

Electronic Supplementary Information

Platinum-complexed phosphorous-doped carbon nitride for electrocatalytic hydrogen evolution

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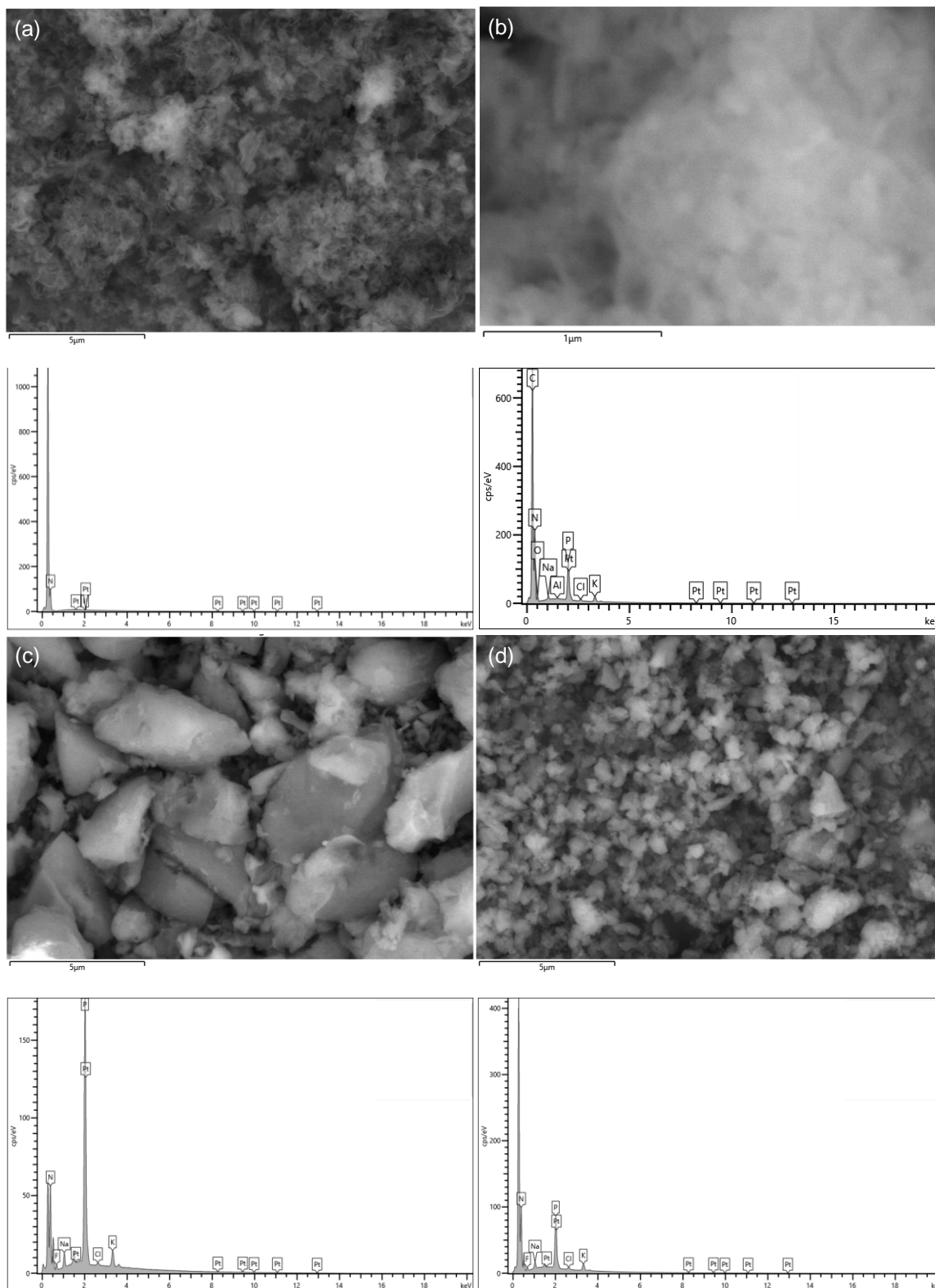


Figure S1. SEM images of (a) PtCNP₁, (b) PtCNP₂, (c) PtCNP₃, and (d) PtCNP₄. The corresponding EDS spectra are included below the respective panel, where Pt signals can be readily identified in all samples.

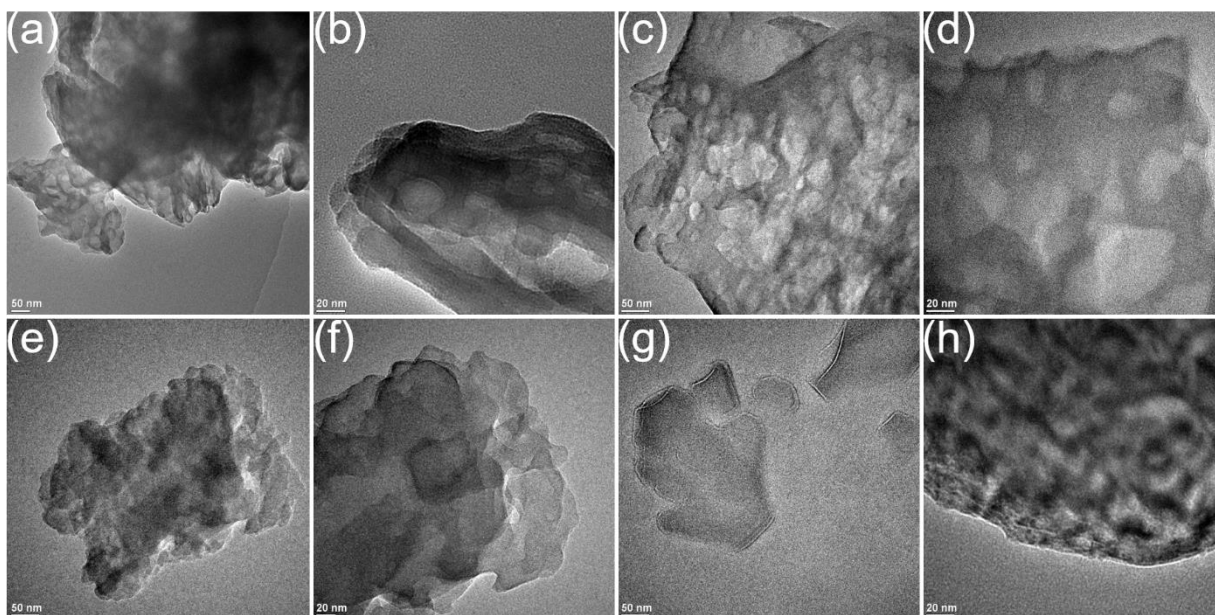


Figure S2. TEM images of (a, b) PtCN, (c, d) PtCNP₁, (e, f) PtCNP₃, (g, h) PtCNP₄. Scale bars are (a, c, e, g) 50 nm and (b, d, f, h) 20 nm.

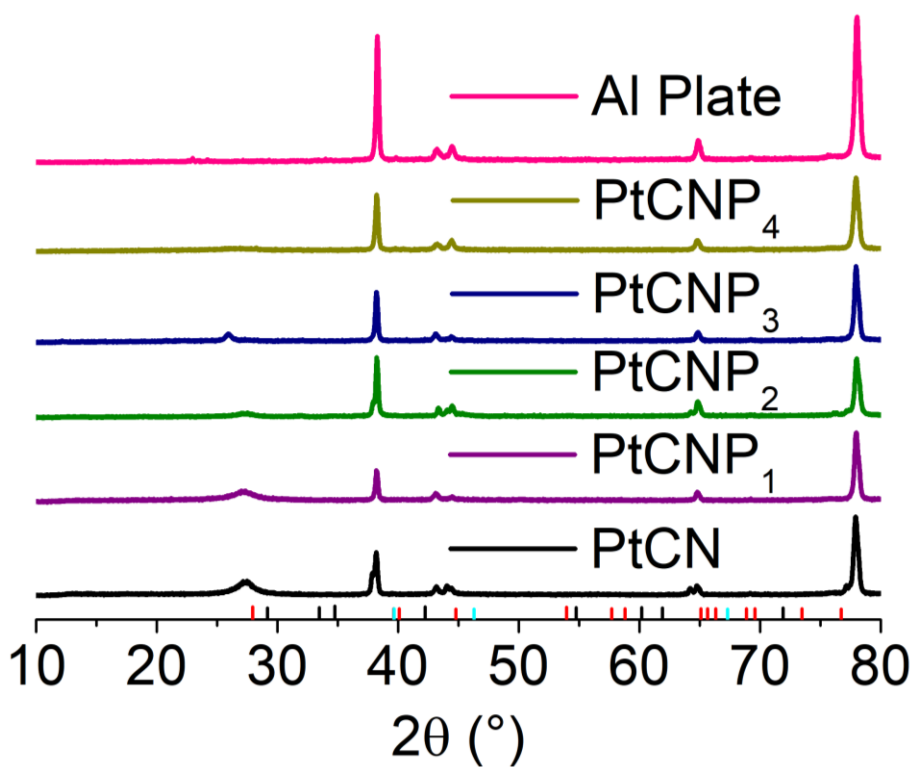


Figure S3. XRD patterns of the sample series deposited onto an aluminum plate. Reference lines are provided at the bottom of the plot and refer to cubic Pt with space group $fm-3m$ (JCPDS: 00-001-1190) (cyan), tetragonal PtO with space group $p42/mmc$ (JCPDS: 00-027-1331) (black), and orthorhombic PtO₂ with space group pnm (JCPDS: 00-023-1306) (red).

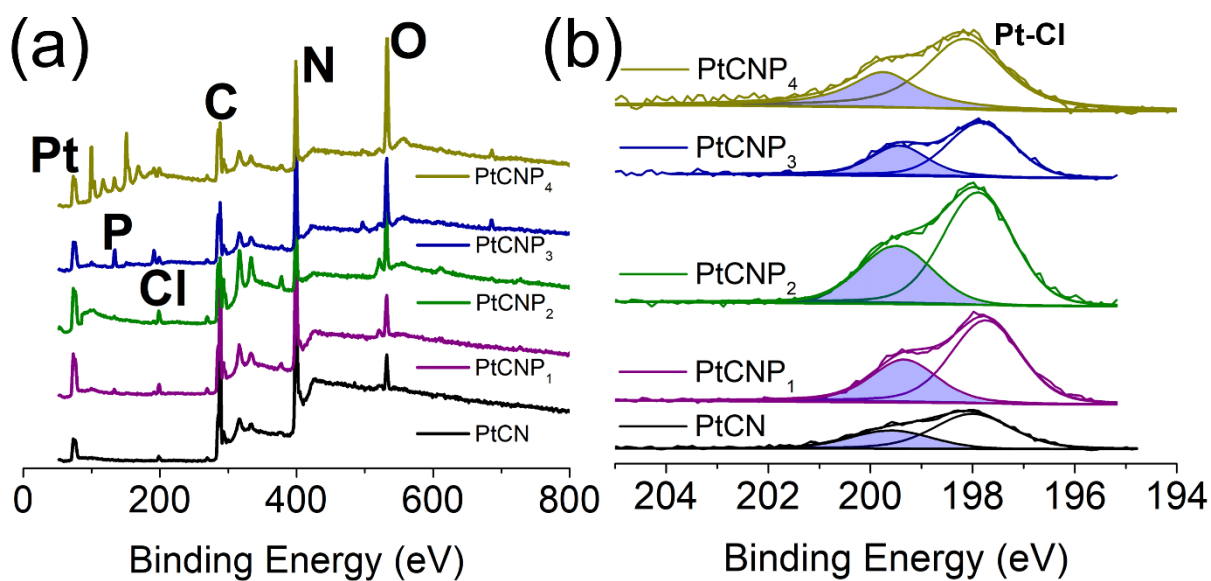


Figure S4. (a) XPS survey spectra of PtCN, PtCNP₁, PtCNP₂, PtCNP₃, and PtCNP₄. (b) High-resolution Cl 2p spectra of the sample series.

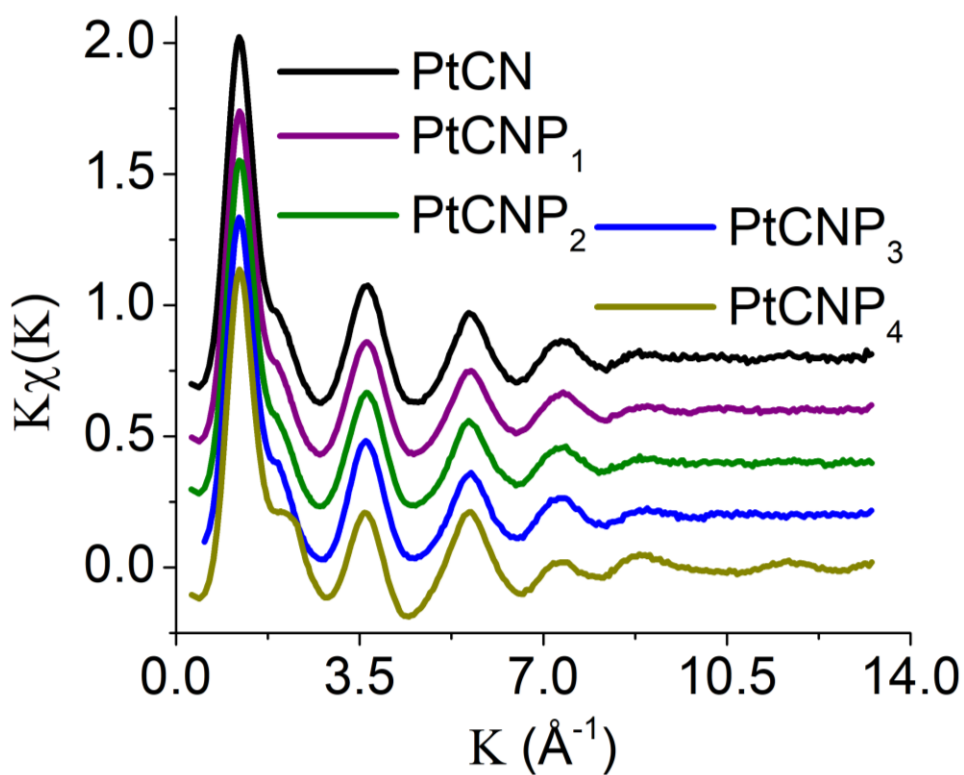


Figure S5. Pt L3 edge k-space data for the sample series collected at 10 K. Plots are produced by averaging 3 traces from for each sample.

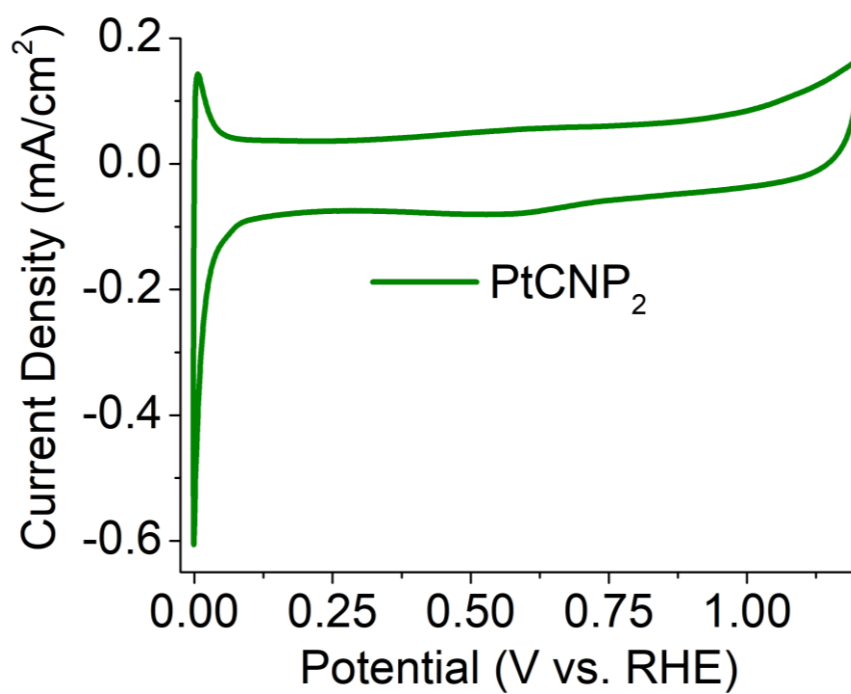


Figure S6. Cyclic voltammogram of the PtCNP₂ sample performed in N₂ saturated H₂SO₄ at a scan rate of 10 mV s⁻¹. Current density is obtained by normalizing the current to the electrode geometrical surface area.

Table S1. Elemental compositions (at%) of the sample series from XPS measurements

Sample	C	N	O	P	Cl	Pt
PtCN	43.98	51.01	3.71	0.00	0.58	0.73
PtCNP ₁	43.66	45.35	6.38	1.31	1.60	1.69
PtCNP ₂	44.39	46.37	4.73	1.11	1.72	1.69
PtCNP ₃	39.63	38.11	13.19	6.32	1.17	1.58
PtCNP ₄	19.91	7.25	55.53	11.03	5.96	0.32

Table S2. Pt 4f binding energy and atomic ratio of the sample series

Sample	Pt(II)		Pt(IV)		Pt(II)/Pt(IV) ratio
	4f _{7/2} (eV)	4f _{5/2} (eV)	4f _{7/2} (eV)	4f _{5/2} (eV)	
PtCN	72.63	75.98	74.35	77.70	4.01
PtCNP ₁	72.40	75.75	74.02	77.37	5.12
PtCNP ₂	72.54	75.89	74.34	77.69	11.80
PtCNP ₃	72.49	75.84	74.29	77.64	4.70
PtCNP ₄	72.41	75.76	73.48	76.83	2.70

Table S3. Binding energy of the P and Cl 2p_{3/2} electrons in the sample series

Sample	P		Cl	
	2p _{3/2} (eV)	2p _{1/2} (eV)	2p _{3/2} (eV)	2p _{1/2} (eV)
PtCN	-		198.00	199.6
PtCNP ₁	133.39	134.26	197.74	199.34
PtCNP ₂	132.88	133.75	197.79	199.39
PtCNP ₃	133.12	133.99	197.83	199.43
PtCNP ₄	133.01	133.88	198.15	199.75