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Hydrogen adsorption on palladium anchored defected graphene with B-doping: A theoretical study

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ABSTRACT

The effect of a combination of B-doping and vacancy-defect on the atomic adsorption of hydrogen on Pd-decorated graphene have been investigated using density functional theory simulations. The introducing of defect and B-dopant enhanced the adsorption of hydrogen molecule and the PDOS results indicated that the enhancement was contributed by the hybridization of B and H atoms. Furthermore, the adsorption of hydrogen molecule on Pd-decorated double-vacancy (DV) defective graphene lead to dissociated and chemisorbed states with the two separated H atoms bonding to the C atoms at vacancy sites. Interestingly, the B-doping decreased the interaction between the Pd-adatom and the defected graphene but increased the stability of the adsorption of dissociated H_2. The activated states of H_2 molecule occurred in the adsorption on single-vacancy (SV) defected graphene with stretched H—H bonds. Our results provide a potential approach for the engineering of graphene for hydrogen storage applications.

Introduction

Recently, the development of hydrogen as energy carrier has attracted significant attention to replace fossil fuel as recyclable and environment friendly source [1,2]. However, the main challenge of developing hydrogen energy economy is the lack of compact, effective, safe and cheap storage media. An ideal storage material is characterized by high

storage capacity [3], excellent ability of absorption and desorption at near room temperature and ambient pressure [4], and reversible hydrogen-releasing. Graphene has been focused for using as new high capacity of hydrogen storage materials, since its first experimental synthesis in 2004 [5]. Whereas, the pristine graphene cannot exhibit sufficient binding energy for hydrogen, which was less than 0.1 eV/H_2 [6] compared with the required value in the range of 0.16–0.4 eV/H_2 [7,8]. A way to overcome this is by adding transition metal (TM) atoms with Kubas interaction [9], namely, the d states of TM atoms hybridize with the hydrogen molecule. The interaction enhances the binding energy through forming H_2-TM complexes and it has been observed experimentally in Ni, Ti and Pd decorated carbon materials [10–12]. Additionally, palladium is prevalently chosen because its distribution over carbon materials improves the activity of surface and then increases the hydrogen storage [13–17]. For instance, Lipson and co-workers [17] found that single-walled carbon nanotubes encapsulated by Pd layers exhibited large hydrogen storage of 8–12 wt%. Psofogiannakis et al. [18] have reported graphite oxide-like carbon foam doped with Pd nanoparticles could be measured to achieve a storage capacity of 3 wt% at room temperature and 2 Mpa, halfway to the DOE (US Department of Energy) target of 5.5 wt% for 2015 [3]. Yang and co-workers [19] explained the mechanism of this activation was due to the hydrogen dissociation on TM particles, which was defined as hydrogen spillover. The phenomena has been observed in many experiments [20–25] and show that H_2 was dissociated into H atoms. Then the H atoms subsequently migrate onto the supporting carbon substrate surface. Therefore, the Pd decorated carbon nanomaterials was expected to be promising candidate for hydrogen storage. Whereas, TM nanoparticles tend to form clusters when disperse on the perfect graphene due to a larger cohesive energy of metal than the binding energy with the graphene [26–29]. To avoid this, a number of methods were attempted to enhance the stabilization of TM atoms on the graphene surface, and the inducing of carbon vacancies was successfully proposed in experimental and theoretical studies [30–33].

Until now, intrinsic point defects on graphene, including vacancies, topological defects and adatoms, have been experimentally observed and their presence influences the physical and chemical characteristics of graphene [34–40]. Among them, vacancy is a typical and common defect produced by missing lattice atom, such as single-vacancy and double-vacancy. Previous experimental studies showed that vacancies could be purposefully created by electron or ion irradiation releasing carbon atoms [41]. For TM-adatoms, it was found that the binding energy on vacancy sites of graphene was much larger than the cohesive energy of metal [42–44]. Therefore, it was reasonable to expect the presence vacancies could enhance the hydrogen storage capacity by increasing the activity of graphene surface. On the other hand, it was reported that Boron doping is a feasible and practical method to alter the binding structure and enhance the adsorption performance of hydrogen [45,46]. Experimentally, B-doped carbon materials were synthesized [47] and the application for hydrogen storage was implemented successfully. Liu and co-workers showed that four polarized H_2

molecules absorbed around one Li-adatom on B-doping graphene exhibited optimal adsorption energy of 0.13 eV/H_2 [48]. Yang et al. reported that hydrogen storage was increased to 1.2 wt% at 298 K and 10 Mpa via spillover on Ru-supported B-doped microporous carbon [49]. Wu and co-workers investigated the hydrogen spillover mechanism on B-doped graphene theoretically and the results indicated that the more H atoms could absorb on the B-doped graphene than the pristine one with sufficient low activation barriers under ambient conditions [50].

In this paper, we investigated the adsorption of hydrogen on Pd-decorated B-doped vacancy-defected graphene via first-principles based on density functional theory (DFT). First, the structures of single-vacancy (SVG), double-vacancy (DVG), and B-doped these two (BSVG and BDVG) were considered. Second, we performed the corresponding parameters detailed describing Pd absorbed on B-doped vacancy-defected graphene. Finally, we investigated the adsorption of hydrogen on the modified graphene substrate and explored the effect of defect–dopant combination on the adsorption process.

Model and computations

All the calculations were performed within the framework of first-principles DFT, implemented in the $Dmol^3$ code [51]. We used the generalized gradient approximation (GGA) for exchange-correlation functional, as described by Perdew-Burke-Ernzerhof (PBE). We selected DFT semicore pseudopotential (DSSP) to replace core electrons as a single effective potential [52]. A double numerical plus polarization (DNP) was employed as the basis set. The DNP basis set corresponds to a double-ζ quality basis set with a p-type polarization functions to hydrogen and d-type polarization functions added to heavier atoms, which is comparable with the Gaussian 6-31G (d, p) basis set and owns a better accuracy [53].

In our work, we used $5 \times 5 \times 1$ supercell with periodic boundary condition on the x and y axes to model the infinite graphene sheet. The vacuum space of 20 Å was set in the direction normal to the sheets to avoid the interactions between periodic images. A $5 \times 5 \times 1$ mesh of k-point and the global orbital cutoff of 5.0 Å were set in the spin-unrestricted calculations. All atoms were allowed to relax. Convergence in energy, force, and displacement was set at 2×10^{-5} Ha, 0.004Ha/Å, and 0.005 Å, respectively. In the present study, we first optimized the geometry structure of pristine graphene, the calculated bond length of C–C was 1.420 Å, which was well agreement with the previous theoretical and experimental results [54]. Then we take two typical vacancy defects in graphene into account, that is, single-vacancy (SVG) and double-vacancy (DVG). The vacancy-defective graphene were created by removing a C atom or a C–C dimmer from perfect graphene. The optimized atomic structures of SVG and DVG were depicted in Fig. 1a and b. Moreover, we doped a B atom to stand for a C atom consisting the vacancy defect, and the most energetically most favorable two systems, namely, B-doped single-vacancy (BSVG) and double-vacancy (BDVG) defected graphene, were also shown in Fig. 1c and d.

In defected systems, the key physical quantity to calculate is the defect formation energy and many properties of a defect