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# 1 Lithium-decorated oxidized porous graphene for hydrogen storage 2 by first principles study

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7 The first-principles calculations are performed to investigate the geometric stability and the hydrogen  
8 storage capacity of lithium-decorated oxidized porous graphene (PG). Due to strong interaction  
9 between Li and O atom, two stable Li decorated structures have relatively high Li binding energies  
10 of 3.84 and 3.04 eV, which could eliminate the clustering problem for Li atoms on PG surface. One  
11 doped Li atom could hold five H<sub>2</sub> molecules and the binding energy of each H<sub>2</sub> is above 0.2 eV. The  
12 interaction of H<sub>2</sub> molecules with Li atom results from charge exchange between H<sub>2</sub>'s  $\sigma$  orbital and  
13 Li's 2s orbital. In the final structure with two Li-O groups in one carbon pore, a hydrogen storage  
14 capacity of 9.43 wt. % could be achieved. By the combination of the advantage of Li decoration and  
15 oxidized porous graphene, Li-OPG possesses remarkable geometric stability and high hydrogen  
16 storage capacity. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4770482>]

## 17 I. INTRODUCTION

18 Hydrogen energy is believed to be a promising energy  
19 source because it is abundant and environmental friendly. In  
20 searching for an ideal H<sub>2</sub> storage medium with high gravi-  
21 metric and volumetric density operating at ambient condi-  
22 tions, a plenty of metal-decorated nanostructures have been  
23 proposed to serve as hydrogen sorbents.<sup>1-4</sup>

24 In these materials, metal atoms distributed on the sur-  
25 face of nanostructures are assumed to be the H<sub>2</sub> adsorbing  
26 centers. To adsorb and desorb H<sub>2</sub> molecule under moderate  
27 temperature and pressure, the suitable H<sub>2</sub> binding energy  
28 should be in the range of 0.2–0.6 eV/H<sub>2</sub>.<sup>5</sup> The transition met-  
29 als, such as Ti<sup>6-8</sup> and Fe,<sup>9</sup> were first tried to serve as doping  
30 metal on the nanostructure. It is proved that they have a  
31 Kubas interaction with H<sub>2</sub> molecules.<sup>10</sup> However, this inter-  
32 action seems to be excessively strong, since the H<sub>2</sub> binding  
33 energy is above 0.6 eV and the H-H bond breaks up. Aside  
34 from transition metals, alkaline metals<sup>11-14</sup> and alkaline  
35 earth metals<sup>15-19</sup> tend to adsorb H<sub>2</sub> molecules through a  
36 moderate interaction with H<sub>2</sub> binding energy around 0.2 eV,  
37 in which H<sub>2</sub> remains in molecule form. According to the pre-  
38 vious calculations,<sup>20-22</sup> a calcium atom could hold up to four  
39 H<sub>2</sub> molecules around, and the moderate interaction with av-  
40 erage H<sub>2</sub> binding energy around 0.2 eV (GGA value) permits  
41 H<sub>2</sub> recycling at ambient conditions. Except the similar bind-  
42 ing mechanism of H<sub>2</sub> molecule, lithium has a more advant-  
43 age of the smallest atomic mass to achieve higher  
44 gravimetric hydrogen storage density. Furthermore, the co-  
45 hesive energy of Li is substantially smaller than those of  
46 transition metals.<sup>23</sup> Thus, Li atoms are not likely to form  
47 clusters because of the repulsion between Li atoms induced  
48 by remaining positive charge of each lithium atom.

49 On the other hand, an appropriate nanostructure should  
50 be chosen to fixate the decorating metal steadily with high

density. So far, a lot of nanostructures, including nanotube,<sup>24-30</sup>  
graphene,<sup>31-36</sup> fullerene,<sup>37-40</sup> metal organic framework,<sup>41-46</sup>  
small organic molecules,<sup>47,48</sup> etc., have been studied. The  
metal binding energy is an important criterion to measure  
nanostructure's ability to fix metal atom. Sun *et al.*<sup>37</sup> pro-  
posed a Li<sub>12</sub>C<sub>60</sub> structure bonding Li atom to every pentago-  
nal face of C<sub>60</sub> fullerene. In a lithium doped graphene  
structure proposed by Ataca *et al.*,<sup>31</sup> metal binding energy is  
1.93 eV and 0.86 eV with a minimum Li-Li distance of  
9.77 Å and 4.92 Å, respectively. Li<sub>12</sub>Si<sub>60</sub>H<sub>60</sub> composite has  
been proposed to study the hydrogen adsorption ability.<sup>49</sup>

Recently, porous graphene (PG), a regular 2D polyphen-  
ylene networks with single atom wide pores and sub  
nanometre periodicity, have successfully fabricated of by  
surface-assisted coupling of specifically designed molecular  
building blocks.<sup>50</sup> PG could be also considered as a defect  
graphene sheet with repeat missed carbon ring that is termi-  
nated by hydrogen bonds. As well as the experimental inves-  
tigations,<sup>51</sup> there were several theoretical works which  
studied the electronic properties,<sup>52</sup> gas separation,<sup>53</sup> and  
hydrogen storage<sup>54</sup> of PG. Du *et al.*<sup>55</sup> have studied the  
hydrogen storage capacity of Li doped porous graphene.

In this work, we designed a novel hydrogen storage  
material named lithium-decorated oxidized porous graphene  
(Li-OPG), based on the experimentally prepared porous gra-  
phene. In Li-OPG structure, lithium atom is expected to have  
a stronger interaction with oxygen than with carbon atom.  
Furthermore, it is able to achieve higher hydrogen storage  
density, because of the lower density of porous graphene  
than that of normal graphene, and the carbon pore in the po-  
rous graphene providing more space for lithium atoms and  
H<sub>2</sub> molecules. To validate the feasibility of Li-OPG, the fol-  
lowing three issues must be addressed. First, is the Li-OPG  
structure stable enough for practical synthesis? Second, how  
many H<sub>2</sub> could one Li atom adsorbed and what is the binding  
mechanism? Third, is the hydrogen storage capacity satisfy-  
ing? We studied these questions by first principle  
calculations.

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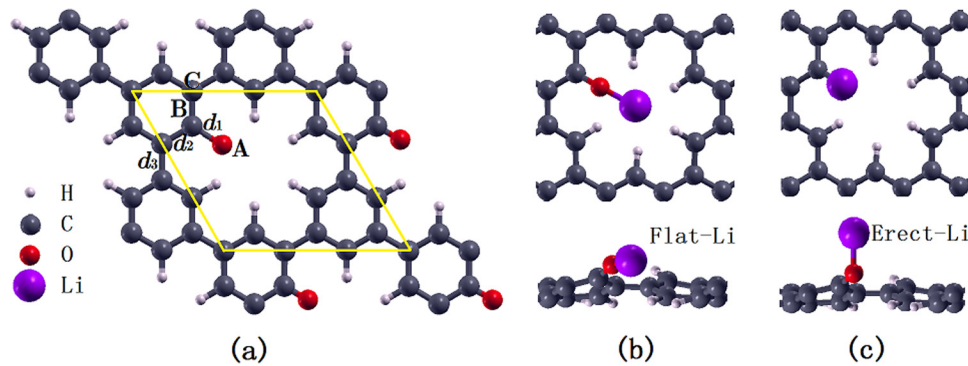


FIG. 1. (a) OPG structure; (b) and (c) top view and side view of two Li-OPG structures.

## 89 II. COMPUTATIONAL METHODS

90 All calculations were carried out by SIESTA code<sup>56</sup> with  
 91 the framework of density function theory (DFT).<sup>57,58</sup> General-  
 92 ized gradient approximation described by Perdew-Burke-  
 93 Ernzerhof (PBE)<sup>59</sup> was chosen as the exchange correlation  
 94 potential, and the Troullier-Martins scheme norm-conserving  
 95 pseudopotentials<sup>60</sup> was employed to represent the interaction  
 96 between localized pseudoatomic orbitals and ionic cores. The  
 97 double- $\zeta$  basis set was adopted to ensure a good computa-  
 98 tional convergence. The energy cutoff was 150 Ry. The  
 99 Brillouin zone sampling was performed using a Monkhorst-  
 100 Pack special  $k$  points grid.<sup>61</sup> All structures were fully relaxed  
 101 with the force on each atom less than 0.05 eV/Å. The lattice  
 102 constants  $a$  and  $c$  of hexangular  $3 \times 3 \times 1$  supercell are  
 103 7.38 Å and 22.14 Å, respectively. The  $c$  parameter of the  
 104 supercell was designed to be large enough to render the inter-  
 105 action between the layer and its periodic image negligible.

## 106 III. RESULTS AND DISCUSSION

### 107 A. Li-OPG structure

108 First of all, we constructed OPG structure based on the  
 109 experimentally prepared porous graphene, by replacing a  
 110 hydrogen atom with an oxygen atom, as shown in Fig. 1(a).  
 111 Like the relationship of graphene and graphene oxide, here  
 112 oxidized porous graphene is constructed by introducing the  
 113 oxygen atoms to the porous graphene, which is expected to re-  
 114 ally in an oxidation process. Furthermore,  
 115 we will discuss the different oxidation  
 116 sites on PG structure (sites A, B, and C in Fig. 1). The com-  
 117 parison of total energy ( $-2368.99$ ,  $-2365.78$ ,  $-2363.94$  eV,  
 118 respectively) of these three configurations shows that the site  
 119 A is most favorable for oxygen atom adsorption, and this  
 120 OPG structure has been chosen for following Li atoms and  
 121  $H_2$  molecules adsorption. Then Li-OPG structure was formed  
 122 by adsorbing a Li atom on the OPG surface near oxygen  
 123 atom, and two stable Li adsorption sites noted as Flat-Li and  
 124 Erect-Li are shown in Figs. 1(b) and 1(c).

125 In the relaxed OPG structure, the carbon plane tends to  
 126 curve a little after oxidizing rather than staying smooth as  
 127 porous graphene does. In Fig. 1(a), the distance  $d_1$  (1.46 Å)  
 128 between oxygen and carbon atoms is very close to that in  
 129 other C=O molecules (about 1.43 Å), which means a strong  
 130 covalent C=O bond has formed here. The calculated C-C  
 131 bond lengths  $d_2$  (1.40 Å) and  $d_3$  (1.38 Å) are also close to the  
 132 original C-C bond (1.42 Å) in graphene, and almost equal to

that in original porous graphene terminated by hydrogen  
 bonds, indicating that this oxygen atom replacing hardly  
 affect the adjacent carbon structure. For the Li-OPG model,  
 there are two stable Li adsorbing structures, in which the dis-  
 tance between Li atom and O atom are both 1.70 Å. This  
 bond is relatively shorter than other Li doped structure,  
 indicating a stronger interaction between Li and O. For con-  
 venience, we denoted these two structures as Flat-Li and  
 Erect-Li afterwards, as the Li-O bonds are parallel and per-  
 pendicular to the carbon plane, respectively.

To characterize the stability of Li adsorbing on  
 OPG, the binding energy of Li atom was calculated as  $E_{MB}$   
 $= E_{Li-OPG} - E_{OPG} - E_{Li}$ . Here,  $E_{Li-OPG}$  and  $E_{OPG}$  are the  
 energies of relaxed Li-OPG and OPG structures, respec-  
 tively.  $E_{Li}$  is the energy of a free Li atom. As a result,  $E_{MB}$  of  
 Flat-Li and Erect-Li turn out to be 3.84 eV and 3.04 eV. To  
 figure out the cause of the  $E_{MB}$  difference, we calculated the  
 charge transfer of Li-OPG structure. The Mulliken charge  
 analysis indicates that Li becomes positively charged by  
 donating 0.319 and 0.433 electrons to O and H bonded to C  
 atoms, respectively. The O and H atoms bonded to C atoms  
 possess charge of around  $-0.2 |e|$ . It is reasonable that the  
 neighboring negatively charged H atoms attract the posi-  
 tively charged Li atom. Therefore, Flat-Li has a higher  $E_{MB}$ .  
 It should be noted that the calculated  $E_{MB}$  are much higher  
 than the Li bulk binding energy (1.6 eV).  
 keep away from each other with a nearest neighbor distance  
 which means doped Li atoms are uniformly distributed in the  
 structure. In addition, we calculated the binding energy of  
 porous graphene to be 1.08 eV (DFT calculation).  
 value to be 1.81 eV based on LDA<sup>55</sup>. Compared to the  $E_{MB}$   
 of Li doped graphene and  $Li_{12}C_{60}$ , which was demonstrated  
 to be 1.93 (LDA)<sup>31</sup> and 1.78 eV (GGA),<sup>37</sup> the  $E_{MB}$  of Li-  
 OPG is significantly higher (Table I).

### 166 B. Hydrogen binding energy of Li-OPG

167 First, we investigated the adsorption of one  $H_2$  molecule  
 168 to the Li atom of Li-OPG structure. Similarly, hydrogen

TABLE I. The distance between Li and O  $d_{Li-O}$ , the Li binding energy  $E_{MB}$ , the charge of Li  $Q_{Li}$  and the charge of O  $Q_O$  of two Li-OPG structures.

	$d_{Li-O}/\text{Å}$	$E_{MB}/\text{eV}$	$Q_{Li}/ e $	$Q_O/ e $
Flat-Li	1.70	3.84	+0.319	-0.125
Erect-Li	1.70	3.04	+0.433	-0.170



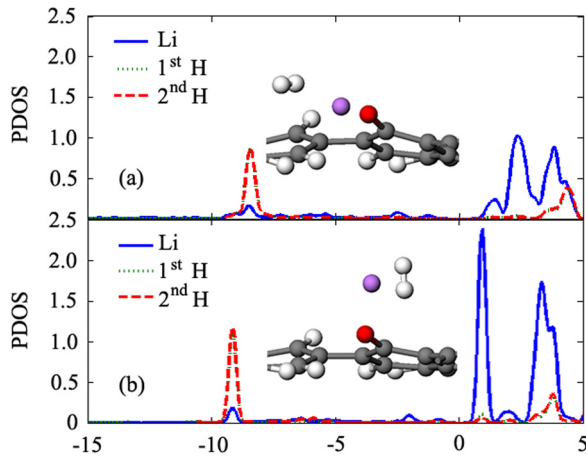


FIG. 2. (a) PDOS of one H<sub>2</sub> molecule adsorbed Flat-Li system; (b) PDOS of one H<sub>2</sub> molecule adsorbed Erect-Li system.

169 binding energy is calculated as  $E_{\text{Hb}} = (E_{\text{H-Li-OPG}} - E_{\text{Li-OPG}} - E_{\text{H}})$ . Here  $E_{\text{H-Li-OPG}}$  and  $E_{\text{Li-OPG}}$  are the energies of relaxed H-Li-OPG and Li-OPG structures, respectively.  $E_{\text{H}}$  is the energy of a H<sub>2</sub> molecule. These two relaxed structures are shown as insets in Figs. 2(a) and 2(b). And  $E_{\text{Hb}}$  along with length of H-H bond and distance from metal atom to H<sub>2</sub> molecule are shown in Table II. As we could see,  $E_{\text{Hb}}$  of Erect-Li structure is much higher than that of Flat-Li structure. Besides, Erect-Li has a longer H-H length and shorter distance between Li and H<sub>2</sub> molecule. According to the charge analysis, Li atom in Erect-Li has a larger positive charge. Therefore, the Li atom is changed to the partial density of states (PDOS) emptier and provide more room for H<sub>2</sub>.

182 To further probe the interaction nature between decorated Li atom and H<sub>2</sub> molecule, PDOS of Li 2s orbital and two H atoms' 1s orbital were shown in Fig. 3. Li atom's 2s orbital has a slight overlap with  $\sigma$  bond of H<sub>2</sub> molecule at 9 eV lower than Fermi Energy. This proves that Li atom's empty 2s orbital exchanges electrons with  $\sigma$  bond of H<sub>2</sub> molecule. Here, the 1st and 2nd hydrogen all belong to the first adsorbing H<sub>2</sub> molecule, and these two distances between hydrogen and Li atom are almost equal with each other after the structure relaxation. So, the interactions of two H atoms with Li atom and corresponding PDOS are very similar. Furthermore, the overlap peak in Figs. 3(a) and 3(b) was compared. We found that the overlap peak is higher in Erect-Li structure. It is indicated that the interaction between Li and H<sub>2</sub> molecule is much stronger in Erect-Li system. Thus, it explains for the higher  $E_{\text{Hb}}$  in Erect-Li system.

TABLE II. The H<sub>2</sub> binding energies  $E_{\text{Hb}}$  and the distances between H<sub>2</sub> and Li  $d_{\text{H-Li}}$  of the 1st to 6th H<sub>2</sub> molecule on two Li-FOPG structures.

$N_{\text{H}_2}$	$E_{\text{Hb}}/\text{eV}$		$d_{\text{H-Li}}/\text{\AA}$	
	Flat-Li	Erect-Li	Flat-Li	Erect-Li
1	0.32	0.59	2.02	1.97
2	0.30	0.54	2.02	2.03
3	0.30	0.32	2.38	2.15
4	0.27	0.27	2.23	2.20
5	0.22	0.21	3.13	2.13
6	0.06	0.05	3.53	2.56

198 Next, more H<sub>2</sub> molecules were added one by one to these two Li-OPG structures to determine their hydrogen absorption abilities, as displayed in Fig. 3. The calculated  $E_{\text{Hb}}$  of the 1st to 6th H<sub>2</sub> molecules were listed in Table II. From the 1st to the 5th H<sub>2</sub> molecule,  $E_{\text{Hb}}$  of Flat-Li system decreases slowly from 0.32 eV to 0.22. The moderate interaction of Li atom and H<sub>2</sub> molecule is similar with the calcium case with H<sub>2</sub> binding energy around 0.2 eV (GGA value).<sup>20</sup> While in Erect-Li system,  $E_{\text{Hb}}$  of the first two H<sub>2</sub> molecules are above 0.5 eV but drops significantly to the same magnitude as that of Flat-Li system from the third H<sub>2</sub> molecule. At the same time, the distance from Li to H<sub>2</sub> increases as  $E_{\text{Hb}}$  decreases. Interestingly,  $E_{\text{Hb}}$  of the 6th H<sub>2</sub> molecule in these two systems falls down simultaneously to around 0.05 eV, which is much lower than 0.2 eV. Thus, one Li atom in these two Li-OPG structures could adsorb a maximum number of five H<sub>2</sub> molecules.

215 We also compared our results to that of other carbon nanostructure based hydrogen storage materials. As Sun *et al.*<sup>37</sup> reported, the total interaction energy of 60 H<sub>2</sub> molecules with Li<sub>12</sub>C<sub>60</sub> is 4.5 eV, which means the average binding energy of 0.075 eV/H<sub>2</sub> molecule (GGA). In the case of Li doped graphene, reported by Ataca *et al.*,<sup>31</sup> four H<sub>2</sub> molecule could be absorbed by Li atom effectively, and the binding energies of the four H<sub>2</sub> are 0.05 eV, 0.41 eV, 0.18 eV, and 0.19 eV (LDA), respectively. Relatively, Li-OPG has a higher hydrogen binding energy. What is more, we also calculated the average  $E_{\text{Hb}}$  of Li doped porous graphene. It turned out to be 0.29 eV, which is comparable to that of Li-FOPG. Since Li-FOPG has a higher  $E_{\text{Mb}}$ , it is apparently more advisable.

### C. Hydrogen storage capacity of Li-OPG

230 So far, the calculations lead to the conclusion that one Li atom could adsorb five H<sub>2</sub> molecules. And next, we demonstrated that two Li-O groups could exist stably in one carbon pore. Three configurations of Flat-Li and six configurations of Erect-Li with two oxygen atoms in the same missing ring are considered as shown in Fig. 4. The total energies of these structures depend on the oxygen atom places and Li adsorption sites, and the relative values  $\Delta E$  are also listed. The three configurations of Flat-Li with lower relative energies about 1.5–2.5 eV are chosen to calculate the hydrogen storage capacity. In these structures shown in

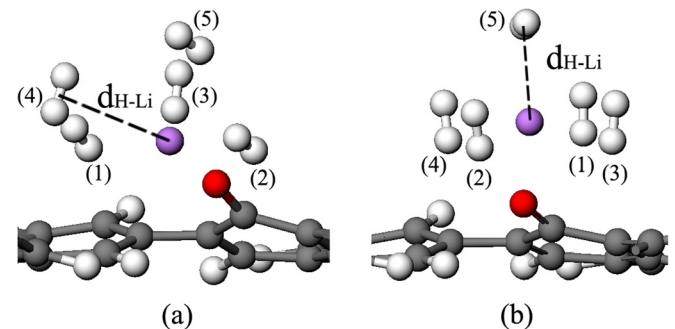


FIG. 3. (a) Side view of Flat-Li structure adsorbing five H<sub>2</sub> molecules; (b) side view of Erect-Li structure adsorbing five H<sub>2</sub> molecules.

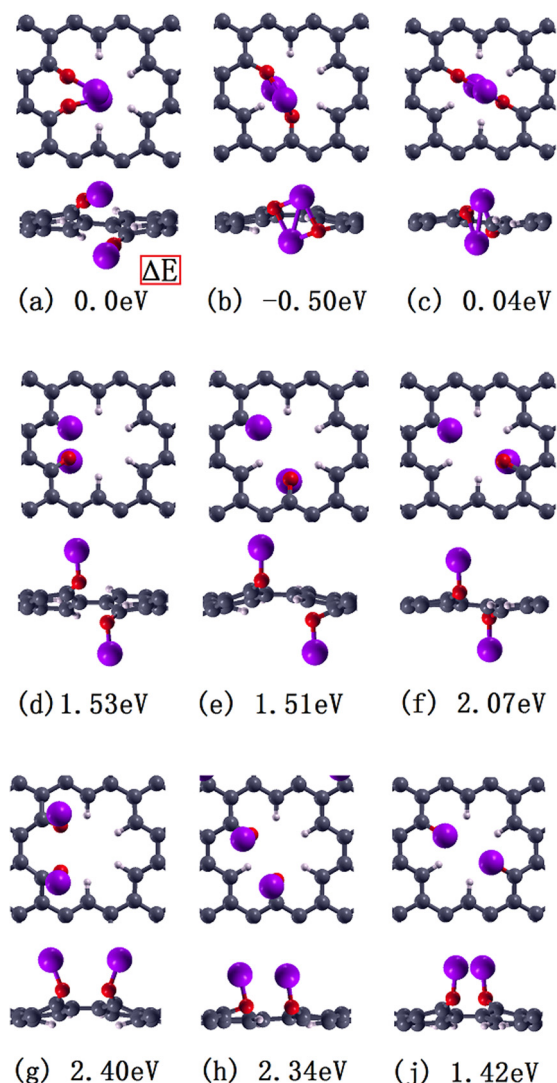


FIG. 4. Decorated OPG structures with two Li atoms, (a)-(c) three configurations of Flat-Li and (d)-(j) six configurations of Erect-Li, the value is relative total energy  $\Delta E$ .

241 Fig. 4, Li atoms remain separate instead of clustering.  
 242 Because Li atoms are positively charged by O atom, they  
 243 tend to repel each other due to the charge repulsion.

244 Since the two Li atoms are adsorbed on different sides  
 245 of OPG at each configuration, the interactions between these  
 246 Li atoms are small. The sufficient space of missed carbon  
 247 ring ensures the five  $H_2$  molecules adsorbing near each Li  
 248 atom like the single Li atom case, as shown in Fig. 5. The  
 249 average binding energies of  $H_2$  molecules are 0.25–0.32 eV.  
 250 We also calculated the binding energies (0.15–0.20 eV) of  
 251 fifth  $H_2$  molecules at these situations, and found appropriate  
 252 adsorptions could be expected for these 5th  $H_2$  molecules. It  
 253 should be noted that the hydrogen storage densities of these  
 254 Li-OPG structures all reach 9.43 wt. %. It is much higher  
 255 than the criteria (6 wt. %) set for on board application.

#### 256 IV. CONCLUSIONS

257 By performing first principles calculations, we have  
 258 demonstrated that lithium-decorated oxidized porous gra-  
 259 phene is a promising hydrogen storage material. It is remark-

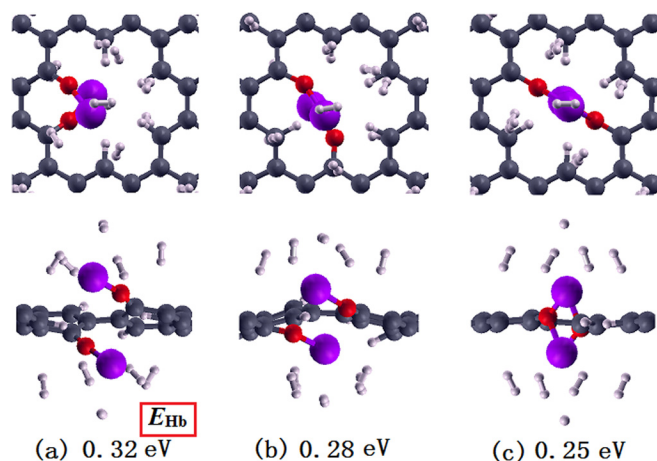


FIG. 5. (a)-(c) Three kinds of double-Li system and corresponding average  $H_2$  binding energies.

able that Li-OPG possess a Li binding energy above 3 eV. 260  
 This large metal binding energy is very important in avoid- 261  
 ing metal clustering. One Li atom in Li-OPG could adsorb 262  
 five  $H_2$  molecules. The adsorption of  $H_2$  on Li atom origi- 263  
 nates from slight charge exchange between 2s orbital of Li 264  
 atom and  $\sigma$  bond of  $H_2$  molecule. Finally, it was shown that 265  
 Li-OPG structure with two Li-O groups in one carbon pore 266  
 could reach storage capacity of 9.43 wt. %. 267

It should be noted that the high ideal value about 9.43% 268  
 profits from the combined contributions of light mass of Li 269  
 atom and sparse structure of OPG with sufficient space for  $H_2$  270  
 adsorption. The hydrogen storage capacity strongly depends 271  
 on density of missing rings and Li atoms in Li-OPG model 272  
 almost proportionally. Theoretically, a perfect repeated oxy- 273  
 gen atom replacing will induce a regular Li adsorption at each 274  
 missing rings, and a maximal hydrogen storage capacity was 275  
 given. Of course, this theoretical limit will be hard to reach, 276  
 especially considering many uncertain factors though the ex- 277  
 perimental preparation. As porous graphene has been success- 278  
 fully synthesized, there is hope to obtain Li-OPG and apply it 279  
 into hydrogen storage in the future. 280

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