Electronic Supplementary Information (ESI)

Phosphorus vacancy-engineered Ce-doped CoP nanosheets for electrocatalytic oxidation of 5-hydroxymethylfurfural

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Experimental Section

Materials and chemicals

Choline chloride (ChCl), oxalic acid ($H_2C_2O_4$), potassium chloride (KCl) and sodium hypophosphite (NaH_2PO_2) were all obtained from Aladdin Chemistry Co., Ltd. P,otassium hydroxide (KOH) and Cobalt chloride hexahydrate ($CoCl_2 \cdot 6H_2O$) were purchased from Sinopharm Chemical Regent Co. Ltd. Cerium nitrate hexahydrate ($Ce(NO_3)_3$) was purchased from Tianjin Kermel Chemical Reagent Co., Ltd. 5-hydroxymethylfurfural (HMF), 2,5-furandicarboxylic acid (FDCA), 5-formyl furan-2-carboxylic acid (FFCA) and 5-hydroxymethyl-2-furan-carboxylic acid (HMFCA) were purchased from Alfa-Aesar. 2,5-diformyl furan (DFF) was purchased from Tokyo Chemical Industry Co., Ltd. 5 wt% nafion solution was purchased from the Sigma Co., Ltd. Carbon cloth was obtained from Changsha Lyrun Material Co., Ltd. Nafion 115 membrane was purchased from Wuhan GaossUnion technology Co., Ltd.

Synthesis of choline chloride/oxalic acid (ChCl/OA) DES

Equimolar oxalic acid reacted with choline chloride by magnetic stirring at 80 °C for 30 minutes, and ChCl/OA DES was then obtained.

Synthesis of Ce-doped CoP nanosheets

The CoP with different Ce doping amount was labelled as *x*Ce-CoP, where *x* represented the actual atomic ratio of Ce/(Co+Ce) in the obtained Ce-CoP. In a typical procedure, 6.09 mg $Ce(NO_3)_3$ and 30 mg $CoCl_2 \cdot 6H_2O$ were dissolved in 1 mL ChCl/OA DES with ultrasonic treatment at 40 °C. Subsequently, the obtained transparent blue liquid was transferred into microwave oven, which was microwave- heated at 100 W

for 15 s to obtain the Ce/Co-based precursor. Then, the precursor was recovered and rinsed with ethanol and desiccated at room temperature overnight in a vacuum.

After that, the NaH_2PO_2 and the dry precursor were placed upstream and downstream in a corundum tube of the tube furnace, respectively. Then, Ce-CoP was obtained by heat-treating the precursor at 350 °C for 2 h with 10 °C min^{-1} in N_2 flow. Finally, the obtained Ce-CoP nanosheets were washed with water and ethanol, then were dried in the vacuum oven. The obtained Ce-CoP was determined to be 5.2% Ce-CoP based on the nergy-dispersive X-ray (EDX) result.

For comparison, 3% Ce-CoP and 10% Ce-CoP were prepared by the same method except that the adding amount of $Ce(NO_3)_3$ were 1.6 mg and 9.65mg respectively. The undoped CoP was synthesized via the same process without addition of $Ce(NO_3)_3$.

Characterizations

Rigaku SmartLab 9KW X-ray diffractometer was used to obtain the X-ray diffraction (XRD) patterns. Transmission electron microscopy (TEM) was performed on a JEM-1400 microscope. Characterization of scanning electron microscopy (SEM) and energy-dispersive X-ray (EDX) were done by Zeiss Sigma 300. High-resolution transmission electron microscopy (HRTEM) images were obtained from JEM-2100 microscope. X-ray photoelectron spectroscopy (XPS) measurements were performed by a Thermo Fisher ESCALAB XI. Nitrogen adsorption-desorption tests were conducted on the micromeritics ASAP 2460. Electron paramagnetic resonance (EPR) measurements were tested on the Bruker A300. High performance liquid chromatography (HPLC) analysis was performed using an Agilent G7114A system.

Electrochemical Measurements

Electrochemical characterizations were tested on a CHI760E workstation. Here, carbon paper-loaded catalysts (working electrode), Ag/AgCl (reference electrode, in saturated KCl solution), and platinum foil (counter electrode) were utilized. 1 M KOH (10 mL) solution with or without 10 mM HMF was used as electrolytes.

For the working electrode fabrication, catalysts (4 mg) were put into the mixture of nafion solution (20 μL, 5 wt%) and ethanol (180 μL). The mixture was then sonicated (30 min) to achieve a catalyst ink. Next, 200 μL of the resulting ink was drop-coated on the carbon paper (1 × 1 cm^2) using a spray gun and dried. All of the potentials were referenced against the reversible hydrogen electrode (RHE) by the formula:

$$E\ (RHE) = E\ (Ag/AgCl) + 0.197 + 0.059 \times pH$$

Products analysis

The concentrations of the components in the electrolyte were determined by high-performance liquid chromatography (HPLC) using a 4.6 mm × 250 mm Zorbax SB-C18 5 μm column and an ultraviolet-visible detector. Specifically, 10 μL electrolyte was taken out and diluted to 0.5 mL with ultrapure water and analyzed by HPLC. The wavelength of UV-Vis detector was 265 nm. HPLC eluents were mixtures of 5 mM aqueous ammonium formate and methanol. The separation and quantification were performed using an isocratic elution with 5 mM aqueous ammonium formate solution (volume: 70%) and methanol (volume: 30%) at a flow rate of 1 mL min^{-1}.

The HMF conversion, selectivity and faradaic efficiency (FE) were achieved according to following equations:

$$\text{HMF conversion}\ (\%) = \frac{n_{\text{HMF consumption}}}{n_{\text{HMF initial value}}} \times 100\%$$

$$\text{Selectivity}\ (\%) = \frac{n_{\text{Product formation}}}{n_{\text{HMF initial value}}} \times 100\%$$

$$\text{Faraday efficiency}\ (\%) = \frac{n_{\text{FDCA formation}} \times 6F}{Q}$$

Where, Q is the total transferred charge and F is 96485 C mol^{-1} (Faraday constant). The quantity of product is determined by HPLC analysis.

Density functional theory (DFT) Calculation

The present first principle DFT calculations were accomplished by Vienna Ab initio Simulation Package(VASP)[1] with the projector augmented wave (PAW) method.[2] The exchange-functional was handled using the generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof (PBE)[3] functional. The energy cutoff for the plane wave basis expansion was set to 450 eV and the force on each atom less than 0.02 eV/Å was set for convergence criterion of geometry relaxation. A 15 Å vacuum was added along the z direction in order to avoid the interaction between periodic structures. The Brillouin zone integration was performed using 2×2×1 k-point sampling. The self-consistent calculations applied a convergence energy threshold of 10^{-5} eV.

The adsorption energy of HMF was calculated according to the following equation:

$$E_{ads} = E_{total} - E_{mol} - E_{sub}$$

where the E_{total} is the total energy of the HMF adsorbed on the CoP or Ce-CoP substrate, E_{mol} and E_{sub} were the energies of the isolated HMF molecule and the substrate, respectively.

The charge density differences were defined as $\Delta\rho=\rho(\text{Ce-CoP})-\rho(\text{CoP})-\rho(\text{Ce})$,

where ρ(Ce-CoP), ρ(CoP)and ρ(Ce) were the unperturbed electron densities of the Ce doped CoP with P vacancy, pure CoP with P vacancy and Ce atom, respectively

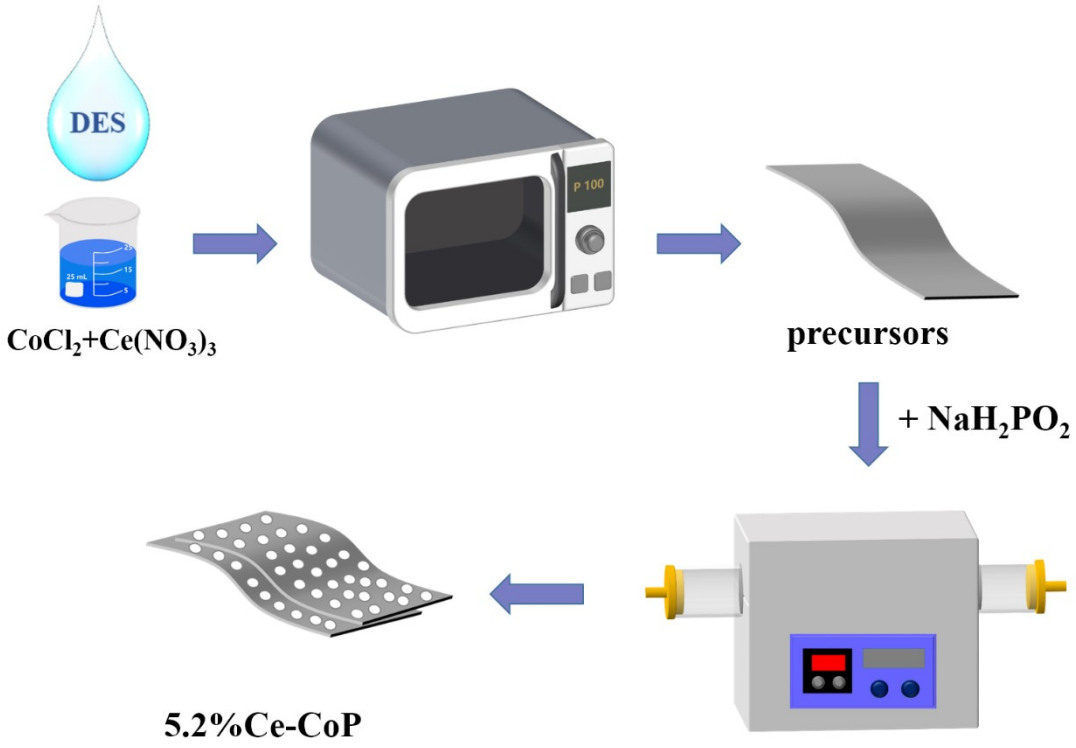

Fig. S1 Schematic diagram of Ce-doped CoP nanosheet synthesis.

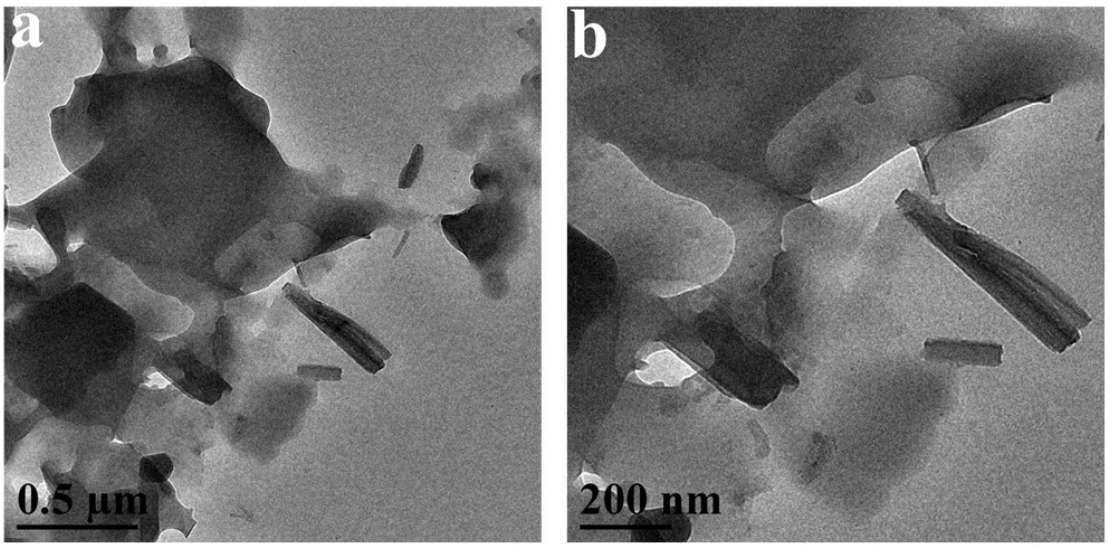

Fig. S2 Low- and high- magnification TEM images of the precursors obtained after microwave heating 1 mL ChCl/OA DES with 6.09 mg $Ce(NO_3)_3$ and 30 mg $CoCl_2$. This obtained precursor will be used for synthesizing 5.2%Ce-CoP nanosheets.

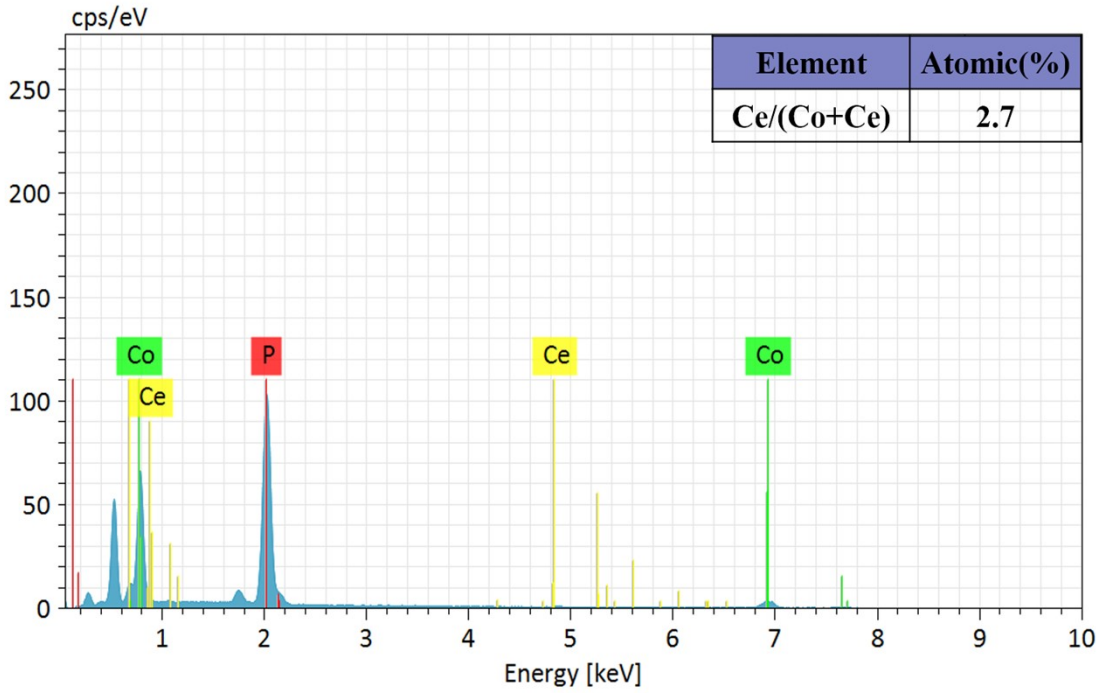

Fig. S3 EDX spectrum of Ce-CoP nanosheets which were synthesized from the precursor obtained after microwave heating 1 mL ChCl/OA DES with 1.6 mg $Ce(NO_3)_3$ and 30 mg $CoCl_2$.

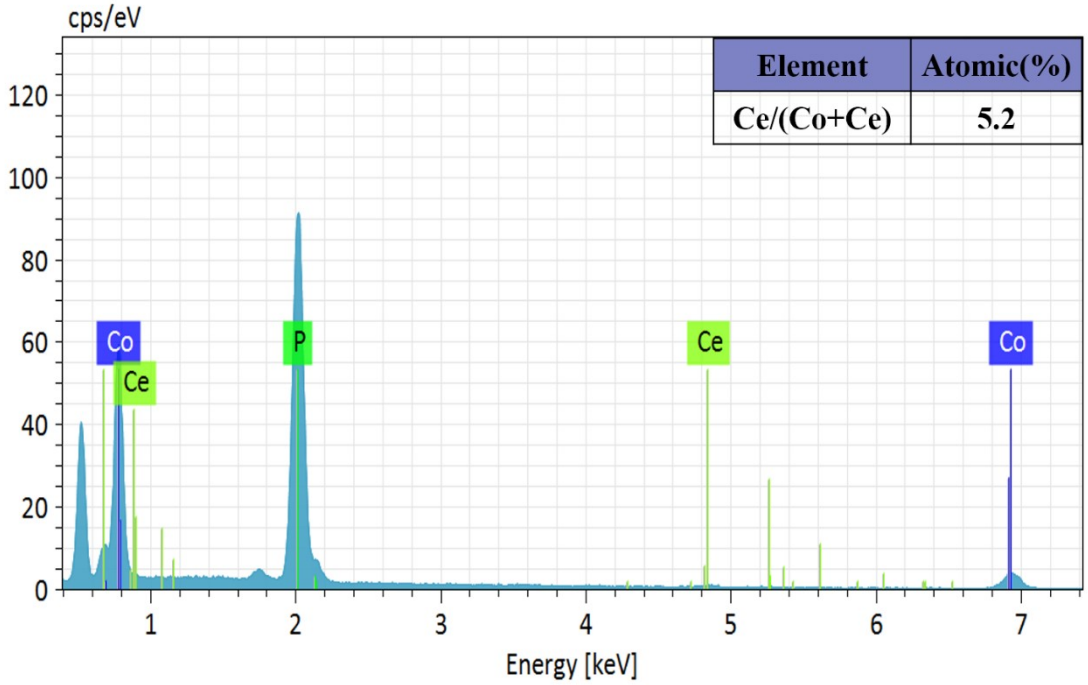

Fig. S4 EDX spectrum of Ce-CoP nanosheets which were synthesized from the precursor obtained after microwave heating 1 mL ChCl/OA DES with 6.09 mg $Ce(NO_3)_3$ and 30 mg $CoCl_2$.

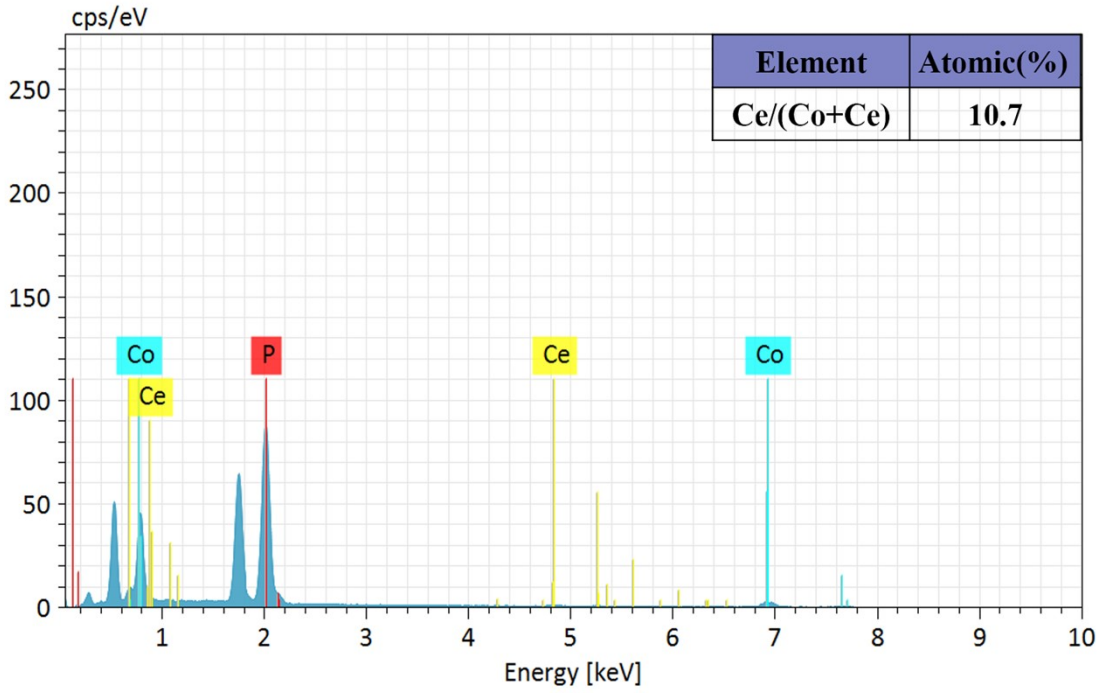

Fig. S5 EDX spectrum of Ce-CoP nanosheets which were synthesized from the precursor obtained after microwave heating 1 mL ChCl/OA DES with 9.65 mg $Ce(NO_3)_3$ and 30 mg $CoCl_2$.

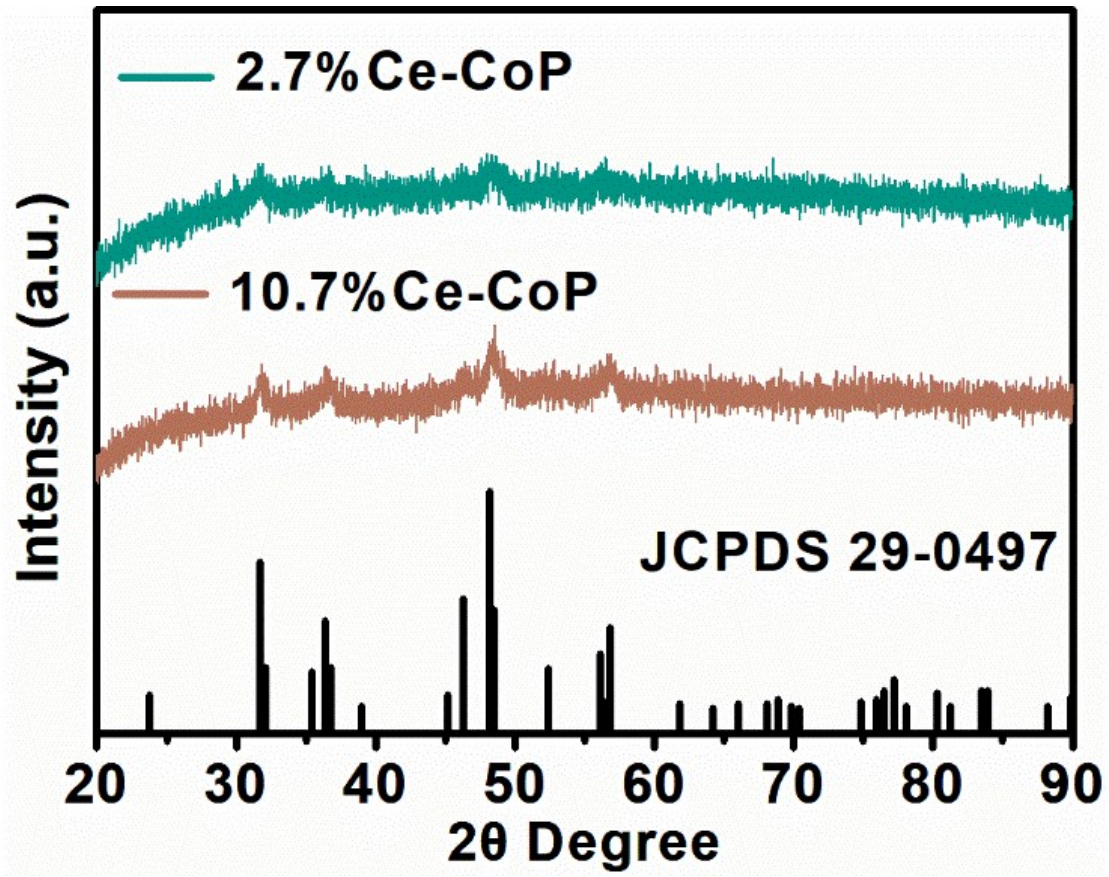

Fig. S6 XRD patterns of 2.7%Ce-CoP nanosheets and 10.7%Ce-CoP nanosheets.

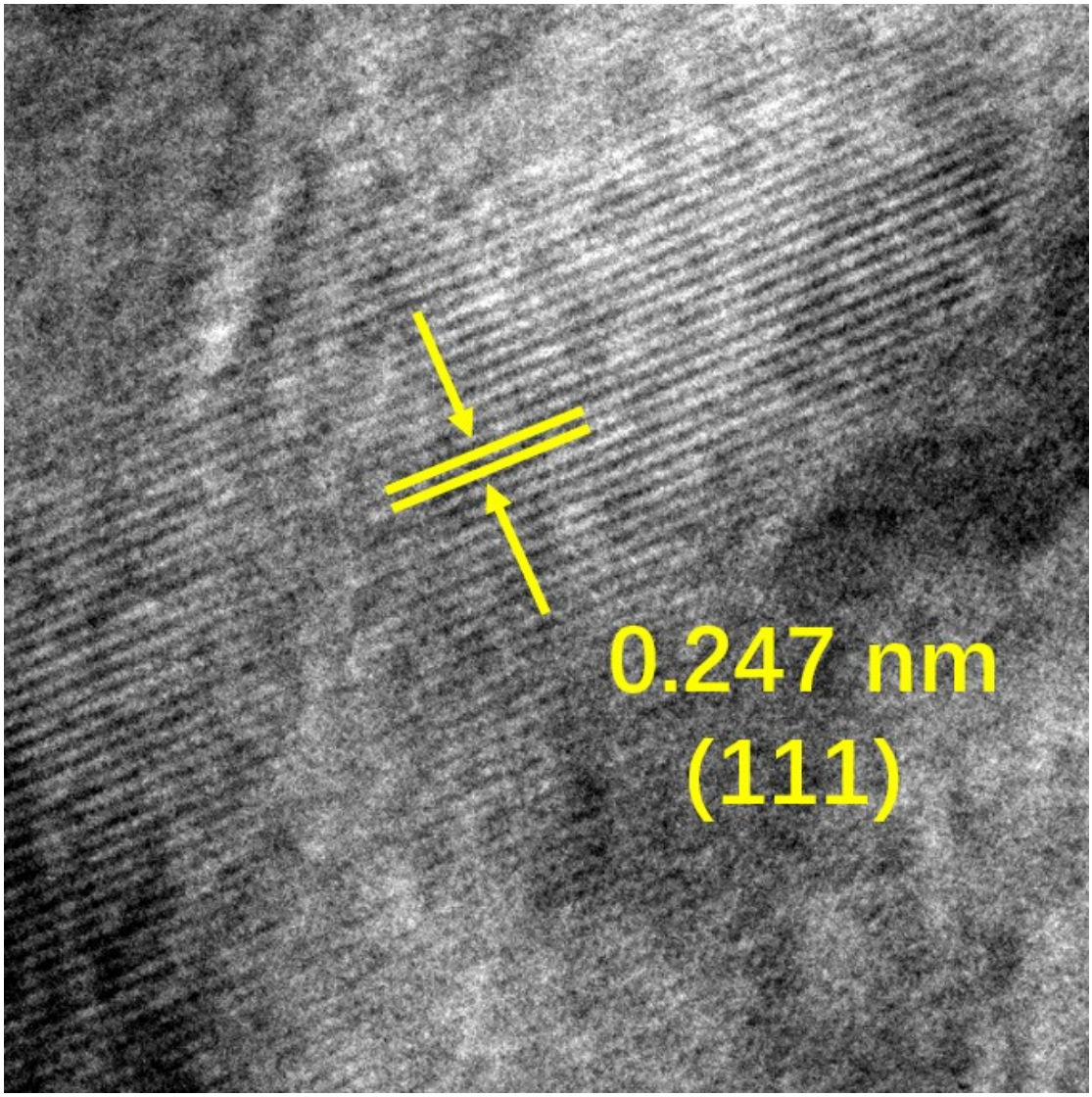

Fig. S7 HRTEM images of CoP nanosheets.

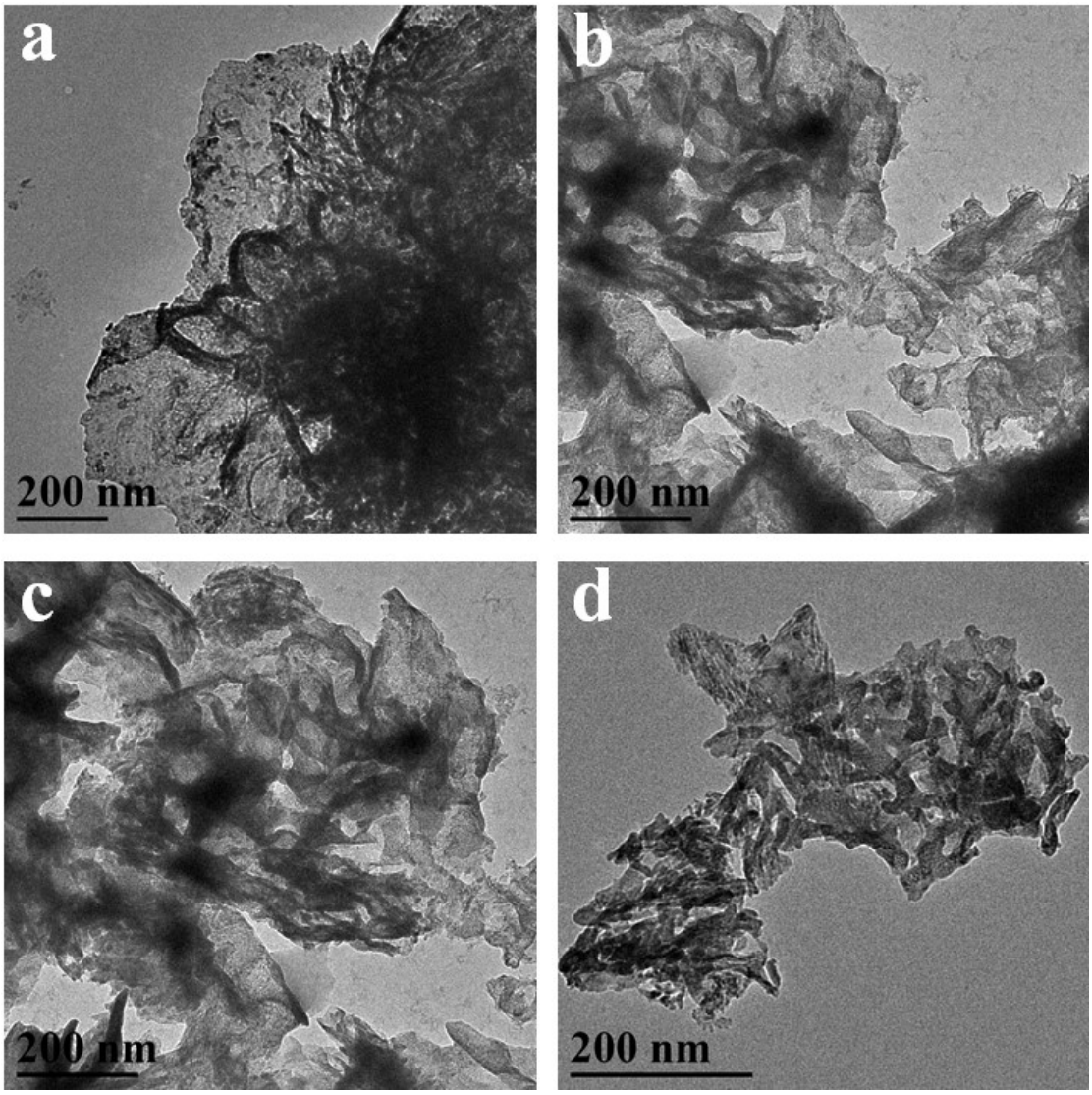

Fig. S8 TEM images of (a) CoP nanosheets, (b, c) 2.7%Ce-CoP nanosheets, (d) 10.7%Ce-CoP nanosheets.

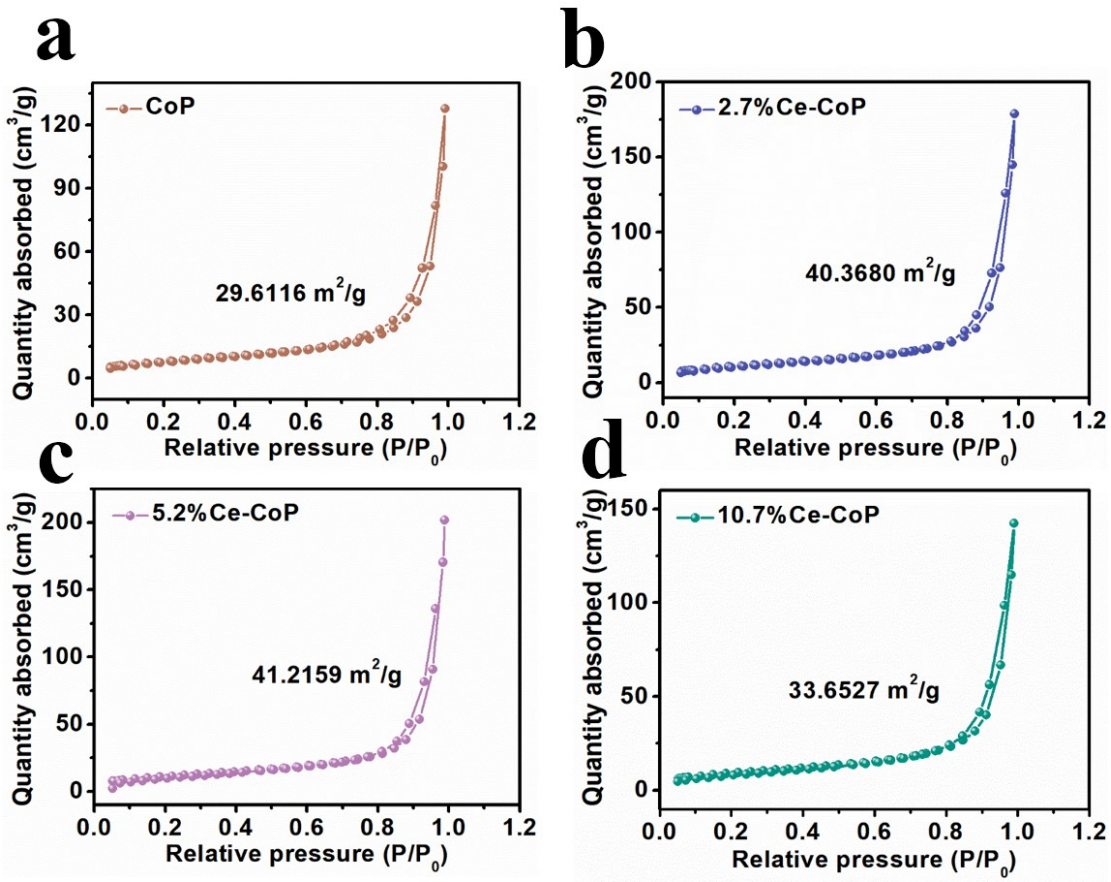

Fig. S9 N_2 adsorption-desorption isotherms of (a) CoP nanosheets, (b) 2.7%Ce-CoP nanosheets, (c) 5.2%Ce-CoP nanosheets and (d) 10.7%Ce-CoP nanohseets.

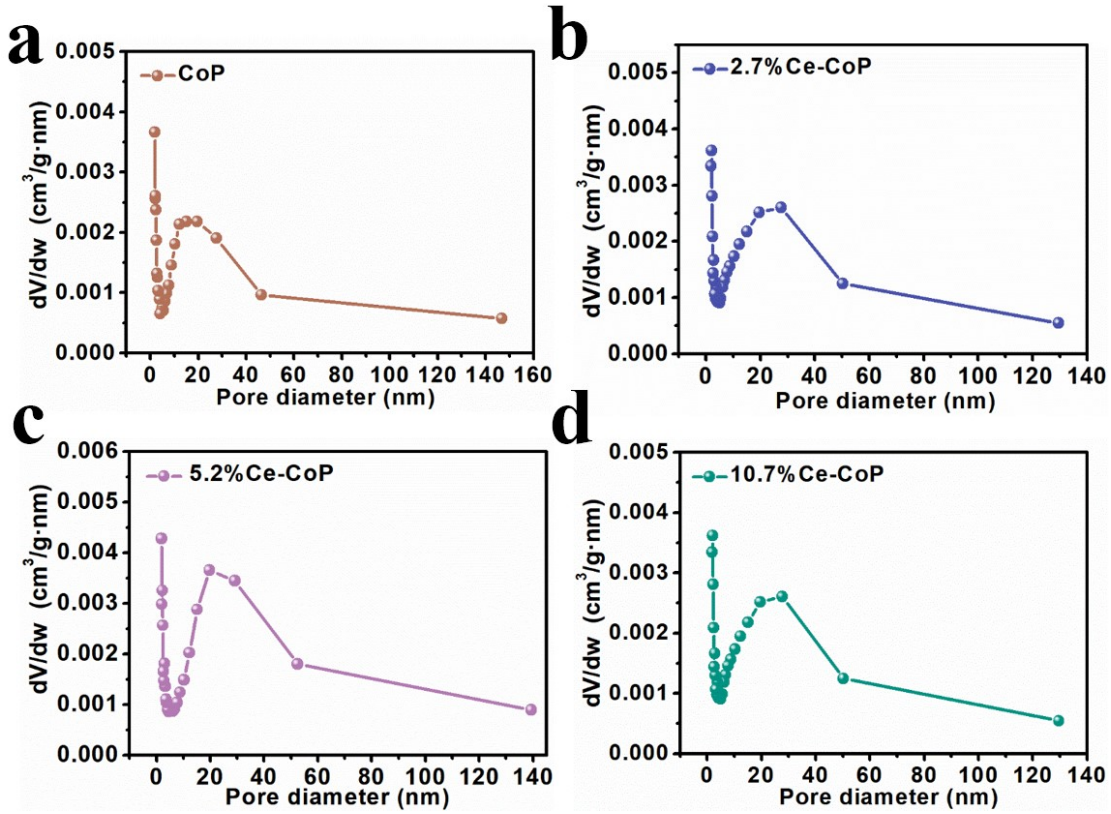

Fig. S10 Pore size distributions of (a) CoP nanosheets, (b) 2.7%Ce-CoP nanosheets, (c) 5.2%Ce-CoP nanosheets and (d) 10.7%Ce-CoP nanosheets.

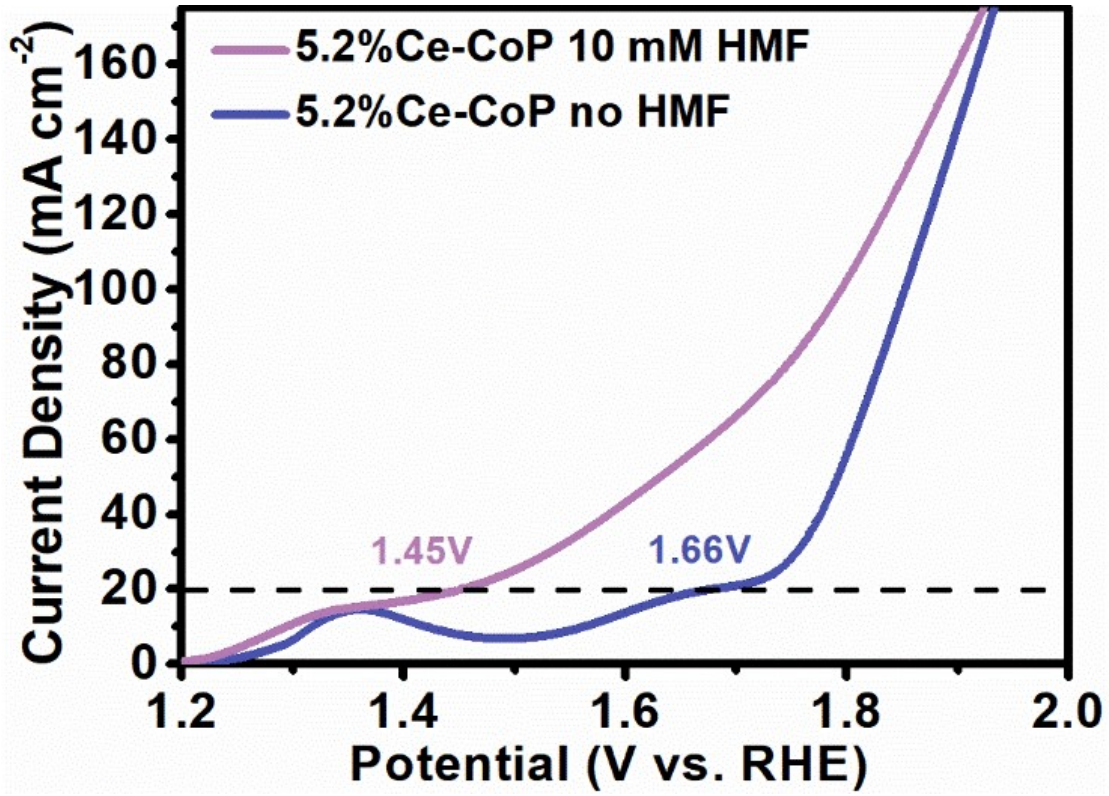

Fig. S11 LSV curves of 5.2%Ce-CoP nanosheets in 1 M KOH with/without HMF.

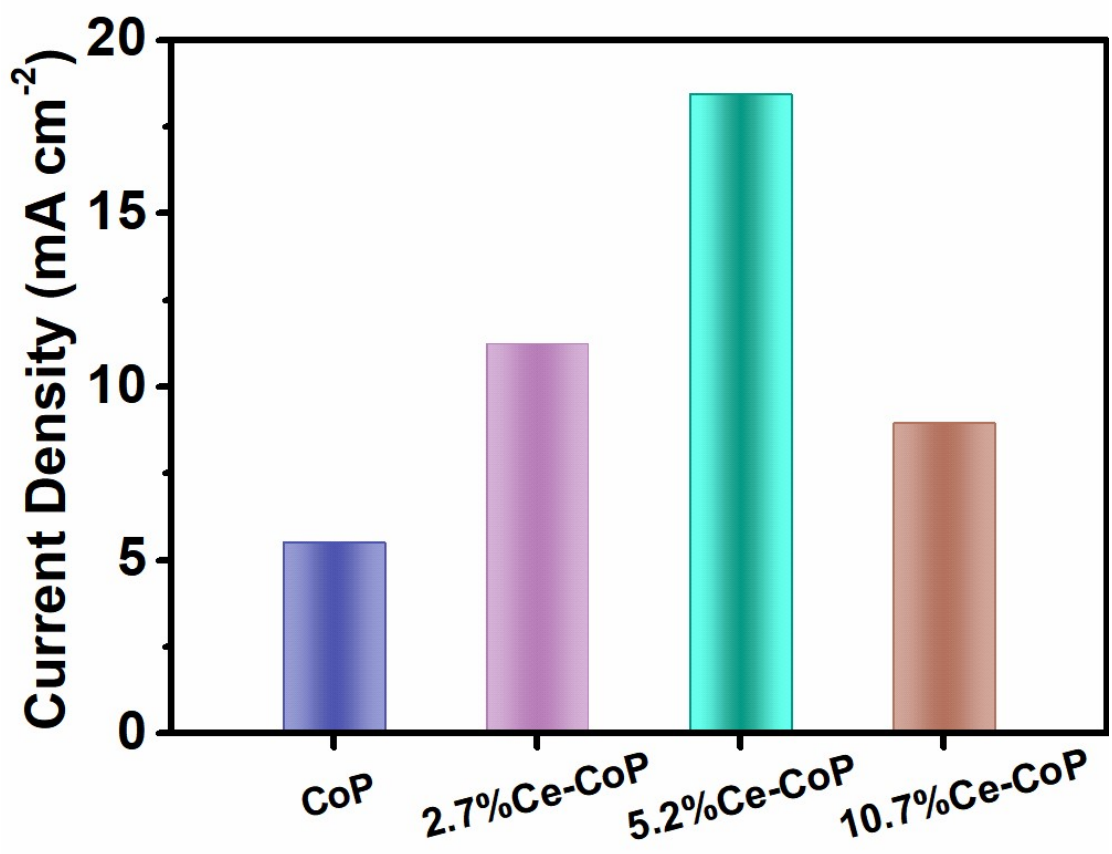

Fig. S12 Corresponding current densities at 1.44 V in 1 M KOH with 10 mM HMF.

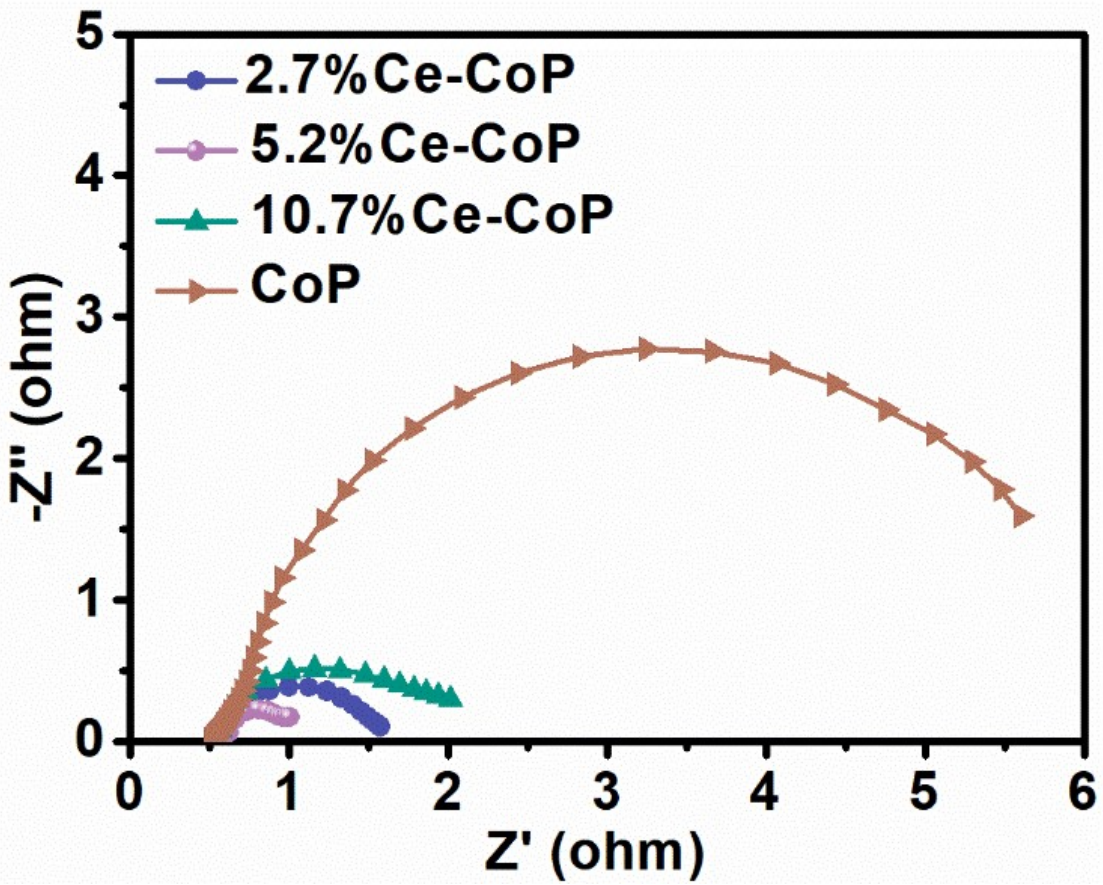

Fig. S13 Nyquist plots of different samples at 1.44 V.

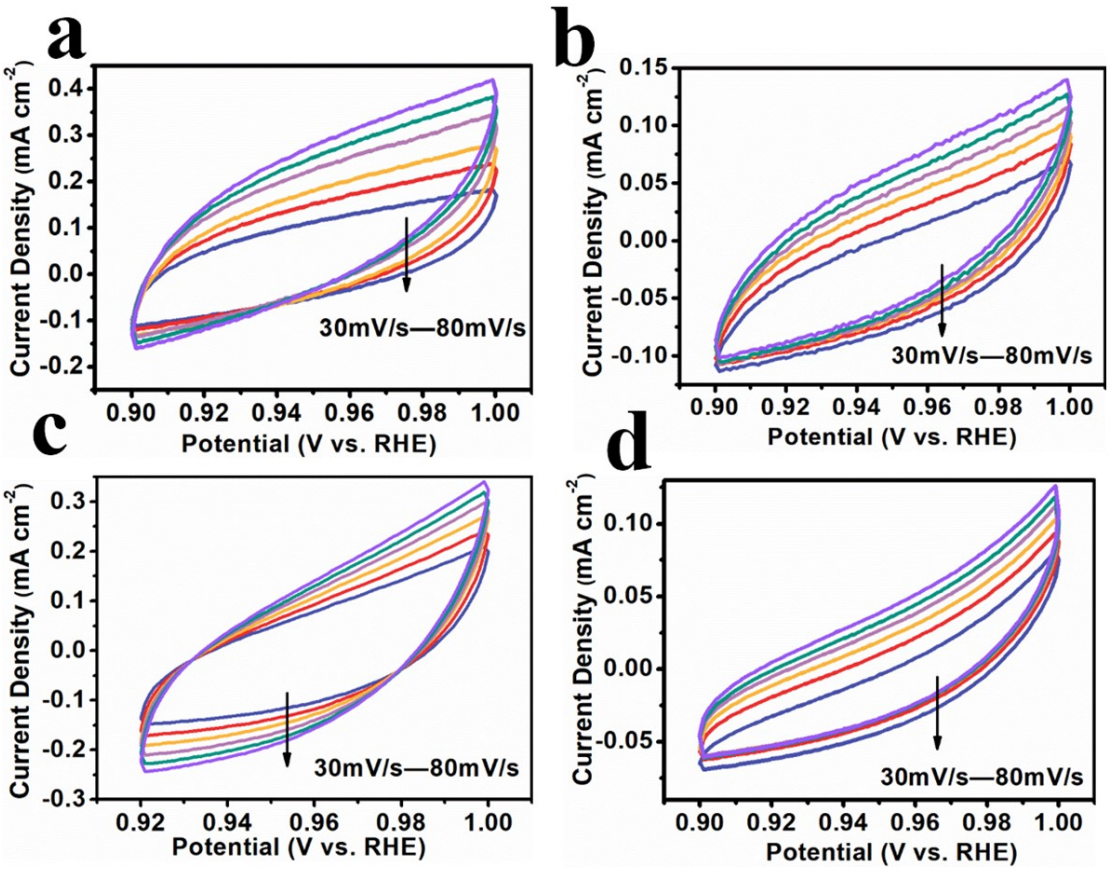

Fig. S14 CV curves of (a) CoP nanosheets, (b)2.7%Ce-CoP nanosheets, (c) 5.2%Ce-CoP nanosheets and (d) 10.7%Ce-CoP nanosheets at different scan rates.

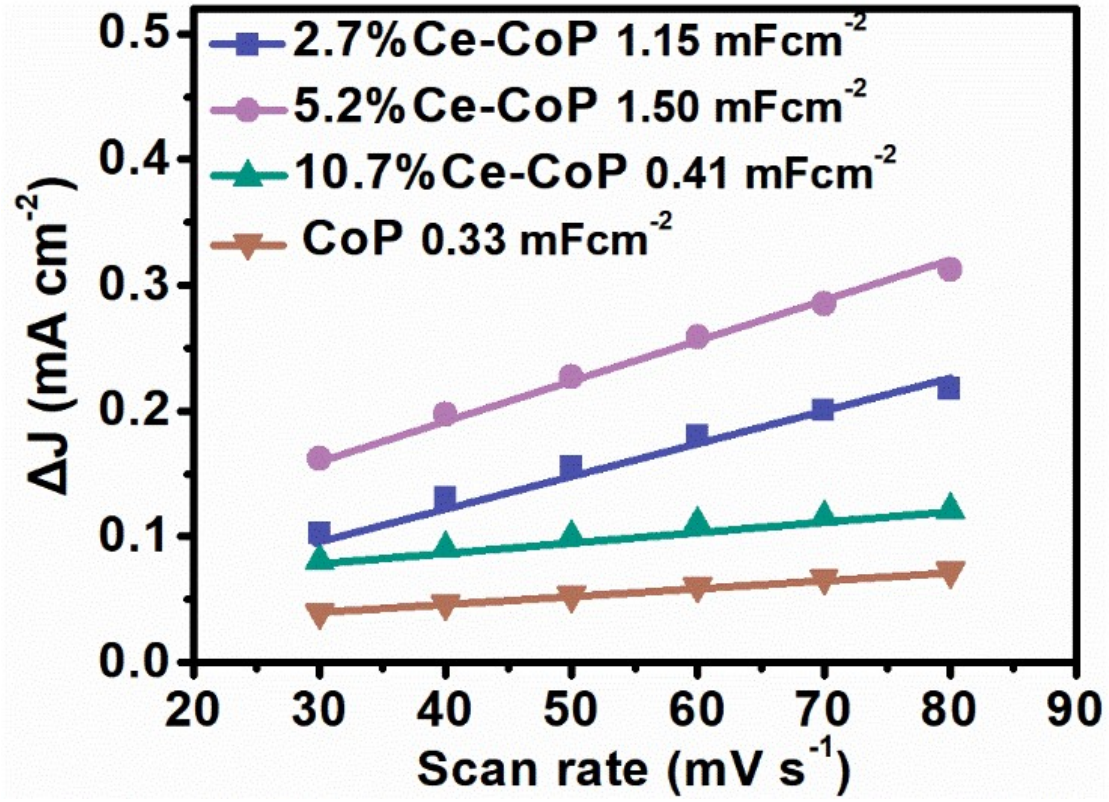

Fig. S15 The corresponding C_{dl} of CoP nanosheets, 2.7%Ce-CoP nanosheets, 5.2%Ce-CoP nanosheets and 10.7%Ce-CoP nanosheets in 1.0 M KOH with 10 mM HMF.

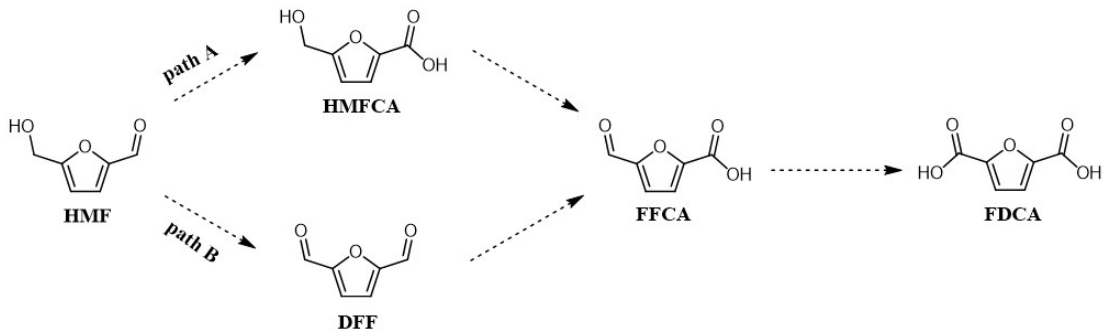

Fig. S16 Two possible pathways of HMF oxidation to FDCA.

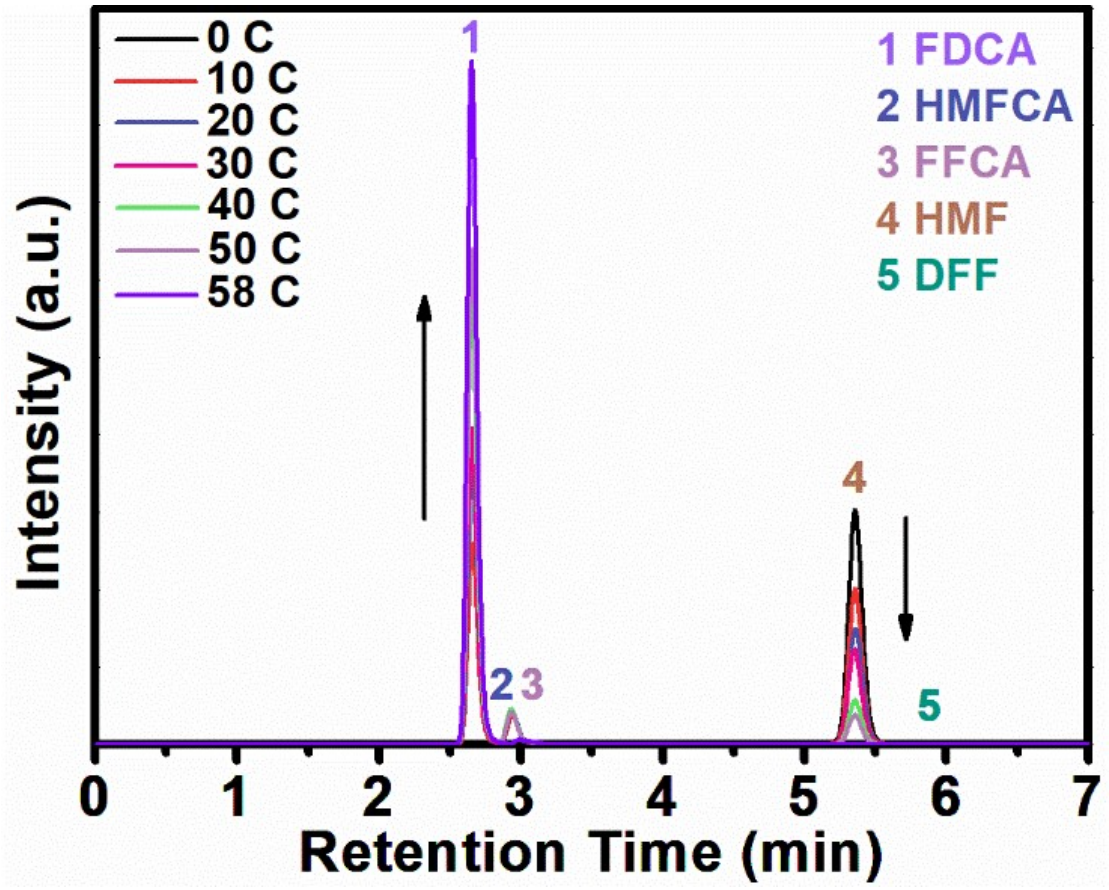

Fig. S17 HPLC traces of electrocatalytic oxidation of HMF by 5.2%Ce-CoP nanosheets at 1.44 V in 10 mL of 1 M KOH with 10 mM HMF.

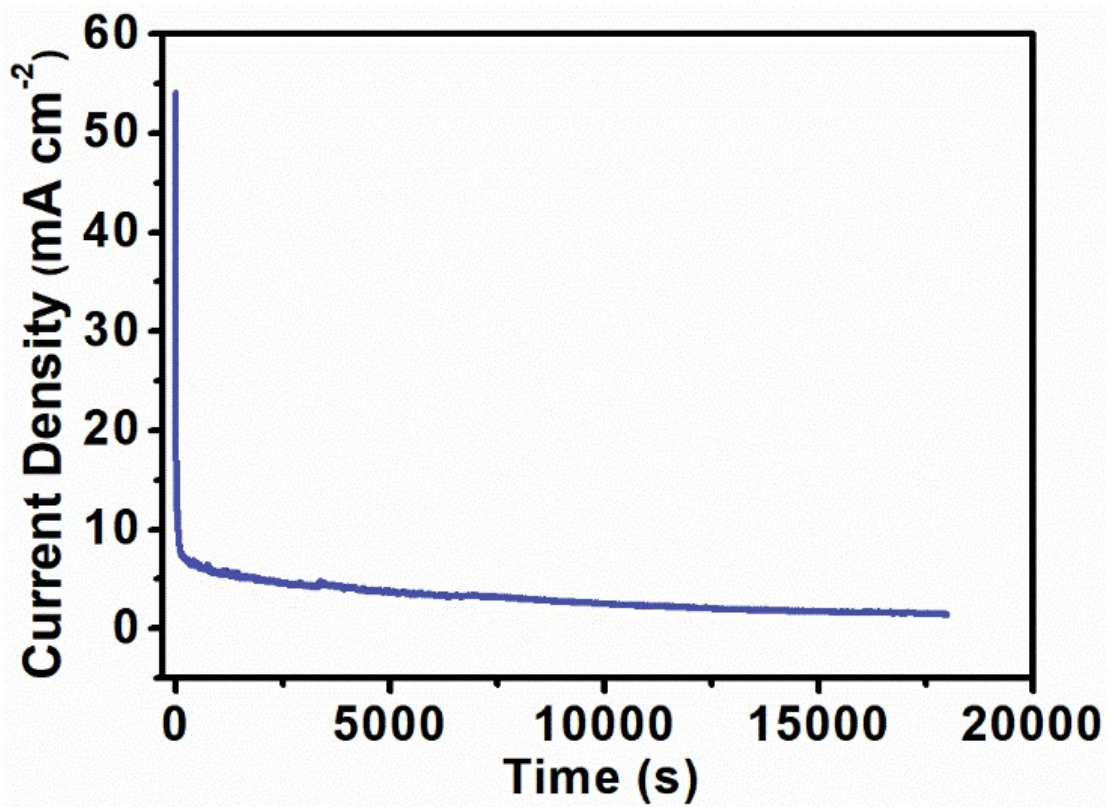

Fig. S18 I-t curve of 5.2%Ce-CoP nanosheets at a constant potential of 1.44 V in 1.0 M KOH with 10 mM HMF.

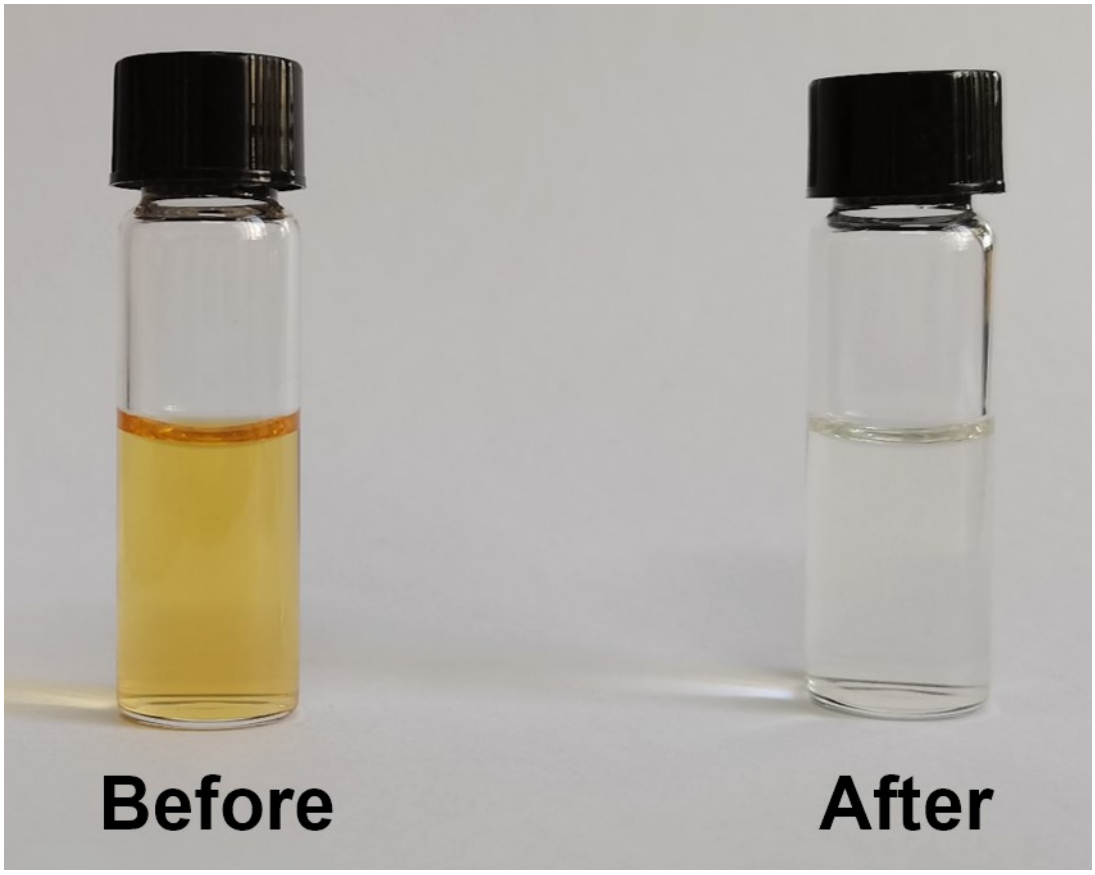

Fig. S19 Color change of the recovered electrolyte before and after reaction.

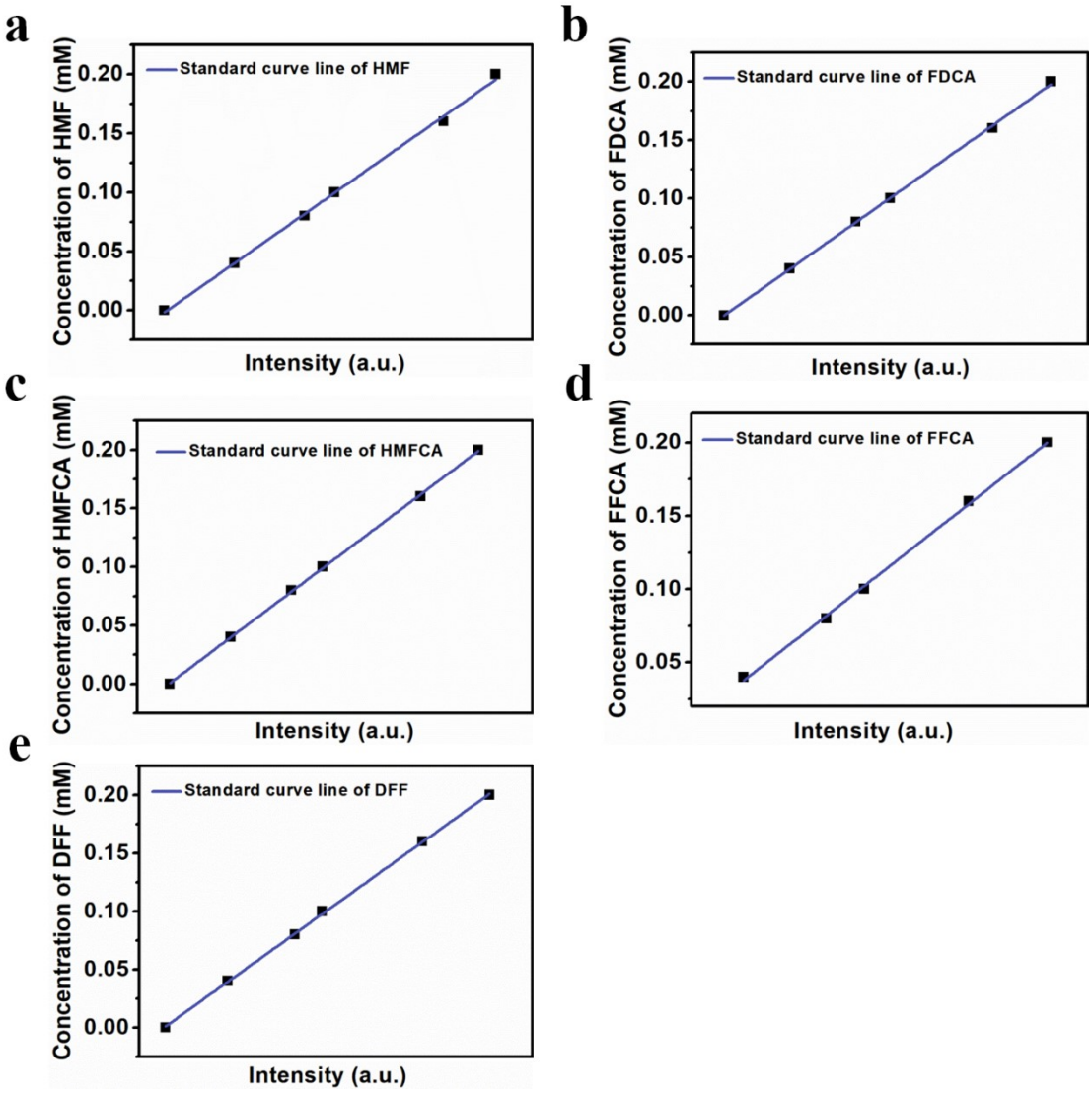

Fig. S20 Calibration curves of the HPLC for (a) HMF, (b) FDCA, (c) HMFCA, (d) FFCA and (e) DFF.

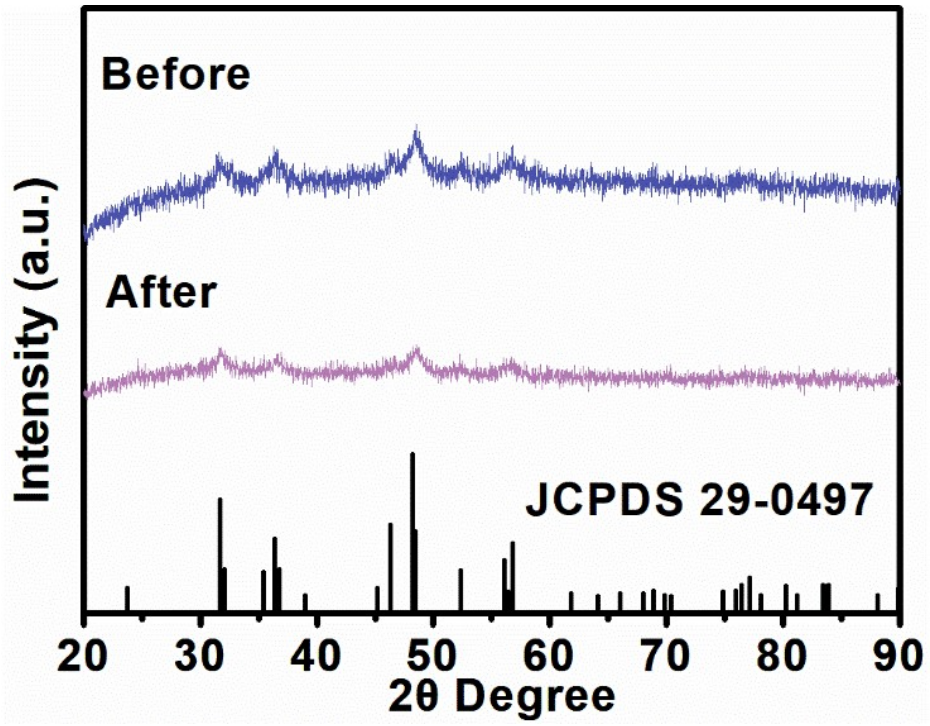

Fig. S21 XRD patterns of 5.2%Ce-CoP nanosheets before and after four electrolysis cycles.

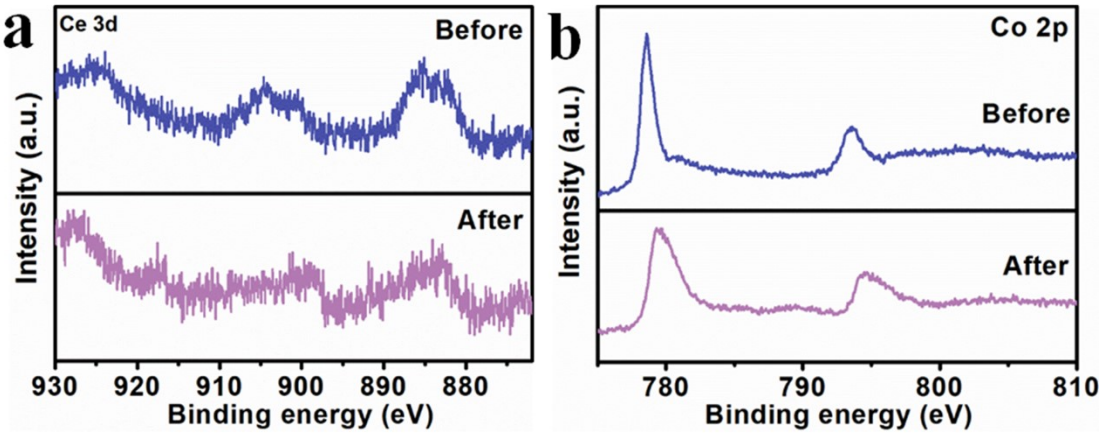

Fig. S22 XPS spectra of 5.2%Ce-CoP nanosheets before and after four electrolysis cycles. (a) Ce 3d, (b) Co 2p.

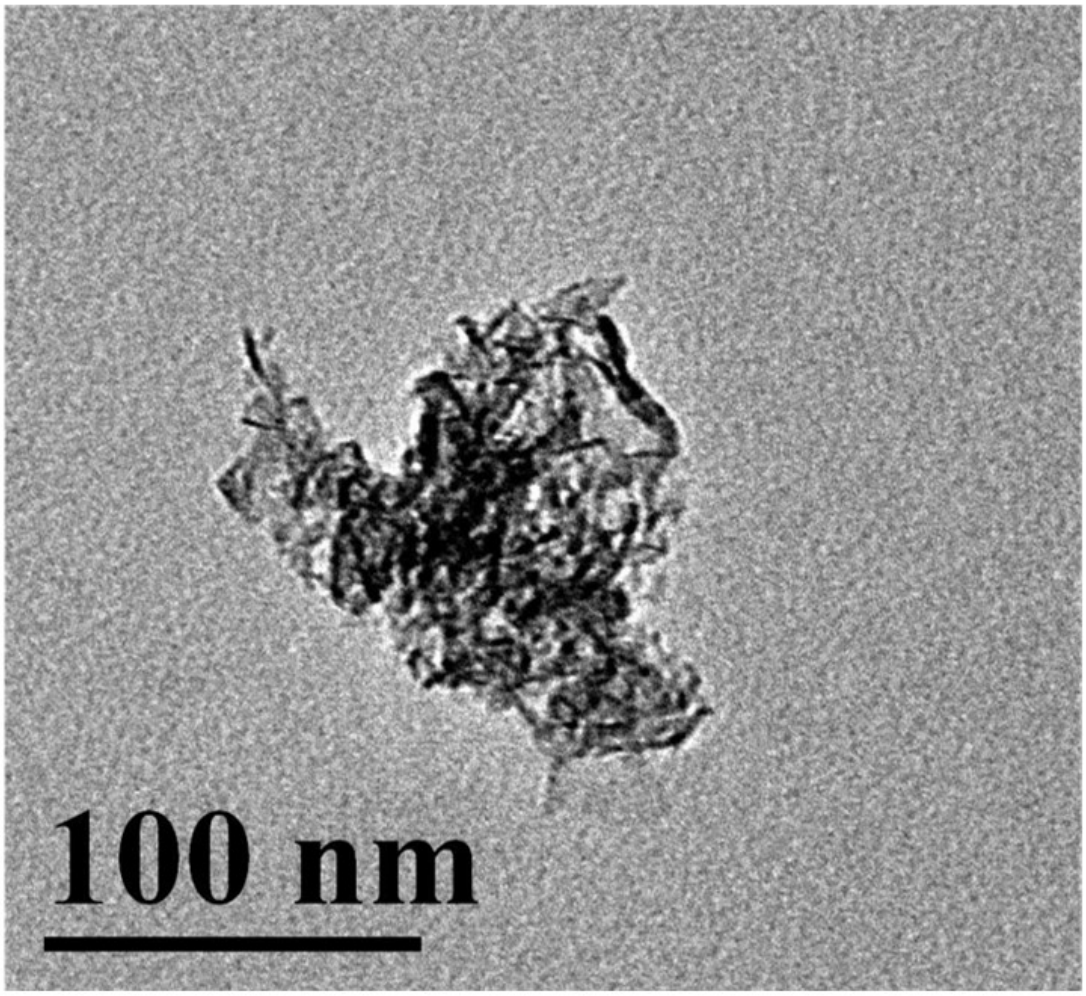

Fig. S23 TEM images of 5.2%Ce-CoP nanosheets after four electrolysis cycles.

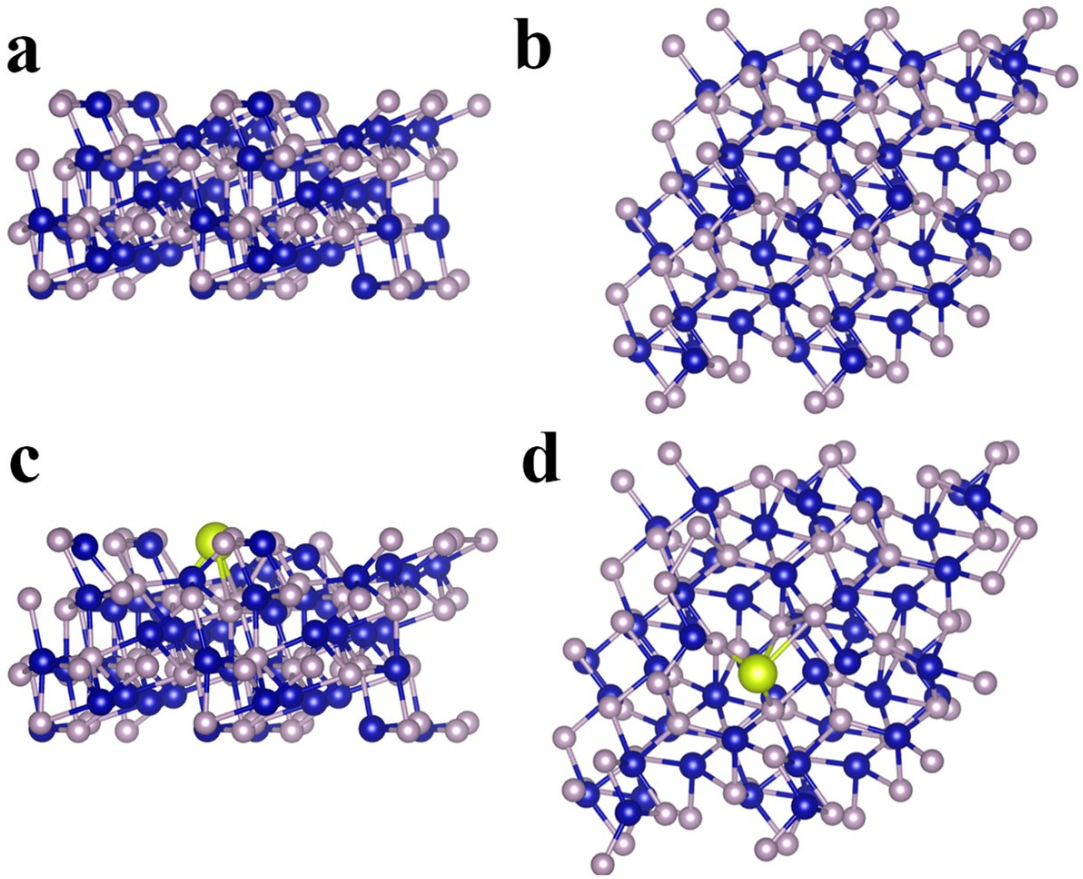

Fig. S24 Optimized structure of (a, b) CoP and (c, d) 5.2%Ce-CoP.

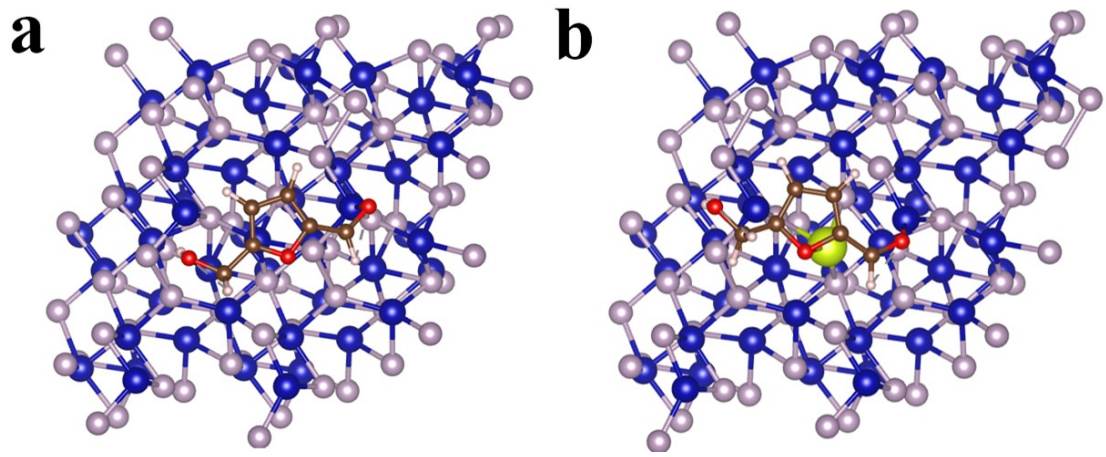

Fig. S25 Optimized structure of HMF on (a) CoP and (b) 5.2%Ce-CoP.

Table S1 Recently reported high performance electrocatalytic HMF-EOR catalysts.

Catalysts	**C_{HMF} (mM)**	**Potential (V *vs.* RHE)**	**Conv. (%)**	**FDCA Yield (%)**	**FE. (%)**
Co-P/CF[4]	50	1.423	100	90	~
Co-P_DES[5]	5	1.45	99	85.3	77.3
NiCoFe-LDH[6]	10	1.55	95.5	84.9	~
$NiCo_2O_4$[7]	5	1.5	99.6	90.8	87.5
NiCoP[8]	300	1.464	99.8	99.6	96.1
$CuCo_2O_4$[9]	~	1.45	~	93.7	94
nanocrystalline Cu[10]	5	1.62	99.9	96.4	95.3
$CuNi(OH)_2$[11]	5	1.45	100	93.3	94.4
NiCoFe-LDHs[12]	10	1.54	95.5	84.9	~
$Ni_{0.9}Cu_{0.1}(OH)_2$[13]	5	1.45	~99	91.2	~
VN/NiF[14]	10	~	99	97	~
N-MoO_2/Ni_3S_2 NF[15]	10	1.623	96	90	~
5.2%Ce-CoP (This work)	**10**	**1.44**	**100**	**98**	**96.4**

Table S2 Adsorption energy of HMF on different surfaces

Adsorbed sites	$\mathbf{E_{total}}$	$\mathbf{E_{sub}}$	$\mathbf{E_{mol}}$	$\mathbf{E_{ads}}$
CoP	-742.055	-645.359	-95.2825	-1.41298
Ce-CoP	-737.895	-640.408	-95.2825	-2.20414

* Where the E_{total} is the total energy of the HMF adsorbed on the CoP or Ce-CoP substrate, E_{mol} and E_{sub} are the energies of the isolated HMF molecule and the substrate, respectively.

Table S3 Unit-cell and position parameters of CoP optimization model

		CoP	
a (Å)		12.06880	
b (Å)		12.89130	
c (Å)		22.27670	
α (deg)		90.0	
β (deg)		90.0	
γ (deg)		74.0	
Atom Coordinates	***x***	***y***	***z***
Co1	0.02027	0.06166	0.45061
Co2	0.40216	0.46033	0.34022
Co3	0.13718	0.15573	0.55414
Co4	0.00837	0.3514	0.43866
Co5	0.12752	0.44011	0.53768
Co6	0.20593	0.02834	0.64384
Co7	0.19848	0.0525	0.38365
Co8	0.31931	0.14703	0.49419
Co9	0.42555	0.22926	0.58801
Co10	0.21205	0.25923	0.39522
Co11	0.32779	0.35775	0.50163
Co12	0.44996	0.44018	0.60447
Co13	0.52026	0.06167	0.45061
Co14	0.90216	0.46033	0.34022
Co15	0.63718	0.15572	0.55413
Co16	0.50837	0.3514	0.43866
Co17	0.62751	0.44012	0.53769
Co18	0.70595	0.02837	0.64386
Co19	0.69848	0.0525	0.38365
Co20	0.81931	0.14702	0.49419
Co21	0.92554	0.22925	0.588
Co22	0.71205	0.25923	0.39522
Co23	0.82778	0.35774	0.50162
Co24	0.94996	0.44019	0.60447

Co25	0.02027	0.56167	0.45061
Co26	0.40216	0.96033	0.34022
Co27	0.13718	0.65572	0.55413
Co28	0.00837	0.8514	0.43866
Co29	0.12752	0.94013	0.5377
Co30	0.20597	0.52835	0.64385
Co31	0.19848	0.5525	0.38365
Co32	0.31931	0.64702	0.49419
Co33	0.42555	0.72924	0.58801
Co34	0.21205	0.75923	0.39522
Co35	0.32778	0.85776	0.50163
Co36	0.44997	0.94018	0.60447
Co37	0.52027	0.56166	0.45061
Co38	0.90216	0.96033	0.34022
Co39	0.63718	0.65571	0.55413
Co40	0.50837	0.8514	0.43866
Co41	0.62751	0.9401	0.53769
Co42	0.70594	0.52836	0.64384
Co43	0.69848	0.5525	0.38365
Co44	0.81931	0.64703	0.49419
Co45	0.92555	0.72925	0.58801
Co46	0.71205	0.75923	0.39522
Co47	0.8278	0.85775	0.50163
Co48	0.94996	0.94019	0.60447
P1	0.40211	0.23206	0.42916
P2	0.01638	0.32106	0.53569
P3	0.12607	0.40019	0.64234
P4	0.00842	0.07968	0.34972
P5	0.1335	0.17404	0.45535
P6	0.23801	0.27684	0.57575
P7	0.05349	0.31808	0.33667
P8	0.17495	0.41676	0.43746
P9	0.28534	0.00919	0.55751
P10	0.35704	0.49365	0.4422
P11	0.47334	0.07397	0.5514

P12	0.06163	0.16481	0.64951
P13	0.90211	0.23206	0.42916
P14	0.51637	0.32105	0.53568
P15	0.62603	0.40019	0.64234
P16	0.50842	0.07968	0.34972
P17	0.6335	0.17404	0.45535
P18	0.73801	0.27683	0.57574
P19	0.55349	0.31808	0.33667
P20	0.67495	0.41676	0.43745
P21	0.78532	0.00915	0.55751
P22	0.85704	0.49365	0.4422
P23	0.97333	0.07397	0.5514
P24	0.56166	0.16485	0.64951
P25	0.40211	0.73206	0.42916
P26	0.01638	0.82106	0.53569
P27	0.12602	0.90016	0.64235
P28	0.00842	0.57968	0.34972
P29	0.1335	0.67404	0.45535
P30	0.23802	0.77683	0.57575
P31	0.05349	0.81808	0.33667
P32	0.17495	0.91676	0.43746
P33	0.28533	0.50916	0.5575
P34	0.35704	0.99365	0.4422
P35	0.47332	0.57399	0.55141
P36	0.06168	0.66483	0.64951
P37	0.90211	0.73206	0.42916
P38	0.51639	0.82104	0.53569
P39	0.62603	0.90019	0.64235
P40	0.50842	0.57968	0.34972
P41	0.63351	0.67403	0.45534
P42	0.73801	0.77683	0.57575
P43	0.55349	0.81808	0.33667
P44	0.67496	0.91675	0.43745
P45	0.78535	0.50916	0.5575
P46	0.85704	0.99365	0.4422

P47	0.97334	0.57397	0.55141
P48	0.56166	0.66482	0.6495

Table S4 Unit-cell and position parameters of 5.2%Ce-CoP optimization model

	5.2%Ce-CoP		
a (Å)	12.06880		
b (Å)	12.89130		
c (Å)	22.27670		
α (deg)	90.0		
β (deg)	90.0		
γ (deg)	74.0		
Atom Coordinates	***x***	***y***	***z***
Ce1	0.43781	0.42265	0.64631
Co1	0.01955	0.0634	0.45051
Co2	0.40216	0.46033	0.34022
Co3	0.13321	0.15394	0.55505
Co4	0.00837	0.3514	0.43866
Co5	0.12603	0.43801	0.53635
Co6	0.16315	0.00952	0.63838
Co7	0.19848	0.0525	0.38365
Co8	0.31909	0.14915	0.49585
Co9	0.42505	0.22769	0.58505
Co10	0.21205	0.25923	0.39522
Co11	0.32825	0.35801	0.50252
Co12	0.52057	0.06053	0.45178
Co13	0.90216	0.46033	0.34022
Co14	0.63839	0.15437	0.55518
Co15	0.50837	0.3514	0.43866
Co16	0.61287	0.42936	0.53112
Co17	0.69653	0.02894	0.64347
Co18	0.69848	0.0525	0.38365
Co19	0.82026	0.14906	0.49654
Co20	0.91888	0.23705	0.58741
Co21	0.71205	0.25923	0.39522
Co22	0.82363	0.36059	0.50085
Co23	0.95748	0.44228	0.60607
Co24	0.01962	0.56172	0.45085

Co25	0.40216	0.96033	0.34022
Co26	0.13605	0.65556	0.55185
Co27	0.00837	0.8514	0.43866
Co28	0.12746	0.93692	0.53381
Co29	0.20694	0.53092	0.64112
Co30	0.19848	0.5525	0.38365
Co31	0.31634	0.64854	0.49166
Co32	0.43168	0.71598	0.59101
Co33	0.21205	0.75923	0.39522
Co34	0.33209	0.85618	0.50353
Co35	0.44609	0.93038	0.60181
Co36	0.51923	0.563	0.44965
Co37	0.90216	0.96033	0.34022
Co38	0.6409	0.64598	0.55545
Co39	0.50837	0.8514	0.43866
Co40	0.62817	0.93701	0.54049
Co41	0.70248	0.45766	0.62171
Co42	0.69848	0.5525	0.38365
Co43	0.82046	0.6486	0.49654
Co44	0.92733	0.73162	0.58947
Co45	0.71205	0.75923	0.39522
Co46	0.826	0.85677	0.50129
Co47	0.95622	0.94456	0.60799
P1	0.40211	0.23206	0.42916
P2	0.015	0.32302	0.53591
P3	0.14138	0.39463	0.6426
P4	0.00842	0.07968	0.34972
P5	0.13486	0.17385	0.45587
P6	0.23864	0.2738	0.5749
P7	0.05349	0.31808	0.33667
P8	0.17495	0.41676	0.43746
P9	0.27759	0.00625	0.56255
P10	0.35704	0.49365	0.4422
P11	0.47155	0.06793	0.55395
P12	0.04667	0.16265	0.65058

P13	0.90211	0.23206	0.42916
P14	0.51554	0.3147	0.53347
P15	0.50842	0.07968	0.34972
P16	0.63559	0.17212	0.45605
P17	0.7316	0.28463	0.57657
P18	0.55349	0.31808	0.33667
P19	0.67496	0.41676	0.43745
P20	0.78806	0.00688	0.55941
P21	0.85704	0.49365	0.4422
P22	0.97649	0.07653	0.55272
P23	0.56047	0.17637	0.65122
P24	0.40211	0.73206	0.42916
P25	0.01335	0.8242	0.5362
P26	0.12998	0.85535	0.64938
P27	0.00842	0.57968	0.34972
P28	0.13073	0.67554	0.45408
P29	0.24434	0.77262	0.57131
P30	0.05349	0.81808	0.33667
P31	0.17495	0.91676	0.43746
P32	0.28324	0.51137	0.55397
P33	0.35704	0.99365	0.4422
P34	0.46753	0.56471	0.54888
P35	0.07753	0.69147	0.65028
P36	0.90211	0.73206	0.42916
P37	0.51973	0.81124	0.53671
P38	0.61697	0.90025	0.6438
P39	0.50842	0.57968	0.34972
P40	0.63561	0.6722	0.45624
P41	0.73811	0.77338	0.5785
P42	0.55349	0.81808	0.33667
P43	0.67496	0.91675	0.43746
P44	0.79932	0.50989	0.55567
P45	0.85704	0.99365	0.4422
P46	0.97897	0.5763	0.55249

P47	0.56216	0.59512	0.6437

Table S5 Unit-cell and position parameters of the optimized model for the adsorption of HMF on CoP

	CoP		
a (Å)	12.06880		
b (Å)	12.89130		
c (Å)	22.27670		
α (deg)	90.0		
β (deg)	90.0		
γ (deg)	74.0		
Atom Coordinates	***x***	***y***	***z***
P1	0.40211	0.23206	0.42916
P2	0.01676	0.32023	0.53554
P3	0.12581	0.39701	0.64341
P4	0.00842	0.07968	0.34972
P5	0.13414	0.17337	0.45555
P6	0.23616	0.27647	0.57536
P7	0.05349	0.31808	0.33667
P8	0.17495	0.41676	0.43746
P9	0.28931	0.00772	0.55877
P10	0.35704	0.49365	0.4422
P11	0.47749	0.07442	0.55154
P12	0.06035	0.16394	0.64933
P13	0.90211	0.23206	0.42916
P14	0.51405	0.32131	0.53569
P15	0.62873	0.41193	0.63507
P16	0.50842	0.07968	0.34972
P17	0.63466	0.1738	0.45606
P18	0.73798	0.27648	0.57526
P19	0.55349	0.31808	0.33667
P20	0.67496	0.41676	0.43745
P21	0.7796	0.00662	0.56198
P22	0.85704	0.49365	0.4422
P23	0.97126	0.0728	0.55217
P24	0.55068	0.16079	0.6501
P25	0.40211	0.73206	0.42916

P26	0.01845	0.81989	0.53509
P27	0.12227	0.89681	0.64407
P28	0.00842	0.57968	0.34972
P29	0.13352	0.67379	0.45534
P30	0.23683	0.77654	0.57656
P31	0.05349	0.81808	0.33667
P32	0.17495	0.91676	0.43746
P33	0.2863	0.50945	0.55664
P34	0.35704	0.99365	0.4422
P35	0.47408	0.57533	0.55115
P36	0.06075	0.6596	0.64924
P37	0.90211	0.73206	0.42916
P38	0.51323	0.82326	0.53599
P39	0.62838	0.8554	0.65044
P40	0.50842	0.57968	0.34972
P41	0.63381	0.67382	0.4552
P42	0.7398	0.77277	0.57094
P43	0.55349	0.81808	0.33667
P44	0.67496	0.91675	0.43746
P45	0.77945	0.50553	0.56272
P46	0.85704	0.99365	0.4422
P47	0.97169	0.57253	0.55131
P48	0.57005	0.69107	0.64939
C1	0.59688	0.4859	0.76915
C2	0.50353	0.57649	0.7749
C3	0.40387	0.53966	0.77967
C4	0.44065	0.42813	0.77724
C5	0.37721	0.3436	0.77929
C6	0.71361	0.4675	0.74951
O1	0.55738	0.39411	0.77211
O2	0.2565	0.38928	0.78326
O3	0.76074	0.54343	0.73669
H1	0.50789	0.65937	0.77405
H2	0.31499	0.58721	0.78448
H3	0.40419	0.29269	0.81939

H4	0.40218	0.29015	0.73974
H5	0.22594	0.40753	0.74246
H6	0.76648	0.38256	0.749
Co1	0.02075	0.06078	0.45155
Co2	0.40216	0.46033	0.34022
Co3	0.13765	0.15475	0.55412
Co4	0.00837	0.3514	0.43866
Co5	0.12812	0.44087	0.53883
Co6	0.20086	0.02537	0.64301
Co7	0.19848	0.0525	0.38365
Co8	0.32016	0.14662	0.49481
Co9	0.42206	0.23228	0.58697
Co10	0.21205	0.25923	0.39522
Co11	0.32626	0.35827	0.50083
Co12	0.45011	0.44304	0.60403
Co13	0.52005	0.06288	0.45035
Co14	0.90216	0.46033	0.34022
Co15	0.63564	0.15467	0.55574
Co16	0.50837	0.3514	0.43866
Co17	0.62191	0.43731	0.53295
Co18	0.66674	0.00735	0.63803
Co19	0.69848	0.0525	0.38365
Co20	0.81845	0.14768	0.49431
Co21	0.92521	0.22861	0.58778
Co22	0.71205	0.25923	0.39522
Co23	0.82836	0.35819	0.50266
Co24	0.94966	0.43863	0.60459
Co25	0.02025	0.56102	0.45082
Co26	0.40216	0.96033	0.34022
Co27	0.137	0.65539	0.55398
Co28	0.00837	0.8514	0.43866
Co29	0.12865	0.94122	0.54112
Co30	0.20528	0.52479	0.64197
Co31	0.19848	0.5525	0.38365
Co32	0.3191	0.64818	0.49486

Co33	0.42527	0.73085	0.58789
Co34	0.21205	0.75923	0.39522
Co35	0.32535	0.85731	0.50081
Co36	0.45634	0.94426	0.60735
Co37	0.51943	0.56288	0.44997
Co38	0.90216	0.96033	0.34022
Co39	0.63555	0.64988	0.55398
Co40	0.50837	0.8514	0.43866
Co41	0.62865	0.93514	0.53414
Co42	0.71079	0.54123	0.65387
Co43	0.69848	0.5525	0.38365
Co44	0.81868	0.6476	0.49408
Co45	0.92639	0.72795	0.58742
Co46	0.71205	0.75923	0.39522
Co47	0.82999	0.85845	0.50174
Co48	0.94793	0.93639	0.60325

Table S6 Unit-cell and position parameters of the optimized model for the adsorption of HMF on 5.2%Ce-CoP

	5.2%Ce-CoP

a (Å)		12.06880	
b (Å)		12.89130	
c (Å)		22.27670	
α (deg)		90.0	
β (deg)		90.0	
γ (deg)		74.0	
Atom Coordinates	***x***	***y***	***z***
C1	0.49202	0.4632	0.75681
C2	0.43904	0.57553	0.75235
C3	0.31956	0.59299	0.74724
C4	0.29198	0.49185	0.74539
C5	0.20051	0.46107	0.78314
C6	0.60431	0.39953	0.74293
Ce1	0.46376	0.42457	0.6471
P1	0.40211	0.23206	0.42916
P2	0.01663	0.32183	0.53474
P3	0.13549	0.40881	0.63849
P4	0.00842	0.07968	0.34972
P5	0.13573	0.1734	0.45628
P6	0.24064	0.27688	0.57557
P7	0.05349	0.31808	0.33667
P8	0.17495	0.41676	0.43746
P9	0.27707	0.0059	0.56335
P10	0.35704	0.49365	0.4422
P11	0.47156	0.0702	0.554
P12	0.04862	0.16528	0.65078
P13	0.90211	0.23206	0.42916
P14	0.52172	0.31818	0.53331
P15	0.50842	0.07968	0.34972
P16	0.63439	0.173	0.45525
P17	0.73733	0.27613	0.5719
P18	0.55349	0.31808	0.33667
P19	0.67496	0.41676	0.43745
P20	0.78943	0.00608	0.55841

P21	0.85704	0.49365	0.4422
P22	0.97731	0.0746	0.55292
P23	0.56227	0.17305	0.64993
P24	0.40211	0.73206	0.42916
P25	0.01256	0.82264	0.53616
P26	0.12658	0.85503	0.65027
P27	0.00842	0.57968	0.34972
P28	0.13232	0.67448	0.45461
P29	0.2382	0.77332	0.57028
P30	0.05349	0.81808	0.33667
P31	0.17495	0.91676	0.43746
P32	0.2847	0.51024	0.56064
P33	0.35704	0.99365	0.4422
P34	0.46973	0.56871	0.5492
P35	0.07483	0.68565	0.64996
P36	0.90211	0.73206	0.42916
P37	0.51902	0.81645	0.53491
P38	0.61879	0.89978	0.64425
P39	0.50842	0.57968	0.34972
P40	0.63614	0.67168	0.45595
P41	0.73794	0.77302	0.57739
P42	0.55349	0.81808	0.33667
P43	0.67496	0.91675	0.43746
P44	0.78354	0.50326	0.56311
P45	0.85704	0.99365	0.4422
P46	0.97443	0.57443	0.55183
P47	0.5546	0.6538	0.64699
Co1	0.01956	0.06331	0.45033
Co2	0.40216	0.46033	0.34022
Co3	0.13537	0.15486	0.55596
Co4	0.00837	0.3514	0.43866
Co5	0.12486	0.43819	0.53537
Co6	0.16098	0.00931	0.63851
Co7	0.19848	0.0525	0.38365
Co8	0.3196	0.15039	0.49582

Co9	0.42842	0.23028	0.58461
Co10	0.21205	0.25923	0.39522
Co11	0.32989	0.36112	0.50375
Co12	0.52081	0.0606	0.4521
Co13	0.90216	0.46033	0.34022
Co14	0.63869	0.15187	0.55309
Co15	0.50837	0.3514	0.43866
Co16	0.6248	0.43616	0.54063
Co17	0.69848	0.02759	0.64254
Co18	0.69848	0.0525	0.38365
Co19	0.82072	0.1483	0.49576
Co20	0.92234	0.23471	0.58622
Co21	0.71205	0.25923	0.39522
Co22	0.8252	0.35898	0.50022
Co23	0.9551	0.43982	0.60372
Co24	0.01983	0.56251	0.45066
Co25	0.40216	0.96033	0.34022
Co26	0.13555	0.65125	0.55271
Co27	0.00837	0.8514	0.43866
Co28	0.12637	0.93577	0.53364
Co29	0.21808	0.53449	0.65391
Co30	0.19848	0.5525	0.38365
Co31	0.31658	0.64885	0.49202
Co32	0.42378	0.72437	0.58467
Co33	0.21205	0.75923	0.39522
Co34	0.32902	0.85946	0.50183
Co35	0.44624	0.93256	0.60251
Co36	0.52087	0.56004	0.45056
Co37	0.90216	0.96033	0.34022
Co38	0.63771	0.64909	0.55484
Co39	0.50837	0.8514	0.43866
Co40	0.6283	0.93764	0.54139
Co41	0.67677	0.50404	0.64323
Co42	0.69848	0.5525	0.38365
Co43	0.81971	0.64795	0.49593

Co44	0.92666	0.72972	0.58893
Co45	0.71205	0.75923	0.39522
Co46	0.82547	0.85658	0.50103
Co47	0.95563	0.9428	0.6082
O1	0.40239	0.40995	0.75289
O2	0.09356	0.54099	0.78295
O3	0.68308	0.44003	0.71872
H1	0.48439	0.63697	0.75679
H2	0.25536	0.67077	0.74916
H3	0.23024	0.45346	0.83017
H4	0.1934	0.38146	0.76815
H5	0.06429	0.5479	0.74159
H6	0.62785	0.3125	0.75236

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