

## Supporting Information

### From highly-oriented bulk black arsenic phosphorus to well-crystallized exfoliated flakes with enhanced anti-oxidation: precise control upon chemical vapor transport

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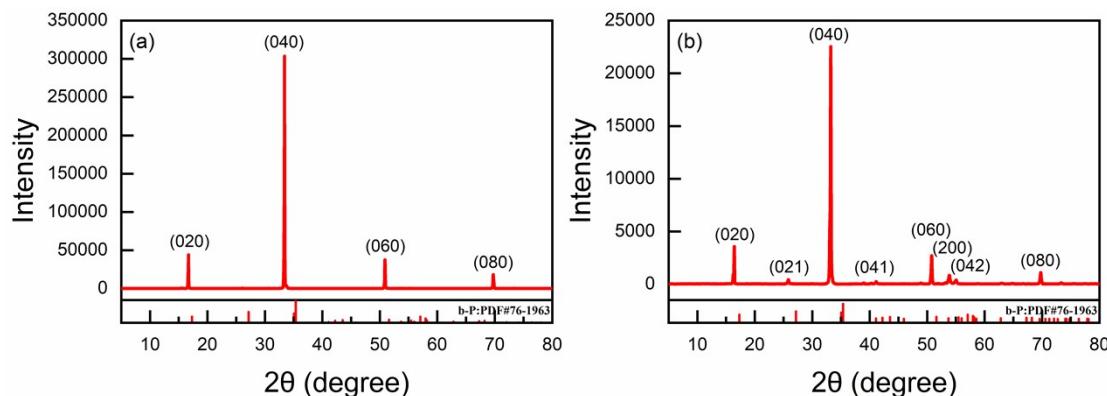


Fig. S1 XRD patterns of (a) highly-oriented b-AsP and (b) b-AsP-Control.

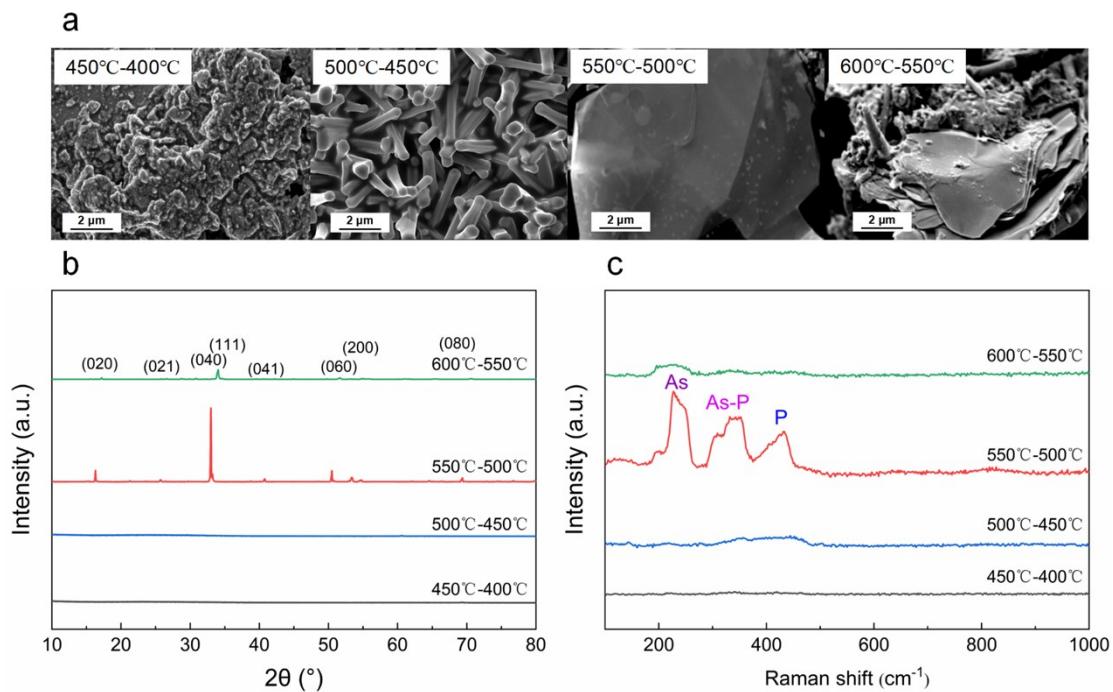


Fig. S2 (a) SEM image, (b) XRD pattern and (c) Raman spectra of products synthesized by different temperature fields (pressure field: 10 atm, atomic ratio of As:P: 4:1, amounts of SnI<sub>4</sub>: 2 wt%, reacting time: 10 h, cooling time: 2 h).

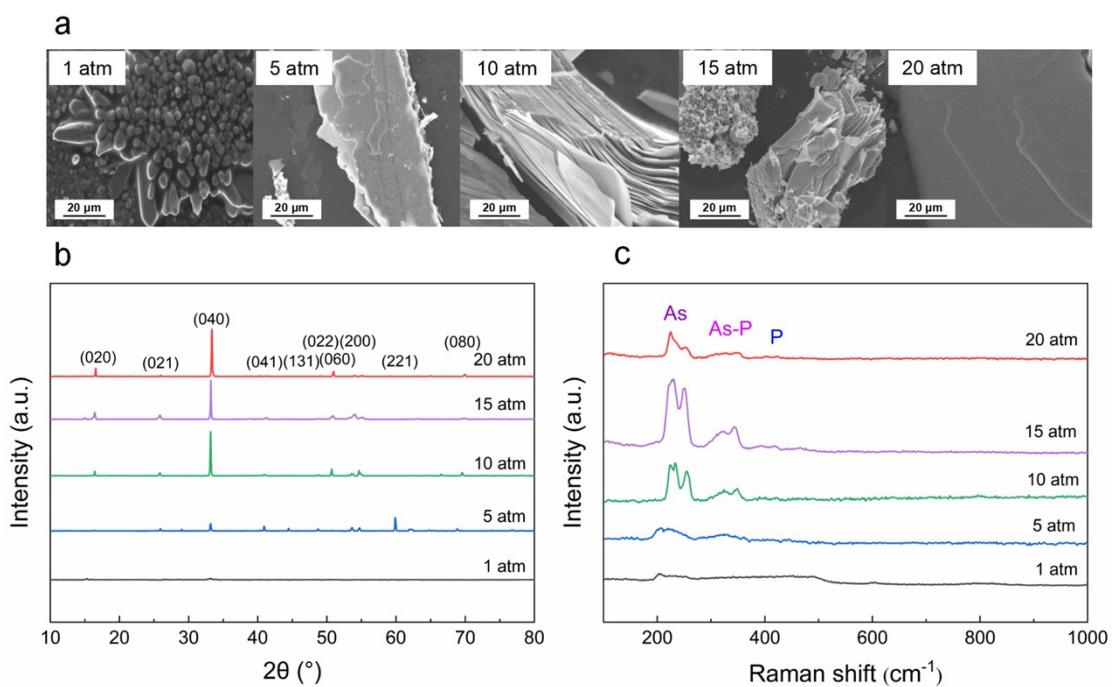


Fig. S3 (a) SEM image, (b) XRD pattern and (c) Raman spectra of products synthesized by different pressure fields (temperature field: 550°C-500°C, atomic ratio of As:P: 4:1, amounts of SnI<sub>4</sub>: 2 wt%, reacting time: 10 h, cooling time: 2 h).

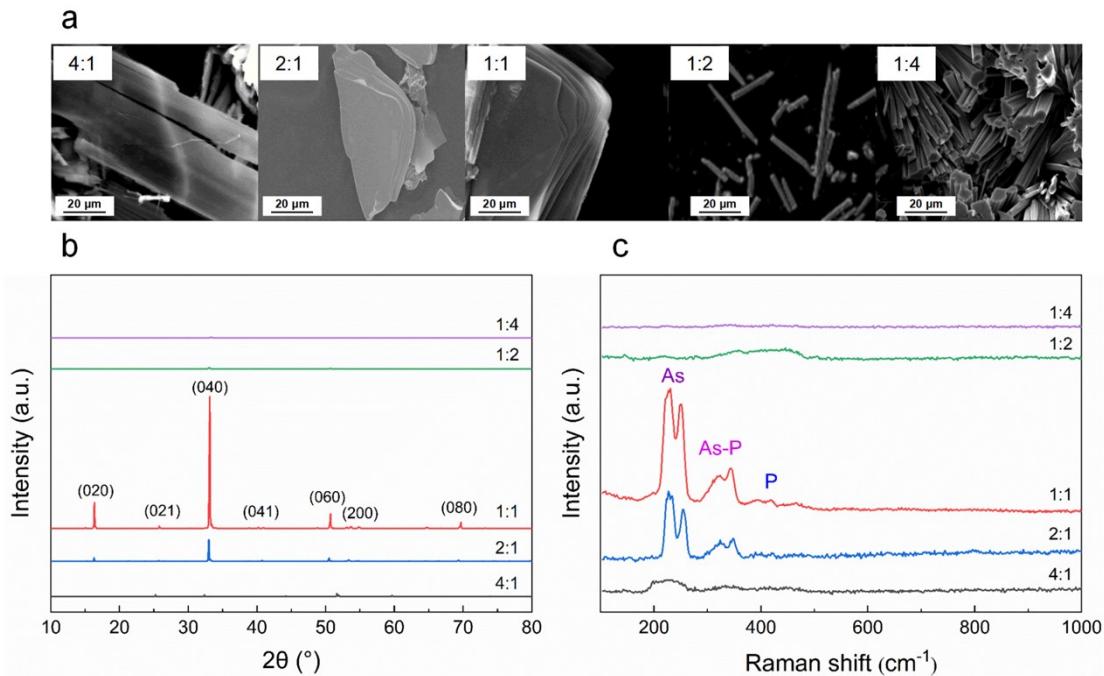


Fig. S4 (a) SEM image, (b) XRD pattern and (c) Raman spectra of products synthesized by different atomic ratio of As:P (temperature field: 550°C-500°C, pressure field: 20 atm, amounts of SnI<sub>4</sub>: 2 wt%, reacting time: 10 h, cooling time: 2 h).

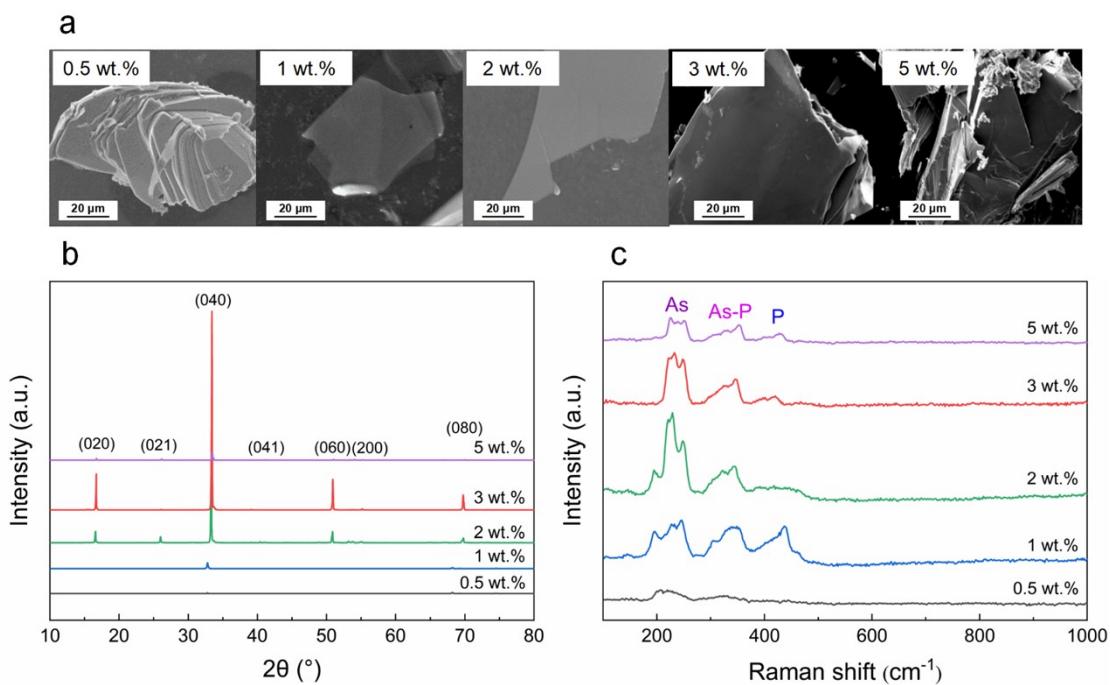


Fig. S5 (a) SEM image, (b) XRD pattern and (c) Raman spectra of products synthesized by different amounts of SnI<sub>4</sub> (temperature field: 550°C-500°C, pressure field: 20 atm, atomic ratio of As:P: 1:1, reacting time: 20 h, cooling time: 2 h).

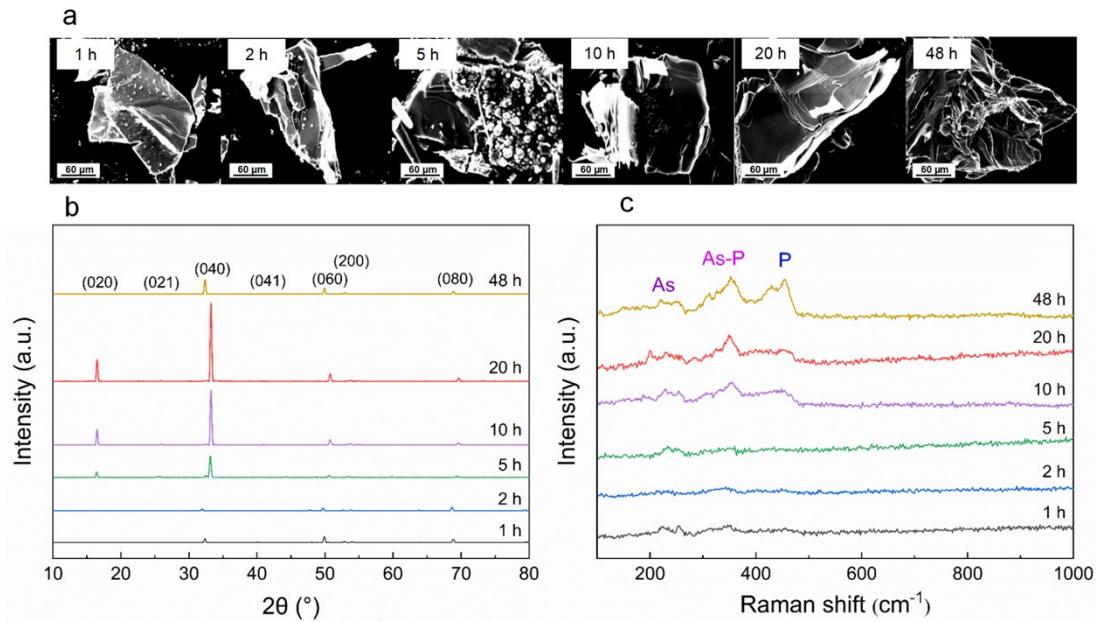


Fig. S6 (a) SEM image, (b) XRD pattern and (c) Raman spectra of products synthesized by different reacting time (temperature field: 550°C-500°C, pressure field: 20 atm, atomic ratio of As:P: 1:1, amounts of SnI<sub>4</sub>: 2 wt%, cooling time: 2 h).

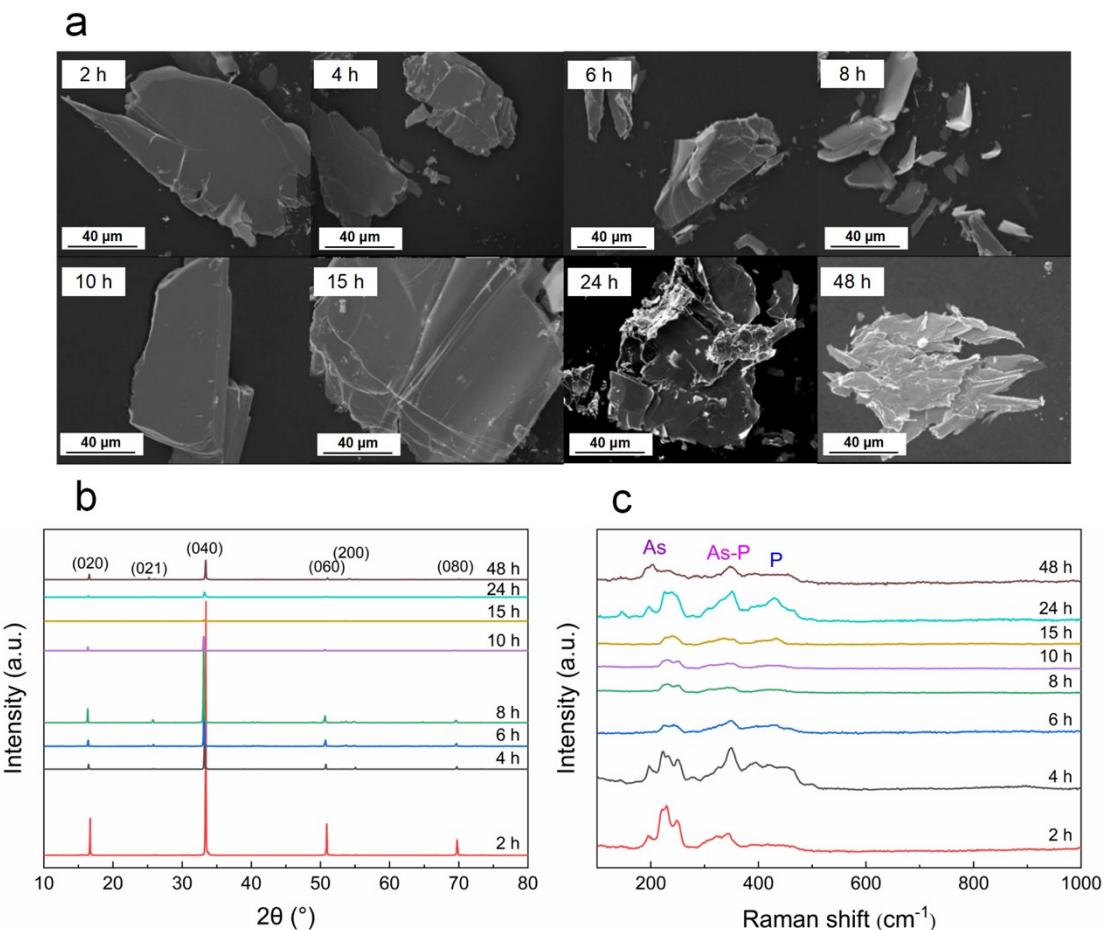


Fig. S7 (a) SEM image, (b) XRD pattern and (c) Raman spectra of products synthesized

by different cooling time (temperature field: 550°C-500°C, pressure field: 20 atm, atomic ratio of As:P: 1:1, amounts of SnI<sub>4</sub>: 3 wt%, reacting time: 20 h,).

Table S1 Elemental composition of highly-oriented b-AsP crystals obtained under optimal conditions by SEM-EDS.

Element type	As	P	Sn	I
Content (atom%)	73.25	26.38	-	0.37

Table S2 Elemental composition of highly-oriented exfoliated b-AsP flakes obtained under optimal conditions by TEM-EDS.

Element type	As	P	Sn	I
Content (atom%)	70.77	27.93	0.63	0.67

Table S3 Elemental composition of products synthesized under different system by SEM-EDS.

Product type	As (at.%)	P (at.%)	I (at.%)	Sn (at.%)
Highly-oriented b-AsP	73.25	26.38	0.37	-
b-AsP-Control	74.56	23.48	0.49	1.47

Table S4 Comparison of peak intensity, (010) degree of orientation and (040) full width at half maxima in XRD patterns between b-AsP products synthesized by different process conditions.

Process conditions types	Parameters	(040) peak intensity (°)	(021) peak intensity (°)	(010) degree of orientation	(040) full width at half maxima
Temperature field	450°C-400°C	-	-	-	-
	500°C-450°C	-	-	-	-
	550°C-500°C	14156	116	122.03	0.13
	600°C-550°C	1833	89	20.60	0.25
Pressure field	1 atm	-	-	-	-
	5 atm	865	273	3.17	0.15
	10 atm	5221	363	14.38	0.13
	15 atm	4613	490	9.41	0.14
	20 atm	5603	131	42.77	0.16
Atomic ratio of As:P	4:1	1009	1231	0.82	0.08
	2:1	14156	383	36.96	0.13
	1:1	86065	1526	56.40	0.13
	1:2	845	-	-	0.22
	1:4	-	-	-	-
Amounts of SnI <sub>4</sub>	0.5 wt.%	863	41	21.05	0.11
	1 wt.%	6993	332	21.06	0.18
	2 wt.%	105682	7453	14.18	0.14
	3 wt.%	243596	667	365.21	0.08
	5 wt.%	9700	1507	6.44	0.13
Reacting time	1 h	1160	35	33.14	0.28
	2 h	559	27	20.70	0.24
	5 h	6723	309	21.76	0.28
	10 h	17283	297	58.19	0.24
	20 h	24797	231	107.35	0.24
	48 h	4537	104	43.63	0.24
Cooling time	2 h	303596	667	455.17	0.07
	4 h	40136	798	50.30	0.12
	6h	60522	2080	29.10	0.14
	8h	89295	3414	26.16	0.13
	10 h	17123	191	89.65	0.16
	15 h	1578	76	20.76	0.11
	24 h	5816	174	33.43	0.22
	48 h	23169	734	31.57	0.13