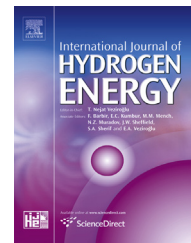


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Electric field induced enhancement of hydrogen storage capacity for Li atom decorated graphene with Stone-Wales defects

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ABSTRACT

The density functional theory calculations are carried out to investigate the enhancement of the hydrogen storage ability induced by the electric field (E-field) vertical to the surface of the Li atom decorated graphene with Stone-Wales defects. When without E-field, the binding energy (E_b) of the Li atoms to the hollow site of the heptatomic ring is 2.89 eV, which is larger than that at the hollow sites of the hexatomic ring and the pentatomic ring, indicating the Stone-Wales defect on the graphene surface can effectively enhance the binding strength of the Li atom. When the upward +0.01 au E-field is imposed, the E_b of the Li atom on the hollow site of the heptatomic ring increases to 3.41 eV, which is larger than the double of the experimental cohesive energy of bulk Li (1.63 eV), consequently allowing the dispersion of Li atoms without clustering, which is the basis for large amount hydrogen storage. The maximum number of H_2 molecules adsorbed by each Li on the surface of the SW defective graphene under the upward 0.01 au E-field is 5, one more than that without E-field. The average adsorption energies of molecular hydrogen around Li in the presence of upward 0.01 au E-field are in the range of 0.21–0.46 eV, which are larger than that in the field-free case and intermediate between physisorbed and chemisorbed states (0.1–0.6 eV). The SW defective graphene adsorbs hydrogen molecules mainly through the polarization interaction. The calculated desorption temperature and molecular dynamic simulation indicate that the H_2 molecules are easier to be desorbed under the downward E-field. Therefore, the Li decorated graphene with SW defects is appropriate for hydrogen storage under near-ambient conditions with the application of an E-field. Keeping five H_2 molecules adsorbed per Li and stabilizing the dispersion of individual Li atoms under the upward E-field, the structure can serve as better building blocks of polymers. These findings suggest an effective route to control the hydrogen storage abilities of nanomaterials.

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Introduction

Hydrogen is a kind of clean energy and an alternative candidate for the synthetic fuel because it is environmental friendly, lightweight and high abundant. The most difficult challenge is to find materials that can store hydrogen with large hydrogen gravimetric density (HGD). The target for the ideal hydrogen storage materials suggested by the Department of Energy of America is that the HGD should reach 5.5 wt % by the year 2017 [1,2]. In addition, the hydrogen storage materials with the average hydrogen adsorption energy (E_{ad}) for molecular hydrogen in the range of 0.1–0.6 eV can realize the reversible storage for hydrogen under near-ambient conditions [3].

The carbon-based nanomaterials such as carbon nanotubes [4], fullerenes [5], and graphene [6] have been widely studied as one kind of the most promising hydrogen storage materials because of their chemical stabilities and high surface area. Due to the simple van der Waals interaction dominates the adsorption of hydrogen molecules to the surface of pure carbon nanomaterials, the carbon surfaces cannot store hydrogen efficiently [7–9]. However, decorating carbon surfaces with metal atoms has recently been proposed to improve their hydrogen storage abilities. The atoms include transition metals [10–12], alkaline metals [13,14], and alkaline earth metals [15]. For example, the transition metal Ti coated graphene nanoribbons could effectively store hydrogen with the HGD of 6 wt% [16]. The HGD of the Li decorated two dimensional carbon allotropes could up to 7.12 wt% [17]. The Li atoms coated BN sheet could take over 12.2 wt% H_2 molecules [18]. Since metal atoms tend to form clusters on the surfaces of nanostructures, consequently the hydrogen storage capacity drops dramatically. Therefore, the binding energy (E_b) of the metal atom to the substrate should be larger than the experimental cohesive energy of bulk metal [19]. As reported, the alkaline metal lithium is known as the smallest and lightest metal and will help to introduce more H_2 molecules in the larger space and increase the HGD. Recently, it has been reported that the E_b for the Li atom to the graphene with the Stone-Wales (SW) defects, which is formed by rotating a C–C bond by 90° with regard to the midpoint of the C–C bond, is 2.16 eV, only 0.53 eV higher than the experimental cohesive energy of bulk Li (1.63 eV) [20]. Thus, in order to effectively avoid the clustering of the Li atoms on the surface of graphene, some approaches should be proposed to enhance the binding strength between Li and graphene.

It has been reported that applying an electric field (E-field) vertical to the substrate should be a good method to improve the E_b of the metal to the graphene [21]. Comparing with other approaches, E-field has many advantages for practical applications, such as clean, easily available, and adjustable in both direction and intensity [22]. Particularly, graphene can exhibit a prominent response to the external perpendicular E-field due to its high electric transferring behaviors [23]. For example, Zhang et al. [24] have pointed out that when a single H_2 is adsorbed on a BCN sheet, the E_{ad} of the H_2 molecule increased to 0.51 eV under the 0.035 au E-field. Each Ca atom of the Ca-silicene system could adsorb nine H_2 molecules with the E_{ad} of 0.37 eV in the upward 0.004 au E-field, much larger

than the 0.19 eV in the field-free case [25]. Liu et al. [26] have reported that the application of upward E-field vertical to the surface of the Li coated single-layer and bilayer graphenes could result in the E_b increased by 88%. Experimentally, Shi et al. [27] have demonstrated that the E_{ad} of hydrogen on the carbonaceous sorbent supported by Pt could be enhanced under an upward E-field. So, when the Li atom is chosen to decorate the planar nanostructures, the higher E_{ad} for H_2 can be obtained under the upward E-field.

In order to further increase the binding strength between the Li atom and the SW defective graphene, we add an E-field perpendicular to the surface. Therefore, the enhanced hydrogen adsorption abilities of the Li decorated graphene with SW defects induced by the perpendicular upward E-field can be expected. The next of the paper is organized as follows. Section Computational details shows the computational details. In Section Results and discussion, we present the results and discussions. The conclusion is given in Section Conclusions.

Computational details

In this paper, all calculations are performed using the density functional theory (DFT) [28] as implemented in the DMol³ code [29]. The generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional [30] is used in our calculations in combination with the van der Waals correction (standard DFT computations with empirical pair potentials, namely, DFT-D). It is well known that the PBE/GGA with the Grimme method considered for the long range dispersion correction can generate remarkable hydrogen adsorption energies for many hydrogen storage systems [31–36], such as the H_2 adsorbed Pd-graphene [37], $C_{60}Ca_{32}-62H_2$ [38] and so on. Therefore, the approximate semi-empirical DFT-D correction scheme proposed by Grimme (PBE-Grimme [33]) is considered in our calculations.

The double-numerical basis sets includes polarization functions (DNP) is employed [37]. All atoms in the structures are allowed to relax without any constraints. Here, the all electron method is used for Li, C, and H. The self-consistent field procedure is done with a convergence criterion of 10^{-5} Hartree on the electron density. [1 Hartree = 27.21 eV] The convergence tolerances are 10^{-5} Hartree for the energy, 2×10^{-3} Hartree/Å for the force, and 10^{-4} Å for the atomic displacement in the optimization. Finally, the natural bonding orbital (NBO) charges are computed to obtain the electronic configurations of all the structures [38–40]. Since the localized natural atomic orbitals can be used to describe the electron density, thus, the NBO charges are much more reliable and can obviously work very well for many structures [39–41]. The ground-state structures are determined by their minimal energies, which are further verified by no imaginary frequency in their harmonic frequency calculations [42]. All the calculations use the 4×4 unit cell of graphene to simulate the infinite graphene sheet. The interlayer distance is set to be 20 Å, which is enough to minimize the artificial interlayer interaction. The external E-field is applied along the Z direction and varies from -0.01 au to $+0.01$ au. [1 au of E-field = 51.40 V/Å].

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