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A comparative study on hydrogen interaction with defective graphene structures doped by transition metals

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HIGHLIGHTS

- Interaction of H₂ molecules with defective graphene doped TM atoms was studied.
- 585 divacancy-TM had the strongest binding energy compared to SW and 555-777.
- 555-777 structure doped by Sc had the maximum capacity for hydrogen molecules.
- H₂ binding energies on 555-777/Sc system were in the favorable range of 0.2–0.4 eV.

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ABSTRACT

In the present work, the interaction of hydrogen molecules with defective graphene structures doped by transition metal (TM) atoms is investigated by using first principles density functional theory (DFT). Defective graphene structures include Stone–Wales (SW), 585 and 555-777 and transition metals include early TMs, i.e. scandium (Sc), titanium (Ti) and vanadium (V). It is found that in comparison with the pristine graphene, presence of defects significantly enhances the metal binding. Among three defects, 585 divacancy leads to the strongest binding between graphene and metal. Hydrogen adsorption is then evaluated by sequential addition of hydrogen molecules to the system. The results reveal that in comparison with other structures, 555-777 defective structure doped by Sc has the maximum capacity for hydrogen molecules. Also it is indicated that none of hydrogen molecules were dissociated during relaxation, indicating that all hydrogen molecules are accessible for reversible storage. Moreover, it is found that binding energies for adsorption of hydrogen molecules over 555-777/ Sc system are in the favorable range of 0.2–0.4 eV/H₂.

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1. Introduction

Hydrogen has been considered as a promising alternative energy carrier due to its abundant reserves, high specific energy and environmental friendliness [1–3]. But the problem with developing hydrogen technology lies in its efficient and safe storage [4,5]. This is particularly essential for on-board hydrogen storage, since for such application reliable storage of hydrogen in low-weight storage systems is very important. Among hydrogen storage technologies, compressed gas storage is not so suitable for transportation applications due to the high weight and size of the tank, whereas cryogenic liquid state storage suffers from evaporative losses and high energy cost for liquefaction. On the other hand, solid state storage technologies such as metal hydride techniques and physisorption on high

surface area materials have the potential to become a viable technology and meet the US DOE targets for hydrogen storage [6,7]. Although there have been a variety of experimental and theoretical research works on solid state hydrogen storage systems, especially on metal hydrides [8–12] and carbon nanomaterials [13–22], finding a suitable novel material for hydrogen storage tanks is still an open-ended problem.

Among different carbon nanomaterials, graphene has gained significant attention in recent years. Indeed, successful isolation of free-standing sheet of graphene in 2004 [23], opened a new branch of research in science. This isolation of carbon atoms arranged in a hexagonal lattice provided the capability of studying a truly two dimensional system with a thickness of just one layer of atoms. Superior properties of graphene such as very low density, enormous mechanical strength, chemical stability and excellent thermal and electrical conductivity make this nanomaterial attractive for many potential applications. These applications range from future electronics such as touch panels and transistors

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to very effective catalysts [24,25]. Due to very high surface area of graphene ($\sim 2600 \text{ m}^2 \text{ g}^{-1}$), this nanomaterial has also been studied for application as the storage media for hydrogen storage [25–31]. However, similar to other carbon nanomaterials, pristine graphene alone does not provide enough binding energy which is necessary for hydrogen adsorption at ambient conditions. It has been shown that the binding energy of hydrogen molecules over pristine graphene is less than 0.1 eV, while the ideal binding energy should be in the range of 0.2–0.4 eV. To overcome this problem, one solution is to dope graphene with transition-metal atoms. It is known that in these systems the Kubas interaction (hybridization of partially filled d orbital of transition metal with σ orbital of H_2 molecule) is responsible for enhanced hydrogen storage [32]. This type of enhancement in binding energies of hydrogen molecules has been the subject of some recent research works [33–35]. But for practical applications, the main issue is that transition metal atoms dispersed on pristine graphene prefer to form clusters rather than being individually dispersed over graphene, since their cohesive energy is larger than their binding energy with graphene. To avoid such clustering problem, it is necessary to increase the binding energy between metal atoms and graphene layer. A novel approach is to introduce defect sites in graphene, so that reactive carbon atoms could provide trapping sites for adsorption. Beside theoretical works on defect formation over graphene sheet, several experimental studies have proved the occurrence of either native or physically introduced defects in graphene [36]. For instance it is known that irradiation of graphene by energetic particles like electrons or ions can lead to generation of different defects [37,38]. Also chemical treatments like oxidation by an oxidizing acid such as HNO_3 or H_2SO_4 are known for defect creation on graphene [39]. Different types of defects that have been mainly studied until now include Stone–Wales, 585, 555–777, single vacancy, and multiple vacancies.

Recently, storage of hydrogen on defective structures doped by different atoms or compounds has been the subject of some research works. For instance Kim et al. used first principles calculations based on DFT to study the adsorption of transition and alkaline earth metals over graphene with vacancy defect as well as hydrogen storage capacity of these systems [40]. In another study Chu et al. used DFT to study the adsorption of titanium over double-vacancy graphene and then they evaluated the hydrogen storage capacity of the system [41]. They found that this structure can hold up to eight hydrogen molecules per unit. Furthermore, Xu and Ge used different defective structures such as single vacancy and 585 to calculate the hydrogen storage capacity of NaAlH_4 supported on graphene [43]. The capability of small Pd clusters adsorbed on double vacancy defective graphene sheet for hydrogen storage was investigated by Sen et al. [42]. They found that 555–777 structure is the most favorable structure for the adsorption of Pd_4 cluster. In comparison with the pristine graphene, 555–777 was found much more efficient energetically for hydrogen storage. Despite these research works on the effect of defects on hydrogen storage, however to the best of authors' knowledge, there isn't any comparative study on hydrogen storage capability of defective graphene structures including SW, 585 and 555–777 doped by transition metals.

The main aim of the present work is to study the interaction of hydrogen molecules with three defective graphene structures doped with transition metals by using density-functional theory. The work is organized as following: at first the adsorption of three transition metal atoms including Sc, Ti and V will be evaluated over three defective graphene structures and the results will be compared with the pristine graphene. The defective structures include SW, 585 and 555–777. Next, effect of dispersive forces will be investigated on the binding energies of metal adsorption. Hydrogen molecules will be then introduced sequentially to the

system of TM-doped defective graphene and adsorption energies of hydrogen molecules as well as maximum capacity of these systems for hydrogen storage will be evaluated.

2. Computational details

A first-principles calculation on the electronic structure has been performed within spin-polarized density functional theory. All calculations are implemented using Quantum ESPRESSO code [44] with plane-wave basis set and generalized gradient approximation (GGA). It has been proved that DFT gives the correct equilibrium structure for carbon nanomaterials [45,46]. However, since in systems containing hydrogen molecules, weak forces are significantly involved, it is important to choose correct exchange-correlation functional. Recently Kelkanen et al. concluded that among GGAs, Perdew–Burke–Ernserhof (PBE) exchange-correlation functional gives better results [47]. Also it has been shown that PBE works better for predicting the geometries of systems with transition metals [48]. Therefore in the present work, PBE in combination with Vanderbilt ultrasoft potential has been used. Energy cutoffs of 30 and 300 Ry are used for plane-wave basis sets and charge density grids, respectively. The occupation state is smearing and Gaussian spreading of Brillouin-zone integration is 0.02 eV. K-points are generated automatically with the size of $2 \times 2 \times 1$ using Monkhorst–Pack scheme [49]. To check that calculations are independent from size of K-points, a number of systems were repeated by the size of $4 \times 4 \times 1$ and it was observed that the binding energy changes only by less than 20 meV. For geometrical optimization, the system was allowed to fully relax until the force acting on any atom was less than 0.05 eV \AA^{-1} .

Pristine graphene was built from a supercell of 32 carbon atoms with lattice parameters of $8.52 \times 9.84 \times 20 \text{ \AA}$. The large vacuum layer in z-direction (20 \AA) was chosen to avoid the interaction between adjacent layers. Three types of defective graphene including, Stone–Wales, 585 and 555–777 were built by pure rearrangement and removal of two carbon atoms from pristine supercell. The transition metals, including Sc, Ti and V were introduced to pristine and defective graphene structures and the adsorption energy between graphene structure and transition metal (E_{ad}) was calculated by:

$$E_b = E_{G-TM} - E_G - E_{TM} \quad (1)$$

where E_{G-TM} is the total energy of graphene-transition metal system and E_G and E_{TM} are energies of isolated graphene and transition metal, respectively.

The binding energy for the adsorption of i th hydrogen molecule over TM doped graphene was evaluated from:

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

where $E_{G-TM-iH_2}$ is the total energy of graphene structure doped by transition metal containing i hydrogen molecules and E_{G-TM} and E_{H_2} are energies of isolated graphene doped by transition metal and isolated hydrogen molecules, respectively.

3. Results and discussions

3.1. Relaxation of different graphene structures

Fig. 1 shows the optimized configuration of four graphene structures including pristine, SW, 585 and 555–777. These structures have been obtained by fully relaxation of carbon atoms. For the pristine graphene the calculated bond length of C–C bond in is 1.42 \AA , which is in very good agreement with the experimental bond length.

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