Supporting Information for "*Ab Initio* Studies of Thermodynamic and Electronic Properties of Phosphorene Nanoribbons"

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I. COMPARISON OF H_2 CHEMICAL POTENTIALS OBTAINED FROM *AB INITIO* CALCULATIONS WITH EXPERIMENTAL DATA

To validate the *ab initio* approach for calculating the H_2 chemical potential, we compared our calculated results with thermochemical data from standard tables within the temperature range of 298-1000 K.[1] Figure S1 displays the calculated H_2 chemical potential along with that obtained from experimental data. As seen, our calculated results are in excellent agreement with experiment the maximum error being ~ 2 meV.

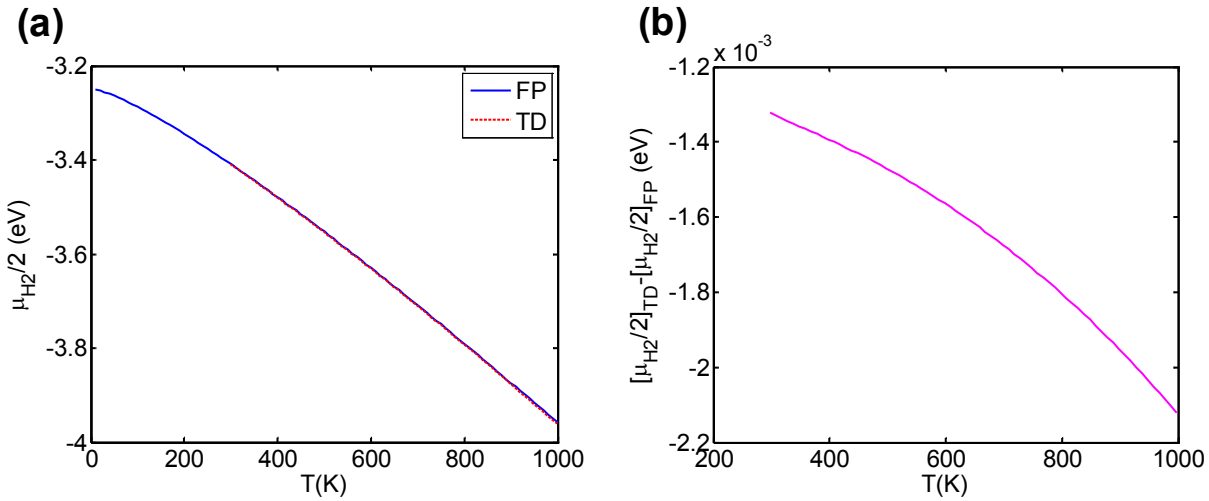

FIG. S1: (a) One half of the H_2 chemical potential computed from first-principles (FP) and thermochemical data (TD) as function of temperature (0-1000 K for FP and 298-1000 K for TD). (b) Deviation between TD and FP predictions for H_2 chemical potential in the range 298-1000 K.

II. ELECTRONIC BAND STRUCTURES FOR PHOSPHORENE NANORIBBONS

For completeness, we present in Fig. S2 electronic band structures of the phosphorene nanoribons—an example for each edge termination—that were not already presented in the main text. Also presented are the partial charge densities arising from the valence band maxima and conduction band minima for semiconducting ribbons. For metallic ribbons, we

display filled and empty states within ±0.2 eV of the Fermi level. As seen from Fig. S2, zigzag ribbons with bare or partially hydrogenated edges all have metallic edges. Ribbons with fully hydrogenated edges are semiconducting. Ribbons with bare armchair edges are semiconducting, but the presence of a mid-gap state makes the band gaps smaller than that of hydrogenated ribbons.

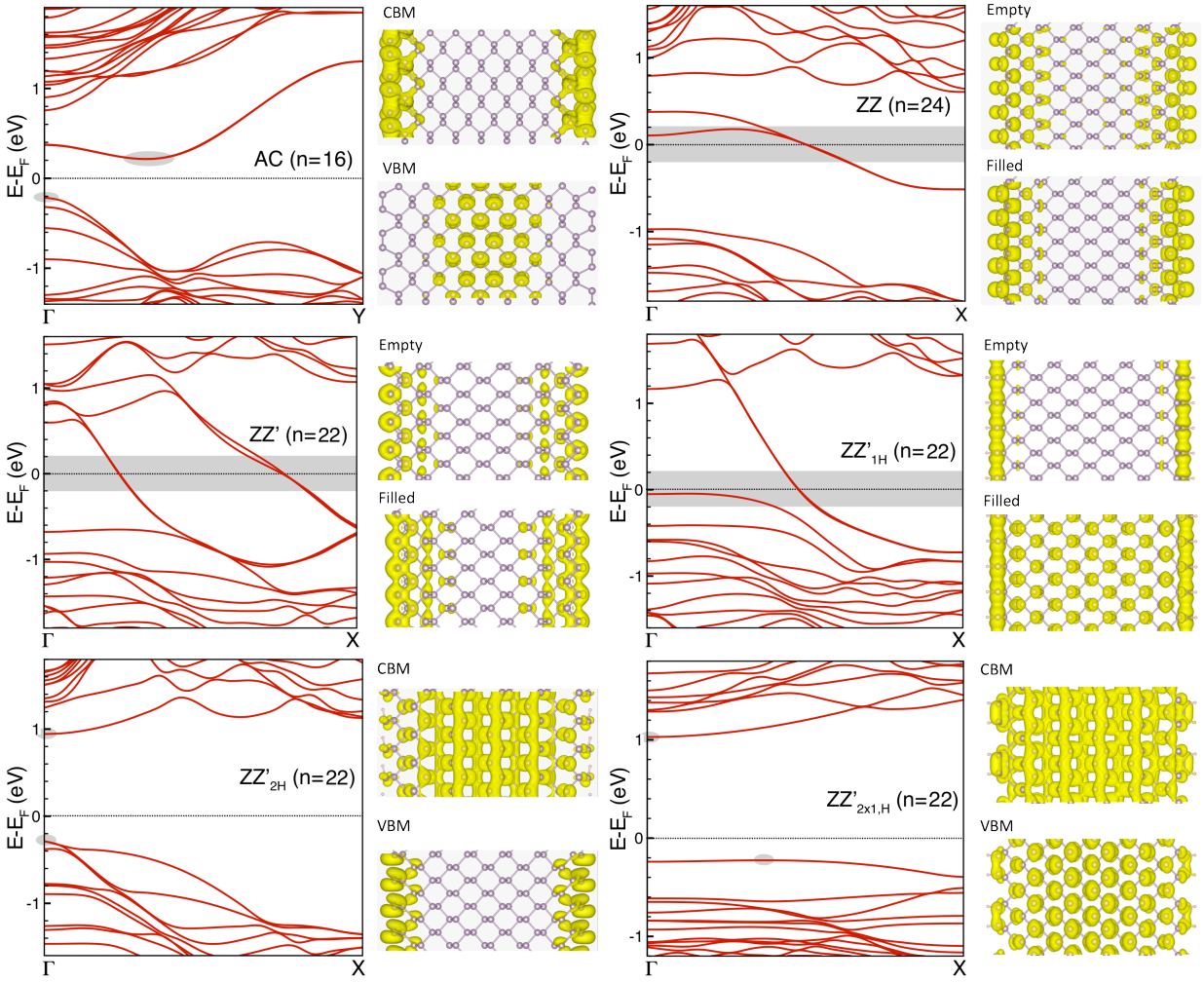

FIG. S2: Electronic band structures of sample nanoribbons with various edge terminations. Ribbon sizes n are assigned as per the indexing scheme in Figs. 2 and 3 of the paper. Also displayed here are the partial charge densities (at arbitrary isosurface levels) of the valence band maxima (VBM) and conduction band minima (CBM) of semiconducting ribbons, which are marked by grey ellipses in the bandstructure plot. For metallic ribbons, filled and empty states within ±0.2 eV of the Fermi level (shaded regions) are displayed.

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[1] *NIST Chemistry WebBook*, Mallard, W.G.; Linstrom, P. J., Eds. NIST Standard Reference Database Number 69; National Institute of Standards and Technology: Gaithersburg, MD, 2003, 20899 http://webbook.nist.gov/chemistry/.