Supplementary Information

Vacancy-Rich Sn-P-I Catalyst for Highly Efficient Black Phosphorus Preparation and Catalytic Mechanistic Investigation

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DFT calculation details

All the density function theory (DFT) calculations were carried out using the Vienna Ab initio Simulation Package (VASP)[1, 2]. The ionic cores were described with projector augmentedwave (PAW) pseudopotential[3, 4] and the valence electrons were into account using a plane wave basis set with a kinetic energy cutoff of 400 eV. The generalized gradient approximation (GGA) was used with the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional to describe exchange-correlation effects of electrons[5]. A4 layered 1 × 1 supercell of Sn-I-P (200) was constructed with 4 P atoms on the surface of the slab. A vacuum layer of 15 Å was inserted in the vertical direction of the model to separating the slabs along the perpendicular c-direction. For the geometrical optimizations, a 3 × 3 × 1 Γ-centered Monkhorst-Pack schemed k-mesh was set to sample the first Brillouin zone. The DFT-D3 method included the long-range van der Waals interaction[6-8]. The convergence criterion for the electronic self-consistent field (SCF) loop was set to 10^{-5} eV/atom. The atomic structures were optimized until the residual forces were below 0.02 eV $Å^{-1}$.

The energy of slabs with n vacancies (E_{nv}) were defined ass

$$E_{nv\text{-}SLAB} = E_{slab} - n \times E_{P4} / 4 \ (E_{P4} \text{ is the energy of } P_4 \text{ molecular})$$

The adsorption energy of Pn (ΔE_{*Pn}) is defined as

$$\Delta E_{*Pn} = E^*Pn - E_{nv\text{-}SLAB} - n \times E_{P4}/4$$

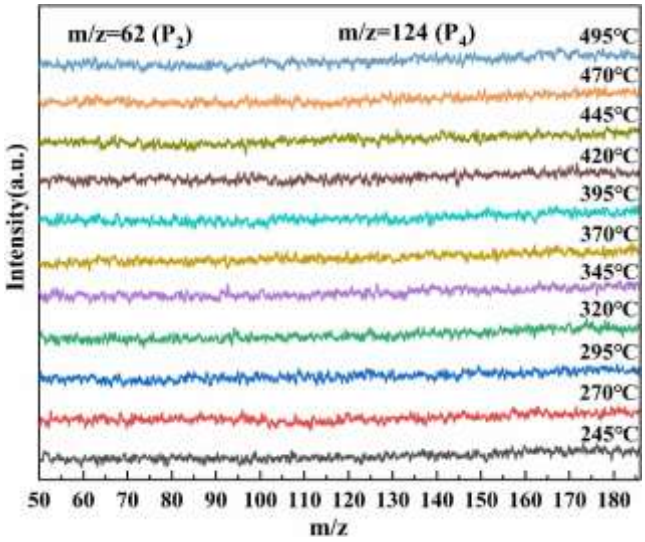

Fig.S1 Mass spectra of Sn-P-I at different temperatures, with no P_2 signal detected.

Fig.S2 Photograph of the quartz tube filled with WP after heating to 800°C, holding for 10 hours, and then slowly cooling to room temperature.

Table S1. Elemental content of different ratios of synthesized catalysts tested by ICP-MS/OES

Samples	Sn（w%）	I（w%）	P（w%）	molecular formula
Content of	61.66	20.06	18.21	$Sn_{24}P_{27.2}I_{7.3}$
sample elements	61.97	22.16	13.69	$Sn_{24}P_{20.3}I_{8.03}$
W (%)	62.69	21.31	12.16	$Sn_{24}P_{17.8}I_{7.63}$

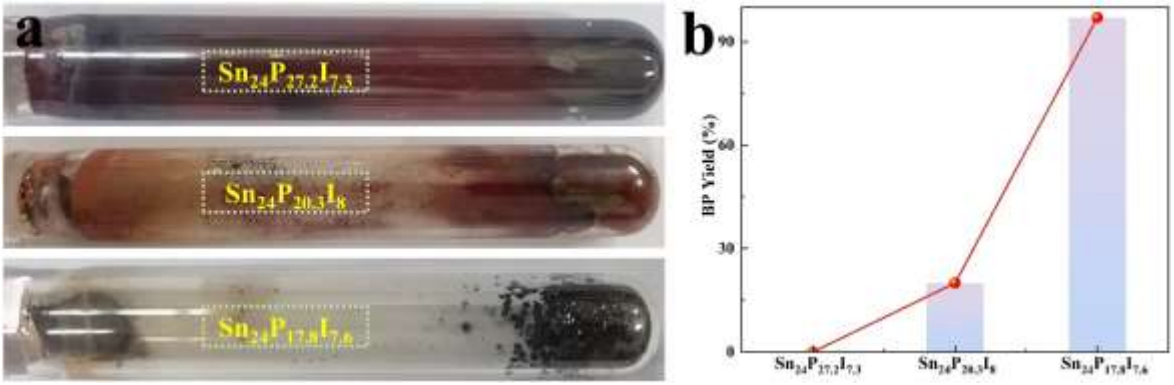

Fig.S3 (a) Photographs of BP grown using different Sn-P-I catalysts; (b) Corresponding PB yield.

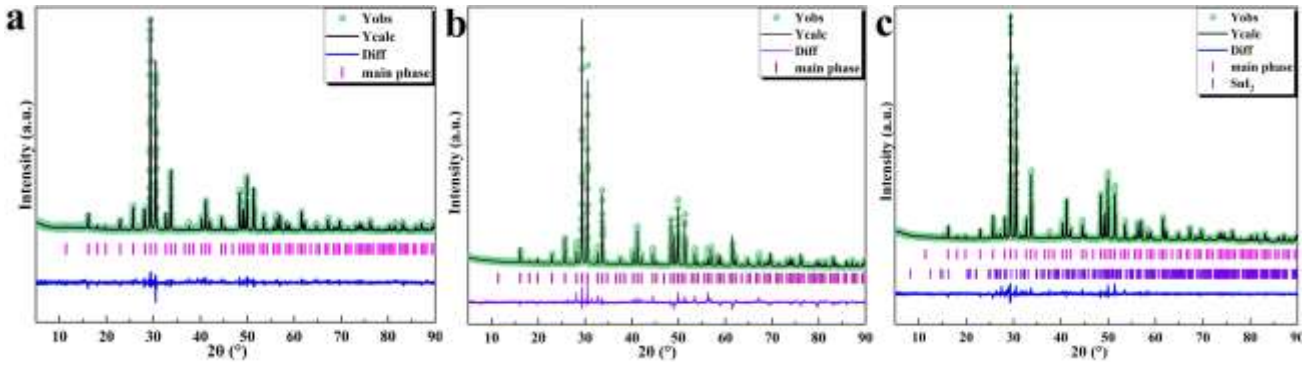

Fig.S4 XRD refined pattern of (a) $Sn_{24}P_{27.2}I_{7.3}$, (b) $Sn_{24}P_{20.3}I_8$, and (c) $Sn_{24}P_{17.8}I_{7.6}$.

Table S2. Cell Parameter of catalysts with different element ratios

ICP test results		$Sn_{24}P_{27.2}I_{7.3}$	$Sn_{24}P_{20.3}I_8$	$Sn_{24}P_{17.8}I_{7.6}$	
Molecular formula		$Sn_{24}P_{20.66}I_{7.94}$	$Sn_{24}P_{19.3}I_8$	$Sn_{24}P_{20.4}I_{7.82}$	SnI_2
Corresponding card		PDF#89-6562	PDF#89-6562	PDF#89-6562	PDF#70-1492
Space group		Pm-3n	Pm-3n	Pm-3n	C2/m
Cell Parameter	a (Å)	10.95788(10)	10.957684(44)	10.96168(21)	14.2021
	b (Å)	10.95788(10)	10.957684(44)	10.96168(21)	4.5470
	c (Å)	10.95788(10)	10.957684(44)	10.96168(21)	10.8409
	α (°)	90	90	90	90
	β (°)	90	90	90	92.10
	γ (°)	90	90	90	90
	Volume($Å^3$)	1315.768(35)	1315.698(16)	1317.137(77)	699.616

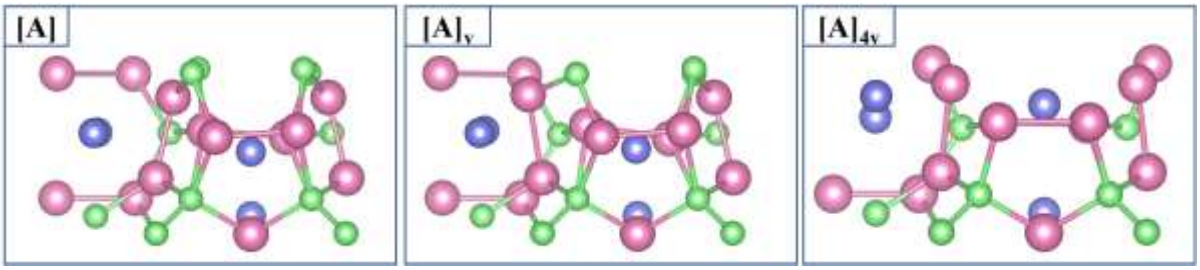

Fig.S5 Sn-P-I model: models of intact Sn-P-I clathrate (denoted as [A]), single phosphorus vacancies ($[A]_v$) and saturated phosphorus vacancies ($[A]_{4v}$)

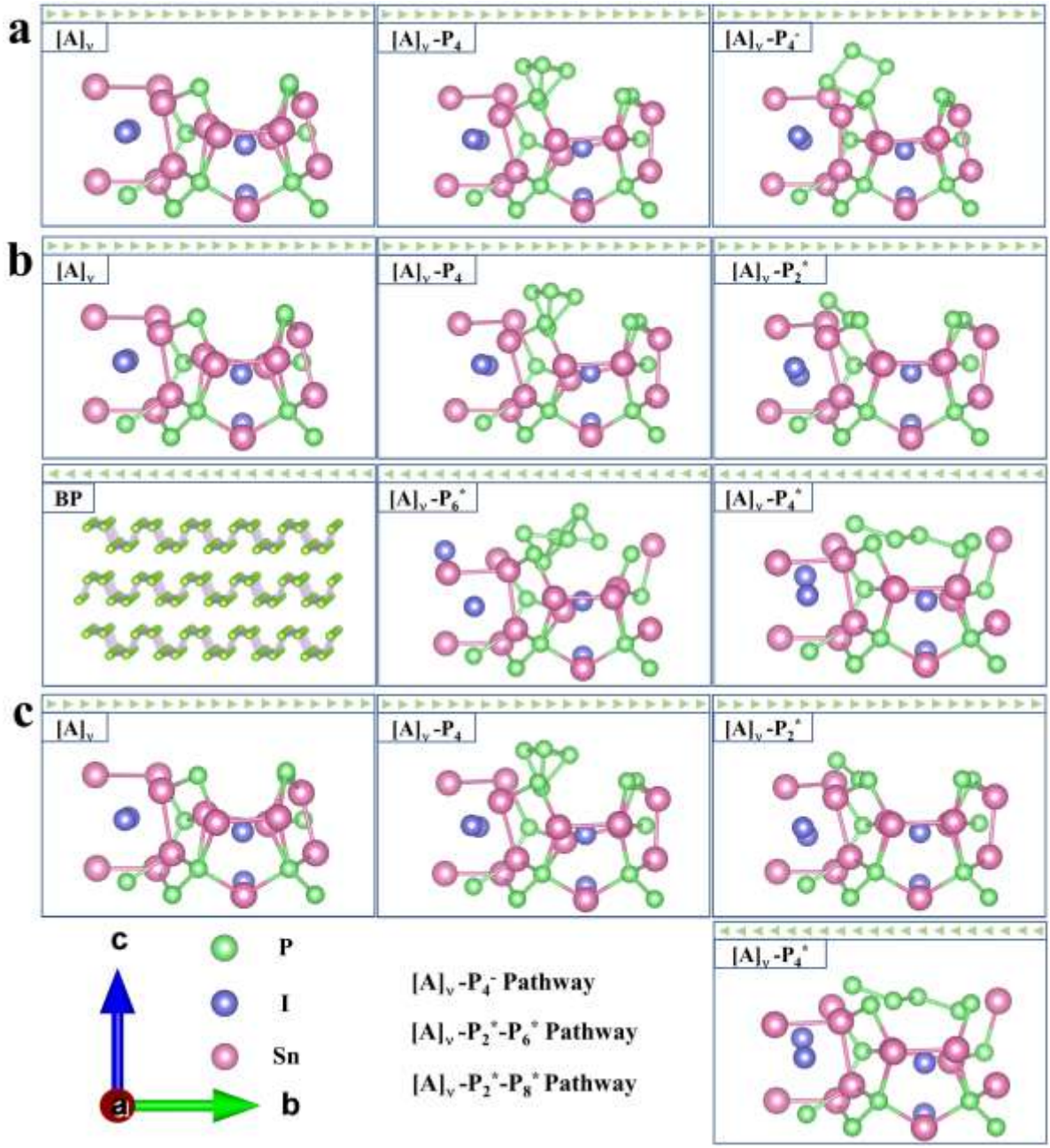

Fig.S6 Several potential reaction pathways with relatively high energy barriers.

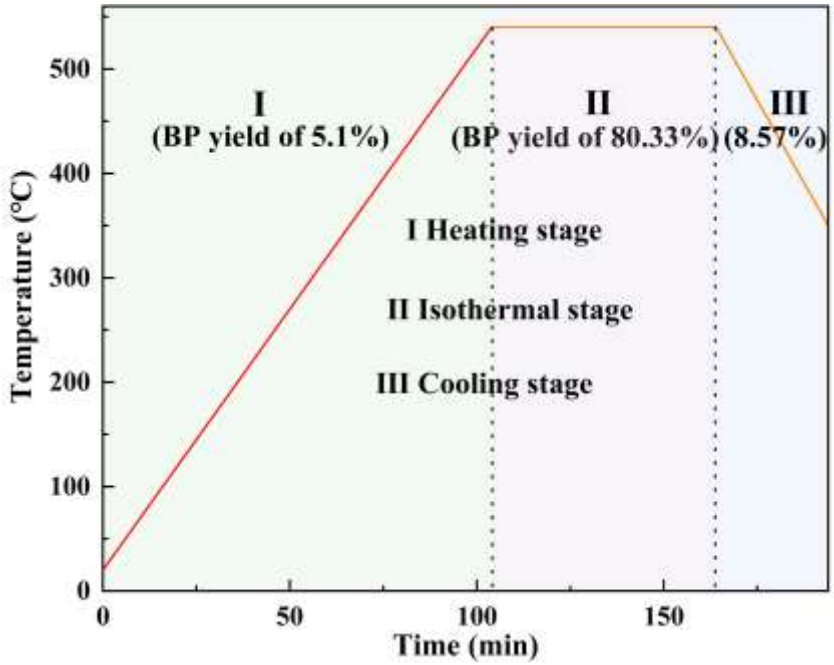

Fig. S7 BP yields at different reaction stages. The reactions were quenched at different time to obtain BP for analysis.

Fig.S8 Physical images of BP prepared by quenching the reaction with liquid nitrogen.

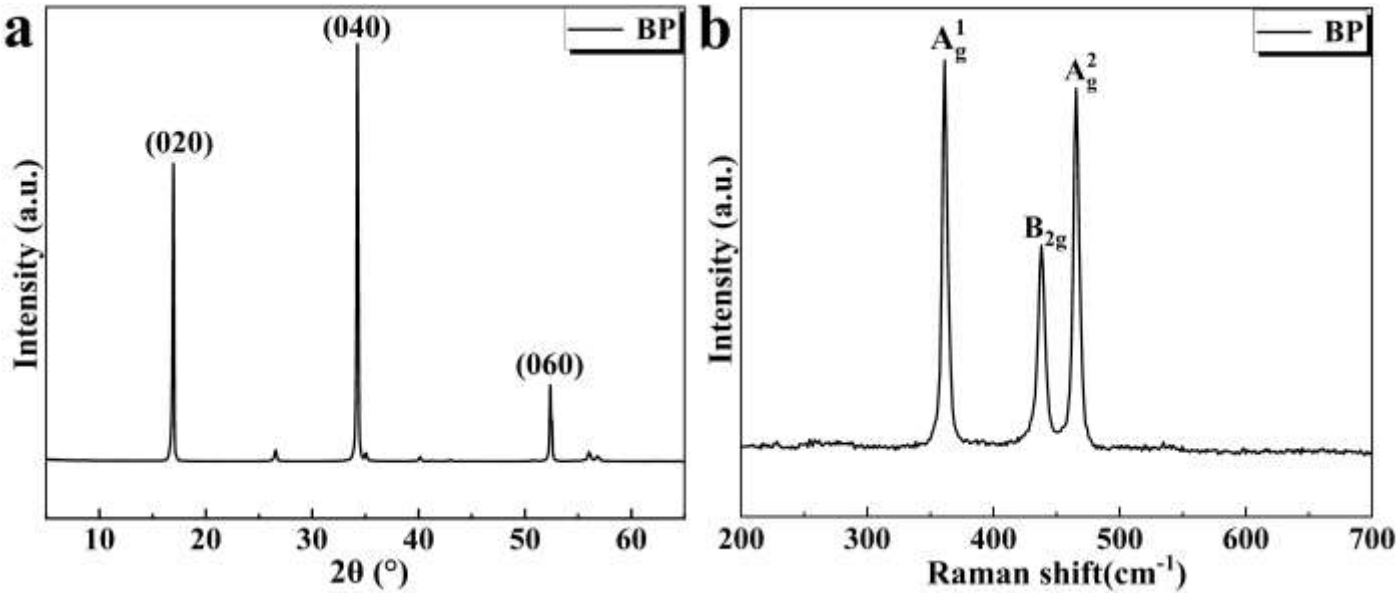

Fig.S9 (a) XRD pattern of BP. (b)Raman spectra of BP. The BP was prepared by quenching the reaction with liquid nitrogen.

Fig S10 Physical images of BP prepared from (a) white phosphorus and (b) red phosphorus at 420℃.

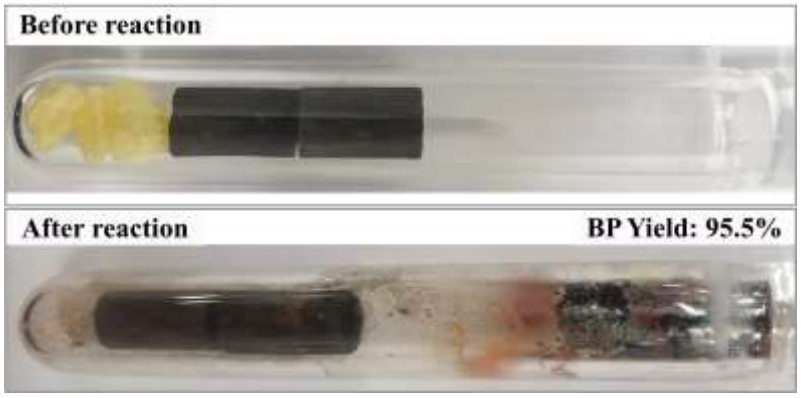

Fig.S11 Physical images of the rapid BP synthesis within 90 min, with a BP yield of 95.5%.

Table S3. Summary of reaction times for black phosphorus preparation

Materials	Temperature	reaction time	BP yield	Reference
WP(1g)、Sn-P-I(0.4g)	540-420℃	90min	95.5%	This work
RP(-)、Sn(-)、I_2(-)	590	-	-	9
RP(-)、Sn(-)、SnI_4(-)	620	25h	88%	10
RP(0.5g)、Sn(1g)、I_2(0.1g)	630-580	36h	90%	11
RP(0.3g)、$Sn_{24}P_{22-x}I_8$(0.02g)	550	30h	-	12
RP(0.3g)、Sn(0.012g)、SnI_4(0.006g)	650	14h	90%	13

Table S4. Statistics of waste generated during the reaction process in this method and the traditional method

Method	Present Method		Traditional Method		
Raw Materials	WP	Sn-P-I	RP	Sn	SnI_4
Amount Used/g	30	5	30	6	3
BP/g	28.65		27		
Total Waste /g	26.75		38.75		
E-factor	0.93		1.44		

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