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Bipolar Doping of Double-layer Graphene Vertical Heterostructures with Hydrogenated Boron Nitride

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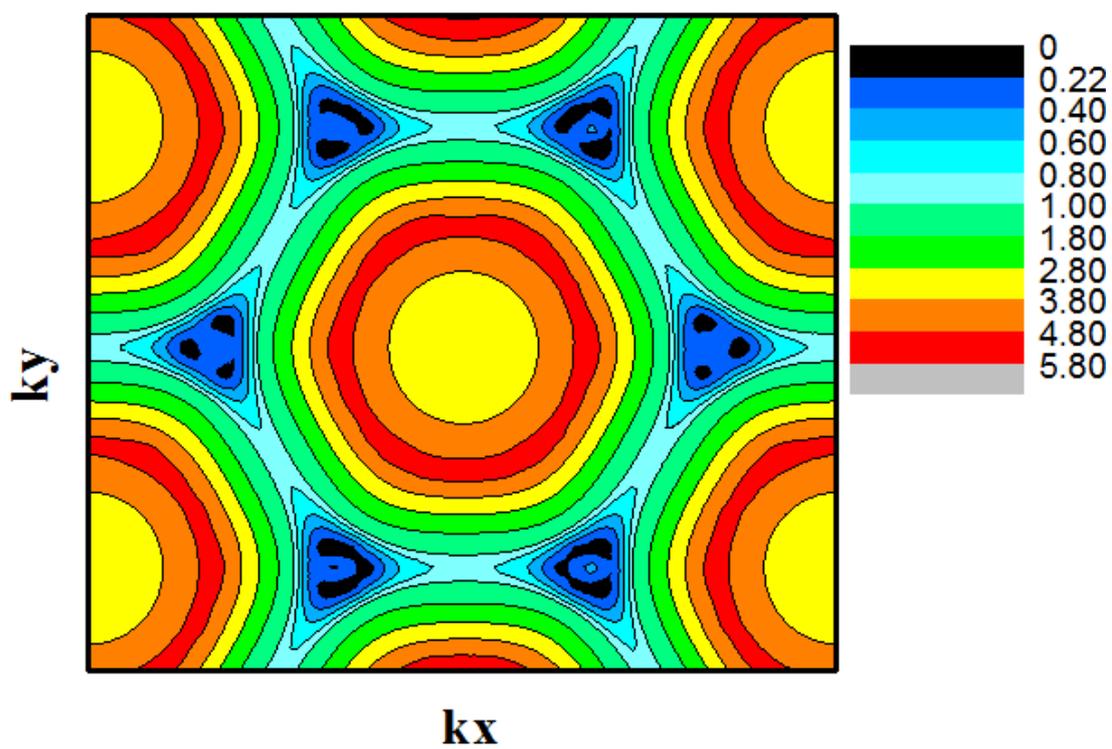
Fig. S1 Calculated Dirac band energy spectrum (above the Fermi level part) of DLG. The Fermi surface is indicated by the black arc regions, which is approximated to a circle due to the two Dirac cones interpenetration.
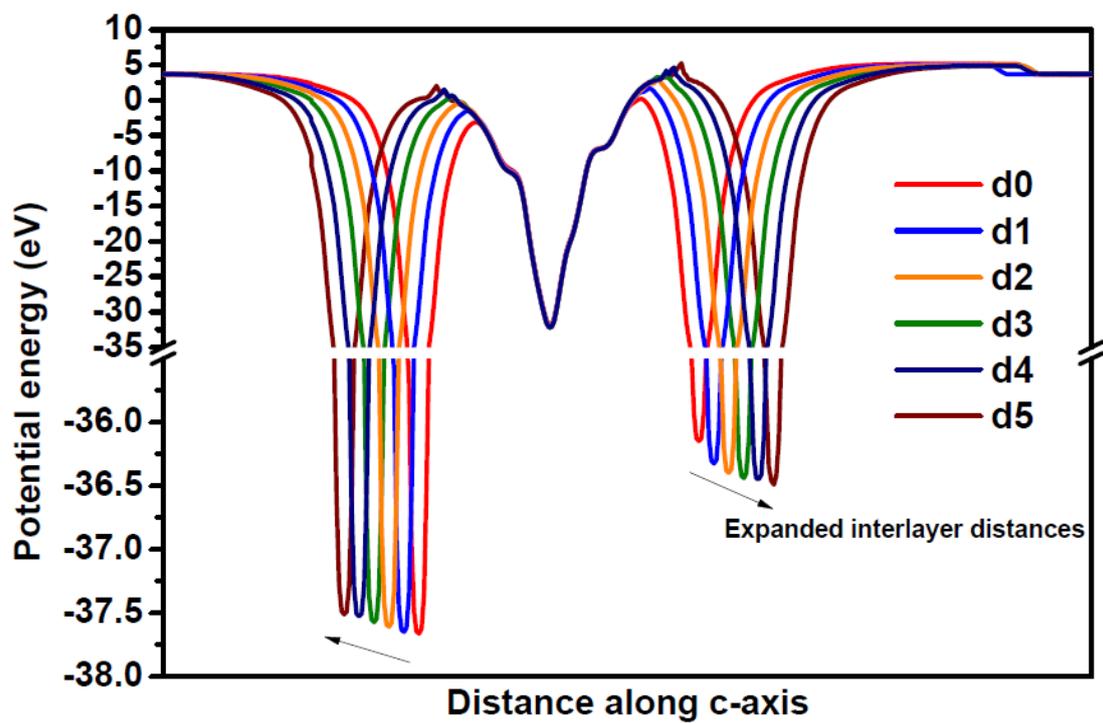
Fig. S2 Plane averaged potential energies of DLG with the expanded interlayer distances ($Z-Z_{equ}$ = ds = $0.4 \times s$ (Å)).
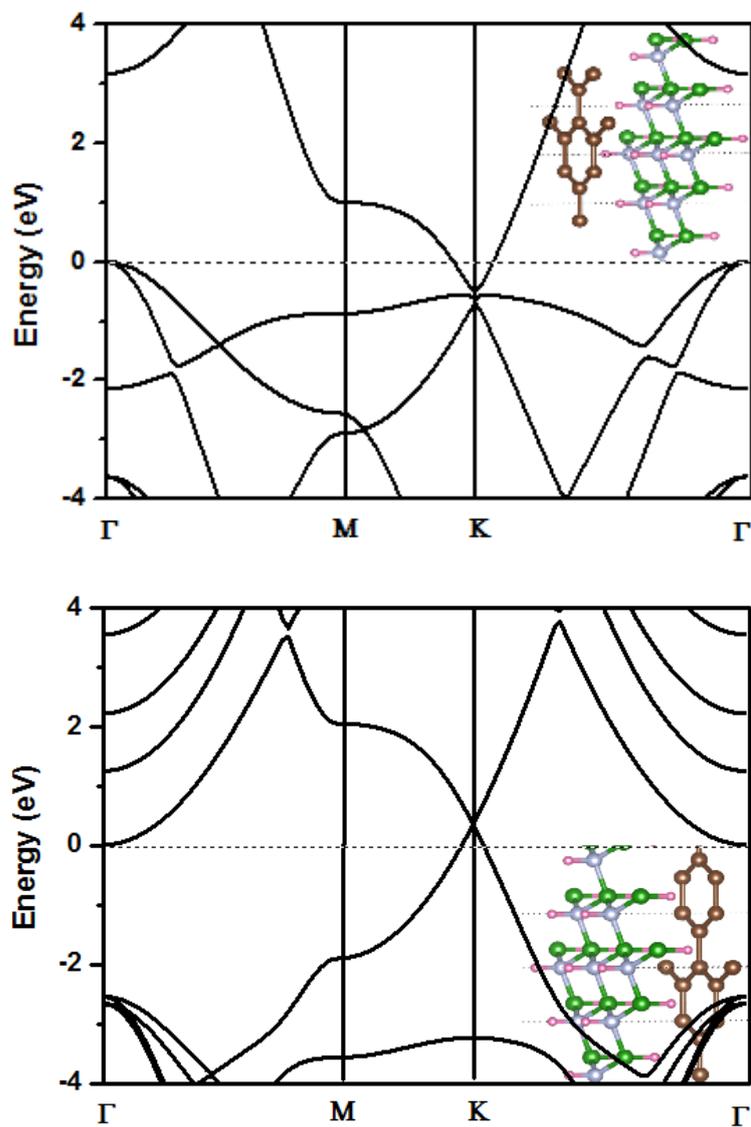
Fig. S3 Band structures of single layer graphene adsorption on HNBH. (Top) The downward shift of Dirac point by -0.5 eV in Gr(N). (Bottom) The upward shift Dirac point by 0.37 eV in Gr(B). The insets show the corresponding optimised atomic structures.
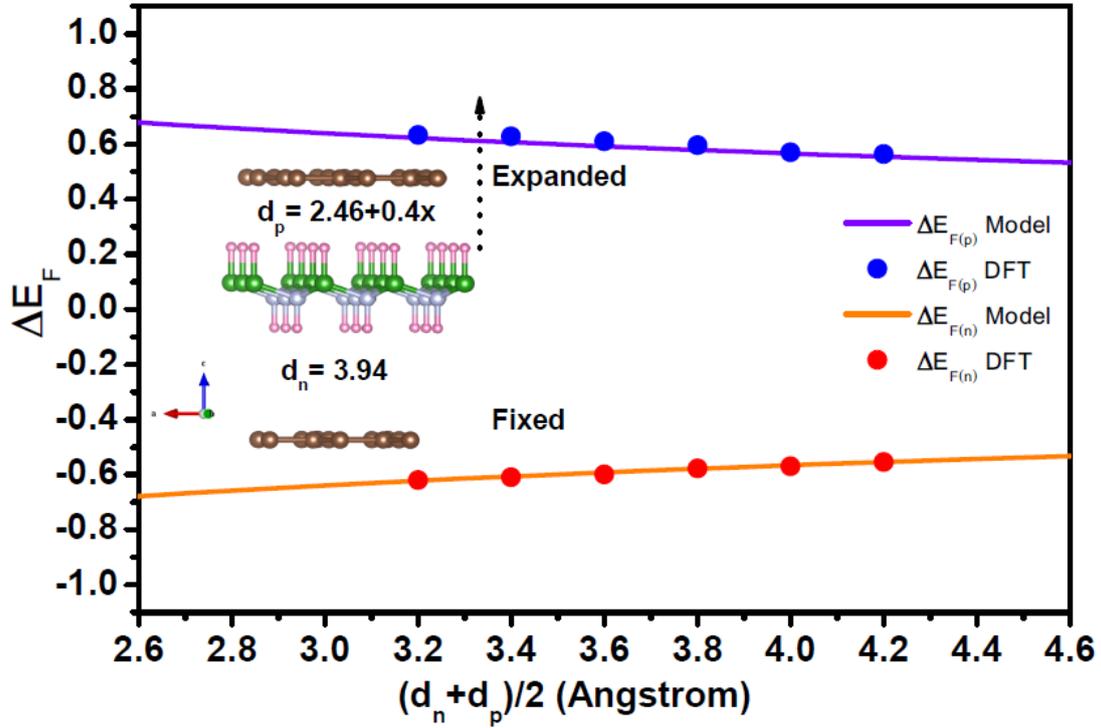
Fig. S4 The Fermi level shifts versus the averaged interlayer distances in two graphene layers with unequal expansions. The interlayer distances between Gr(N) and HNBH are fixed (d_n = 3.94 Å), while distances between Gr(B) and HNBH are gradually increased (d_p = 2.46 + 0.4x, x = 0-5). The results given by sloid lines represent the model predictions, the dots are obtained from the DFT caculations.
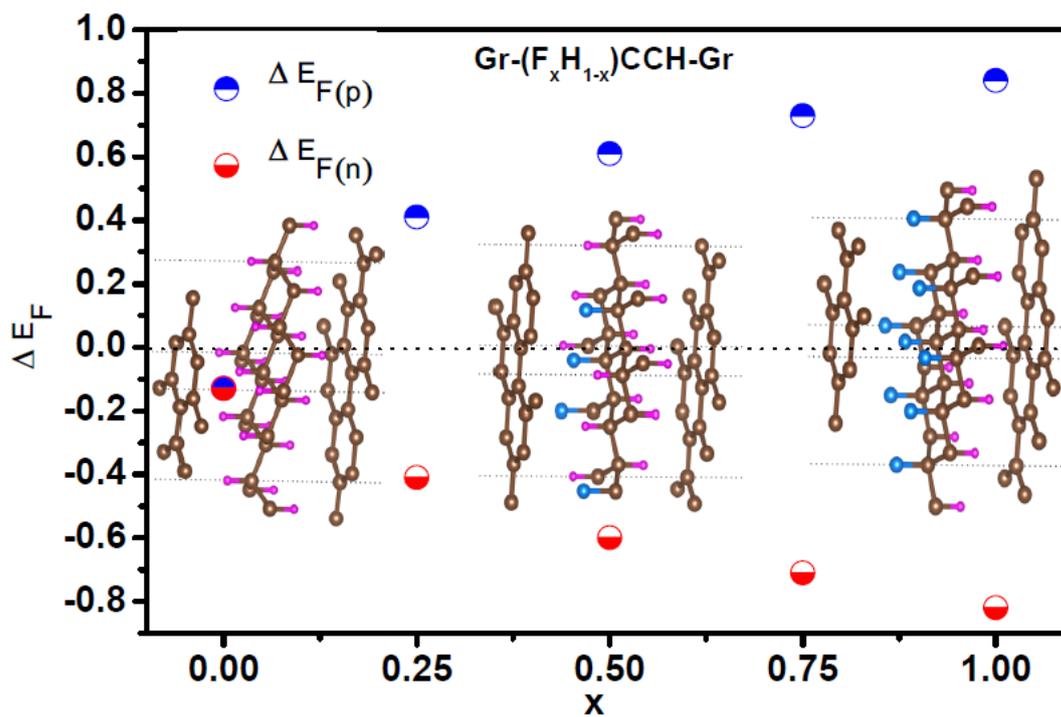
Fig. S5 Using hydrofluorinated graphene Gr-(F_xH_{1-x})CCH-Gr as the sandwich layer, the DLG with controllable doping level by adjusting the F atom concentrations. Note that, when the middle layer is fully hydrogenated, i.e. the $x = 0$, the graphene bands are degenerated and both Dirac points are slightly shift of -0.19 eV by n-type doping.
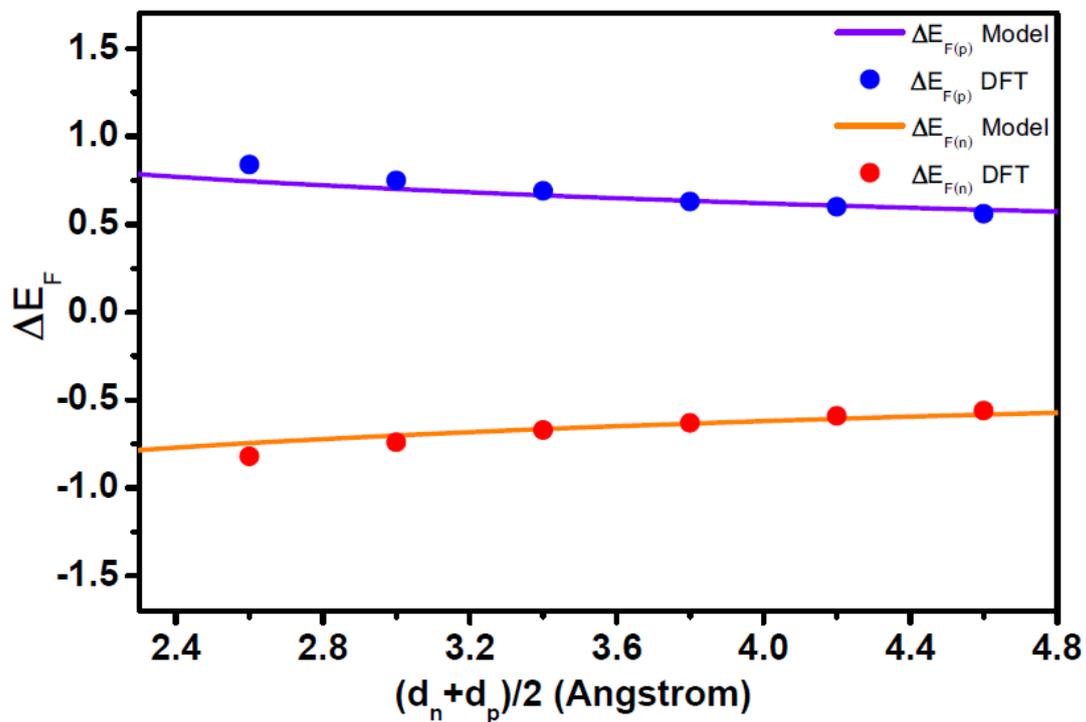
Fig. S6 Using the hydro-fluorinated graphene (take the Gr-FCCH-Gr as an example) as the the sandwich layer, the Fermi level shifts in two graphene layers versus the averaged interlayer distances. (Note: the ΔV_{di}=5.4eV is the potential energy difference in FCCH by our caculation)

S2. Electrostac doping model for DLG
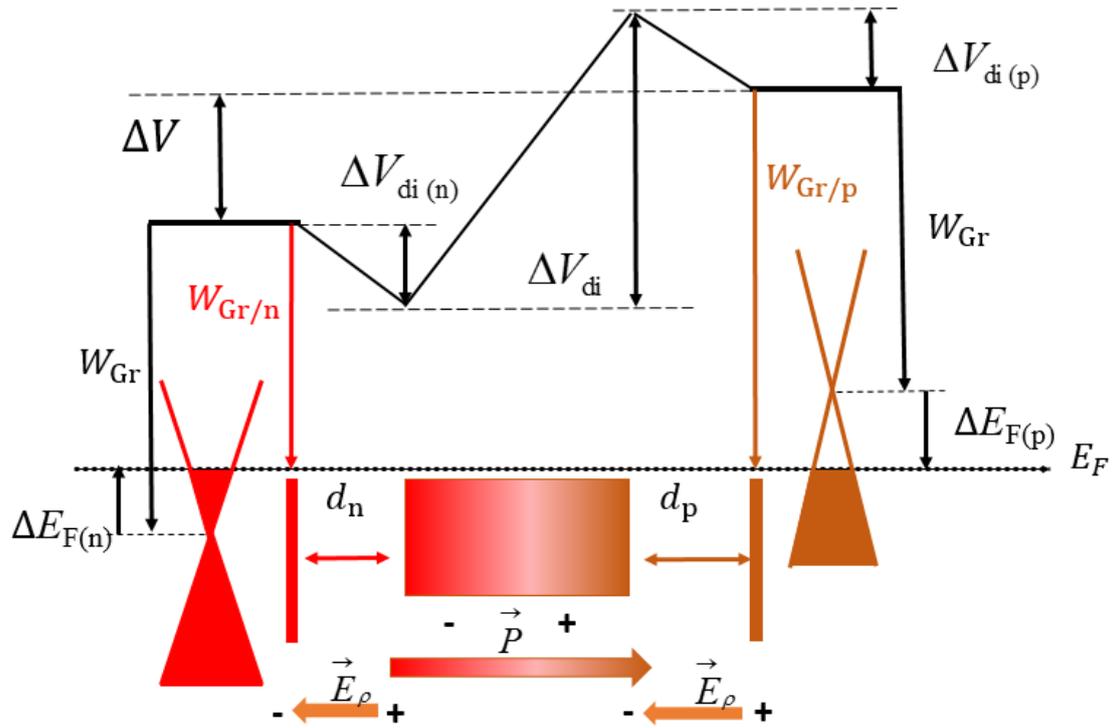
Schematic 1

Schematic illustration of the DLG structure. The electrostatic potential profile is drown by black line, and the spontaneous polarization field $\vec{P}$ and charge-transfer screening feild $\vec{E}_\rho$ are indicated at the bottom. It should be noticed that the doping level of single layer graphene adsorption on hydrogenated BN (see Fig. S3) are appreciably lower than that in DLG. This indicates that the bipolar doping is mutual enhanced by the balance of screening charges between the two graphene layers, i.e., the polar charge on the B-end surface should be keep equal but opposite in sign to the charge on N-end surface. Therefore, the reduction of positive polar charge on B-end surface by transfer electrons from Gr(B) synergistically diminishes the negative polar charge on N-end surface by transfer electrons to Gr(N). Under ideal conditions, the amount of charge transfer is almost equal and give rise to same magnitude but

opposite direction in shifts of Fermi level in the graphene layers (i.e. the p-type doping of Gr(B) is coupled with the n-type doping of Gr(N) by the relationship: $\Delta E_{F(p)} = -\Delta E_{F(n)}$).

The potential difference can be approximated as follows,

$$\Delta V = \Delta V_{di} - \Delta V_{di(n)} - \Delta V_{di(p)} = W_{Gr/p} - W_{Gr/n} \approx -\Delta E_{F(n)} + \Delta E_{F(p)} \approx -2\Delta E_{F(n)}, \quad (1)$$

where $W_{Gr/p}$ and $W_{Gr/n}$ are, repectively, the work function of the p-type and n-type doped graphene. $\Delta E_{F(n)} \approx \left| W_{Gr(n)}\text{-}W_{Gr} \right|$ is the Fermi energy level shift of n-type doped graphene. The ΔV_{di}=4.6 eV is the potential energy difference in HNBH. The $\Delta V_{di(n/p)}$ are the potential steps between the n(p)-type doped graphene and the dielectric layer, which can be quantilized by a plane capacitor modle,

$$\Delta V_{di(n(p))} = \alpha N(d_{n(p)})d_{n(p)} + \Delta_{ch}, \quad (2)$$

$$\alpha = e^2 / A\varepsilon_0, \quad (3)$$

$$N(d_{n(p)}) = \pm \frac{D_0}{2} \left| \Delta E_{F(n(p))} \right|^2, \quad (4)$$

where α = 33.88 eV/Å with A = 5.37 Å^2 the area of the unit cell, and $D_0 = D(E)/\left| E \right| \approx 0.08$ per (eV^2 unit cell) is the slop of the linear density of states for $\left| E \right|$ within 0.85 eV. The $d_{n(p)}$ are the interlayer diatances between the graphene and the HNBH. When the graphene layers with large seperations, the chemical contribution $\Delta_{ch} \approx 0eV$ are insignificant and the two Dirac points are distributed symmetrically around the Fermi level.

Using the above relations, we can get:

$$\Delta V_{di} - \alpha \frac{D_0}{2} \left| \Delta E_{F(n(p))} \right|^2 (d_n + d_p) + \Delta_{ch} = -2 \left| \Delta E_{F(n(p))} \right|, \quad (5)$$

$$\Delta E_{F(n(p))} = \mp 2 \frac{\sqrt{1 + \frac{\alpha D_0}{2}(d_n + d_p)\left| \Delta V_{di} + \Delta_{ch} \right|} - 1}{\alpha D_0 (d_n + d_p)} = \mp \frac{\sqrt{\frac{(d_n + d_p)}{2}*12.468 + 1} - 1}{2.71 * \frac{(d_n + d_p)}{2}} \quad (6)$$

We further confirm this coupled bipolar doping mechanism by investigating the Fermi level shifts in two graphene layers with unequal interlayer expansions. As shown in Fig. S4, the Fermi level shifts $\Delta E_{\text{Fn(p)}}$ are still agree well with the model predictions. This result indicates that tuning the interplanar strain on one graphene can control the doping level of other one by the interlayer coupling effect in DLG, which makes it a promising candidate for future mechanical-electric devices. As shown in the following schematic 2(a), we illustrate the possible methold to fabricate the device with desired interpalane strain by compressing the outermost layers.

Another posssible approach to achieve the tunable interlayer spacing is grafing functional molecules as the building blocks to pattern the graphene (see the schematic 2(b)). The synergistic interfacial interactions, such as hydrogen bonds, ionic bonds, π-π interactions, and covalent bonding, enable interface design for high mechanical performance graphene-based artificial nacres with engineered interlayer distances. The configurations of the functional groups can be switched by the temperature or optical excitation. Combining optics, strain, and temperature to modulate the doping properties, these functional molecule decorated DLG promise their utilities in switchable optoelectrinic devices.

Schematic 2