

**Hydrogen adsorption on boron nitride nanotubes: A path to room-temperature hydrogen storage**

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The adsorption of molecular hydrogen on boron nitride nanotubes is studied with the use of the pseudopotential density functional method. The binding energy and distance of adsorbed hydrogen is particularly calculated. It is found that the binding energy of hydrogen on boron nitride nanotubes is increased by as much as 40% compared to that on carbon nanotubes, which is attributed to heteropolar bonding in boron nitride. The effect of substitutional doping and structural defects on hydrogen adsorption is also studied and we find a substantial enhancement of the binding energy from that on perfect boron nitride. The current study demonstrates a pathway to the finding of proper media that can hold hydrogen at ambient conditions through physisorption.

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**I. INTRODUCTION**

Hydrogen is an ideal material as an alternative energy source. A serious bottleneck for the full usage of hydrogen is the lack of appropriate storage materials. Metal hydrides, high-pressurized tanks, and liquid hydrogen have been tested and investigated as possible storage forms or materials, which, however, have several drawbacks such as low capacity, safety problems, or impractical release temperatures. The recent focus of developing hydrogen storage has shifted to nanostructured materials with physisorption. Materials at nanoscale have advantages over their bulk structures such as large surface area and potentially high binding energy. Single-wall carbon nanotubes, for example, have all their atoms at the surface and have been tested as a hydrogen storage for the past several years.<sup>1-3</sup> However, their reported desorption temperature and capacity have not been confirmed.<sup>4-7</sup> The goal in hydrogen storage is a capacity of about 6% by weight at ambient temperature and pressure, which is gauged by the surface area and hydrogen binding energy.<sup>8</sup> The key is therefore to find materials that have the hydrogen binding energy of 0.2–0.3 eV as estimated from the van't Hoff equation<sup>9</sup> and a sufficient surface area of a few thousands m<sup>2</sup>/g.

In this paper, we report our study on boron nitride (BN) as a potential hydrogen storage through pseudopotential density functional calculations. The adsorption of molecular hydrogen on surfaces is in nature a physisorption due to strong H-H bond and closed-shell electronic configuration. The binding energy of H<sub>2</sub> on solid surface is thus usually very small. For example, the binding energy of hydrogen on activated carbons is about 60 meV which inevitably leads to very high pressure (several hundred bars) and/or very low temperature (~77 K) to store meaningful amounts of hydrogen in activated carbons despite their high surface area of up to 2600 m<sup>2</sup>/g.<sup>10,11</sup> We focused on BN because it is light and similar in structure to carbon so that high surface area BN can be synthesized. An interesting feature of BN is that the B-N bond has ionic character, which may induce an extra dipole moment and hence a stronger adsorption of hydrogen. This feature may in fact be true for all ionic materials be-

cause the (induced) dipole moment of hydrogen is sensitive to local electric fields.

Hexagonal boron-nitride (*h*BN) consists of heteropolar *sp*<sup>2</sup>-like bonding, and Rubio *et al.*<sup>12</sup> showed that BN could form tubular structures through *ab initio* calculations. In fact, various nanostructural forms of BN are synthesized including nanotubes and nanococoons.<sup>13,14</sup> An intriguing observation in computational simulations is that BN nanotubes have substantial bucklings of B-N bonds and hence a dipole layer of boron-atom and nitrogen-atom shells.<sup>15,16</sup> Even a permanent axial dipole moment was suggested in a recent tight-binding calculation.<sup>17,18</sup> These observations indicate that hydrogen adsorption on BN nanotubes can be significantly different from that on carbon nanotubes.

**II. COMPUTATIONAL METHOD**

In order to investigate the binding of hydrogen on BN, we perform a series of total energy calculations using pseudopotential density functional methods.<sup>19</sup> Exchange-correlation of electrons is treated with the generalized gradient approximation (GGA) of Perdew, Burke and Ernzerhof,<sup>20</sup> which, as it is believed to be better than the local density approximation (LDA), has been successful in describing a wide range of interactions. However, it has been controversial whether the GGA (or LDA) could describe correctly van der Waals (vdW) interactions because of their long-range nature. There have been several approaches to describe van der Waals interactions within density functional theory recently (for example, see Refs. 21–24 and references therein), but none of them have yet been established as a widely accepted and reliable methodology. Further developments of exchange-correlation functionals for DFT are needed for better description of vdW interactions, while some *ad hoc* approaches can be used to produce potentials for describing the physisorption (Refs. 25–27, and references therein). We caution the reader that our goal here is not to predict the hydrogen physisorption energy with extreme accuracy but rather to give guidance for the search of better hydrogen storage materials. Hence the results in this study can be understood as a reference within a given frame of computational methods. For

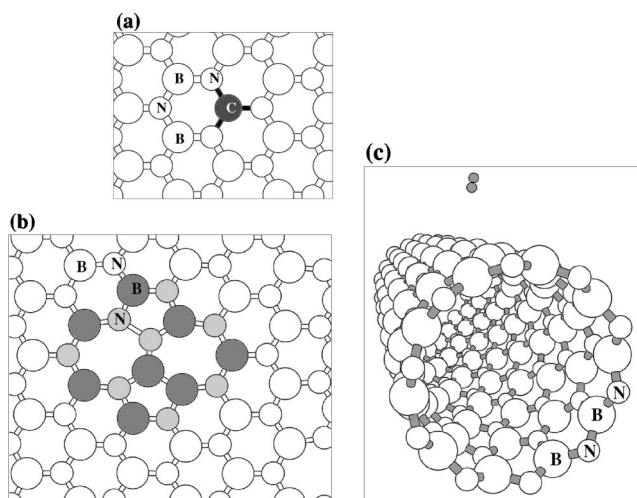


FIG. 1. Schematic drawing of various BN structure. (a) A graphitic sheet of hexagonal boron nitride with carbon (dark filled circle) doping, (b) *h*BN with  $5 \times 7$  defects denoted by gray filled circles, and (c) (10,0) boron nitride nanotube with hydrogen (small gray circles) on top of it. Boron and nitrogen atoms are depicted as larger and smaller empty circles in all three figures.

comparison, we also used the LDA and checked whether the trends obtained from the GGA calculations are consistent with the LDA results.

Atomic orbitals with double zeta polarization are used to expand single-particle wave-functions<sup>28,29</sup> with a cutoff energy of 60 Ry. We use 0.01 Ry of the confinement energy shift, which defines the cutoff radii of the atomic orbitals. Binding energy curves are obtained by performing successive calculations of total energy at varying distance between the hydrogen molecule and the adsorbates. Full relaxations of atomic positions are carried out with the center of mass of hydrogen being fixed until their Hellmann-Feynman forces are less than  $0.01 \text{ eV}/\text{\AA}$ . We studied three types of materials as depicted in Fig. 1: perfect *h*BN (not shown), *h*BN with substitutional doping [Fig. 1(a)] or structural defects [Fig. 1(b)], and BN nanotubes [Fig. 1(c)]. For substitutional doping, we replace a boron or nitrogen atom by a carbon atom and as a structural defect we introduce a pair of pentagon-heptagon (5-7) (Stone-Wales defect) to study their effects on hydrogen adsorption. A  $4 \times 4$  supercell is used to emulate a section of *h*BN. For nanotubes, we put (10,0) zigzag type tubes in a triangular lattice with  $25 \text{ \AA}$  tube-tube distance. The wall-to-wall distance is  $17 \text{ \AA}$  for the (10,0) tube, which is enough to minimize the effect from adjacent tubes on hydrogen binding. The  $\text{H}_2\text{-H}_2$  distance along the tube axis is about  $8.6 \text{ \AA}$ .

### III. RESULTS AND DISCUSSION

Figure 2 shows the binding curves of hydrogen molecule on BN graphitic sheet for various binding sites: top of boron (B), nitrogen atoms (N), and hexagon center (HC). The binding energy of  $\text{H}_2$  on the BN sheet is calculated to be about  $90 \text{ meV}$ . We note that the difference in binding energy for different sites is quite small that the diffusion of hydrogen

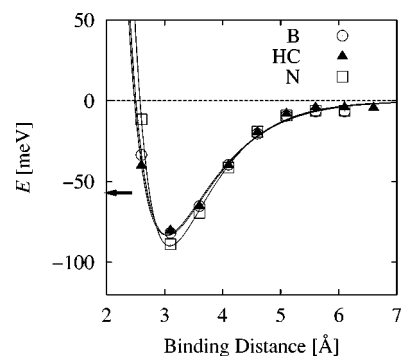


FIG. 2. Binding energy curves of hydrogen at various sites of a graphitic sheet of *h*BN. Open circles denote the calculated values on top of boron (B), filled triangles on top of hexagon center (HC), and open squares on top of nitrogen (N), respectively. Note that the binding energy at different sites is quite similar. The binding energy of hydrogen on graphite is indicated by an arrow for comparison.

can be fast in BN at moderate temperatures. The binding distance is found to be about  $3.1 \text{ \AA}$  for all sites studied. The calculated binding energy of  $90 \text{ meV}$  is significantly higher than that in graphite [ $\sim 60 \text{ meV}$  (Refs. 30–34)]. From the van't Hoff equation,<sup>9</sup> the desorption temperature of  $\text{H}_2$  in BN is estimated to be about  $115 \text{ K}$  assuming the change of entropy in adsorption to be the same as the gas-liquid entropy difference of hydrogen.<sup>35</sup> Although the desorption temperature of hydrogen in BN is still well below the room temperature, our calculated value is significantly larger than that in graphite, which is estimated to be about liquid nitrogen temperature. Since the desorption temperature in BN is above the liquid nitrogen temperature, BN can be a more efficient and cost-effective hydrogen storage than carbon.

Next we studied the change in hydrogen binding by defects, which inevitably leads to the modification of  $sp^2$  bonding and hence to the local charge and electric field distribution. First we substitute a boron or nitrogen atom in the supercell by a carbon atom, which can readily form  $sp^2$ -like bonding with surrounding B or N atoms. After structural relaxation, it is found that the bond length of C-B and C-N is  $1.55$  and  $1.47 \text{ \AA}$ , respectively, which are very close to the bond length in  $\text{BC}_3$  nanotube<sup>36</sup> and hexagonal carbon nitride,<sup>37</sup> respectively. Carbon, boron, and nitrogen atoms stay in the same plane without noticeable protrusion from the plane. Figure 3(a) shows the binding curves of hydrogen on carbon-doped BN graphitic sheet. The binding energy is surprisingly increased by as much as 50% on top of carbon that substitutes boron. The increase in binding energy for carbon substituting nitrogen is a little smaller than that for carbon substituting boron but it is still a 20% enhancement from that in perfect BN sheet. The binding distance is reduced to about  $2.95 \text{ \AA}$  for both substitutions. We note that the enhancement of the binding energy is maximum at the top of carbon atom and becomes less significant at other sites. Therefore, a moderate doping rate is necessary to have a global increase of the binding energy.

It is reported that several types of defects, such as vacancy or 5-7 defect pairs (Stone-Wales defect) can be generated during the growth or by irradiations in carbon nanotubes. Although the 5-7 defects in BN lead to N-N or B-B

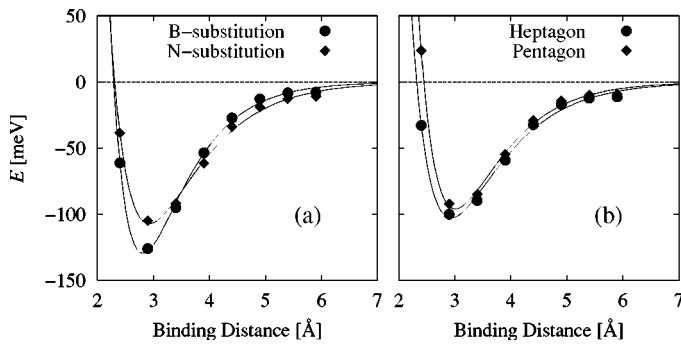


FIG. 3. Binding energy curves of hydrogen on top of (a) carbon-doped BN with carbon substituting for boron (filled circles) and for nitrogen (filled diamonds) and (b) 5-7 defect pairs in BN for heptagon ring (filled circles) and pentagon ring (filled diamonds).

bond, which are energetically unfavorable compared to B-N bond, it is worth investigating the adsorption of hydrogen on such defects. Similar to the above procedure, we relax the structure of BN with 5-7 defect pairs and then calculate the binding energy of hydrogen at various sites as shown in Fig. 3(b). The bond length of B-B and N-N bonds is found to be 1.72 and 1.57 Å, respectively. No significant protrusion is observed either in this case. Calculated binding energy is about 100 meV on top of heptagon and pentagon center of the 5-7 defect, which is about 10% increase from that on perfect BN sheet. The binding distance is about 2.97 Å.

The enhancement of binding energy of hydrogen in defects suggests that modifications of  $sp^2$  bonding in BN can lead to higher binding energies. Nanostructure of *h*BN can thus not only provide a high surface area but also have a higher adsorption energy of hydrogen because its surface is more reactive. Now we calculate the adsorption energy of hydrogen on boron nitride nanotubes. We choose (10,0) zig-zag type nanotube as depicted in Fig. 1(c). After a full atomic relaxation, it is found that nitrogen atoms are displaced outward by about 0.005 Å from boron atoms, which is consistent with previous calculations.<sup>15,16</sup> Figure 4 shows the binding energy curves of hydrogen on top of hexagon center

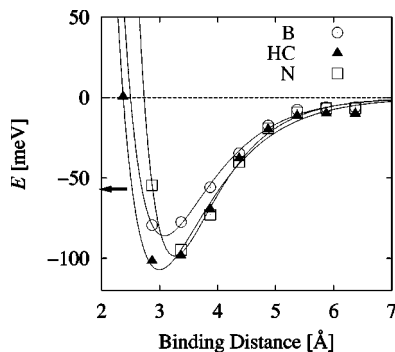


FIG. 4. Binding energy curves of hydrogen on (10,0) boron nitride nanotube with hydrogen on top of hexagon center (HC, filled triangles), boron (B, open circles), and nitrogen (N, open squares), respectively. Note that the difference in binding energy at different sites is quite significant compared to that on *h*BN sheet as shown in Fig. 2. The binding energy of hydrogen on graphite is also indicated by an arrow for comparison.

(HC), boron (B), and nitrogen (N) in BN nanotubes. Calculated binding distances on the tops of HC, B, and N sites are about 3.0, 3.05, and 3.3 Å, respectively, and corresponding binding energies are 110, 85, and 100 meV, respectively. Compared to carbon nanotubes,<sup>33</sup> BN nanotubes have about 40% larger binding energy, and the desorption temperature is therefore expected to be about 125 K. The binding energy in BN nanotubes is even larger by about 10% than in planar BN sheet, which is presumably due to the buckling of BN bonds. Another interesting observation is that the binding energy in BN nanotube has a more variance for different sites than in planar BN, which is also due to the corrugation of B-N bonds in BN nanotube. The diffusion of hydrogen is therefore slower in small diameter BN nanotubes than in larger diameter ones.

We also performed the LDA calculations of hydrogen adsorption on *h*BN and BN nanotubes (with or without defects) and found that the LDA produces similar trends while it gives bigger binding energy of as much as twice the GGA results. We also investigated hydrogen adsorption on graphite, carbon nanotubes, and boron oxide with the same computational methods and observed a similar tendency.<sup>33,38</sup> Their GGA values then were in reasonably good agreement with experiment.<sup>38</sup> We believe that present results could provide a practical guidance for searching hydrogen storage materials and for future experiments.

In recent experiments, Ma *et al.* showed that boron nitride nanotube can adsorb hydrogen up to 2.6 wt.% at about 10 MPa at room temperature, which is larger in capacity than multiwall carbon nanotubes.<sup>39,40</sup> The nanotube in that study has bamboolike structure and its surface area is not significant (about 200 m<sup>2</sup>/g) compared to that of high surface-area activated carbon (~2600 m<sup>2</sup>/g).<sup>11</sup> Since the capacity of hydrogen storage depends on the surface area, the study demonstrated that BN can be a hydrogen storage material with a strong binding energy and hence is in support of our calculations. Synthesis of high surface-area BN at large quantities is required for further studies and applications.

#### IV. SUMMARY

We have shown through computational simulations that BN can be a good hydrogen storage medium. Our study also shows that deviations from  $sp^2$  bonding tends to increase the binding energy of hydrogen in BN. This study suggests that a systematic increase of binding energy of hydrogen can be achieved for  $sp^2$ -like bonding nanostructure materials by modifying the  $sp^2$  bonding. Similar effects are also observed for carbon nanotubes.<sup>33</sup> It is possible that layered materials of ionic character, more ionic than boron nitrides, with a moderate substitutional doping would have a substantially large binding energy enough for storing hydrogen at room temperatures. Studies of carbon nitrides, beryllium borides, and other heteropolar layered materials are underway.

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