

Metal-dispersed porous graphene for hydrogen storage

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First-principles calculations are carried out to study the role of various metal atoms on porous graphene for molecular hydrogen (H_2) adsorption. The binding sites of each metal atom on porous graphene are investigated and the binding energies are determined. It is shown that H_2 exhibits different adsorption characteristics onto alkaline, alkaline-earth, or transition metals in porous graphene. In particular, Ca-decorated porous graphene is investigated and found to be feasible for high-capacity hydrogen storage. Our results provide a general picture on the interactions of H_2 with porous graphene decorated with various metals. © 2011 American Institute of Physics.

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Metal-decorated nanostructures have been theoretically demonstrated to be excellent H_2 sorbents with optimal binding energies for hydrogen storage.^{1–12} The favorable H_2 binding to transition metal (TM) results from Kubas-type interactions between the metal and hydrogen,^{1–7} which are much stronger than static Coulomb interactions.^{8–12} TM-decorated materials have H_2 -binding strength of as high as 0.4 eV via the hybridization of TM d - H_2 σ and σ^* states, which forms the donation and the back-donation channel, respectively.¹³ However, TM tends to cluster due to its high cohesive energy, and the storage capability falls short of theoretical predictions.¹⁴ Also excessive back-donation from TM d to σ^* states leads to the dissociation of H_2 , particularly often for late $3d$ TMs such as Ni. Alkaline metals (AMs) and alkaline-earth metals (AEMs) are likely to have less tendency of clustering because of their relatively small cohesive energies. Particularly Ca has been considered as a decorating metal superior to TMs due to its small cohesive energy and a capability of holding multiple H_2 with binding energies of about 0.2 eV.^{15–21} Other non-TMs, such as Be and Al, were also considered for decorating nanostructures to store hydrogen.^{22,23}

Since successful production of single graphene, similar graphitic two-dimensional layers have been proposed and/or synthesized. Porous graphene²⁴ is a graphenelike polymer with well-defined atomic scale pores. This material is of particular interest as pore size, pore density, and subsequently its electronic structure can be tailored. First-principles calculations showed that porous graphene is direct-gap semiconductor.²⁵ Porous graphene was also proposed as a hydrogen purification membrane²⁶ and hydrogen storage.²⁵

In this letter, we study metal-doped porous graphene and their interactions with H_2 using first-principles methods. Metals considered here include AMs (Li, Na, and K), AEMs (Be, Mg, and Ca), TMs (Sc, Ti, and V), and the simple metal (Al). The favorable binding sites of a single metal atom on porous graphene as well as binding energies are determined. The adsorption characteristics of H_2 on metal-doped porous graphene are also investigated. Finally, we study the adsorp-

tion of H_2 on Ca-decorated porous graphene, which is found to be feasible for hydrogen storage.

Our first-principles calculations were performed using the Vienna *ab initio* simulation package²⁷ within the generalized gradient approximation.²⁸ The energy cutoff of 400 eV was used for plane-wave basis set. All atoms were relaxed until the Hellmann–Feynman forces on each atom are less than 0.01 eV/Å. The supercell approach is used where the adjacent porous graphene sheets are separated by over 25 Å. The calculated lattice constant is 7.514 Å, which is in good agreement with experiment.²⁴

First, we investigate the binding of single metal atoms on porous graphene. Metal atoms can be deposited atomistically on graphitic surfaces without clustering by, for example, substitutional boron doping.⁴ There are six available sites for metal binding as shown in Fig. 1, which are the hollow center of the C hexagon (H1), the hollow center of the C-H hexagon (H2), the bridge of C–C bond type-I (B1), the bridge of C–C bond type-II (B2), the top of C atom type-I (T1), and the top of C atom type-II (T2). The hollow center of six H atoms is energetically unfavorable compared to other sites for all metals. All metal atoms except Mg were found to bind to porous graphene. The H1 site is energetically favorable for most bound metals atoms except Be which prefers B2 and the sites slightly off from H1. Aluminum, calcium, and large size AMs such as Na do not exhibit a preference for specific sites. The site preference of small AMs is due to their small ionic radius compared to the cor-

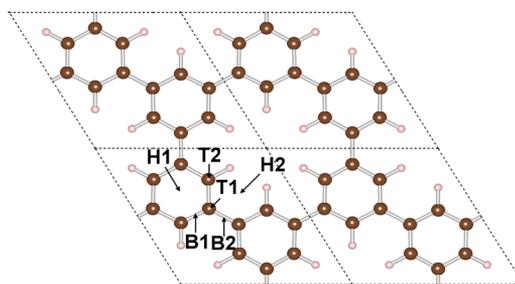


FIG. 1. (Color online) Optimized atomic geometry of (2×2) porous graphene large dark gray (brown) balls, C and small light gray (pink) balls, H. The unit cell (separated by dashed lines) is also shown along with the adsorption sites considered.

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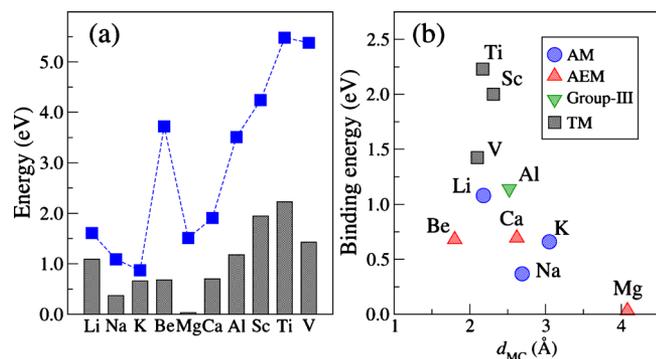


FIG. 2. (Color online) (a) Calculated metal binding energies (solid bars) on porous graphene together with calculated metal cohesive energies, as denoted by solid (blue) squares. Our calculated cohesive energies of metals are in good agreement with experiment (Ref. 31) (b) The metal binding energies on porous graphene are plotted with respect to metal-porous graphene distance (d_{MC}).

rugation of porous graphene.²⁹ Figure 2(a) shows that the ratio of calculated binding energy to calculated cohesive energy is relatively large for AMS and AEMS (except for Be and Mg) compared to other metals. However, TMs and Al have much larger cohesive energies than AMs, indicating that they have a stronger tendency of clustering. The metal diffusion can also affect the clustering tendency particularly for TMs. The binding energy is correlated with the metal-carbon distance (d_{MC}) as shown in Fig. 2(b). This is obvious for group I-III metals in the periodic table that make ionic bonding to porous graphene. Nevertheless, Be $2s$ orbital is found to hybridize with the porous graphene π states, giving small d_{MC} . On the other hand, TMs have almost the same d_{MC} with relatively large binding energies due to their covalent bonding to porous graphene.

Next, we calculate H_2 adsorption on metal-decorated porous graphene (Fig. 3). There is a significant difference in adsorption energy of the first hydrogen by about 0.5–1.0 eV between TM-, AM-, and AEM-decorated porous graphene. Be is an exception in this respect, having a quite strong adsorption for the first H_2 . The difference in adsorption energy indicates that these metals have different type of interactions with the first H_2 . AM atoms that become ionized due to charge transfer to porous graphene mostly bind H_2 with static multipole Coulomb interaction whereas TMs mostly bind H_2 with strong Kubas interaction. The H–H bond length

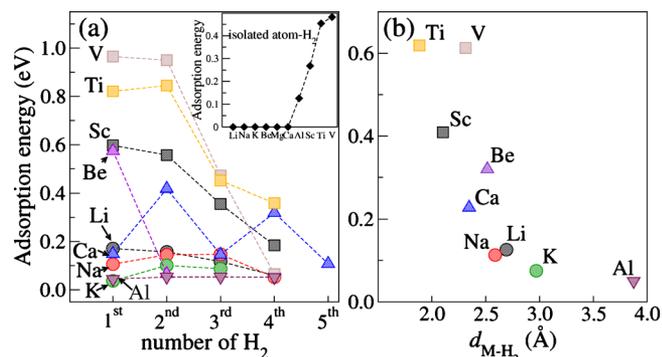


FIG. 3. (Color online) (a) Calculated H_2 adsorption energy (eV/ H_2) on metal-porous graphene complexes. The abscissa denotes the order of attached H_2 . The inset shows the average H_2 adsorption energy of isolated neutral metal atom. (b) The average H_2 adsorption energy with respect to metal- H_2 distance (d_{M-H_2}).

of adsorbed H_2 (d_{H_2}) reflects a characteristic of the interaction types. Calculated d_{H_2} of the first H_2 adsorbed on Li, Na, K, and Ca is about 0.76–0.78 Å while it is about 0.81–0.86 Å on Sc, Ti, and V due to the back-donation from metal d orbitals to hydrogen σ^* orbital (calculated d_{H_2} of isolated H_2 is about 0.75 Å). The large binding energy of the first H_2 adsorbed on Be arises from the hybridization of Be s and p orbitals with H_2 σ states,³⁰ and d_{H_2} is elongated to about 0.82 Å. Since Al is slightly ionized (by about +0.78| e |) on porous graphene, Al on porous graphene weakly binds H_2 compared to AMs.

While H_2 on AMs is mainly mediated by static multipole Coulomb interaction, Ca-porous graphene shows a mixed character of hydrogen adsorption. The first adsorbed H_2 on Ca atom is mostly mediated by multipole Coulomb interaction and a charge transfer by very small amount from the sorbent to H_2 is observed. As more H_2 molecules are adsorbed on Ca, the Kubas interaction becomes dominant for H_2 adsorption, leading to larger adsorption energies.¹⁷ However, the fifth H_2 adsorbed on Ca is again mediated by static Coulomb interaction. For Be, only two H_2 are bound to Be-porous graphene for both binding sites at most. While the first adsorbed H_2 is mediated by Kubas-type orbital interaction, the second H_2 is mediated by weak static Coulomb interaction, as indicated by small binding energy. All TM-porous graphene can bind up to four H_2 molecules. The first three H_2 molecules are bound to the metal with Kubas interaction, as indicated by high binding energies and largely elongated d_{H_2} . The fourth H_2 is mostly bound to TM with static Coulomb interaction but weak hybridization between metal d orbitals and H_2 σ^* states is still observed for Sc and Ti case. We note that, while multiple H_2 bind on TM with Kubas interaction without dissociation, a single H_2 tends to dissociate into 2H on TM and this should be taken into account when kinetic process of uptake and release of hydrogen is studied.

Figure 3(b) shows the average H_2 adsorption energy with respect to average distance between adsorbed H_2 and metal (d_{M-H_2}). We observe that the average adsorption energy scales inversely with d_{M-H_2} . This can be understood by the different H_2 adsorption characteristics of metals. The positively charged Li, Na, and K atoms dominantly adsorb H_2 with Coulomb interaction. The amount of electrons transferred to porous graphene from Li, Na, and K are calculated to be ~ 0.87 , 0.63, and 0.60 electrons, respectively. Hence, the strength of Coulomb interaction and the adsorption energy tend to decrease from Li to Na. On the other hand, the Kubas interaction is dominant for the H_2 adsorption on TM-porous graphene. The hybridization between metal d orbitals and H_2 σ^* states is the origin of relatively small d_{M-H_2} and large adsorption energy compared to the corresponding values of AMs. The H_2 adsorption energies in Fig. 3 generally increase from Sc to V, indicating the increase in degree of hybridization.¹ It is worth noting that adsorbed metal atoms on porous graphene (except for Al) have much enhanced binding strength of H_2 , compared to their neutral isolated atomic state, as shown in the inset of Fig. 3(a).

Since Ca exhibits favorable characteristics for hydrogen binding in terms of energies and the number of H_2 , we now focus on Ca-decorated porous graphene for hydrogen storage. Isolated Ca atom on porous graphene can bind up to five H_2 with adsorption energy of ~ 0.23 eV. To test the Ca clus-

tering, we calculated the binding of the second Ca atom on a H1 site nearest to the one that is already occupied by another Ca using a (2×2) supercell. The second Ca atom is found to energetically prefer the H1 site rather than forming Ca–Ca dimer. Ca is thus expected to adsorb on porous graphene in a high coverage without clustering. If we utilize both sides of porous graphene, the number of H_2 that can adsorb on a Ca atom is four in such case. Simple estimation of maximal capacity by the mass ratio is about 6~9 wt % depending on available surface area of porous graphene (i.e., utilizing single or both sides). The usable hydrogen will be less than the maximal capacity as it is limited by preset pressure and temperature for uptake and release of hydrogen in the storage.³

In summary, metal-porous graphene complexes are investigated by first-principles calculations for H_2 adsorption. Most metals except Mg in our study bind to porous graphene at H1 site and are able to adsorb multiple H_2 molecules. Calculated H_2 adsorption energy and atomic geometry provide a general trend of H_2 binding on porous graphene decorated with various metals. We have shown that high storage capacity can be obtained for Ca decorated-porous graphene when we make use of both sides of the graphene. Our results can serve as a guide for further studies of metal-decorated nanomaterials for hydrogen storage.

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¹Y. Zhao, Y.-H. Kim, A. C. Dillon, M. J. Heben, and S. B. Zhang, *Phys. Rev. Lett.* **94**, 155504 (2005).

²T. Yildirim and S. Ciraci, *Phys. Rev. Lett.* **94**, 175501 (2005).

³H. Lee, W. I. Choi, and J. Ihm, *Phys. Rev. Lett.* **97**, 056104 (2006).

⁴G. Kim, S.-H. Jhi, N. Park, S. G. Louie, and M. L. Cohen, *Phys. Rev. B* **78**, 085408 (2008).

⁵G. Kim, S.-H. Jhi, and N. Park, *Appl. Phys. Lett.* **92**, 013106 (2008).

⁶S. A. Shevlin and Z. X. Guo, *J. Phys. Chem. C* **112**, 17456 (2008).

⁷S. Meng, E. Kaxiras, and Z. Zhang, *Nano Lett.* **7**, 663 (2007).

⁸W.-Q. Deng, X. Xu, and W. A. Goddard, *Phys. Rev. Lett.* **92**, 166103 (2004).

⁹Q. Sun, P. Jena, Q. Wang, and M. Marquez, *J. Am. Chem. Soc.* **128**, 9741 (2006).

¹⁰K. R. S. Chandrakumar and S. K. Ghosh, *Nano Lett.* **8**, 13 (2008).

¹¹G. K. Dimitrakakis, E. Tyliaakis, and G. E. Froudakis, *Nano Lett.* **8**, 3166 (2008).

¹²C. Ataca, E. Akturk, S. Ciraci, and H. Ustunel, *Appl. Phys. Lett.* **93**, 043123 (2008).

¹³G. J. Kubas, R. R. Ryan, B. I. Swanson, P. J. Vergamini, and H. J. Wasserman, *J. Am. Chem. Soc.* **106**, 451 (1984).

¹⁴Q. Sun, Q. Wang, P. Jena, and Y. Kawazoe, *J. Am. Chem. Soc.* **127**, 14582 (2005).

¹⁵H. Lee, J. Ihm, M. L. Cohen, and S. G. Louie, *Phys. Rev. B* **80**, 115412 (2009).

¹⁶C. Ataca, E. Akturk, and S. Ciraci, *Phys. Rev. B* **79**, 041406 (2009).

¹⁷G. Kim, S.-H. Jhi, S. Lim, and N. Park, *Phys. Rev. B* **79**, 155437 (2009).

¹⁸Y. Y. Sun, K. Lee, Y.-H. Kim, and S. B. Zhang, *Appl. Phys. Lett.* **95**, 033109 (2009).

¹⁹Q. Wang, Q. Sun, P. Jena, and Y. Kawazoe, *J. Chem. Theory Comput.* **5**, 374 (2009).

²⁰X. Yang, R. Q. Zhang, and J. Ni, *Phys. Rev. B* **79**, 075431 (2009).

²¹M. Yoon, S. Yang, C. Hicke, E. Wang, D. Geohegan, and Z. Zhang, *Phys. Rev. Lett.* **100**, 206806 (2008).

²²H. Lee, B. Huang, W. Duan, and J. Ihm, *J. Appl. Phys.* **107**, 084304 (2010).

²³Z. M. Ao and F. M. Peeters, *Phys. Rev. B* **81**, 205406 (2010).

²⁴M. Bieri, M. Treier, J. Cai, K. Ait-Mansour, P. Ruffieux, O. Gröning, P. Gröning, M. Kastler, R. Rieger, and X. Feng, *Chem. Commun. (Cambridge)* **2009**, 6919.

²⁵A. Du, Z. Zhu, and S. C. Smith, *J. Am. Chem. Soc.* **132**, 2876 (2010).

²⁶Y. Li, Z. Zhou, P. Shen, and Z. Chen, *Chem. Commun. (Cambridge)* **46**, 3672 (2010).

²⁷G. Kresse and J. Furthmüller, *Comput. Mater. Sci.* **6**, 15 (1996).

²⁸J. P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.* **77**, 3865 (1996).

²⁹K.-H. Jin, S.-M. Choi, and S.-H. Jhi, *Phys. Rev. B* **82**, 033414 (2010).

³⁰H. Lee, B. Huang, W. Duan, and J. Ihm, *Appl. Phys. Lett.* **96**, 143120 (2010).

³¹C. Kittel and P. McEuen, *Introduction to Solid State Physics*, 8th ed. (Wiley, New York, 2005).