Electronic Supplementary Information

Hittorf's Phosphorus: the Missing Link during Transformation of Red Phosphorus to Black Phosphorus

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Experimental section

Crystals growth: (1) Bulk BP/HP crystals were synthetized by the reaction of red phosphorus (RP, 400 mg, 99.999+%, lump, Alfa Aesar), tin (Sn, 30 mg, 99.999%, granule, Alfa Aesar) and iodine (I_2, 20 mg, 99.99+%, crystalline, Alfa Aesar) in an evacuated silica glass ampule (p=0.1 Pa, length 130 mm, inner diameter 8 mm and wall thickness 1 mm). The ampule was horizontally placed in a tube furnace with an independent heating zone (MTI KJ OTF−1200X−S, Hefei, China). The reaction solid starting materials were put at one side of the silica ampule and located at the hot zone (T_1) of the furnace. The hot zone (T_1) was heated from room temperature to 600 °C in 120 min, and then kept for ~60 min at 600 °C. Meanwhile, the temperature gradient of silica ampule has been determined by using an external thermocouple. It was shown that a temperature gradient between the hot zone (T_1) and the cold zone (T_2) of silica ampule was about 150 °C. After that, the silica ampule was cooled to ambient temperature through a natural cooling-off process. Finally, the as-grown crude products were obtained. (2) 400 mg RP (99.999+%, lump, Alfa Aesar) and 30 mg tin (II) iodide (SnI_2, 99.999%, granule, Alfa Aesar) were employed to synthesize BP single crystals by using the above-mentioned synthetic strategy and controlled the reaction time (about 120 min) of the constant-temperature (600 °C) heating process at the hot zone (T_1), and the temperature of cold zone (T_2) was ~450 °C at this moment. (3) Bulk BP single crystals were grown by using the above-mentioned synthetic strategy but precisely controlled the reaction time (about 120 min) of the constant-temperature (600 °C) heating process at the hot zone (T_1), and the temperature of cold zone (T_2) was ~450 °C at this moment.

Characterizations: The phase analysis was carried out by using X-ray diffraction (XRD) (Bruker D8 Advance, Germany) with Cu Kα radiation (λ = 1.5406 Å) at 40 kV and 40 mA. The crystalline quality was examined by using the X-ray rocking curve measurement (S2, Japan) and the field emission transmission electron microscopy (FETEM, JEOL JEM 2100F, Japan). The chemical compositions were identified by using a scanning electron microscope (SEM) (Hitachi SU8010, Japan) equipped with an energy dispersive X-ray spectroscope (EDX). Optical microscope (OM) images were taken by a microscope with a CCD camera (Olympus BX51, China) in ambient atmosphere. The micro-Raman spectra and Raman intensity mapping were collected via a high-resolution confocal Raman system (Horiba Jobin Yvon LabRAM HR Evolution, France) equipped with a 532 nm laser source.

S1. Photograph of as-grown crude products

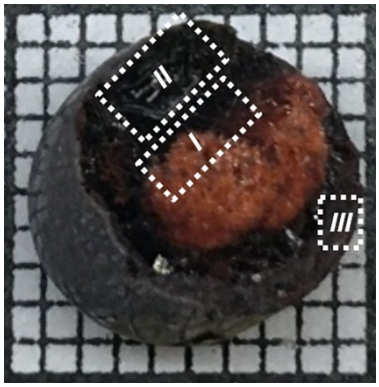

Fig. S1 A photograph of the as-grown crude products, the grid scale is 1mm.

S2. Photograph of crystal *ii* and solid *iii*

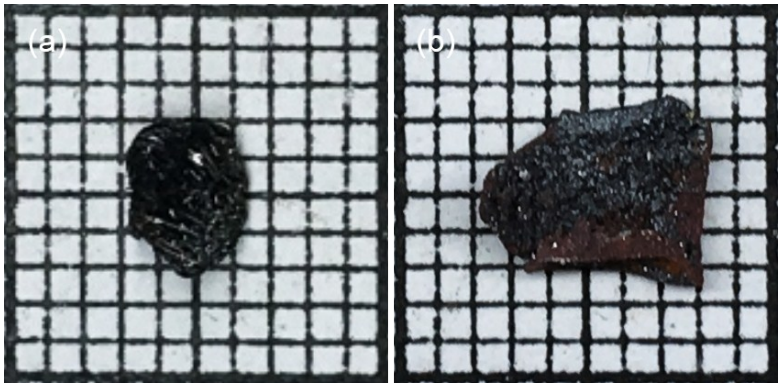

Fig. S2 Photographs of (a) crystal ***ii*** separated from compound ***II***, (b) solid ***iii*** separated from compound ***III***. The grid scale is 1mm.

S3. Optical and structural characterizations of crystal ii

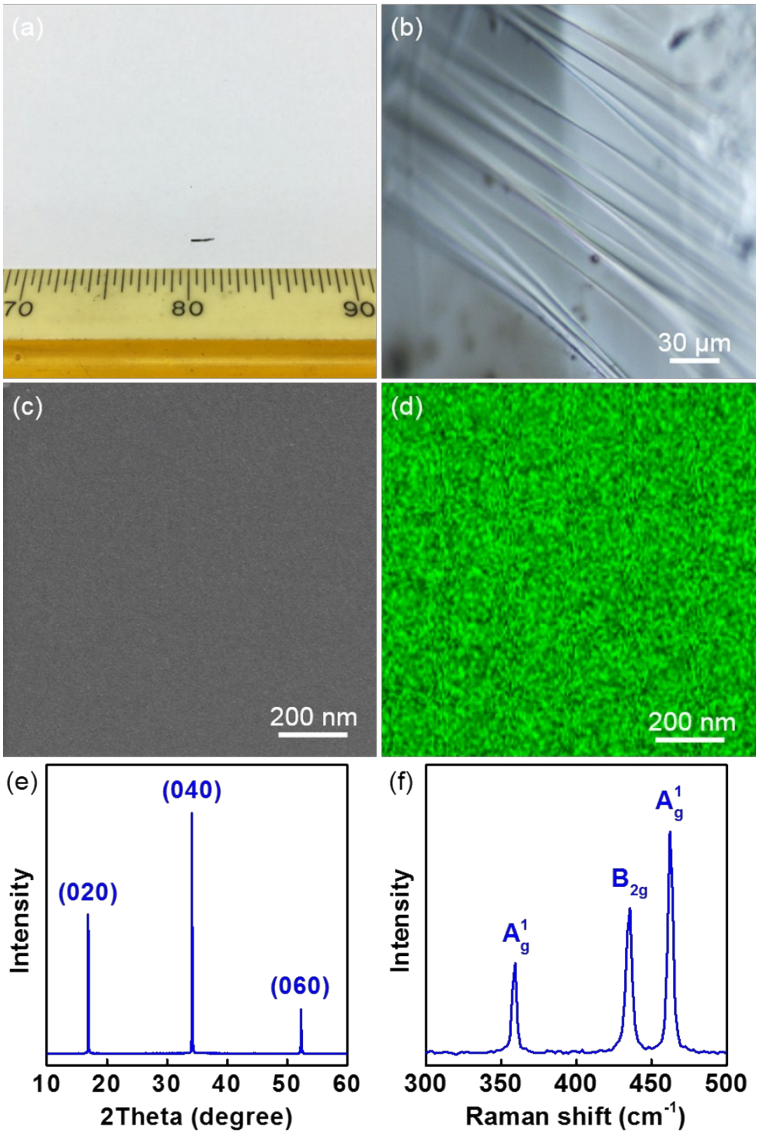

Fig. S3 Characterizations of the crystal ***ii***. (a) A photograph of a typical BP single crystal selected from the crystal ***ii*** (Figure S2a). (b) OM image of the BP single crystal. (c) SEM image of the BP single crystal. (d) EDX mapping of element phosphorus, corresponding to the SEM image in (c). (e) XRD pattern of the BP single crystal. (f) Micro-Raman spectrum of the BP single crystal.

S4. Schematic diagram of the unit cell of HP

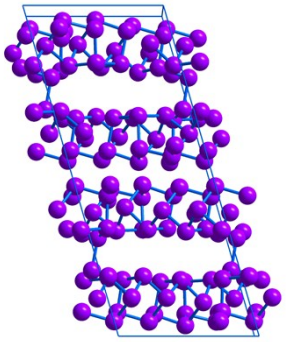

Fig. S4 Schematic diagram of the unit cell of HP.

S5. Photograph of some evacuated silica glass ampules

We directly employed the solid SnI_2 and RP as the source materials to synthesize the BP single crystals. It demonstrated that no formation of BP single crystals at the end of CVT reaction (Fig. S6a, b). However, bulk BP single crystals were grown by the reaction of solid Sn, I_2 and RP via the same synthetic strategy (Fig. S6c).

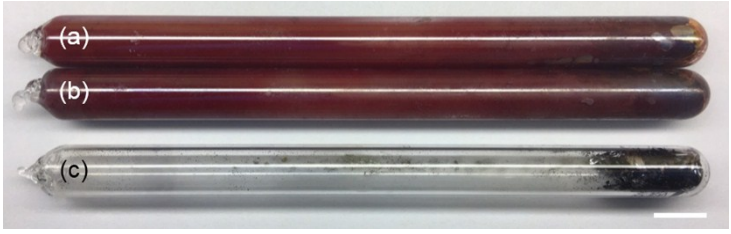

Fig. S5 A photograph of some evacuated silica glass ampules at the end of CVT reaction. (a, b) The solid SnI_2 and RP as the source materials. (c) The solid Sn, I_2 and RP as the source materials. Scale bar is 1 cm.

S6. Photograph of as-grown bulk BP single crystals

Fig. S6 A photograph of the as-grown bulk BP single crystals, the grid scale is 1mm.

S7. Photograph of a large size BP single crystal

Fig. S7 A photograph of a BP single crystal of about 7.0 mm × 5.0 mm × 0.2 mm in size, the grid scale is 1mm.

S8. TEM image of multilayer phosphorene

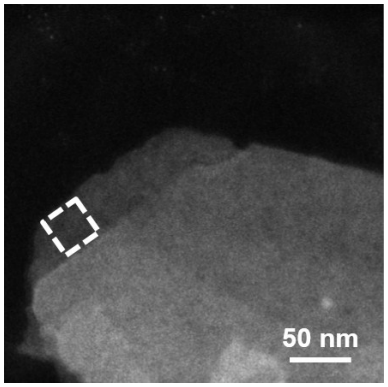

Fig. S8 Typical TEM image of multilayer phosphorene on copper-carbon support.

S9. Theoretical and computational details

The theoretical studies of the two crystalline forms of black phosphorus (BP) and Hittorf's phosphorus (HP) were carried out by using density functional theory (DFT).[1] The calculations were performed through Dmol^3 package[2,3] by using a spin-polarized Kohn-Sham formalism[4] and gradient corrected Perdew-Burke-Ernzerhof (PBE) functional.[5,6] The Kohn-Sham orbitals were constructed by a basis set spanned by double-numeric quality basis functions with polarization functions (DNP). DFT semi-core pseudo-potential (DSPP) were utilized to replaces core electrons of P [$1s^2 2s^2 2p^6$] by a single effective potential.[7] For HP, the cell parameters a = 9.21, b = 9.15, c = 22.6, α = 90.0, β = 106.1, γ = 90.0 were taken from standard experimental crystalline data.[8] The cell was used with the k-point in the Brillioun Zone setting to be 2 × 2 × 1. For BP, the experimental cell parameters a = 3.3136, b = 10.48, c = 4.38, α = 90.0, β = 90.0, γ = 90.0 were adopted without further relaxation.[9] The k-point used for BP is 7 × 2 × 5 to be consistent with that of HP. Convergence tolerance of energy was set to be 1.0×10^{-6} Hatree.

The vibrational frequencies were calculated using double harmonic approximation without considering the relaxation of the cell. The vibrational entropies were calculated using equation (1) of the paper to generate the Gibbs free energies by using the total energies from the quantum-mechanical calculations and zero-point vibrational energies from the unscaled harmonic vibrational frequencies.

S10. Physical properties of inorganic compounds

Table S1. Physical constants of inorganic compounds

Name	Formula	Melting point, °C	Boiling point, °C
Iodine[10]	I_2	113.60	185.24
Phosphorus (red)[10]	P_4	597	Subl 416
Tin (white)[10]	Sn	231.928	2602
Phosphorus (III) iodide[11]	PI_3	61	–

References

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