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Supporting Information

Engineering Mo_xC nanoparticles confined in N, P-codoped porous carbon hollow spheres for enhanced hydrogen evolution reaction

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Experimental section

Materials: Phosphotungstic acid ($H_3PW_{12}O_{40}$·nH_2O, PMo_{12}), pyrrole (C_4H_5N, Py), and tetraethyl orthosilicate (TEOS) were purchased from Alfa Aesar Co. Ltd. Commercial 20% Pt/C was bought from Johnson Matthey. All reagents were used without further treatment.

Synthesis of S-1. The SiO_2 nanospheres with positive charges (SiO_2 (+)) were synthesized according to the reported literature.[1] 0.1 g of SiO_2 (+) nanospheres were first dispersed into 100 mL of ultra-purified water by sonicating. After 5 h, 1.7 g of PMo_{12} was added and vigorously stirred for 3 h. Afterward, Py solution (0.5 mL in 30 mL absolute alcohol) was added to the mixture following by stirring for 12 h. The SiO_2@PMo_{12}@PPy composite was obtained by centrifugation and then washed with ethanol/water for five times, respectively. Then, the resulting SiO_2@PMo_{12}@PPy hybrid was annealed under Ar atmosphere at 900 ^{o}C for 4 h (denoted as SiO_2@Mo_xC@NPC). Finally, the SiO_2@Mo_xC@NPC was etched by 10% HF solution to gain the S-1 composite. The yield of S-1 is about 83.2%.

Synthesis of S-2. The S-2 sample was prepared under the similar condition except that the SiO_2 templates were not used. The yield of S-2 is about 91.3%.

Instruments. The scanning electron microscope images were obtained from JSM-7600F. The transmission electron microscopy (TEM) and high-resolution TEM images were collected on JEOL JEM-2100F with an accelerating voltage of 200 kV. The powder X-ray diffraction (PXRD) tests were carried out on D/max 2500VL/PC diffractometer with Cu Kα radiation. X-ray photon spectroscopy (XPS) was measured on PHI 5000 Verasa utilizing Al k_α radiation. In terms of N_2 sorption isotherm, the specific surface area and pore size distribution calculated by density functional theory (DFT) method were evaluated, which was acquired on Micromeritics ASAP 2050.

Electrochemical measurements. The HER electroactivity was investigated on an electrochemical work station (CHI 760D) in N_2-saturatd 0.5 M H_2SO_4 solution, wherein a graphite rod and a saturated calomel electrode (SCE) were elected as the counter electrode and reference electrode, respectively. The reversible hydrogen electrode (RHE) calibration were carried out according to the reported literature (*ACS Energy Lett.* 2020, 5, 1083-1087.). $E_{\mathrm{RHE}} = E_{\mathrm{SCE}} + 0.258$. Linear sweep voltammetry (LSV) was tested at 2 mV s^{-1} with 95% *iR* drop compensation. To assess the electrochemical active surface area of the resultant catalysts, cyclic voltammograms (CV) cycles were carried out from 108 to 208 mV with different scan rates of 20-200 mV s^{-1}. The electrochemical impedance spectroscopy (EIS) analysis was performed over the range of 100 kHz - 100 mHz at an overpotential of -152 mV.

To fabricate the working electrode, 2 mg of the as-synthesized material, 0.2 mL of Nafion (5 wt%), and 0.9 mL of ethanol were dispersed to form uniform ink with sonication. Subsequently, 5 µL of the resulting ink was loaded on a glassy carbon electrode. The mass loading of the catalyst is 0.142 mg cm^{-2}.

1. Chen, Y.; Li, Z.; Zhu, Y.; Sun, D.; Liu, X.; Xu, L.; Tang, Y. *Adv. Mater.* 2019, **31**, 1806312.

S1. Figures in Supporting Information

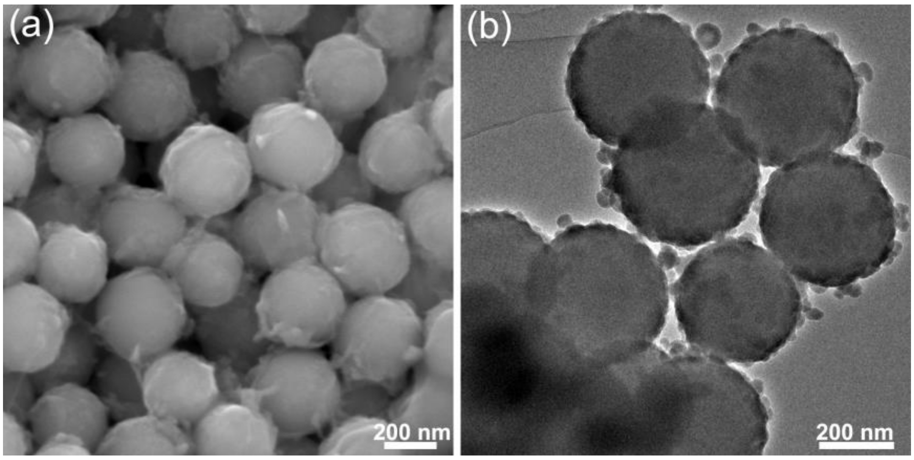


Fig. S1 (a) SEM and (b) TEM images of $SiO_2/PMo_{12}@PPy$.

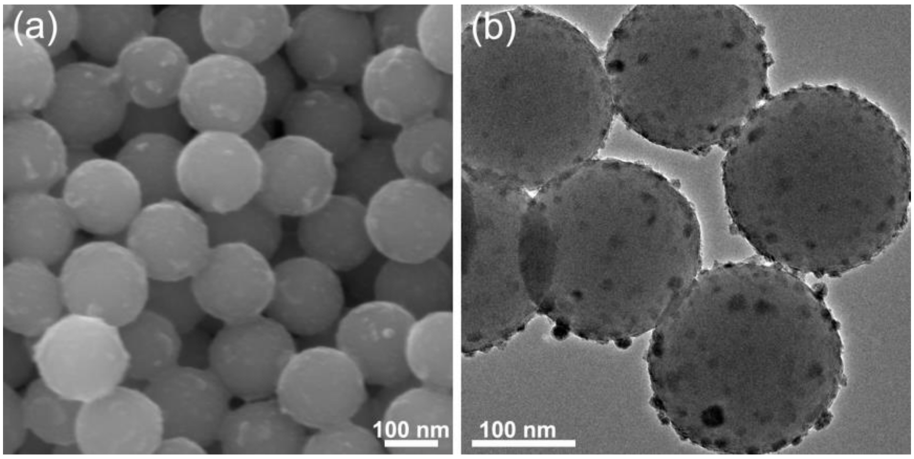


Fig. S2 (a) SEM and (b) TEM images of SiO_2/Mo_xC@NPC.

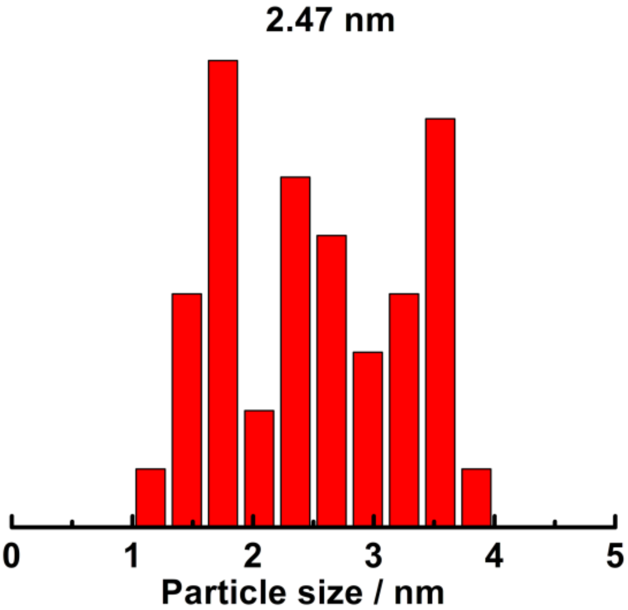


Fig. S3 The particle size distribution of Mo_xC for S-1.

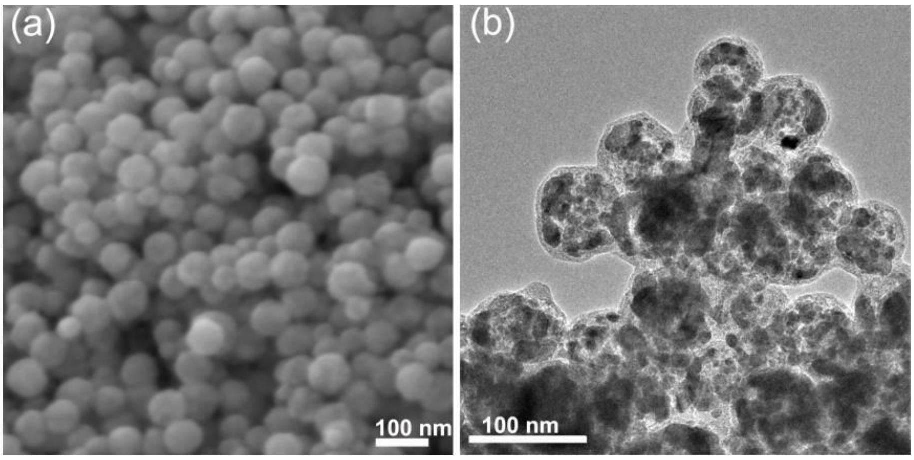


Fig. S4 (a) SEM and (b) TEM images of S-2.

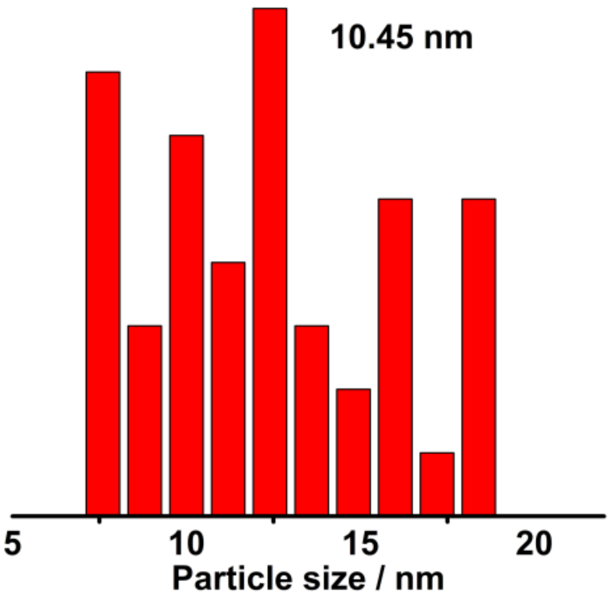


Fig. S5 The particle size distribution of Mo_xC for S-2.

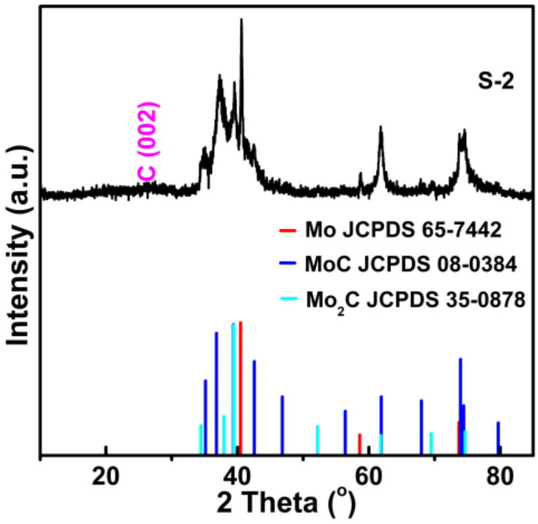


Fig. S6 PXRD pattern of S-2.

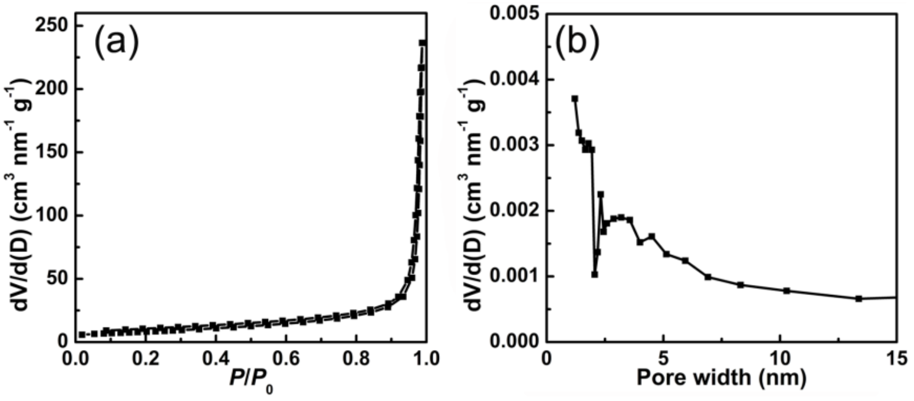


Fig. S7 (a) N_2 sorption isotherm and (b) pore size distribution of S-2.

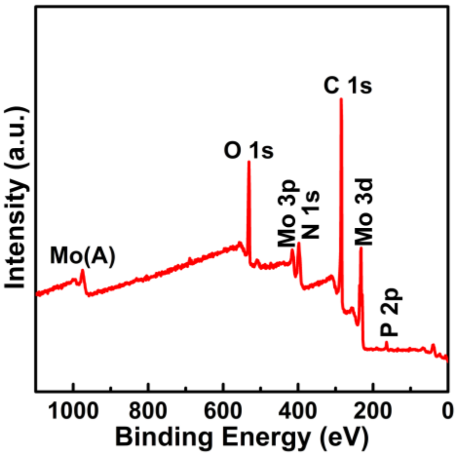


Fig. S8 XPS survey spectrum of S-1.

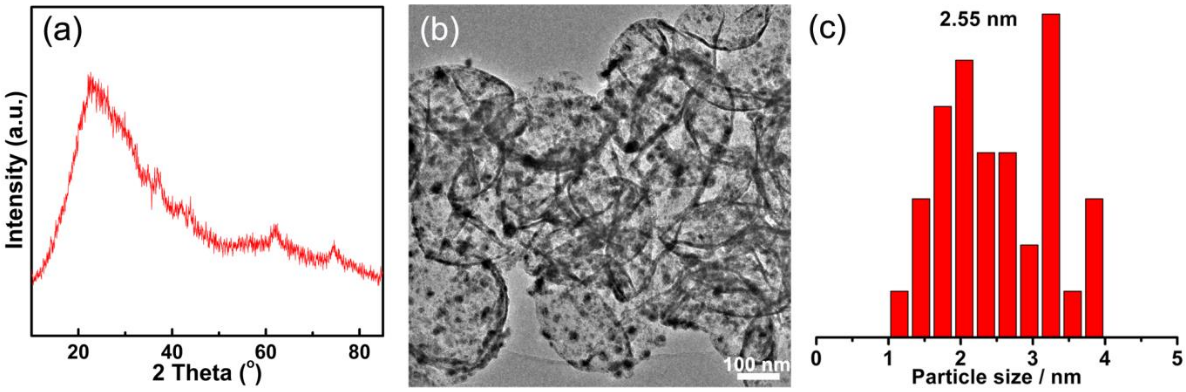


Fig. S9 (a) PXRD, (b) TEM image and (c) particle size distribution of Mo_xC for S-1 after long-term stability.

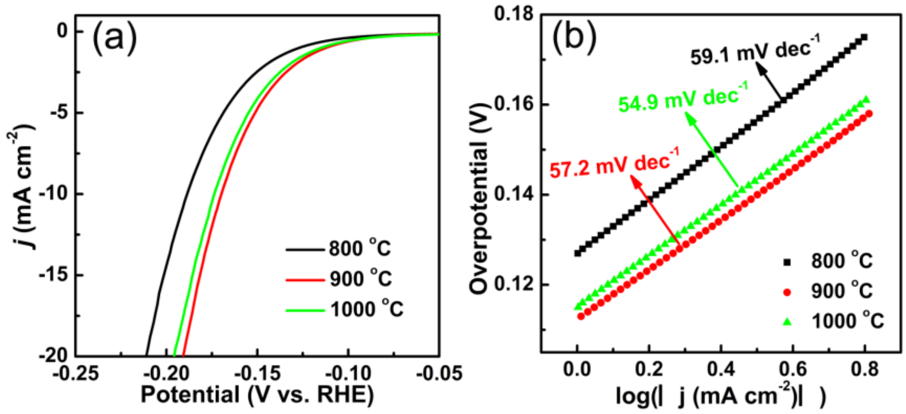
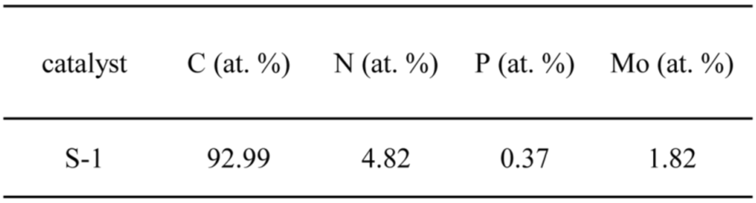


Fig. S10 Electrocatalytic performance of different samples carbonized at 800, 900, and 1000 °C, respectively. (a) Polarization curves and (b) Tafel plots.

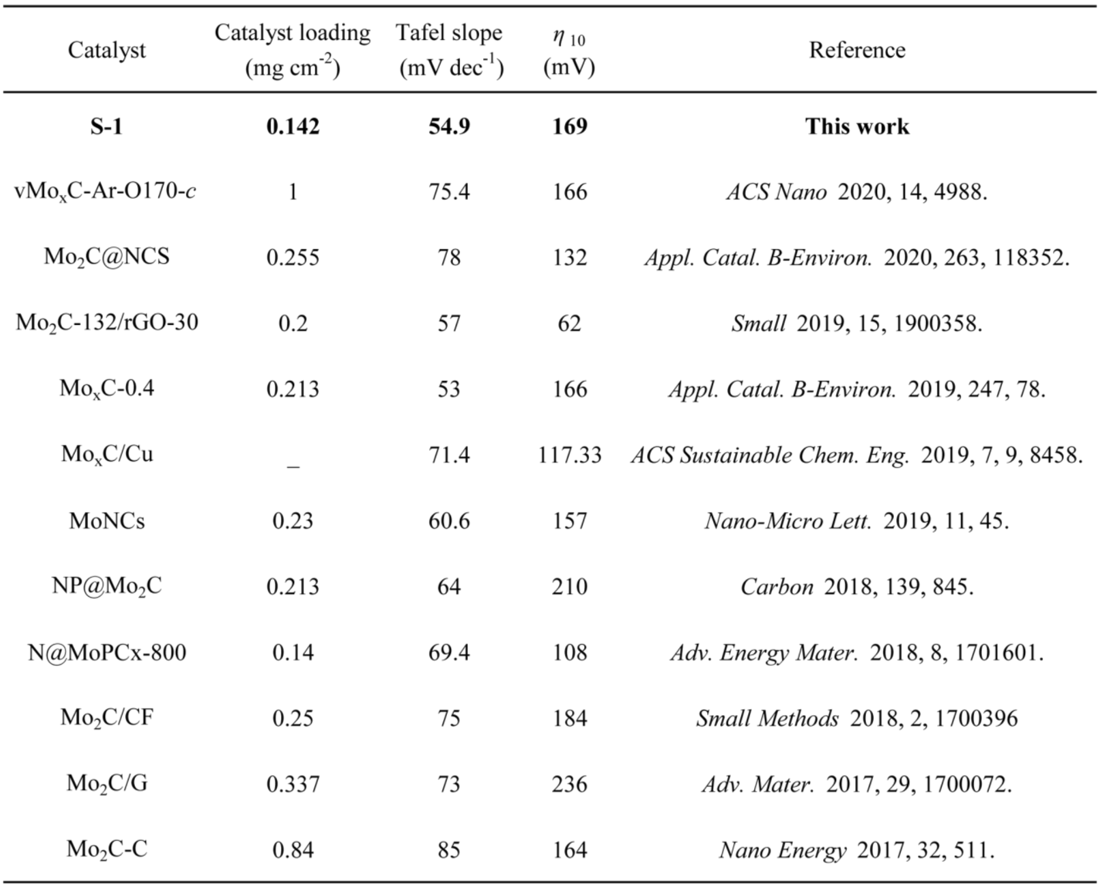
S2. Tables in Supporting Information

Table S1. Elemental compositions of S-1 determined by EDS.



catalyst	C (at. %)	N (at. %)	P (at. %)	Mo (at. %)
S-1	92.99	4.82	0.37	1.82

Table S2. Comparison of electrocatalytic performance of Mo_xC-based HER catalysts.



Catalyst	Catalyst loading (mg cm^{-2})	Tafel slope (mV dec^{-1})	η_{10} (mV)	Reference
S-1	**0.142**	**54.9**	**169**	**This work**
vMo_xC-Ar-O170-*c*	1	75.4	166	*ACS Nano* 2020, 14, 4988.
Mo_2C@NCS	0.255	78	132	*Appl. Catal. B-Environ.* 2020, 263, 118352.
Mo_2C-132/rGO-30	0.2	57	62	*Small* 2019, 15, 1900358.
Mo_xC-0.4	0.213	53	166	*Appl. Catal. B-Environ.* 2019, 247, 78.
Mo_xC/Cu	_	71.4	117.33	*ACS Sustainable Chem. Eng.* 2019, 7, 9, 8458.
MoNCs	0.23	60.6	157	*Nano-Micro Lett.* 2019, 11, 45.
NP@Mo_2C	0.213	64	210	*Carbon* 2018, 139, 845.
N@MoPCx-800	0.14	69.4	108	*Adv. Energy Mater.* 2018, 8, 1701601.
Mo_2C/CF	0.25	75	184	*Small Methods* 2018, 2, 1700396
Mo_2C/G	0.337	73	236	*Adv. Mater.* 2017, 29, 1700072.
Mo_2C-C	0.84	85	164	*Nano Energy* 2017, 32, 511.