Supplementary Information for

In Situ TEM Study of Edge Reconstruction and Evolution in Monolayer Black Phosphorus

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This files includes:

Supplementary Figures S1 to S6. Table 1.

Other Supplementary Information for this manuscript includes the following:

Movie S1: Edge evolution of ML-BP in Figure 1 (AVI).

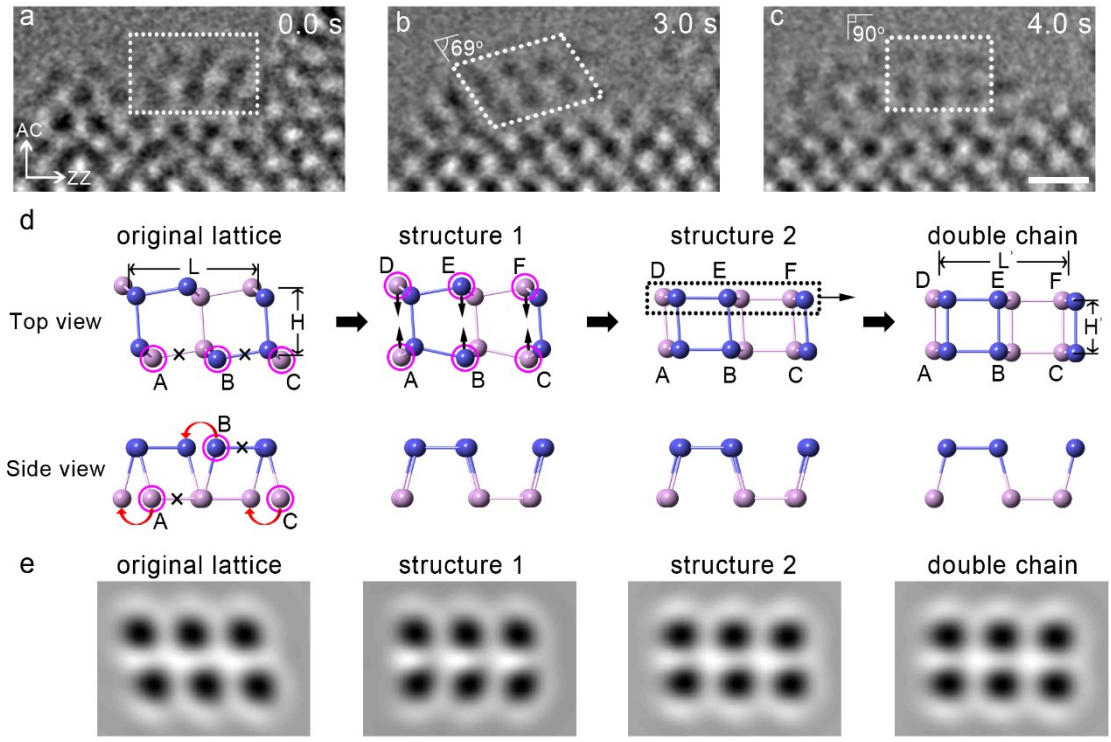

Figure S1. Time sequential HRTEM images of the formation of a double armchair chain. (a) A local disordered edge fragment on the ML-BP. (b) Detachment of an original lattice from the host ML-BP body. (c) Formation of a double armchair chain structure. (d-e) Crystal structures and corresponding simulated images of the formation process of the double armchair chain. Scale bar is 0.5 nm.

Figure S1a shown a local disordered edge fragment on the ML-BP edge as marked with dashed rectangle. At t = 3.0 s, this disordered edge fragment detached from the host ML-BP body and kept an original lattice with two armchair chains ('original lattice' in Figure S1d was its corresponding crystal structure), and then further transform into a double armchair chain configuration in next second. The possible formation mechanism of this double armchair chain was further provided and shown in Figure S1d. Simulated TEM images based on the crystal structures in Figure S1d further validated the structure of double armchair chain.

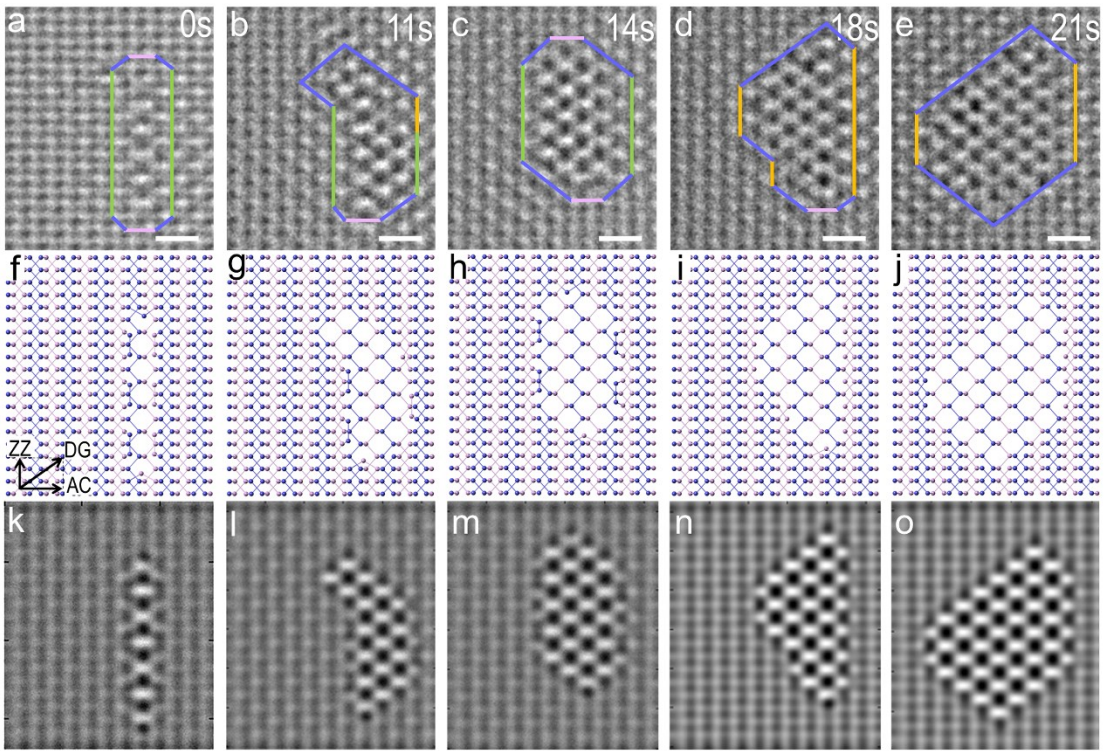

Figure S2. (a-e) Time-sequential HRTEM images of edge evolution in bilayer BP, (f-j) corresponding atomic structures and (k-o) simulated TEM images of (a-e). The $rZZ_{[1, 0]}$, $rZZ_{[1, 0]}$(K), $rDG_{[1, 1]}$ and five-membered ring edges are marked with orange, green, blue and pink lines. Simulated parameters are listed as: Cs = 4 μm, defocus = -6 nm, A1 = 2 nm. The scale bars are 0.5 nm.

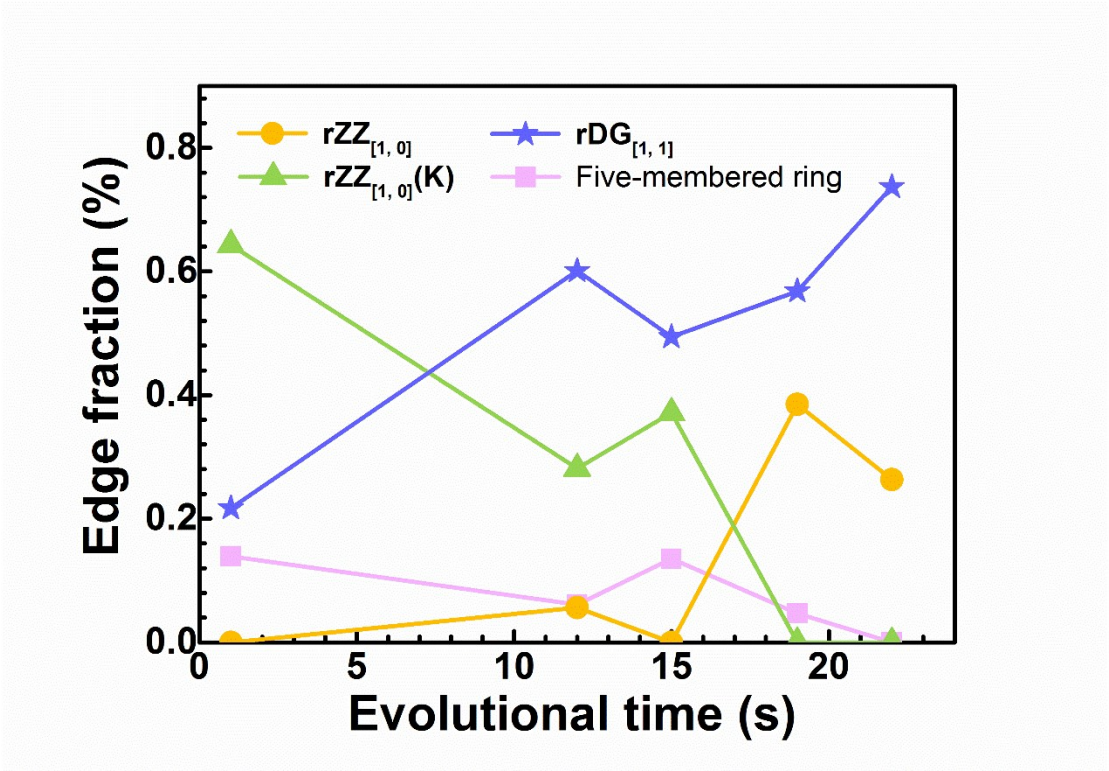

Figure S3. Plot of time evolution of observed edge fractions, including $rZZ_{[1, 0]}$, $rZZ_{[1, 0]}(K)$, $rDG_{[1, 1]}$, and five-membered ring edge from the series HTREM images in Figure S1.

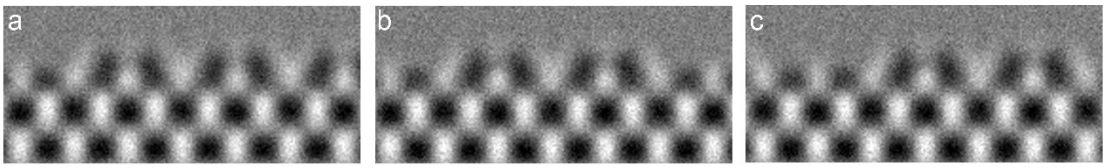

Figure S4. (a-c) Corresponding simulated TEM images of Figures. 2a-2c. Simulated parameters are listed as: Cs = 4 μm, defocus = -6 nm, A1 = 2 nm.

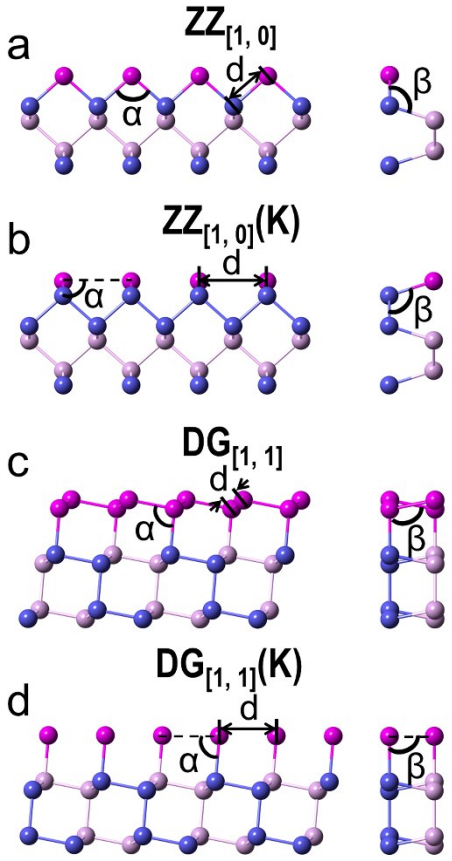

Figure S5. (a-d) Atomic structures of pristine $ZZ_{[1, 0]}$, $ZZ_{[1, 0]}$(K), $DG_{[1, 1]}$, and $DG_{[1, 1]}$(K) edges after total energy relaxed via DFT calculation. Symbols d, α and β represent projected bond length and projected bond angles, respectively, the corresponding values are listed in Table 1.

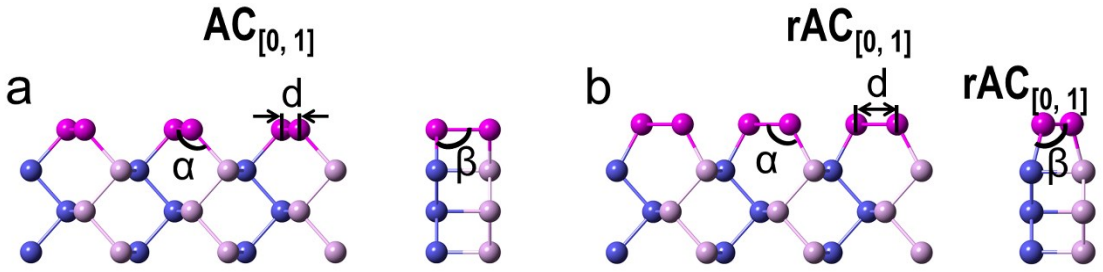

Figure S6. DFT calculated atomic structures of (a) pristine and (b) reconstructed $rAC_{[0, 1]}$ edge. Symbols d, α and β are projected bond length and projected bond angles, respectively.

Table S1. DFT calculated bond length, bond angle and formation energy of pristine and reconstructed AC edge.

Edge	Projected bond length (Å)	Projected bond angle	Formation energy (eV/Å)
$AC_{[0, 1]}$	0.7	$\alpha = 131.7^{o}$, $\beta = 90.0^{o}$	1.084
$rAC_{[0, 1]}$	1.7	$\alpha = 115.7^{o}$, $\beta = 103.4^{o}$	0.671