Supporting Information

In-situ removal of surface molybdenum oxide making binder-free porous $Mo_{1.98}C_{1.02}$ film as a more efficient electrocatalyst for alkaline than for acidic hydrogen production

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Supporting discussion 1. Estimation of the PMC weight content in the composite

The porous film of $Mo_{1.98}C_{1.02}$ (PMC) was exfoliated from the carbon fiber paper (CFP) via ultrasonic vibration, and subjected to thermogravimetric analysis (TGA). All $Mo_{1.98}C_{1.02}$ nanoparticles were oxidized to MoO_3, and all carbon atoms (including residual carbon and those in $Mo_{1.98}C_{1.02}$) were removed during the oxidation process at 650 °C. The weight percent of $Mo_{1.98}C_{1.02}$ in PMC is computed according to the follow equation:

$$\frac{1.98W_{Mo1.98C1.02}}{M_{Mo1.98C1.02}} = \frac{W_{remain}}{M_{MoO3}}$$

Where $W_{Mo1.98C1.02}$ is the weight percent of $Mo_{1.98}C_{1.02}$, $M_{Mo1.98C1.02}$ is the molecular weight of $Mo_{1.98}C_{1.02}$, W_{remain} is the weight of MoO_3 suggested by the TGA curve, M_{MoO3} is the molecular weight of MoO_3. According to the TGA curve, W_{remain} is 121.74%, and then $W_{Mo1.98C1.02}$ is computed to be 86.38%. Therefore, the weight percent of residual carbon is 1 – 86.38% = 13.62%.

Supporting discussion 2. **Estimation of the electrochemically active surface area**

To measure the electrochemical capacitance, the potential was swept in the range 0.10 to 0.20 V vs. RHE at different scan rates.[1, 2] The capacitance current density ($\Delta J = J_a - J_c$ at 0.15 V vs. RHE) was plotted and the C_{dl} was obtained by a data fitting of the plot. Electrochemical surface areas (ECSA) was estimated from the C_{dl} using the specific capacitance value for a flat standard with 1 cm^2 of real surface area. In general, the C_{dl} for a flat surface ranges from 20 to 60 μF cm^{-2}, so in our calculations a specific capacitance for a flat surface area of 40 μF cm^{-2} was adopted.

A EASA = C_{dl}/(40 μF cm^{-2} per cm2 ECSA)

Table R1. Diffraction peaks of $Mo_{1.98}C_{1.02}$, PMC and all the Mo_2C samples from Jade 6.0 software.

Sample	Peak (°)							
PMC	34.4	37.7	39.3	51.9	61.5	69.2	74.5	75.5
$Mo_{1.98}C_{1.02}$ 65-8364	34.4[100]	37.7[002]	39.3[101]	51.9[102]	61.5[110]	69.1[103]	74.5[112]	75.5[201]
Mo_2C 31-871	34.3[021]	38.0[200]	39.3[121] 39.5[102]	52.1[221] 52.2[202]	61.4[040] 61.6[023]	69.5[321]	74.5[240] 74.7[223]	75.5[142] 75.8[104]
Mo_2C 35-787	34.4[100]	38.0[002]	39.4[101]	52.1[102]	61.5[110]	69.6[103]	74.6[112]	75.5[201]
Mo_2C 65-8766	34.5[100]	38.0[002]	39.6[101]	52.3[102]	61.9[110]	69.8[103]	75.0[112]	76.0[201]
Mo_2C 71-242	34.3[021] 34.4[002]	38.0[200]	39.4[121] 39.5[102]	52.1[221] 52.2[202]	61.4[040] 61.4[132] 61.6[023]	69.6[321]	74.5[240] 74.7[223]	75.5[142] 75.8[104]
Mo_2C 72-1683	34.5[021] 34.5[002]	38.1[200]	39.5[121] 39.5[102]	52.3[221] 52.3[202]	61.8[040] 61.8[023]	69.8[321] 69.8[302]	74.9[240] 74.9[223]	75.8[142] 75.8[104]
Mo_2C 77-720	34.4[201] 34.5[002]	38.1[020]	39.5[211] 39.6[012]	52.2[221] 52.3[022]	61.5[312] 61.5[400] 61.7[203]	69.7[231] 69.7[032]	74.7[420] 74.9[223]	75.7[412] 75.9[014]
Mo_2C 79-744	34.4[021] 34.4[002]	38.0[200]	39.4[121] 39.4[102]	52.1[221] 52.1[202]	61.6[040] 61.6[023]	69.6[321] 69.6[302]	74.7[240] 74.7[223] 75.0[133]	75.6[142] 75.7[104]

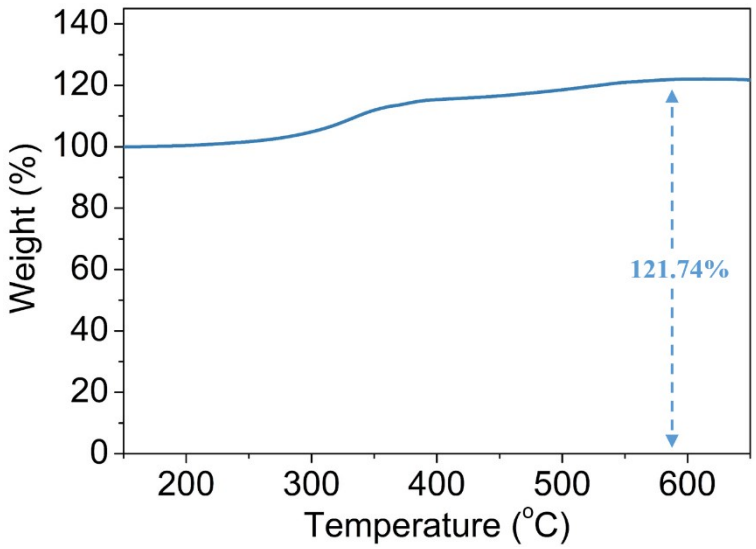

Figure S1. TGA curve of PMC measured in O_2 atmosphere.

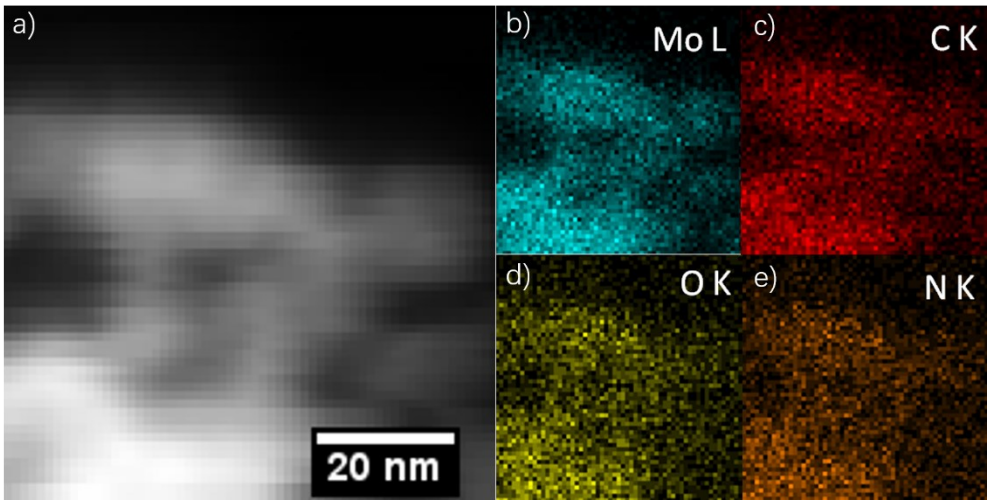

Figure S2. (a) Dark-field STEM image of the PMC and corresponding elemental mapping images of (b) Mo, (c) C, (d) O and (e) N.

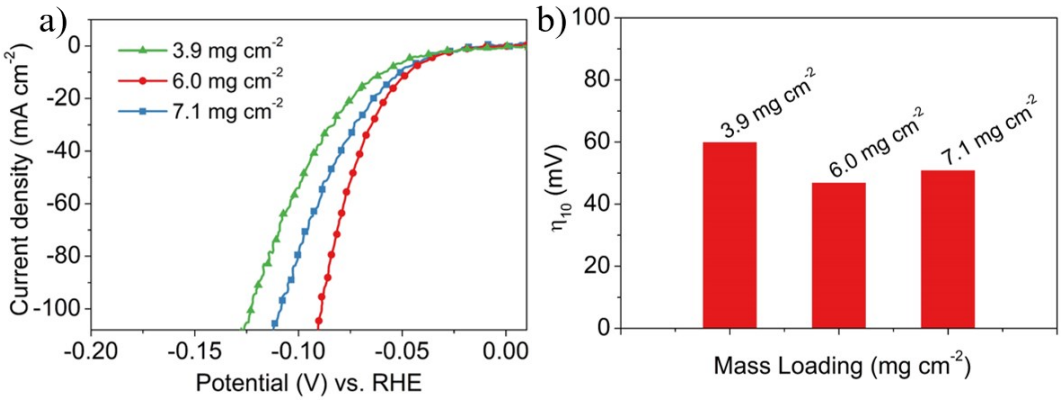

Figure S3. (a) Polarization curves and (b) η_{10} of PMC with different loading amounts in alkaline media.

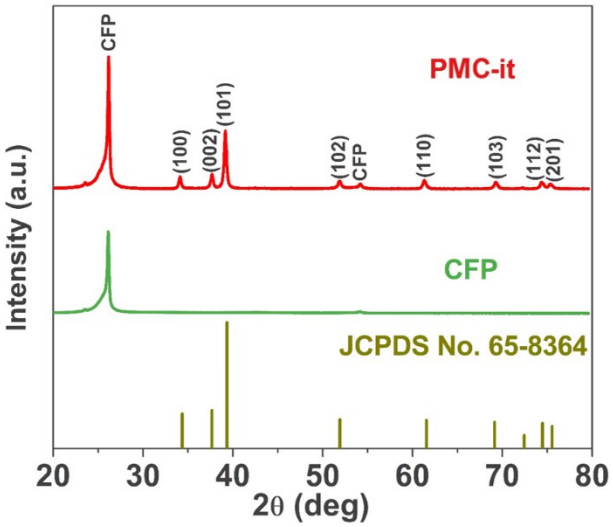

Figure S4. XRD pattern of the PMC-it.

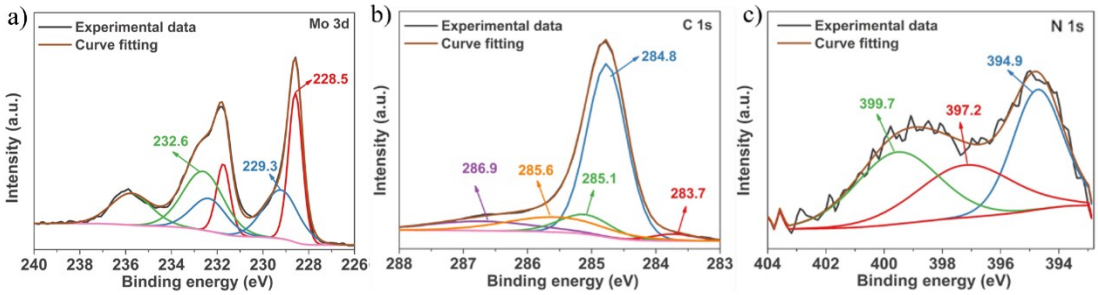

Figure S5. (a) Mo 3d, (b) C 1s and (c) N 1s windows of XPS spectra of the PMC-it.

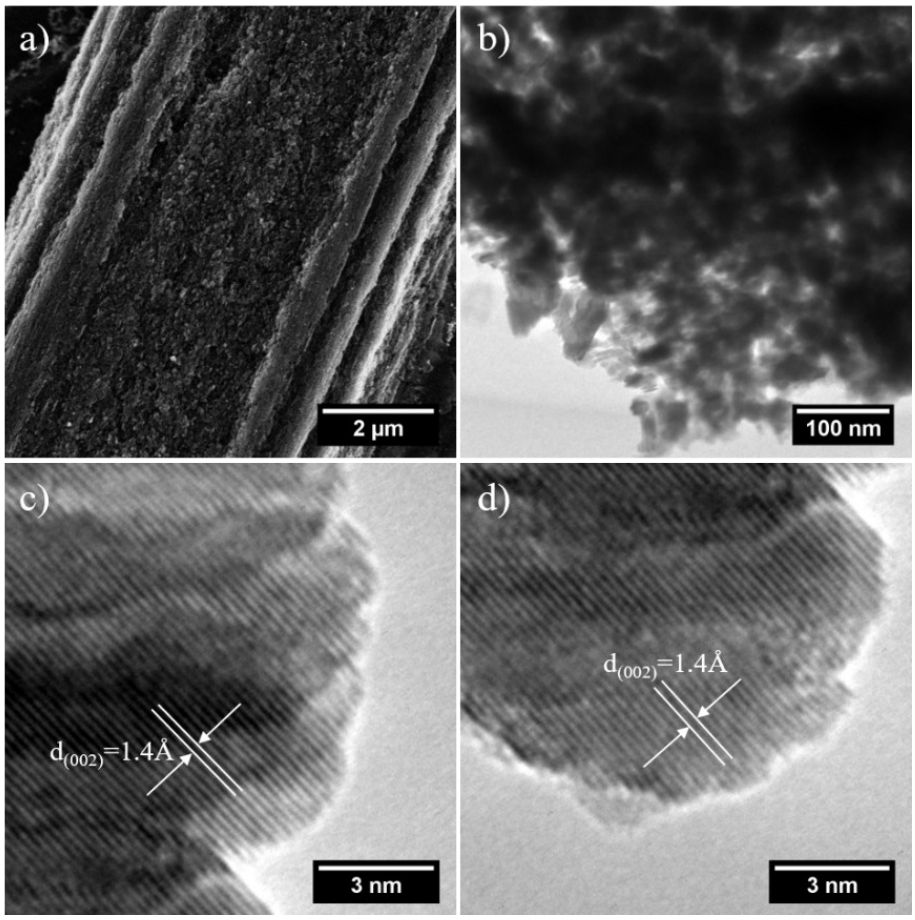

Figure S6. (a) SEM, (b) TEM, and (c-d) HRTEM images of the PMC-it.

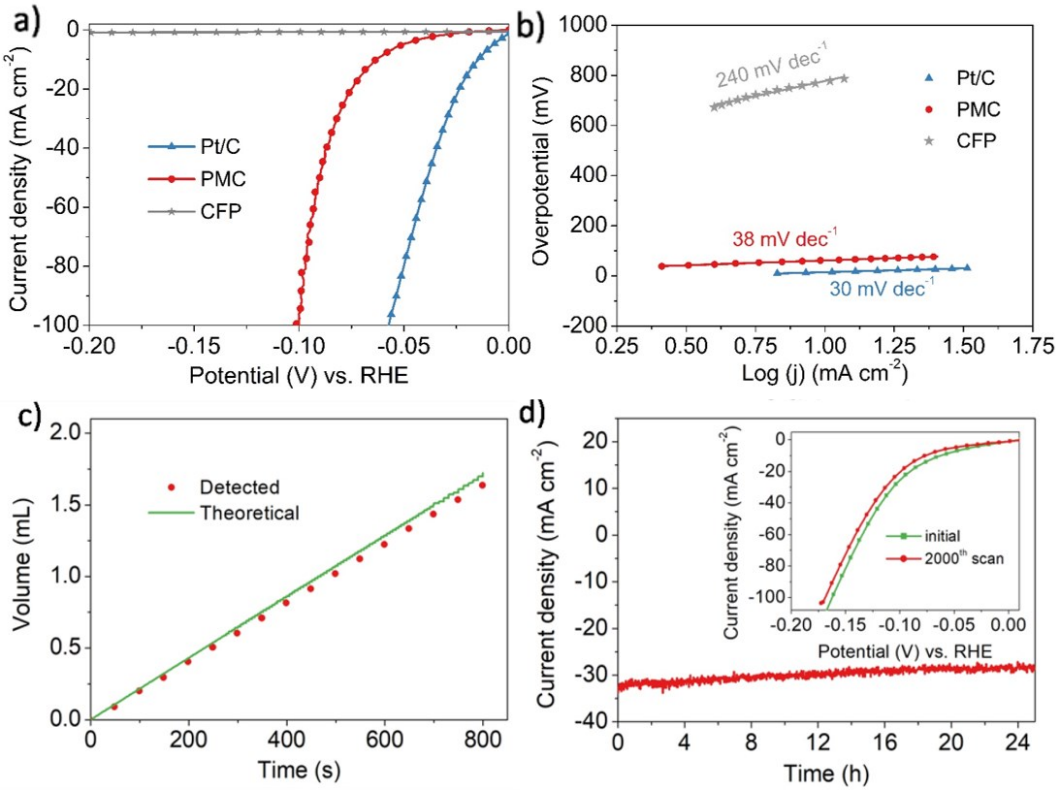

Figure S7. (a) Polarization curve of PMC, CFP, and commercially available Pt/C. (b) Tafel plot of PMC, CFP, and Pt/C. (c) Faradaic efficiency of PMC. (d) Long-term potentiostatic experiment of PMC. And insert of (d) shows polarization curves of PMC derived from the 1st and 2000th CV scan. All measurements were carried out in acidic media.

Table S2. Summary of HER performance of representative molybdenum carbide electrocatalysts in acidic media.

Catalyst	Mass density ($mg\ cm^{-2}$)	η_{10} (mV)	Tafel slope (mV/dec)	Reference
PMC	6.0	63	38	This work
Mo_2C@NPC /NPRGO	0.14	34	33.6	Nature Commun. 2016, 7, 11204-11211
Mo_xC-Ni@NCV	1.1	75	45	J. Am. Chem. Soc. 2015, 137, 15753–15759
β-$Mo_{0.06}W_{0.94}C$/CB	0.724	220	---	Angew. Chem. Int. Ed. 2014,53, 5131-5136
Mo_2C@NC	0.28	124	60	Angew. Chem. Int. Ed. 2015, 54, 10752-10757
Mesoporous Mo_2C nano-octahedrons	0.8	142	53	Nature Commun. 2015, 6, 6512
Mo_2C/CNT	2	140 (η_8)	55.2	Energy Environ. Sci. 2013, 6, 943-951
$Mo_2F_xC_{1-x}$/rGO	--	95	86	ACS Sustain. Chem. Eng. 2020, 8, 10284−10291
Mo_2C nanobelts	0.5	140	51.3	Appl. Catal. B: Environ. 2018, 224, 533–540
B-MoC	--	285	128	Int. J. Hydrogen Energy 2020, 45, 30659-30665
$Mo_2C/MoSe_2$	--	80	49.8	J. Mater. Chem. A 2020,8, 6692-6698
$Mo_xW_{2-x}C$@NC/CC	1.5	115	58.5	Adv. Funct. Mater. 2020, 2003198
Ni-Mo_2C_{CB}/CFP	0.86	121.4	116.9	Electrochim. Acta 2019, 319, 293-301
Mo_2C/VC@C	0.28	122	43.8	Nano Energy 2019, 60, 520–526

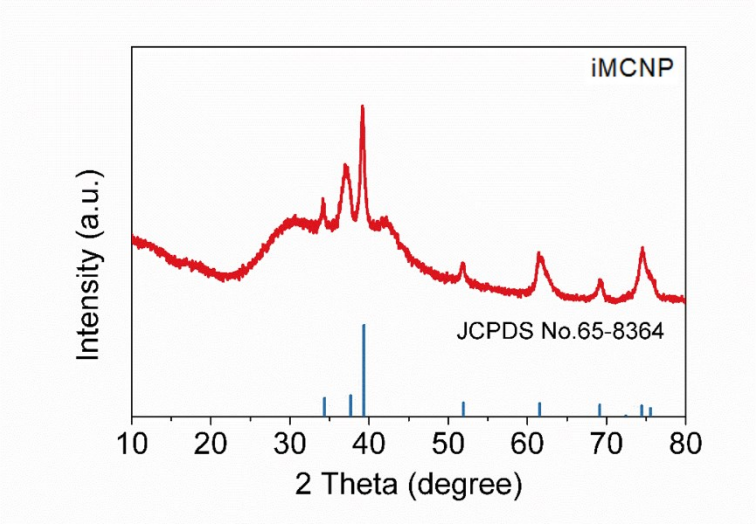

Figure S8. XRD pattern of iMCNP.

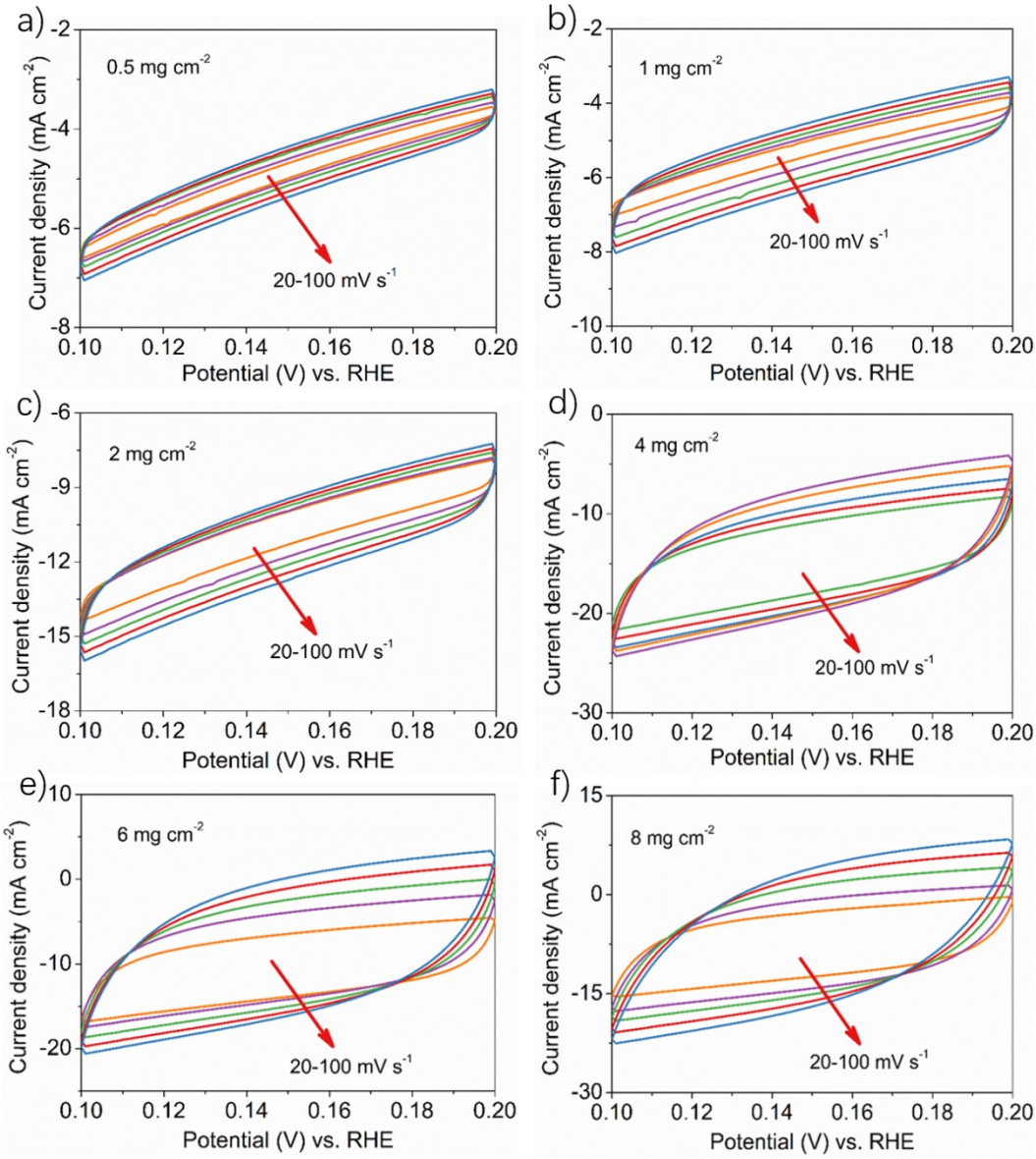

Figure S9. CV curves of iMCNP electrode with different loading amounts: (a) 0.5 mg cm^{-2}, (b) 1 mg cm^{-2}, (c) 2 mg cm^{-2}, (d) 4 mg cm^{-2}, (e) 6 mg cm^{-2} and (f) 8 mg cm^{-2}.

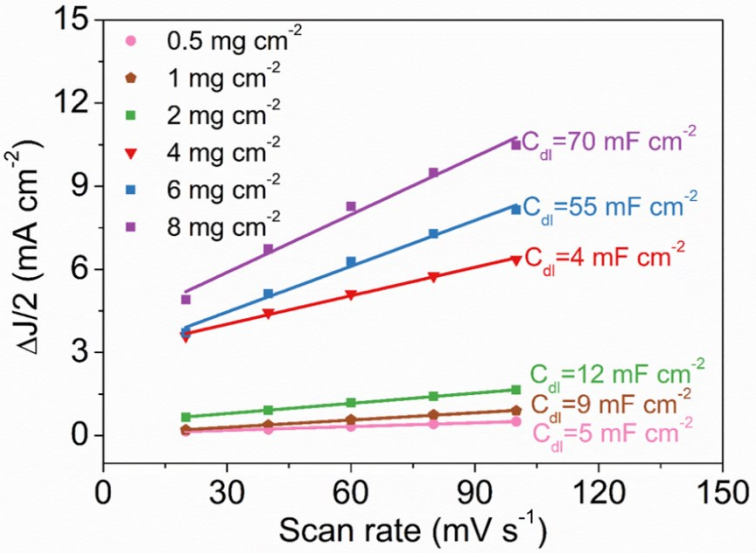

Figure S10. C_{dl} of the iMCNP electrode with different loading amounts in basic solution.

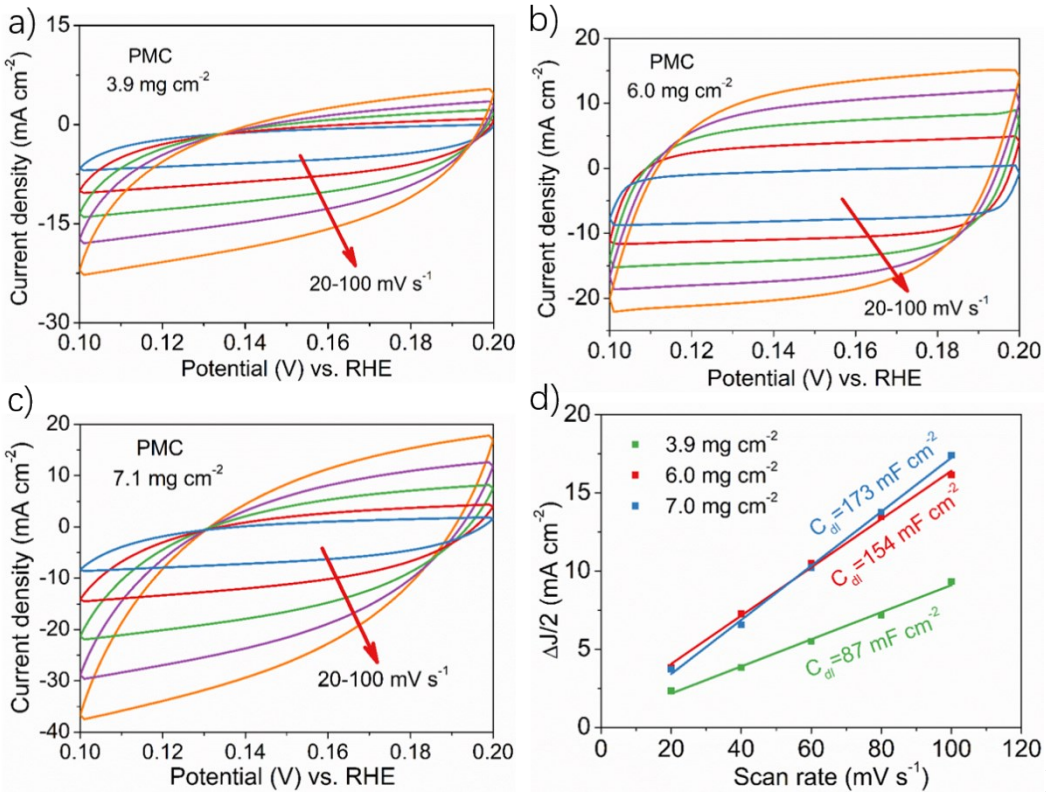

Figure S11. (a-c) CV curves and (d) C_{dl} of PMC with different loading amounts.

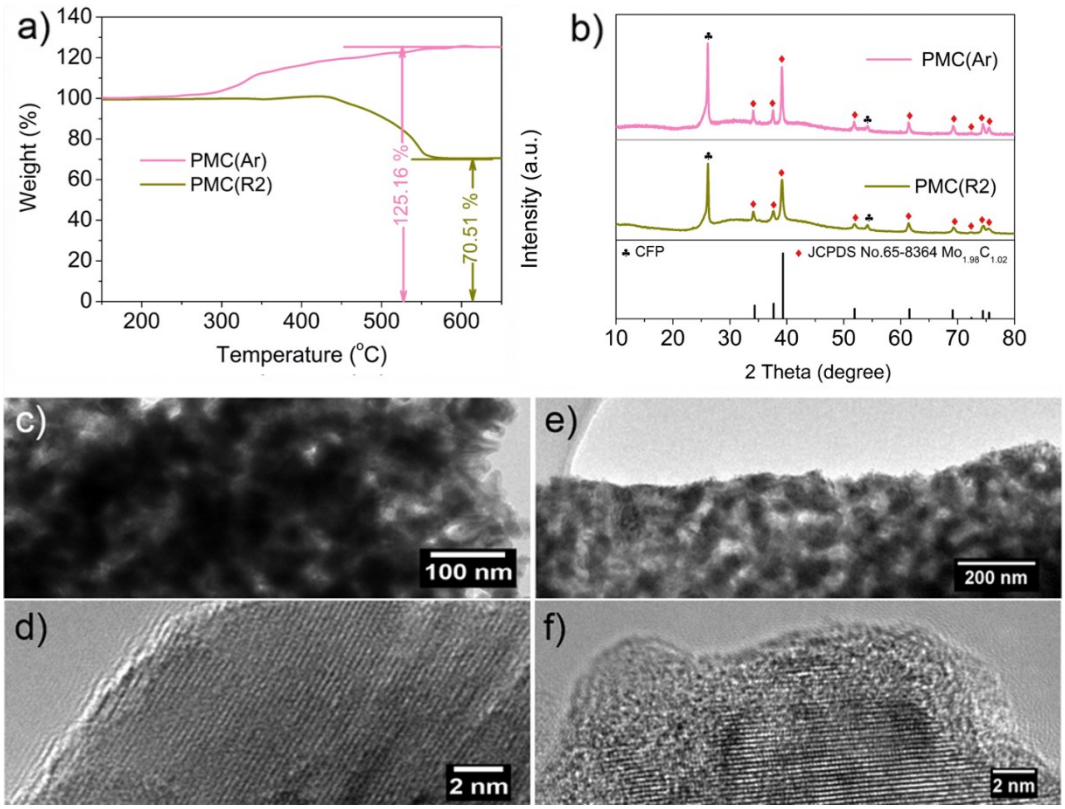

Figure S12. (a) TGA curve and (b) XRD pattern of PMC(Ar) and PMC(R2). (c, d) TEM images of PMC(Ar). (e, f) TEM images of PMC(R2).

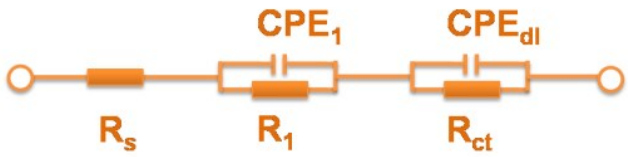

Figure S13. Equivalent circuit was used to fit the EIS data. R_s is the overall series resistance, CPE_1 and R_1 are the constant phase element and resistance describing electron transport at substrate/catalyst interface, respectively, CPE_{dl} is the constant phase element of the catalyst/electrolyte interface, and R_{ct} is the charge transfer resistance at catalyst/electrolyte interface.

Table S3. Fitting results from the EIS spectra of PMC and comparative samples in alkaline solution

Sample	R_s (Ω)	R_1 (Ω)	Q_1 (F S^{n-1})	n_1	R_{ct} (Ω)	Q_{dl} (F S^{n-1})	N_{dl}
PMC	3.466	1.034	0.1977	0.6058	57.66	7.874e-3	0.9408
PMC(Ar)	23.05	5.052	5.266e-5	0.5206	328.2	5.414e-3	0.8877
PMC(R2)	0.01	5.727	4.831e-7	0.3269	89.22	9.597e-3	0.8626

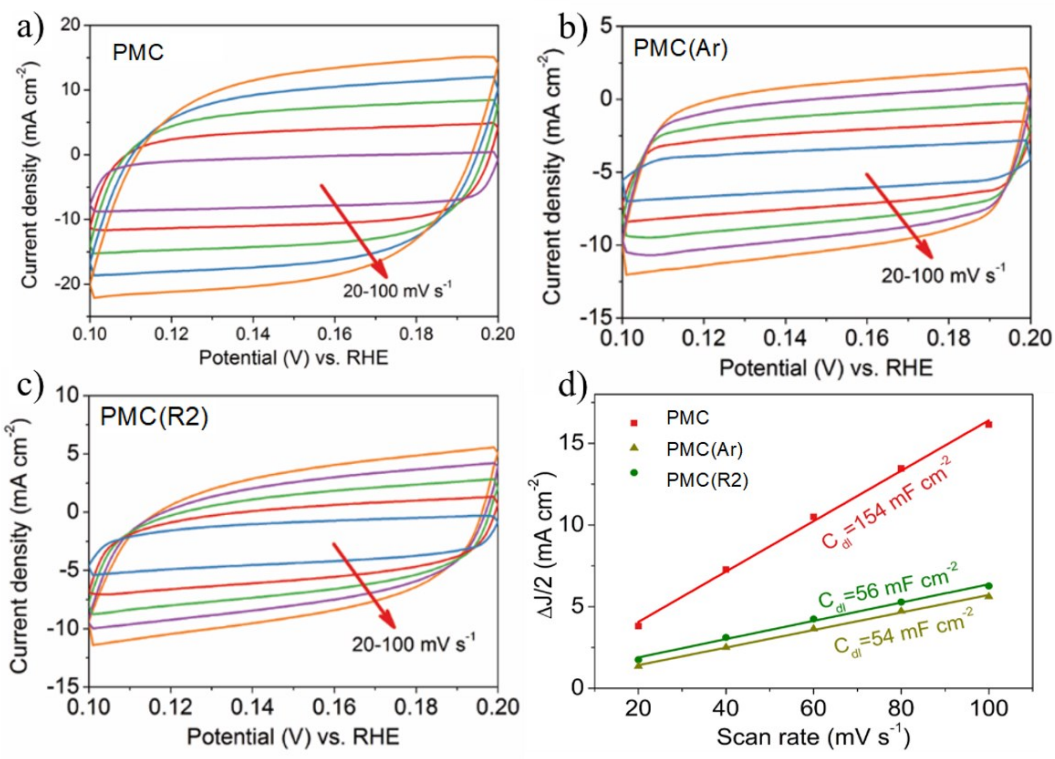

Figure S14. CV curves of (a) PMC, (b) PMC(Ar) and (c) PMC(R2). (d) C_{dl} of the PMC, PMC(Ar) and PMC(R2). All measurements were carried out in 1 M KOH.

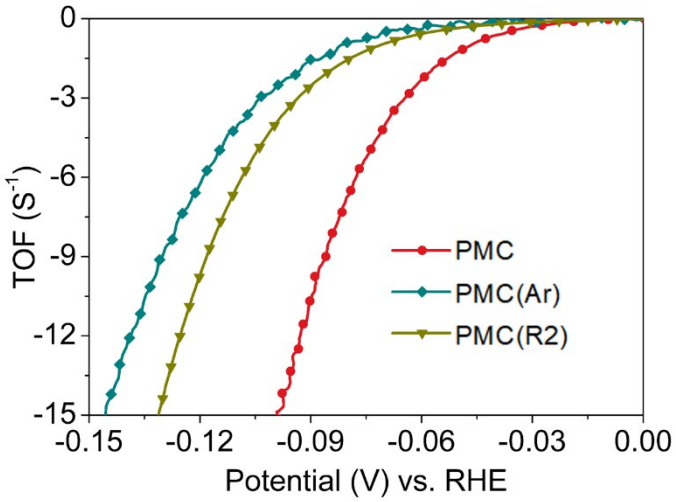

Figure S15. TOF plots of PMC, PMC(Ar) and PMC(R2).

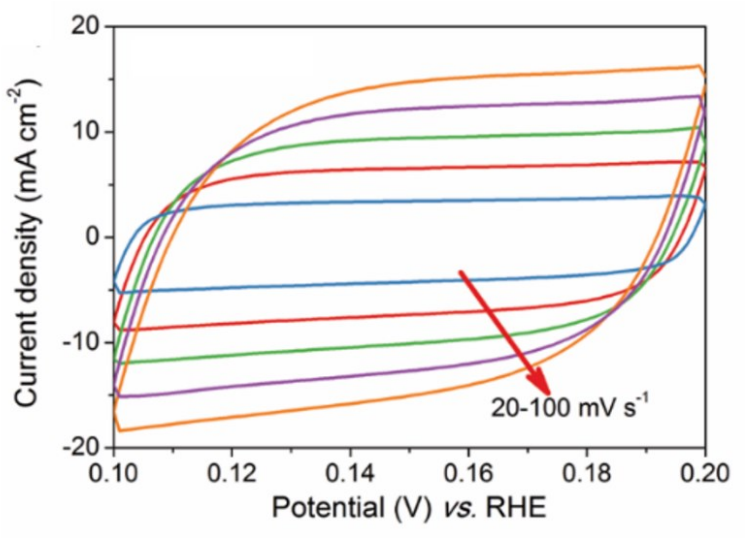

Figure S16. CVs scan of PMC in acidic solution.

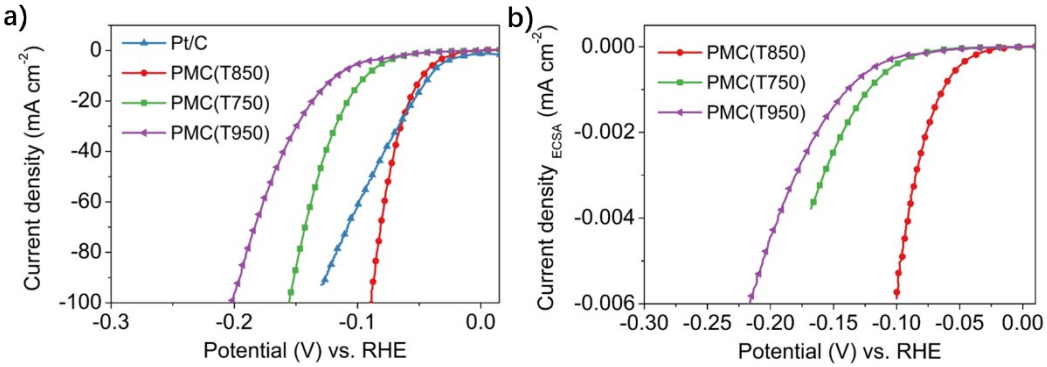

Figure S17. (a) Polarization curves and (b) reductive current normalized by the ECSA of PMC(T750), PMC(T850) and PMC(T950). All measurements were carried out in alkaline media.

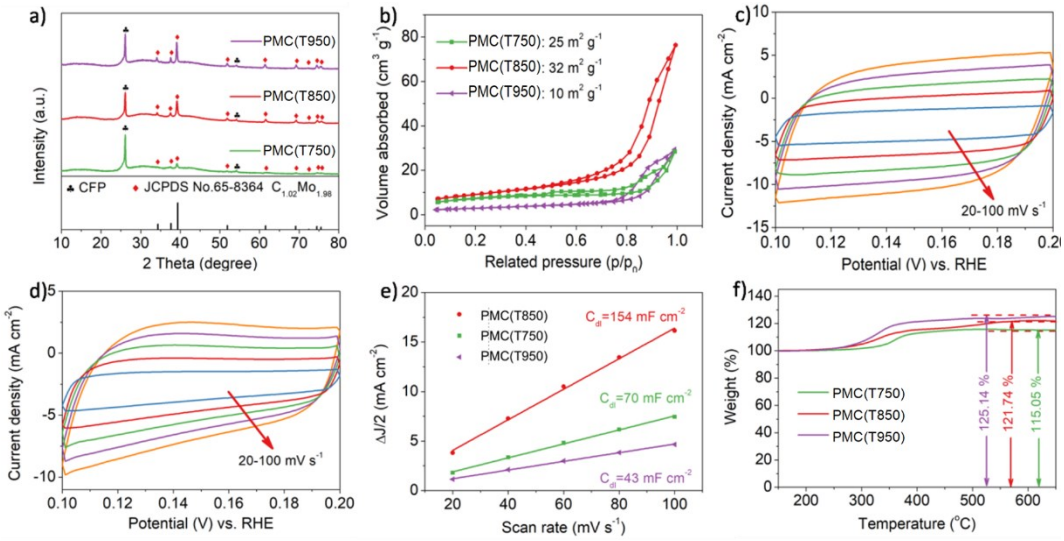

Figure S18. (a) XRD patterns, (b) nitrogen adsorption-desorption isotherms of PMC(T750), PMC(T850) and PMC(T950). CV in the region of 0.1-0.2 V vs. RHE for the (c) PMC(T750) and (d) PMC(T950). (e) Plots of the current density versus the scan rate, (f) TGA curves of PMC(T750), PMC(T850) and PMC(T950). All electrochemical measurements were carried out in alkaline media.

References

1. M. A. Lukowski, A. S. Daniel, F. Meng, A. Forticaux, L. Li and S. Jin, *J. Am. Chem. Soc.* , 2013, **135**, 10274-10277.
2. J. Xie, J. Zhang, S. Li, F. Grote, X. Zhang, H. Zhang, R. Wang, Y. Lei, B. Pan and Y. Xie, *J. Am. Chem. Soc.*, 2013, **135**, 17881-17888.