Supporting Information for:

Flexible Direct Synthesis of Phosphorus-Rich CoP_3 on Carbon Black and its Examination in Hydrogen Evolution Electrocatalysis

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Table S2. Literature comparison table for carbon-supported cobalt phosphides HER in 0.5 M H_2SO_4.

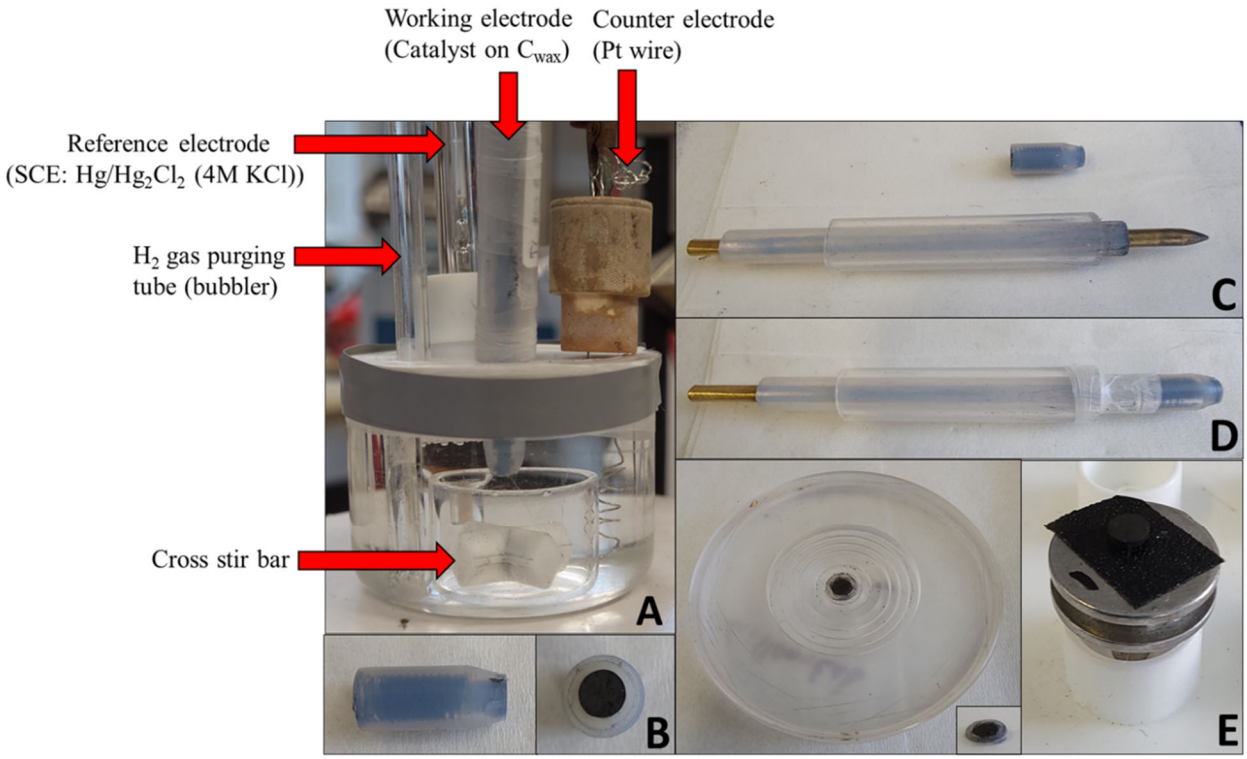


Figure S1. Images of electrochemical cell and working electrode: (A) Three electrode, single compartment cell, (B) coned, C_{wax} electrode tip in different geometries, (C) disassembled C_{wax} electrode tip + brass current collector, (D) assembled C_{wax} working electrode, and (E) cut slice C_{wax} tip geometries for post electrochemical XRD and SEM-EDS analysis.

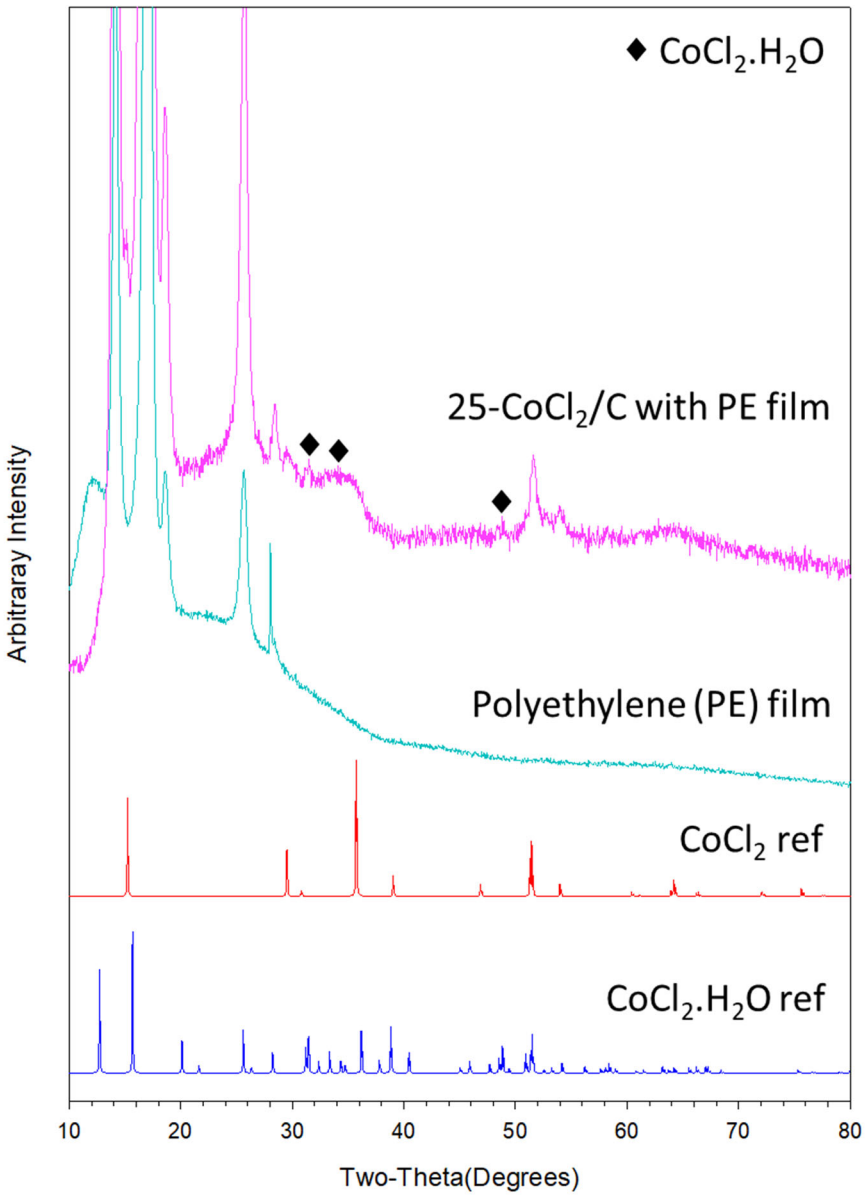


Figure S2. XRD results of 25-$CoCl_2$/C (25 mol% $CoCl_2$ deposited onto carbon black) product after methanol evaporation followed by heated evacuation (180 ° C, 15 min).

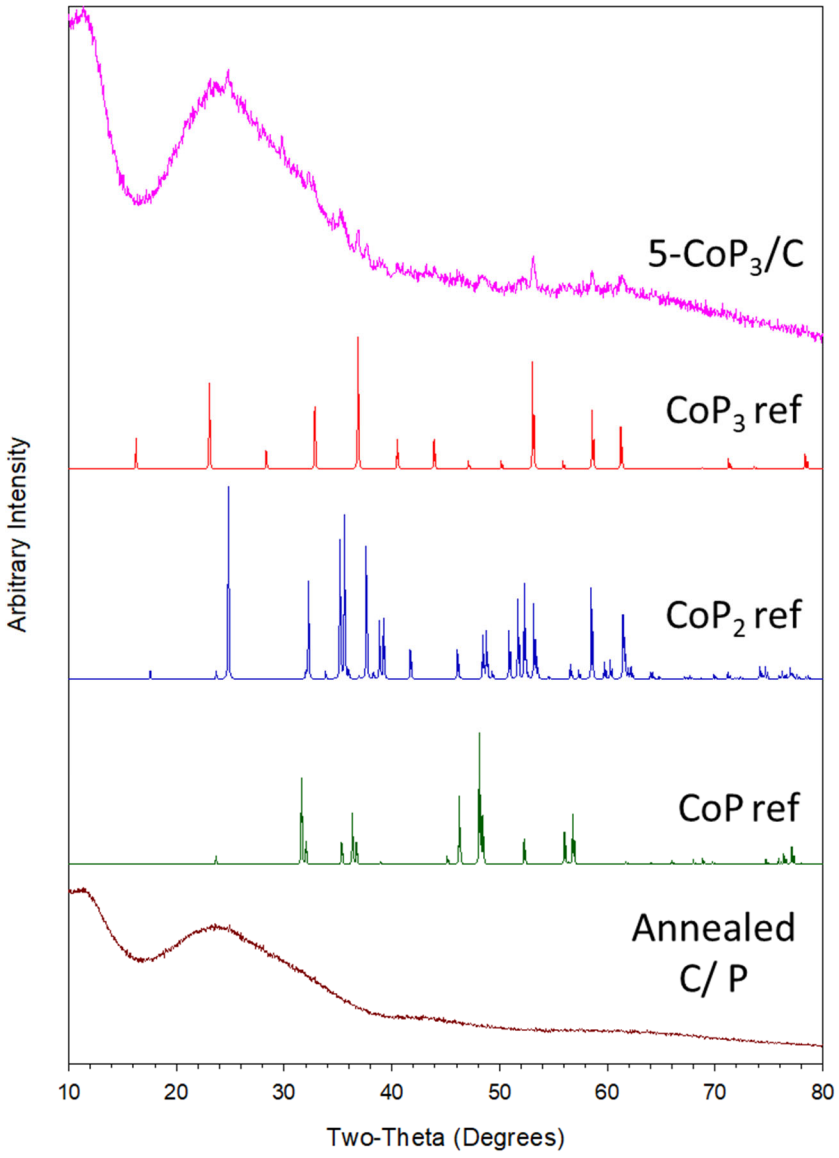


Figure S3. XRD results of targeted 5-CoP_3/C reaction using 3-fold excess phosphorus relative to stoichiometric amounts. The 5-CoP_3/C composite and carbon black (C/P) were annealed with 3-fold excess phosphorus at 500 °C for 48 hours.

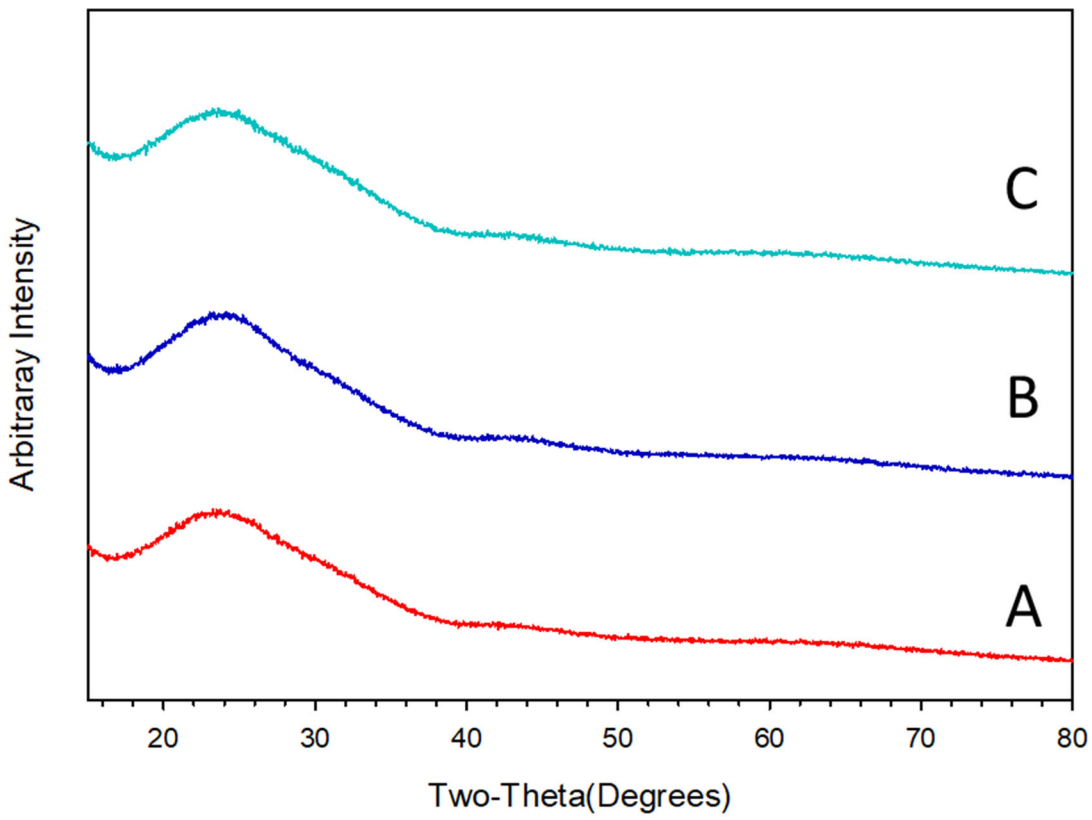


Figure S4. XRD results of (A) pristine carbon black (XC-72), annealed carbon black at 500 °C for 48 hours (B) without and (C) with excess phosphorus.

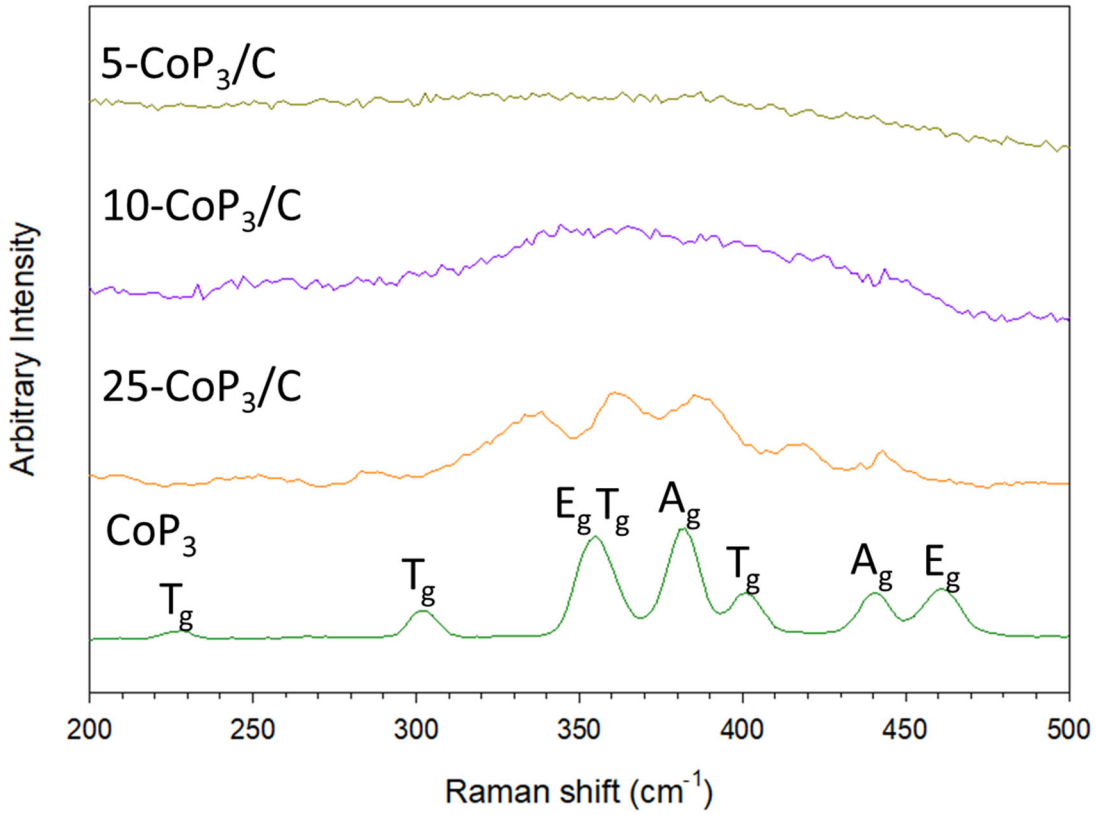


Figure S5. An overlay of Raman spectra of CoP_3, x-CoP_3/C (x = 5,10, 25) in the zoomed in region of 200-500 cm^{-1}.

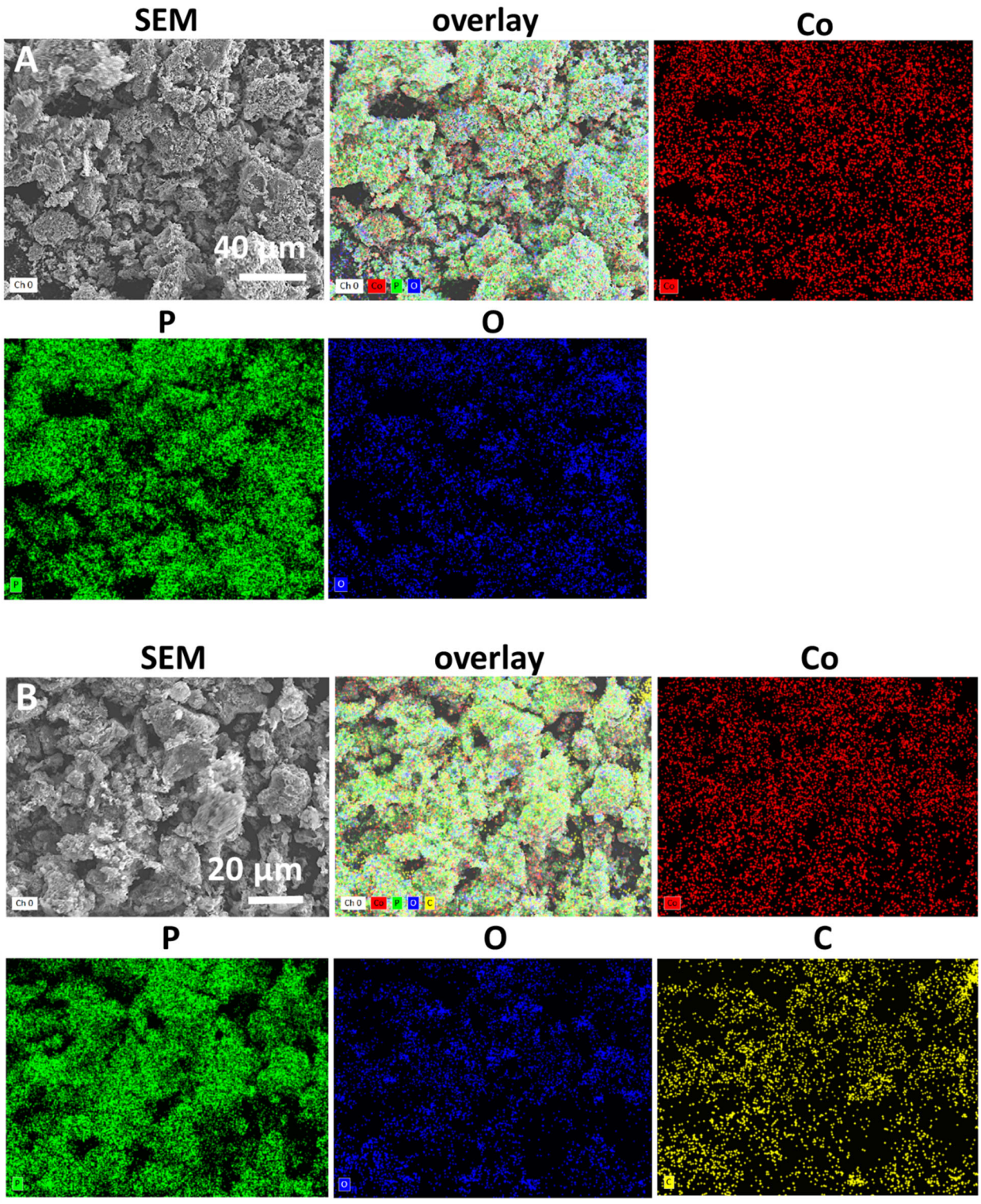


Figure S6. EDS elemental maps of (A) CoP_3 and (B) 25-CoP_3/C.

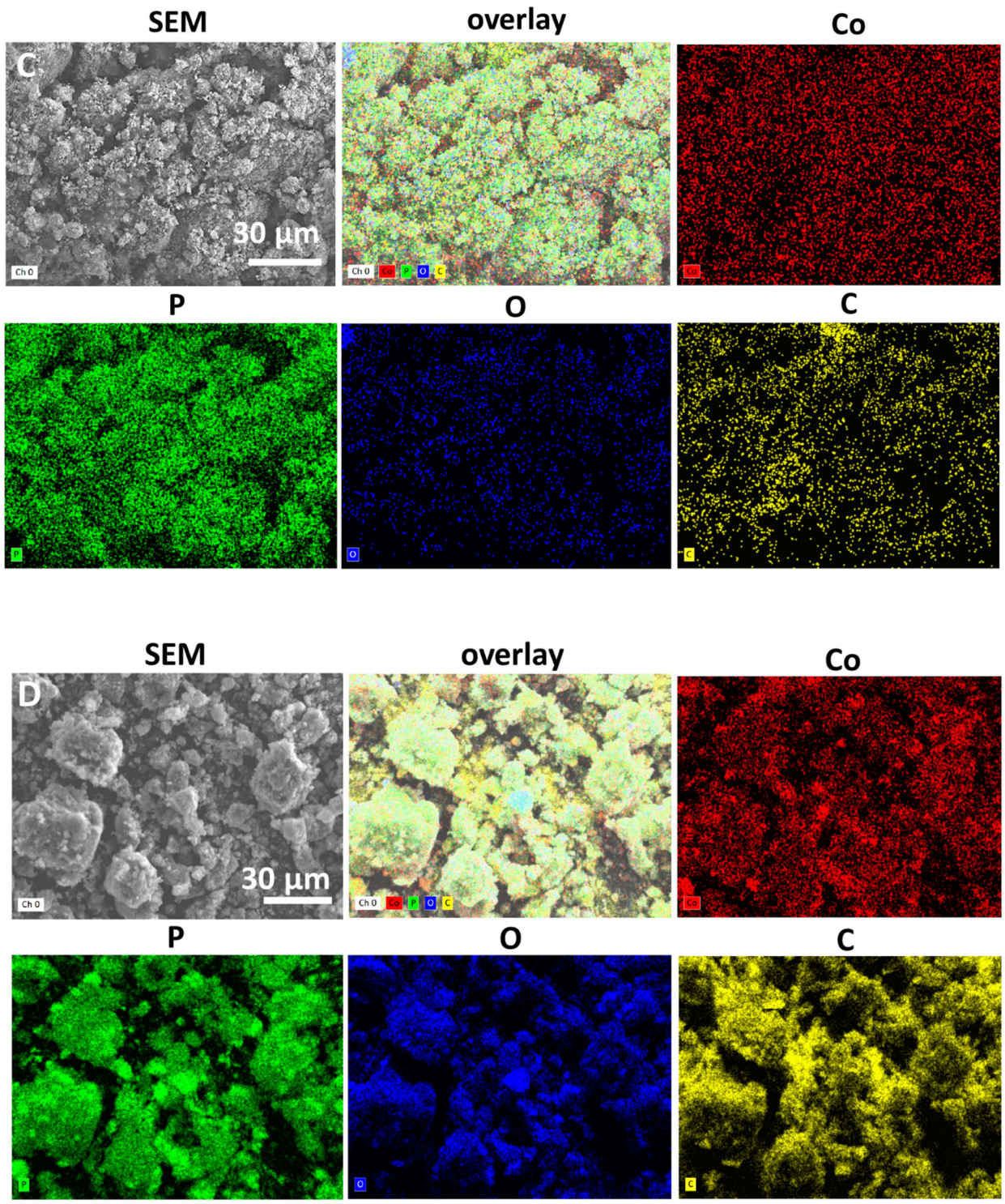
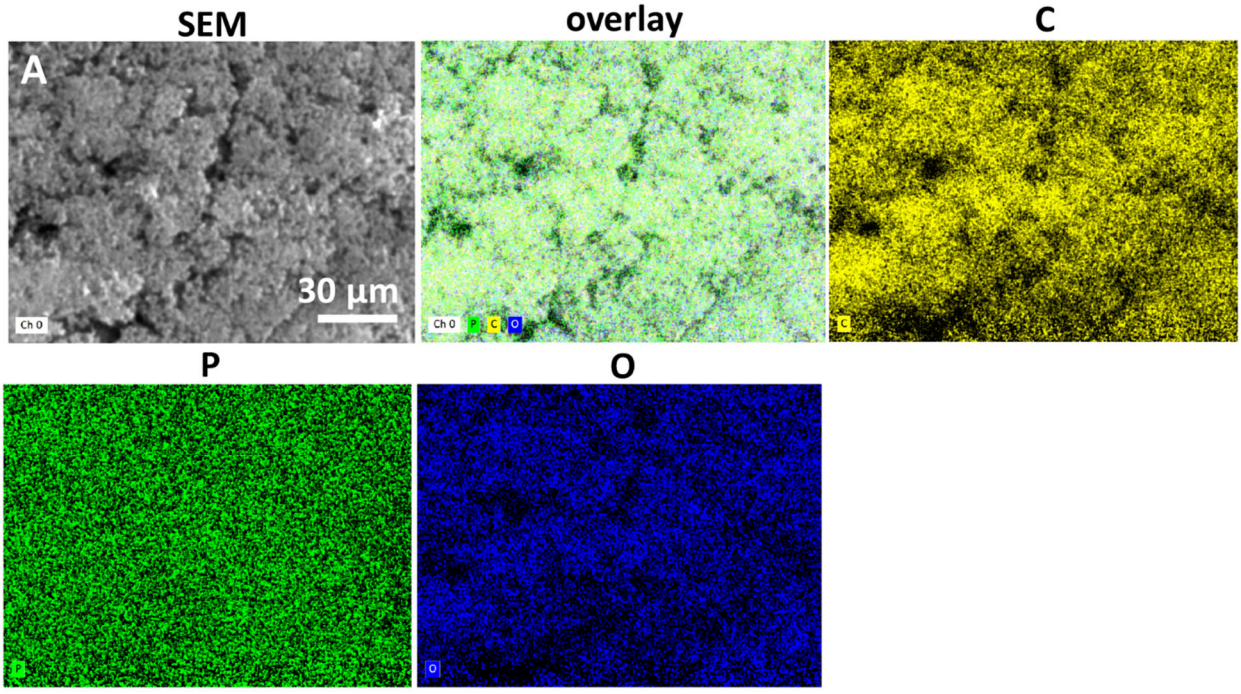
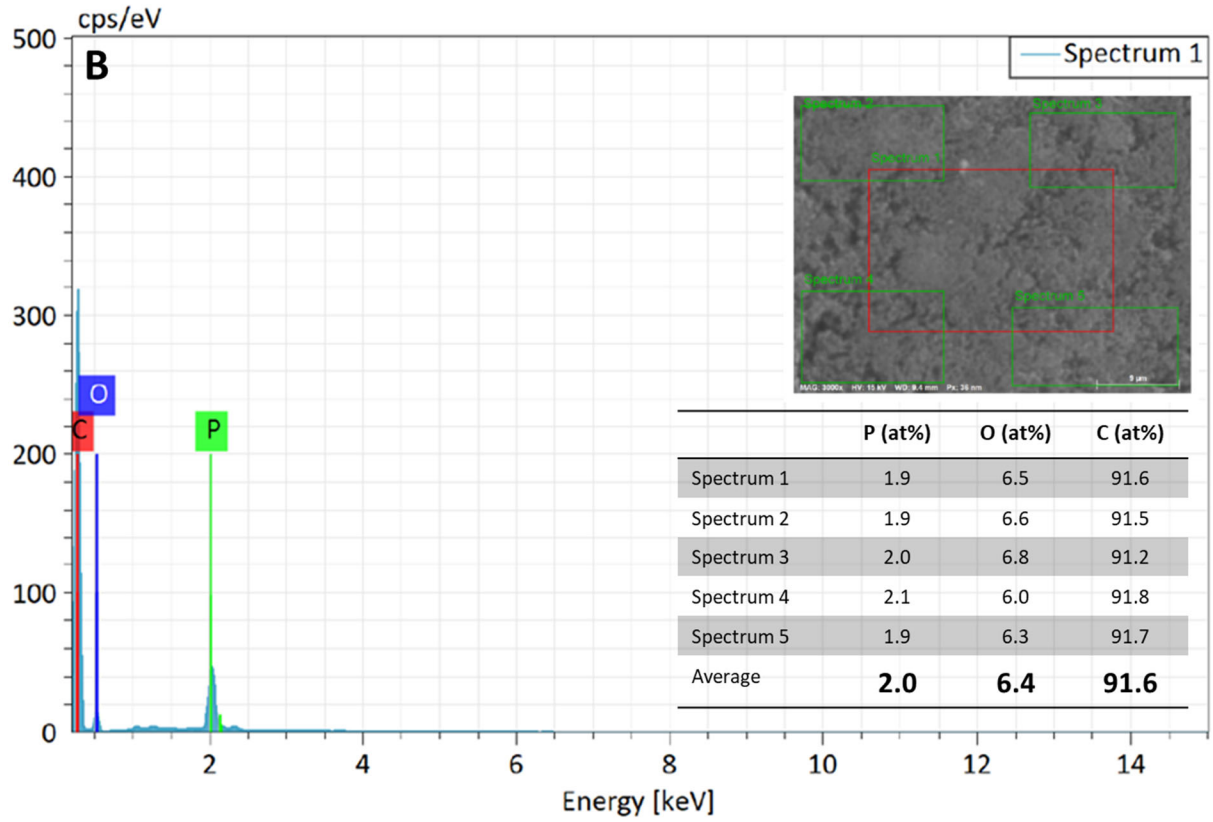


Figure S7. EDS elemental maps of (C) 10-CoP_3/C and (D) 5-CoP_3/C.





	P (at%)	O (at%)	C (at%)
Spectrum 1	1.9	6.5	91.6
Spectrum 2	1.9	6.6	91.5
Spectrum 3	2.0	6.8	91.2
Spectrum 4	2.1	6.0	91.8
Spectrum 5	1.9	6.3	91.7
Average	**2.0**	**6.4**	**91.6**

Figure S8. (A) EDS elemental maps and (B) analysis of annealed carbon black with phosphorous.

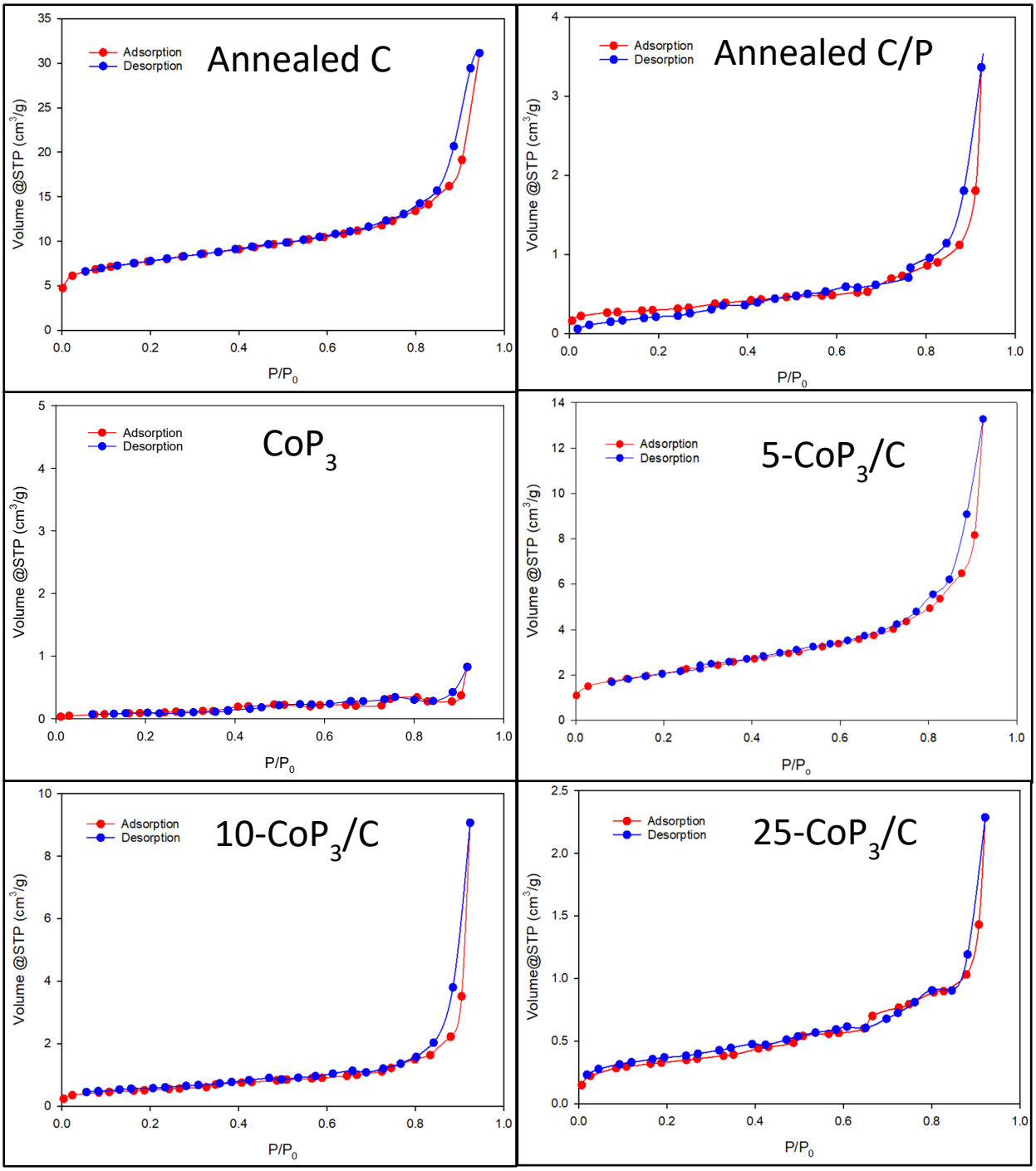


Figure S9. 50-point BET full isotherms of annealed carbon black with or without phosphorus, CoP_3 and x-CoP_3/C (x = 5, 10, 25) materials.

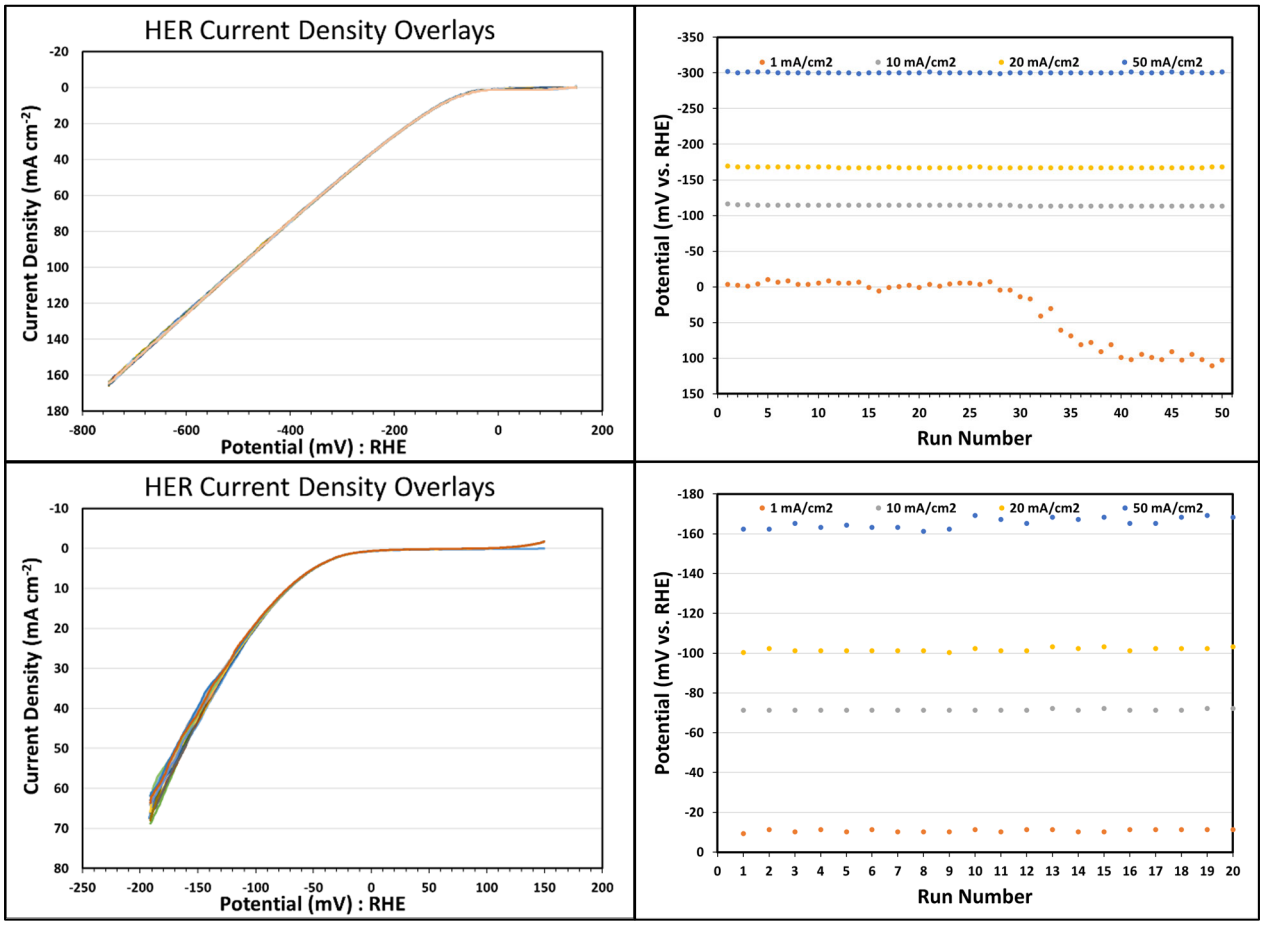


Figure S10. Left column: Overlay plots of iR uncompensated (50 LSV runs, top) and 85% iR compensated (20 LSV runs, bottom) of CoP_3 for HER experiments in 0.5 M H_2SO_4 at 5 mV/s scan rate. Right column: Plots of run number versus applied potentials to produce 1, 10, 20, 50 mA/cm^2 current densities using the LSV overlap plots shown in the left column.

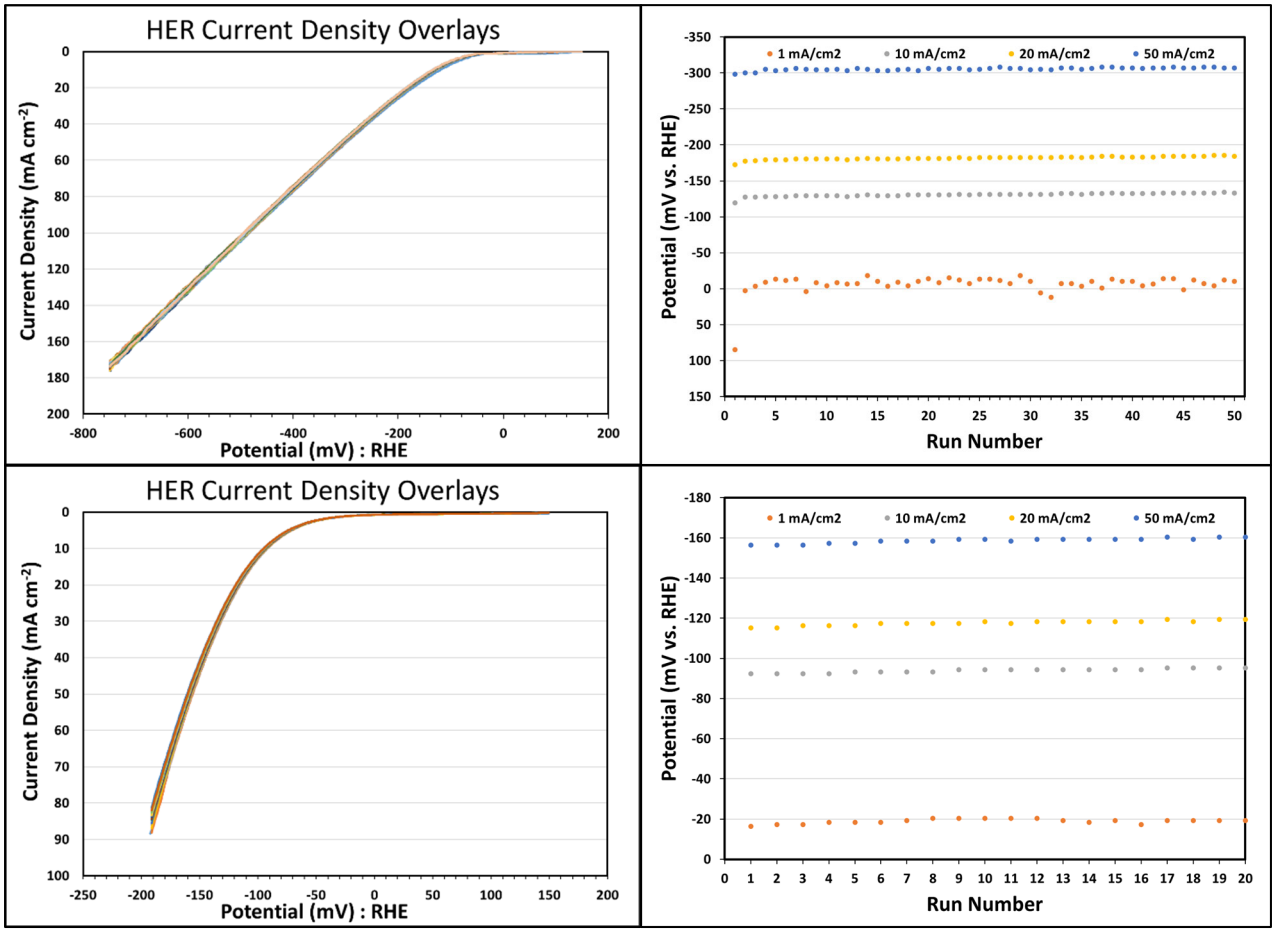


Figure S11. Left column: Overlay plots of iR uncompensated (50 LSV runs, top) and 85% iR compensated (20 LSV runs, bottom) of 25-CoP_3/C for HER experiments in 0.5 M H_2SO_4 at 5 mV/s scan rate. Right column: Plots of run number versus applied potentials to produce 1, 10, 20, 50 mA/cm^2 current densities using the LSV overlap plots shown in the left column.

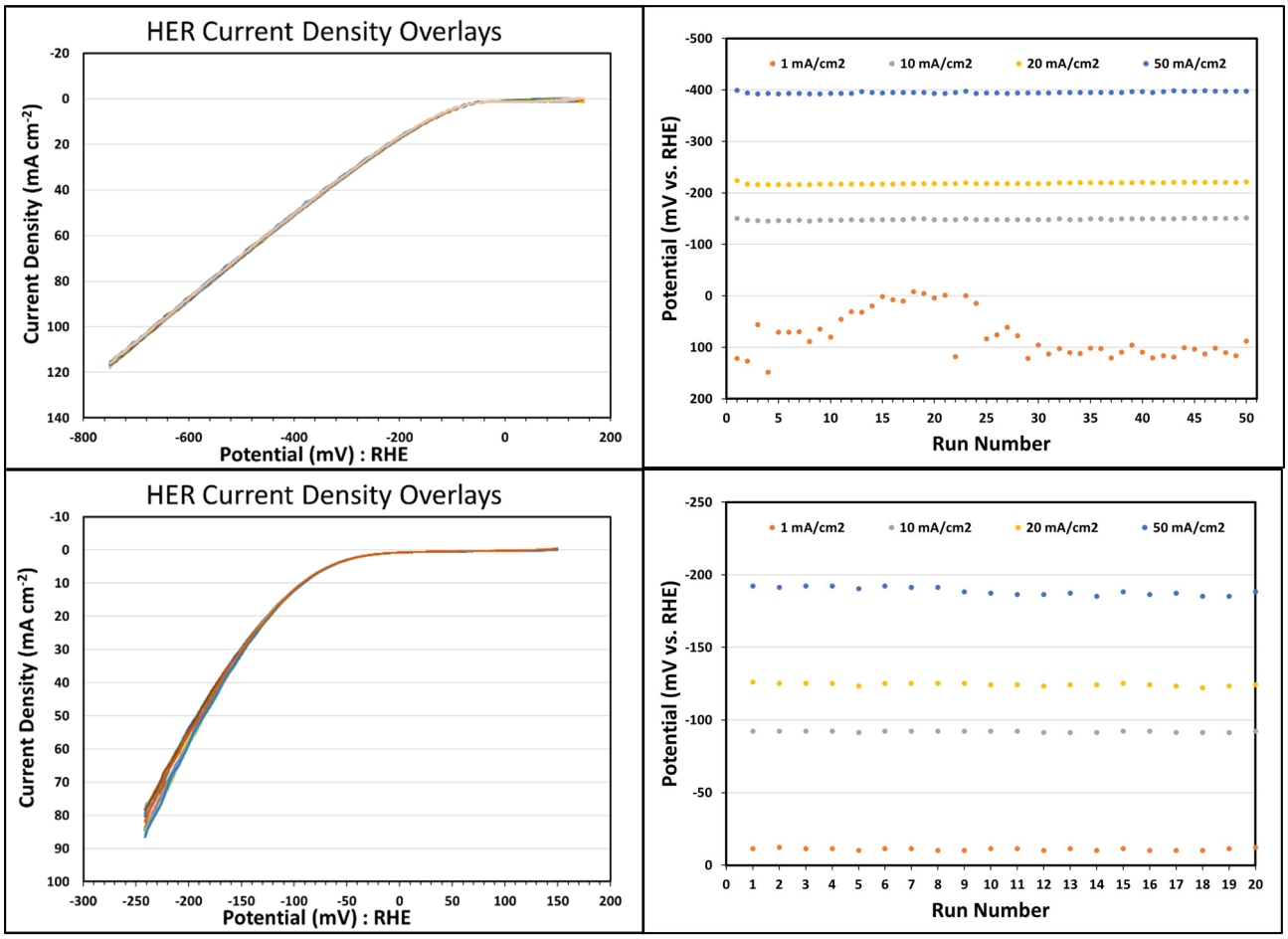


Figure S12. Left column: Overlay plots of iR uncompensated (50 LSV runs, top) and 85% iR compensated (20 LSV runs, bottom) of 10-CoP_3/C for HER experiments in 0.5 M H_2SO_4 at 5 mV/s scan rate. Right column: Plots of run number versus applied potentials to produce 1, 10, 20, 50 mA/cm^2 current densities using the LSV overlap plots shown in the left column.

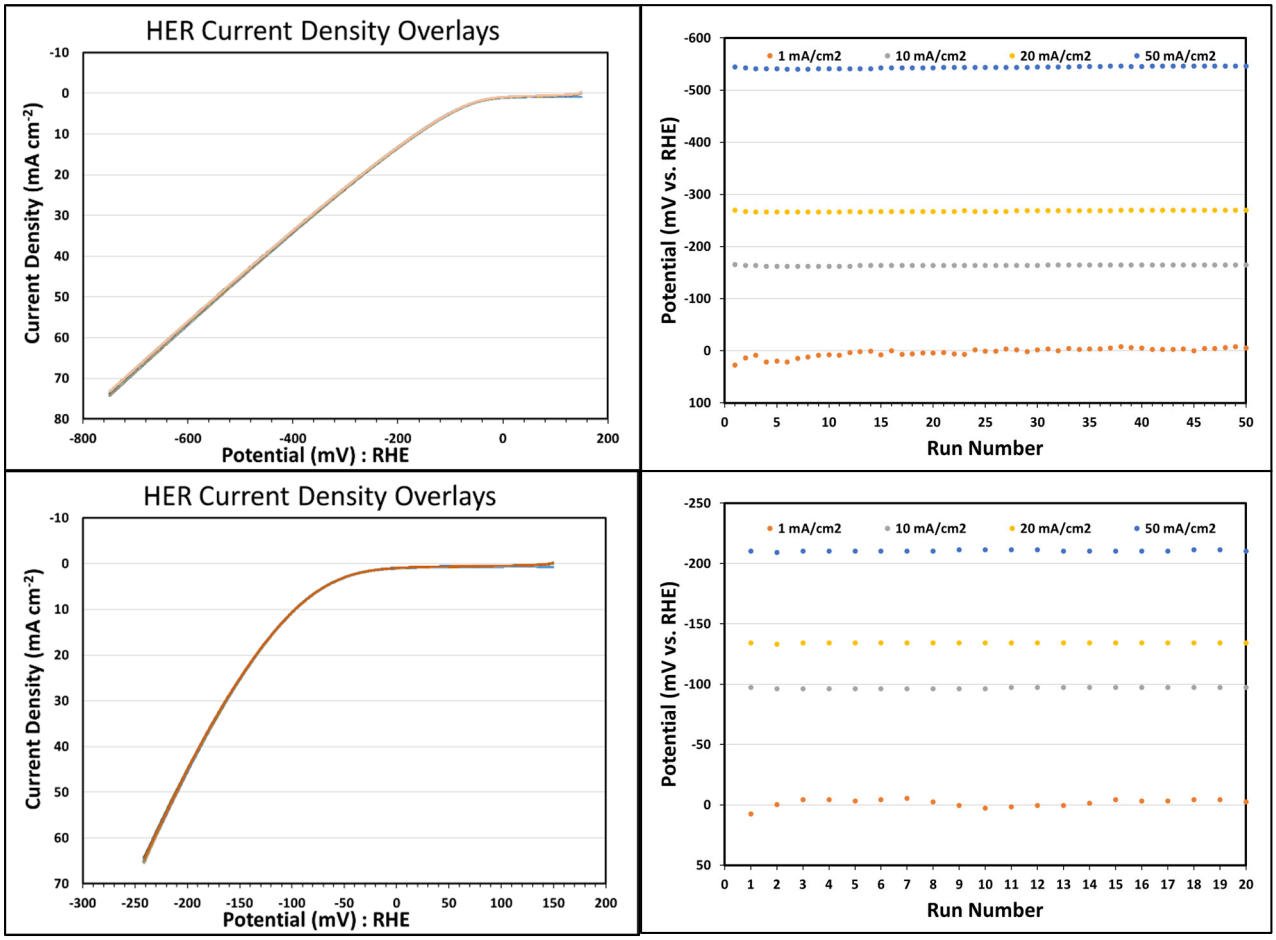


Figure S13. Left column: Overlay plots of iR uncompensated (50 LSV runs, top) and 85% iR compensated (20 LSV runs, bottom) of 5-CoP_3/C for HER experiments in 0.5 M H_2SO_4 at 5 mV/s scan rate. Right column: Plots of run number versus applied potentials to produce 1, 10, 20, 50 mA/cm^2 current densities using the LSV overlap plots shown in the left column.

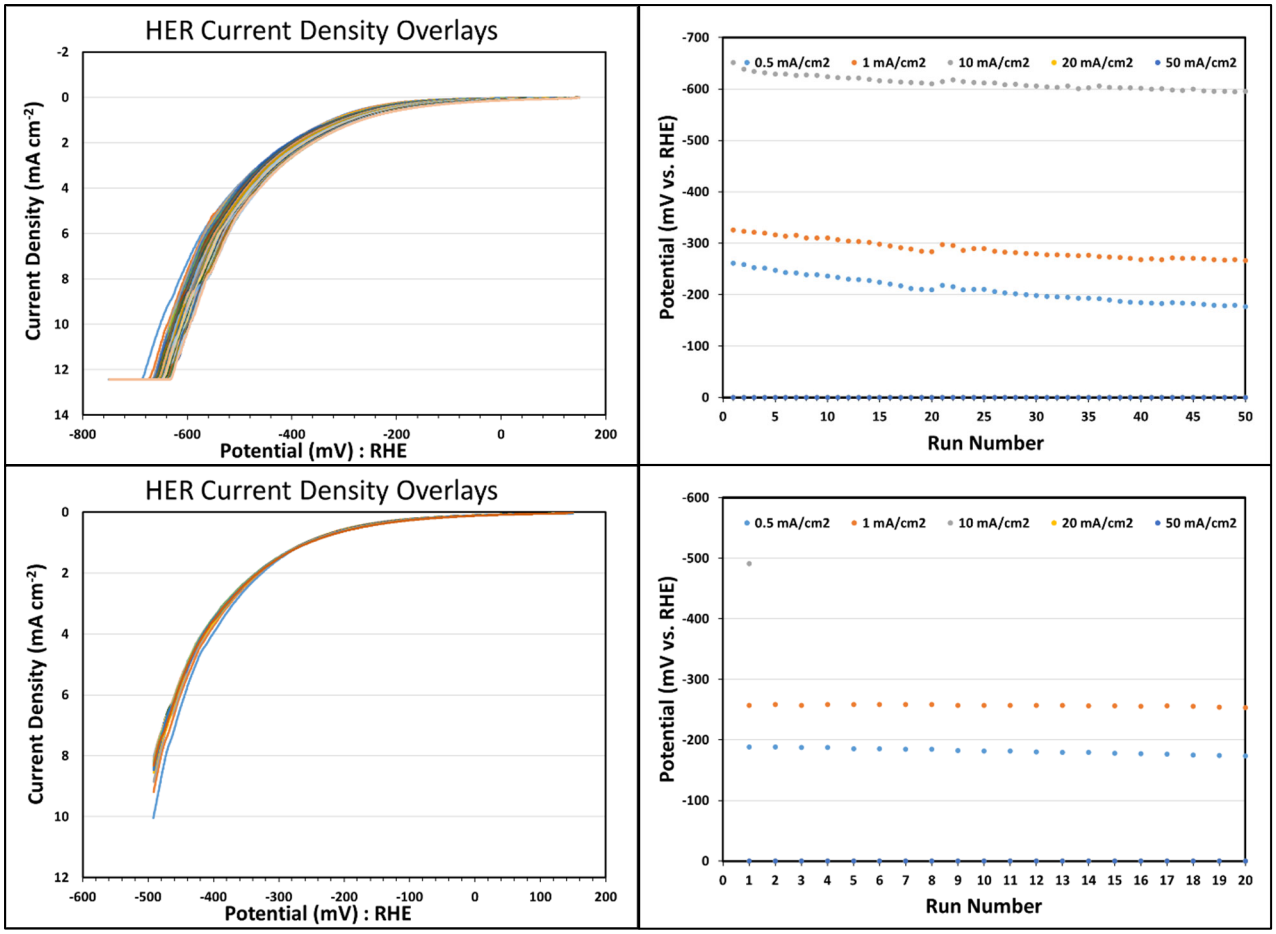


Figure S14. Left column: Overlay plots of iR uncompensated (50 LSV runs, top) and 85% iR compensated (20 LSV runs, bottom) of carbon black annealed with phosphorus for HER experiments in 0.5 M H_2SO_4 at 5 mV/s scan rate. Right column: Plots of run number versus applied potentials to produce 1, 10, 20, 50 mA/cm^2 current densities using the LSV overlap plots shown in the left column.

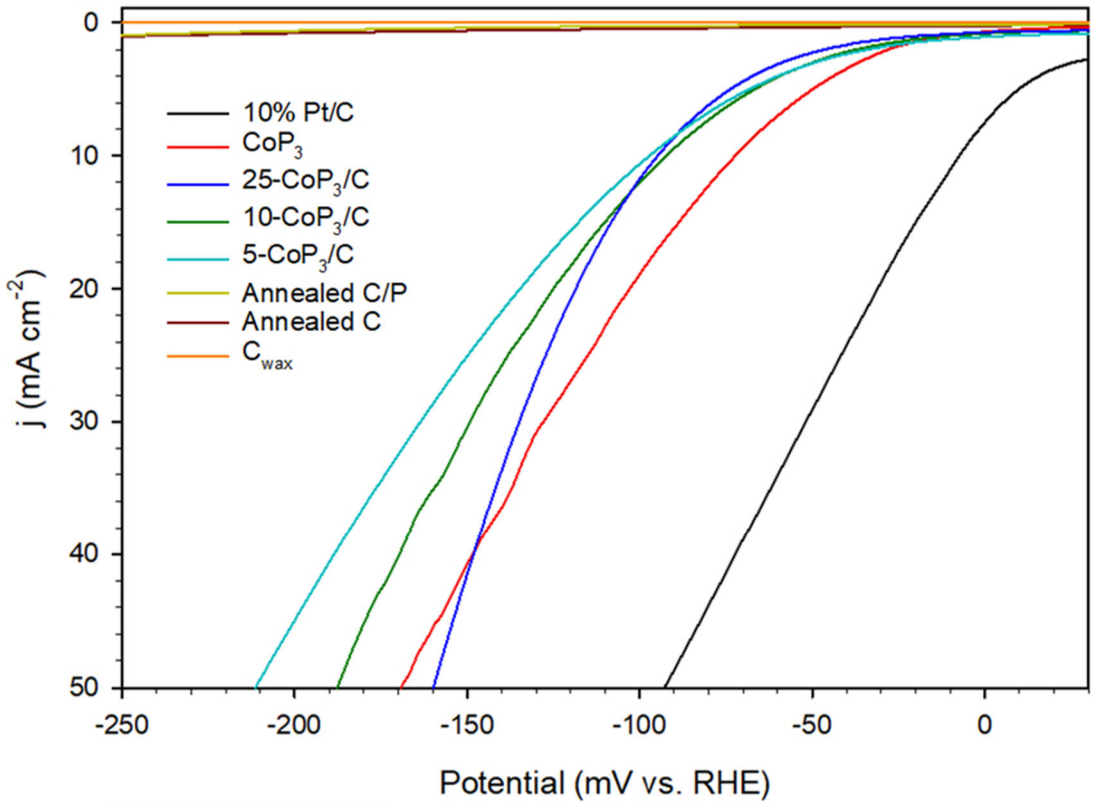


Figure S15. Representative 85% *iR* compensated LSV overlay plot of HER results for CoP_3, x-CoP_3/C (x = 5, 10, 25) and carbon black annealed with phosphorus.

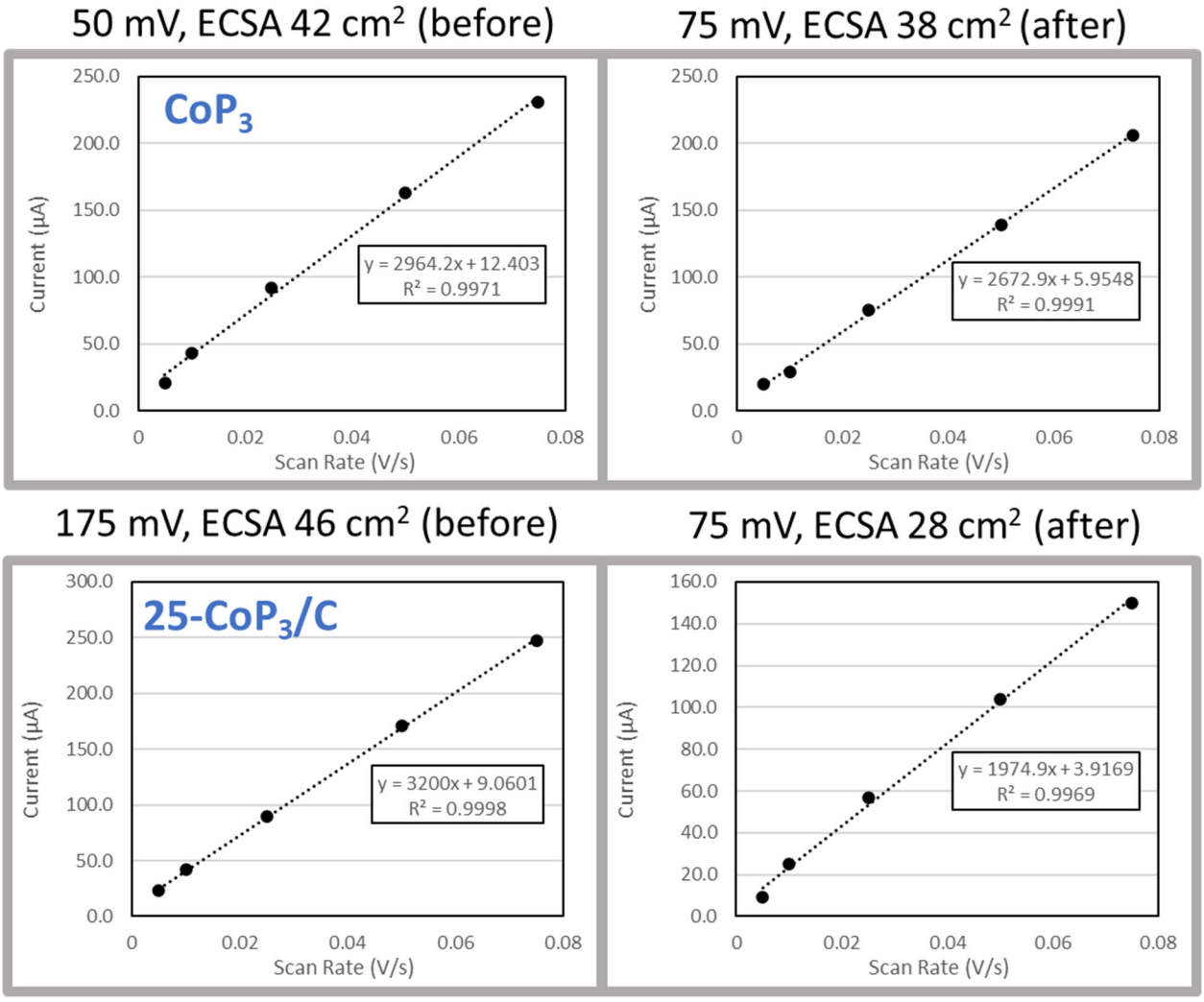


Figure S16. Analysis of scan rate data from CV runs to calculate ECSA values before and after 50 LSV scans (*iR* uncompensated) for CoP_3 and 25-CoP_3/C materials from Table 2.

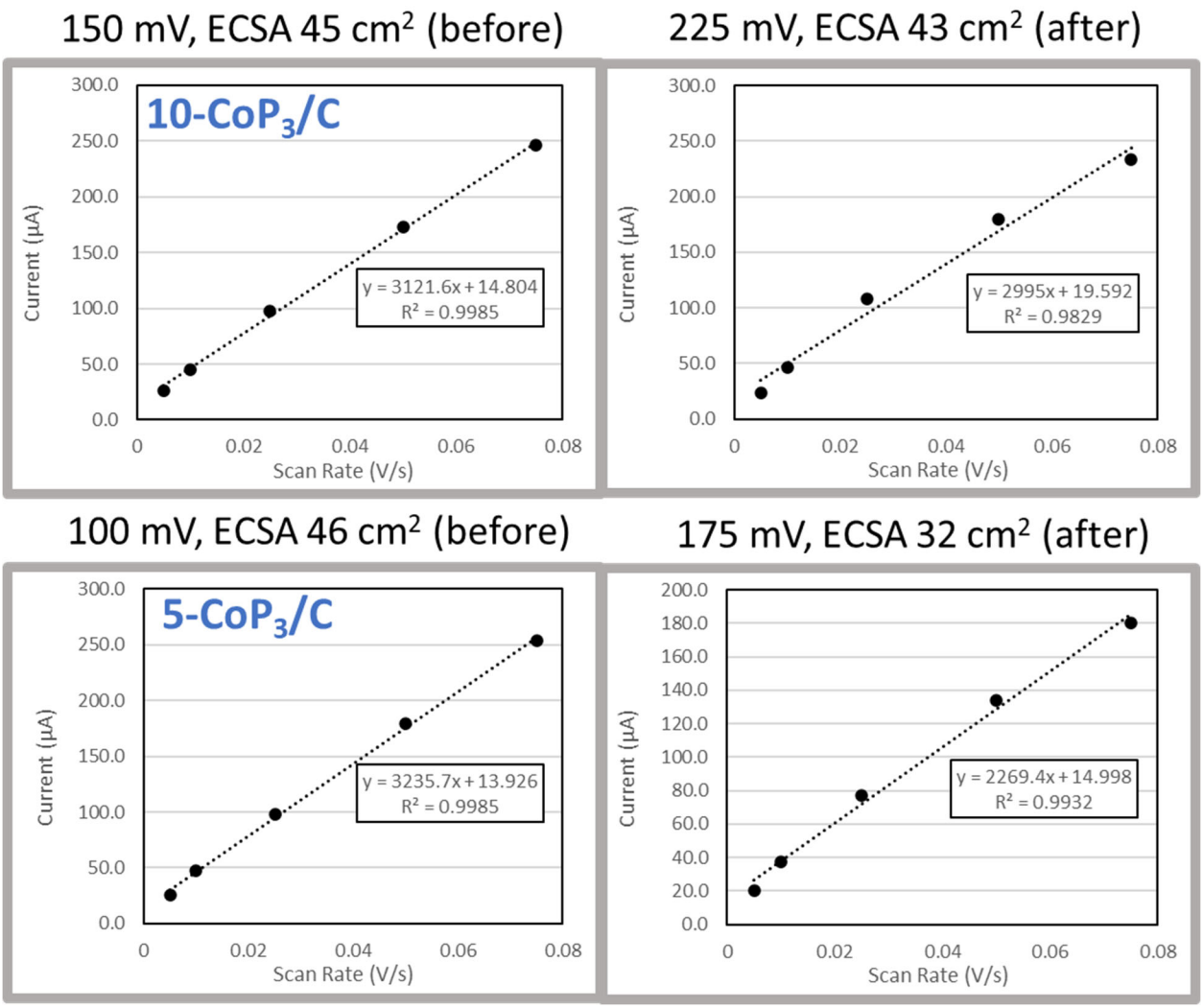


Figure S17. Analysis of scan rate data from CV runs to calculate ECSA values before and after 50 LSV scans (*iR* uncompensated) for 10-CoP_3/C and 5-CoP_3/C materials from Table 2.

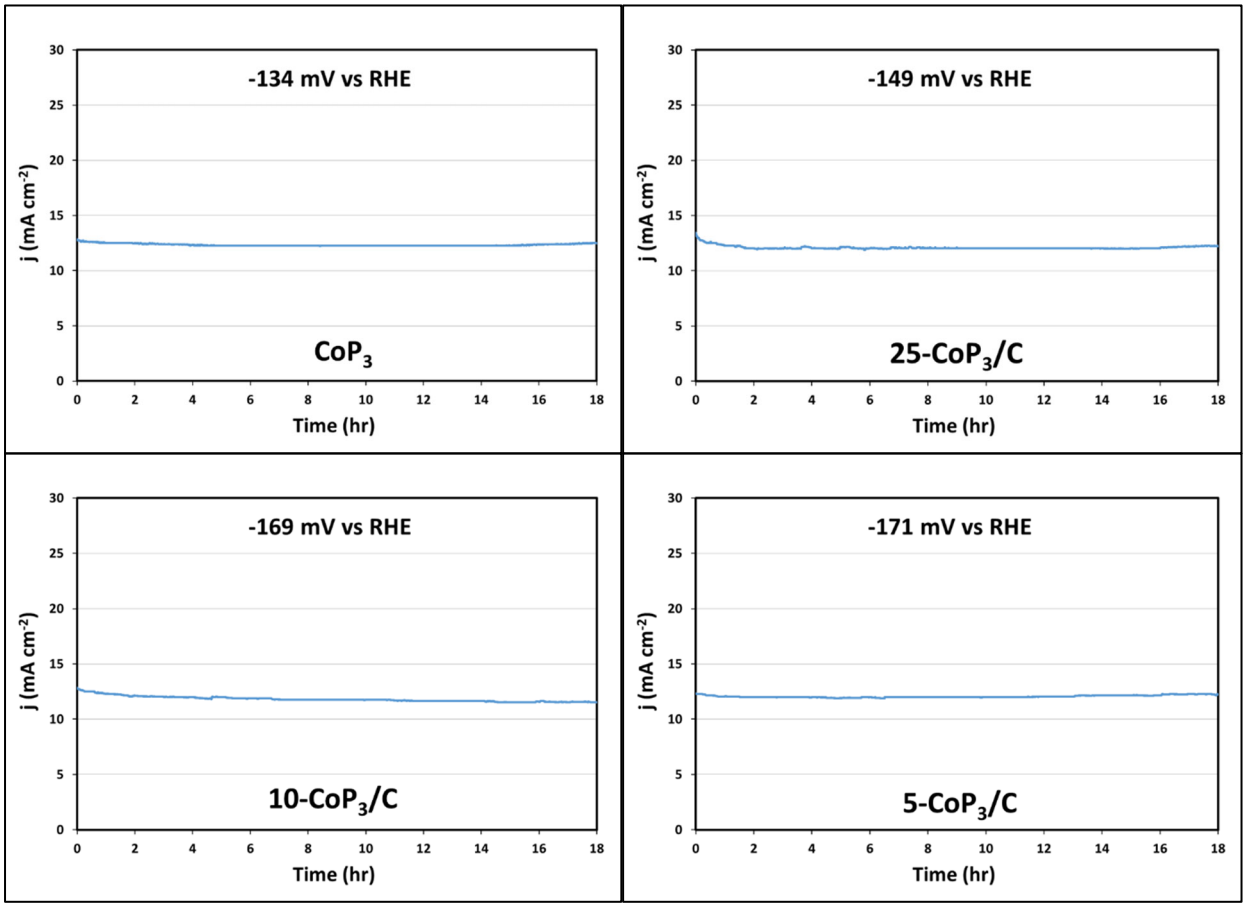


Figure S18. 18-hour constant potential chronoamperometry (CA) HER experiments for CoP_3 and x-CoP_3/C (x = 5, 10, 25) catalysts using a platinum counter electrode.

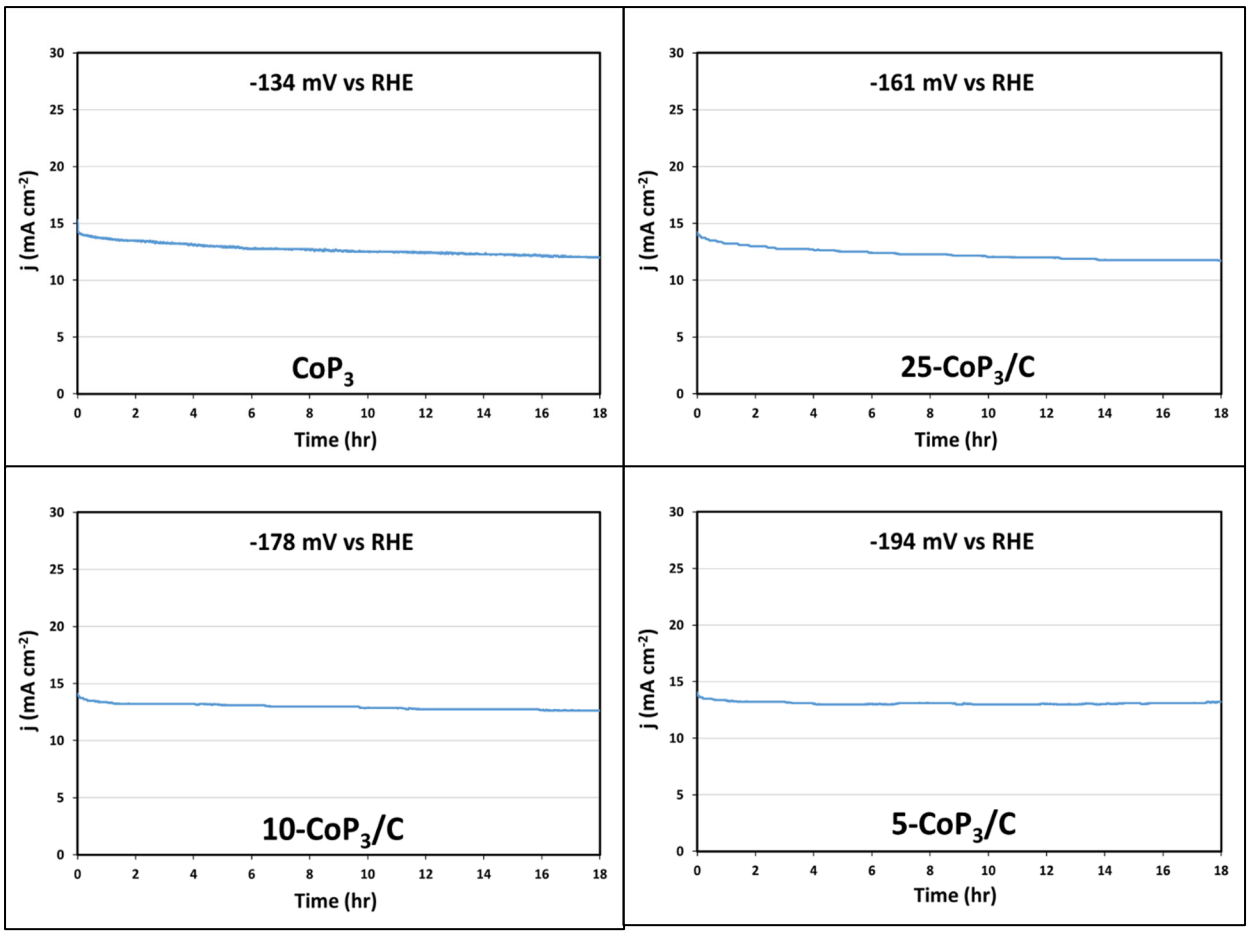


Figure S19. 18-hour constant potential chronoamperometry (CA) HER experiments for CoP_3 and x-CoP_3/C (x = 5, 10, 25) catalysts using graphite rod counter electrode.

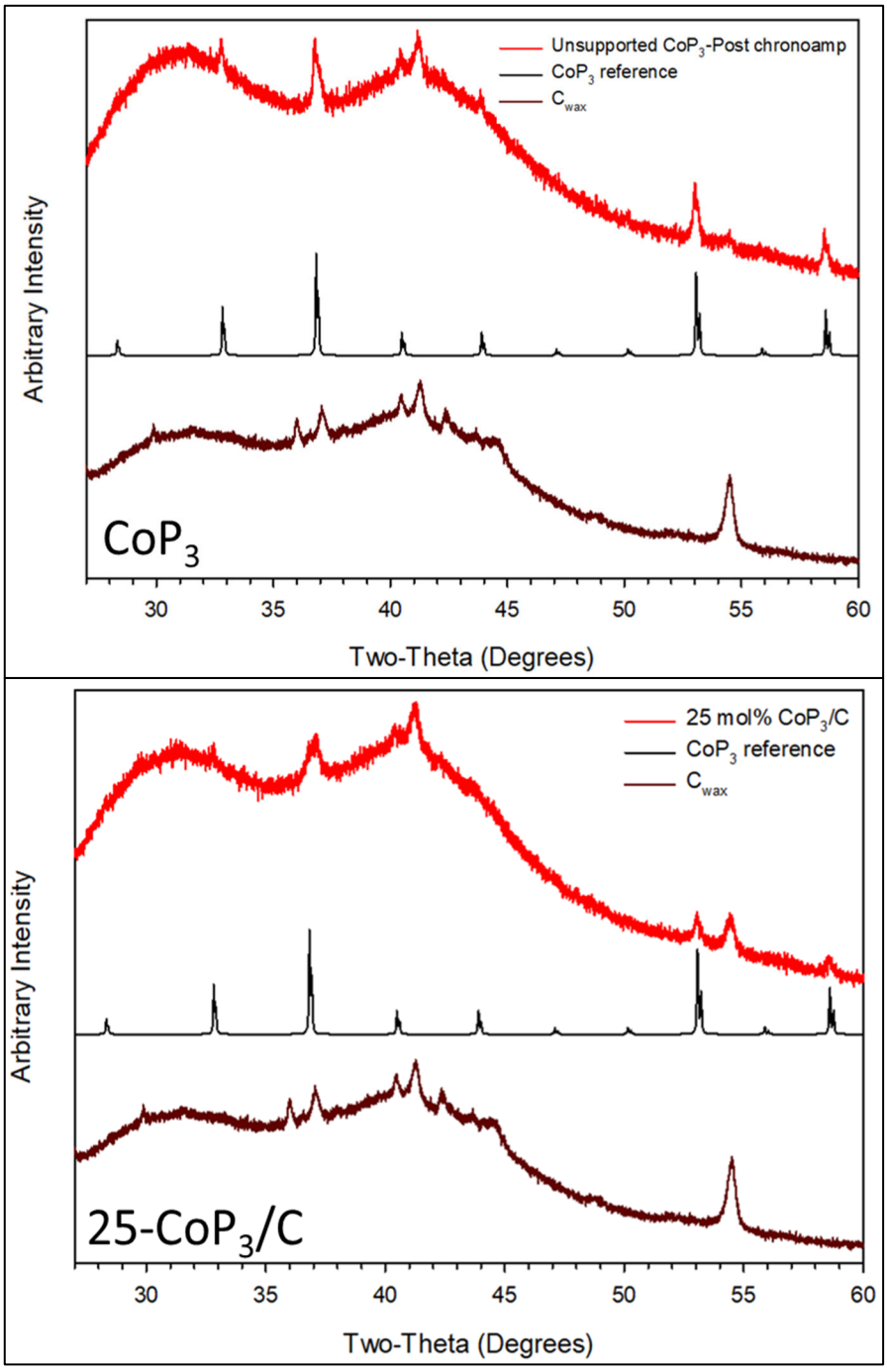


Figure S20. XRD results of CoP_3, and 25-CoP_3/C materials embedded on C_{wax} tips before and after 18-hour constant potential chronoamperometry (CA) HER experiments.

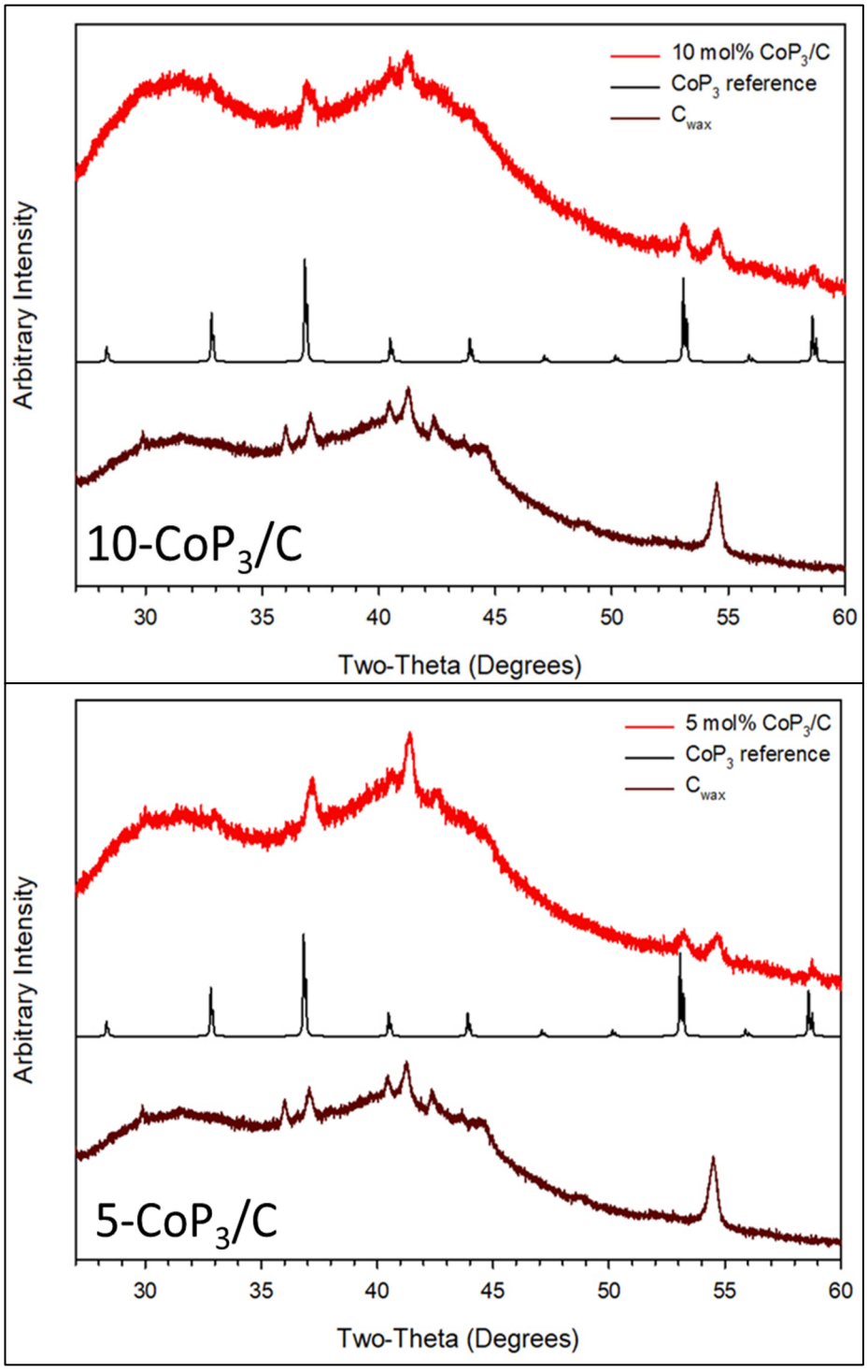


Figure S21. XRD results of 10-CoP_3/C and 5-CoP_3/C materials embedded on C_{wax} tips before and after 18-hour constant potential chronoamperometry (CA) HER experiments.

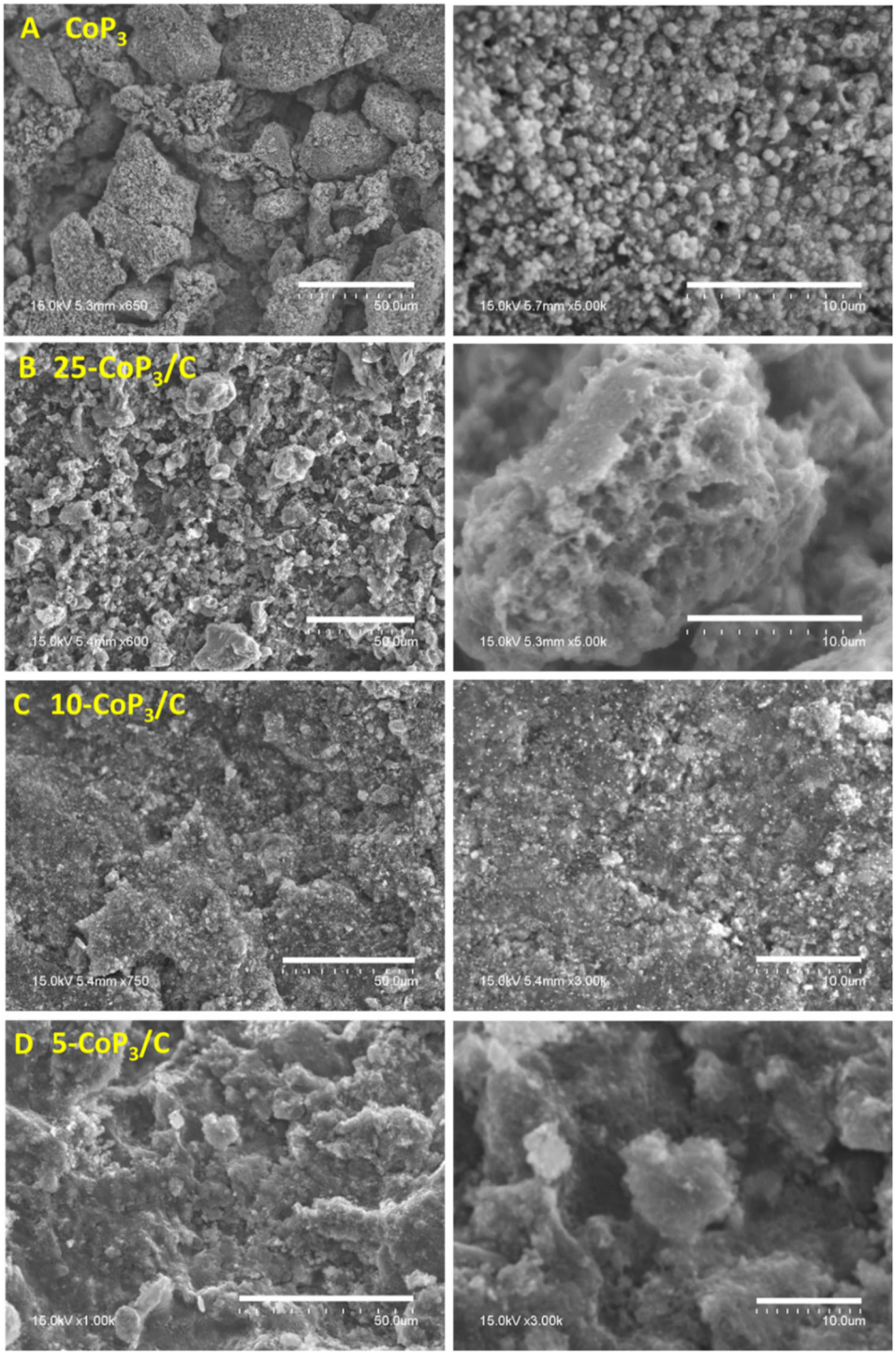


Figure S22. Scanning electron microscopy (SEM) images of (A) CoP_3, (B) 25-CoP_3/C, (C) 10-CoP_3/C, and (D) 5-CoP_3/C embedded on a C_{wax} electrode tip after 18-hour CA HER experiments.

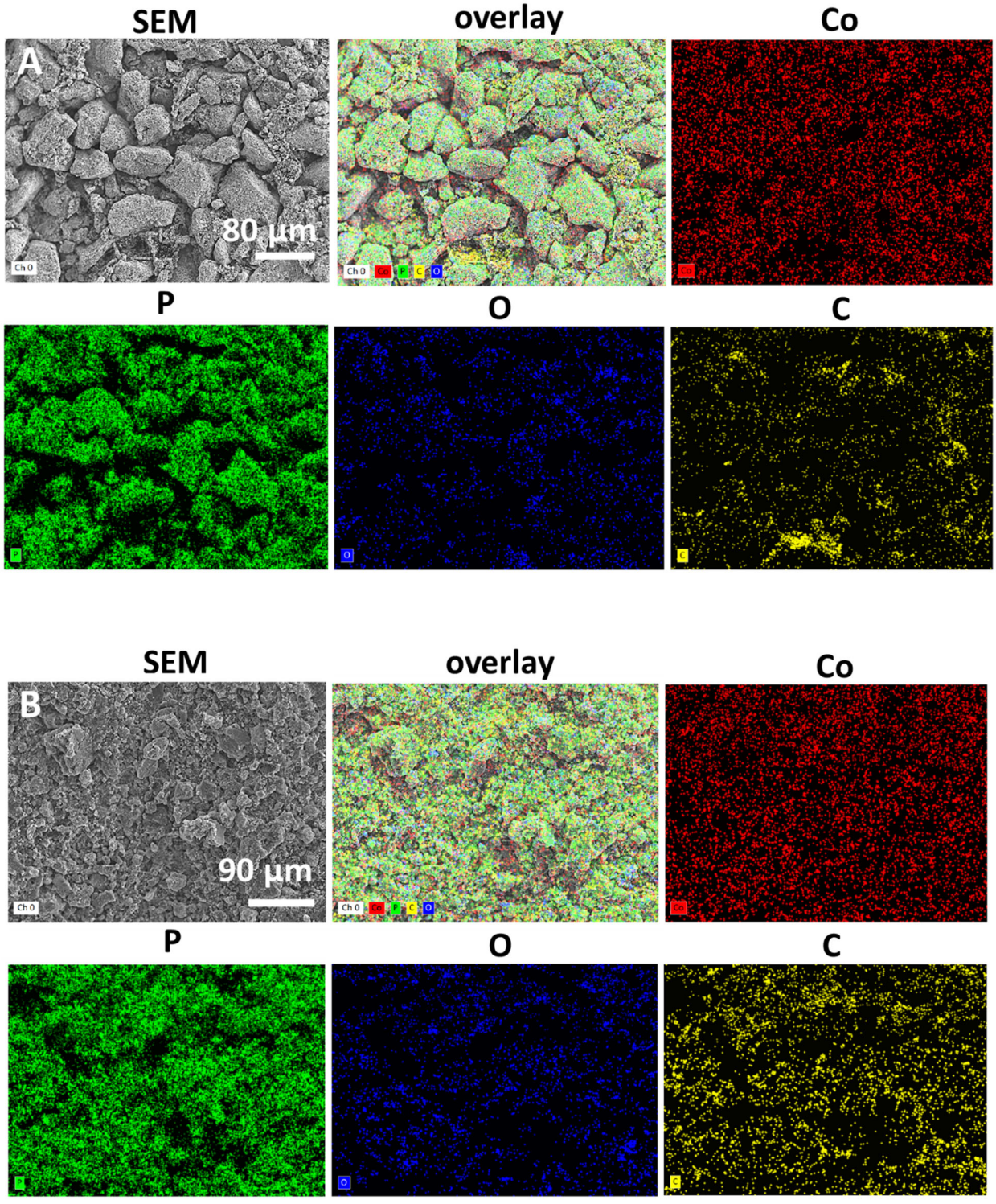


Figure S23. EDS maps of (A) CoP_3 and (B) 25-CoP_3/C embedded on C_{wax} electrode tips after 18-hour CA HER experiments.

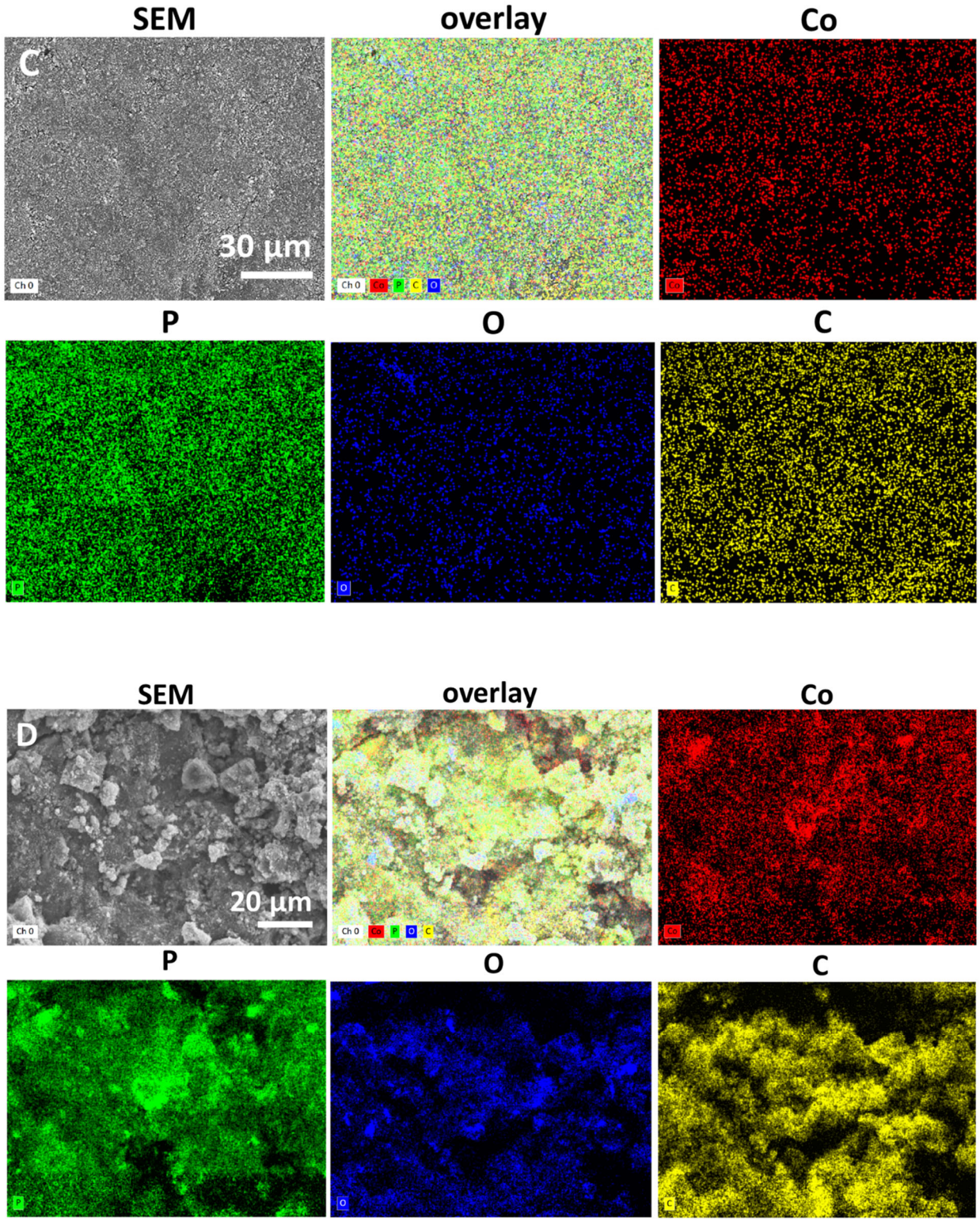


Figure S24. EDS maps of (C) 10-CoP_3/C and (D) 5-CoP_3/C embedded on C_{wax} electrode tips after 18-hour CA HER experiments.

Table S1. EDS compositional analysis of CoP_3, and x-CoP_3/C materials embedded on C_{wax} tips after 18-hour constant potential chronoamperometry (CA) HER experiments.

Sample	Co (at%)	P (at%)	O (at%)	C (at%)
CoP_3	6.8	13.8	34.6	44.8
25-CoP_3/C	6.2	12.2	30.5	51.1
10-CoP_3/C	3.8	8.4	21.0	66.8
5-CoP_3/C	1.0	2.3	8.7	88.0

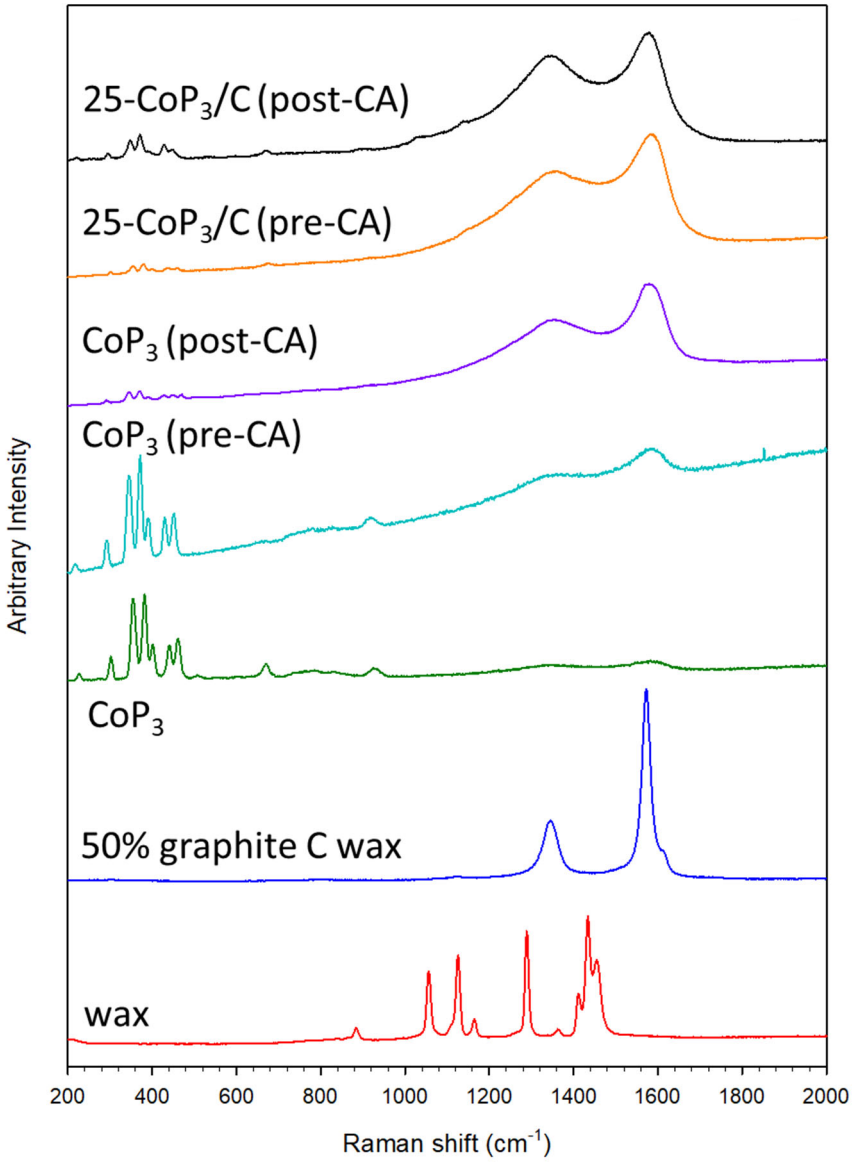


Figure S25. Raman spectra of CoP_3 and 25-CoP_3/C materials embedded on C_{wax} tips before 18-hour constant potential chronoamperometry (pre-CA) and after CA (post-CA) HER experiments in the region of 200-2000cm^{-1}.

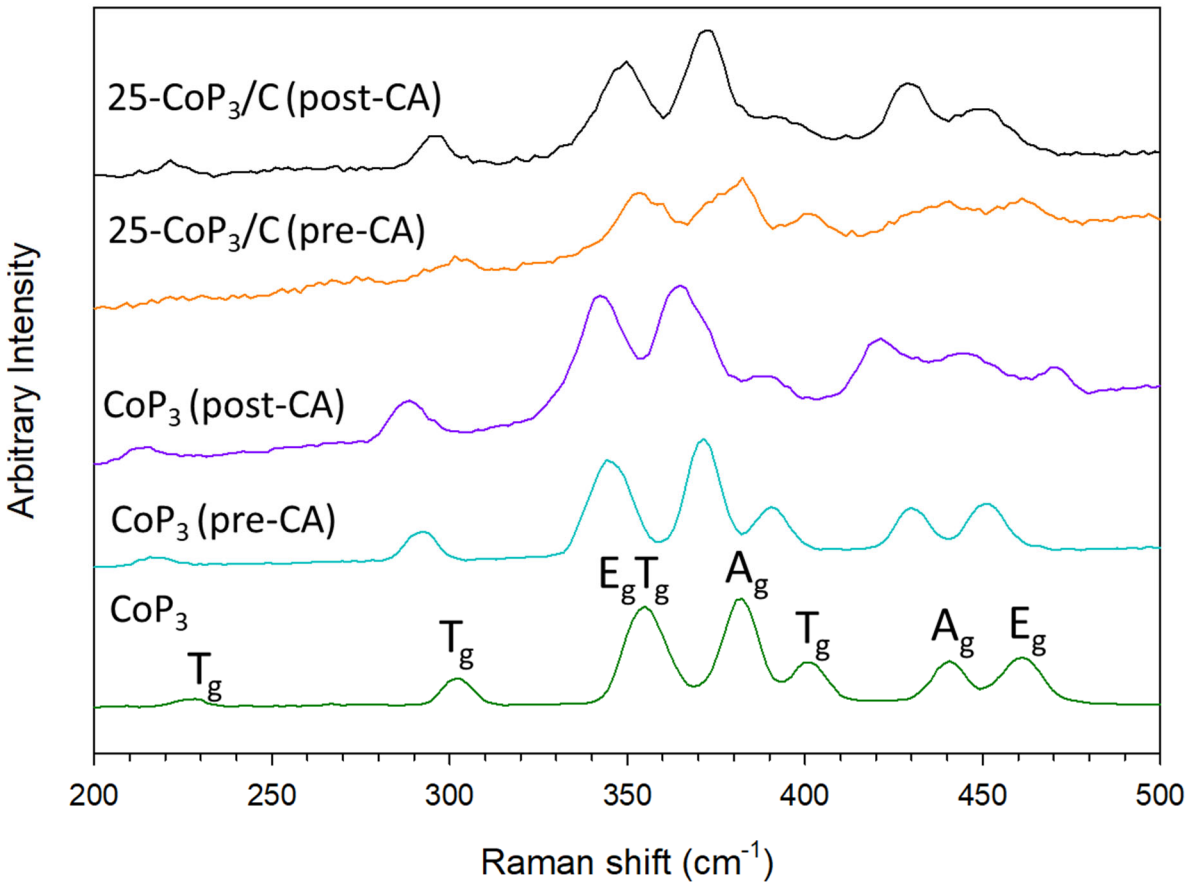


Figure S26. Raman spectra of CoP_3 and 25-CoP_3/C materials embedded C_{wax} tips before 18-hour constant potential chronoamperometry (pre-CA) and after CA (post-CA) HER experiments in a zoomed in region of 200-500 cm^{-1}.

Table S2. Literature comparison table for carbon-supported cobalt phosphides HER in 0.5 M H_2SO_4. All current densities are normalized for the geometrical surface area of the electrode. a) Values estimated from plots and graphical data in reference. GCE = Glassy carbon electrode, NRs = Nanorods, NPs = Nanoparticles, CNTs = Carbon nano tubes, NCNT = N-doped CNTs, NCNW = N-doped bundled carbon nanowires, PNC = P, N co-doped carbon, NWs = Nanowires, RGO = Reduced Graphene Oxide, NAs = nanoarrays, CP = Concave Polyhedrons, CFP = Carbon Fiber Paper.

Supported Cobalt phosphide	**Electrode, Geometric area (cm^2)**	**10 mA/cm^2 (mV)**	**20 mA/cm^2 (mV)**	**Tafel slope (mV/dec)**	**Ref.**
Co_2P NRs	Ti foil (0.5)	-134	-167	52	1
Co_2P NPs	Ti foil (0.2)	-95	-109	45	2
Co_2P/CNT	GCE (0.09)	-195	-219	74	3
Co_2P/NCNT	GCE (0.09)	-170[a]	-190[a]	62	3
CoP/NCNWs	GCE (0.09)	-95	-120[a]	50	4
CoP@PNC	GCE (0.09)	-84	-110[a]	57	4
CoP/CNT	GCE (0.09)	-122	-180[a]	54	3
CoP/CNT	GCE (0.09)	-165	-198	68	3
CoP/NCNT	GCE (0.09)	-79	-99	49	3
CoP NPs	Ti foil (0.2)	-75	-85	50	5
CoP NWs	GCE (0.09)	-110	-142	54	6
CoP	CC (6)	-67	-100	51	7
CoP/RGO	GCE (0.09)	-157	-190[a]	70	8
CoP_2	GCE (0.09)	-120	-150[a]	73	9
CoP_2/RGO	GCE (0.09)	-88	-106[a]	50	9
CoP_3 NAs	CFP (5.4)	-65	-100[a]	46	10
CoP_3 CPs	CFP (0.25)	-78	-110[a]	53	11

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