

Supporting Information

# Atomic-scale Dynamics of Triangular Hole Growth in Monolayer Hexagonal Boron Nitride under Electron Irradiation

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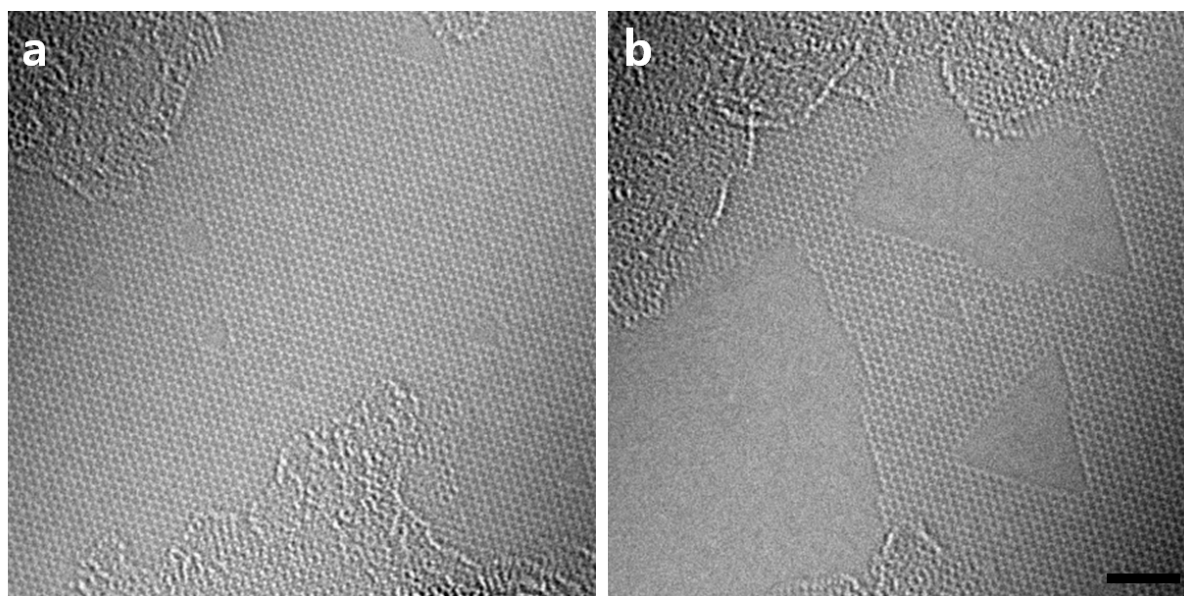
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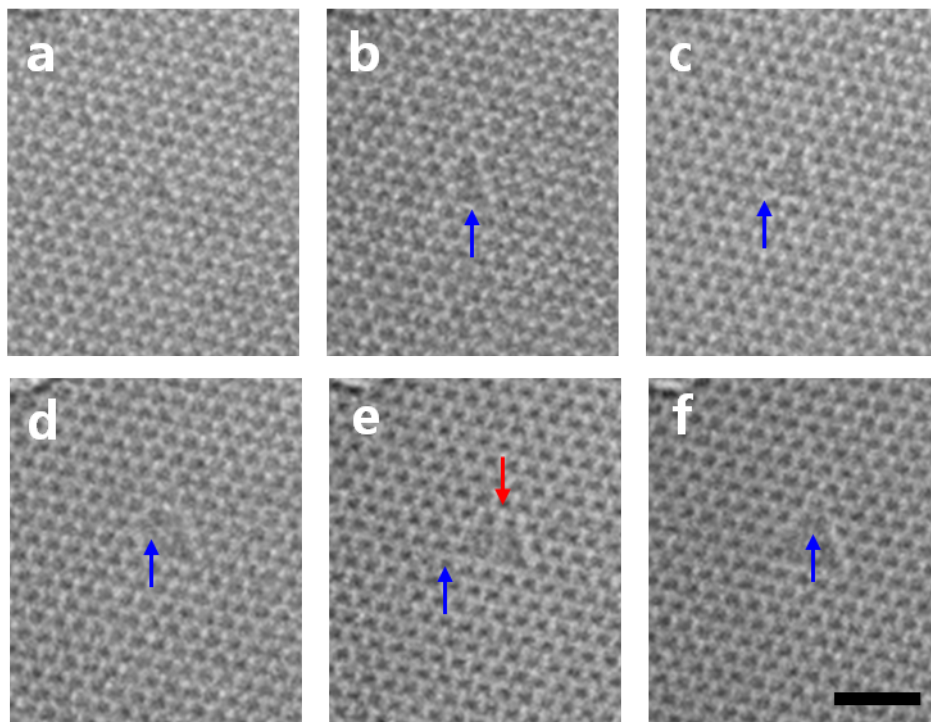
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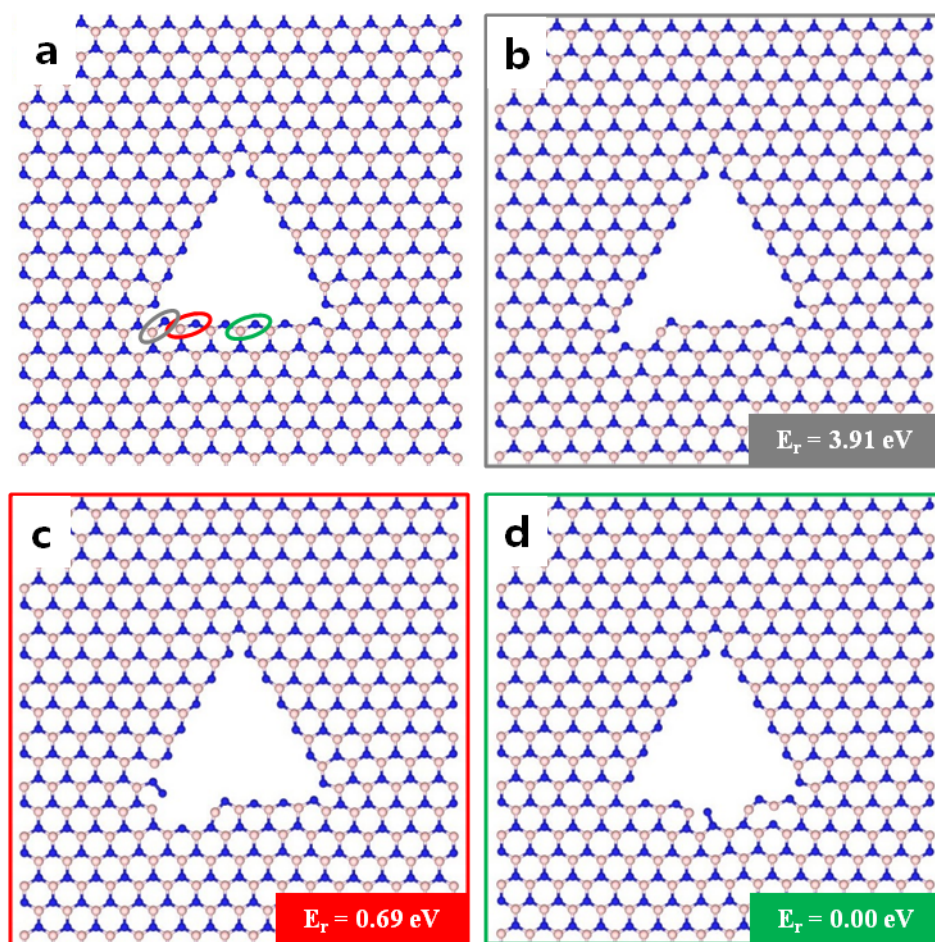
<sup>‡</sup> G.H. Ryu and H.J. Park contributed equally to this work.



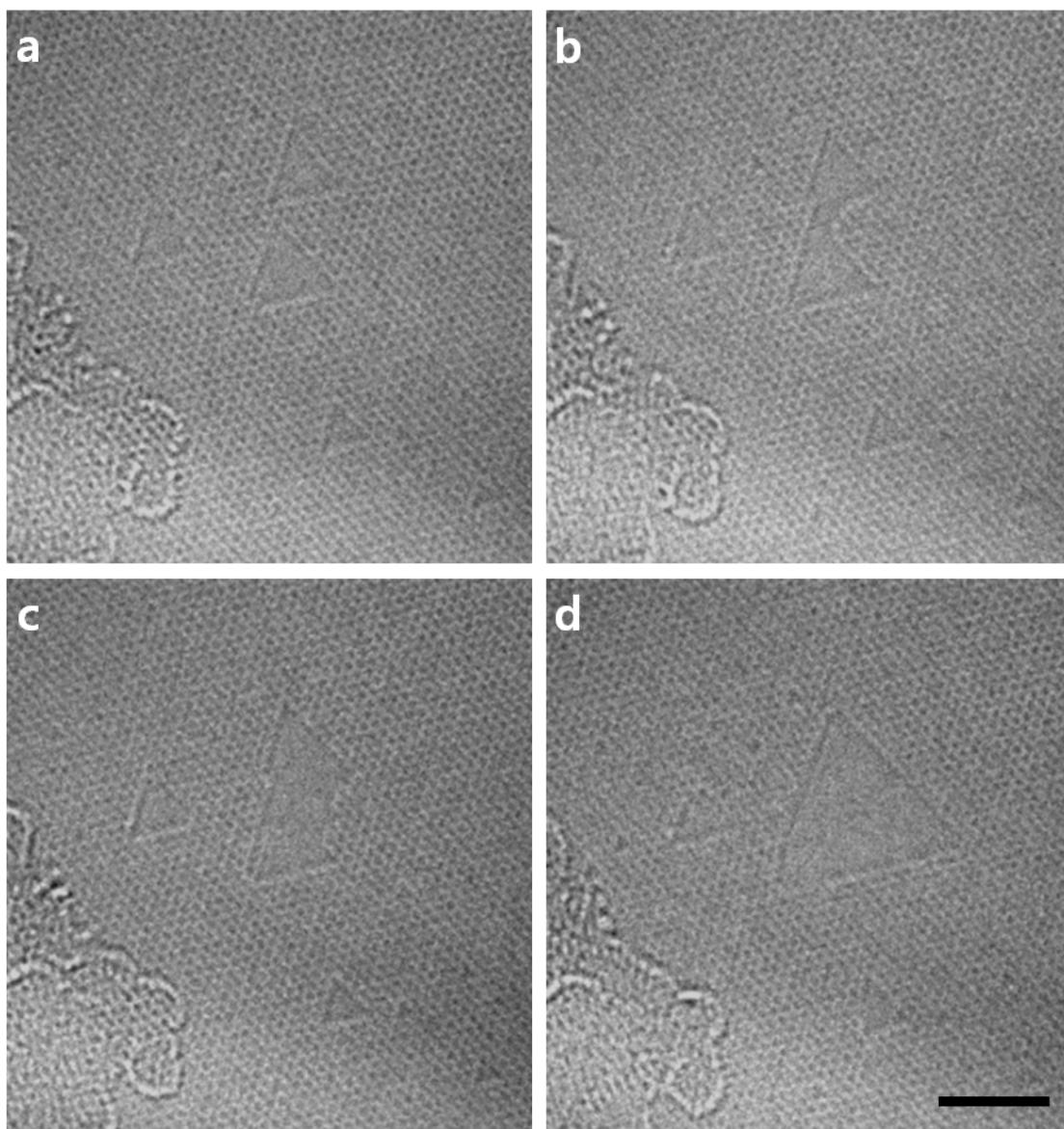
**Fig. S1.** Formation and growth of large triangular holes in monolayer hBN by electron beam irradiation. The TEM images show (a) the initial defects and (b) an enlarged area of the same region. Scale bar is 2nm.



**Fig. S2.** Raw atomic scale images of the growth of a triangular hole found in monolayer hBN. Blue arrows indicate the removal of atoms while the red arrow points to an area where atoms have been added. Scale bar is 1 nm.

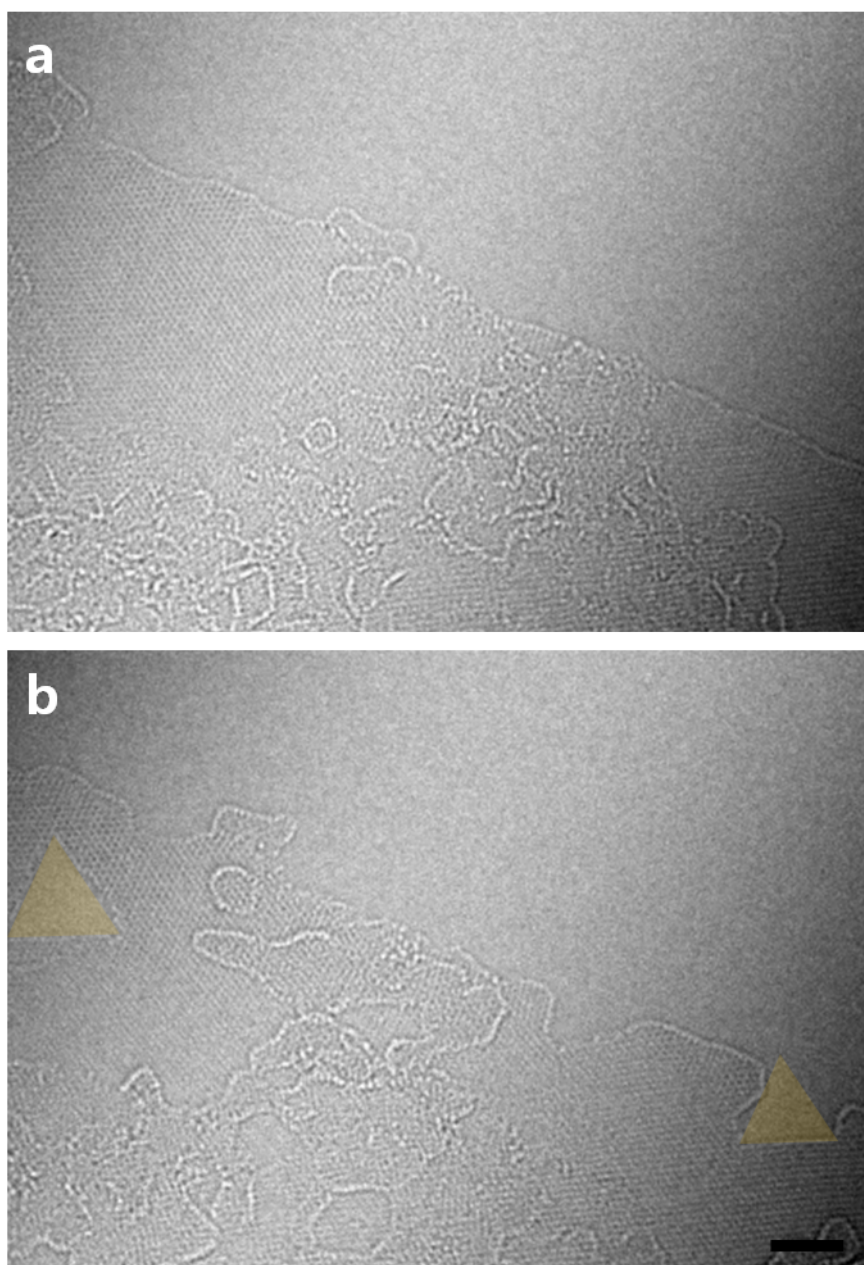


**Fig. S3.** (a) Models for paired B–N atoms missing at an edge of a triangular hole defect in a monolayer hBN sheet with their relative energies: (b) at a corner; (c) near the corner; and (d) near the middle region of a defect edge. Paired B–N atoms missing near the middle of an edge appear to be more stable than those missing at a corner or near a corner.

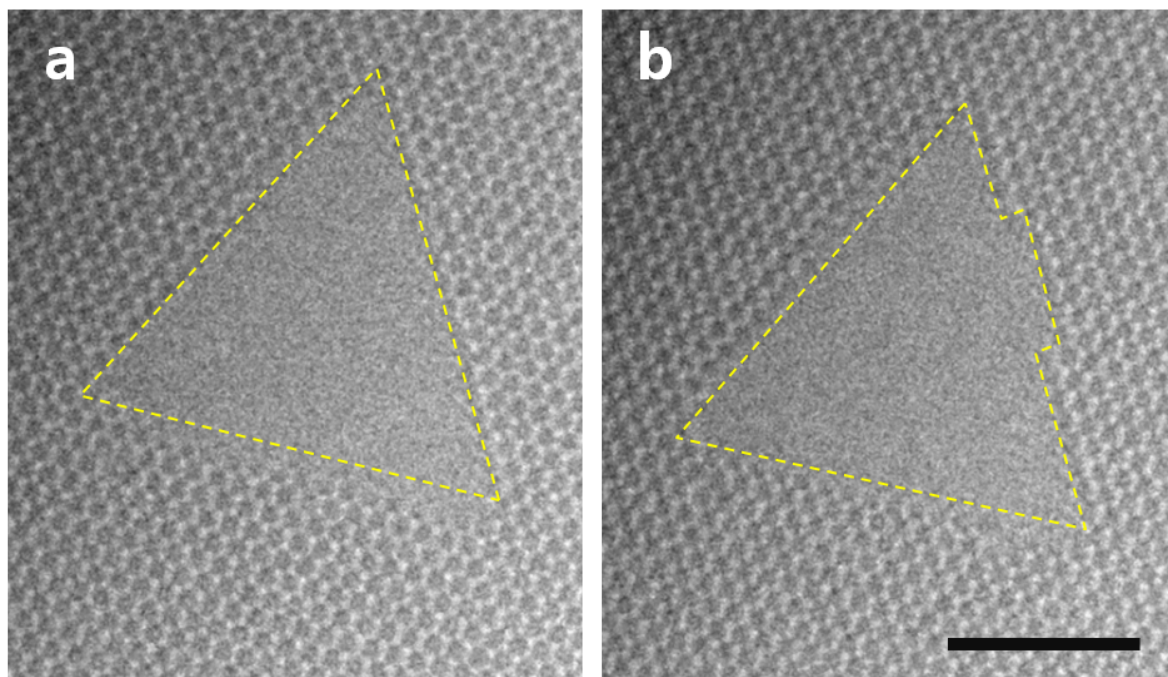


**Fig. S4.** A series of sequential atomic resolution images of monolayer hBN showing how the merging of two holes ultimately maintains a triangular shape. The scale bar represents 2 nm.

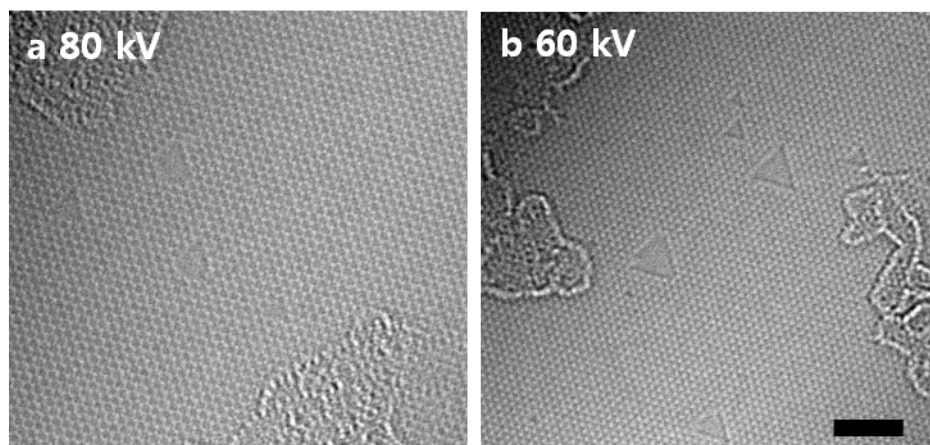




**Fig. S5.** Triangular hole formation on a random edge found in a monolayer of hBN. The images represent (a) an edge followed by (b) the formation of structures with N terminated edges after electron beam irradiation. The scale bar is 2 nm.



**Fig. S6.** Growth of a triangular hole. Comparing the TEM images shown in (a) and (b) reveals that bundles of B and N atoms are removed at a defect edge within the acquisition time of one frame (0.5 sec). Scale bar is 2 nm.



**Fig. S7.** Triangular holes in hBN sheet after electron beam irradiation with different acceleration voltages. Although triangular holes are formed at 80 kV as well as 60 kV, our experiments were performed at 80 kV. Scale bar is 2 nm.

#### **The contribution of oxygen containing species in hole formation mechanism.**

When studying damage mechanism of materials inside TEM, one should consider both physical knock-off of atoms by electron beam irradiation and chemical etching of material by oxygen or other chemicals existing inside TEM. For example, amorphous carbon reacts with oxygen inside TEM and etched away.<sup>1</sup> In addition, oxidation of graphene is expected to require low energy and be irreversible with significant desorption barriers.<sup>2</sup> Contrast to graphene, however, hBN is known to be a chemically inert material. Only weak interaction between oxygen and pristine monolayer hBN is expected. O-containing species such as O<sub>2</sub>, OOH, O and H<sub>2</sub>O are physisorbed on pristine monolayer hBN sheet with very small binding energy.<sup>3</sup> While the defect-free hBN rarely react with oxygen, defect-possessing hBN is reported to absorb oxygen due to the dangling bond, changing the electronic state of hBN.<sup>4,5</sup>

To avoid oxygen-mediated etching effect, defect-free regions where oxygen is hard to attach are carefully selected and observed from the start of forming a monovacancy. As electron beam is continuously irradiated on the hBN sheet as hole grows, oxygen atom may not be able to cling to the defect site of hBN. Therefore, we only address the knock-on damage<sup>6,7</sup> in hole forming mechanism in this paper. Even though our careful selection of defect-free regions, residual oxygen inside TEM may contribute to the hole growth speed or atoms migration. But the triangular hole shape was constantly maintained all in our experiment in any condition.

## References

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