In contrast to quick degradation of exfoliated as-grown BP (AG-BP) flakes, hydrogen treated BP (H₂-BP) flakes only undergo a few percent of corrosion even after long exposure of 4 weeks under ambient conditions. More impressively, the H₂-BP FET devices still deliver high values of mobility and $I_{ON}/I_{OFF}$ ratio, retaining ~ 85% of their initial values.

1. AFM studies on AG and H₂-BP flakes under ambient exposure

BP flakes were mechanically exfoliated from AG and H₂-BP crystals onto oxidized Si substrates. AG and H₂-BP flakes were kept under the same ambient condition, and atomic force microscopy (AFM) was used to keep track of degradation-induced changes in the surface morphologies with exposure time (see Fig. 1a, b). Initially, as-exfoliated AG and H₂-BP flakes both have a smooth surface. Degradation under ambient exposure leads to formation of bubbles on the surface, similar to the previous reports. The AG-BP flake exhibits fast ambient degradation, as shown in Fig. 1a. With increase of exposure time, degradation-produced bubbles
on the surface grow quickly in size, and they merge together to form the larger ones. On the ninth day, the AG-BP flake was partially corroded away owing to deep degradation. With further exposure, more and more of the AG-BP flake were corroded away. On the twentieth day, the AG-BP flake was almost completely corroded away, and just a few large bubbles are clearly observable. In comparison, the H$_2$-BP flake displays much slower ambient degradation. As shown in Fig. 1b, degradation-produced bubbles on the surface of H$_2$-BP flake exhibit much slower growth in size with increase of exposure time up to 28 days, and no sign of complete corrosion was observable. The extracted roughness and height from AFM images and their dependences on exposure time are shown in Fig. 1c, d. Under ambient exposure up to 22 days, the AG-BP flake of 10.5 nm thickness exhibits a quick increase in surface roughness by more than 500% and a fast reduced thickness by $\sim$ 90%. In contrast, the H$_2$-BP flake of 10.2 nm thickness under ambient condition shows a much slower increase in roughness and a much smaller reduction in thickness with exposure time. Even after exposure of 28 days, the surface roughness is increased just by $\sim$250% and the thickness is reduced just by $\sim$10%.
Fig. 1 AFM characteristics of BP flake upon ambient exposure. (a) AFM image of as-growth (AG) BP flake with a thickness of \(\approx 11\) nm. (b) AFM image of a hydrogen treated BP (H$_2$-BP) flake with a thickness of \(\approx 10.5\) nm. The height profile was obtained along the white dash line in (a) and (b). (c) Variation of surface roughness with increasing exposure time. (d) Variation of retained BP thickness with increasing exposure time. Scale bars in (a) and (b) represent 1 \(\mu\)m. Dashed lines in (c) and (d) are the guide lines. (e) Real-time $^{31}$P MAS NMR spectra of AG-BP flakes day by day. (f) Real-time $^{31}$P MAS NMR spectra of H$_2$-BP flakes day by day.
2. Transport characteristics of AG and H$_2$-BP FETs for comparison

Based on the mechanically exfoliated few-layer AG and H$_2$-BP flakes, a series of FET devices have been fabricated to investigate their transport characteristics for comparison. The electrical transport properties were measured at ambient condition.

Among 20 as-fabricated H$_2$-BP FET devices, five ones were randomly selected to experience exposure test under ambient condition. Their performances with increase of exposure time were monitored and compared with those of five AG-BP FET devices. Fig. 2a, b display the typical evolution of transfer characteristics with increasing exposure time for AG-BP and H$_2$-BP FET devices, respectively. The AG-BP device exhibits sharp drop of ON current by increasing exposure time, similar to the previous observation in BP FETs. By exposure up to 15 days, ON current was greatly reduced to just a few percent of the initial value, indicating almost complete failure of the AG-BP device. In contrast, the H$_2$-BP FET device presents much slower decay of ON current with increase of exposure time and 67% of the initial ON current value was still retained even after long exposure of 4 weeks. For five tested AG (H$_2$)-BP devices, the values of mobility and $I_{ON}/I_{OFF}$ ratio were determined and normalized with the corresponding initial values for proper comparison. As shown in Fig. 2c, d, the AG-BP devices display fast decrease in normalized mobility and $I_{ON}/I_{OFF}$ ratio with increase of exposure time, and they generally tend to fail when exposure is longer than 9 days. In contrast, the H$_2$-BP devices exhibit well-retained mobility and $I_{ON}/I_{OFF}$ ratio. Some H$_2$-BP devices even show slight increase of mobility and closely constant $I_{ON}/I_{OFF}$ ratio with increasing exposure up to 15 days and then a very slow drop with further exposure. In average over the values of five tested H$_2$-BP devices, the mobility and
$I_{ON}/I_{OFF}$ ratio still keep $\sim 85\%$ of their initial values even after long exposure of 28 days. Obviously, hydrogen treatment greatly suppresses not only the degradation but also the deterioration of electric transport performance for BP flakes under ambient exposure.

**Fig. 2** Comparison of as-growth (AG) and hydrogen treated BP (H$_2$-BP) FETs on electronic characteristics under ambient conditions. (a-b) Typical transfer characteristics on linear of a H$_2$-BP and AG-BP device at different exposure days under ambient environment, respectively. (c-d) Normalized carrier mobilities and normalized $I_{ON}/I_{OFF}$ ratios by the initial values for AG-BP (dots) and H$_2$-BP (star symbols) BP devices, respectively. The solid and dotted lines in (c) and (d) represent normalized carrier mobility and $I_{ON}/I_{OFF}$ ratio in average over five devices, respectively.
3. Method

*Hydrogen treatment of BP crystals:* The hydrogen treated experiment of BP crystals was performed as follows. First, BP crystal was synthesized from red phosphorus under high temperature of 1000 °C and high pressure of 2 GPa. Then little size lamellar BP was stripped from BP crystal in the glove box and was put into an airtight container full of hydrogen. At the beginning, hydrogen pressure was set to about 4.5 Mpa for 30 min, then the pressure was improved to 5.5 MPa for 30 min. According to the ideal gas state equation the hydrogen absorption capacity was calculated to be 3~5 wt%.

*Fabrication of BP FETs:* BP nanoflakes were mechanically exfoliated in ambient conditions (45 ~ 50% humidity) via standard Scotch tape from bare and hydrogen treated BP crystals to 300 nm thick SiO$_2$ on Si substrate. Back-gated FETs were prepared by patterning resist layer using electron beam lithography (EBL), followed by electron-beam evaporator of Ti (10 nm)/Au (70 nm).