Supplementary information

Direct imaging of the nitrogen rich edge in monolayer hexagonal boron nitride and Its Band Structure Tuning

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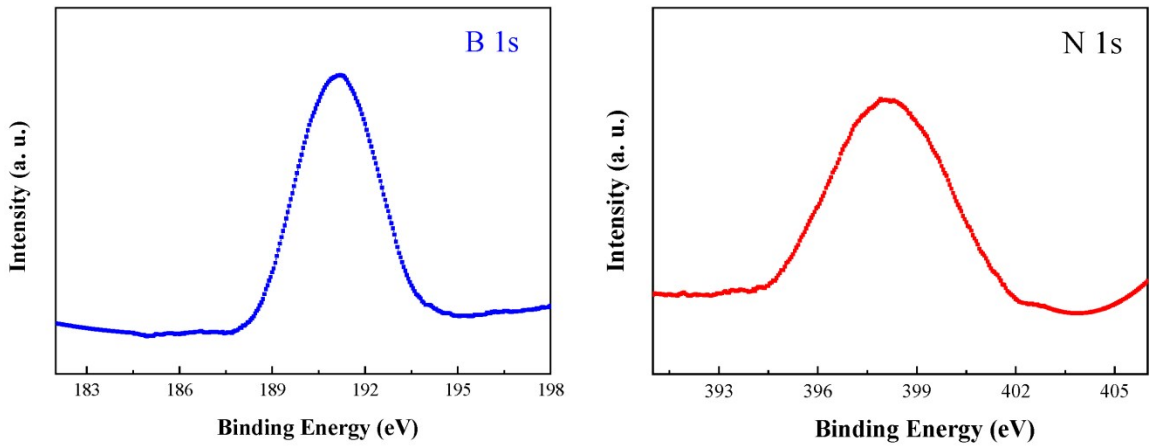

Fig. S1. XPS characterization of CVD grown h-BN. The binding energies of B 1s and N 1s state are 191.2 eV and 398.3 eV respectively, indicating the sp^2 bonding and therefore the hexagonal phase of BN sheets[1].

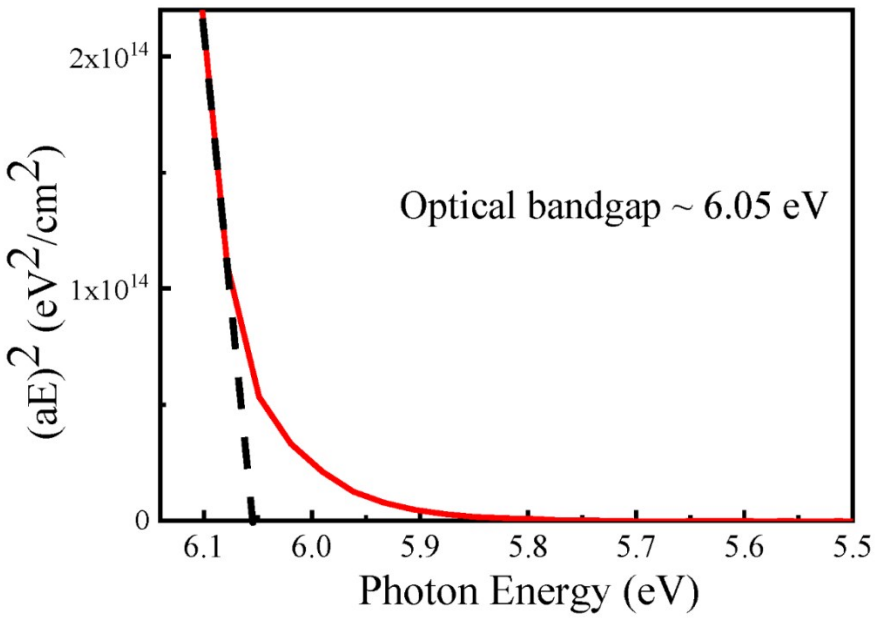

Fig. S2. Bandgap measurement of BN crystallites with ultraviolet-visible absorption spectra. The extrapolation of the linear part of the $(\alpha E)^2$ — $(E - E_g)$ plot intersect X-axis at 6.05 eV.

Ultraviolet-visible absorption spectra were applied to measure the bandgap of h-BN. For direct bandgap semiconductors, the absorption coefficient α is proportional to $\sqrt{(E-E_g)}/E$, where E is the incident photon energy and E_g the optical bandgap[2] . Thus the curve of $(\alpha E)^2$ vs $(E-E_g)$ can be used to determine the bandgap of h-BN. The extrapolation of linear part of the curve intersected X-axis at 6.05 eV, which is the bandgap of h-BN, and the measurement is consistent with our HSE06 calculation result of 5.91 eV.

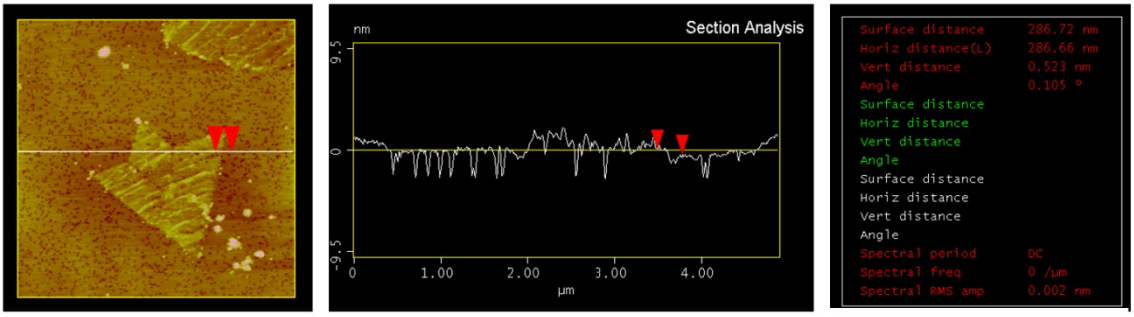

Fig. S3. AFM characterization of single layer h-BN. CVD grown h-BN domains transferred on a silicon wafer was characterized with atomic force microscopy, and the vertical distance of 0.523 nm between the edge of an h-BN domain and the substrate (denoted with the 2 red markers on the AFM image and the line profile across the μm-size h-BN domain) indicates that the h-BN domain is a monolayer.

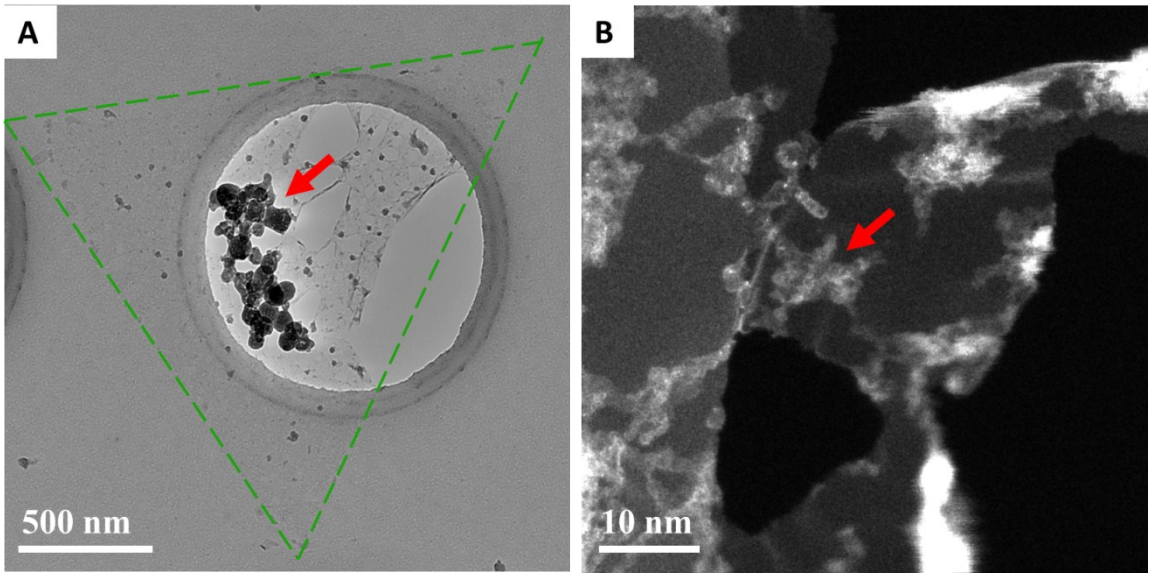

Fig. S4. h-BN monolayer on TEM grid. (**A**) An overview of a triangular h-BN monolayer suspending on a hole of a gold Quantifoil TEM grid. Edges of the triangular h-BN flake are highlighted with dashed green line in this TEM image. (**B**) A zooming in STEM image of the suspended h-BN flake, on which a triangular hole and clean edges can be observed. Red arrows denote junks on the h-BN monolayer.

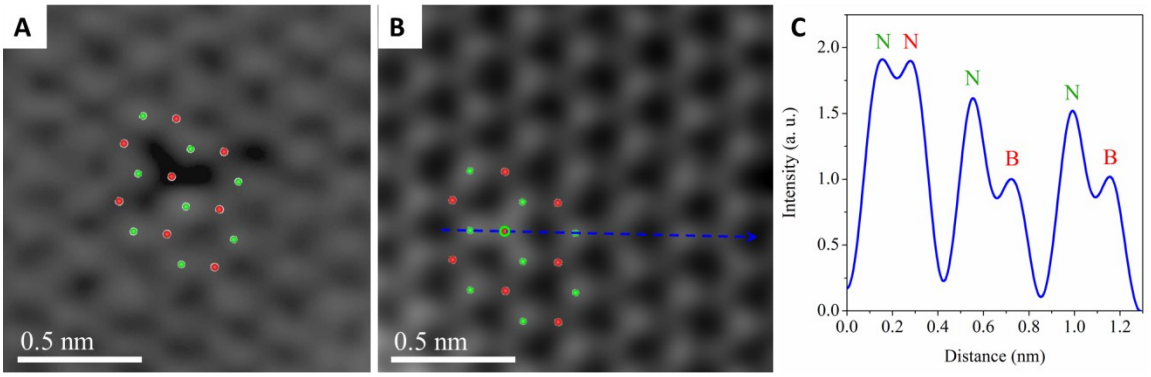

Fig. S5. Native defects in h-BNmonolayer. (**A**) MAADF image of a boron vacancy V_B in h-BN monolayer. Lattice positions near the defect are overlaid with h-BN atomic models for visual guidance. Green and red spots represent N and B atoms respectively, and a red spots in the center of the black tripod hole shows the missing of a B atom. (**B**) MAADF image of a nitrogen anti-site N_B in h-BN monolayer. The red spot with green outline represents the N_B. (**C**) The intensity profile along the blue arrow in (B), convinces that a boron atom on B site was substituted by a N atom.

A defect free h-BN monolayer can sustain a long time scan under a 60 keV electron beam and gives a high quality atomic resolution images. However, intrinsic defects in h-BN will cause unstable and thus holes are common to be created under a focused electron beam. Boron vacancy V_B is one of the sources of producing holes in h-BN, and Fig. S5A is a V_B captured under our low dose MAADF imaging. The overlaid atomic model demonstrates an absence of B, leaving a dark tripod shape in the h-BN monolayer, which is the same configuration as the exit-wave reconstructed image of an aberration corrected HRTEM observation [3]. Nitrogen anti-site N_B in h-BN monolayer is shown in Fig. S5B. h-BN atomic structure model on top of the image demonstrates atomic positions of B and N clearly, and N_B is denoted as the red dots with green outline. A line profile of image intensity along B-N bond (blue line with an arrow end in Fig. S5B) was plot and shown in Fig. S5C. The profile conformed that at this site boron was substituted by nitrogen and thus N-N couple gives a higher intensity due to the stronger electron scattering possibility of nitrogen than that of boron.

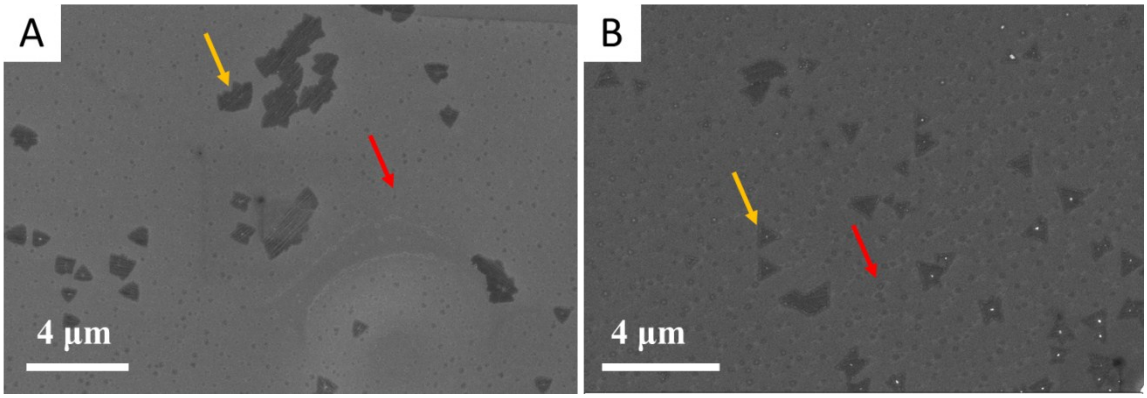

Fig. S6. SEM images of nanosized h-BN islands prepared by the bottom-up CVD growth. (**A**) and (**B**) shows the typical SEM images of morphologies of h-BN islands grown with the duration of less than 1 minute. Small h-BN islands with the lateral size of sub-100 nm and μm-size h-BN monolayer domains are marked with red and orange arrows, respectively.

With the cold-wall furnace system, the CVD growth with the duration of less than 1 min has been performed, giving rise to the small h-BN islands (marked by the red arrows)

with the lateral size of sub-100 nm. Also, the h-BN monolayer domains with larger sizes ($\sim \mu m$) have been observed and highlighted by orange arrows.

References

1. T.H.Yuzuriha and D.W.Hess, *Thin Solid Films*, 1986,**140**, 199-207.
2. X. Blase, Angel Rubio, Steven G. Louie, and Marvin L. Cohen, *Phys. Rev. B*, **51**, 6868.
3. C. H. Jin, F. Lin, K. Suenaga and S. Iijima, *Phys. Rev. Lett.*, 2009, **102**, 195505.