Electronic Supplementary Information

Atomic Layer Deposition of Photoelectrocatalytic Material on 3D-Printed Nanocarbon Structures

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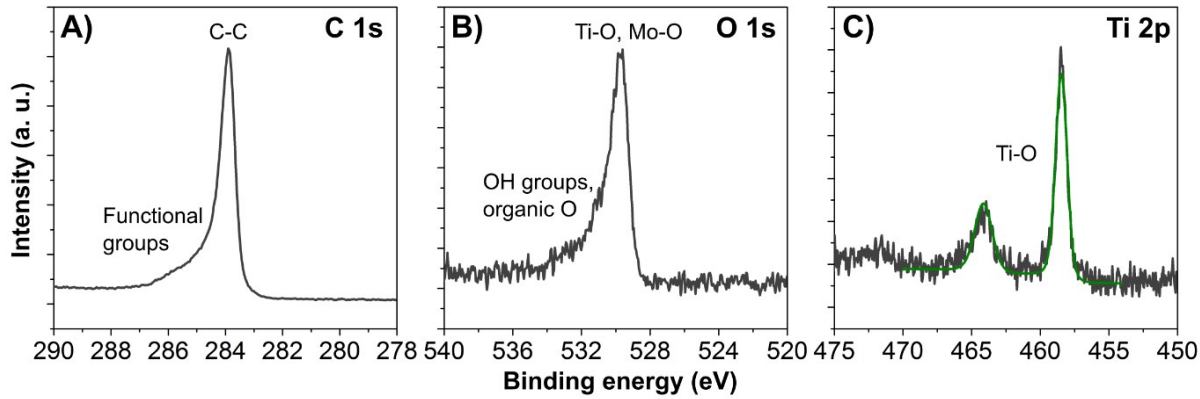

Fig. S1 XPS high-resolution core level spectra for (A) C 1s, (B) O 1s, and (C) Ti 2p of 300 ALD cycles MoS_2 coated 3D-printed nanocarbon electrodes.

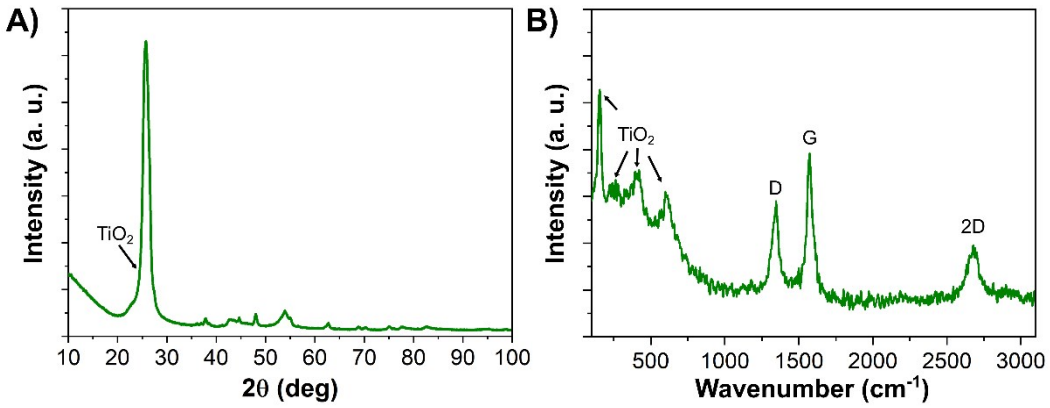

Fig. S2 (A) XRD pattern and (B) Raman spectrum of 300 ALD cycles MoS_2 coated 3D-printed nanocarbon electrode. The peaks are originated from the nanocarbon electrode or TiO_2 inherent impurities presence within the electrode.

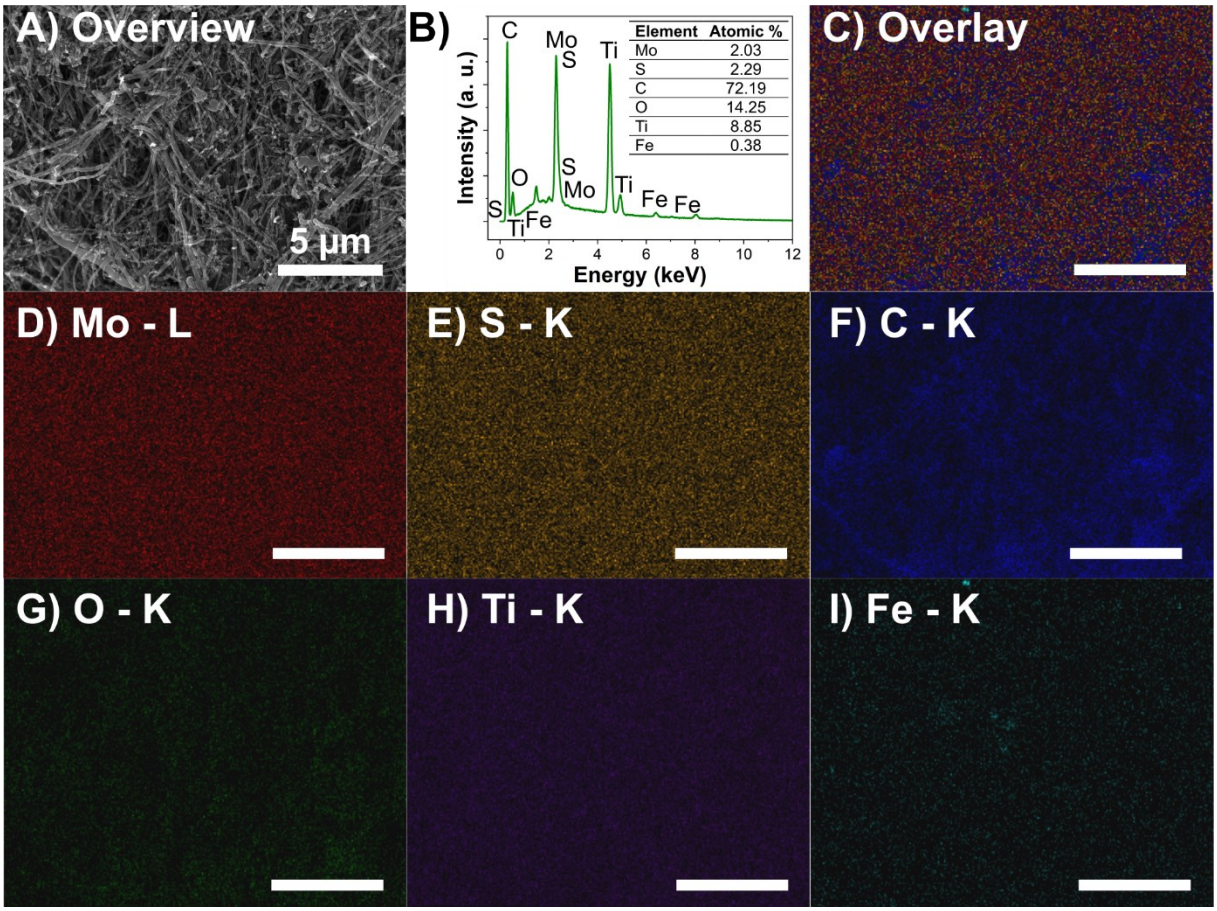

Fig. S3 SEM-EDX spectroscopy elemental mapping of a large area of 600 ALD cycles MoS_2 coated 3D-printed nanocarbon electrode for (A) SEM image for an overview of the area, (B) EDX spectrum with the atomic percentage of each element in the table in inset, (C) overlay of all elemental maps, individual map of (D-I) molybdenum, sulfur, carbon, oxygen, titanium, and iron.

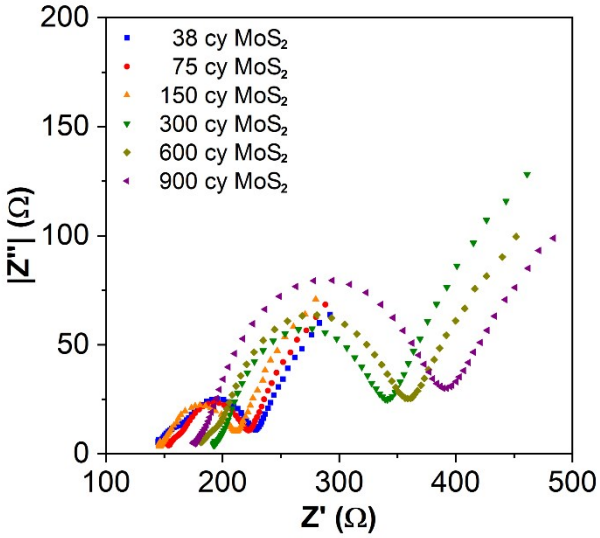

Fig. S4. Electrochemical impedance spectroscopy (EIS) Nyquist plots of 38 to 900 ALD cycles MoS_2 coated 3D-printed nanocarbon electrodes recorded at open-circuit potential (OCP) in the frequency range from 10 kHz to 50 mHz in an electrolyte consists of 10 mM $[Fe(CN)_6]^{3-/4-}$ and 0.1 M KCl.

Table S1 Comparison of MoS_2 supported by 3D-printed electrodes for hydrogen evolution reaction.

MoS_2 deposition method	**Material of 3D electrode**	**Electrolyte**	**Overpotential (mV) *vs.* RHE at -10 mA cm^{-2}**	**Reference**
Electrodeposition	Steel	1 M KOH	≈350	[1]
Spray-coating	Carbon	0.5 M H_2SO_4	≈550	[2]
Electrodeposition	Carbon	0.5 M H_2SO_4	≈390	[3]
Atomic layer deposition	Carbon	0.5 M H_2SO_4	≈480	This work

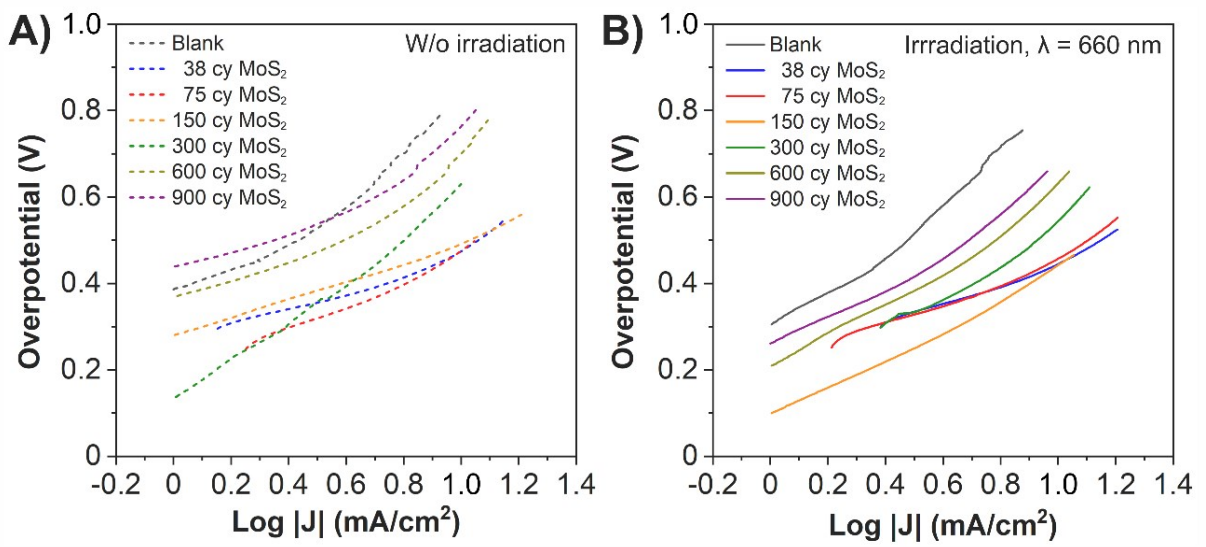

Fig. S5 HER Tafel plot of blank and 38 to 900 ALD cycles MoS_2 coated 3D-printed nanocarbon electrodes, extracted from LSV curves in Fig. 5, (A) without and (B) with irradiation, $\lambda = 660$ nm.

Table S2 Tafel slope of blank and 38 to 900 ALD cycles MoS_2 coated 3D-printed nanocarbon electrodes by fitting the linear portion of the Tafel plot in Figure S5.

Electrode	**Tafel slope (mV dec^{-1})**	
	Without irradiation	**With irradiation**
Blank	464	531
38 cycles MoS_2	238	256
75 cycles MoS_2	275	272
150 cycles MoS_2	225	341
300 cycles MoS_2	468	409
600 cycles MoS_2	455	408
900 cycles MoS_2	430	406

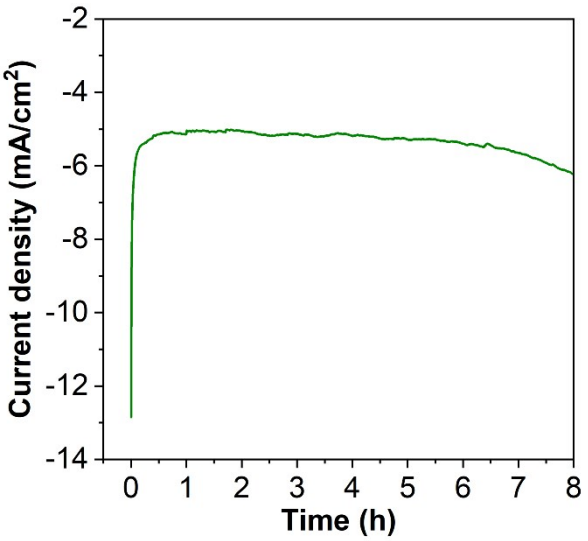

Fig. S6 Chronoamperometry profile for the stability test of 300 ALD cycles MoS_2 coated 3D-printed nanocarbon electrodes in 0.5 M H_2SO_4 with an applied potential of -0.45 V_{RHE} for 8 h.

References

1 A. Ambrosi and M. Pumera, *ACS Sustain. Chem. Eng.*, 2018, **6**, 16968–16975.
2 R. Gusmão, Z. Sofer, P. Marvan and M. Pumera, *Nanoscale*, 2019, **11**, 9888–9895.
3 C. Iffelsberger, S. Ng and M. Pumera, *Appl. Mater. Today*, 2020, **20**, 100654.