Electronic Supplementary Material (ESI) for Nanoscale Horizons.

Self-passivation leads to semiconducting edges of black phosphorene

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Outline

Table S1 The edge formation energies for the most stable edge reconstructed structures and pristine edged structures based on three different methods. The unit of energy is eV

Structures		E_{edge-f} (eV/Å)		
		DFT	DFT+D3	DFT+D2
AC	AC-I	0.202	0.276	0.292
	Pristine	0.242	0.302	0.312
	ΔEedge-f	0.040	0.026	0.020
ZZ	ZZ-I	0.131	0.156	0.169
	Pristine	0.435	0.280	0.308
	ΔEedge-f	0.304	0.124	0.139
ZZ1	ZZ1-I	0.163	0.221	0.241
	Pristine	0.383	0.460	0.465
	ΔEedge-f	0.220	0.239	0.224

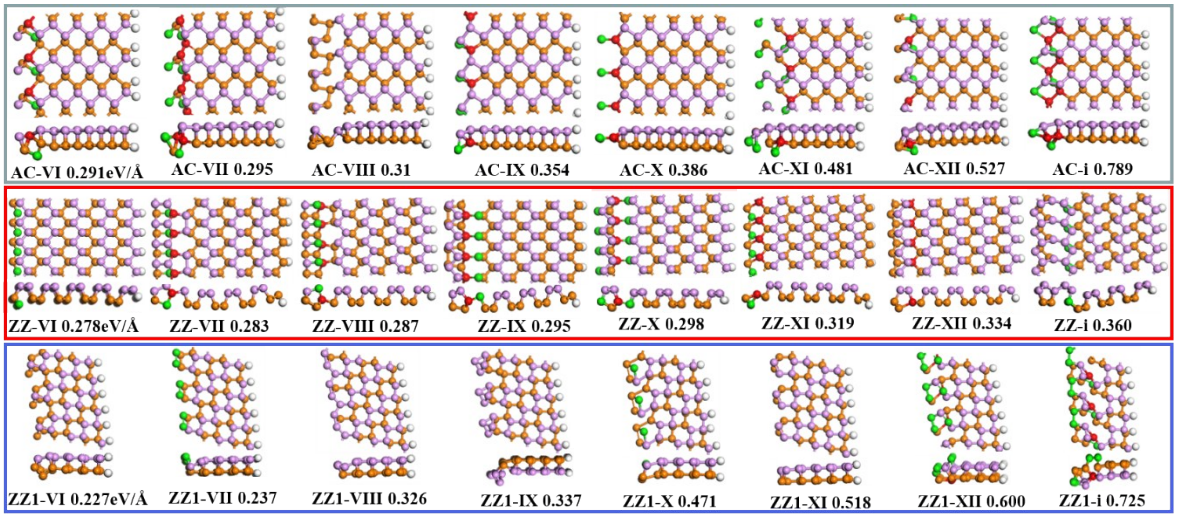

Fig. S1 The top and side views of the other low-lying structures of AC, ZZ and ZZ1 reconstructed edges together with their edge formation energies (unit in eV/Å). The different structures are labeled f-m according to their edge formation energies from low to high. The orange spheres, pink spheres, red spheres, green spheres and gray spheres represent the lower level phosphorus atoms, the upper level phosphorus atoms, the phosphorus atom has four sp^3 bonds, the phosphorus atom has two sp^3 bonds and the hydrogen atoms, respectively.

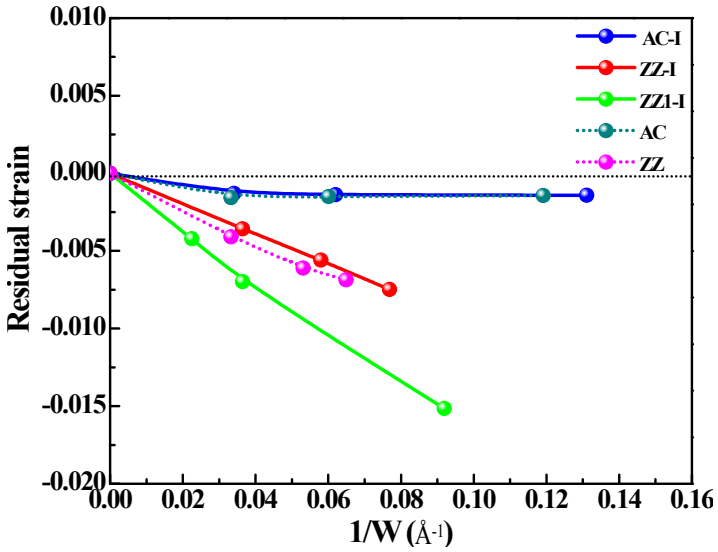

Fig. S2 Residual strains verus the inverse width of the BP ribbons for edge reconstructed AC-I, ZZ-I, ZZ1-I structures (solid lines) and pristine AC, ZZ structures (short dot lines).

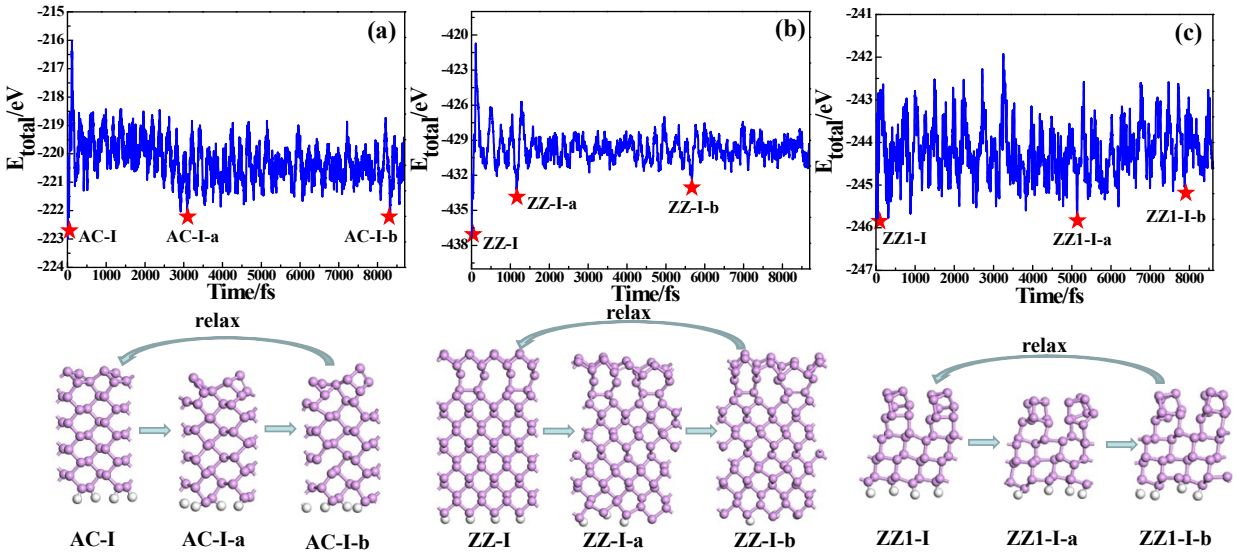

Fig. S3 Phase separations and energy profiles of BP nanoribbons with edge reconstruction (a) AC-I, (b) ZZ-I and (c) ZZ1-I during MD simulations.

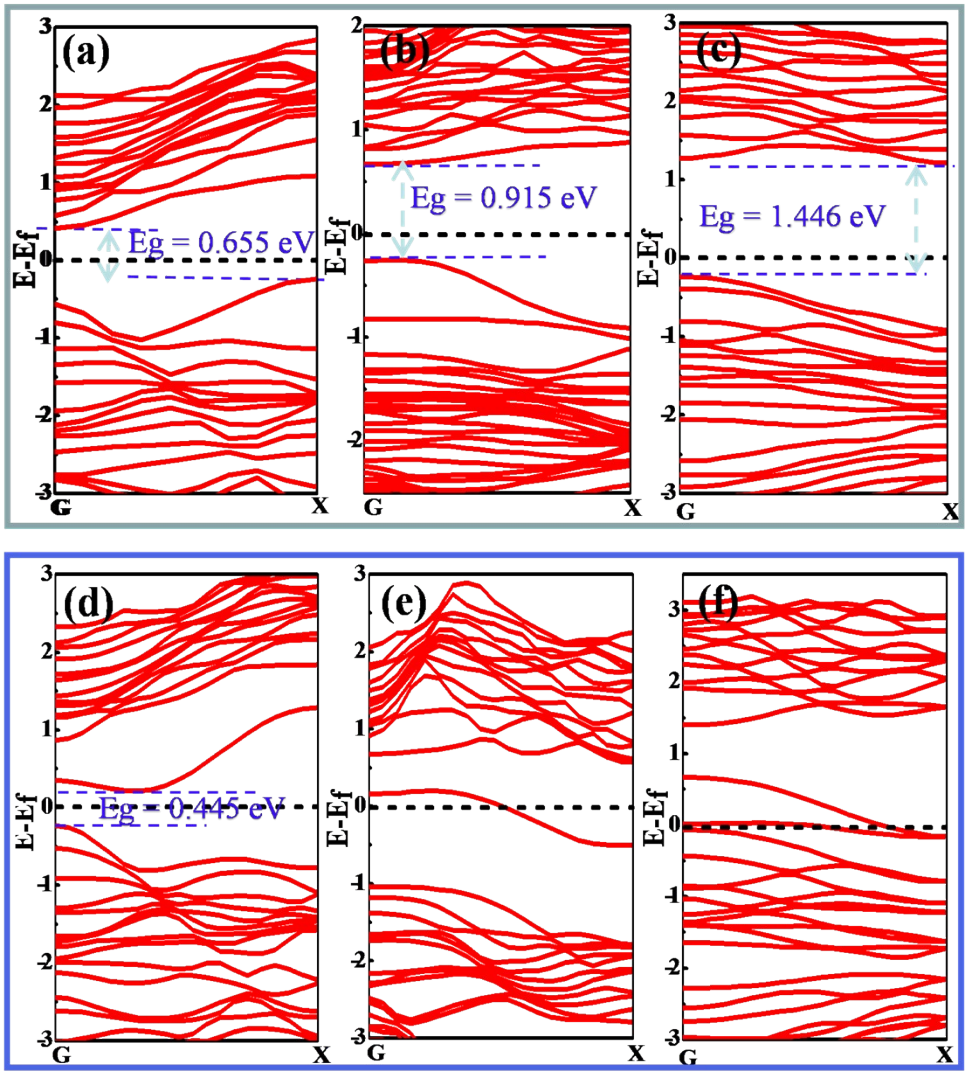

Fig. S4 (a-c) The band structures of AC-I, ZZ-I and ZZ1-I black phosphorene nanoribbons (BPNRs) with edge reconstructions based on PBE method. (d-f) The band structures of AC, ZZ and ZZ1 PNRs without considering edge reconstructions based on PBE method. The Fermi level is set at 0 eV.

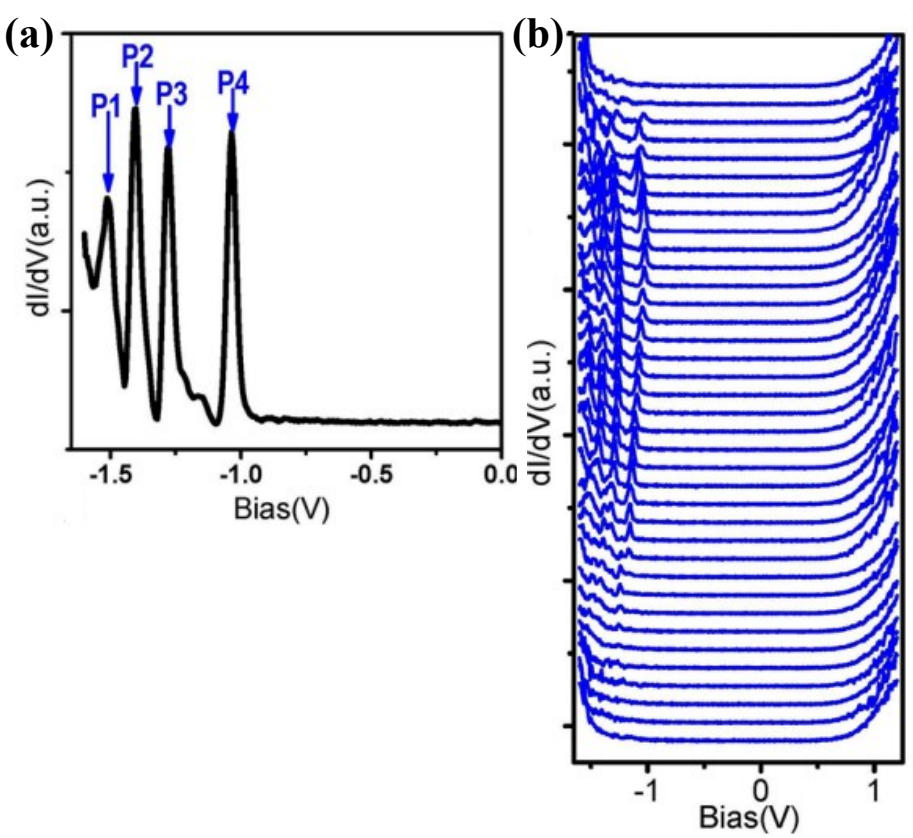

Fig. S5 (a) A typical dI/dV spectrum measured by Meunier *et al*. A series of peaks (labeled as P1 to P4) near the negative gap edge. (b) A series of dI/dV spectra measured along the "*x*" direction across the step edge. Adopted with permission. Copyright 2014, American Chemical Society.

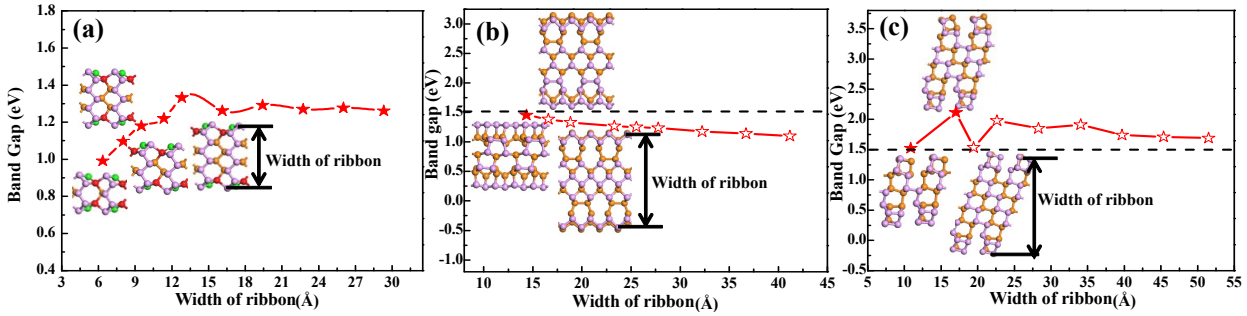

Fig. S6 The band gaps of BPNR structures with (a) AC-I, (b) ZZ-I and (c) ZZ1-I edge reconstruction as the function of nanoribbon width. The definition of the PNR width is also shown in (a), (b) and (c) respectively. The black dashed line shows experimental values of mono-layer BP. The orange spheres, the pink spheres, the red sphere and the green spheres indicate the lower level phosphorus atoms, the upper level atoms, and the phosphorus atoms which has four sp^3 bonds and two sp^3 bonds, respectively. Solid and empty star symbols indicate indirect and direct band gaps, respectively.

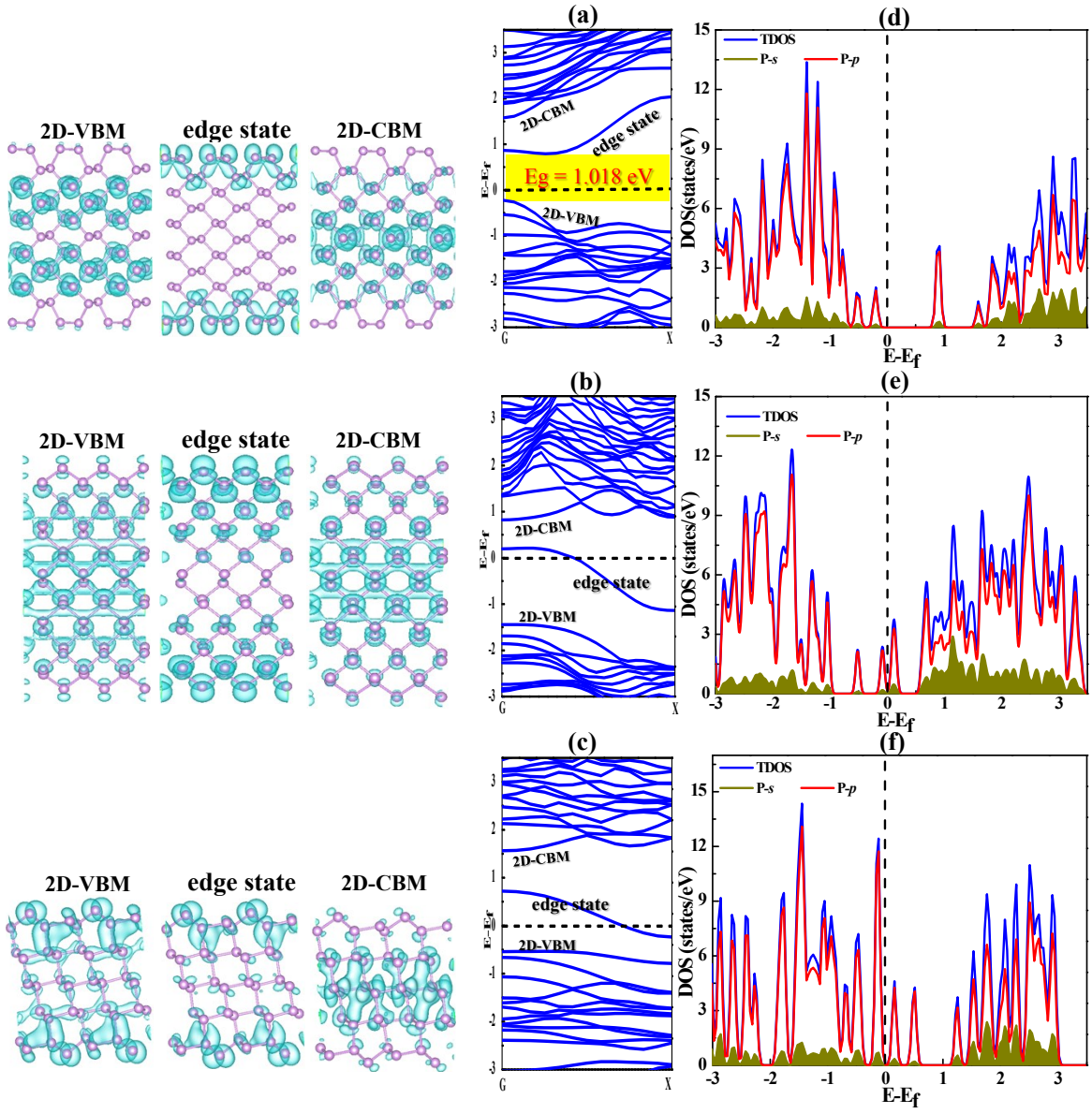

Fig. S7 The band structures and band decomposed charge densities of black phosphorene nanoribbons (BPNRs) with pristine AC (a), ZZ (b) and ZZ1 (c) edges. These BPNRs are saturated by hydrogen atoms on one side. The bands corresponding to 2D phosphorene's valence band maximum and conduction minimum are denoted as 2D-VBM and 2D-CBM, respectively. Edge states around Fermi level are also labeled. (d-f) The corresponding density of states (DOSs) for PNRs with various edges. The Fermi level is set at 0 eV.