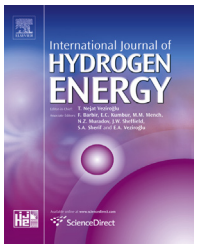
Available online at www.sciencedirect.com

ScienceDirect

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



Li-decorated double vacancy graphene for hydrogen storage application: A first principles study

S. Seenithurai, R. Kodi Pandyan, S. Vinodh Kumar, C. Saranya, M. Mahendran *

Smart Materials Lab, Department of Physics, Thiagarajar College of Engineering, Madurai 625015, India

ARTICLE INFO

Article history:
Received 23 March 2014
Received in revised form
8 May 2014
Accepted 12 May 2014
Available online 11 June 2014

Keywords:
Hydrogen storage
Adsorption
DFT
Li-decoration
Binding energy
Defected graphene

ABSTRACT

Lithium decoration is an effective strategy for improving the hydrogen adsorption binding energy and the storage capacity in carbon nanostructures. Here, it is shown that Li-decorated double carbon vacancy graphene (DVG) can be used as an efficient hydrogen storage medium by means of Density Functional Theory (DFT) based calculations. The Li binding energy in DVG is 4.04 eV, which is much higher than that of pristine graphene. A maximum of four hydrogen molecules adsorb on Li decorated on one side of DVG and this leads to a gravimetric storage capacity of 3.89 wt% with an average adsorption binding energy of 0.23 eV/H_2. When Li is decorated on both sides of DVG, the gravimetric storage capacity reaches 7.26 wt% with a binding energy of 0.26 eV/H_2 which shows that desorption would take place at ambient conditions.

Introduction

Hydrogen is one of the alternative energy resources with high abundance on the earth in the form of water. It is a clean energy carrier and produces water vapor as the only effluent during the combustion of the engine. It has high energy content in terms of mass (~143.0 MJ/kg) which is three times larger than the gasoline (44.4 MJ/kg). However, in terms of volume, its efficiency is very low (0.0108 MJ/L), compared to gasoline (34.8 MJ/L) [1]. Thus, efficient storage and transportation are to be accomplished to use hydrogen as a fuel in fuel-cell controlled vehicles (FCV). A normal car would consume 4 kg of hydrogen to travel a distance of ~400 km. Since hydrogen is a molecular gas, in order to store 4 kg of hydrogen at normal temperature and pressure (NTP), a volume of ~45 m^3 is required and this size would be larger than the car itself. Thus, storing hydrogen in a smaller, lightweight and safe container is one of the important problems that has to be addressed for onboard automobile applications [2,3].

Hydrogen is stored using physical method or chemical methods. Conventional physical hydrogen storage method is a high-pressure method where H_2 molecules are compressed to a high pressure in the aluminum cylinders or carbon fiber

* *Corresponding author*. Tel.: +91 452 2482430x723; fax: +91 452 2483427.
E-mail addresses: manickam-msahendran@tce.ed, perialangulam@gmail.com (M. Mahendran).
http://dx.doi.org/10.1016/j.ijhydene.2014.05.068

reinforced tanks [4]. Present day high pressure tanks (Type IV) made of carbon fiber reinforced plastic (CFRP) can withstand upto 690 atm, which would have a storage capacity of 5.6 kg of recoverable hydrogen [5]. However, the storage at high pressure is not a viable option for onboard vehicles since there is an associated risk of outburst during cataclysmic events. Another physical method is storage of H_2 in liquid phase at temperatures below 20 K, using Liquid Helium as a coolant. The hydrogen was first liquefied by Dewar in 1898 and now actively used in space explorations during rocket launch and aircrafts [6]. The storage density in liquid hydrogen is ~70.8 kg/m^3 and this is larger than the density achieved through other hydrogen storage methods. Nevertheless, there is a need of a cryogenic unit, which would increase the cost, and more importantly, the weight of the onboard vehicles. The loss of liquid hydrogen (~0.4% per day) is also a major problem. Due to these reasons, cryogenic storage method does not meet the requirements of lightweight onboard automobile applications.

Alternative storage method that is widely used now is solid-state storage method in which hydrogen is stored by means of chemical interaction. At present, the well-developed and widely used method is storage of hydrogen in the form of hydrides [7]. Simple and complex metal hydrides are used wherein the interaction involves breaking/creating covalent and/or ionic bonds [8]. Thus, even though metal hydrides such as AlH_3, MgH_2, $LiBH_4$ and $NaAlH_4$ have high hydrogen uptake, desorption temperature is very high in metal hydrides and kinetics is very slow [7,9–11]. In fact, hydrogen decomposition temperatures in the range of 60 °C–120 °C is advantageous, since this is the waste heat of the fuel cell. None of the metal hydride satisfies all the required conditions in order to use as an efficient storage media in onboard vehicles [12]. An ultimate gravimetric hydrogen storage capacity of 7.5 wt% is proposed with a fast fueling rate of 2 kg/minute [13]. Apart from the gravimetric density, the volumetric density should also be 70 g/L (2.3 kWh/L). The adsorption binding energy per H_2 molecule in the range of 0.2–0.6 eV would be desirable, since this can be used in ambient condition [14,15].

Search for efficient hydrogen storage media has resulted in a wide range of experimental and theoretical works as well as reviews [10,16–40]. Dillon et al. proposed carbon nanotube for hydrogen storage and projected a storage capacity of upto 5–10 wt% [26]. In pure carbon nanostructures, H_2 interacts with a weak binding energy of 0.11 eV/H_2 or less which is insufficient to hold the adsorbed molecules at near ambient conditions and therefore, all the adsorbed H_2 molecules are desorbed well below the room temperature [41–43]. On the other hand, the storage methods, which use a pure chemisorption, have high desorption temperature [33,44]. Thus, enhanced interaction through physisorption or modified chemisorption is necessary to obtain suitable storage media. Polarization of H_2 molecules by the positive ions anchored on host materials like carbon nanotube and graphene, Kubas interaction where donation of filled states of hydrogen molecule to the empty d orbitals and back donation from the filled states of d, and electric field enhanced interaction are suitable mechanisms of molecular hydrogen storage [45–47].

Since the work of Chen et al. and Ciraci et al., carbon-based nanomaterials functionalized with metals and metal hydrides are proposed to be potential candidates for the hydrogen storage media [22,48]. These carbon-based nanostructures are opted because of their lightweight that is necessary for achieving high gravimetric storage capacity. Since carbon exhibits enormous allotropes such as C60, carbon nanotube, graphene, cones, graphyne, linear atomic chains etc. and the possibility of arranging these carbon nanostructures into three-dimensional networks has also motivated this direction of investigation [20,49]. Extensive research shows that suitable hydrogen storage capacity and H_2 adsorption binding energies can be achieved by doping these carbon-based nanomaterials with boron, aluminum or decorating with light alkali metals (Li and Na), alkaline earth metals (Ca and Sr), light transition metals (Sc through Ni) and other metals such as Yttrium (Y), Palladium (Pd) and Platinum (Pt) [18,29,39,50–55]. Among these, B-, Al-doped and Li, Al, Ca, Sc, Ti, Pd, Pt decorated carbon nanostructures are extensively studied because they lead to high storage capacity with desirable binding energies [31,32,40,51,53,56–60].

The alkaline metal Li is preferable because of its lightweight, which will increase the gravimetric density. Li doped carbon nanotubes were first used for hydrogen storage by Chen et al. [48]. A reversible storage capacity of 4.2 wt% was obtained by Liu et al. in Li doped carbon nanotubes at room temperate and 10 MPa [61]. On theoretical side, Dag et al. studied the co-adsorption of Li and H_2 molecules in (8,0) CNTs and found that there is a strong interaction between the Li and H_2 even though no significant indirect adsorption occurs [62]. Recently, graphene has been proven to be a good hydrogen storage media owing to their high surface area of 2600 m^2/g [63]. Besides, since both sides of the graphene can be used for the hydrogen adsorption, graphene may be superior to other carbon-based nanostructures and a storage capacity of upto 12.8 wt% is predicted [23]. Pellenq et al. investigated the strong physisorption sites in Li intercalated graphene sheets and found that a separation of 6 Å gives the minimum adsorption energy [64]. Huang et al. showed a storage capacity of 9.43 w% in an Li decorated oxidized porous graphene [65]. Wang and Jena's study brings out that 6 Li atom decorated C60 could store upto 5wt%. Li decorated (8,0) CNTs were shown to adsorb a storage capacity of 13.45 wt% through a systematic study of Li decoration with an adsorption binding energy of 0.17 eV/H_2 [66].

Most of these studies report Li decoration and its hydrogen storage on defect free graphene and carbon nanostructures. In pure carbon nanostructures, clustering of decorated atoms is a main problem [67]. Boron doping is proved to be a promising approach for enhancing the Li binding energy and reducing the clustering [68]. Other remarkable strategies are co-doping of fluorine atom with Li atom, and application of strain in the preferred orientation [16,24]. The binding energy of the decorated metal atom can be enhanced by making defects also. In fact, experimentally prepared graphene always has defects such as single carbon atom vacancy, called mono vacancy (MV), double carbon atoms vacancy (DV), Stone-Wales defect etc [69]. These defects can be introduced in pure graphene using electron, protons or ion irradiation in controlled environments such as inside a Tunneling Electron Microscope [70]. Yadav et al. have studied the H_2 adsorption in double vacancy and Ni decorated double vacancy graphene [71]. Park and