Electronic Supplementary Information (ESI)

Long-Term Can-Sealing Protection: Stable Black Phosphorus Nanoassembly Achieved through Heterogeneous Hydrophobic Functionalization

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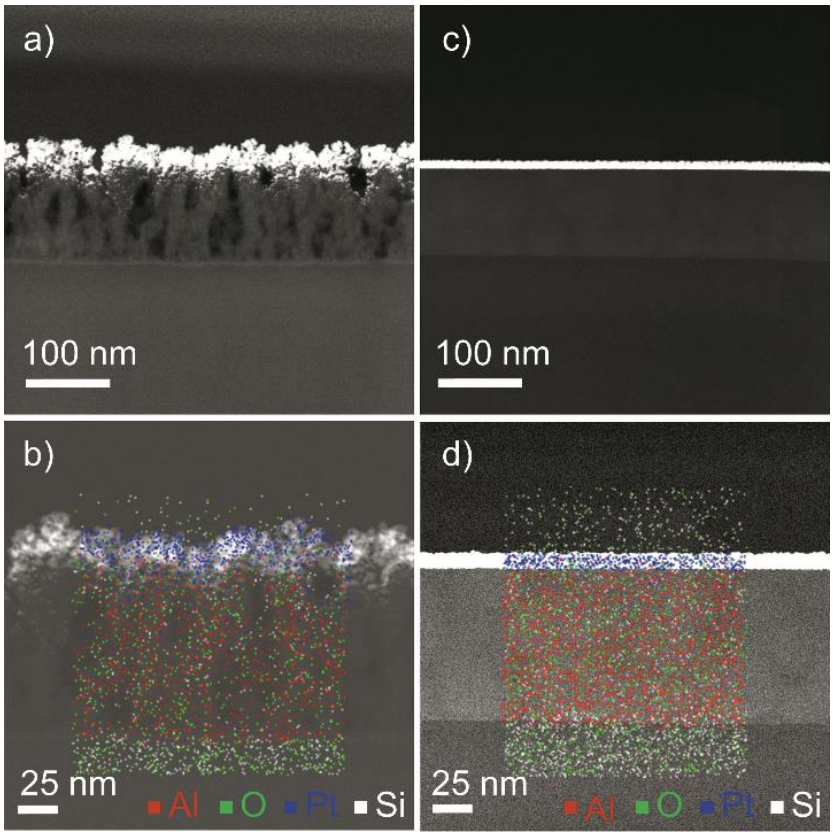

Figure S1. (a-d) Cross-sectional HAADF images and corresponding EDS mappings of Al (red), O (green), Pt (blue), and Si (white) taken from Column-LP and Dense-HT.

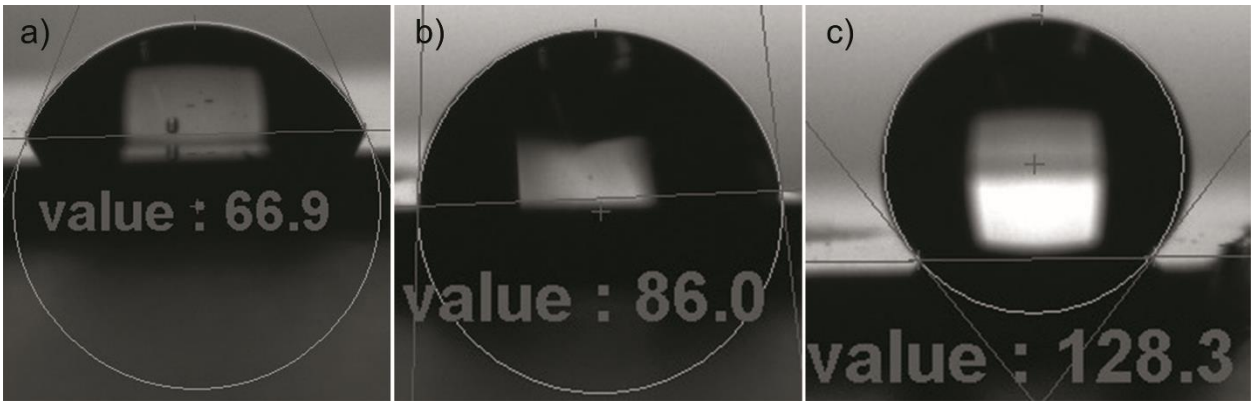

Figure S2. Contact angle images for droplets of water on (a) SiO_2/Si substrate, (b) hydrophilic dense Al_2O_3, and (c) hydrophobic columnar Al_2O_3 layer.

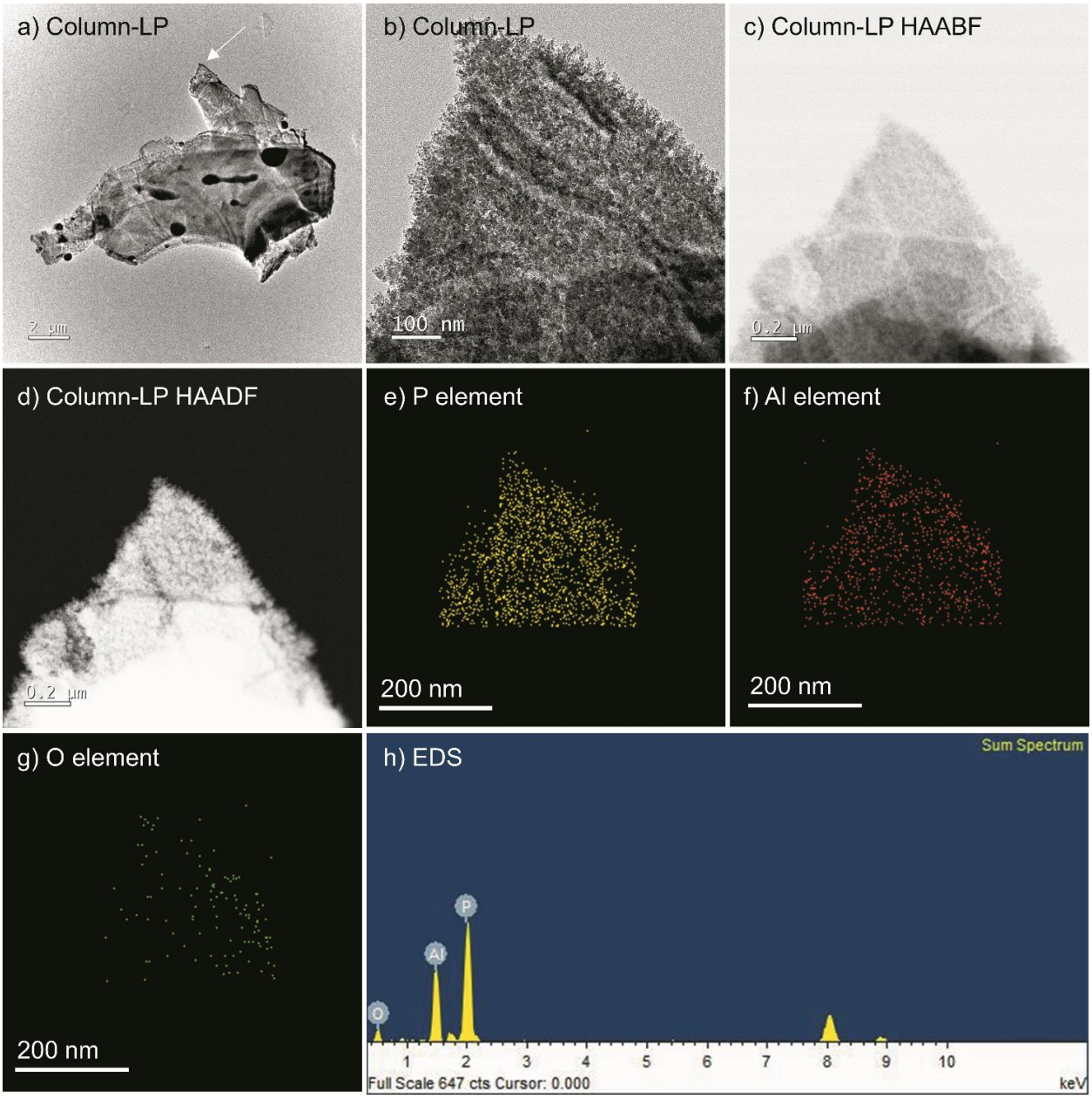

Figure S3. TEM images of (a) an isolated BP flake capped with hydrophobic Al_2O_3 layer and (b) enlarged image from (a). (c) HAABF and (d) HAADF STEM images, the corresponding (e-g) EDS-STEM mappings of P, Al, and O elements, and (h) EDS spectrum of (d).

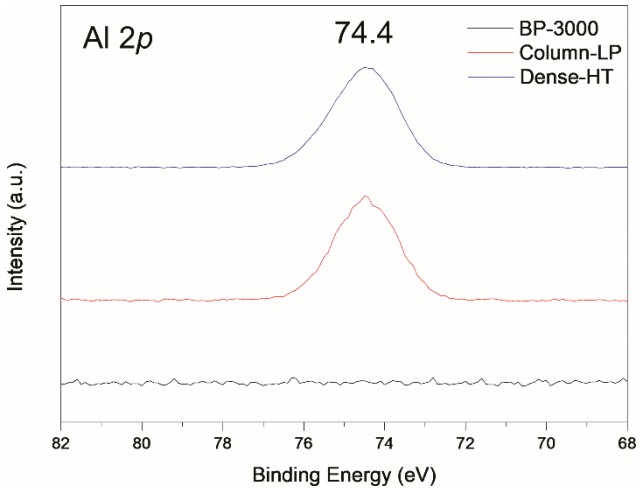

Figure S4. XPS binding energy around Al 2*p* core-levels recorded from the pristine BP flakes collected with a centrifugal speed of 3K rpm (BP-3000) and the Al_2O_3 capped BP flakes assemblies (Dense-HT and Column-LP).

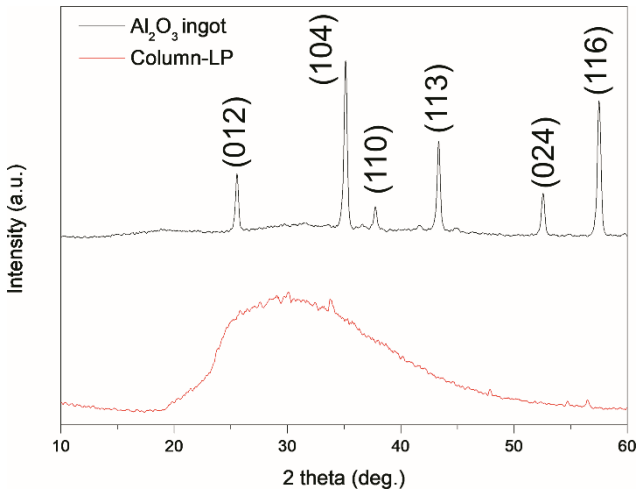

Figure S5. The XRD patterns were recorded from the Al_2O_3 ingot for laser ablation and the obtained Al_2O_3 layer deposited at a substrate temperature of 25 ^oC.

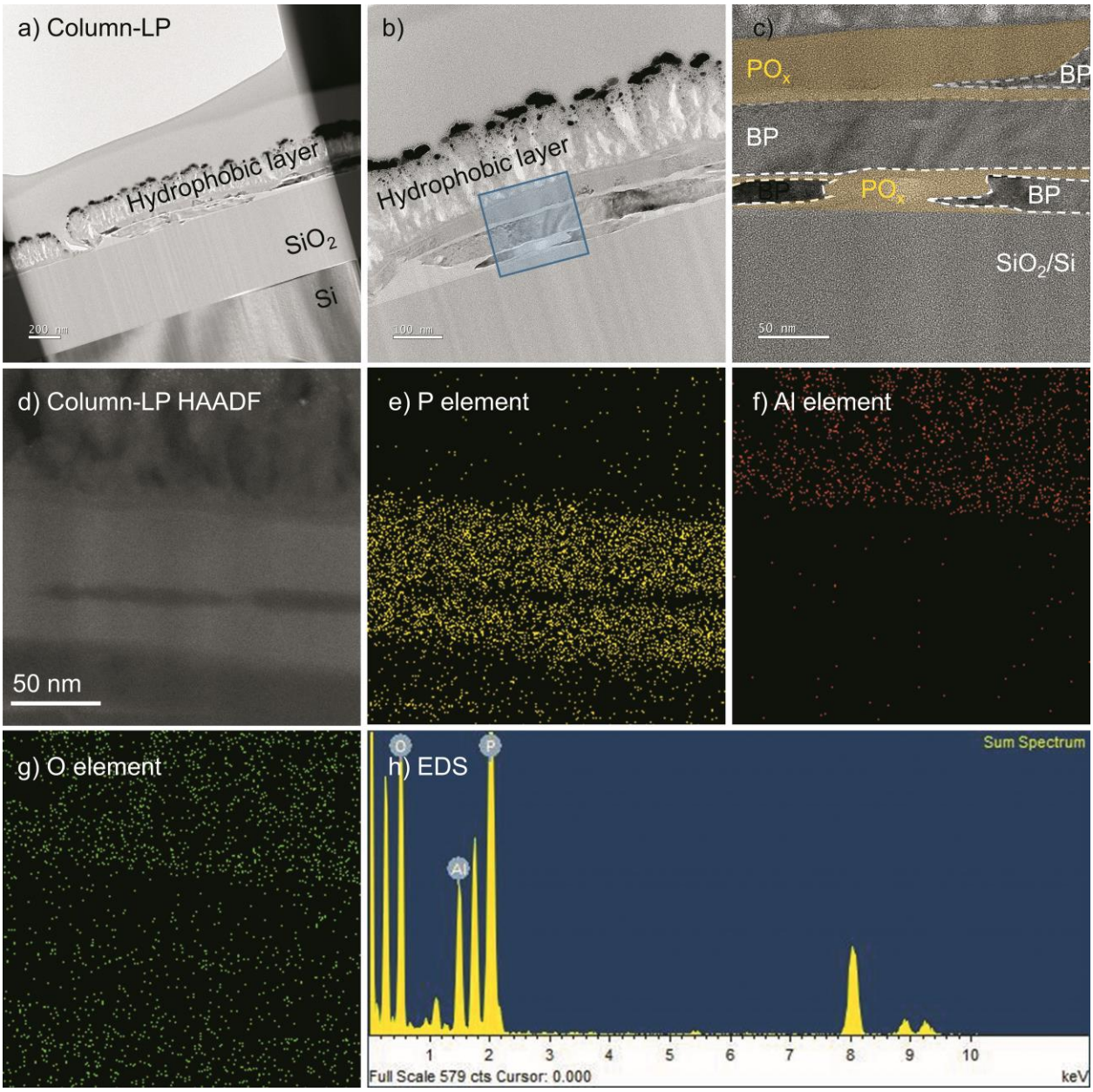

Figure S6. Cross-sectional TEM images are taken from the BP flakes assemblies capped with (a-b) the hydrophobic layer (from Column-LP), (c) enlarged image from (b), and the image shows the PO_x-BP-PO_x sandwich structure. (d) HAADF STEM image, the corresponding (e-g) EDS-STEM mappings of P, Al, and O elements, and (h) EDS spectrum of (d).

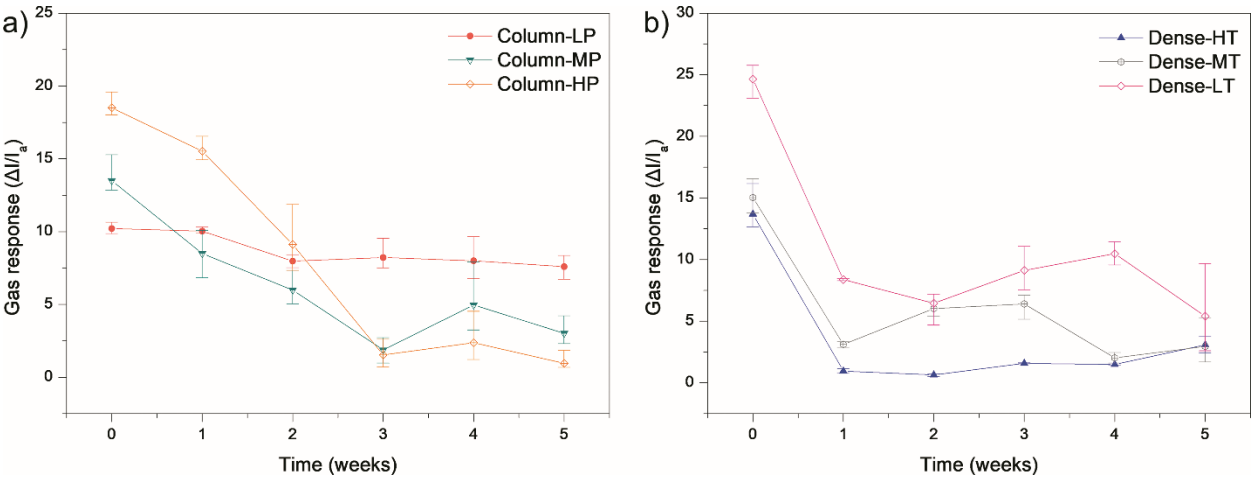

Figure S7. The stored-time dependent saturated response ($\Delta I_{max}/I_a$ collected from the humidity sensing curves measured at the setting stored time) of the BP flakes assemblies capped with (a) the columnar Al_2O_3 layers and (b) the dense ones.

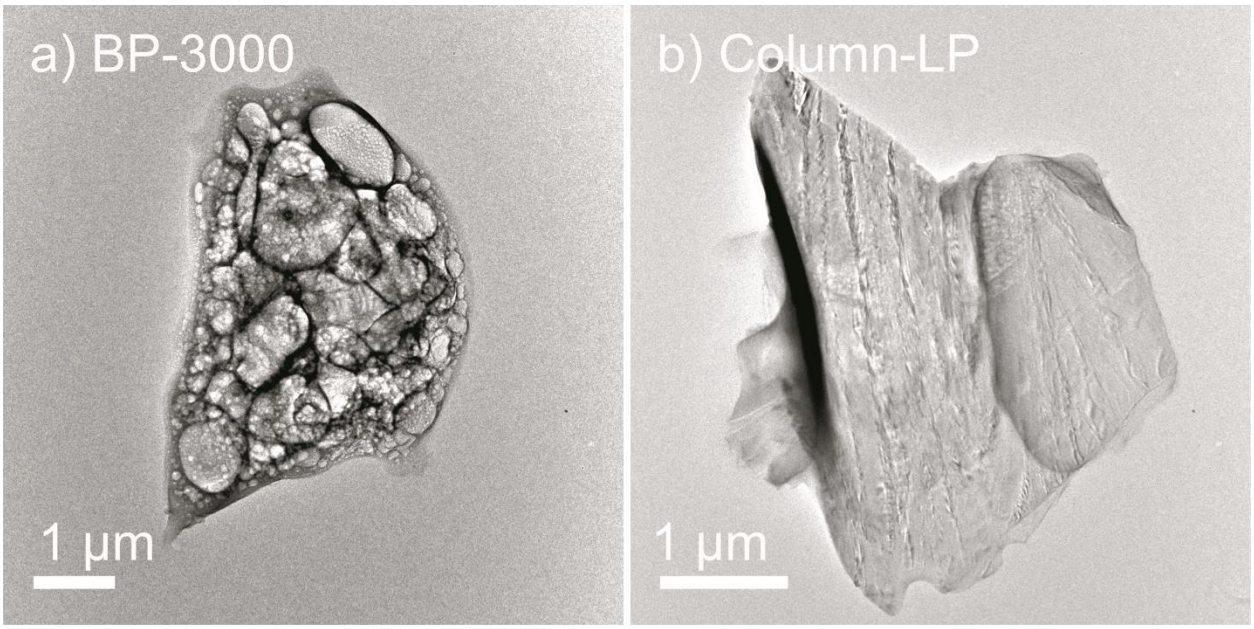

Figure S8. The TEM images of (a) an isolated bare BP flake and (b) a separated columnar Al_2O_3 layer capped BP flake after being exposed to the atmosphere (RH = 70%) at room temperature for 35 days. The numerous circular patterns were the sign indicating the degradation, more precisely, the formation of phosphoric acids on the BP surface while exposing to a humid atmosphere. In contrast, the relatively smooth surface found from the columnar Al_2O_3 capped BP flake reveals the success of the proposed can-sealing concept using hydrophobic Al_2O_3 nanostructures as the passivation layers for preventing the rapid degradation of BP.

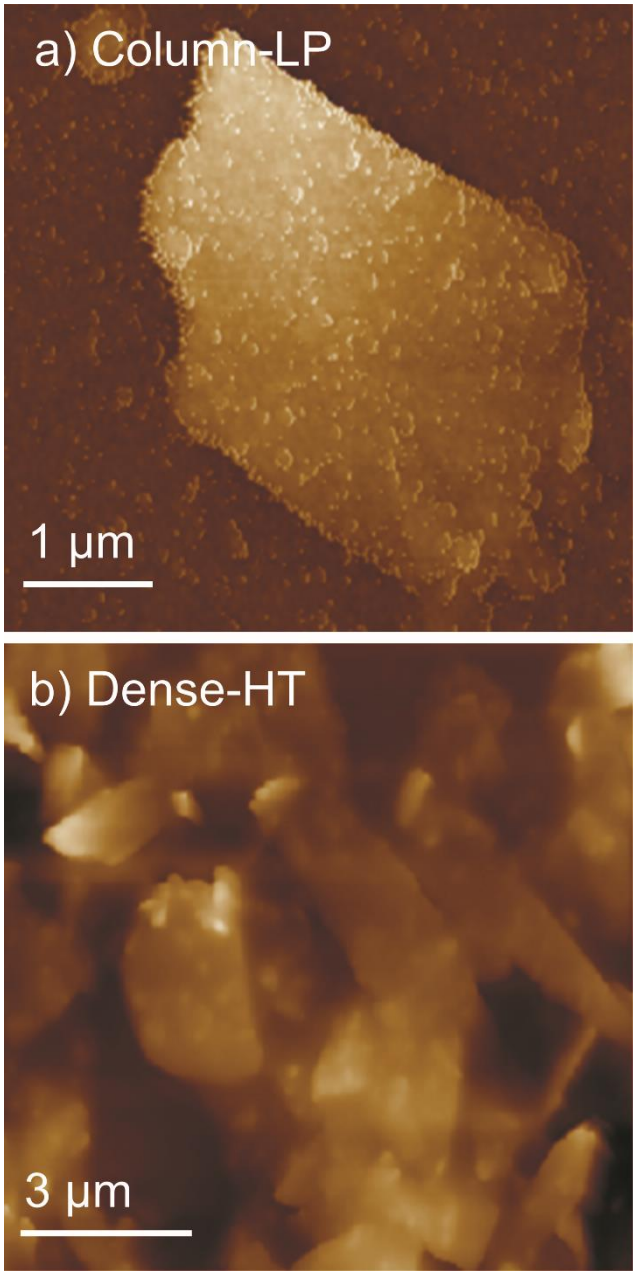

Figure S9. The AFM images of (a) an isolated columnar Al_2O_3 layer capped BP flake and (b) bare BP flake after being exposed to the atmosphere (RH = 70%) at room temperature for 35 days.