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Supporting Information

Hierarchical MoS_2 nanosheets on flexible carbon felt as an efficient flow-through electrode for dechlorination

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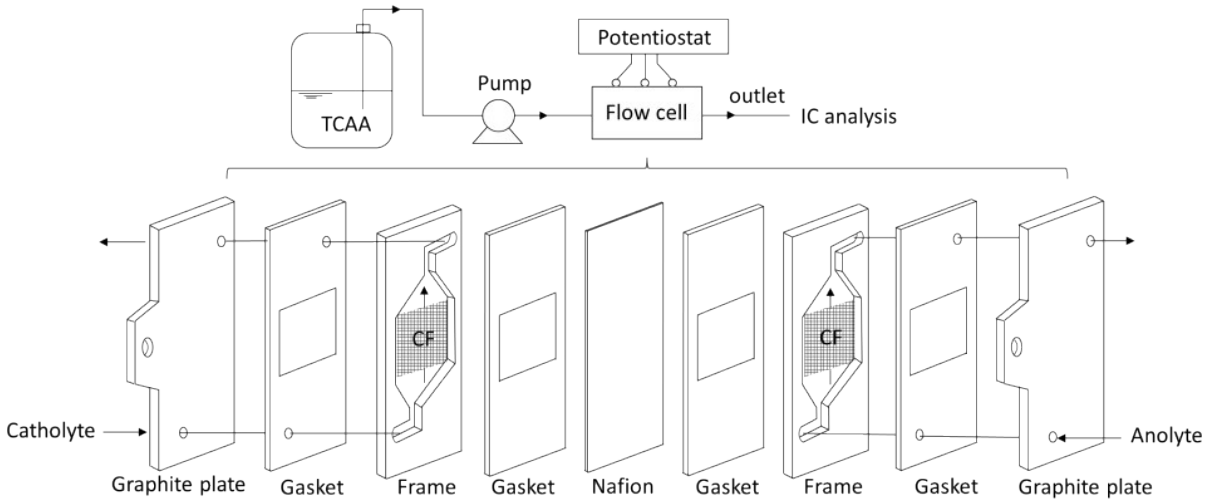
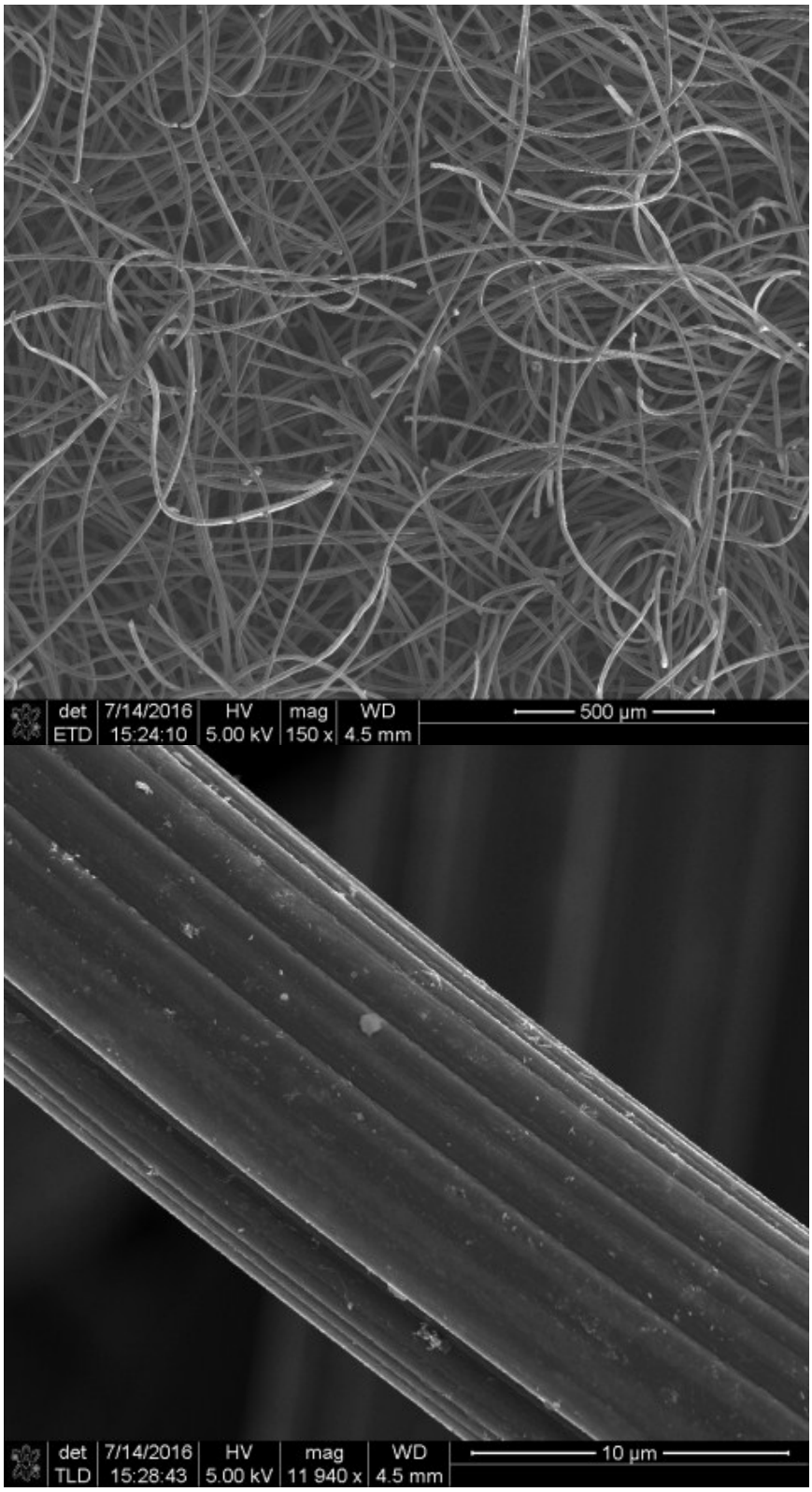


Figure S1. Schematic illustration of the flow cell used in this work.

Figure S2. Photo of the monolith electrodes (30 × 34 × ~4 mm) used in the flow cell.


det
ETD
7/14/2016
15:24:10
HV
5.00 kV
mag
150 x
WD
4.5 mm
500 µm
det
TLD
7/14/2016
15:28:43
HV
5.00 kV
mag
11 940 x
WD
4.5 mm
10 µm

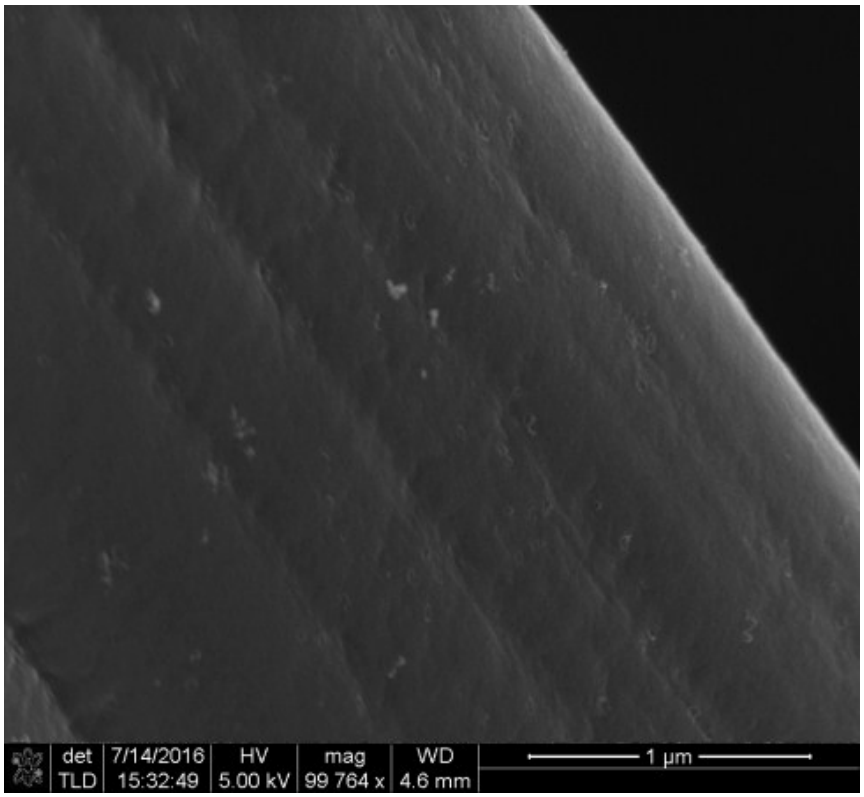


Figure S3. SEM images of bare carbon felt.

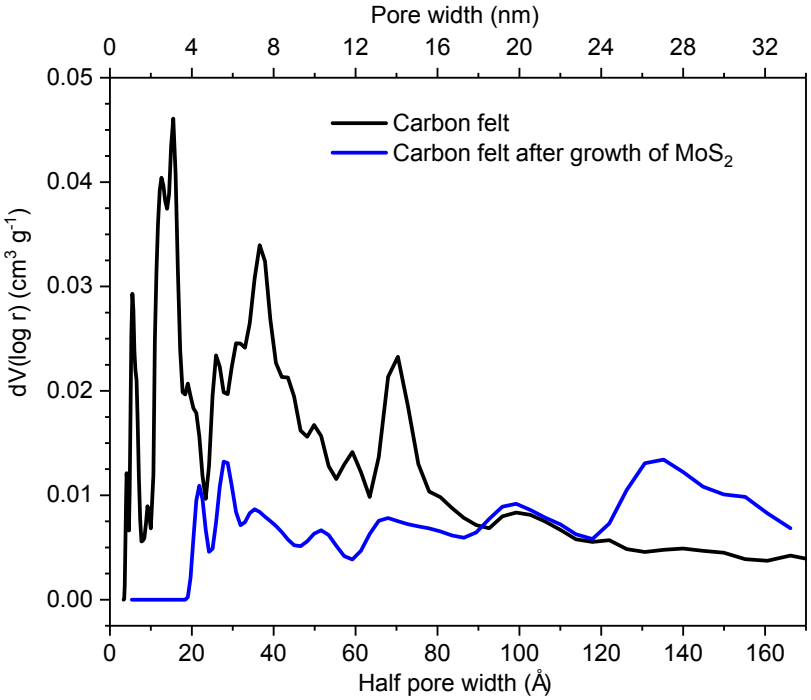


Figure S4. Pore size distribution of carbon felt electrode before (black) and after (blue) growth of MoS_2 nanosheets.

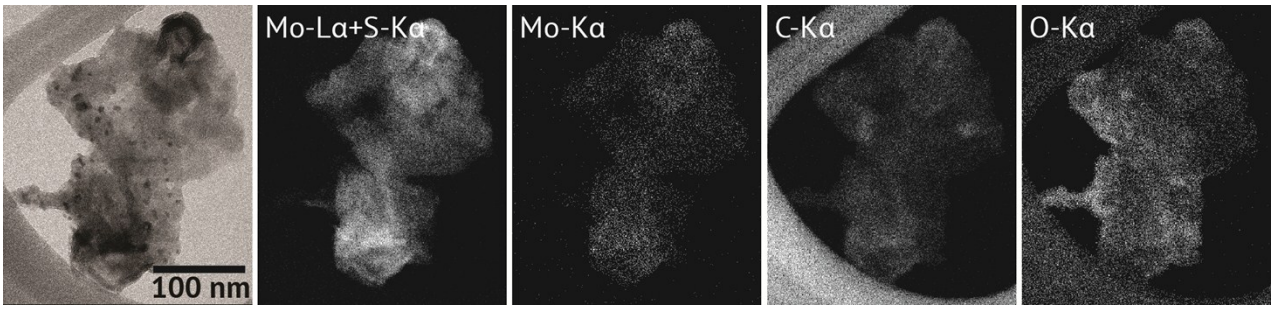


Figure S5. TEM images of MoS_2 with elemental mapping of Mo+S, Mo, C, and O. The mapping of S is not possible due to its spectrum overlapping with that of Mo.

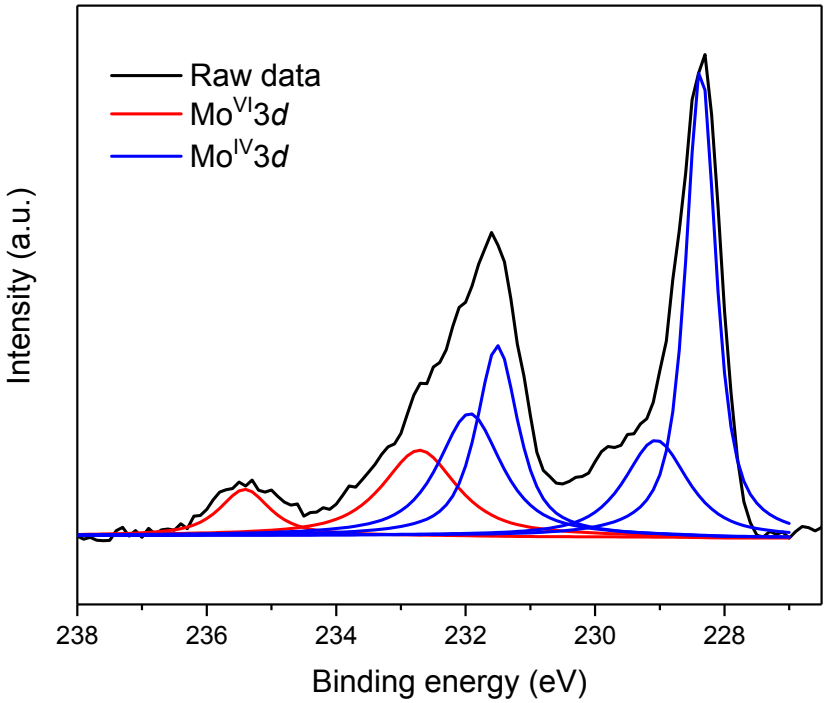


Figure S6. Mo 3d XPS spectra of MoS_2 catalyst on CF.

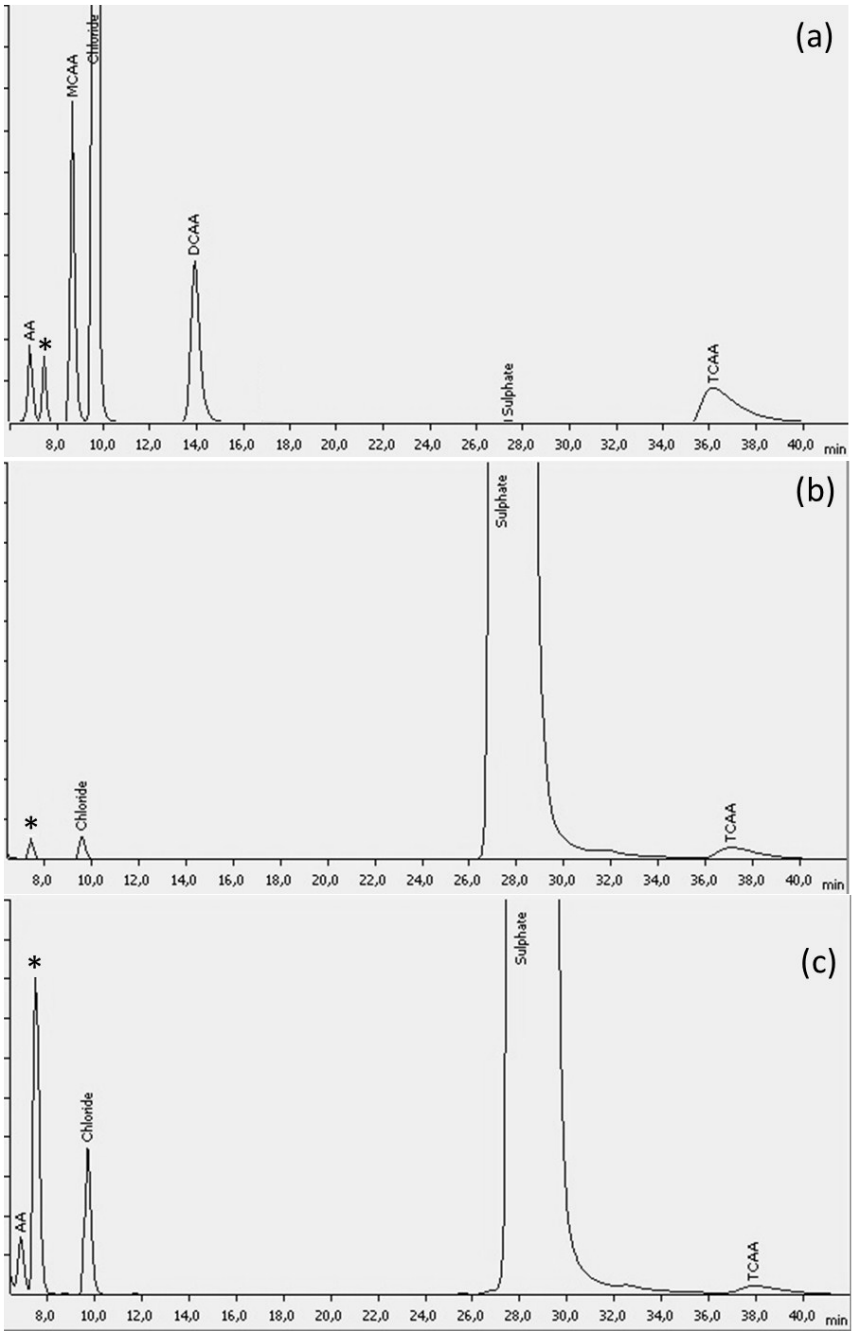
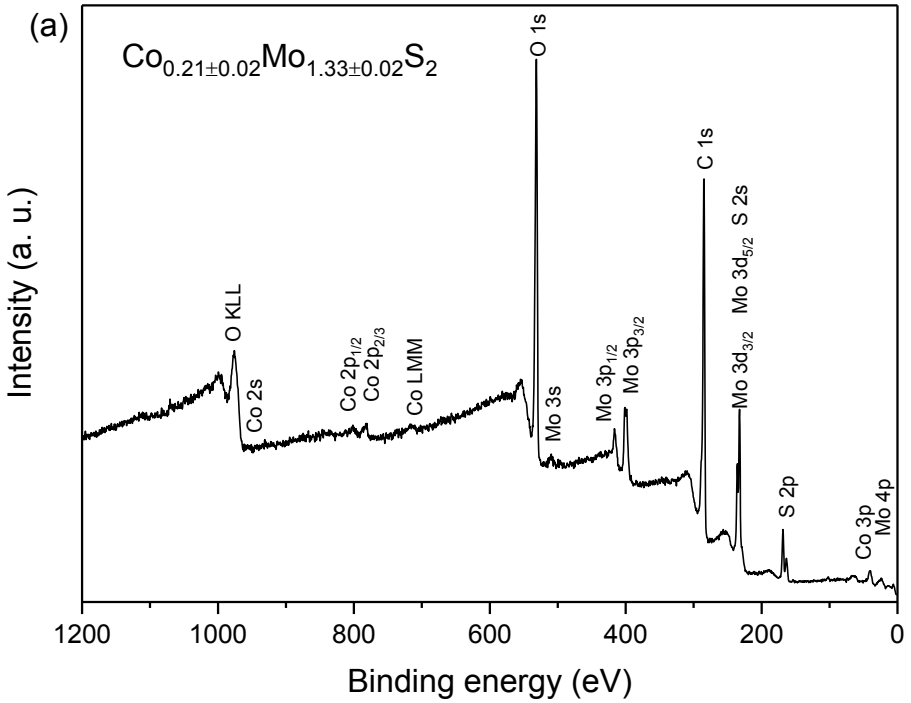
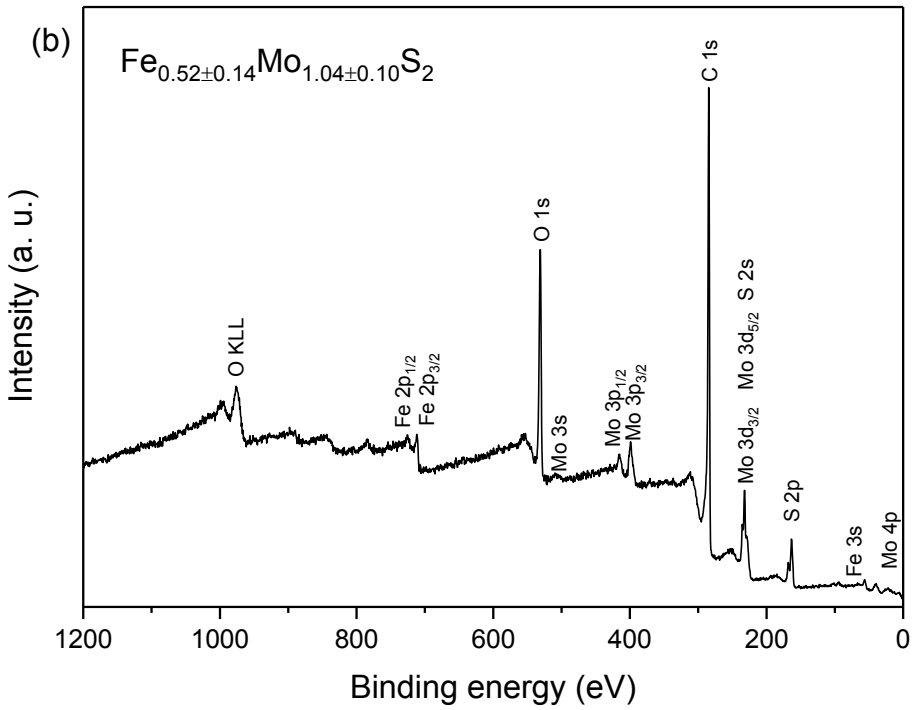
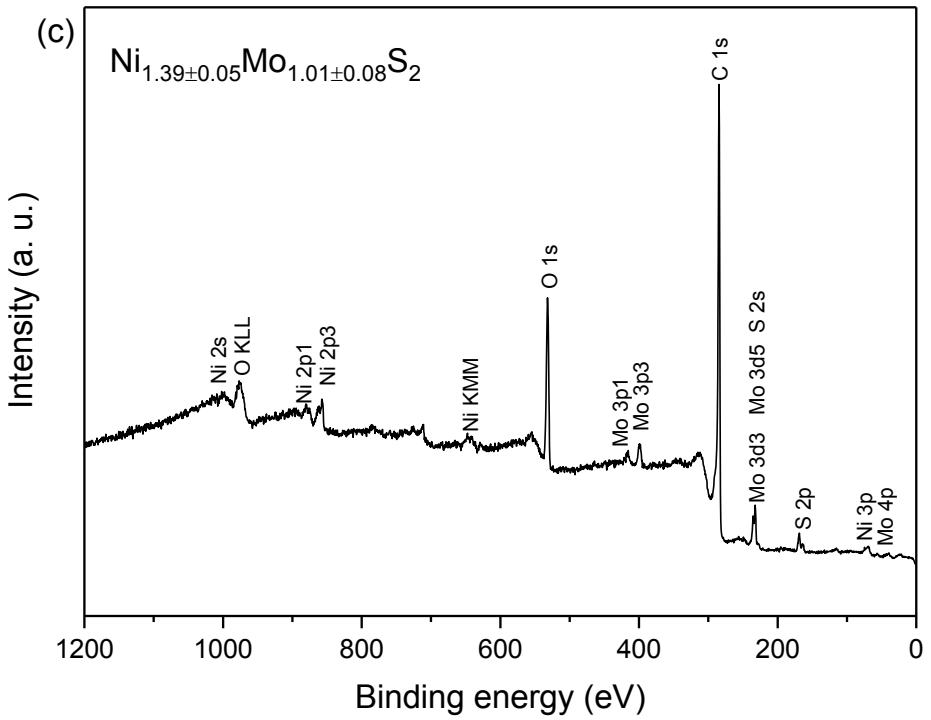


Figure S7. IC chromatography of (a) standard prepared from commercial available chemicals showing the retention time of TCAA and possible reduction products, (b) inlet of synthetic contaminated water containing 10 μM TCAA, and (c) outlet after flow cell treatment using MoS_2 catalyst. The inlet water contain Cl impurities which was subtracted to obtain the produced Cl from TCAA dechlorination. The peak indicated by "*" is an impurity peak from the filter.


(a)
$Co_{0.21\pm0.02}Mo_{1.33\pm0.02}S_2$
Intensity (a. u.)
Binding energy (eV)
1200
1000
800
600
400
200
0
O KLL
Co 2s
Co $2p_{1/2}$
Co $2p_{2/3}$
Co LMM
O 1s
Mo 3s
Mo $3p_{1/2}$
Mo $3p_{3/2}$
C 1s
Mo $3d_{3/2}$
Mo $3d_{5/2}$
S 2s
S 2p
Co 3p
Mo 4p


(b)
$Fe_{0.52\pm0.14}Mo_{1.04\pm0.10}S_2$
Intensity (a. u.)
Binding energy (eV)
1200
1000
800
600
400
200
0
O KLL
Fe $2p_{1/2}$
Fe $2p_{3/2}$
O 1s
Mo 3s
Mo $3p_{1/2}$
Mo $3p_{3/2}$
C 1s
Mo $3d_{3/2}$
Mo $3d_{5/2}$
S 2s
S 2p
Fe 3s
Mo 4p


(c)
$Ni_{1.39\pm0.05}Mo_{1.01\pm0.08}S_2$
Intensity (a. u.)
Binding energy (eV)
1200
1000
800
600
400
200
0
Ni 2s
O KLL
Ni 2p1
Ni 2p3
Ni KMM
O 1s
Mo 3p1
Mo 3p3
C 1s
Mo 3d5
S 2s
Mo 3d3
S 2p
Ni 3p
Mo 4p

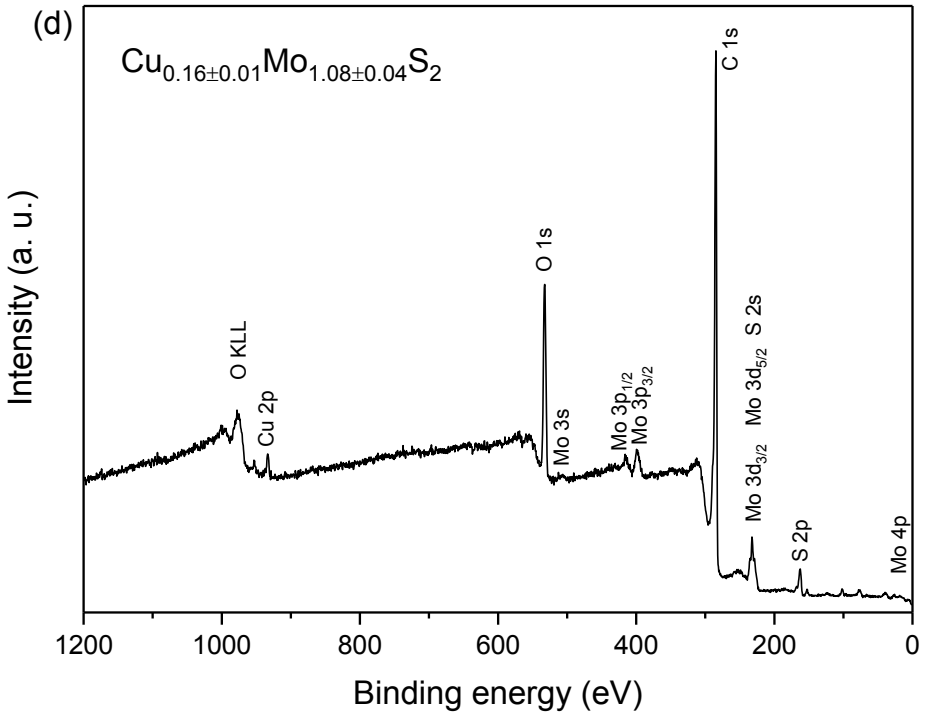

(d)
$Cu_{0.16\pm0.01}Mo_{1.08\pm0.04}S_2$
Intensity (a. u.)
Binding energy (eV)
1200
1000
800
600
400
200
0
O KLL
Cu 2p
O 1s
Mo 3s
Mo $3p_{1/2}$
Mo $3p_{3/2}$
C 1s
S 2s
Mo $3d_{5/2}$
Mo $3d_{3/2}$
S 2p
Mo 4p

Figure S8. XPS survey spectra giving the chemical formula of (a) Co, (b) Fe, (c) Ni, and (d) Cu doped MoS_2 on CF electrodes.

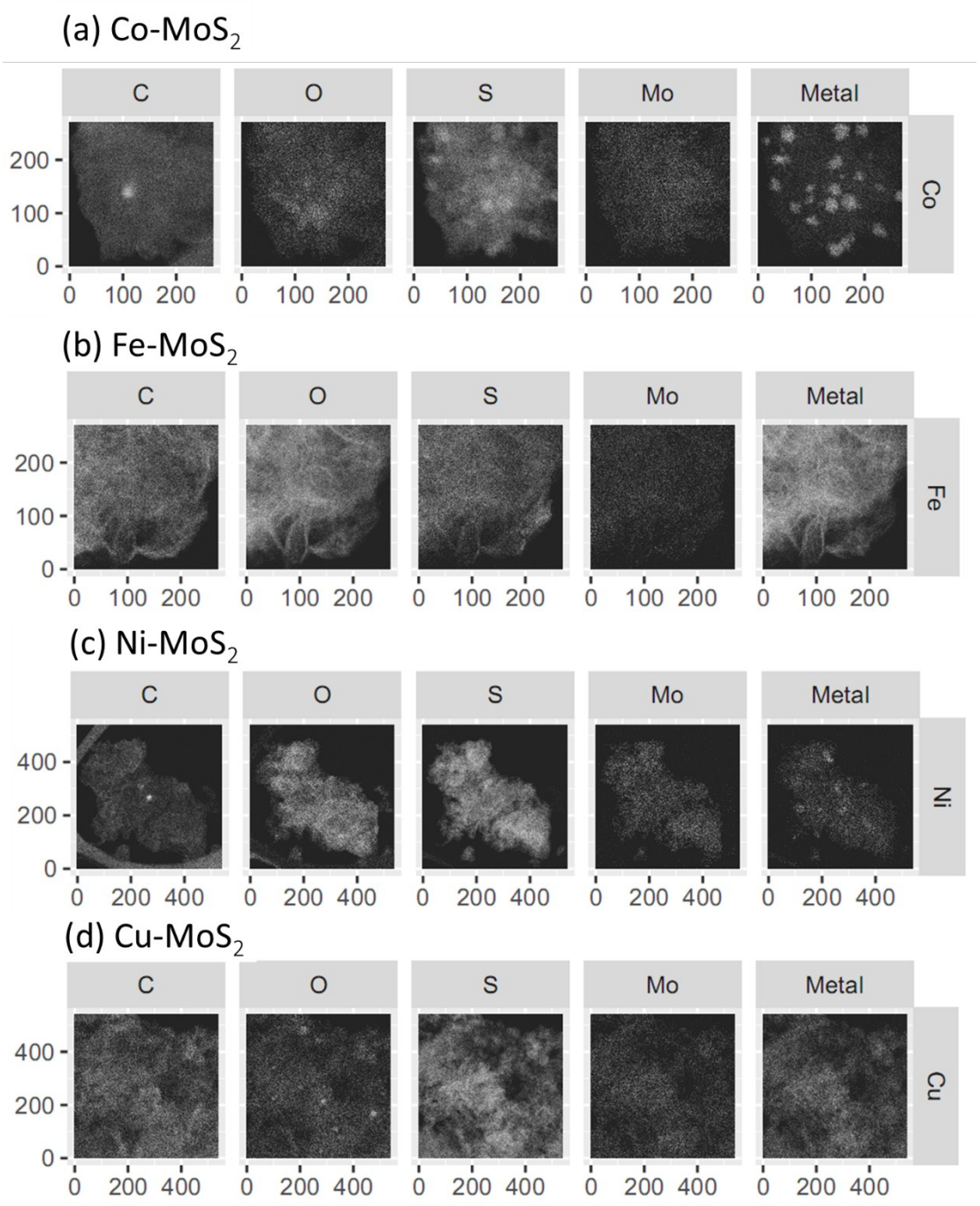


Figure S9. STEM-EDS chemical maps of C, O, S, Mo, and other metals in the MoS_2 nanosheets doped with (a) Co, (b) Fe, (c) Ni, and (d) Cu. Lengths are in nm.

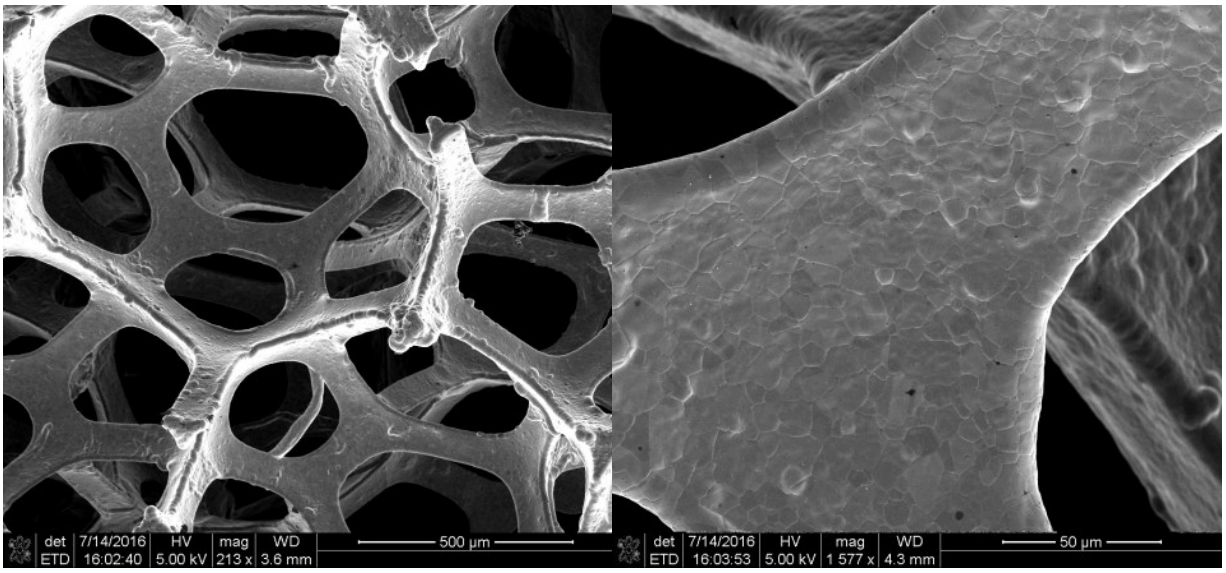


Figure S10. SEM images of Ni foam.

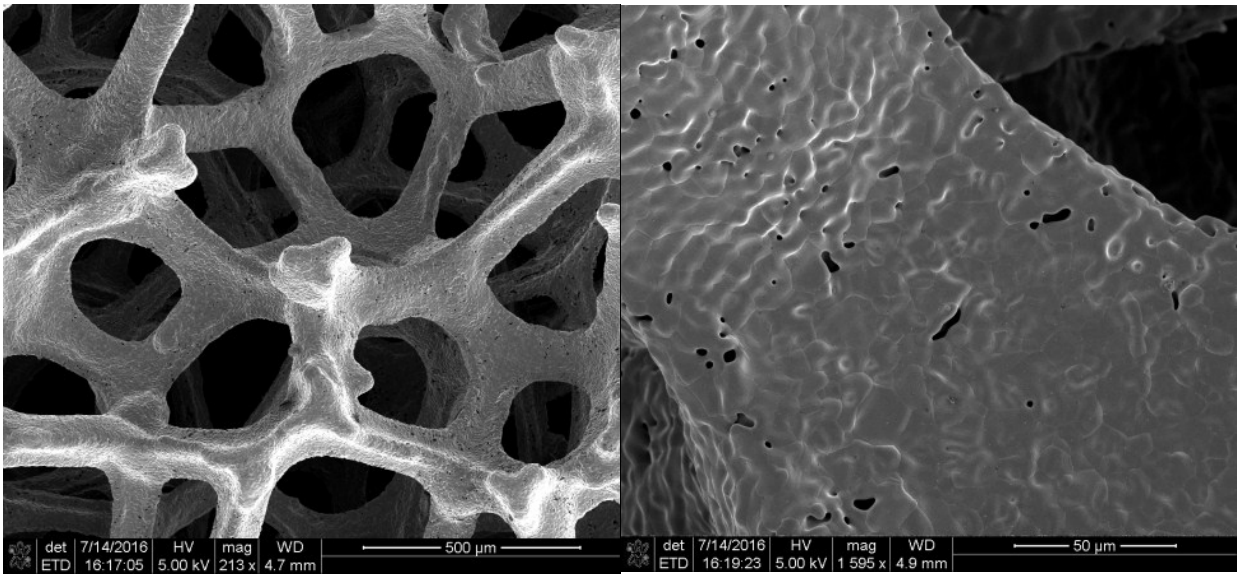


Figure S11. SEM images of Cu foam.

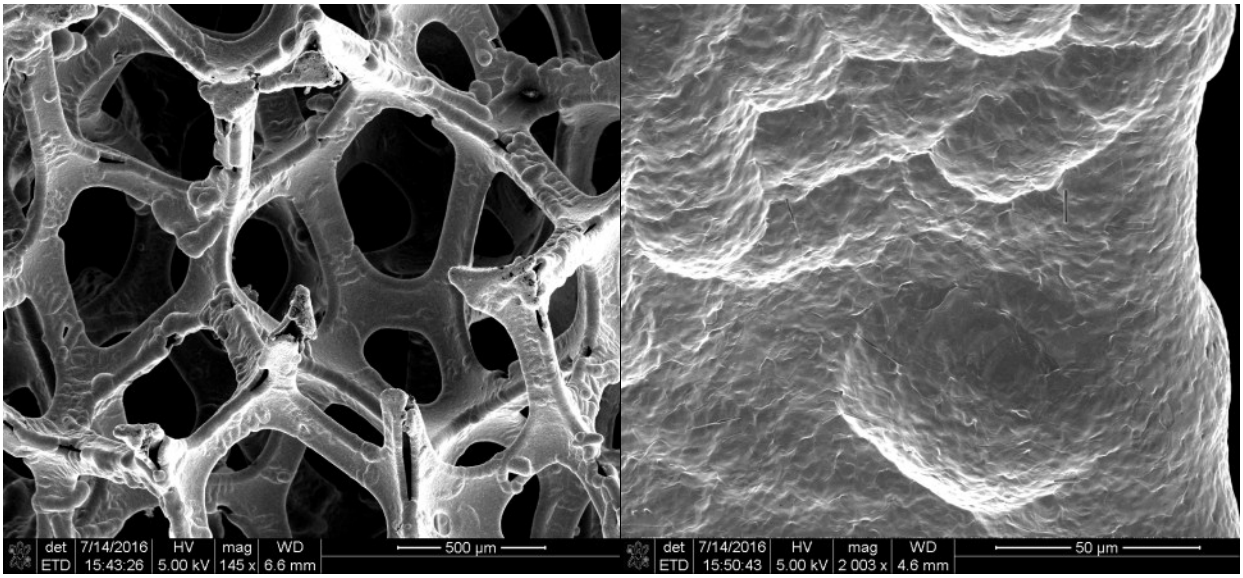


Figure S12. SEM images of stainless steel foam.

The catalyzed HER follows the reaction scheme:[S1]

$$H^+ + e^- + cat \rightarrow H^*\text{-}cat \quad \text{Volmer step}$$

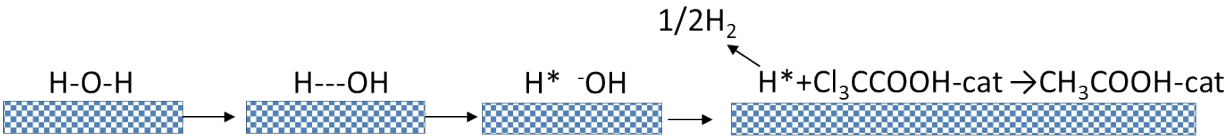
$$2H^*\text{-}cat \rightarrow \uparrow H_2 \quad \text{Tafel step}$$

$$H^*\text{-}cat + H^+ + e^- \rightarrow cat + \uparrow H_2 \quad \text{Heyrovsky step (in acidic solution)}$$

$$H^*\text{-}cat + H_2O + e^- \rightarrow cat + {}^-OH + \uparrow H_2 \quad \text{Heyrovsky step (in alkaline solution)}$$

Here "*" denotes a site on the catalyst surface able to bind to hydrogen.

Table S1. DFT Calculations of the Energetics (in eV) of the Electrocatalytic HER on the Surfaces of Different Catalysts.[S1]



Catalyst	$\Delta G(H_2O)$	$G(OH)$	$\Delta G(H)$
MoS_2	1.17	-4.95	0.60
Ni-MoS_2	0.66	-3.36	-0.07
Co-MoS_2	0.76	-3.46	0.13
Fe-MoS_2	0.96	-3.46	-0.11

The parameters $\Delta G(H_2O)$ and $\Delta G(H)$ are the kinetic energy barriers for the Volmer ($H^+ + e^- +$ cat → H*-cat) and Tafel (2H*-cat → $\uparrow H_2$) steps, respectively, and $G(OH)$ is the Gibbs free energy of the adsorbed ^-OH on the surfaces of catalysts. The symbol "*" denotes a site on the catalyst surface able to bind to hydrogen, while Cl_3CCOOH-cat denotes a Cl_3CCOOH molecule adsorbed on the catalyst surface.

Table S2. Equilibrium Mass Distribution Calculated by VMINTEQ.[a]

Component	**Total dissolved (mol L^{-1})**
H^+	4.6447×10^{-7}
HS^-/S^{2-}	1×10^{-16}
Na^+	4×10^{-3}
SO_4^{2-}	2×10^{-3}

[a] The parameters used are: pH is fixed at 6.4, the ionic strength is calculated from the supporting electrolyte of 2 mM Na_2SO_4, and the temperature is 25 °C. Solid "MoS_2" was added as an infinite solid phase which means that the concentration of the MoS_2 solid is sufficient to maintain equilibrium in the solution at all times.

Reference

[S1] J. Zhang, T. Wang, P. Liu, S. Liu, R. Dong, X. Zhuang, M. Chen, X. Feng, Engineering water dissociation sites in MoS_2 nanosheets for accelerated electrocatalytic hydrogen production, Energy Environ. Sci., (2016).