Supplementary Information

Synthesis of InP nanofibers from tri(m-tolyl)phosphine: An alternative route to metal phosphide nanostructures

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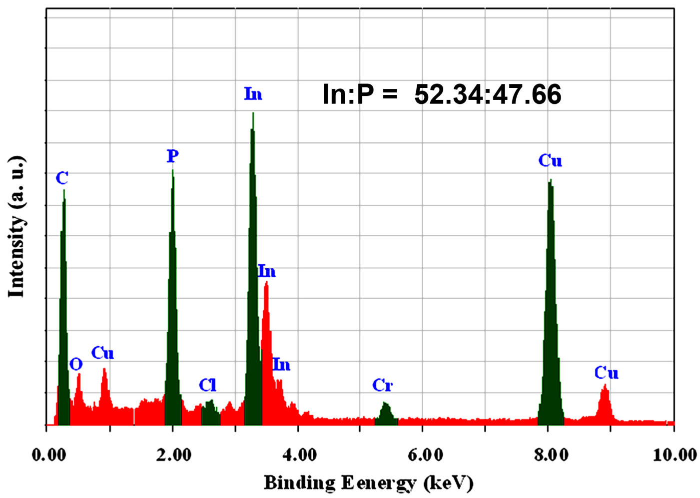


Fig. S1 Energy-dispersive X-ray (EDX) spectrum of InP nanofibers. The peaks of C, Cr and Cu are from the carbon-coated copper grid of TEM, and O and Cl from surface oxides and adsorbed species.

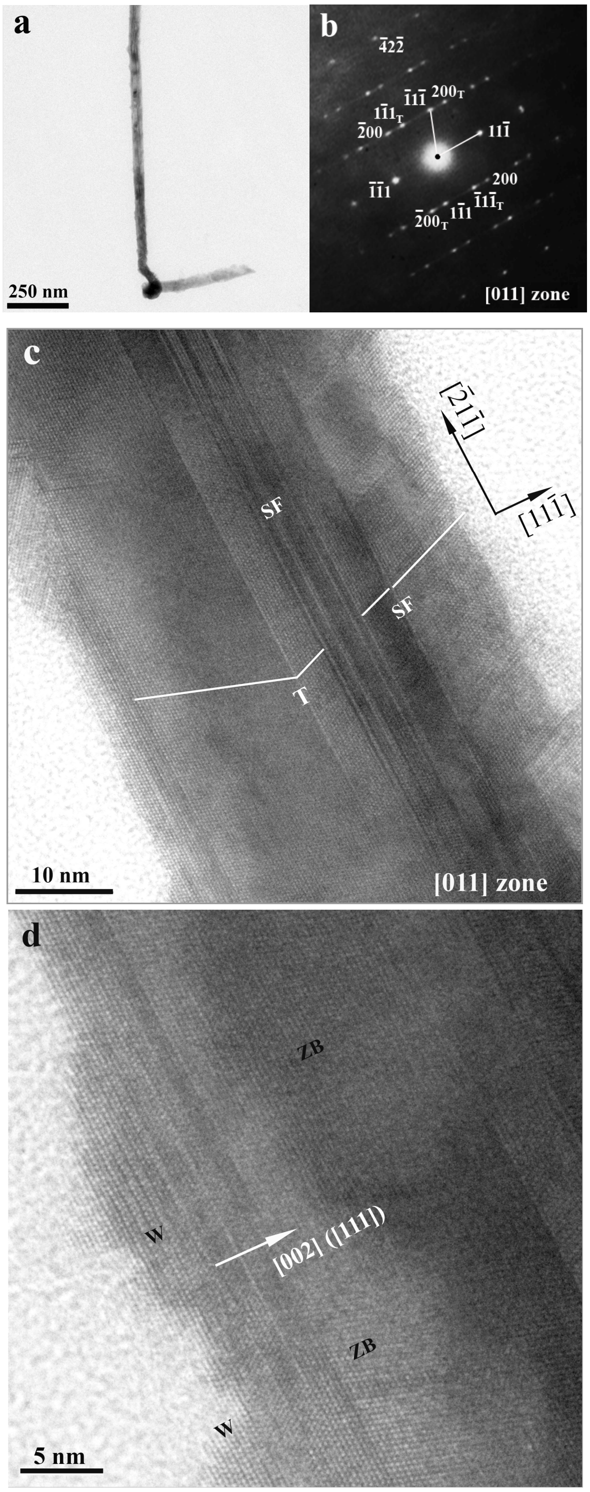


Fig. S2 (a) TEM image of a typical individual InP nanofiber; (b) ED pattern, (c) and (d) HRTEM images taken on the InP nanofiber in (a).

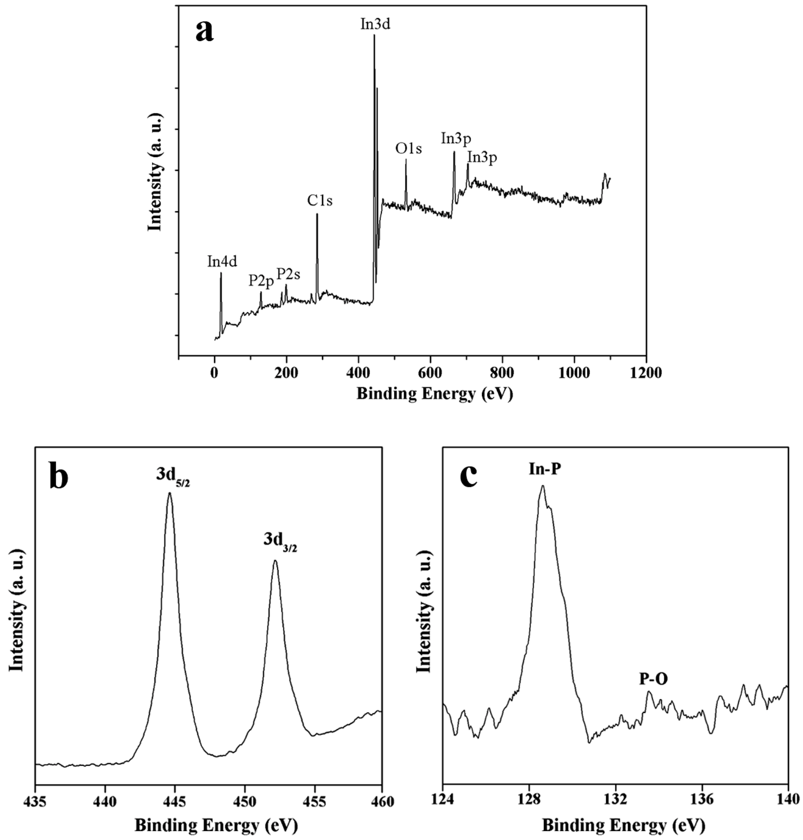
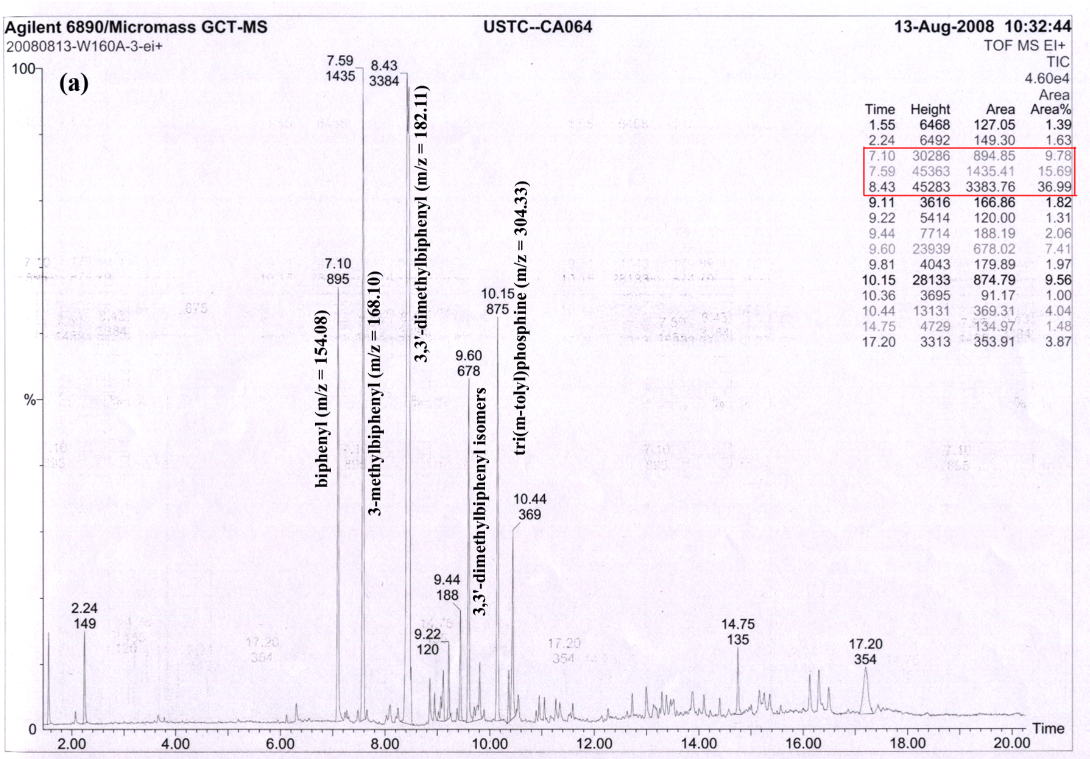
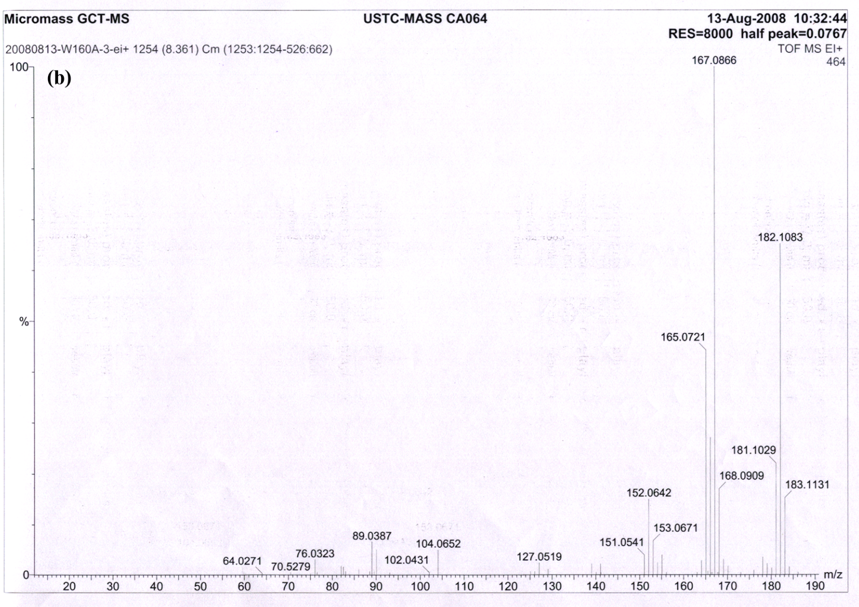


Fig. S3 XPS spectra of InP nanaofibers. (a) the survey of XPS spectrum, (b) the high-resolution spectrum of In 3d core, and (c) the high-resolution spectrum of P 2p core.





Multiple Mass Analysis: 54 mass(es) processed - displaying only valid results

(c) Tolerance = 4.0 mDa / DBE: min = -3.0, max = 50.0

Monoisotopic Mass, Odd and Even Electron Ions
447 formula(e) evaluated with 26 results within limits (up to 50 closest results for each mass)

Minimum:	0.10				-3.0	
Maximum:	100.00		4.0	60.0	50.0	

Mass	RA	Calc. Mass	mDa	PPM	DBE	Formula
76.0323	3.06	76.0313	1.0	13.2	5.0	C6 H4
86.0140	1.09	86.0157	-1.7	-19.2	7.0	C7 H2
89.0387	6.59	89.0391	-0.4	-4.8	5.5	C7 H5
90.0461	5.03	90.0470	-0.9	-9.4	5.0	C7 H6
93.0729	0.44	93.0704	2.5	26.6	3.5	C7 H9
102.0431	0.44	102.0470	-3.9	-37.7	6.0	C8 H6
104.0652	5.03	104.0626	2.6	25.0	5.0	C8 H8
125.1329	0.66	125.1330	-0.1	-1.0	1.5	C9 H17
127.0519	2.41	127.0548	-2.9	-22.6	7.5	C10 H7
129.0713	1.10	129.0704	0.9	6.8	6.5	C10 H9
151.0541	3.93	151.0548	-0.7	-4.5	9.5	C12 H7
152.0642	15.07	152.0626	1.6	10.5	9.0	C12 H8
153.0671	6.77	153.0704	-3.3	-21.7	8.5	C12 H9
154.0768	2.40	154.0783	-1.5	-9.4	8.0	C12 H10
155.0897	3.93	155.0861	3.6	23.4	7.5	C12 H11
164.0598	2.84	164.0626	-2.8	-17.1	10.0	C13 H8
165.0721	44.24	165.0704	1.7	10.1	9.5	C13 H9
166.0774	27.09	166.0783	-0.9	-5.1	9.0	C13 H10
167.0866	100.00	167.0861	0.5	3.1	8.5	C13 H11
168.0909	17.04	168.0939	-3.0	-17.9	8.0	C13 H12
170.1076	1.75	170.1096	-2.0	-11.5	7.0	C13 H14
173.0411	0.44	173.0391	2.0	11.4	12.5	C14 H5
178.0810	3.49	178.0783	2.7	15.4	10.0	C14 H10
181.1029	22.07	181.1017	1.2	6.5	8.5	C14 H13
182.1083	65.23	182.1096	-1.3	-6.9	8.0	C14 H14
186.1370	0.44	186.1409	-3.9	-20.7	6.0	C14 H18
115.0532	4.10	115.0548	-1.6	-13.7	6.5	C9 H7
116.0599	0.26	116.0626	-2.7	-23.3	6.0	C9 H8
125.0399	0.26	125.0391	0.8	6.2	8.5	C10 H5
126.0460	1.50	126.0470	-1.0	-7.5	8.0	C10 H6
127.0514	2.02	127.0548	-3.4	-26.6	7.5	C10 H7
128.0615	4.94	128.0626	-1.1	-8.6	7.0	C10 H8
129.0720	0.37	129.0704	1.6	12.2	6.5	C10 H9
138.0494	0.31	138.0470	2.4	17.7	9.0	C11 H6
139.0538	3.55	139.0548	-1.0	-7.0	8.5	C11 H7
140.0595	0.71	140.0626	-3.1	-22.1	8.0	C11 H8
141.0686	34.26	141.0704	-1.8	-12.9	7.5	C11 H9
143.0822	0.28	143.0861	-3.9	-27.1	6.5	C11 H11
144.0912	0.11	144.0939	-2.7	-18.7	6.0	C11 H12
145.0996	0.20	145.1017	-2.1	-14.6	5.5	C11 H13
149.0377	0.37	149.0391	-1.4	-9.6	10.5	C12 H5
150.0494	1.73	150.0470	2.4	16.3	10.0	C12 H6
151.0555	4.44	151.0548	0.7	4.8	9.5	C12 H7
152.0614	15.02	152.0626	-1.2	-7.9	9.0	C12 H8
153.0687	18.29	153.0704	-1.7	-11.3	8.5	C12 H9
154.0762	42.92	154.0783	-2.1	-13.3	8.0	C12 H10
157.1048	0.17	157.1017	3.1	19.6	6.5	C12 H13
158.1101	0.28	158.1096	0.5	3.5	6.0	C12 H14
162.0442	0.20	162.0470	-2.8	-17.0	11.0	C13 H6
163.0536	1.40	163.0548	-1.2	-7.2	10.5	C13 H7
164.0615	1.28	164.0626	-1.1	-6.7	10.0	C13 H8
165.0685	17.56	165.0704	-1.9	-11.7	9.5	C13 H9
166.0768	13.30	166.0783	-1.5	-8.7	9.0	C13 H10
167.0841	25.93	167.0861	-2.0	-11.8	8.5	C13 H11

Fig. S4 (a) GC Spectrum for the benzene solution of organic sideproducts produced form the reaction of In/tri(m-tolyl)phosphine at 370 ^{o}C for 12 h; (b) and (c) MS data for 3,3'-dimethylbiphenyl produced in the synthesis. The above GC-MS results show that the production of biaryls, such as 3,3'-dimethylbiphenyl, methyl biphenyl and biphenyl (the total content > 60%), and the reaction between In (or other metals) and tri(m-tolyl)phosphine is similar to the traditional Ullmann reaction for the synthesis of biaryls catalyzed by Cu.

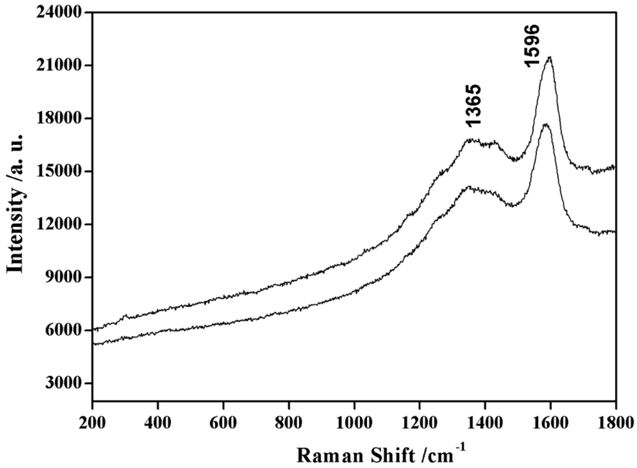


Fig. S5. Raman spectra for the InP samples prepared at 370 °C for 12h from the reactions of In nanoparticles with tri(p-tolyl)phosphine (the top spectrum) or diphenyl(p-tolyl)phosphine (the down one). The InP sample synthesized from tri(o-tolyl)phosphine at 370 °C has a similar Raman spectrum to that the InP sample prepared from tri(p-tolyl)phosphine at 390 °C for 12h.

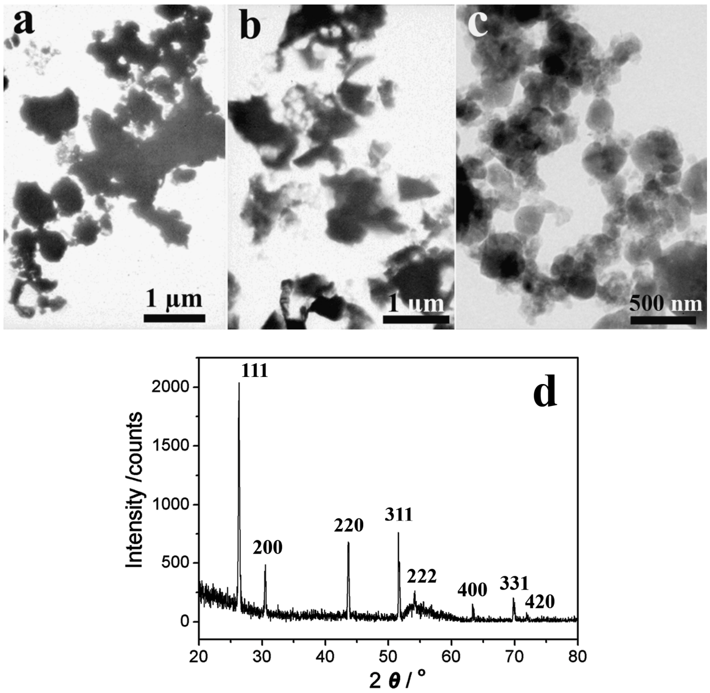


Fig. S6 TEM images of the InP products prepared at 370 °C from the reactions of In nanoparticles with (a) tri(p-tolyl)phosphine, (b) tri(p-tolyl)phosphine, and (c) diphenyl(p-tolyl)phosphine, respectively. (d) The XRD pattern of the InP products synthesized from In/tri(p-tolyl)phosphine at 370 °C for 12 h, which shows the good crystallinity of the resulting InP products.

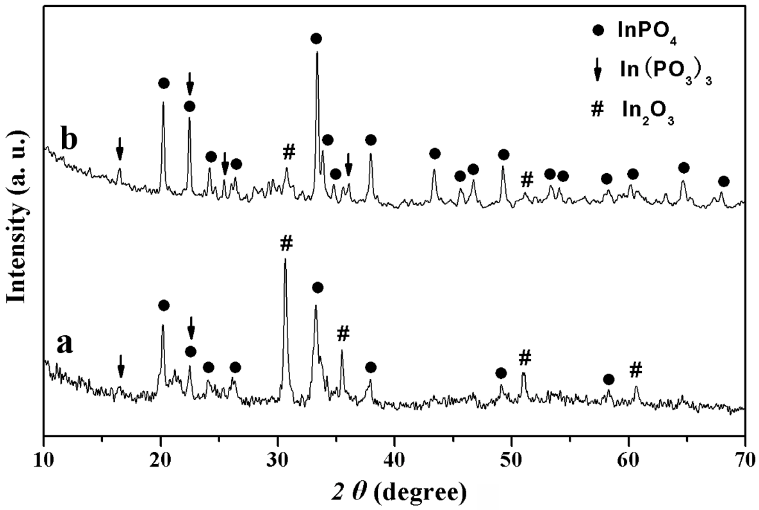


Fig. S7 XRD patterns of the products produced from thermal-treatment of (a) the InP nanofibers synthesized from tri(m-tolyl)phosphine at 370 ^{o}C for 12h, and (b) from thermal-treatment of the InP sample synthesized from tri(m-tolyl)phosphine at 390 ^{o}C. The peaks in the XRD patterns can be well indexed to $InPO_4$ (JCPDS No. 08-0052), $In(PO_3)_3$ (JCPDS No. 51-1644) and In_2O_3 (JCPDS No. 01-0929). The thermal-treatment was carried out in air from room temperature to 800 ^{o}C at the heating rate of 10 ^{o}C/min.

No. Name	Weight [mg]	Date	Time	C/N Ratio		Content [%]	Peak Area
36 W216A	2.5810	25.09.09	14:52	8617	N:	0.008	6
					C:	72.31	39892
					H:	3.942	7132
37 W216B	3.6880	25.09.09	15:01	89.80	N:	0.017	17
					C:	1.494	1236
					H:	0.433	1317
38 W216C	2.7420	25.09.09	15:12	1819	N:	0.038	29
					C:	69.46	40705
					H:	3.652	7019

Fig. S8 The CH elemental analysis results for (A) the InP sample synthesized from In/tri(m-tolyl)phosphine at 390 ^{o}C for 12h; (B) the InP nanofibers synthesized from In/tri(m-tolyl)phosphine at 370 ^{o}C for 12h; and (C) the InP sample synthesized from In/tri(p-tolyl)phosphine at 370 ^{o}C for 12h. The CH analyses show that higher temperature and more reactive triarylphosphines will lead to a higher C content in the resulting products, and more stable triarylphosphines, such as tri(m-tolyl)phosphine and triphenylphosphine, favor the production of InP nanofibers or nanowires. It is noted that the C content (72.31 %) determined by CH analysis is much higher than that detected by TGA (30.78%), and the difference could be probably attributed to the small variations in two experiments for the synthesis of InP samples from In/tri(m-tolyl)phosphine at 390 ^{o}C. However, both of the above analyses confirm the fact that a higher C content will take place at the higher temperature (390 ^{o}C) in the synthesis of InP samples from In/tri(m-tolyl)phosphine.

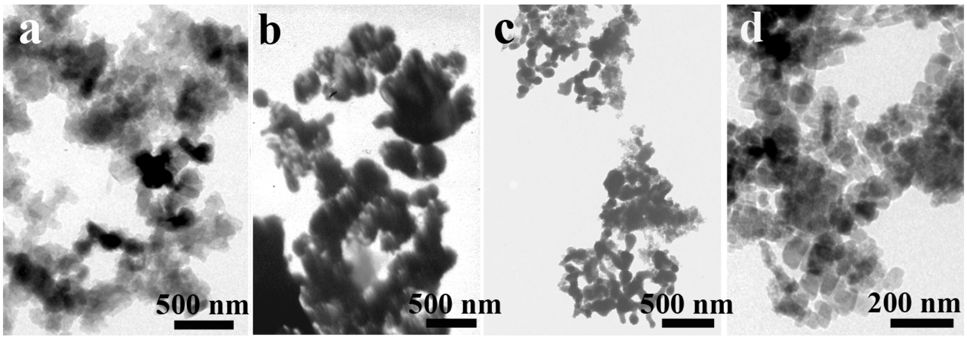


Fig. S9 TEM images of (a) GaP, (b) MnP, (c) CoP and (d) Pd_5P_2 samples synthesized from the corresponding metals with tri(m-tolyl)phosphine at 370 °C for 12 h.

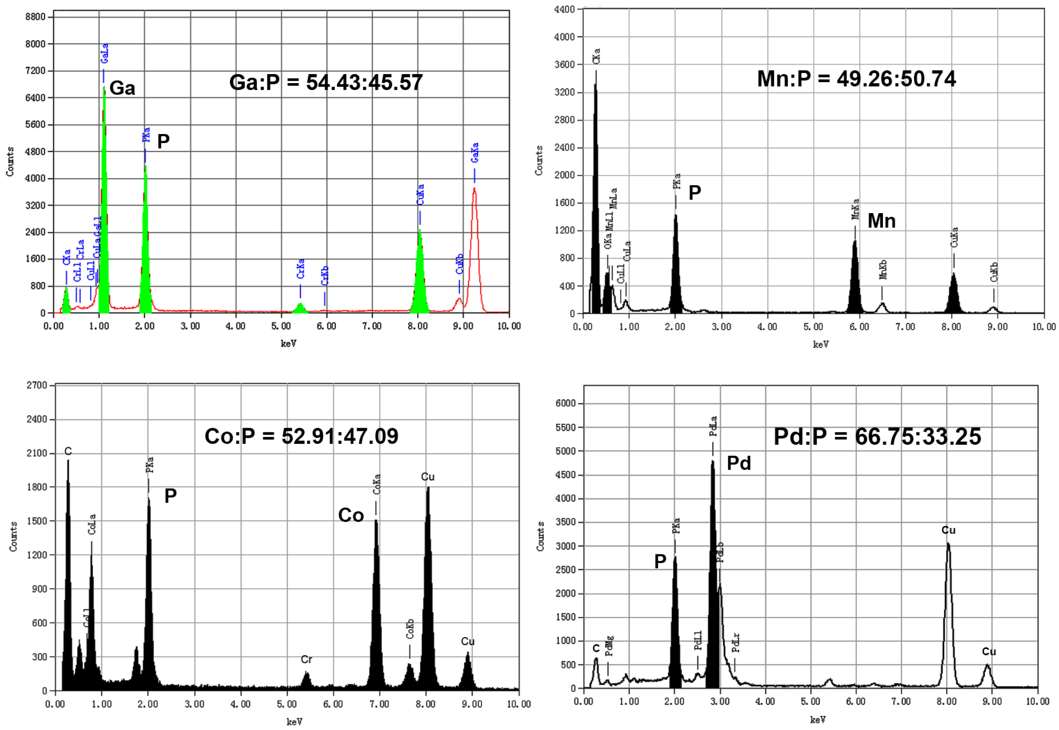


Fig. S10 EDX spectra taken on the samples: (a) GaP, (b) MnP, (c) CoP, and (d) Pd_5P_2. The chemical compositions of the phosphide products are close to the stoichiometric ratios of their bulk counterparts.