INTERNATIONAL JOURNAL OF HYDROGEN ENERGY 39 (2014) 13189–13194

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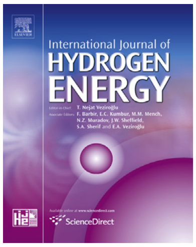

Hydrogen storage in Li dispersed graphene with Stone–Wales defects: A first-principles study

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ARTICLE INFO

Article history:
Received 7 January 2014
Received in revised form
25 June 2014
Accepted 30 June 2014
Available online 23 July 2014

Keywords:
Hydrogen storage
Stone-Wales defect
Graphene
Density functional theory
Ab initio

ABSTRACT

Li dispersed graphene with Stone–Wales (SW) defects was investigated for geometric stability and hydrogen storage capability using density functional theory (DFT) calculations. When the graphene with SW defects, which has the internal strain derived from rotated C–C bond, adsorbs Li adatoms, the strain is relieved by generating the buckling of graphene. This effect plays a crucial role in enhancing the binding energy (E_b) of Li adatoms, consequently allowing the atomic dispersion of Li adatoms on the graphene without clustering. The Li dispersed graphene with SW defects can accommodate four H_2 molecules with the range of 0.20–0.35 eV. This falls in a desirable range for feasible applications under ambient conditions. It is therefore anticipated that Li dispersed graphene with SW defects may be an ideal hydrogen storage media due to its geometric stability and high hydrogen storage capacity.

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Introduction

Hydrogen has received a great deal of interest as a promising alternative energy source in combination with the development of fuel cell technology for on-board vehicles [1,2]. However, for the development and viability of hydrogen powered vehicles, there remains a major challenge to find the appropriate storage media with high gravimetric density and modest binding energy (E_b) (0.2–0.7 eV per H_2 proposed by the U.S. Department of Energy (DOE) [3,4]. Such demands have led researchers to investigate carbon-based nanomaterials as potential hydrogen storage media due to their light weight, mechanical property, and thermal stability [5–8]. In particular, among the other types of carbon-based materials, metal-decorated graphene has been shown to be the most promising candidate for hydrogen storage media due to the high surface–volume ratio of graphene and the enhancement of the adsorption energy of H_2 by metal decoration [9–12]. However, it has been also reported that metal adatoms tend to aggregate easily instead of being atomistically dispersed owing to their strong cohesive energy [13–15]. This severely limits the hydrogen storage performance of metal-decorated graphene.

As a way to overcome such a clustering tendency, the introduction of defects such as substitutional doping and vacancy for anchoring metal adatoms has been suggested [16–20]. Because new acceptorlike states near the Fermi level can be formed in the presence of defects on the graphene, the bond strength between the metal atoms and modified graphene sheet is enhanced, and this prevents adatoms from clustering. However, excessively strong interaction between the metal adatoms and the defective graphene curtails their

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http://dx.doi.org/10.1016/j.ijhydene.2014.06.163

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hydrogen storage capacity as the charge of adatom, which is able to participate in the interaction with H_2 molecules, falls relatively short [21]. Thus, it is necessary to find an efficient and practical defective structure that can fix metal atoms on the graphene while maintaining a sufficient hydrogen storage capacity.

Recently, it has been reported that Li atom adsorbed on graphene with the Stone–Wales (SW) defect, which is formed by rotating a C–C bond by 90° with regard to the midpoint of the bond, showed slightly high E_b compared to the cohesive energy of the Li metal bulk [22]. In contrast with other point defective structures that pin metal adatoms too strongly [17,21,23], the SW defective structure showed comparatively weak bonding with metal adatoms. Thus, it can be anticipated that its ability to adsorb H_2 molecules is not hindered by the interaction between the adatoms and the defective structure. Furthermore, because the SW defect has the lowest formation energy and the highest migration energy among all the intrinsic defects in graphene [24], it is expected that the SW defect in graphene will be easily formed, and maintain its structure stably [25]. From these studies, we may conclude that the SW defective structure, easily produced from an industrial point of view, could be an effective means not only to stabilize metal atoms but also to have remarkable hydrogen storage capability.

In this paper, detailed studies of Li dispersed SW defective graphene for its potential as an efficient hydrogen storage medium were conducted. Here, the Li metal atom was adopted since Li is the lightest alkali metal atom and adsorbs H_2 molecules with the proper binding energy (E_b) range for applications at ambient conditions [26–28]. Thus, for this SW defective system, the structural stability of the Li atom on SW defective graphene was first studied and then the bonding characteristics and energetics of the H_2 molecules adsorbed on the system were systematically investigated. All studies were performed using first-principles calculations based density functional theory (DFT), known to be a suitable method for predicting the geometric stability and adsorption behavior [18].

Calculation method

DFT calculations [29] were performed using the Vienna *ab initio* simulation package (VASP) code [30]. Projector-augmented waves(PAW) [31] were used to describe the ion cores, and the exchange–correlation interactions were expressed with a generalized gradient approximation (GGA) in the form of the Perdew, Burke, and Ernzerhof (PBE) functional [29]. Here, the effect of the van der Waals (vdW) interactions was included explicitly by using the empirical correction scheme of Grimme's DFT-D2 method [32], as implemented by Bucko et al. for periodic systems [33]. The plane-wave basis set was expanded to a cutoff energy level of 500 eV. All of the self-consistent loops were iterated until the total energy difference of the systems between the adjacent iterating steps was less than 10^{-5} eV. The calculations were performed with a Γ-point centered (4 × 4 × 1) *k*-point generated by the Monkhorst-Pack scheme [34]. The effective range of the cutoff energy and the validity of the mesh density used in this calculation were determined by a convergence test using the theoretically estimated lattice constants of the pristine graphene, 2.464 Å. Ionic relaxation was executed with the conjugate gradient method. The constituent atoms in the Li dispersed SW defective graphene systems were fully relaxed until the maximum Hellmann-Feynman forces were in the range of $\hat{A} \pm 0.01$ eV $Å^{-1}$. The electronic structure was calculated using the Gaussian-smearing method with a width of 0.1 eV. To simulate the Li dispersed graphene with SW defects, a 4 × 4 supercell that contains 32 carbon atoms with an interlayer distance of 20 Å was chosen.

Results and discussion

The structural properties of graphene with SW defects were first investigated compared to those of pristine graphene. This defect was obtained by optimizing the structure after rotating the C1–C2 bond of graphene by 90° with regard to the midpoint of the bond as shown in Fig. 1. In contrast to other vacancy defects, graphene with SW defects has considerable internal strain induced by the bond rotation. As described in Fig. 1(b), the rotated defect core bond length is compressed to 1.301 Å, which is much shorter than the bond length of pristine graphene (1.426 Å). Based on this noticeable structural change, internal compressive strain occurs along the zig-zag direction of graphene, whereas elongation of the bond lengths was observed along the armchair direction of graphene. From these results, it is supposed that this unstable defective structure itself has the strong reactivity with metal adatoms.

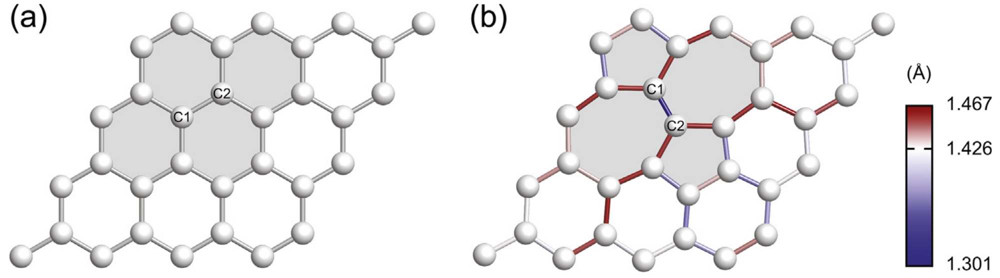

Fig. 1 – The optimized structures of graphene 4 × 4 supercell (Top view): (a) pristine graphene, (b) SW defective graphene, where gray balls represent the carbon atoms and two carbon atoms placed at the SW defects core are labeled by C1 and C2. C–C bond lengths of SW defective graphene are distinguished by color of the bond as described in scale bar. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).

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