Supplementary Information

Fluorination Activates the Basal Plane HER Activity of ReS_2: A Combined Experimental and Theoretical Study

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Table S1. Atomic concentration of the samples measured by XPS.

	Atomic concentration at.%		
Peaks	ReS_2	ReS_2-$F_{4.69}$	ReS_2-$F_{5.93}$
Re 4f	33.28	34.09	34.80
S 2p	66.72	61.22	59.27
F 1s	0	4.69	5.93

Table S2. Re L3-edge EXAFS curve fitting parameters of ReS_2 and ReS_2-$F_{5.93}$.

Sample	path	*N*	*R* (Å)	σ^2 ($\times10^{-3}$ Å^2)	ΔE_0 (eV)	*R*, %
ReS_2	Re-S	4.9	1.963	0.0056	8.7	0.01
	Re-Re	2.3	2.786	0.0059		
ReS_2-$F_{5.93}$	Re-S	4.8	1.994	0.0062	7.6	0.01
	Re-Re	2.5	2.778	0.0071		

N is the coordination number; *R* represent the distance between absorber and backscatter atoms; σ^2 is regarded as Debye-Waller factor to account for both thermal and structural disorders; ΔE_0 is used as inner potential correction; The goodness of the fit is assessed by *R* factor (%). Error bounds (accuracies) that characterize the structural parameters obtained by EXAFS spectroscopy were estimated as *N* ± 20%; *R* ± 1%; σ^2 ± 20%; ΔE_0 ± 20%. S_0^2 was fixed to 1.0. Bold numbers indicate fixed coordination number (*N*) according to the crystal structure. Fitting range: 2.0 ≤ *k* (/Å) ≤ 14.5 and 1.0 ≤ *R* (Å) ≤ 3.5.

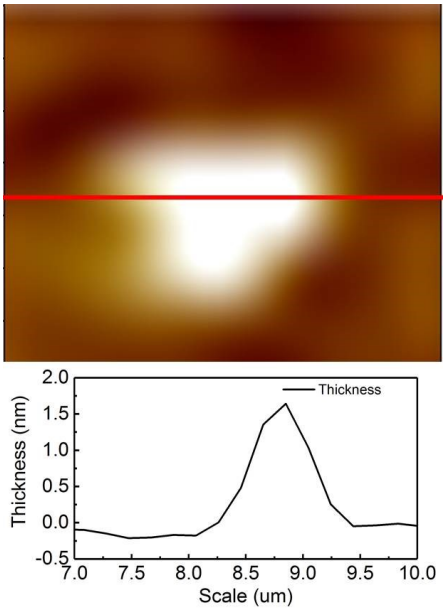

Figure S1. The AFM image and the corresponding height profile of ReS_2-$F_{5.93}$.

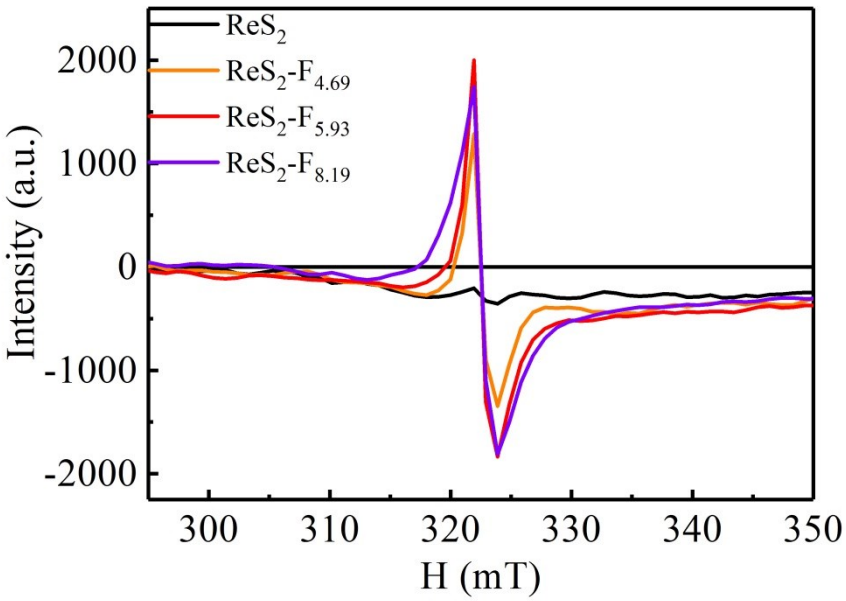

Figure S2. The ESR results ReS_2-$F_{5.93}$.

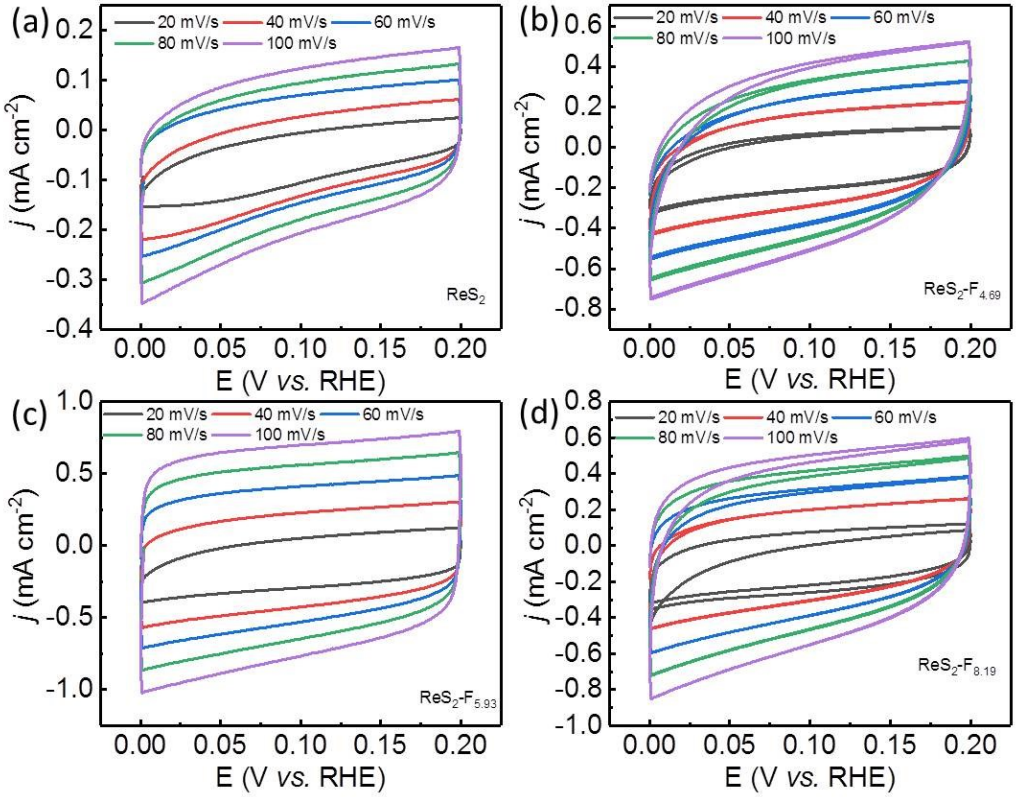

Figure S3. The CV curves of (a) ReS_2, (b) ReS_2-$F_{4.69}$, (c) ReS_2-$F_{5.93}$, and (d) ReS_2-$F_{8.19}$ at scan rates of 20, 40, 60, 80, and 100 mV s^{-1} in 0.5 M H_2SO_4.

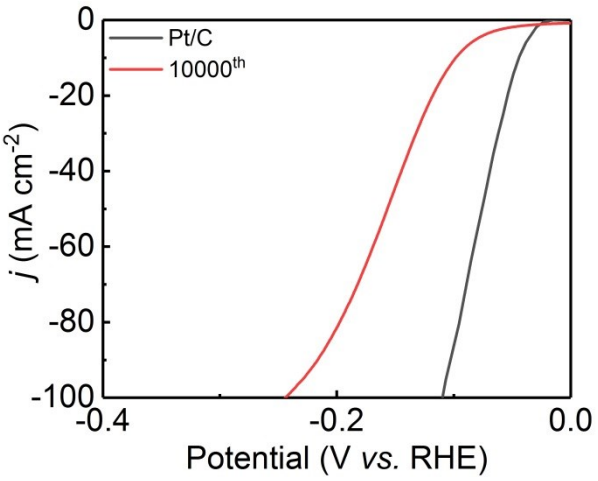

Figure S4. LSV curves of the Pt/C catalyst before and after 10000 CV cycles.

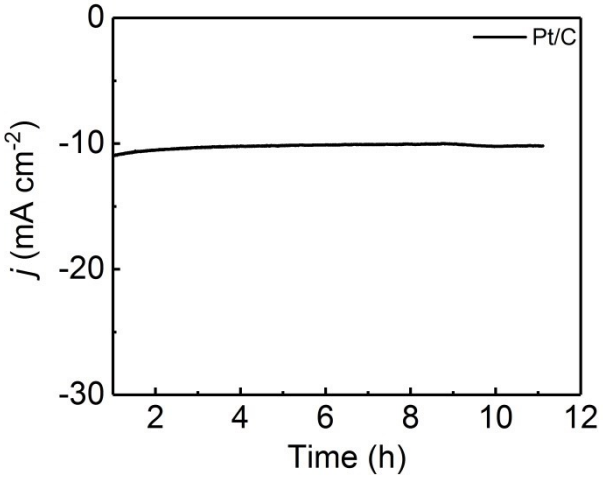

Figure S5. The Time-dependent current density curve of the Pt/C catalyst.

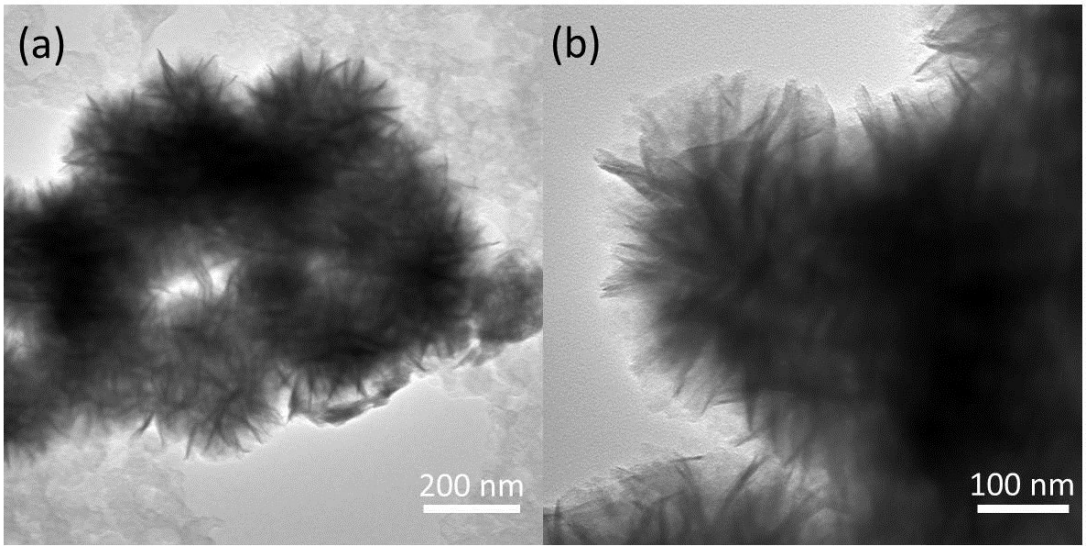

Figure S6. The SEM image of (a) pristine ReS_2 and (b) ReS_2-$F_{5.93}$ measured after the HER test.

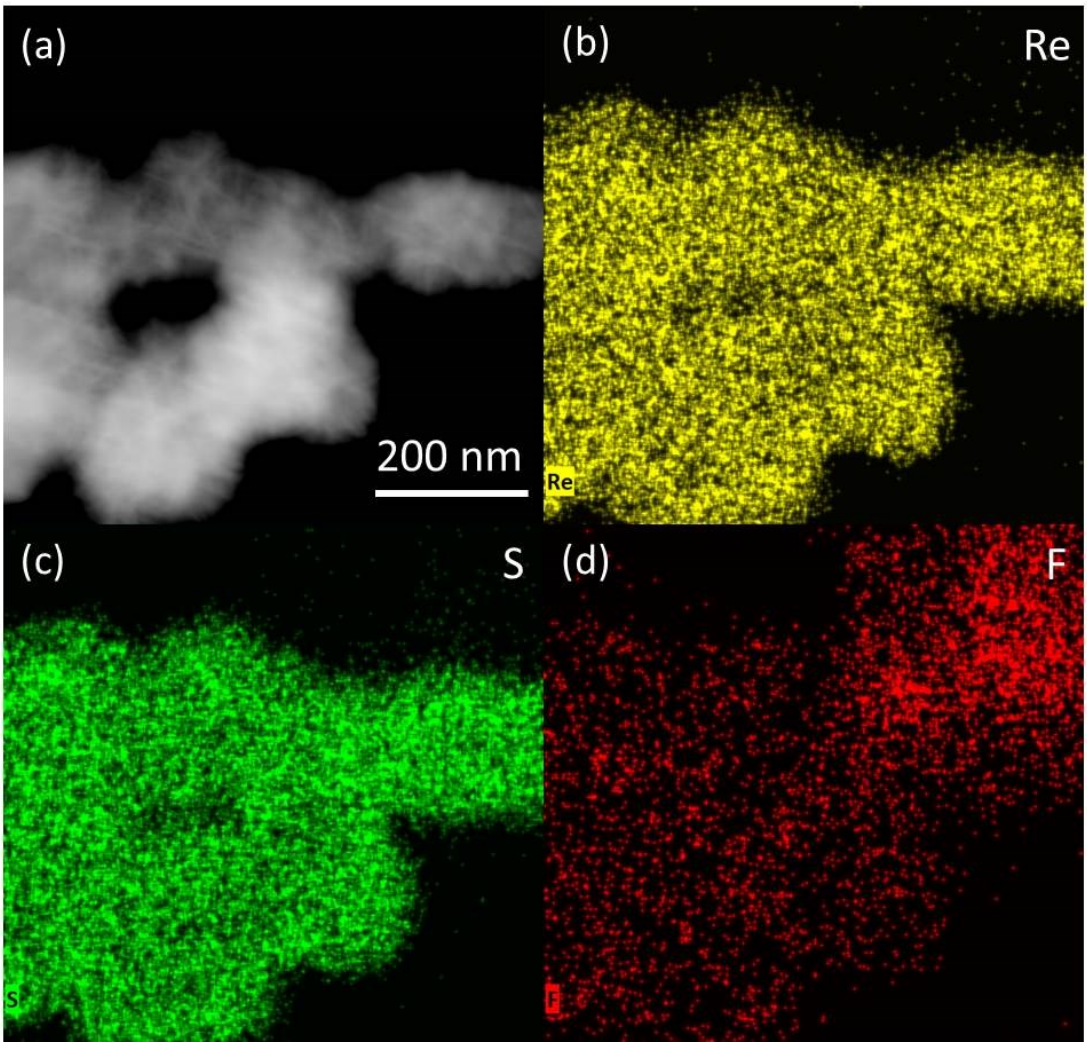

Figure S7. HAADF image and the EDX mapping of the ReS_2-$F_{5.93}$ measured after the HER test.

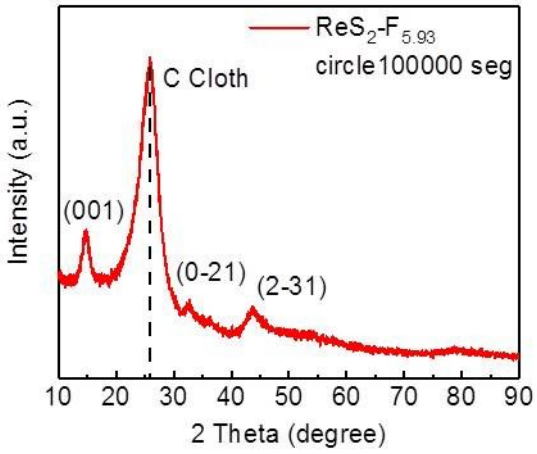

Figure S8. XRD pattern of the ReS_2-$F_{5.93}$ measured after the HER test.

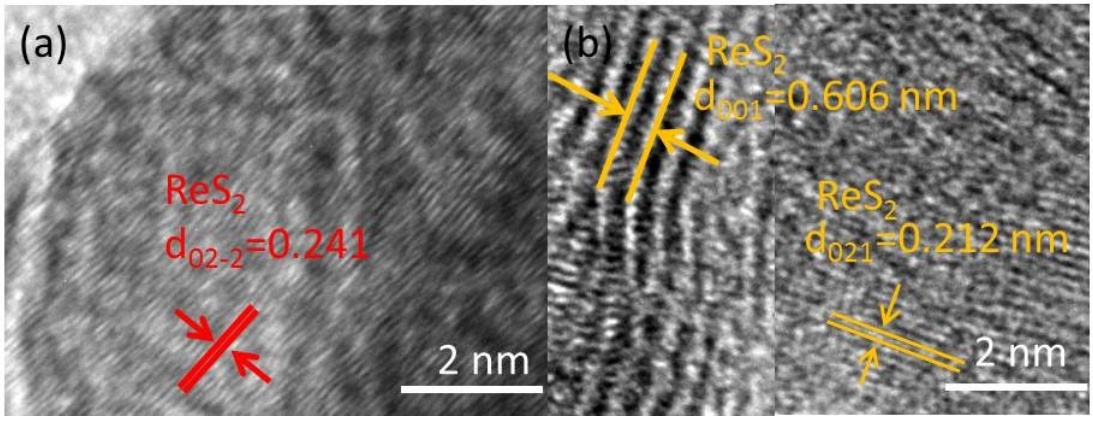

Figure S9. HRTEM image of the (a) pristine ReS_2 and (b) ReS_2-$F_{5.93}$ measured after HER test.

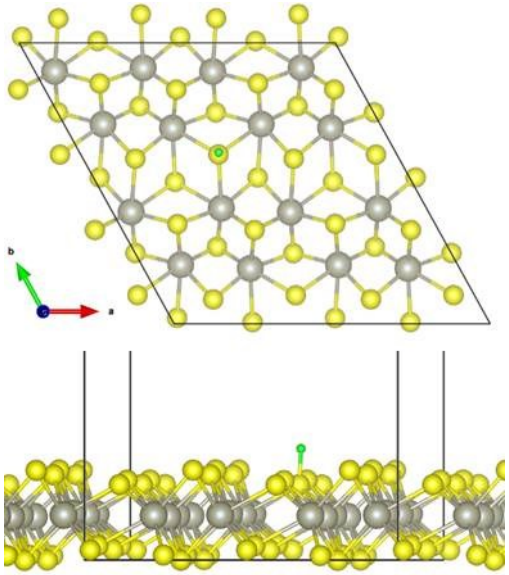

Figure S10. The calculation models of ReS_2.

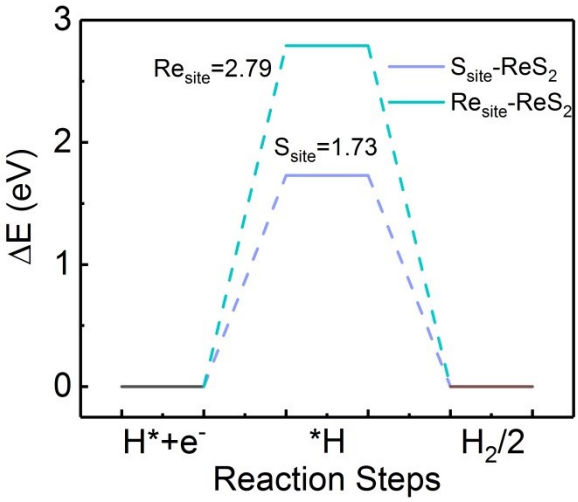

Figure S11. HER free energy diagram calculation at equilibrium potential for Re and S site of the ReS_2.