

Electric field enhanced hydrogen storage on polarizable materials substrates

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Using density functional theory, we show that an applied electric field can substantially improve the hydrogen storage properties of polarizable substrates. This new concept is demonstrated by adsorbing a layer of hydrogen molecules on a number of nanomaterials. When one layer of H₂ molecules is adsorbed on a BN sheet, the binding energy per H₂ molecule increases from 0.03 eV/H₂ in the field-free case to 0.14 eV/H₂ in the presence of an electric field of 0.045 a.u. The corresponding gravimetric density of 7.5 wt% is consistent with the 6 wt% system target set by Department of Energy for 2010. The strength of the electric field can be reduced if the substrate is more polarizable. For example, a hydrogen adsorption energy of 0.14 eV/H₂ can be achieved by applying an electric field of 0.03 a.u. on an AlN substrate, 0.006 a.u. on a silsesquioxane molecule, and 0.007 a.u. on a silsesquioxane sheet. Thus, application of an electric field to a polarizable substrate provides a novel way to store hydrogen; once the applied electric field is removed, the stored H₂ molecules can be easily released, thus making storage reversible with fast kinetics. In addition, we show that materials with rich low-coordinated nonmetal anions are highly polarizable and can serve as a guide in the design of new hydrogen storage materials.

energetics | kinetics | nanomaterials | polarization | reversibility

Hydrogen, the simplest and most abundant element in the universe, is an energy carrier which is expected to play a critical role in a decentralized energy infrastructure with many important advantages over other fuels. Unlike fossil fuels such as oil, natural gas, and coal that contain carbon, pollute the environment, contribute to global warming, and have limited supply, hydrogen is clean, environmentally friendly, nontoxic, and abundant. In addition, it is renewable and packs more energy per unit mass than any other fuel. However, its commercial use as an alternate energy source has substantial difficulties to overcome. Among these, the most difficult challenge is to find materials that can store hydrogen with large gravimetric and volumetric density and operate under ambient thermodynamic conditions. The Department of Energy (DOE) has set a target for the ideal hydrogen storage material system to have a gravimetric density of hydrogen of 6 wt% by 2010. Furthermore, the storage materials should be able to reversibly adsorb/desorb H₂ in the temperature range of -20 to 50 °C under moderate pressures (maximum 100 atm). The first requirement limits the choice of storage materials to elements lighter than Al, whereas the latter requires hydrogen binding to be between physisorption and chemisorption energies. Recently Bhatia and Myers (1) studied the optimum thermodynamic conditions for hydrogen adsorption employing the Langmuir equation and then derived relationships between the operating pressure of a storage tank and the enthalpy of adsorption required for storage near room temperature. They have found that the average optimal adsorption enthalpy should be 15.1 kJ/mol, if operated between 1.5 and 30 bar at 298 K. When the pressure is increased to 100 bar, the optimal value becomes 13.6 kJ/mol. Therefore the optimal adsorption energy for H₂ should be in the range of 0.1 ~ 0.2 eV/H₂. Unfortunately, the

above two requirements are difficult to satisfy simultaneously. The bonding of hydrogen in light elements is either too strong, as in light metal hydrides and organic molecules, or too weak, as in graphite and carbon and BN fullerenes and nanotubes (2–5). For example, although BH₃, NH₃, and B₁₂H₁₂ contain a high weight percentage of hydrogen, the kinetics of hydrogen release is poor because of the strong bonding of H with N or B.

To overcome the above problems and to balance both energetics and weight percentage, recent efforts have been devoted to design new materials with exposed metal sites following the mechanisms proposed by Kubas (6) and Niu et al. (7). The Kubas mechanism takes advantage of the unfilled *d* orbitals of transition-metal atoms where H₂ molecules donate electrons to the unfilled *d* orbitals and the transition metals back donate the electrons to the H₂ molecules. As a result, H₂ retains its molecular bond, but in a slightly stretched form. The work of Niu et al. (7) focused on metal cations where stretching of the molecular bond of H₂ is caused by charge polarization. The difficulty with the former approach is that transition-metal atoms tend to cluster (8–11), whereas in the latter the binding energy tends to be lower than the desired value, especially when hydrogen coverage increases (12, 13). Recent attempts have concentrated on using metal ions that carry multiple charges such as Mg²⁺ and Al³⁺ in light porous materials (14–16). Three different strategies have been employed to introduce exposed metal sites (14): (i) remove the metal-bound volatile species which typically function as terminal ligands, (ii) incorporate metal species, and (iii) impregnate materials with excess metal cations. However, experimentally these techniques are complicated and difficult to control because any available atoms or molecules in the environment saturate the exposed metal sites, thus diminishing expected hydrogen adsorption capacity.

In this study, we propose a different approach that would make materials synthesis less complicated while improving the thermodynamics and reversibility of hydrogen storage. Note that the mechanism that allows exposed metal cations to store hydrogen in quasi-molecular form is the polarization of the H₂ molecule caused by the electric field associated with point ions (7, 11). Can the same objective be achieved by directly applying an external electric field to hydrogen storage materials? We show that this is indeed possible by considering a single BN sheet, an AlN sheet, a silsesquioxane molecule, and a silsesquioxane sheet. Using first-principles calculations we find that in an applied electric field the electrons of the hydrogen molecules are polarized. The electrostatic interactions between the hydrogen molecules and the substrates greatly improve the storage performance. For example, when one layer of H₂ is adsorbed on the BN sheet with an electric field of 0.045 a.u., the binding energy is 0.14 eV/H₂, five times larger than the binding energy of 0.03 eV/H₂ in the

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absence of the electric field. The corresponding gravimetric density of hydrogen is 7.5 wt%. Once the applied electric field is removed, the system goes back to its original state and hydrogen molecules easily desorb, yielding good reversibility and fast kinetics.

We chose to begin our study with BN sheets. Since the discovery that graphene, a single sheet of graphite, can be experimentally isolated (17), considerable attention has been focused on synthesizing similar BN-based materials because *h*-BN manifests a structural variety similar to that of *h*-C and possesses the same crystal structure with very similar cell parameters. However, the electronic properties of BN are distinctly different. For example, *h*-C can be metallic, semiconducting, or semimetallic depending upon its dimensionality, size, and coordination, whereas *h*-BN is typically a wide-band gap semiconductor. Very recently, Han et al. (18) successfully synthesized a *mono-atomic-layered* BN sheet by using a chemical-solution-derived method starting from single-crystalline hexagonal boron nitride. Currently the single-layered BN sheet has become a new nanopatform for manipulating the electronic structures and magnetism for various applications (19–22).

Results and Discussion

We first consider the interaction between a single H₂ molecule and a BN sheet. The relative stability of different configurations of the H₂ molecule on a BN sheet in an external electric field (selected as 0.040 a.u.) vertical to the sheet has been studied (Fig. 1). We considered four adsorption sites for the H₂ molecule on the BN sheet: directly on top of a B or N atom (on-top site), above the midpoint of a bond linking the B and N atoms (bridge site), and above the center of a honeycomb-like hexagon (hollow site). For each site, various initial orientations of the H₂ molecule have been studied. After optimization, we found that the H₂ molecule prefers to align along the *z* direction, parallel to the electric field. The lowest energy is found when the H₂ molecule adsorbs on the N atom.

With the help of Mulliken population analysis, we determined that the upper H atom is negatively charged, whereas the charge on the lower one is positive. This can be understood by the polarization effects of the electric field, because it “pushes” positive charges along its direction. Due to its large electronegativity, N attracts electrons from B. Thus, on the BN sheet, the N sites are electron rich and are easily polarized in the applied electric field in a way similar to the H₂ molecule. The electrostatic interaction between the H₂ and N makes N the favored site for H₂ adsorption (Fig. 1C).

We have further studied the effect of electric field strength on hydrogen adsorption by focusing on the “on-top-site” N. The H–H bond length (R_1), distance between N atom and H₂ molecule (R_2), the dipole moment of H₂ molecule, and binding energy per H₂ are plotted as a function of the magnitude of the electric field in Fig. 2. The data are fitted with the curves. We see that the H–H bond length increases exponentially with increasing electric field strength. This is due to the polarization interaction induced by the electric field and concurrent binding with the BN sheet. Simultaneously, the distance between the H₂ molecule and the substrate decreases linearly as the electric field increases. This indicates that the interactions between the H₂ molecule and BN sheet can be easily tuned by the electric field. When the electric field reaches 0.050 a.u., the H–H bond length R_1 becomes 0.815 Å and the distance to the substrate is 2.255 Å, resulting in adsorption energy of 0.48 eV. When the electric field reaches 0.060 a.u., the H₂ molecule is dissociated and atomically bonded to the BN sheet, indicating that molecular hydrogen adsorption can be achieved only below a certain critical electric field. Furthermore, from Fig. 2C we find that the induced dipole moment of the H₂ molecule changes linearly with electric field. Thus, in a weak electric field, contributions from higher-order nonlinear terms can be neglected.

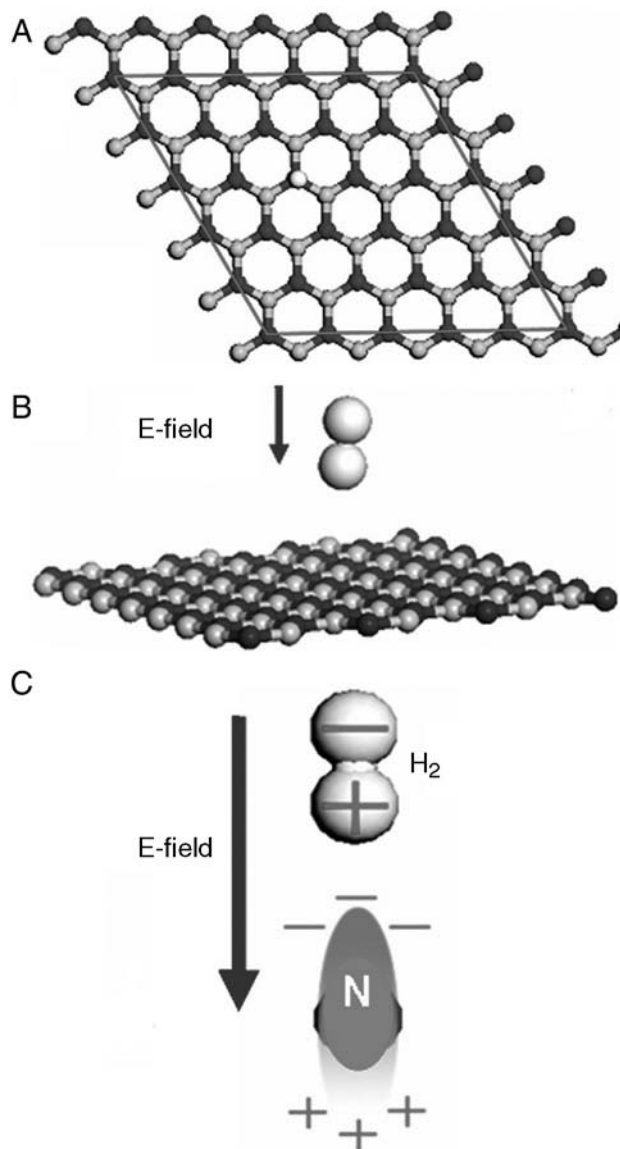


Fig. 1. Single H₂ molecule adsorbed on the BN sheet: (A) Top view; lines show the supercell used in simulations. (B) Side view; vertical electric field is applied in the $-z$ direction. (C) Model demonstrating the polarized H₂ molecule and the polarized electrons at N site on the BN sheet.

We also quantitatively analyzed the adsorption energy, defined as, $E_b = E(\text{BN}) + E(\text{H}_2) - E(\text{BN} + \text{H}_2)$. We found that the adsorption energy (E_b) changes with the applied field (E) in the following way (Fig. 2D):

$$1/E_b = 12.7684 - 10319.39E^2 + 4.19 \times 10^6 E^4 - 7.179 \times 10^8 E^6$$

According to classical physics’s dipole–dipole interaction, E_b should scale with the distance R as $E_b \sim 1/R^3$. Because of the complicated induced polarization, in our case the relationship scales as $E_b \sim 1/R^{5.5}$ (as shown in Fig. 3), suggesting that the interactions between the polarized H₂ molecules and the polarized substrate are very short-ranged as compared to the classical long-range dipole–dipole interactions.

To investigate the effect of the electric field on the electronic structure, we plot the partial density of states of the system with and without the electric field (Fig. 4). In the absence of the electric field (Fig. 4A), the semiconductor nature of the BN sheet can be clearly seen. The corresponding energy band gap of 3.52 eV is less than that of the gap in the bulk phase, namely 5.97 eV (23).

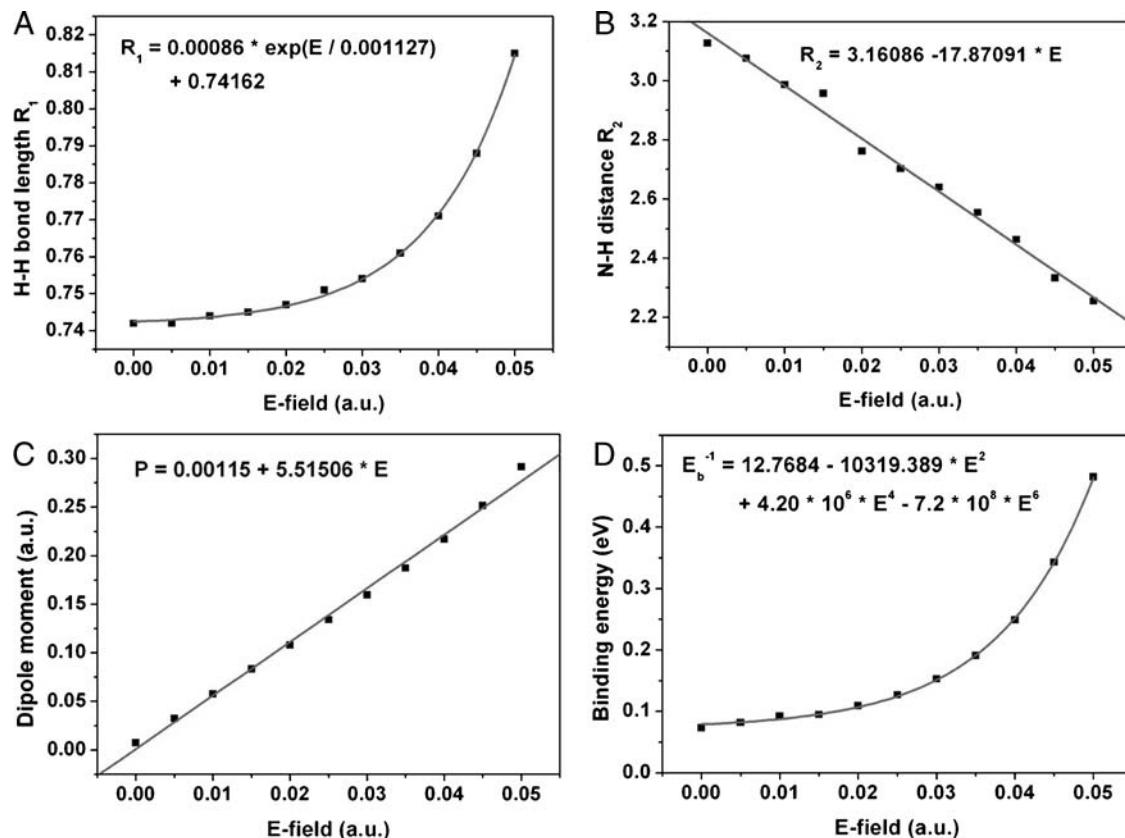


Fig. 2. Calculated data and fitted curve of (A) H-H bond length R_1 (in angstrom), (B) N-H distance R_2 (in angstrom), (C) induced dipole moment of H_2 molecule, and (D) binding energy as a function of electric field strength.

When the electric field of 0.05 a.u. is applied, the adsorption energy of the H_2 molecule is increased to 0.48 eV while the semiconductor property of the system is still retained (Fig. 4B), indicating that the BN sheet is not electrically broken down in an applied electric field. We also see that the peak in the s density of states at ~ -0.23 a.u. contributed by the H_2 orbital in the absence of the field shifts to a higher energy range (~ -0.12 a.u.) when the electric field is applied. Only the $2p$ orbitals of B and N atoms contribute to density of states at the Fermi level.

Next we study the case when one layer of H_2 molecule is adsorbed on the BN sheet (Fig. 5). We initially placed H_2 mole-

cules with various orientations on four different adsorption sites as mentioned above. Once again, we found that the optimized H_2 molecules remain vertical to the sheet, i.e., parallel to the external electric field and the N on-top sites remain the favored adsorption sites. The changes in binding energy per H_2 molecule with different electric field are shown in Fig. 5C. We see that the binding energy increases from 0.03 eV/ H_2 in the absence of the

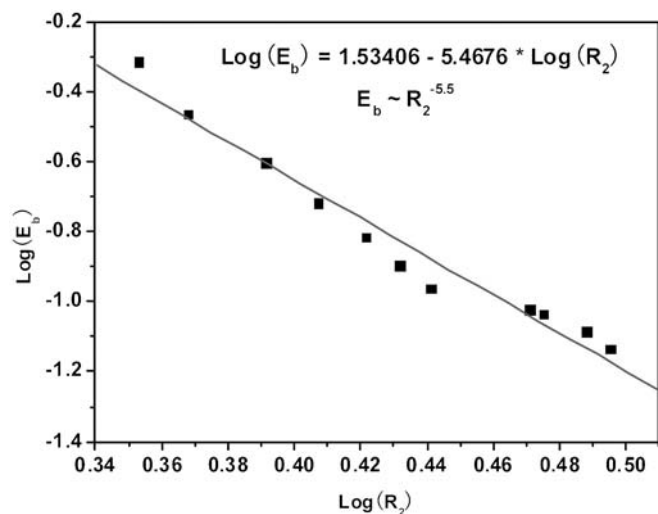


Fig. 3. Changes of adsorption energy E_b with distance R_2 .

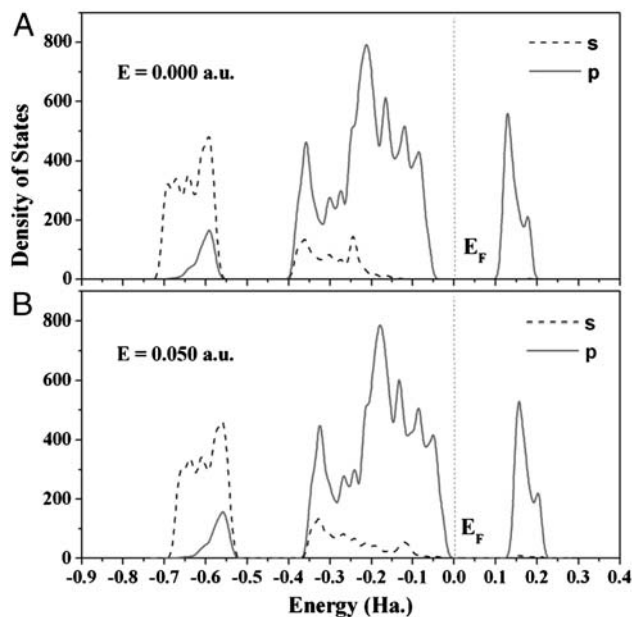


Fig. 4. Density of states of BN- H_2 with and without electric field. The vertical dashed line is for Fermi level.

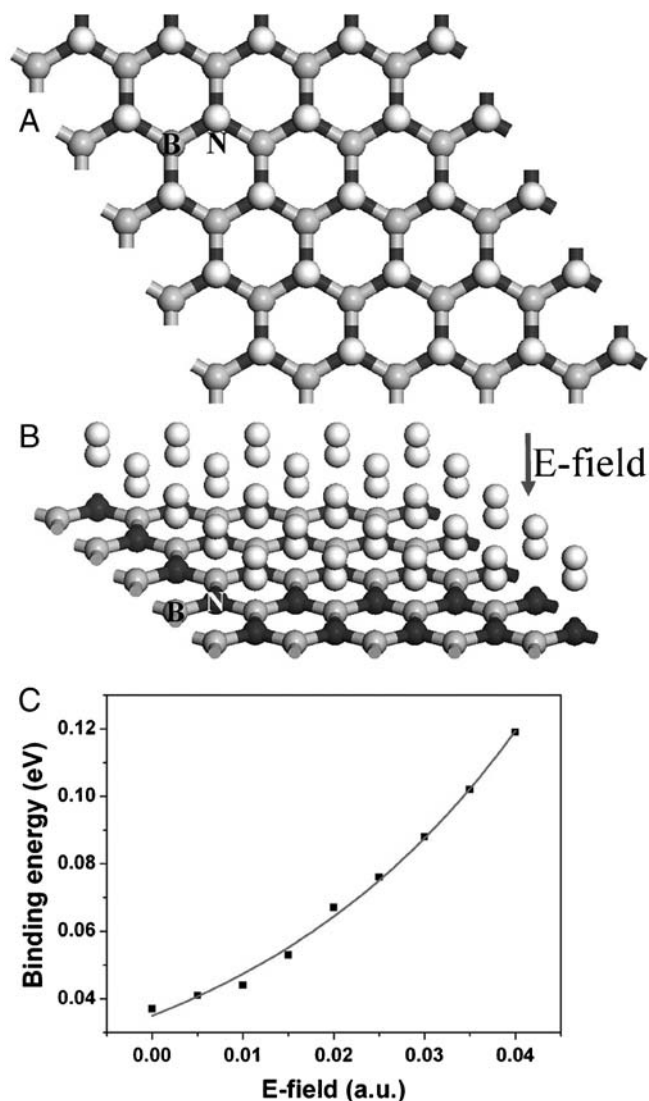


Fig. 5. Layer of H₂ molecules adsorbed on the BN sheet: (A) top view, (B) side view, (C) changes of binding energy with electric field.

electric field to 0.14 eV/H₂ in a field of 0.045 a.u. For a single H₂ molecule in the electric field of 0.045 a.u., the adsorption energy is much higher, 0.35 eV/H₂. There are two factors that account for this energy difference: (i) When one layer of H₂ molecules is introduced, their distance to the substrate increases due to steric hindrance. (ii) When a single H₂ molecule is adsorbed on the BN sheet, because of the nonuniform adsorption, the substrate shows some geometric distortion near the adsorbing N site. However, the adsorption energy of 0.14 eV/H₂ is already within the energy window required for applications under ambient thermodynamic conditions (1). Equally important, the gravimetric density of stored hydrogen is 7.5 wt%. This is consistent with the 6 wt% system target set by DOE for 2010. To check the reversibility of hydrogen storage, we removed the external electric field and, as expected, found that all the adsorbed H₂ molecules become weakly bound with a binding energy of 0.03 eV/H₂. Therefore, storage and release of hydrogen can be easily achieved via switching on/off the external electric field.

To assess the feasibility that our study can lead to the focused discovery of unique hydrogen storage materials for practical applications, it is necessary to examine some of the assumptions we have made, the results we have obtained, and the conclusions we have drawn.

1. Because of the experimental success in synthesizing a single atomic BN layer (18), we chose a single BN sheet in our calculation to illustrate the mechanism. In fact, before the experimental synthesis, a single atomic BN layer was used as a theoretical model for hydrogen storage (20). However, it was found that the adsorption energy is only 0.04 eV/H₂, in agreement with our result of 0.03 eV/H₂ in the field-free case. Here we show that the applied external electric field can significantly enhance the hydrogen adsorption on a BN sheet. In practice, however, a single BN sheet is not enough for hydrogen storage and these sheets have to be assembled. Thus, one has to see if these sheets will collapse and adversely affect their hydrogen storage capacity. For this purpose, we have calculated the equilibrium distance (D) between two BN sheets stacked with five different stacking patterns and found that D lies in the range of 4.46 ~ 5.38 Å. Because the equilibrium distance between the H₂ layer and the BN sheet is only 2.65 Å, the space between BN sheets for certain stacking configurations is enough to store H₂ molecules. One can also use some molecular linkers to assemble the sheets if larger separation is required.
2. We have used density functional theory with Becke-Lee-Yang-Parr (BLYP) exchange-correlation functional to calculate the adsorption energies of H₂ molecules. It is well known that density functional theory (DFT) does not treat van der Waals interactions accurately (24) and hence the accuracy of the calculated energetics of weakly bound systems can be called into question. Recently several authors (25, 26) have incorporated long-range dispersive interactions into DFT to treat weakly bound systems. They have found that the inclusion of long-range interaction increases the binding energies obtained using generalized gradient approximation (GGA) functionals in DFT. For example, Grimme (27) found that binding energy calculated using BLYP is about 2 kcal/mol (i.e., 0.087 eV) less than that calculated using quantum chemical method such as MP2. Therefore, our computed binding energy of 0.14 eV/H₂ is an underestimate and can increase to 0.23 eV/H₂ if more rigorous methods are used. This would bring our computed hydrogen adsorption energies even closer to the desirable energy window for applications.
3. Because DFT is not accurate in treating long-range interactions, one may wonder if it can accurately treat the interaction between the polarized H₂ molecules and substrate under the influence of an electric field. As mentioned above, DFT cannot treat long-range dispersive forces in van der Waals interaction properly. However, there is a difference between the range of dispersive force and the polarization force discussed here. In the former, the range has been experimentally identified to vary from 15 to 130 Å (28) where the electron densities nearly vanish. In the latter case, the distance between H₂ and the substrate is smaller than 3 Å, which is much less than the range of the dispersive force. Furthermore, the extended wave functions of 2p electrons in N sites and 1s electrons in H₂ result in a nonvanishing overlap of the electron densities between H₂ and the substrate. Consequently, the binding energy of hydrogen varies as $1/R^{5.5}$ where R is the distance between the H₂ molecule and the substrate. Note that the interaction energy due solely to dipole-dipole interaction varies as $1/R^3$. Therefore, we believe that the leading part of interaction between H₂ and the substrate can be calculated using DFT.
4. The electric field required to yield a binding energy of 0.14 eV/H₂ for H₂ adsorbed on a BN sheet is 0.045 a.u. This corresponds to an electric field of 23,000 MV/m which is very large. Therefore, the challenge now becomes how to reduce the required electric field. Based on the mechanism involved, we can expect that when a substrate is more polarizable than BN the required H₂ adsorption energy can be achieved with a lower electric field. To demonstrate this possibility, we repeated the calculations for H₂ adsorption on a single AlN

has the following advantages: (i) Contrary to the local electric field produced by exposed metal sites embedded in a substrate or a matrix, an external applied electric field is more effective and provides better control for reversible hydrogen storage. In particular, the energetics and kinetics can be manipulated by tuning the field strength. (ii) This process avoids complicated synthesis routes for embedding metal ions and does not suffer from the possibility that these ions may either cluster during repeated hydrogenation/dehydrogenation processes or be poisoned by other gases such as oxygen. (iii) In contrast to the ionic hydrides and alanates where the release of H₂ might render the materials unstable or incapable of reabsorption of H₂ if its chemical nature is altered, here the H₂ release can be very easily achieved by removing the electric field. (iv) The reversibility, kinetics, and material stability can be controlled by choosing appropriate electric field strength. (v) No catalysts are needed. (vi) The required external electric field can be smaller than the local electric field produced by metal ions.

Although many challenges still lie ahead in finding the right hydrogen storage material for practical applications, the aim of the present article is to demonstrate that an electric field can be used as an alternate parameter to tailor the thermodynamic and kinetic properties of storage materials. We not only provide a paradigm shift in our thinking of hydrogen storage but also provide a route to synthesize highly polarizable materials that are rich with *low-coordinated nonmetal anions*. We hope that this work will stimulate experimental research in this direction.

Methods

Our calculations are based on DFT with GGA for exchange and correlation potential for which BLYP (35) functional is used as implemented in DMol³ package (36–38). The DMol³ code has been extended to include not only the potential arising from the nuclear charges as “external” potential, but also the static potentials arising from an externally applied electric field. The Hamiltonian is composed of the potential arising from the external elec-

tric field (E_{ext}), kinetic operator T , and Hatree (V_H), and exchange-correlation (V_{xc}) potential.

$$H = T + V_H + V_{\text{xc}} - eE_{\text{ext}} \quad [1]$$

Using this prescription, Delley (39) studied the dissociation of molecules in strong electric fields and found that the bond length and vibrational frequency as a function of the field can be fit very well all the way up to the dissociation limit by an analytical formula derived from a Morse potential model, including an additional external electric field term.

All our calculations have been carried out using periodic boundary conditions on the x and y axes to simulate an infinite BN sheet. The electric field was applied in the z direction. The vacuum space of 15 Å is used in the direction normal to the BN sheet in order to avoid interactions between two layers. We have also repeated our calculations by using a larger vacuum space of 18 Å, but the results were found to be the same as those using 15 Å. Integrations over reciprocal space are based on Monkhorst-Pack scheme with $2 \times 2 \times 1$ and $9 \times 9 \times 1$ k -points grid meshes when either a single or a layer of H₂ is considered, respectively. We used a semicore pseudopotential with double-numerical basis set plus d functions. The orbital cutoff was set to be global and with a value of 3.4 Å. The atoms were relaxed without any symmetry constraints. Convergence in energy, force, and displacement was set at 2×10^{-5} Ha, 0.001 Ha/Å, and 0.005 Å, respectively. The accuracy of our exchange-correlation functional and basis set was tested through the following data. The bond length, binding energy, and polarizability of the H₂ molecule parallel to its axis are calculated to be 0.741 Å, 4.42 eV, and 6.0 a.u., respectively, which agree well with corresponding experimental values of 0.741 Å, 4.45 eV, and 6.3 a.u. The in-plane lattice parameter of the BN sheet has been optimized and the calculated value of 2.5 Å is also in good agreement with the experimental value of 2.505 Å.

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