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Supporting Information

Pressure Quenching: A New Route for the Synthesis of Black Phosphorus

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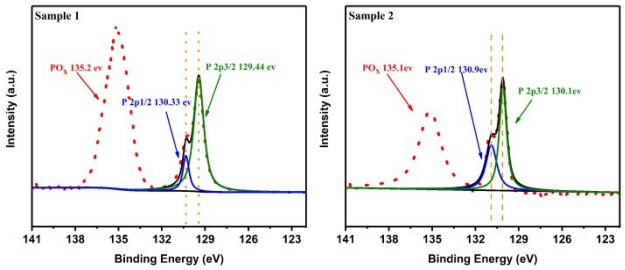

Fig. S1 Shows the high resolution XPS of P 2p for sample 1 and sample 2.

The P 2p high resolution XPS of as-synthesized sample were obtained to evaluate the bonding information. The data of sample 1 shows the P 2p3/2 and P 2p1/2 doublet at 129.44 eV and 130.33 eV, which is one of the characteristics of orthorhombic BP. According to the Moffat's work, [1] this result is reliable. As controllable part, the coexistence of P 2p3/2 and P 2p1/2 peaks at 130.1 eV and 130.9 eV in XPS spectra of sample 2. Based on our analysis, the P2p peak of sample 2 have a higher binding energy than that of sample 1, which due to the sample 2 exhibited more compact structure with high-pressure. Meanwhile, the POx peak (135.2 eV in sample 1 and 135.1 eV in sample 2) also proved the fact, that few-layered BP are more prone to oxidation, which was consistent with Martin Pumera's work.[2]

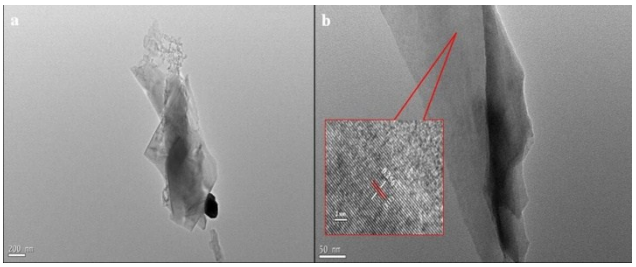

Fig. S2 Illustrates TEM images (a) and (b) shows sample 1 in scale bar : 200nm and 50nm, and HR-TEM image of Sample 1 in scale bar : 2nm.

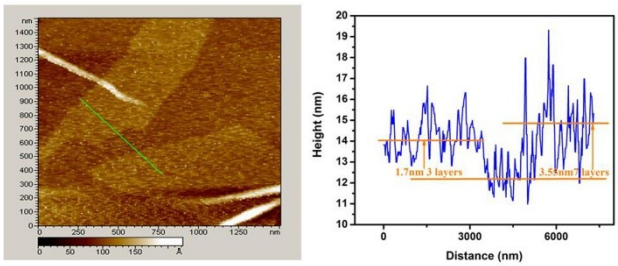

Fig. S3 Show AFM image of Sample 1 deposited on SiO_2/Si substrate and height profile along the line in image.

The thickness was determined by atomic force microscopy (AFM) pattern of sample 1 in Fig. S3. Both of the route and height was shown in the Fig S3. First step height of ~1.7 nm and second step height of ~ 3.55 nm measured at the crystal edge confirms the presence of three layers and seven layers phosphorene. Even though the step height is slightly thinner than the theoretical value of single-layer (0.54 nm) phosphorene, we generally expect that the AFM-measured thickness value of a single-layer 2D crystal on SiO_2/Si substrate is higher than the theoretical value; this is widely observed in graphene and MoS_2 cases. It can be seen that through the pressure quenching method was one step synthesis, due to the pressure quenching is an instant process, the phase transformation process was finished in a very short duration of crystallization, so as to obtain the few-layer sample.

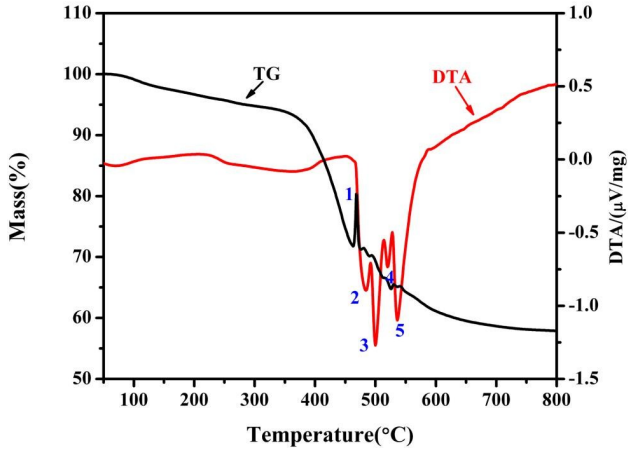

Fig. S4 Shown TG and DTA curve of the sample 1, peak 1 represents a reaction of phosphorus pentoxide, and the peaks 2, 3, 4, 5 represent melting points of Phosphorus pentoxide, RIP, BIP and Black, respectively.

To investigate four contents obviously, the tested sample was synthesized at 450 °C and 0.4 GPa. As shown in Fig S4, five peaks had been found. The peak 1 on the TG curve shown a weight gain, the phenomenon means a reaction occurred during the testing process. This is because the high reactivity of the surface of Black P, which would occur a reaction with oxide, and the product maybe phosphorus pentoxide. And the peaks 2, 3, 4, 5 represent melting points of Phosphorus pentoxide, RIP, BIP and BP, respectively. Upon above analysis, at 450 °C and 0.4 GPa, the products is not only BP, but also other components, such as RP, RIP and BIP. The content of BP can be analyzed according to Fig S4. The mass percent decreased to 60% at 800 °C, that

due to the sublimation of RP and RIP. And according to our date, the melting point of BP was around 550 ^{o}C at an atmospheric pressure, which may be the reason of the reduction in success ration beyond 550^{o}C.

Reference

1. T. P. Moffat, R. M. Latanision and R. R. Ruf, *Electrochimica Acta*, 1995, **40**, 1723-1734.
2. A. Ambrosi, Z. Sofer and M. Pumera, *Angewandte Chemie International Edition*, 2017, **56**, 10443-10445.