Supplementary Information

Highly dispersed CoP on three-dimensional ordered mesoporous FeP for efficient electrocatalytic hydrogen production

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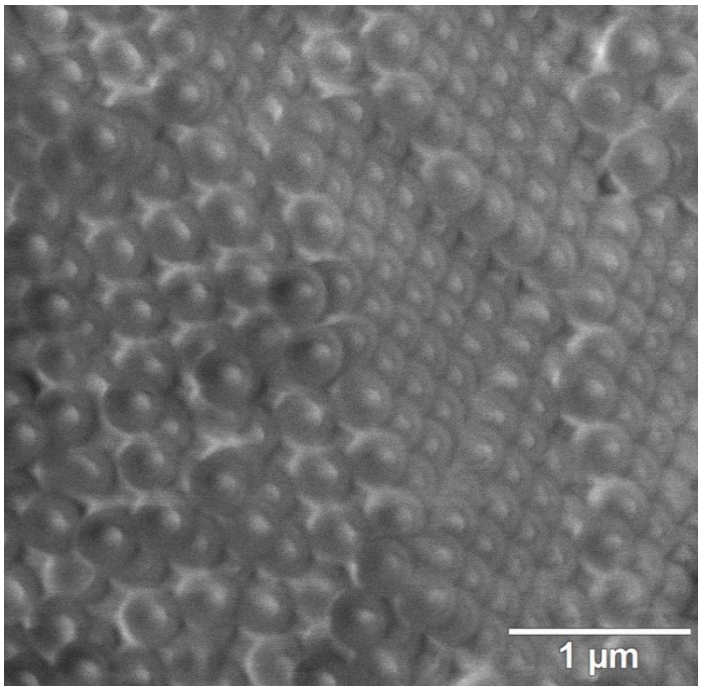

Fig. S1 A typical SEM image of the Co-MOF embedded 3-dimensional ordered PS template.

Preparation and yield of the CoP@3DOM-FeP and the Bulk-Co(0.1)FeP

For synthesizing the Co(0.1)P@3DOM-FeP, 2.0 g ferrous (II) acetate ($Fe(II)Ac_2$, 222.1 g mol^{-1}) and 0.1 g ZIF-67 (71.84 g mol^{-1}) were used. Assuming all the cobalt and iron formed ideal CoP and FeP, the theoretical mass of the final product should be 1.596 g. While the weight of the synthesised product in a single batch is around 1.1~1.3 g. Thus, the yield percentage is around 69%~82%. The main reasons for the loss include the inevitable residues in the combustion boat (20mm×20mm×40mm, Fig. S2), the transfer loss in each step of the synthesis and the influence of the gas flow in the annealing process. Clearly these types of loss can be greatly reduced if larger batch are considered in the future.

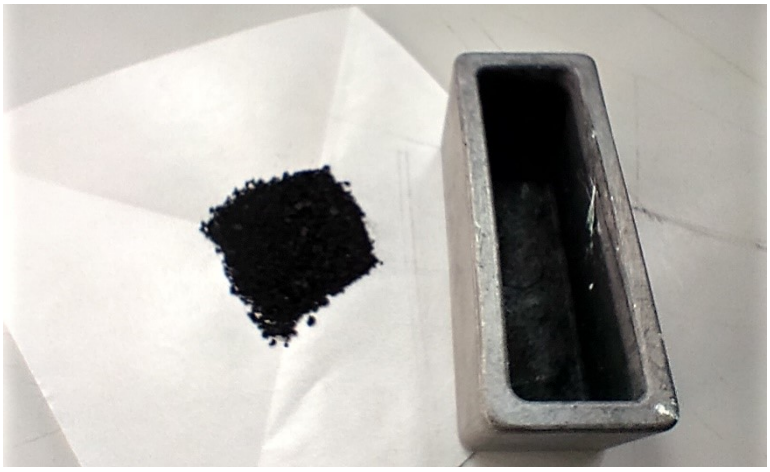

Fig. S2 A picture of the ceramic combustion boat and the Co(0.1)P@3DOM-FeP samples.

For synthesizing the Bulk-Co(0.1)FeP, 2.0 g ferrous (II) acetate ($Fe(II)Ac_2$) and 1.8 g (1 mM) cobalt nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$) were dissolved in the mixed solution of 4 mL ethylene glycol (EG) and 0.1 mL acetate acid. The solution was

then kept vigorous stirring for 30 mins in a sealed vial to avoid oxidation. Next, without PS template added, the sample was dried in an oven for several hours until the ethanol evaporated, and the Fe-Co mixed metal salt was recrystallized. The mixed salt was washed and dried with ethanol for several times and then grinded into powders. The powders was calcinated in furnace tube and treated with the phosphide CVD with the same protocol for synthesizing the Co(0.1)P@3DOM-FeP. The yield of the synthesised Bulk-Co(0.1)FeP is 1.39 g, while the theoretical value (1.596 g) is the same with Co(0.1)P@3DOM-FeP. Thus, the yield rate for Bulk-Co(0.1)FeP is 87.0%."

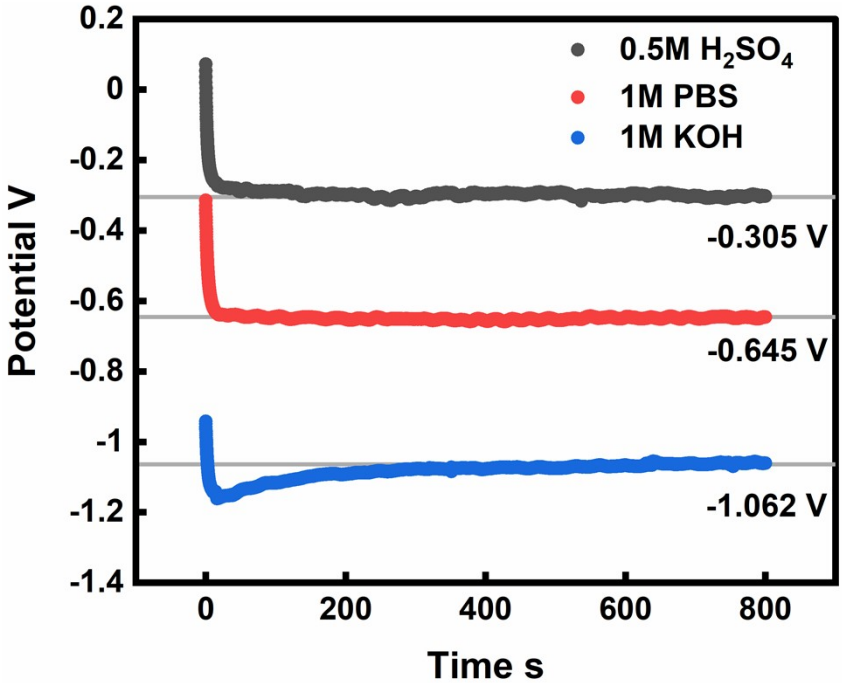

Fig. S3 Calibration curves of SCE vs RHE in 0.5M H_2SO_4, 1M PBS and 1M KOH electrolyte solution.

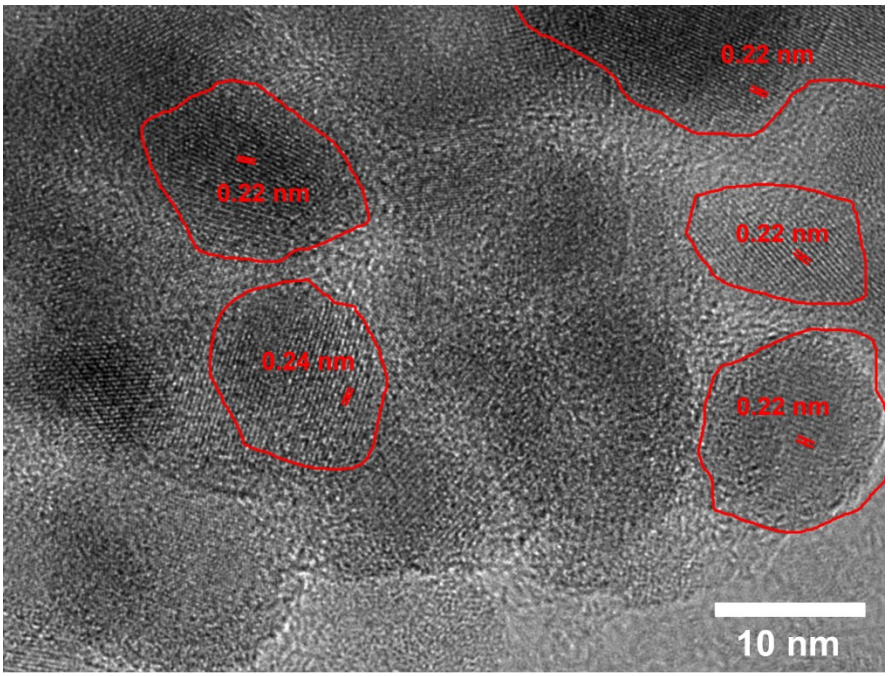

Fig. S4 HRTEM images of FeP crystalline regions.

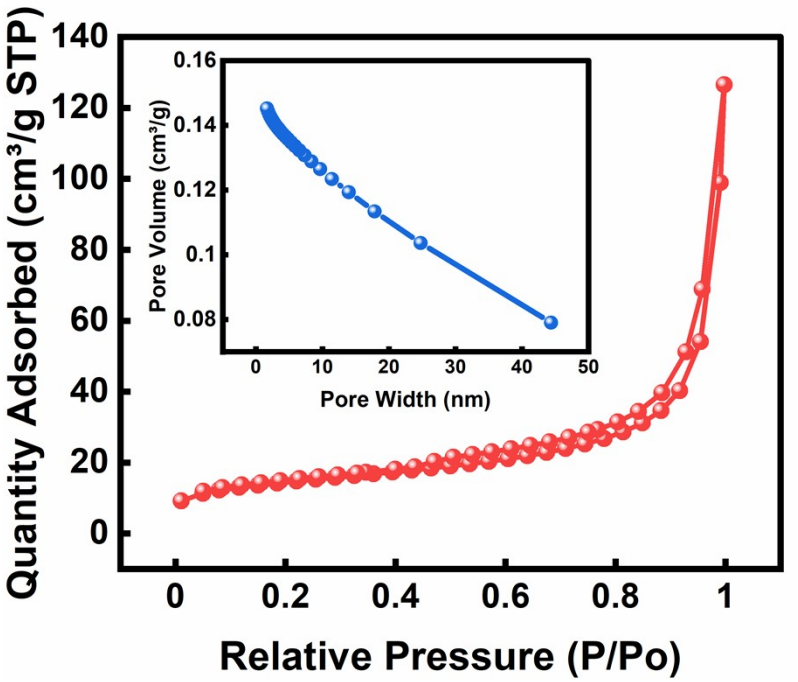

Fig. S5 BET isotherm and pore distribution of Bulk-Co(0.1)P@FeP.

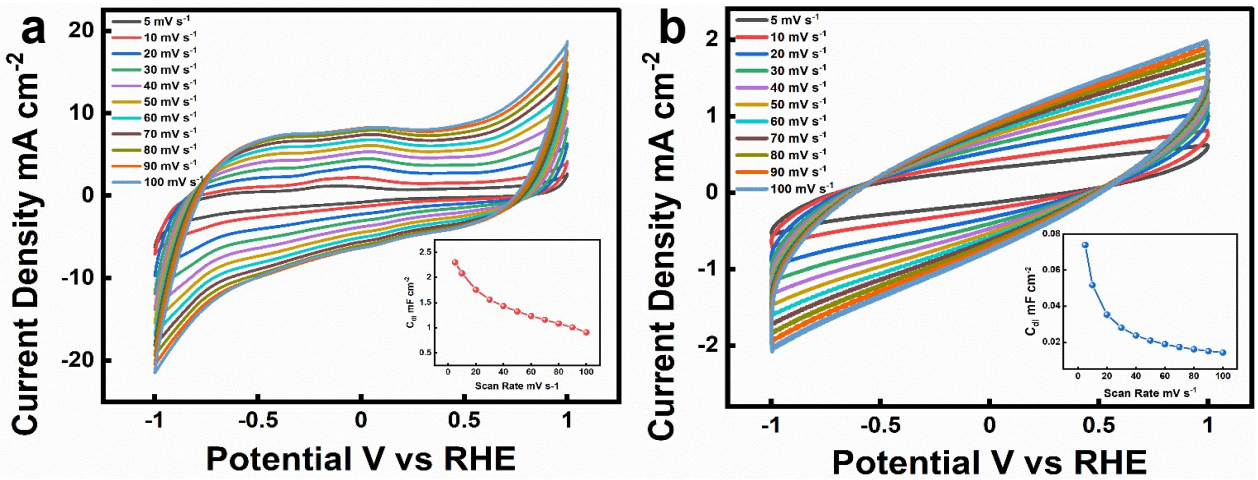

Fig. S6 Cyclic voltammograms of a) Co(0.1)P@3DOM-FeP and b) Bulk-Co(0.1)FeP at the scan rates of 5~100 mV s^{-1}.

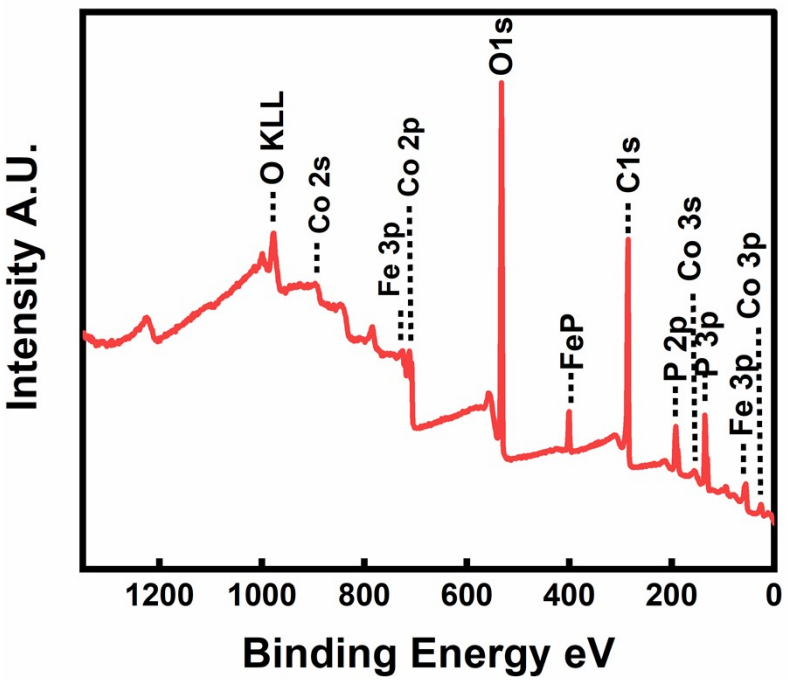

Fig. S7 XPS survey spectra of Co(0.1)P@3DOM-FeP.

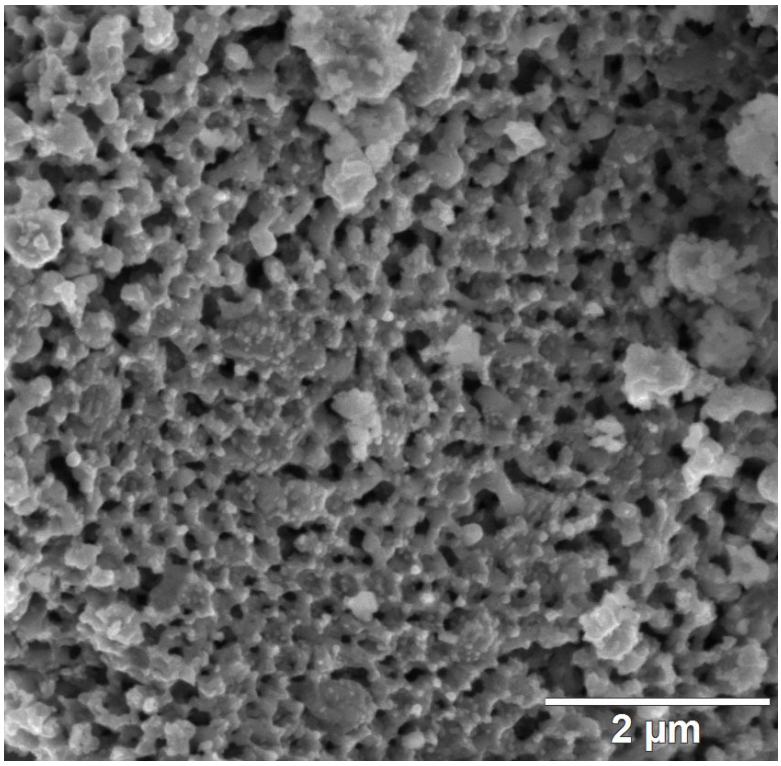

Fig. S8 A typical SEM image of the Co(0.2)P@3DOM-FeP.

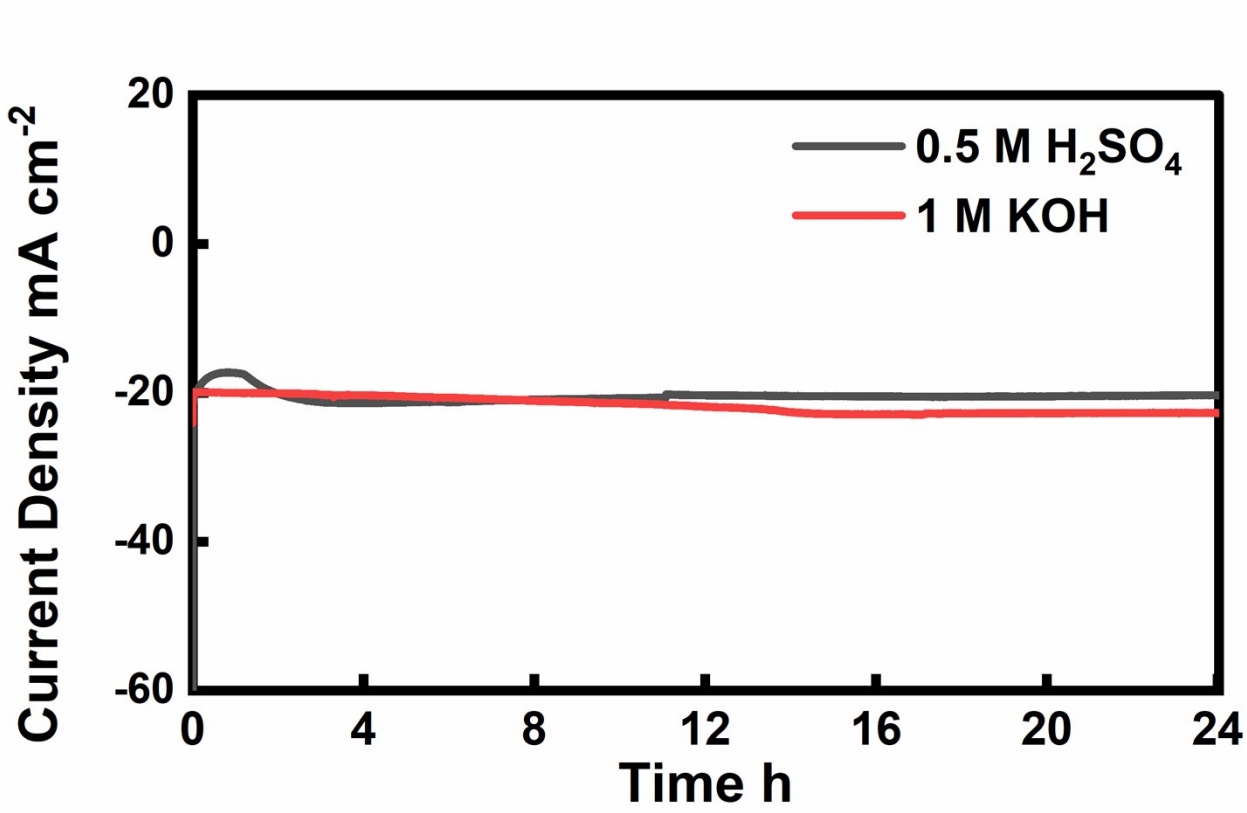

Fig. S9 Chronoamperometric i-t test of the Co(0.1)P@3DOM-FeP catalyst with constant overpotentials of 107 mV and 135 mV applied in alkaline and acidic media respectively.

Table S1 HER performance comparison of several up-to-date cobalt based electrocatalysts.

Electrocatalyst	Electrolyte	Overpotential mV (@10mA cm^{-2})	Tafel Slop mV dec^{-1}	References
Pt/C	Universal PH	53.7~64.5	36.2~46.5	This work
CoP@3DOM-FeP	Universal PH	67.2~76.5	66.3~77.5	This work
N-CoP/ CC	Universal PH	25~74	49~69	1
Cu-CoP NRAs/CC	Universal PH	44~137	86~144	2
W-CoP NAs/CC	Universal PH	89~102	58~87	3
V-CPNA/CC	Universal PH	87~98	65.4~83.7	4
$CoS_{1.097}/MoS_2$	Universal PH	228~341	59~85	5
CoP NFs	Universal PH	122~136	54.8~56.2	6
Mn−Co−P/Ti	Universal PH	49~86	55~82	7
$Ni_{0.89}Co_{0.11}Se_2$ MNSN/ NF	Universal PH	52~85	39~78	8
CoP/Co-MOF	Universal PH	27~49	43~63	9
CoP@3D-NPC	Universal PH	127~333	58~71	10
CoP@NG	Universal PH	158~182	59.6~63.8	11
CoP/NF	Universal PH	41.1~83.9	55~65.3	12
CoP/Mo_2C-NC	Universal PH	68~81.8	49~68	13
CoP/CoMoP	Alkaline	34	33	14
CoP@NC-350	Alkaline	75	55	15
CoPS/N–C	Alkaline	148	78	16
CoMoCH@NiCoP/NF	Alkaline	45	63	17
CoP/PNC	Alkaline	165	70	18
Mo-CoP	Alkaline	118	69	19
Bi/CoP	Alkaline	122	60.2	20
NiCoP-8.0	Alkaline	34.3	49.9	21

Amorphous CoP/NF	Alkaline	143	63	[22]
CoFeO@BP	Alkaline	88	51	[23]
CeO_2/Co_4N	Alkaline	30	66	[24]
Mn_3O_4/CoP PNRs	Alkaline	43	28.9	[25]
N-CNTs@Co_4N@NF	Alkaline	67	46.5	[26]
O,Mo-CoP/NF-2	Alkaline	59	65.4	[27]
HP-CoP NA/NF	Alkaline	70	83.2	[28]
$Co_{0.2}$-VOOH	Alkaline	130	58.2	[29]
CoP/SPNF	Alkaline	45	65.9	[30]
Cu_3P–CoP/CC	Acidic	59	58	[31]
CoP/rGO-400	Acidic	105	50	[32]
Ni_2P–CoP	Acidic	105	64	[33]
CoP_2/CC	Acidic	72	67	[34]
NiCoP	Acidic	160	70	[35]
NiCoP/MoxC-15	Acidic	116	57.4	[36]
Co-MoS_2-0.5	Acidic	60	64.72	[37]
Fe–Co_2P/ NCNTs	Acidic	104	68	[38]
CoP-N-C-400	Acidic	31	42	[39]
MoS_2@CoS_2	Acidic	96	60	[40]

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