Supporting Information

Design the graphene as a new Frustrated Lewis Pair catalyst for the hydrogen activation by co-doping

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Computational Setup

The calculations reported here are performed by using periodic, spin-polarized DFT as implemented in Vienna *ab initio* program package (VASP).[1,2] The electron-ion interactions are described by the projector augmented wave (PAW) method proposed by Blöchl[3] and implemented by Kresse.[4] TPSS functional[5] is used as exchange-correlation functional approximation and a plane wave basis set with an energy cutoff of 400 eV is used. The van der Waals correction is accounted by using DFT-D3 methods proposed by Grimme.[6] The value of the *S6*, *SR*, and *S8* is 1.0, 1.166, and 1.105 respectively. The combination of TPSS and DFT-D3 is recommended to treat the Frustrated Lewis Pair system.[7] A 6x6 unit cell is employed for the boron and nitrogen doped bilayer graphene and a 3x3 kpoint mesh is used for the Brillioune zone sampling. The boron and nitrogen doped graphene ribbon is placed in a cubic cell with a 24.23x14.76x15.00 Å for x, y, z dimension and the periodic condition is employed along the y direction. Only gamma point is used for the doped graphene ribbon calculations. The reaction pathway and barriers are calculated by using the climbing image nudged elastic band (CI-NEB) method.[8] The Mayer bond order calculations is performed by using Gaussian 09.[9]

References

(1) Kresse, G.; Furthmüller, J. *Comput. Matt. Sci.* **1996**, *6*, 15.

(2) Kresse, G.; Furthmüller, J. *Phys. Rev. B* **1996**, *54*, 11169.

(3) Blöchl, P. E. *Phys. Rev. B* **1994**, *50*, 17953.

(4) Kresse, G.; Joubert, D. *Phys. Rev. B* **1999**, *59*, 1758.

(5) Tao, J.; Perdew, J. P.; Staroverov, V. N.; Scuseria, G. E. *Phys. Rev. Lett.* **2003**, *91*, 146401.

(6) Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. *J. Chem. Phys.* **2010**, *132*.

(7) Schirmer, B.; Grimme, S. In *Frustrated Lewis Pairs I*; Erker, G., Stephan, D. W., Eds.; Topics in Current Chemistry; Springer Berlin Heidelberg, 2013; Vol. 332; pp 213–230.

(8) Henkelman, G.; Uberuaga, B. P.; Jonsson, H. *J. Chem. Phys.* **2000**, *113*, 9901–9904.

(9) Frisch, M. J. et al. Gaussian 09 D.01. Gaussian Inc. Wallingford CT 2009.

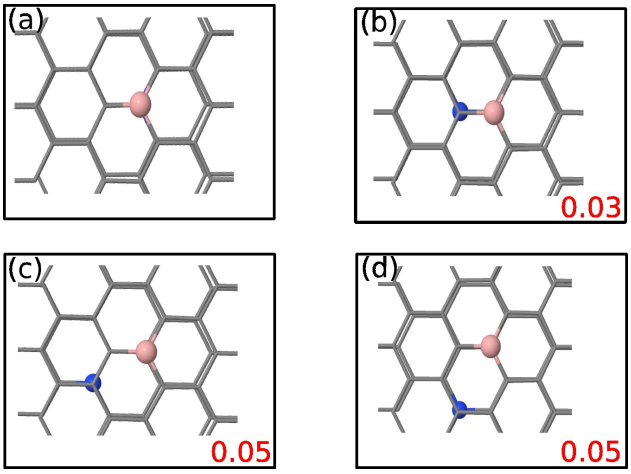

Figure S1: The relative stability of the boron and nitrogen doped AA-stacking bilayer graphene. The number at the right corner in each frame is the energy difference relative to the most stable configuration which is in (a) and unit is in eV. Color code: carbon is gray, boron is pink, nitrogen is blue.

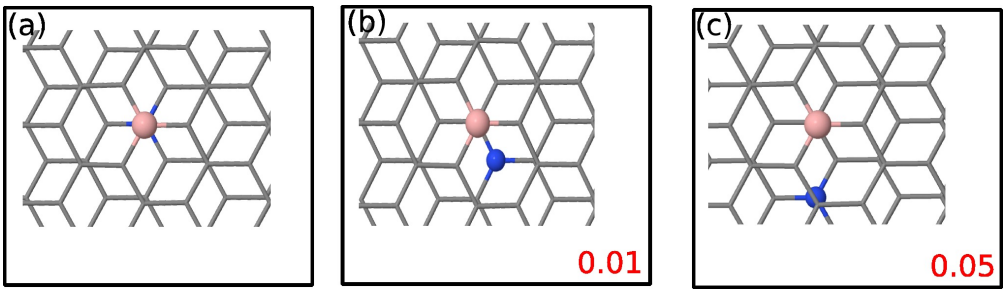

Figure S2: The relative stability of the boron and nitrogen doped AB-stacking bilayer graphene. The number at the right corner in each frame is the energy difference relative to the most stable configuration which is in (a) and unit is in eV. Color code: carbon is gray, boron is pink, nitrogen is blue.

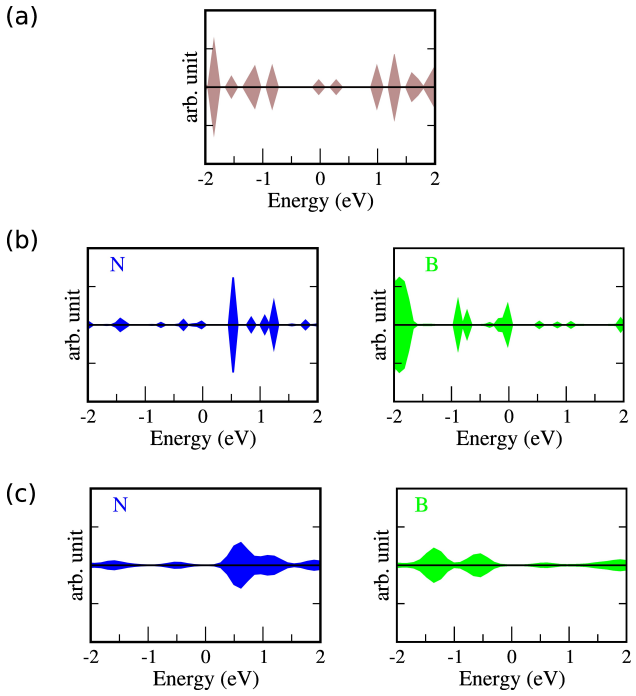

Figure S3: The density of states (DOS) and the partial density of states (PDOS) analysis. (a) DOS of the pristine bilayer graphene (b) PDOS of nitrogen and boron on the AA-stacking bilayer graphene (c) PDOS of nitrogen and boron on the AB-stacking bilayer graphene. The energy zero is Fermi level.

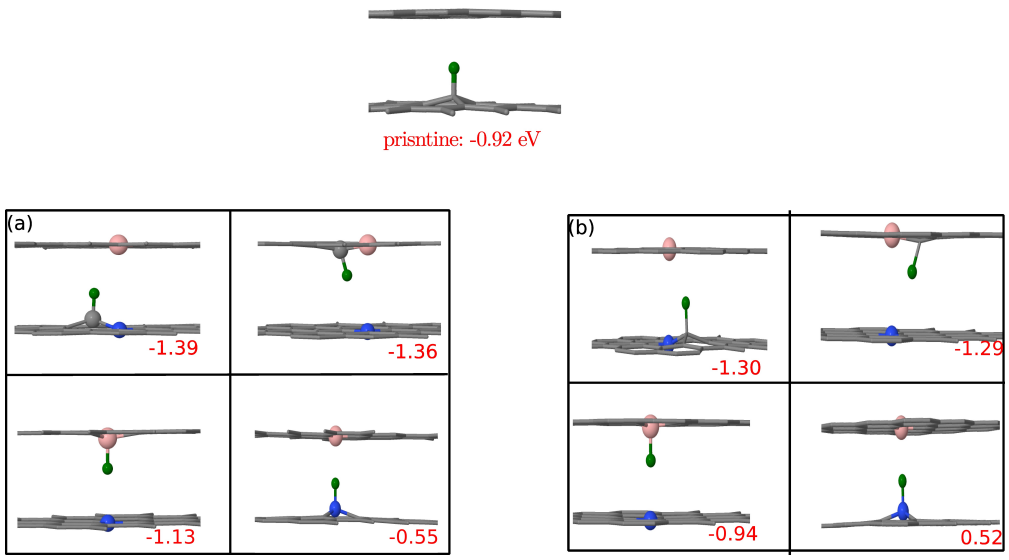

Figure S4: The binding energy of the hydrogen atom. (a) AA-stacking doped (b) AB-stacking doped bilayer graphene. The binding energy on the pristine bilayer graphene is also presented. The negative binding energy means exothermic.

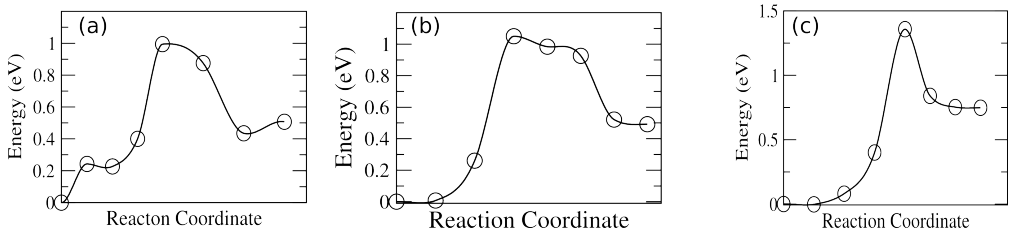

Figure S5: The minimum energy path of the hydrogen activation on BN-G. (a) AA-01 (b) AB-01 (c) AB-02

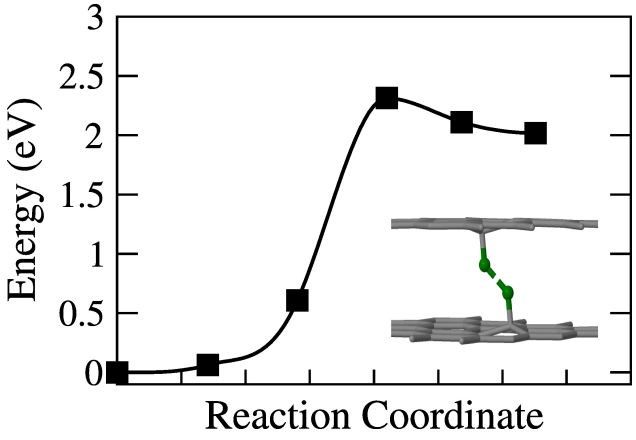

Figure S6: The minimum energy path of the hydrogen dissociation on the pristine bilayer graphene. The inset figure is the structure of the transition state.

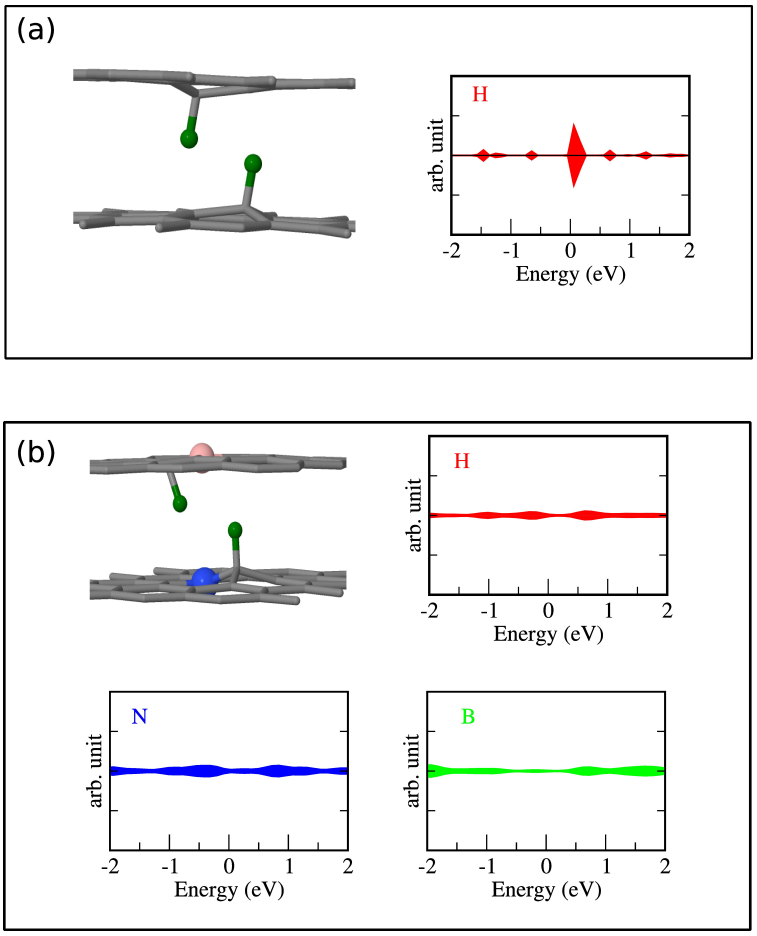

Figure S7: The optimized dissociated structure of H_2 and PDOS. (a) the pristine bilayer graphene (b) AB-stacking doped bilayer graphene.

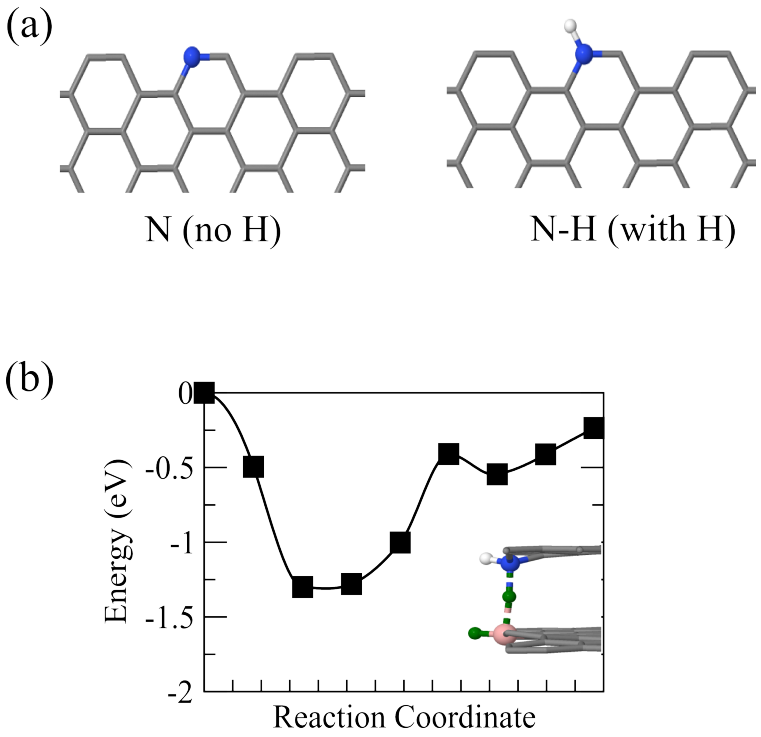

Figure S8: (a) the free nitrogen site without hydrogen (left) and the hydrogen covered nitrogen site (right). (a) The minimum energy path of the hydrogen activation at the hydrogen covered nitrogen site. The inset figure is the structure of the transition state.