Supporting Information for

Flexible and Free-Standing Hetero-electrocatalyst of High-Valence-Cation Doped MoS_2/MoO_2/CNT Foam with Synergistically Enhanced Hydrogen Evolution Reaction Catalytic Activity

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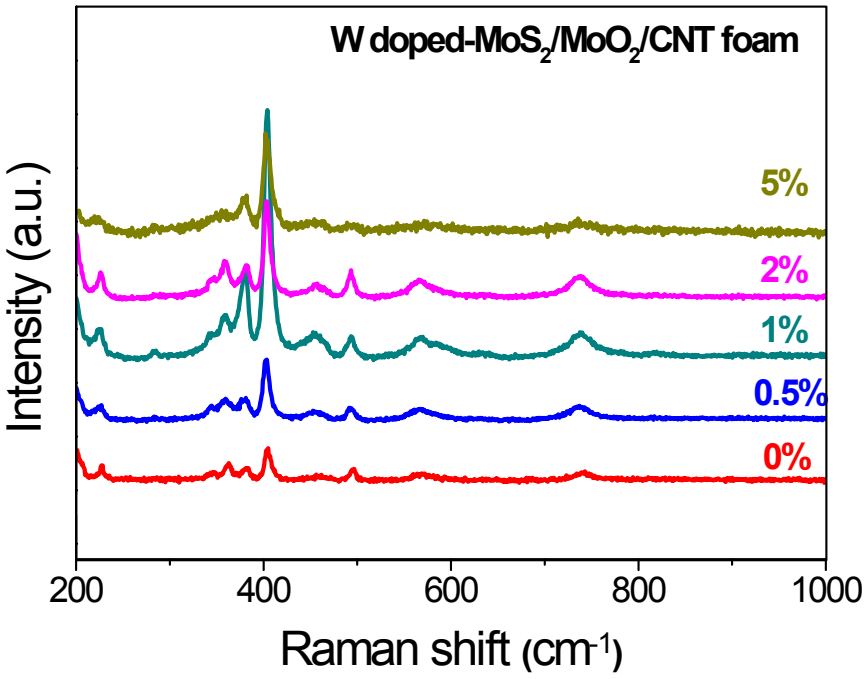


Fig. S1 Raman scan curve at different doping concentrations. As shown in the figure, the peak position and number of peaks hardly change with the change of doping concentration.

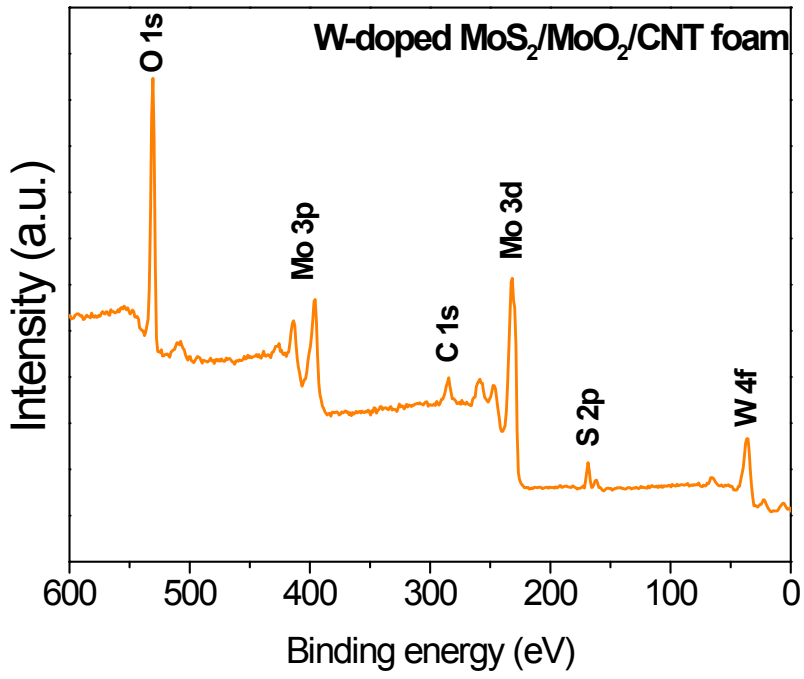


Fig. S2 X-ray photoelectron spectroscopy (XPS) of W-doped MoS_2/MoO_2/CNT foam.

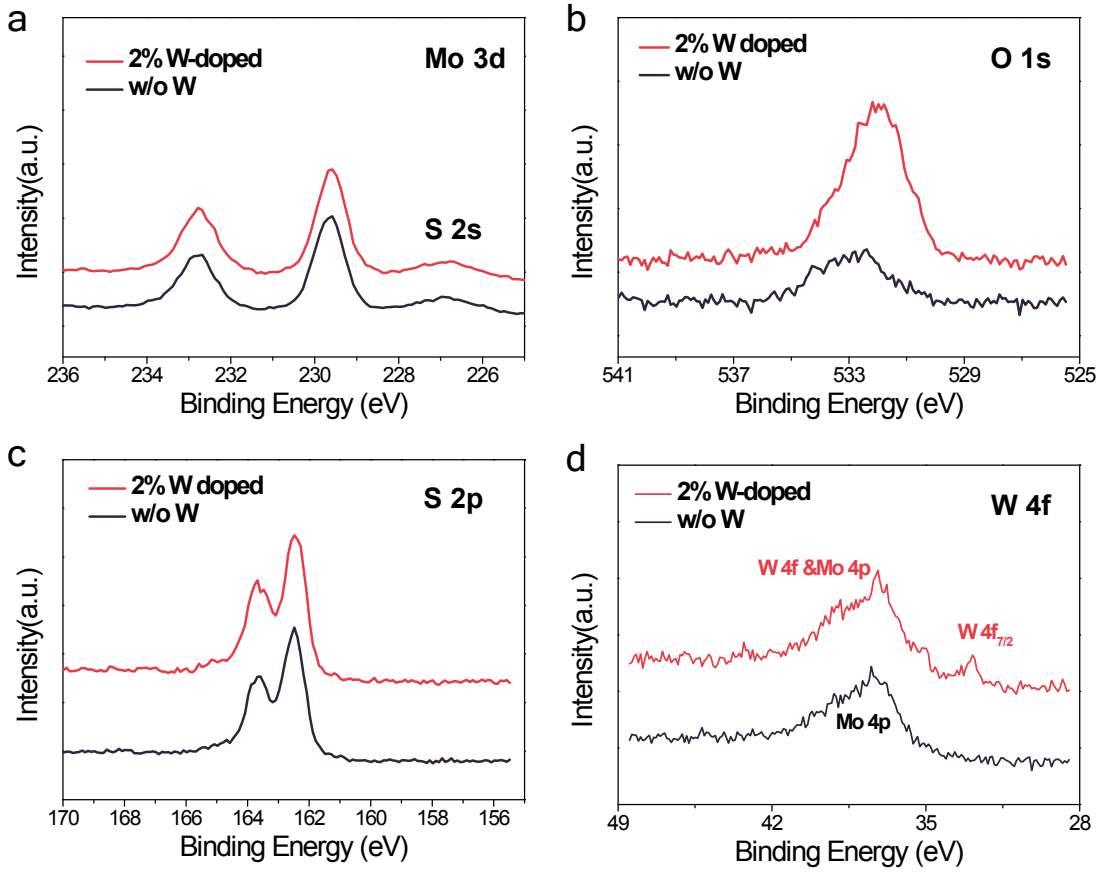


Fig. S3 X-ray photoelectron spectroscopy (XPS) of a)Mo 3d, b)O 1s , c)S 2p and W 4f in 2% W-doped MoS_2/MoO_2/CNT foam and non-doped MoS_2/MoO_2/CNT foam.

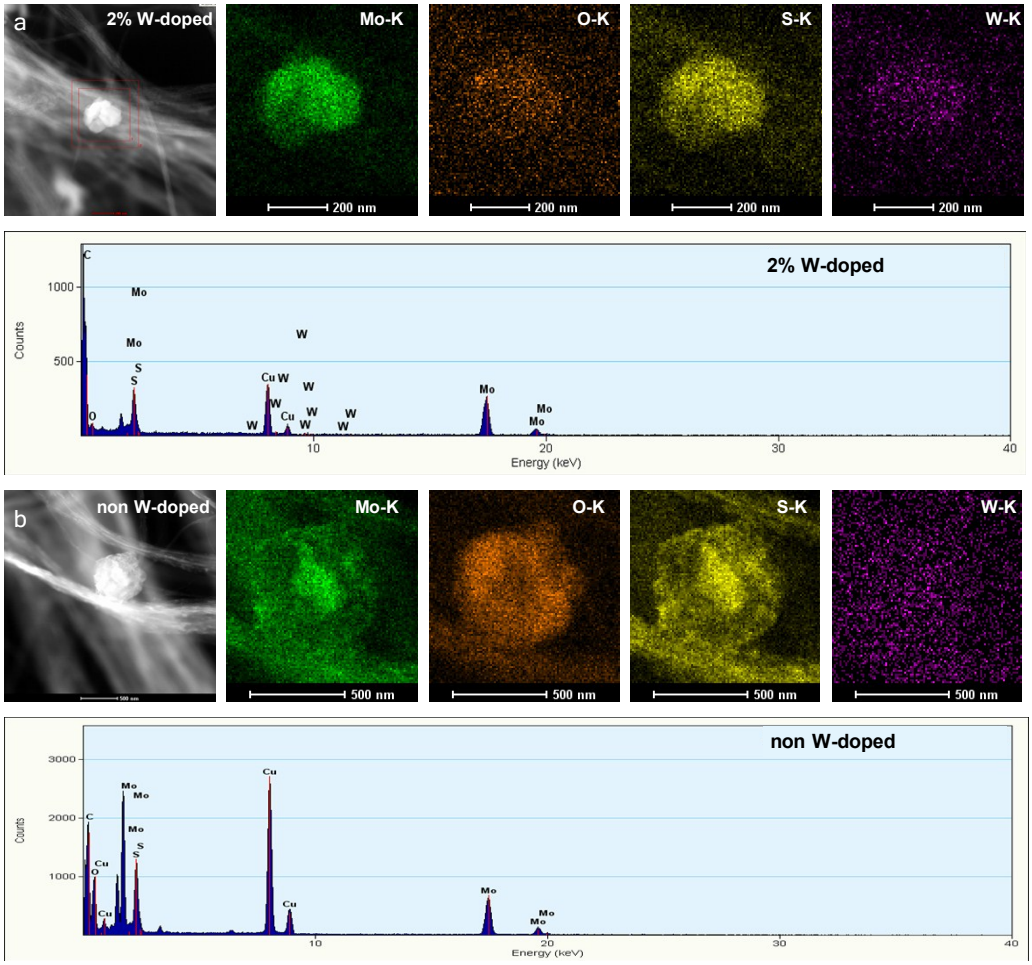


Fig. S4 Energy-dispersive spectroscopy (EDS) elemental mapping of Mo, O, S and Wo in 2% W-doped MoS_2/MoO_2/CNT foam and non-doped MoS_2/MoO_2/CNT foam.

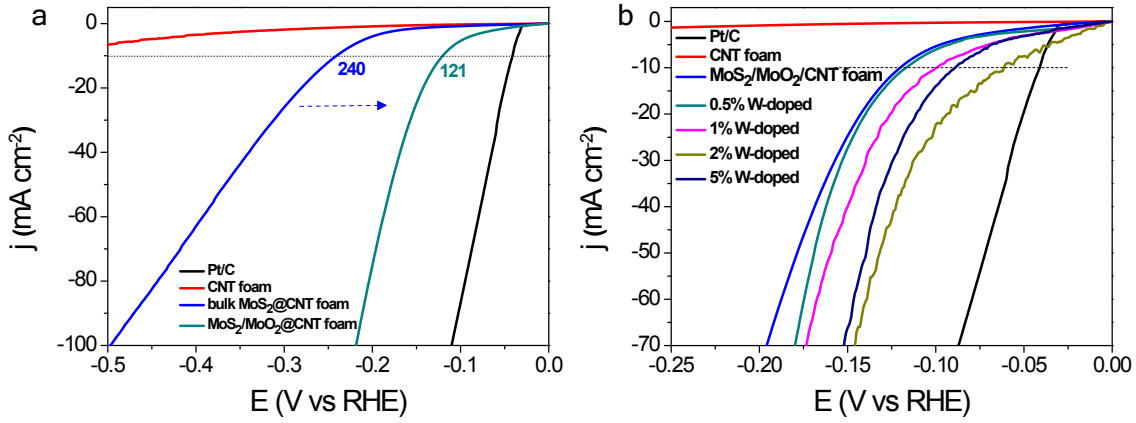


Fig. S5 Electrochemical properties of W-doped MoS_2/MoO_2/CNT foam. a) Comparison of bulk MoS_2/CNT foam and MoS_2/MoO_2/CNT foam prepared by our experimental method,

proving that our method method is effective. b) Performance obtained by doping different concentrations of W atoms, best performance at 2%.

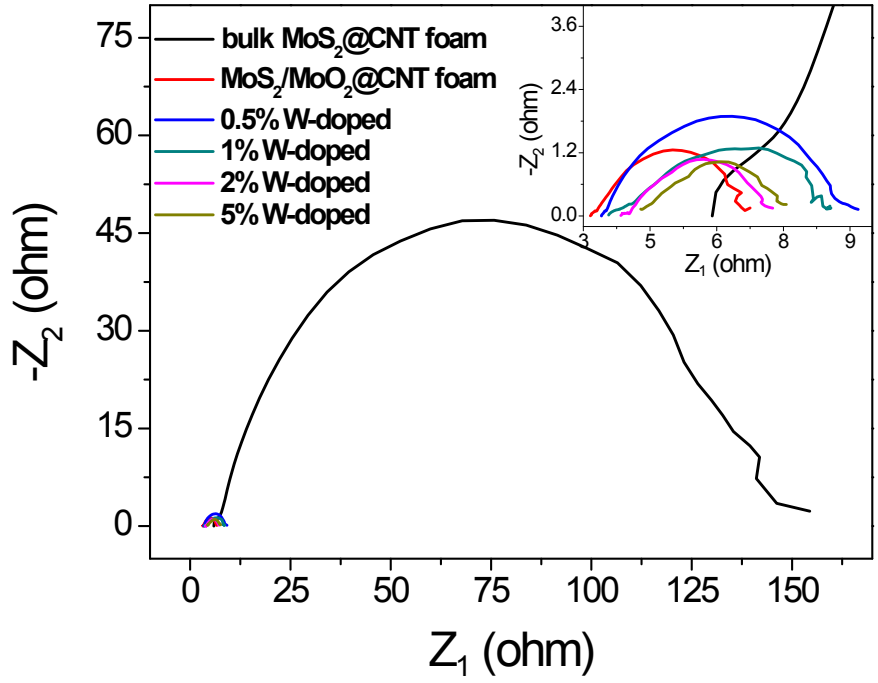


Fig. S6 Electrochemical impedance spectroscopy (EIS) data of samples under different conditions. Because the surface area is different, the absolute values cannot be compared, but it can be seen that the charge transfer impedance of the sample obtained by our method is very small.

Table S1. XPS determined Mo, W, S, C and O atoms amounts in 2%W-doped sample.

Name	Start BE	Peak BE	End BE	Atomic %	PP At. %
W 4f	47.78	37.18	30.68	0.24	0.12
S 2p	171.98	162.45	159.48	3.84	2.61
Mo 3d	238.88	229.59	224.18	1.99	1.09
C 1s	295.38	284.81	282.18	88.21	93.78
O 1s	540.18	532	527.68	5.72	2.4

Table S2. EDS determined C, O, S, Cu, Mo and W atoms amounts in 2%W-doped sample.

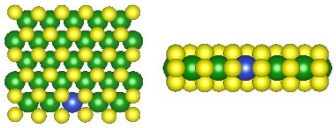
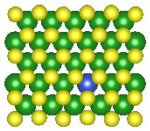
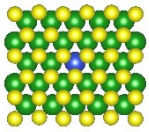
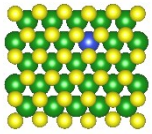
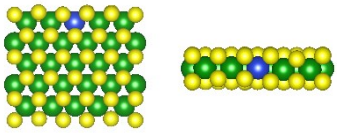
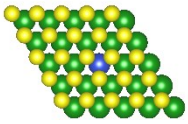
Element	Weight %	Atomic %
C(K)	33.35	75.83
O(K)	1.38	2.35
S(K)	1.80	1.53
Cu(K)	15.33	6.58

Mo(K)	47.99	13.66
W(L)	0.14	0.02

Table S3. ICP determined Mo, W, S and O atoms amounts in 2%W-doped sample.

Sample	**Mo(at.%)**	**W(at.%)**	**S(at.%)**	**O(at.%)**	**Mo/W**
2%W-doped	33.17	0.48	4.90	61.44	69.1

Table S4. Formation energies of W atom substituted Mo atom at edge and basal plane of MoS_2 under the S-rich or Mo-rich condition.

		W_{Mo} doping Structure	Formation energy of W_{Mo} doping (eV)
edge	$W_{edge\text{-}Mo}$		-2.94 (S-rich) -0.30 (Mo-rich)
	$W_{edge\text{-}1}$		-2.74 (S-rich) -0.10 (Mo-rich)
	$W_{edge\text{-}2}$		-2.76 (S-rich) -0.12 (Mo-rich)
	$W_{edge\text{-}3}$		-2.74 (S-rich) -0.10 (Mo-rich)
	$W_{edge\text{-}S}$		-2.95 (S-rich) -0.31 (Mo-rich)
basal plane	W_{plane}		-2.35 (S-rich) 0.29 (Mo-rich)