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In-situ TEM imaging of Novel Edge Reconstruction in Bilayer Phosphorene

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Edges of two-dimensional (2D) crystals are crystal factors which determine various properties of the system ranging from electrical, optical, and chemical properties. The true atomic scale configuration and morphology of 2D crystal's edge are far from simply cleaved edge termination due to possible intrinsic edge reconstruction and extrinsic defects or contamination. Therefore, the direct atomic-scale imaging of intrinsic edge configuration for a given 2D crystals will enhance our fundamental understanding of 2D crystal. Transmission electron microscopy (TEM) has been previously employed to observe atomic scale edge structure of various 2D materials. Moreover, via in-situ TEM capabilities, the controlled edge formation under various environments and stimuli can be achieved.

Here, we report the atomic scale TEM observation of ultra-stable self-passivated phosphorene edges in bilayer phosphorene. Previously, the atomic-scale TEM imaging of crystalline edges of phosphorene has been quite challenging compared to other 2D crystals due to sample's vulnerability to ambient exposure and characterization process. To suppress electron-beam induced radiolysis effect during TEM measurement, we use graphene as supporting layer for phosphorene.[1] We prepare phosphorene/graphene vertical heterostructure samples on in-situ heating microchip by dry-transfer technique. Using in situ heating, the prepared phosphorene/graphene samples suffer from little residues and adsorbates.[2] At elevated temperature, the layer-by-layer etching of phosphorene has been observed, which leads to formation of monolayer and bilayer phosphorene regions. We observe that the edge of bilayer phosphorene with zigzag edge configuration shows high stability under electron beam. (Figure 1)

To investigate the detailed edge configuration of stable bilayer ZZ phosphorene edge, we perform TEM imaging at various defocus values as well as tilting configurations. Based on first principles calculations and TEM image simulations, we confirm that bilayer ZZ edge undergoes edge reconstruction with self-passivating interlayer covalent bonds. (Figure 2) Our theoretical calculations also confirm the low formation energy of the observed edge configuration compared to other possible configurations. Our study demonstrates that atomic-scale reconstruction of phosphorus can be harnessed to fabricate stable phosphorene nanostructures with precisely controlled thickness and edge configuration.

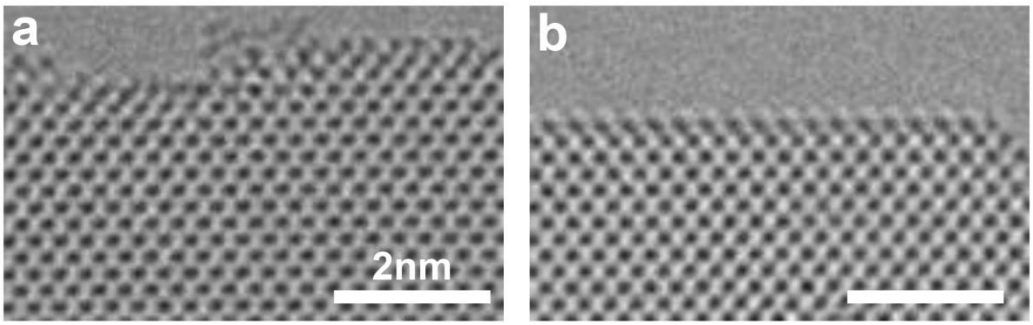

Figure 1. Time-series atomic resolution TEM images of etching of black phosphorus. (a) Non-reconstructed and (b) reconstructed zigzag edges of bilayer phosphorene.

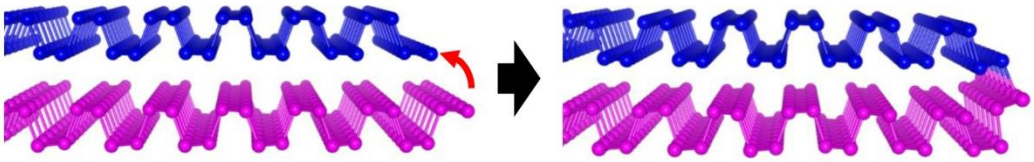

Figure 2. Atomic structures of zigzag edges of bilayer phosphorene before and after reconstruction.

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[1] Y. Lee et al. Nano Lett. **20**, 559-566 (2020).
[2] K. He et al. ACS Nano. **9**, 5, 4786-4795 (2015).
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