Supplementary Material

Single-Atomic Mn Sites of Electronic Configuration Regulation mediated by Mo/Mn Clusters for Efficient Hydrogen Evolution Reaction

Chengyu Zhang [a,b,c], Xiangyang Wang [a,b,c], Renyuan Zhao [a,b,c], Fabrice Ndayisenga [a,b,c], Zhisheng Yu [a,b,c] *

[a] College of Resources and Environment, University of Chinese Academy of Sciences, 19 A Yuquan Road, Beijing 100049, P.R. China;

[b] Binzhou Institute of Technology, Weiqiao-UCAS Science and Technology Park, Binzhou City 256606, Shandong Province, P.R. China;

[c] RCEES-IMCAS-UCAS Joint-Lab of Microbial Technology for Environmental Science, Beijing 100085, China.

* Corresponding author.

Correspondence should be addressed to Prof. Zhisheng Yu (yuzs@ucas.ac.cn), Tel.: +86-10-88256057; Fax: +86-10-88256057.

Text S1 Experimental Procedures

Electrochemical measurement

The electrochemical research uses a standard three-electrode electrolytic cell with 0.5 M H_2SO_4, in which the saturated calomel electrode (SCE) is used as the reference electrode, the graphite rod is used as the counter electrode, and the glass carbon electrode with a diameter of 5 mm is used as the working electrode. All potentials were referenced with a reversible hydrogen electrode (RHE).

5 mg of each catalyst was added 1000 uL anhydrous ethanol and 20 uL Nafion 117 solution respectively, and ultrasonic dispersion was carried out for 50 min to form a uniform catalyst ink. 40 uL of the ink was added to the surface of a glassy carbon electrode (5 mm in diameter, superficial area: 0.19625 cm^2) and dried under ambient conditions for 4 h. The mass loading on the glassy carbon electrode was 1 mg cm^{-2}. A commercial Pt (20 wt %) on carbon was used as the reference sample.

The HER polarization curve of the catalyst-loaded glassy carbon electrode was obtained by Linear sweep voltammetry (LSV), the potential window was 0 ~ -0.6 V vs. RHE, and at a scan rate of 1 mV s^{-1}. Electrochemical impedance measurements (EIS) were carried out from 100 kHz to 100 mHz and obtained at a current density of 10 mA cm^{-2}. All subsequent measurements were corrected to an uncompensated resistance of 85% of the R_u value. The overpotential of the catalyst was obtained at current densities of 10 mA cm^{-2}. To estimate the electroactive surface area (ECSA) of the catalyst, we measured cyclic voltammograms between -0.07 ~ -0.17 V vs. RHE at scan rates of 10, 20, 40, 80, 120, 160, and 200 mV s^{-1}, respectively. The calculation of the Turnover frequency (TOF) value of the catalyst was based on the equation TOF = I/2nF. Where I, n, and F represent the current (A) obtained during the LSV test in 0.5 M H_2SO_4 solution, and the active site number of points (mol) and Faraday constant (96485 C mol^{-1}). The number 2 represents the number of moles of electrons consumed to liberate 1 mol H_2 from water.

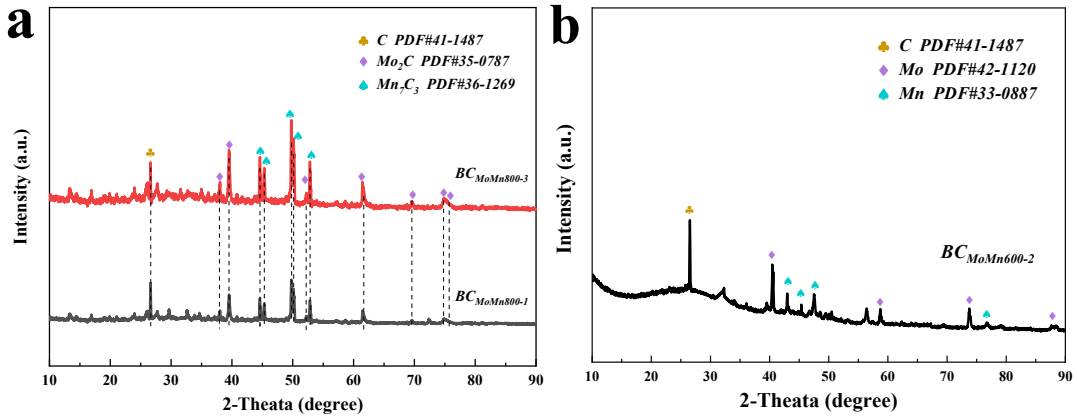


Figure S1. The XRD spectra of a) $BC_{MoMn800\text{-}1}$ and $BC_{MoMn800\text{-}3}$, b) $BC_{MoMn600\text{-}2}$.

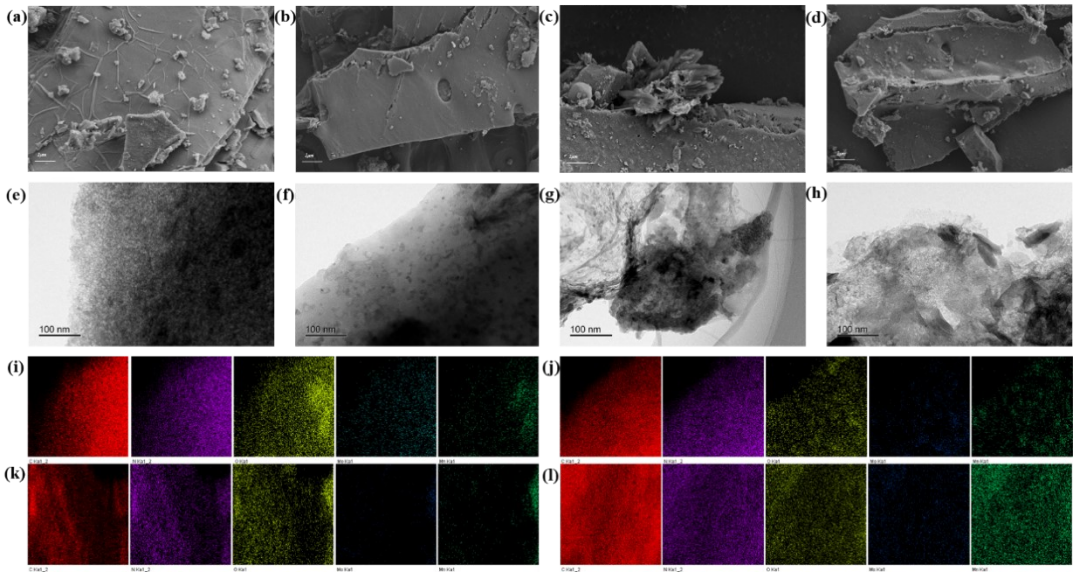
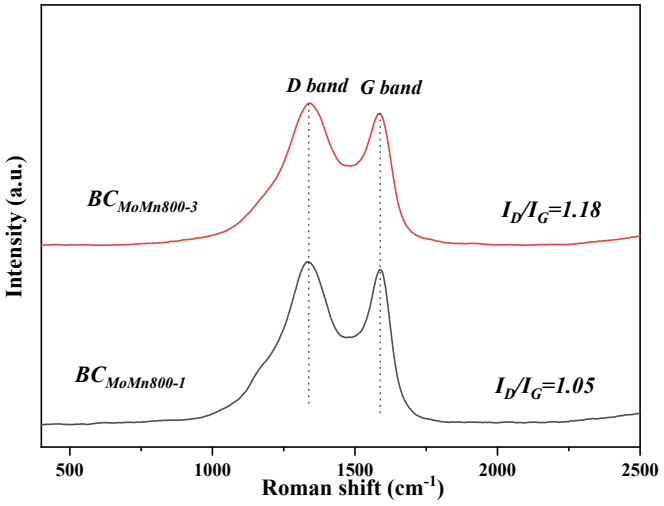
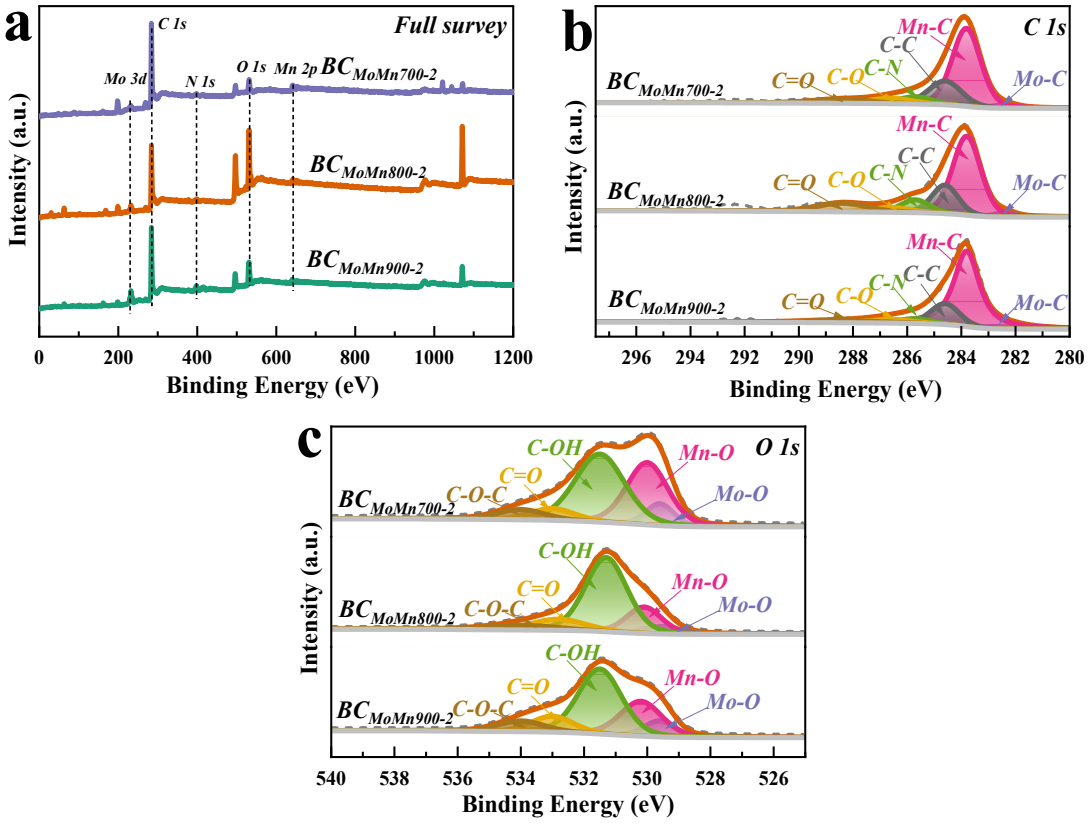


Figure S2. a-d) FESEM, e-h) TEM, and i-l) corresponding EDS line-scan elemental of $BC_{MoMn700\text{-}2}$, $BC_{MoMn800\text{-}1}$, $BC_{MoMn800\text{-}3}$, and $BC_{MoMn900\text{-}2}$.



57

58 **Figure S3.** The Raman spectra of $BC_{MoMn800-1}$ and $BC_{MoMn800-3}$.



59

60 **Figure S4.** The a) full survey, b) high-resolution C 1s, and c) O 1s $BC_{MoMn700-2}$, $BC_{MoMn800-2}$, and $BC_{MoMn900-2}$.

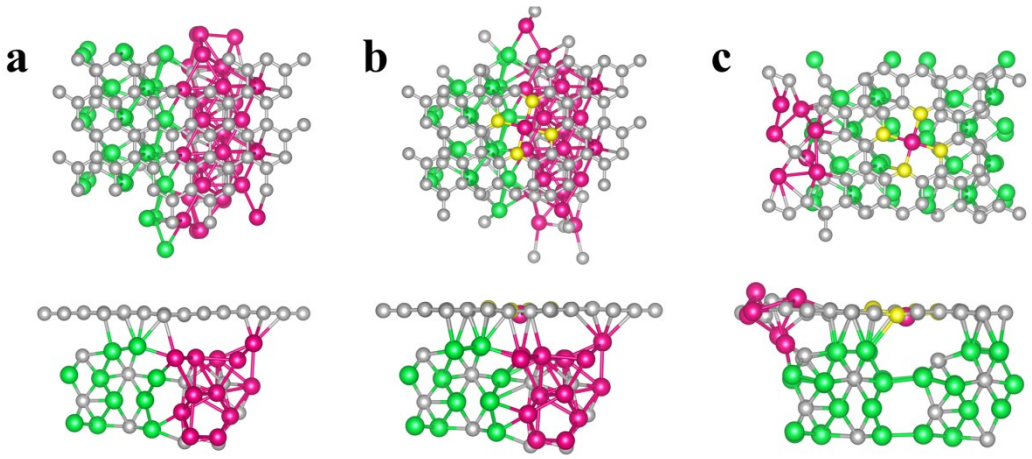


Figure S5. Different views of the optimized structural model. Top and side views of a) Mo_2C-Mn_7C_3/graphene, b) Mo_2C-Mn_7C_3/MnN_4-graphene, and c) Mo_2C/Mn_7C_3-MnN_4-graphene with H adatom.

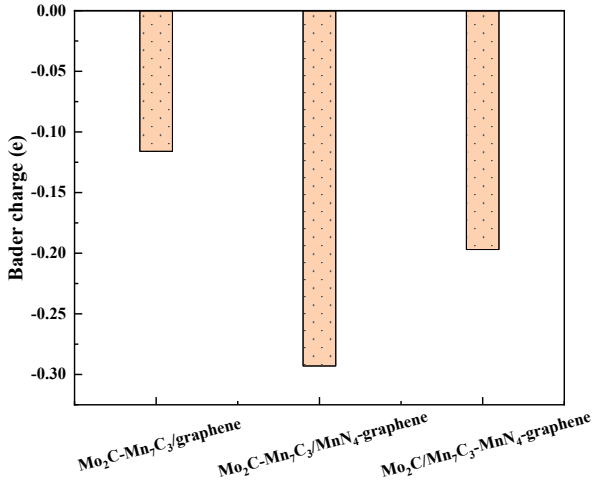
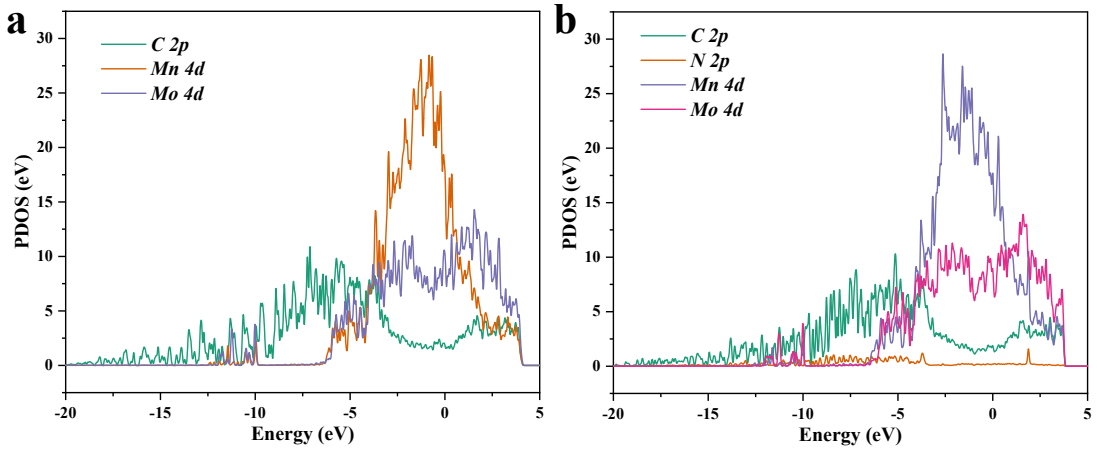
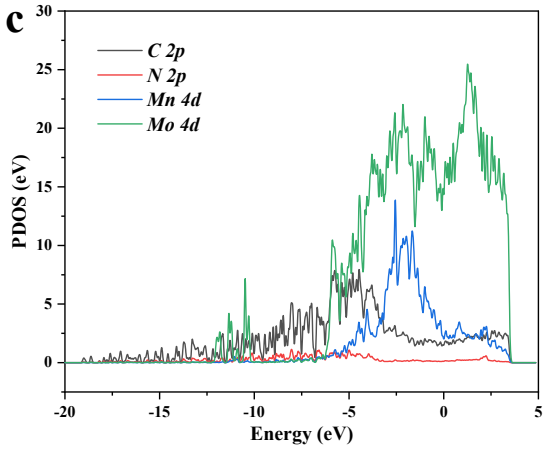


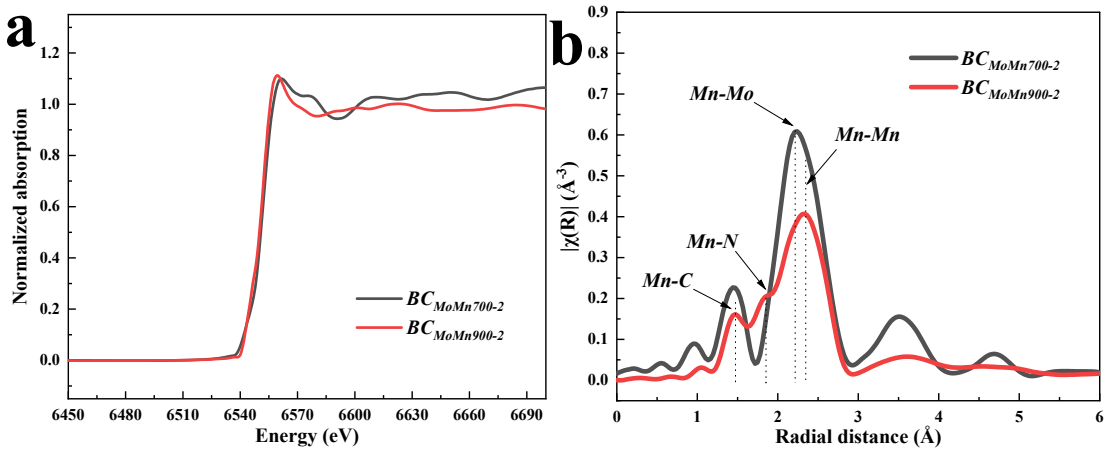
Figure S6. Calculation of Bader charge on Mo_2C-Mn_7C_3/graphene, Mo_2C-Mn_7C_3/MnN_4-graphene, and Mo_2C/Mn_7C_3-MnN_4-graphene.





68

69 **Figure S7.** Density of states of a) Mo_2C-Mn_7C_3/graphene, b) Mo_2C-Mn_7C_3/MnN_4-graphene, and c) Mo_2C/Mn_7C_3-
70 MnN_4-graphene systems.



71

72 **Figure S8.** a) Mn K-edge XANES and b) Fourier transforms of EXAFS spectra of $BC_{MoMn700\text{-}2}$ and $BC_{MoMn900\text{-}2}$.

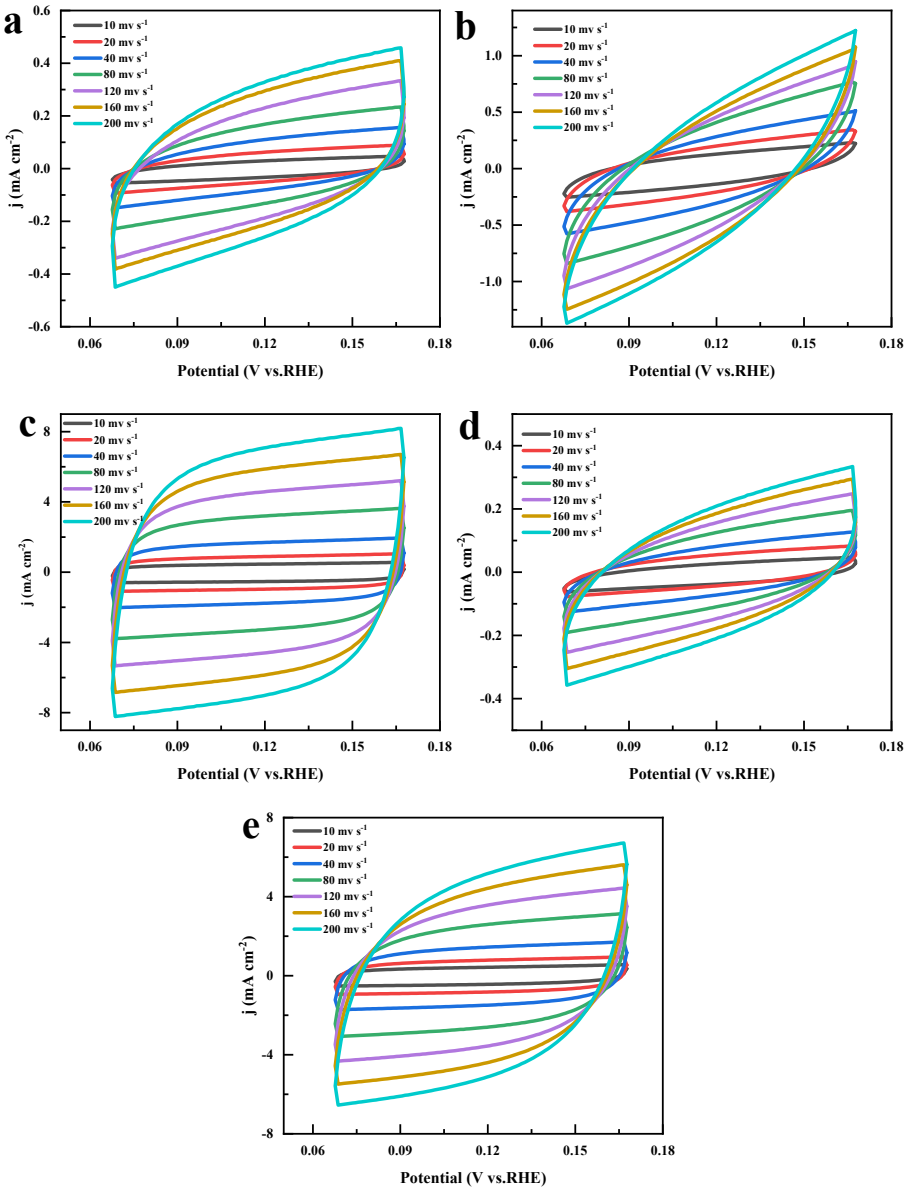


Figure S9. CV curves at different scan rates (10, 20, 40, 80, 120, 160, 200 mV s^{-1}) of a) $BC_{MoMn700\text{-}2}$, b) $BC_{MoMn800\text{-}1}$, c) $BC_{MoMn800\text{-}2}$, d) $BC_{MoMn800\text{-}3}$, and e) $BC_{MoMn900\text{-}2}$.

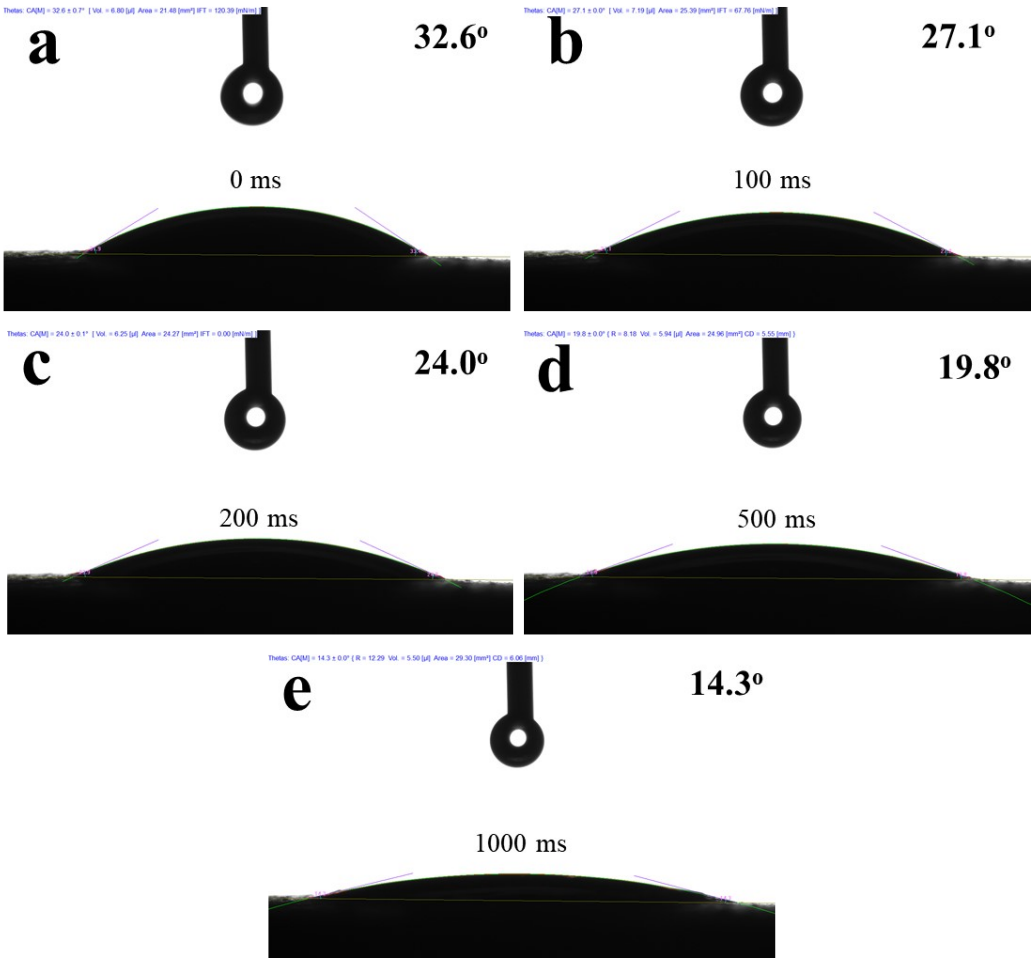


Figure S10. Contact angle images between water and electrodes of $BC_{MoMn800\text{-}2}$.

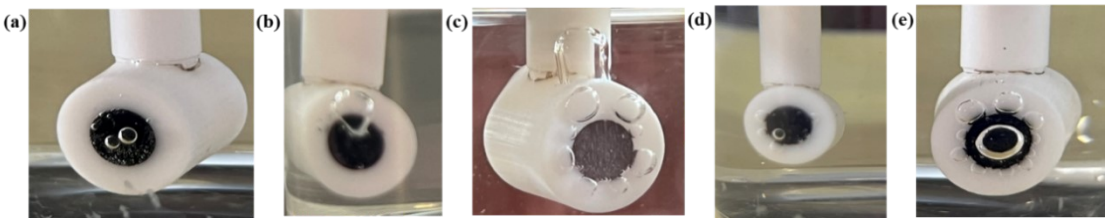


Figure S11. A map of the bubbles on the electrode surface. a) $BC_{MoMn700\text{-}2}$, b) $BC_{MoMn800\text{-}1}$, and c) $BC_{MoMn800\text{-}2}$, d) $BC_{MoMn800\text{-}3}$, e) $BC_{MoMn900\text{-}2}$.

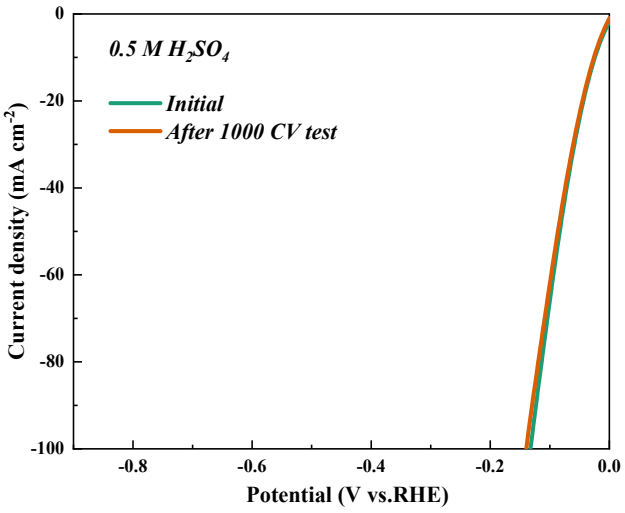


Figure S12. HER polarization curves of $BC_{MoMn800-2}$ after 1000 CV cycles test at the scan rate of 100 mV s^{-1}.

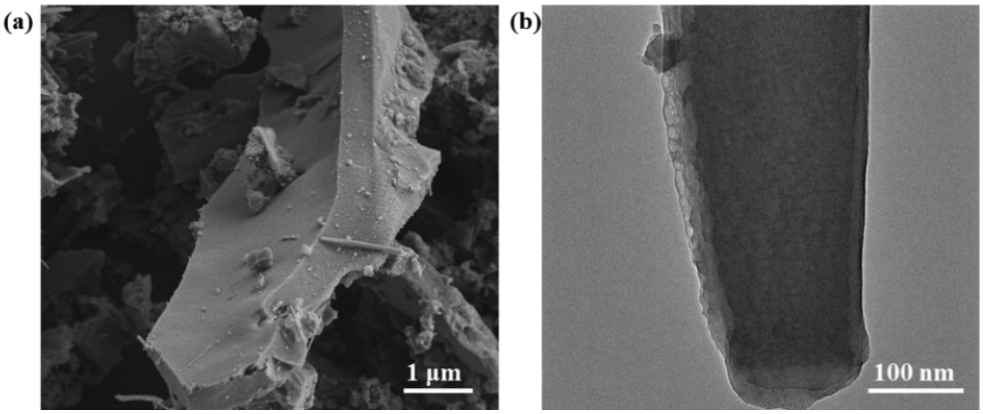


Figure S13. SEM and TEM images of $BC_{MoMn800-2}$ after CV tests.

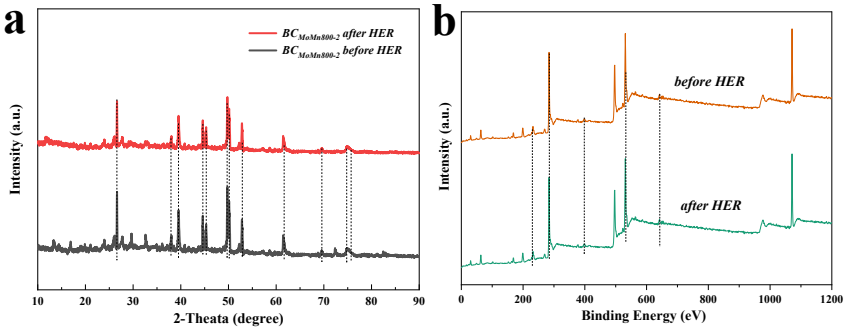
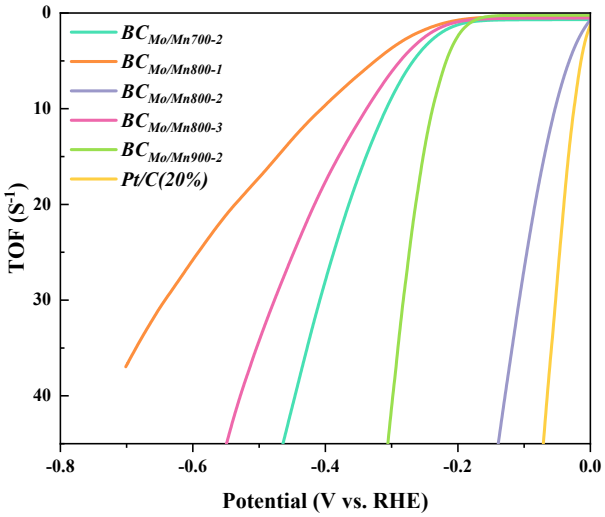
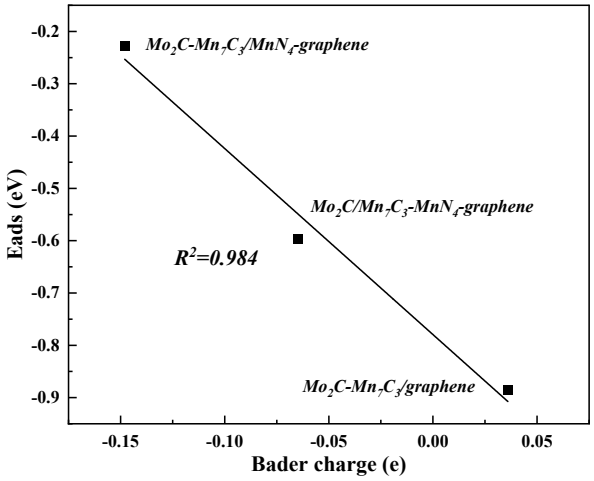


Figure S14. XRD and XPS spectra of $BC_{MoMn800-2}$ after CV tests.



87

88 **Figure S15.** TOF curves of $BC_{MoMn700-2}$, $BC_{MoMn800-1}$, $BC_{MoMn800-2}$, $BC_{MoMn800-3}$ and $BC_{MoMn900-2}$.



89

90 **Figure S16.** The correlation of atomic H adsorption energy with the charge transfer. R^2, coefficient of

91 determination.

92

93 **Table S1**

94 **Table S1** The content of Mo and Mn elements were detected by ICP-OES.

Samples	The content of Mo element in the samples (wt%)	The content of Mn element in the samples (wt%)
$BC_{MoMn700-2}$	4.12	6.15
$BC_{MoMn800-1}$	4.41	3.86
$BC_{MoMn800-2}$	6.53	8.61
$BC_{MoMn800-3}$	9.79	11.21
$BC_{MoMn900-2}$	8.58	10.93

95

96

Table S2

Table S2 Quantitative analysis of functional groups in XPS spectra.

N 1s

Sample	Surface functional group	Group content on the surface (at.%)
$BC_{MoMn700-2}$	oxidized-N	39.6
	graphitic-N	27.7
	pyrrolic-N	15.0
	pyridinic-N	17.7
$BC_{MoMn800-2}$	oxidized-N	24.2
	graphitic-N	42.6
	Mn-N	21.4
	pyridinic-N	11.8
$BC_{MoMn900-2}$	oxidized-N	14.4
	graphitic-N	41.4
	Mn-N	19.9
	pyridinic-N	24.3

Mo 3d

Sample	Surface functional group	Group content on the surface (at.%)
$BC_{MoMn700-2}$	Mo^{2+}	57.2
	Mo^{4+}	16.6
	Mo^{6+}	26.2
$BC_{MoMn800-2}$	Mo^{2+}	51.3
	Mo^{4+}	28.2
	Mo^{6+}	20.5
$BC_{MoMn900-2}$	Mo^{2+}	24.4

	Mo^{4+}	54.4
	Mo^{6+}	21.2

Mn 2p

Sample	Surface functional group	Group content on the surface (at.%)
$BC_{MoMn700-2}$	Mn^{2+}	41.6
	Mn^{3+}	58.4
$BC_{MoMn800-2}$	Mn^{2+}	47.7
	Mn^{3+}	52.3
$BC_{MoMn900-2}$	Mn^{2+}	55.0
	Mn^{3+}	45.0