Supporting Information

Interfacial Electron Transfer Relay Center for Accelerating the Hydrogen Evolution Reaction

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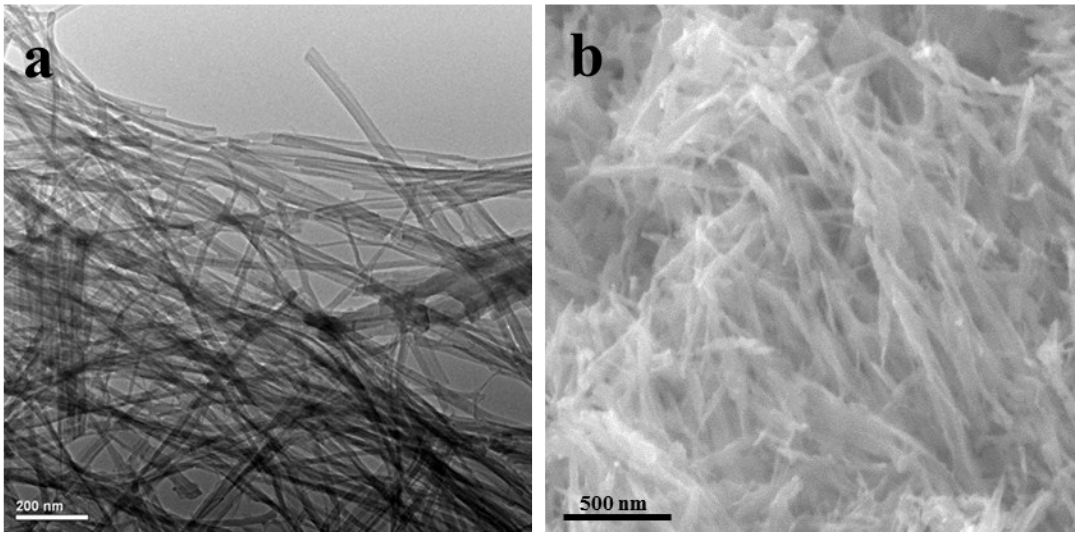

Figure S1. (a) TEM image of Mo-polymelamine precursor; (b) SEM image of S-800.

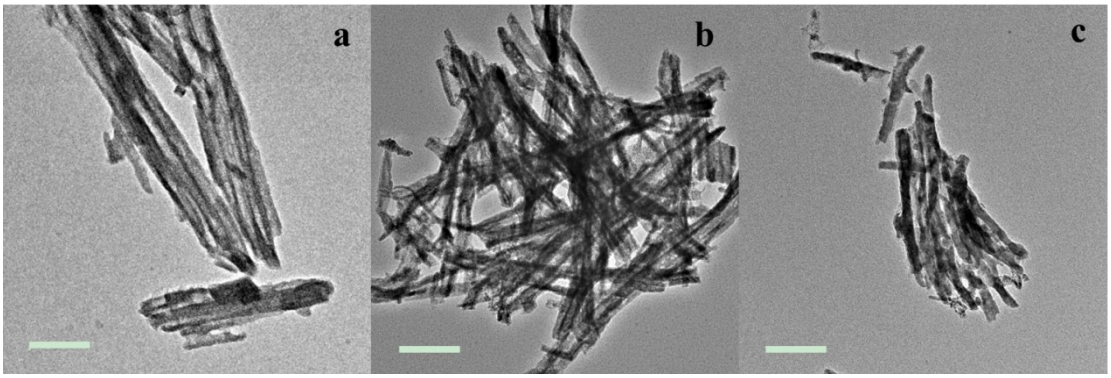

Figure S2. TEM images of S-700 (a), S-750 (b), and S-850 (c). The scar bar is 100 nm.

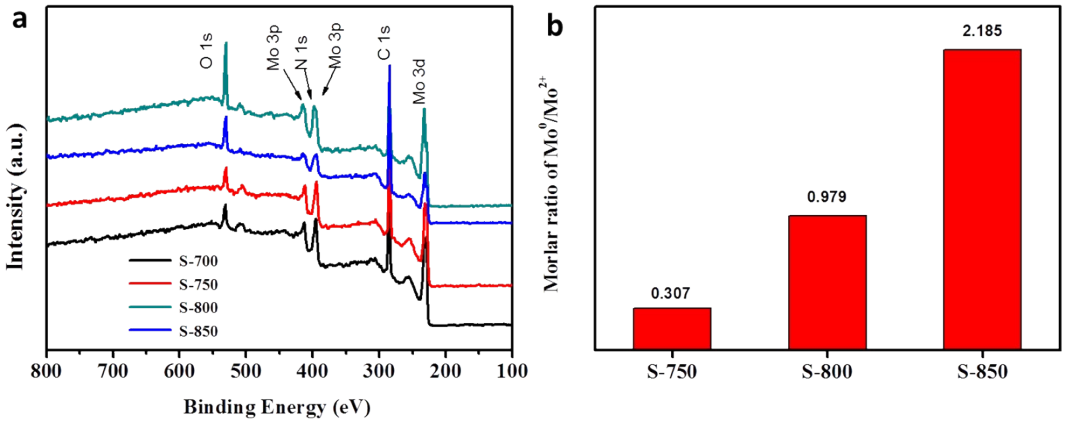

Figure S3. (a) XPS spectra of S-700, S-750, S-800, and S-850; (b) molar ratio of Mo^0/Mo^{2+} of S-750, S-800, and S-850.

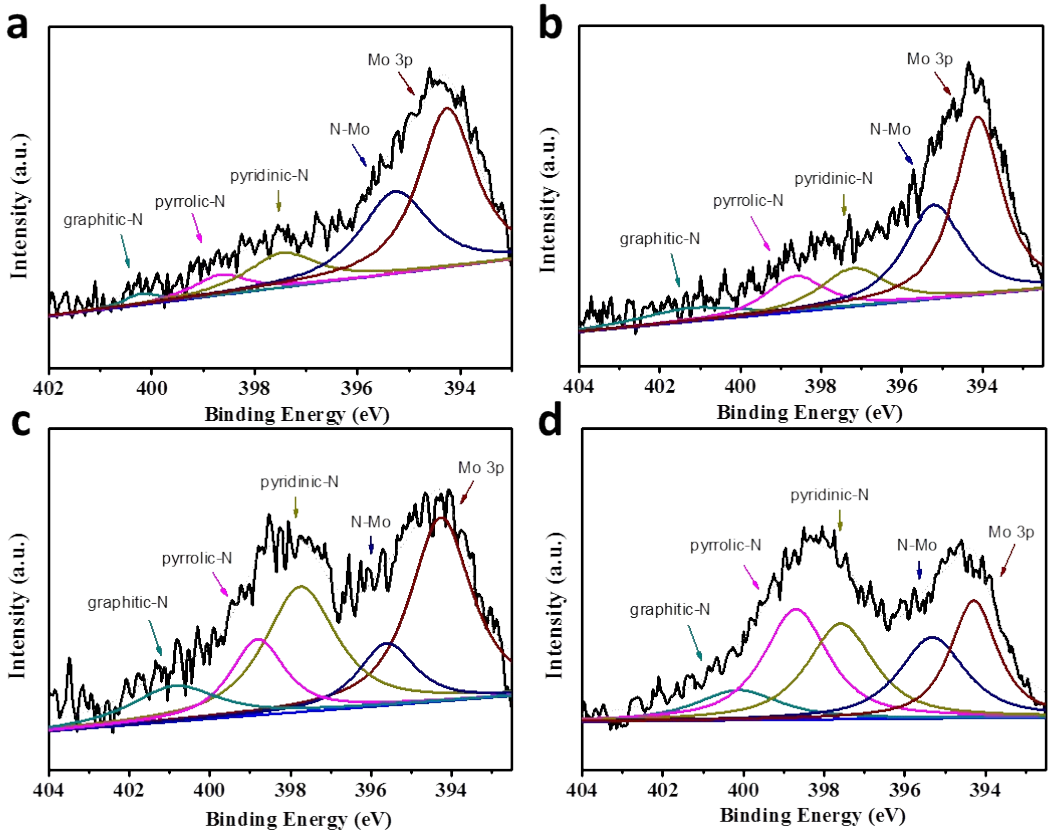

Figure S4. N1s high-resolution XPS spectra of S-700 (a), S-750 (b), S-800 (c), and S-850 (d).

As shown in Figure S4, the N 1s spectrum is deconvoluted into three peaks at 397.5, 398.7, and 400.8 eV, corresponding to pyridinic-N, pyrrolic-N, and graphitic-N, respectively. It's noteworthy that the product of S-800 exhibits the highest ratio of pyridinic-N, which has been proved to be beneficial for enhancing the catalytic performance of water splitting.

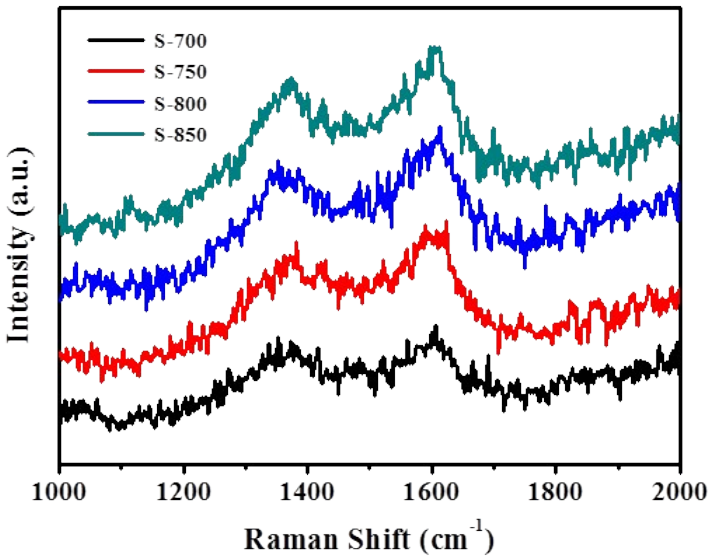

Figure S5. Raman spectra of S-700, S-750, S-800, and S-850.

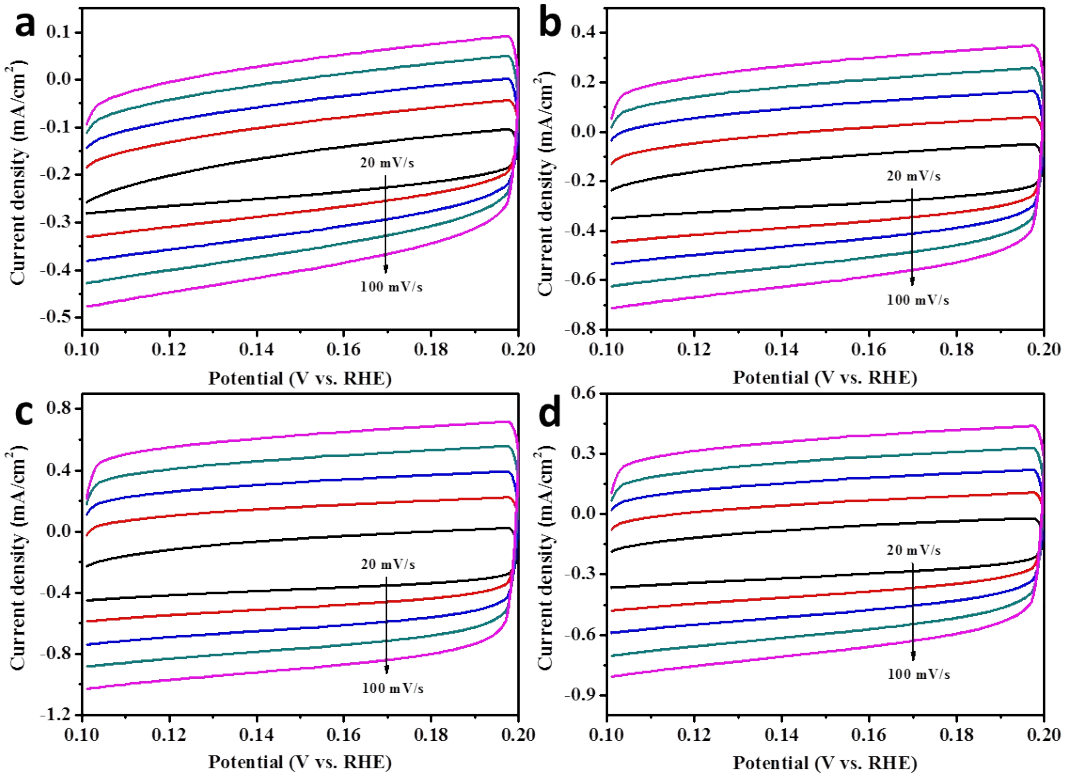

Figure S6. Cyclic voltammograms (CV) at different scan rate from 20 to 100 mV/s of S-700 (a), S-750 (b), S-800 (c), and S-850 (d).

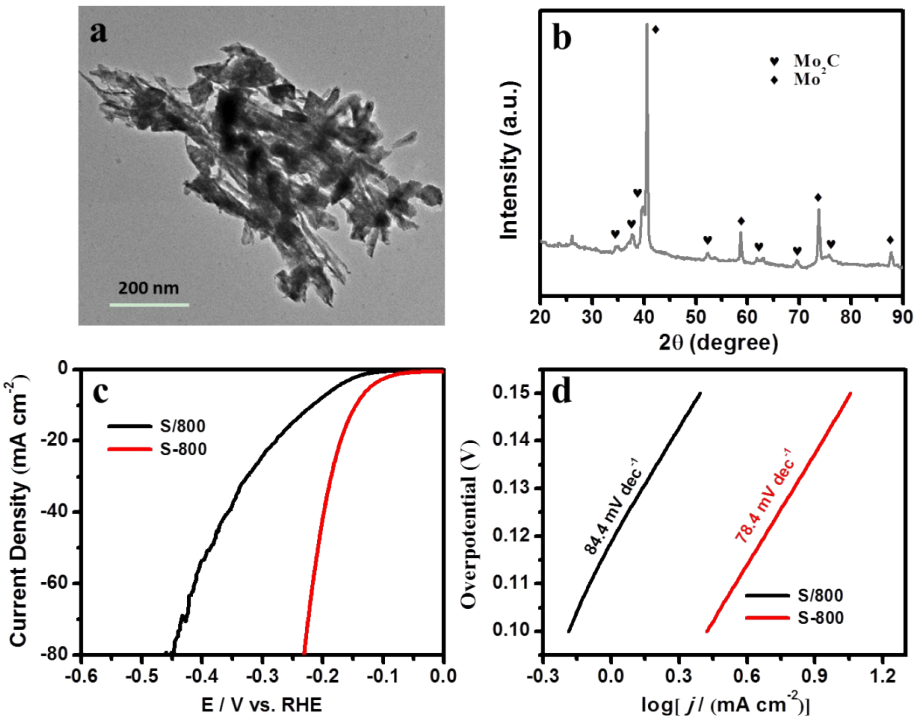

Figure S7. (a) TEM image and (b) XRD pattern of S/800; (c) LSV curves and (d) Tafel plots of S/800 and S-800. S/800 was prepared by calcinating Mo-polymelamine precuesor at 800 oC for 1h directly.

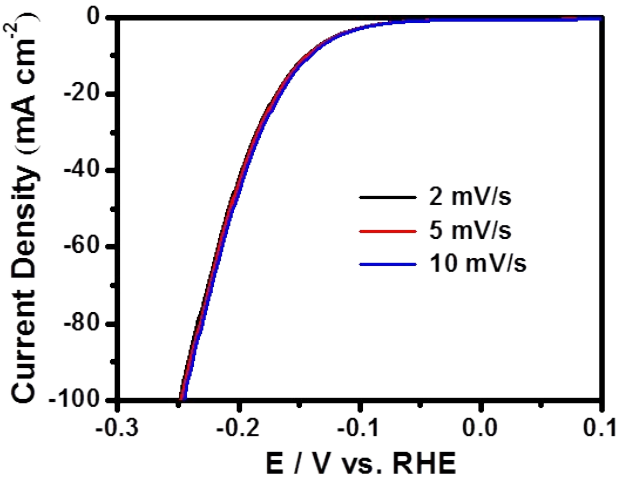

Figure S8. LSV curves of S-800 at different scan rates.

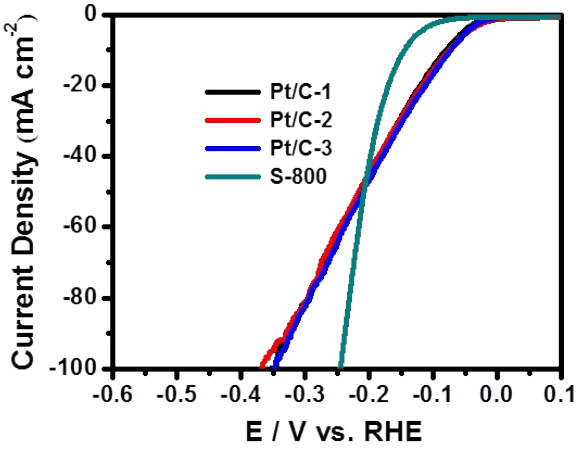

Figure S9. Polarization curves of Pt/C for three times and S-800.

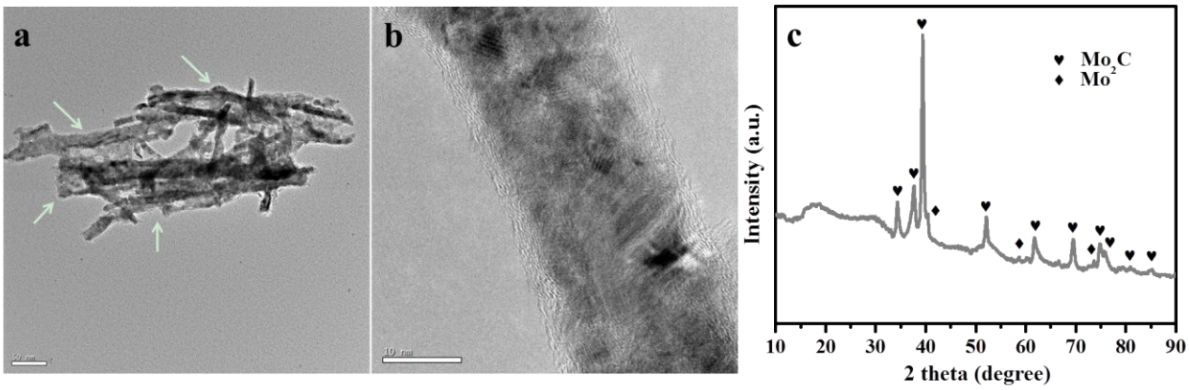

Figure S10. (a, b) TEM images, (c) XRD of S-800 after long-term stability test for 30h.

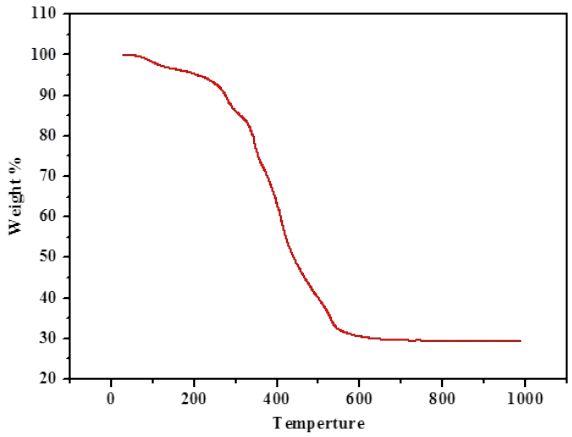

Figure S11. Thermal gravimetric analysis of the Mo-polymelamine precursor.

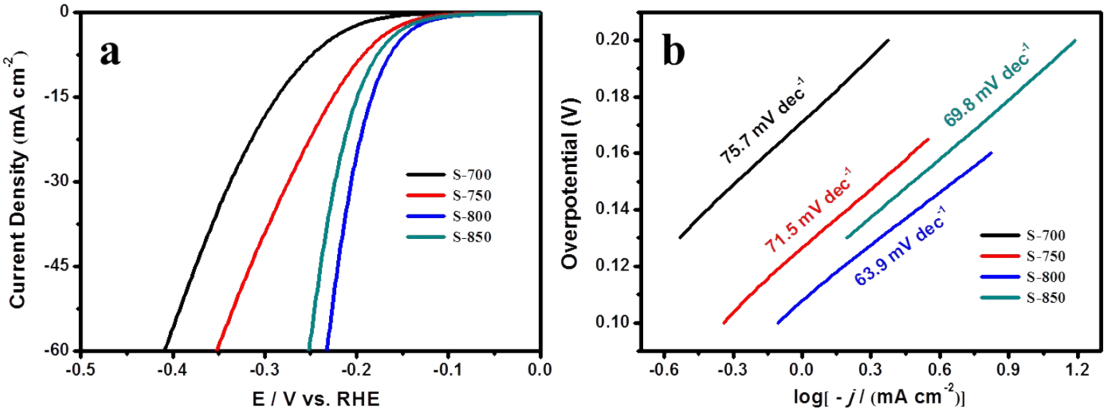

Figure S12. (a) LSV curves and (b) Tafel plots of S-700, S-750, S-800, and S-850 in 0.5 M H_2SO_4.

Table S1. Comparison of catalytic parameters of different HER catalysts.

Catalyst	Onset potential (mV)	Overpotential at 10 mA cm^{-2} (mV *vs* RHE)	j_0 (mA cm^{-2})	Tafel slope (mV dec^{-1})
S-700	304	430	0.0036	139.5
S-750	180	323	0.047	123.8
S-800	58	145	0.24	78.4
S-850	90	219	0.023	118
Pt-C	0	81	0.67	63.2

Table S2. Summary of Mo-based electrocatalysts for HER in alkaline electrolytes.

Materials	Overpotential at 10 mA cm^{-2} (mV *vs* RHE)	Tafel slope (mV dec^{-1})	j_0 (mA cm^{-2})	Mass loading (mg cm^{-2})	Electrolyte	Ref.
MoC_x	151	59	0.029	0.8	1 M KOH	1
$MoC_{0.654}$@CNS	220	\	\	\	0.1 M KOH	2
Mo_2C/C	165	63.6	\	1	1 M KOH	3
MoB	250	59	0.002	2.3	1 M KOH	4
Ni/Mo_2C	179	101	0.2	0.5	1 M KOH	5
$NiMo_3S_4$	252	98	0.039	0.3	1 M KOH	6
Mo_2C MPs	190	59	0.0038	1.1	1 M KOH	7
Mo_2N-Mo_2C/HGr-3	154	68	0.497	0.337	1 M KOH	8
Mo_2C/CNT	160	72	0.071	0.28	1 M KOH	9
MoC HNWs	221	101	0.00058	0.14	1 M KOH	10
Mo/Mo_2C@G core-shell heterointerface nanostructure	**145**	**78.4**	**0.24**	**0.28**	**1 M KOH**	**This work**

References

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