (DOE) goal. However, the TM atoms are shown to have a strong tendency of clustering that deteriorates the storage capability. The origin of such clustering is the large cohesive energy of TM, and thus chemically active sites are required to hold TM atoms so strongly as to overcome the metal cohesion [25]. In view of this point, later works have suggested that modification of carbon nanostructures by doping other atoms such as B and N or forming an intentional vacancy can effectively strengthen the metal binding to the defects and successive enhancement in the hydrogen adsorption [25–39]. Kim et al. [35] reported that the graphene with Stone–Wales (SW) defects can prevent the clustering of Li atoms and the Li dispersed SW defective graphene systems can accommodate four H_2 molecules with the range of 0.20–0.35 eV, which falls in a desirable range for feasible applications under ambient conditions. Nachimuthu et al. [36] performed first-principles calculation to study the adsorption of hydrogen on combined TM-decorated B-doped graphene surface and found that Ni, Pd and Co atoms show a great advantage of both hydrogen adsorption and H spillover method in the hydrogen storage process. Except for enhancement in the hydrogen adsorption, introduction of defects and B or N doping are two of the most pursued methods for better suitability to applications in oxygen reduction reaction catalysis capabilities. For instance, Sen et al. [37] proposed that B–N codoping in defective graphene sheets perform significantly better than the platinum surface, undoped defect graphene, and the single N or B atom doped defect graphene system for dioxygen adsorption. Significant stretching of the O–O bond indicates a lowering of the bond breakage barrier, which is advantageous for applications in the oxygen reduction reaction. Lim et al. [38] demonstrated that defective graphene-supported Cu nanoparticles can enhance electrochemical reduction of carbon dioxide (CO_2) into hydrocarbon fuels. In addition, B-doped graphene was proposed as an anode candidate for a rechargeable Na-ion battery by Ling et al. [39].

Among TM atoms, Pd is five times cheaper than Pt and electrochemically more stable than other TM atoms like Fe, Co and Ni [40], and Pd adsorbed carbon nano-materials can also be utilized as a promising catalyst [41]. For instance, Xiao et al. [42] have found that five H_2 molecules can bind to two adjacent Pd atoms and the hydrogen storage capacity reaches to 2.88 wt% for Pd-decorated (8,0) single-walled (SW) CNTs. Sen et al. [43] have shown that Pd_4 cluster adsorption on “555-777”-type double carbon vacancy (555-777 DCV) defect graphene adsorbs up to five H_2 molecules at maximum with adsorption energy per H_2 molecule lying well within the desirable energy window. Vinayan et al. [44] experimentally studied the hydrogen storage capacity on Pd nanoparticles decorated pristine graphene, only a 0.63 wt % of hydrogen can be stored at 2 MPa and 25 °C, and it is also found that these Pd nanoparticles are weakly adhered to the carbon support, and easily tend to cluster. Thus the problem of Pd′s aggregation cannot be avoided. In order to solve it, Vinayan et al. successfully synthesized the N-doped graphene and showed that the Pd decoration over the N-doped graphene can be used to enhance the hydrogen uptake capacity by almost 272% at ambient temperature and under moderate pressure of 2 MPa. Unfortunately, according to our previous theoretical work [45], although the Pd′s binding energy on the N-doped graphene layer evidently increases, it is still lower than the Pd′s cohesive energy of 3.89 eV [46].

These experimental and theoretical works as well as the questions mentioned above, motivate our investigation on search for better approach to hinder Pd′s aggregation. To achieve this goal, we perform first-principles calculations based on density functional theory (DFT) for a systematic study on geometric stability and hydrogen capacity of Pd-decorated graphene with B dopants and various vacancy defects including single carbon vacancy (SV), “585”-type double carbon vacancy (585 DCV) and (555-777 DCV). We introduce B dopants and different vacancy defects, which can generate acceptorlike state that will efficiently enhance the interaction between metal and graphene and then increase hydrogen storage capacity. We will calculate the binding energies and electronic structures of Pd-decorated B-doped and defective graphene sheets to investigate such effects on Pd atom anchoring and hydrogen binding affinity.

2. Calculation methods

All calculations are carried out using the first-principles method based on DFT as implemented in the Vienna ab initio simulation package (VASP) with a projector augmented wave (PAW) method [47–50]. The electron exchange–correlation interactions are expressed with a generalized gradient approximation (GGA) in the form of the Perdew–Burke–Ernzerhof [51] functional. In fact, GGA and local densities approximation (LDA) with DFT calculations are unable to describe correctly van der Waals (vdW) interactions resulting from dynamical correlations between fluctuating charge distributions. Previous studies have shown that GGA underestimates the relatively weak binding energies, whereas LDA overestimates them [52,53]. A pragmatic method to work around this problem has been given by the DFT-D approach, in which a dispersive force correction based on interatomic potentials of the $C^6 \cdot R^{-6}$ form is added to a standard DFT exchange–correlation functional-allowing for a facile energy decomposition to vdW and electronic parts. Representatives of DFT-D methods are the implementations of Ortmann, Grimme and Tkatchenko [54]. Grimme′s DFT-D2 method is adopted in our work. In the method, the vdW interactions are described via a simple pair-wise force field, which is optimized for several popular DFT functionals [55]. The cutoff energy for the plane-wave basis expansion is chosen to be 400 eV. A conjugate-gradient algorithm is used to relax the ions into their ground-states, and the energies and the forces on each ion are converged within 10^{-4} eV and 0.02 eV/Å, respectively. Integration over the Brillouin zone is performed by using the gamma-centered Monkhorst–Pack scheme [56] with $(4 \times 4 \times 1)$ k-points, together with a Gaussian smearing broadening of 0.2 eV.