Hydrogen-Coverage-Dependent Stark Effect in Bilayer Graphene and Graphene/BN Nanofilms

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ABSTRACT: Hydrogenation and electric field are used to tailor the electronic structures of hybrid graphene/hexagonal boron nitride (Gr/BN) and bilayer graphene (Gr/Gr). Without hydrogen adsorption, the electronic structure of Gr/BN is only slightly affected by the electric field, but energy gaps are induced in Gr/Gr because of the breaking of inversion symmetry. Under partial hydrogenation conditions, more interlayer bonds tend to form in Gr/BN than that in Gr/Gr because of the inherent Coulomb attraction, and a band gap is created in Gr/BN even at low hydrogen coverage. The electronic structures of partially hydrogenated Gr/BN and Gr/Gr are both rather insensitive to the electric fields. Under full hydrogenation conditions, Gr/BN and Gr/Gr evolve into diamond-like nanofilms: Gr/BN-BC (interlayer B–C bonding) and Gr/Gr-CC (C–C bonding). Because of the interface-dipole-induced electric field, the band gap of Gr/BN-BC is rather small compared to that of the Gr/Gr-CC. Depending on the direction of the external electric field, the band gap of Gr/BN-BC is linearly increased or decreased, whereas that of Gr/Gr-CC is only decreased. These electric-field-induced band gap modulations in Gr/BN and Gr/Gr as well as their hydrogenation derivatives are results of the Stark effect; they are dependent on the hydrogen coverage and can be understood in terms of the charge distribution of the valence-band maximum and conduction-band minimum.

INTRODUCTION

The emergence of graphene, the first two-dimensional material to be experimentally obtained, has attracted widespread attention.1–4 Because of its remarkable physical properties, such as massless Dirac Fermion behavior, ballistic charge transport, and high carrier mobility, it is regarded as one of the most promising materials for use in future electronic devices.5–7 However, the semimetallic nature of pristine graphene with zero band gap greatly limits its application in electronic devices.8 The exploration of effective methods of tailoring the band structure of graphene is essential to its future applications. Various methods have been proposed: among them, the most typical involve creating defects in the graphene,9 functionalizing the graphene with small atoms or atomic groups (H, F, Cl, O, NH2, etc.),10–14 or cutting the graphene into nanoribbons.15,16 Many studies have shown that band gaps can be easily induced in bilayer graphene, unlike monolayer graphene, because of the presence of the interlayer interaction.17 For example, in AB-stacked bilayer graphene (Gr/Gr), band gaps can be easily induced by a vertical electric field because of the inversion symmetry breaking.18 In addition, extensive research has demonstrated that the proper choice of substrate can also be used to modulate the electronic structure of graphene by introducing stress and breaking the pristine symmetry. For instance, many types of transition-metal substrates have been adopted to tailor the electronic structure of graphene.19–22 Hexagonal boron nitride (h-BN) is another promising substrate material for graphene.23,24 By taking advantage of its excellent lattice matching with graphene as well as its flat surface, absence of local charge, and dangling bonds, h-BN can be used to maintain the properties of the suspended graphene. In particular, inspired by the advantages of graphene, recent experiments have been conducted regarding the synthesis of single-layer h-BN, which has the same layer structure as graphene.25 Unlike graphene, however, h-BN is a type of wide-band-gap insulator because of the ionic covalent bonds between boron and nitride atoms.26–29 This similarity in lattice structure but large difference in electronic structure has attracted a great deal of interest in the hybrid structures of h-BN and graphene, inspiring the hope of identifying new methods of tailoring the electronic structure of graphene. Hybrid multilayer structures of graphene and h-BN have been synthesized via chemical vapor deposition and other methods in a number of experiments; these structures are uniform and continuous and can be transferred to other substrates for device fabrication.30,31
Theoretical simulations have demonstrated that small energy gaps can indeed be created in graphene in such interlaminar hybrid structures because of the breaking of the pristine symmetry of graphene.

However, for both Gr/Gr and Gr/BN, the energy gap induced by the interlayer interaction is relatively small (0.2 eV for Gr/Gr under a rather high electric field and 0.053 eV for Gr/BN). Moreover, in the case of Gr/BN, there remains some controversy over whether such a small energy gap can exist. Hydrogenation is one of the common methods of tailoring the electronic structure of graphene or h-BN layer. Under hydrogenation conditions, both the electronic structure of graphene and that of h-BN are considerably altered: graphene transforms into a wide-band-gap insulator, whereas the energy gap of h-BN is greatly reduced. For graphene and single-layer h-BN, the differing responses of their electronic structures to the hydrogenation have raised a question: how will the electronic structure of hybrid Gr/BN and Gr/Gr change upon hydrogenation? Moreover, unlike monolayer graphene or h-BN, interlayer bonds will form in Gr/BN or Gr/Gr upon hydrogen adsorption; the number of bonds is dependent on the hydrogen coverage, and the formation of these interlayer bonds also significantly influences the stability and the electronic structure of the final systems. Thus, for the further use of hydrogenated Gr/BN and Gr/Gr, it is essential to investigate the combined impact of hydrogenation and interlayer interaction on the configuration and electronic structure of Gr/BN and Gr/Gr under various levels of hydrogen coverage.

Furthermore, for low-dimensional nanosystems, the response of their electronic structures to external electric fields is extremely important to their future applications in electronic and optoelectronic devices. For one-dimensional nanosystems (nanotubes, nanoribbons), the effects of an electric field on their electronic structures have been thoroughly studied. Some unique laws have been identified; for example, because of the Stark effect, the energy gap of armchair nanoribbons and nanotubes can only be decreased by a transverse electric field, whereas that of the zigzag nanoribbons can be increased or decreased depending on the field direction. For Gr/BN and Gr/Gr as well as their hydrogenated nanofilms, their diverse electronic structures suggest that they should exhibit different responses to the electric fields. Hence, it is necessary to investigate their response to electric fields, with the hope of identifying universal laws such as those that operate in the one-dimensional nanosystems.

In this study, the combined effects of hydrogenation and a vertical electric field on the electronic structures of Gr/BN and Gr/Gr are systematically investigated. In the absence of hydrogen adsorption, the electronic structure of Gr/BN is quite insensitive to the electric field. However, because of the field-induced redistribution of the conduction-band minimum (CBM) and the valence-band maximum (VBM), an energy gap is created in Gr/Gr. Under partial hydrogenation conditions, more interlayer bonds tend to form in Gr/BN than that in Gr/Gr because of the inherent Coulomb attraction between the carbon atoms in graphene and the corresponding boron atoms in h-BN. As a result, a sizable energy gap is created in Gr/BN, even at relatively low hydrogen coverage. Moreover, for all these partially hydrogenated nanosystems, their electronic structures are quite insensitive to external electric fields, which can be understood in terms of the distribution and localization of the VBM and the CBM. Under full hydrogenation conditions, all the Gr/BN and Gr/Gr layer structures spontaneously evolve into diamond-like nanofilms. Because of the presence of a dipole-induced electric field in Gr/BN-BC, its energy gap is lower than that of Gr/Gr-CC. Moreover, the energy gap of Gr/BN-BC is effectively increased or decreased by the vertical electric field depending on the electric-field direction. However, in the case of Gr/Gr-CC, its energy gap is only slightly reduced, regardless of the electric-field direction. Such electric-field-controllable behaviors in these two-dimensional nanofilms are similar to those observed in one-dimensional nanoribbons and nanotubes; this phenomenon is attributed to the Stark effect and can be explained in terms of the VBM and CBM locations.

**COMPUTATIONAL METHODS**

The stable configurations of Gr/BN and Gr/Gr stacked in the AB pattern are chosen as the models for our calculations (Figure 1). For Gr/BN, the B atoms are directly below C atoms, and the N atoms are underneath the corner of the graphene hexagon; this configuration has been found to be the most stable among all possible configurations. To simulate the change in the geometrical structures and the corresponding electronic structures of Gr/BN and Gr/Gr under various levels of electric fields, with the hope of identifying universal laws such as those that operate in the one-dimensional nanosystems.

![Figure 1](https://example.com/figure1.png)

**Figure 1.** Top view and side view of the configurations of Gr/BN (a) and Gr/Gr (b) and the corresponding electronic structures. The N, B, and C atoms are represented by red, green, and pale brown balls, respectively, in Gr/BN. In Gr/Gr, the C atoms in the bottom layer are indicated in white. (c) The variation in the energy gaps of Gr/Gr and Gr/BN with respect to the vertical electric field. The VBM and CBM distributions of Gr/Gr (d) and Gr/BN (e) under the electric field.
of hydrogen coverage \((H_{\text{cov}})\), \(6 \times 6\) Gr/BN and Gr/Gr supercells are used with various number of hydrogen atoms adsorbed on them. The hydrogen coverage is defined as \(n_{H}/n_{\text{tot}}\) where \(n_{H}\) is the number of H atoms included and \(n_{\text{tot}}\) is the total number of C, B, and N atoms. The stability of the various hydrogenated Gr/BN and Gr/Gr structures is analyzed in terms of per hydrogen formation energy, which is defined as

\[
E_f = \frac{1}{n_{H}}(E_{\text{GR+BN}+n_{H}} - E_{\text{GR}+BN} - n_{H}\mu_H)
\]

where \(E_{\text{GR, BN}}\) and \(E_{\text{GR+BN}+n_{H}}\) are the energies of an isolated graphene layer, an isolated BN layer, and the hydrogenated Gr/BN, respectively; \(\mu_H\) is the chemical potential of a hydrogen atom. The formation energy of hydrogenated bilayer graphene is also calculated using an analogous definition in which \(E_{\text{BN}}\) is replaced by \(E_{\text{GR}}\).

All our calculations are performed within the density functional theory (DFT) formalism as implemented in the Quantum Espresso package. Ultrastiff pseudopotentials\(^{49}\) are used to describe the electron–ion interaction. It is well-known that the semilocal generalized gradient approximation (GGA) fails to yield the correct interlayer distance in graphite or hexagonal boron nitride, whereas, because of a delicate error cancellation between the exchange and correlation potentials, the local density approximation (LDA) can yield reasonable interlayer distances in these systems. Hence, the LDA is used here to describe the electron’s exchange and correlation interactions. The electron wave function and charge density are expanded in plane waves, and the energy cutoffs thereof are 30 and 300 Ry, respectively. The corresponding Brillouin zone is sampled in a \(36 \times 36 \times 1\) mesh for Gr/BN and Gr/Gr, as well their fully hydrogenated systems and in an \(8 \times 8 \times 1\) mesh for the corresponding partially hydrogenated systems using the Monkhorst–Pack scheme.\(^{50}\) All structures are fully optimized within the force threshold of \(1 \times 10^{-3}\) Ry/bohr. The Methfessel–Paxton smearing\(^{41}\) technique with a width of 0.02 Ry is used to speed up the convergence. The electric field is applied in the vertical direction with respect to the layer structure and is simulated with the addition of a saw-like potential.\(^{52}\)

## RESULTS AND DISCUSSION

The stable configurations of Gr/BN and Gr/Gr are in the AB-stacked configuration (Figure 1). As mentioned above, single-layer BN is an insulator with a wide band gap (3.6–6.0 eV, as measured in several different experiments\(^{53–56}\)), whereas graphene is a semimetal with zero band gap. The results presented in Figure 1a show that the electronic structure of Gr/BN can be considered to be approximately a superposition of the structures of h-BN and graphene with a very small band gap (50 meV). The linear dispersion in the band structure of graphene is preserved, with the states around the Fermi level being contributed entirely by the 2p states of C atoms. The states contributed by the B and N atoms are far from the Fermi level, outside the energy region \([-1.2\text{ eV}, 3.2\text{ eV}]]\) with an observed energy gap of 4.4 eV. All of these findings indicate that the interlayer interaction between graphene and h-BN is very weak, and the electronic structure of the graphene layer in such a composite structures is negligibly affected by the BN sheet. For bilayer graphene (Figure 1b), however, the strong interlayer coupling greatly changes the electronic structure of the graphene, which causes the dispersion around the Dirac point to be parabola-like.

The difference in the interlayer coupling of Gr/BN and Gr/Gr contributes to their different responses to the vertical electric field. As illustrated in Figure 1c, because of the breaking of the inversion symmetry,\(^{57–59}\) a finite band gap is induced in Gr/Gr, with a magnitude that is dependent on the field intensity. The electronic structure of Gr/BN, conversely, is quite insensitive to the electric field (Figure 1c). To explain these differences, the state distributions of the CBM and VBM of these two systems under an electric field (0.4 V/Å) are given in Figure 1d,e. For bilayer graphene, both the VBM and the CBM redistribute in the presence of an electric field, with the CBM mainly on the top layer and the VBM on the bottom layer (Figure 1d), which is in clear contrast with the zero-field case, in which the VBM and CBM states are evenly distributed between the two layers. Hence, the potential difference between the CBM and VBM contributes to the creation of a band gap in the bilayer graphene. However, for Gr/BN, both the VBM and CBM are located on the graphene layer (Figure 1e), and the electric potentials on them are nearly identical. Consequently, the energy levels can be simultaneously increased or decreased by the electric field, but the energy gap of Gr/BN does not significantly change. Such electric-field-induced band gap modulation in Gr/BN is universal and it is also applicable to Gr/BN with other stacked ways (see Supporting Information).

Upon hydrogen adsorption, both the configurations and the electronic structures of these bilayer systems will change, and these transformations are dependent on the hydrogen coverage. To illustrate the impact of the hydrogenation, the typical structures under various levels of hydrogen coverage are illustrated in Figure 2 and Figure 3. In Gr/BN, the C atoms (Figure 2) are divided into two categories: α C atoms with neighbor B atoms directly below and the β C atoms above the centers of the BN hexagons. Similarly, the α C atoms in Gr/Gr have direct interlayer neighbor C atoms on the other layer and the β C atoms are located above the centers of the C hexagons. For fully hydrogenated graphene or bilayer graphene (also referred to as graphene or bilayer graphene in the literature), the most stable hydrogen configuration has been recognized to

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**Figure 2.** (a–f) Configurations of hydrogenated Gr/BN under various levels of hydrogen coverage. Atoms of C, N, B, and H atoms are represented by pale brown, red, green, and blue balls, respectively. The names of the corresponding configurations are provided.

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be the chair configuration with hydrogen atoms alternatively adsorbed on the both sides of the graphene.\textsuperscript{10,60} In this study, we also consider such a hydrogen-adsorption state. As shown in Figure 2, hydrogen atoms are adsorbed on the $\beta$ carbons and their bottom neighbor nitrogens. Such hydrogen adsorption contributes to the formation of interlayer $C\cdash B$ bonds, which greatly stabilize the final hybrid structures.\textsuperscript{10} A very similar situation also exists in the response of Gr/Gr to different level of hydrogen coverage (Figure 2), where hydrogen adsorption contributes to the formation of interlayer $C\cdash C$ bonds, leading to the stabilization of the final structures.

For the sake of convenience in later descriptions, the hydrogenated Gr/BN and Gr/Gr structures are labeled as $n$CH-$n$NH and $n$CH-$n$CH, where $n$ is the number of hydrogens on the top or bottom layer. The relatively large values of the formation energy ($E_f$) in Table 1 imply that all these hydrogenated Gr/BN and Gr/Gr structures are stable configurations. The structures illustrated in Figure 2 demonstrate that because of the hydrogen adsorption, the average interlayer distance ($D_{av}$) of Gr/BN and Gr/Gr decreases (see Table 1), and sp$^3$ bonds gradually form between the two layers in both Gr/BN and Gr/Gr; the number of these bonds is dependent on the hydrogen coverage. With the formation of sp$^3$ bonds, the interlayer van der Waals bonding changes into chemisorption. Moreover, the comparison indicates that, on the whole, more interlayer bonds tend to form in Gr/BN than in Gr/Gr (Table 1). For example, three interlayer bonds are formed in 3CH-3NH, but only one is formed in 3CH-3CH (Figure 2c, Figure 3c).

To explain the relatively facile formation of the interlayer bonds in the hydrogenated Gr/BN, the bond-formation processes are analyzed by considering 3CH-3NH as an example. The differential charge density in Figure 4a indicates that the C atoms provide most of the charge for the interlayer $C\cdash B$ bond formation, even though the electronegativity of the C atom is larger than that of the B atoms. This situation arises from the fact that in the bottom BN layer, the N atoms with large electronegativity attract most of the electrons, which causes the 2p states of the N atoms to be fully occupied and those of the B atoms to be nearly empty (Figure 1a). Thus, in the interlayer $C\cdash B$ bond-formation process, the empty 2p states of the B atoms accept electrons from the C atoms in the graphene above. As shown in Figure 4b, when hydrogen adsorption occurs, there is electron accumulation in the 2p states of the C atoms, and the 2p states of the B atoms below are empty or effectively occupied by the positive holes. Therefore, there is inherent Coulomb attraction between the C atoms in the graphene and the corresponding B atoms in BN layer, which leads to the facile formation of interlayer bonds. In comparison, in the hydrogenated Gr/Gr, the interlayer bonds are nonpolar covalent $C\cdash C$ bonds (Figure 4c,d), and in the bond-formation processes, the Coulomb attraction that exists in the Gr/BN system is absent.

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**Figure 3.** (a−f) Configurations of differently hydrogenated Gr/Gr, with C indicated in pale brown and H indicated in blue.

**Table 1.** Formation Energy $E_f$ (eV), Average Interlayer Distance $D_{av}$ (Å), Number of Interlayer Bonds $N_b$, and the Energy Gap $E_g$ (eV) of Hydrogenated Gr/BN and Gr/Gr under Various Levels of Hydrogen Coverage $H_{cov}$

<table>
<thead>
<tr>
<th>structure</th>
<th>$H_{cov}$</th>
<th>$E_f$</th>
<th>$D_{av}$</th>
<th>$N_b$</th>
<th>$E_g$</th>
<th>$E_f$</th>
<th>$D_{av}$</th>
<th>$N_b$</th>
<th>$E_g$</th>
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</thead>
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<tr>
<td>1CH-1N(C)H</td>
<td>0.014</td>
<td>2.45</td>
<td>3.15</td>
<td>0</td>
<td>0.075</td>
<td>1.68</td>
<td>3.30</td>
<td>0</td>
<td>0.00</td>
</tr>
<tr>
<td>2CH-2N(C)H</td>
<td>0.028</td>
<td>2.16</td>
<td>3.06</td>
<td>1</td>
<td>0.057</td>
<td>1.33</td>
<td>3.14</td>
<td>1</td>
<td>0.00</td>
</tr>
<tr>
<td>3CH-3N(C)H</td>
<td>0.042</td>
<td>2.07</td>
<td>3.00</td>
<td>3</td>
<td>0.651</td>
<td>1.39</td>
<td>3.09</td>
<td>1</td>
<td>0.00</td>
</tr>
<tr>
<td>4CH-4N(C)H</td>
<td>0.056</td>
<td>2.10</td>
<td>2.96</td>
<td>5</td>
<td>0.507</td>
<td>1.22</td>
<td>3.07</td>
<td>1</td>
<td>0.00</td>
</tr>
<tr>
<td>5CH-5N(C)H</td>
<td>0.069</td>
<td>1.88</td>
<td>2.89</td>
<td>5</td>
<td>0.755</td>
<td>1.45</td>
<td>2.97</td>
<td>3</td>
<td>0.00</td>
</tr>
<tr>
<td>6CH-6N(C)H</td>
<td>0.083</td>
<td>2.04</td>
<td>2.86</td>
<td>5</td>
<td>0.568</td>
<td>1.76</td>
<td>2.95</td>
<td>3</td>
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</table>
Because of the facile formation of interlayer bonds in Gr/BN, the electronic structures of these hydrogenated Gr/BN films are quite sensitive to the hydrogen coverage. In Figure 5, the electronic structures that correspond to differently hydrogenated Gr/BN structures (Figure 2) are presented. At low hydrogen coverage (1CH-1NH), the interlayer C–B bonds are not formed, and the quasi-localized states induced by the hydrogen adsorption pass through the Fermi level without effectively inducing a band gap. When the hydrogen coverage is increased (Figure 2b,c), more interlayer bonds are formed, and the corresponding structures become semiconductors with relatively large direct band gaps at the $\Gamma$ point (Figure 5). For Gr/Gr, however, an energy gap can only be induced at relatively high hydrogen coverage (6CH-6CH of Figure 6), when more interlayer bonds are formed. Under low hydrogen coverage (1CH-1CH to 5CH-5CH), the quasi-localized states induced by the hydrogenation pass through the Fermi level, and the corresponding hydrogenated Gr/Gr films exhibit metallic characteristics.

Furthermore, to investigate the response of these partially hydrogenated nanofilms to the electric field, we have simulated their band gap variations under various electric fields. The results for 3CH-3NH and 6CH-6CH are shown as examples, because relatively large band gaps begin to arise in these systems, and the mechanisms involved can be easily extended to other partially hydrogenated systems. As shown in Figure 7, both the band gap of 3CH-3NH and that of 6CH-6CH are quite insensitive to the external electric field. However, some difference is still observed between these two cases, as the band gap of 3CH-3NH remains nearly unchanged throughout the entire considered range of electric fields, whereas that of 6CH-6CH is slightly increased at higher electric field. This difference can be explained in terms of the field-induced redistribution of VBM and CBM. It can be clearly seen in Figure 7 that both the VBM and the CBM of 3CH-3NH are located on the graphene layer, just as in Gr/BN bilayer structure (Figure 1e). Consequently, under a vertical electric field, the changes in the electric potentials on the VBM and CBM are nearly identical, and the energy gap between them is negligibly affected. In the case of 6CH-6CH, under a vertical electric field, its VBM and CBM are redistributed, with the CBM (VBM) mainly on the top (bottom) graphene layer. Because of this redistribution, the electric potentials on the VBM and CBM become different, thereby enlarging the energy gap in the system. The electric-field-induced band gap variation in 6CH-6CH is similar to that in Gr/Gr (Figure 1c, d), with the
exception that the energy-gap modulation in 6CH-6CH is rather small (Figure 7). The reason for this difference is that in Gr/Gr, the VBM and CBM are composed of and states, respectively, and can be easily driven from one layer to the other by electric fields in either direction. In 6CH-6CH, however, because of the adsorption of the hydrogen atoms, the bonds are partially broken, meaning that the VBM and CBM contain contributions from quasi-localized states, which are much less sensitive to the external electric field.

Under full hydrogenation conditions, the configurations of Gr/BN and Gr/Gr transform into two-dimensional diamond-like nanofilms (Figure 8). For convenience, these fully hydrogenated nanofilms are labeled as Gr/BN-BC and Gr/Gr-CC to represent the interlayer B−C bonding and C−C bonding. The phonon spectrum shows that all these configurations are dynamically stable (Figure S5 in Supporting Information). The parameters of the configurations illustrated in the upper panels of Figure 8 indicate that these two-dimensional nanofilms are quite similar in the structure, but the band gap of Gr/BN-BC (0.851 eV) is rather small compared to that of Gr/Gr-CC (2.837 eV) (middle panels of Figure 8). To determine the underlying mechanism of the band gap difference between Gr/BN-BC and Gr/Gr-CC, the densities of states (DOSs) of the corresponding systems are presented in the bottom panels of Figure 8. For Gr/BN-BC, the VBM is contributed entirely by the 2p states of the C atoms, whereas the CBM is primarily composed of the 1s states of the H atoms. The VBM of Gr/Gr-CC originates from the C 2p states, and the CBM originates from the H 1s and C 2p states. It is the difference in the compositions of the VBM and CBM as well as their locations in these two configurations that ultimately lead to their difference in the band gaps of the systems.

In Figure 9, the real-space distributions of the VBM and CBM are shown. For Gr/BN-BC, the VBM is located on the hydrogenated graphene layer, whereas the CBM is mainly distributed on two planes that are well-separated from the hydrogenated BN layer (see Figure 9a). Thus, the VBM and CBM are spatially separated from each other. Moreover, the plane-averaged electrostatic potential indicates that the potential on the CBM is larger than that on the VBM. Therefore, there is an equivalent electric field in the direction pointing from the CBM to the VBM; this field is induced by the spontaneous dipoles at the interface of the graphene and BN layers that form because of the electronegativity difference between the C atoms and the B atoms immediately below. It is this dipole-induced electric field that increases (decreases) the energy of the VBM (CBM) and results in the relatively small band gap of Gr/BN-BC. Accordingly, it is possible to tune the band gap of Gr/BN-BC by applying an external electric field that is either parallel or antiparallel to the inherent electric field. In Figure 10, the variations in the energy gaps and the energy levels of the VBM and CBM are given as functions of the external electric field, and the results appear to imply that the
energy gap of Gr/BN-BC can be linearly modulated by the electric field. If the external electric field is applied along the same direction as the inherent one, the energy gap will be reduced by increasing the energy level of the VBM and decreasing that of the CBM, and vice versa. This finding confirms that the dipole-induced electric field is very important in determining the energy gaps of Gr/BN-BC. Moreover, the fully hydrogenated Gr/BN with interlayer carbon-nitrogen bonds (Gr/BN-NC) has also been investigated (see Supporting Information). The phenomena obtained on it are almost the same as those on Gr/BN-BC, which further confirms that the dipoles at the interface play an important role in the electronic structures of these fully hydrogenated systems.

Unlike the case of Gr/BN-BC, in Gr/Gr-CC, the interlayer bonds are nonpolar covalent C−C bonds, so there is no interface-dipole-induced electric field, which is demonstrated above to be closely related with the band gap reduction in Gr/BN-BC. Moreover, as shown in Figure 9b, the distributions of the VBM and CBM in Gr/Gr-CC are symmetrical, which produces a unique response to the external electric field in this electronic structure. In fact, our simulation demonstrates that the band gap of this structure can only be slightly reduced by a vertical electric field, regardless of the field direction. For simplicity, in Figure 10c, the results in only one direction are presented. The relation between the energy gap and the electric field is quadratic at low field intensity, and it becomes linear when the field intensity is sufficiently high. In addition, the band gap modulation in Gr/Gr-CC is primarily affected by the energy-level variation of the CBM, which is in contrast with the case of Gr/BN-BC, in which changes in the energy levels of both the CBM and the VBM contribute to the band gap variation (Figure 10). The reason for this difference is that the CBM in Gr/Gr-CC contains the nearly free electron state (NFE) and is distributed on both sides of the Gr/Gr layers (Figure 9b). One well-known feature of NFE state is that the energy level of such a state can be easily affected by an external electric field.39 The VBM of Gr/Gr-CC, on the other hand, is contributed by the 2p states of all the C atoms, and thus, it is extended along the normal direction of Gr/Gr layers (Figure 9a), in comparison with Gr/BN-BC, in which the VBM is localized only on the graphene layer (Figure 9b). This extended character causes the VBM to be quite insensitive to the external electric field, as can be clearly seen in the right-hand panel of Figure 10d, where the energy of the VBM changes very little with the electric field.

The phenomena discussed above are all related to the electric-field-induced redistribution of the VBM and the CBM, which is the result of the Stark effects. By analogy with the one-dimensional nanosystems,40−42 we can safely declare that in these two-dimensional fully hydrogenated Gr/BN and Gr/Gr nanofilms, there exists the same law driven by the Stark effect. In this respect, depending on the direction of an applied vertical electric field, the energy gap of Gr/BN-BC can be linearly increased or decreased, whereas that of Gr/Gr-CC can only be reduced.

**SUMMARY**

In this study, we have systematically investigated the hybrid graphene/BN bilayer structure (Gr/BN) and bilayer graphene (Gr/Gr) as well as the corresponding partially and fully hydrogenated two-dimensional nanofilms. Without hydrogenation, the relatively weak interaction in Gr/BN causes its electronic structure to be insensitive to an external vertical electric field. By contrast, because of the facile redistribution of the VBM and CBM, an energy gap is induced in bilayer graphene with an amplitude that is dependent on the field intensity. Under partial hydrogenation conditions, more interlayer bonds tend to form in Gr/BN than that in Gr/Gr because of the inherent Coulomb attraction between the C atoms and the B atoms below, and a considerable energy gap is induced in these hybrid structures even at relatively low hydrogen coverage. Moreover, the vertical electric field exerts little influence on the electronic structures of partially hydrogenated Gr/BN and Gr/Gr structures because of the distributions and localization of the VBM and CBM. Under full hydrogenation conditions, Gr/BN and Gr/Gr evolve into two-dimensional diamond-like nanofilms with direct band gaps. Because of the presence of electronic dipoles at the interface between the graphene and BN layers, the potential difference between the VBM and CBM reduces the energy gap in Gr/BN-BC with respect to that in Gr/Gr-CC. Moreover, the energy gap of Gr/BN-BC can be linearly modulated (increased or decreased, depending on the field direction) by an external electric field, whereas the energy gap of Gr/Gr-CC can only be reduced by such an electric field. All these electric-field-dependent band gaps in Gr/BN and Gr/Gr as well as their hydrogenated derivations arise from hydrogen-coverage-dependent Stark effects and can be understood in terms of the distributions of the VBM and CBM. These hydrogen- and electric-field-induced band gap variations in Gr/BN and Gr/Gr not only offer an additional approach to the electronic-structure modulation of graphene, but also demonstrate the potential of these materials for possible applications in electronic or optic devices.

**ASSOCIATED CONTENT**

Supporting Information

In the Supporting Information, the following information is provided: (1) PDOS of 3CH-3NH, 3CH-3CH; (2) configurations, electronic structures and electric-field-induced band gap modulations in NC-Gr/BN and Gr/BN-NC; and (3) phonon spectra of these fully hydrogenated Gr/BN and Gr/Gr. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

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