

Multifunctional Porous Graphene for Nanoelectronics and Hydrogen Storage: New Properties Revealed by First Principle Calculations

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The discovery of single layer graphite or graphene has opened up exciting opportunities for the design of novel electronic devices and interconnects¹ due to its unique electronic properties.² Among them, the use of making a truly tiny transistor offers much hope for making faster, smaller electronics devices once silicon reaches its limits.³ However, the lack of an obvious “band gap” is a formidable problem that hinders the practical application of graphene-based nanoelectronics.⁴ In the area of clean energy, graphene doped with Li atoms has been predicted to be a promising candidate for hydrogen storage.⁵ Li-doped graphene is expected to be superior to a Li-doped carbon nanotube because both sides might be readily utilized to ensure efficient hydrogen storage.^{5,6} However, with a high coverage of Li atoms on graphene, the adsorption of hydrogen will be significantly weakened by the strong electrostatic interaction between Li cations.⁵

Most recently, Bieri et al. have for the first time succeeded in synthesizing a well-defined porous graphene.^{7,8} With the insertion of holes of specific size and distribution into graphene sheets, the electronic structure is expected to be greatly modified. Additionally, the separation of Li dopants on porous graphene is expected to be large (4.23 Å) compared to that on Li-doped graphene and hence the electrostatic interaction between Li cations should be lower, leading to enhanced adsorption of hydrogen molecules. Moreover, the hydrogen storage capacity may also be significantly increased.⁵

In this communication, we report a series of calculations to explore (1) whether the creation of porous graphene may open a band gap and (2) whether hydrogen storage performance in Li-decorated porous graphene can be greatly improved compared to that in Li-doped graphene. Remarkably, we find that porous graphene has a direct gap (3.2 eV), which is similar to that of TiO₂ and graphitic C₃N₄ materials with high photocatalytic activities.⁹ Importantly, the adsorption energy of hydrogen on Li-decorated porous graphene is 0.26 eV on average (0 K), which is much closer to the optimal adsorption enthalpy (−0.155 eV) at ambient conditions.¹⁰ Additionally, the adsorption energy of the first hydrogen molecule is at least 50% larger than that in Li-doped graphene as reported by all the existing studies.⁵ Our results predict porous graphene to be a promising optical and hydrogen storage material for nanoelectronics and clean energy application.

First, we will explore the electronic structure of porous graphene by using the plane-wave basis VASP code¹¹ implementing the projector augmented wave method.¹² Figure 1a and 1b present the optimized geometry and band structure for porous graphene based on the local density approximation (LDA).¹³ The lattice constant is calculated to be 7.45 Å, which is in good agreement with the experimental value.⁶ The LDA calculations predict a direct gap of

2.34 eV. It is well-known that LDA underestimates the band gap and hybrid functionals such as HSE06¹⁴ are better able to predict experimentally measured band gaps with high accuracy. Figure 1c presents the calculated band structure for porous graphene using the HSE06 functional. Clearly, valence bands have similar dispersions for both the LDA and HSE06 functional calculations, but the conduction band minimum computed with the hybrid functional is shifted to higher energy relative to the Fermi level. The band gap is increased to 3.2 eV, i.e. in the range of UV light. This is comparable to TiO₂ and graphitic C₃N₄ materials, which have shown potential application in photocatalyzed splitting of water into hydrogen.⁹ These results suggest that porous graphene may solve the obvious “band gap” problem of graphene for nanoelectronics applications and display a photocatalytic activity similar to those of TiO₂ and graphitic C₃N₄ materials.

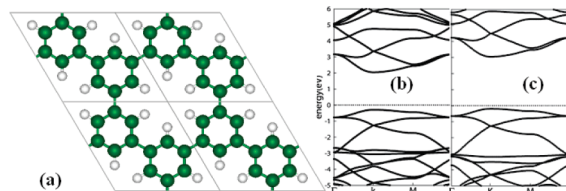


Figure 1. (a) Optimized geometry for 2D porous graphene (dark atoms C and light atoms H). Calculated band structures are shown based on LDA (b) and HSE06 (c) exchange correlation functional, respectively. The dotted line at zero indicates the Fermi level.

We now turn to examine the adsorption of Li atoms on porous graphene. Similar to graphene,⁵ we find the hexagonal center is still the most energetically favorable adsorption site for a Li atom on porous graphene. However, the adsorption energy (−1.81 eV) for a Li atom onto porous graphene (7.45 Å × 7.45 Å) is much stronger than that (−0.86 eV) on a (2 × 2) graphene (5.92 Å × 5.92 Å).⁵ It is however very close to that (−1.65 eV) on a (3 × 3) graphene (7.38 Å × 7.38 Å). Clearly, this effect may therefore be attributed to the natural separation of Li adsorption sites on porous graphene, which avoids strong electrostatic interactions between the Li cations. To examine (and discount) the likelihood of Li clustering, we computed the adsorption of a second Li atom onto porous graphene in a large (3 × 3) supercell (22.35 Å × 22.35 Å) and found that it adsorbs preferentially on another hexagonal center, which can be understood by the fact that the cohesive energy of bulk Li (−1.795 eV per Li atom)¹⁵ is very close to the calculated Li atom adsorption energy.

Figure 2a presents the adsorption energies and optimized geometries for first, second, third and fourth hydrogen molecules around the adsorbed Li atom on porous graphene. In contrast with previous studies on Li-doped graphene,⁵ the adsorption energy for the first hydrogen molecule is calculated to be as high as −0.265

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eV and the H–H bond length was elongated to 0.80 Å. Interestingly, the adsorption energies for the second and third hydrogen molecules remain nearly unchanged (−0.27 and −0.256 eV, respectively). There is a sudden drop (−0.206 eV) for the fourth hydrogen molecule due to the strong steric interaction between the adsorbed H₂ molecules. To explore the adsorption mechanism, three-dimensional charge density differences for Li-decorated porous graphene in the presence of one and three adsorbed hydrogen molecules are plotted in Figure 2b and 2c, respectively. Charge depletion and accumulation at both sides of the H₂ molecule clearly indicate a polarization mechanism. The above calculations are based on LDA, since the van der Waals contribution in alkali doped carbon materials has been shown to be better accounted for by LDA.¹⁶ Similar calculations based on the PW91 functional¹⁷ were performed for comparison. The adsorption energies are calculated to be −0.153, −0.125, and −0.095 eV for first, second, and third hydrogen molecules on Li-decorated porous graphene, which are much higher than that reported in Li-decorated C₆₀ (−0.075 eV).¹⁸

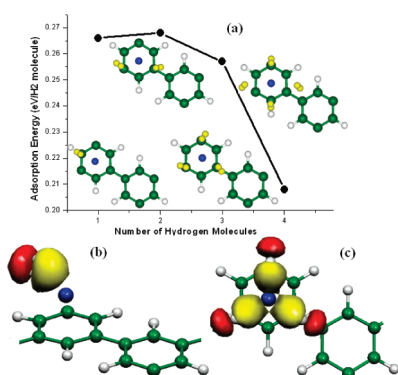


Figure 2. (a) Adsorption energies and optimized geometries for first, second, third, and fourth hydrogen molecules on Li-decorated porous graphene. Green, white, blue, and yellow balls represent C, H, Li, and adsorbed hydrogen molecules, respectively. (b) and (c) present plots of charge density difference with an isovalue of 0.01 e/Å³ for Li-decorated porous graphene in the presence of one and three hydrogen molecules. The red and yellow iso-surface indicates space charge depletion and accumulation.

Lithium atoms can form a dense coverage on porous graphene with a Li–Li distance of 4.23 Å and are expected to resist clustering due to electrostatic interaction between the cationic adsorbed Li atoms. The maximum number of adsorbed Li atoms in one unit cell of porous graphene is two and four for one and both sides, respectively. We examine the case of three adsorbed hydrogen molecules around each Li atom since this ratio retains the higher adsorption energies as shown in Figure 2a. Figure 3a and 3b present the optimized geometries for 6 and 12 hydrogen molecules adsorbed on 2 and 4 Li-decorated porous graphene, respectively. The average adsorption energies of H₂ molecules are calculated to be around 0.255 and 0.243 eV in both cases, respectively. The H₂ storage capacities corresponding to Figure 3a and 3b are 7.0 and 12 wt %, respectively. These are much higher than the limit (6 wt %) set for the feasible hydrogen storage capacity. Recently, unphysical overbinding by density functional calculations in the Ca–H₂ system¹⁹ has been revealed with the correct description of hybridization involving the d orbital on Ca being implicated. This is not expected to be problematic in the Li–H₂ system, however, due to the absence of d orbitals on the Li atom. Previous MP2 calculations have indeed also shown favorable adsorption of H₂ in Li–H₂ system.²⁰

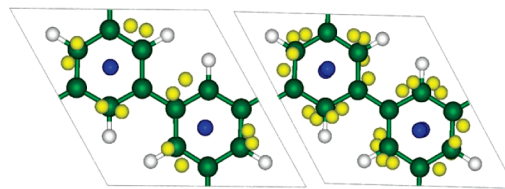


Figure 3. Top views of the optimized geometries for (a) 6 and (b) 12 hydrogen molecules adsorbed on two and four Li-decorated porous graphene. Green, white, blue, and yellow balls represent C, H, Li, and the physisorbed hydrogen molecules, respectively.

In summary, we offer a new prediction that porosity in graphene opens a direct band gap. The predicted band gap (3.2 eV) is comparable to the case of TiO₂ and graphitic C₃N₄ materials with potential applications in photocatalysis.⁹ Most interestingly, the adsorption of hydrogen molecules on Li-decorated porous graphene is significantly enhanced with up to a 12 wt % hydrogen storage capacity potentially feasible, in significant contrast to the case of Li-doped graphene. In light of the recent experimental synthesis of porous graphene,^{7,8} our results suggest multiple new potential applications for this fascinating material.

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Supporting Information Available: Computational details and a side view of Figure 3. These materials are available free of charge via the Internet at <http://pubs.acs.org>.

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