Electronic Supplementary Material (ESI) for Nanoscale.

Electronic Supplementary Information

MoS_2 versatile spray-coatings of 3D electrodes for hydrogen evolution reaction

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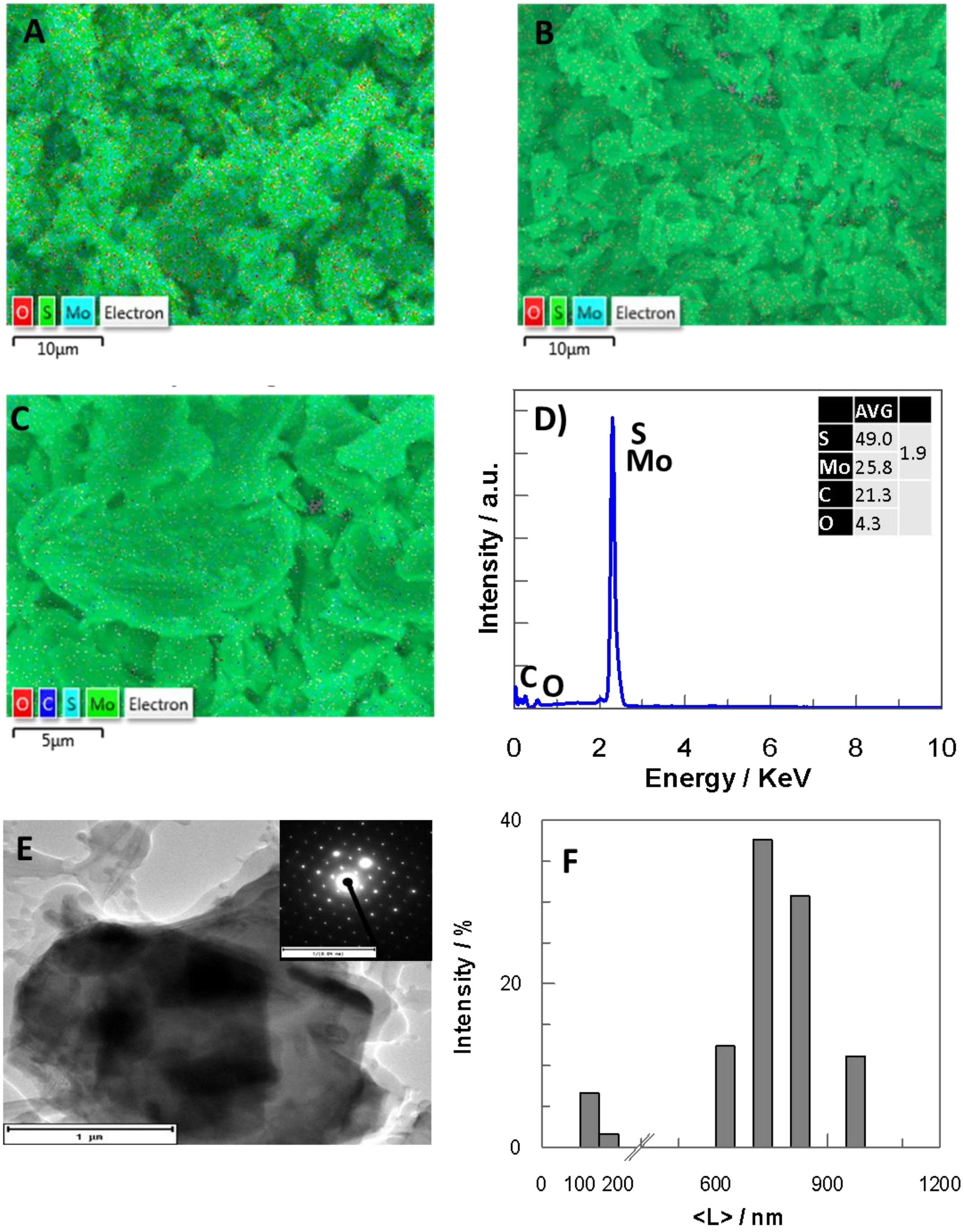


Figure S1. SEM micrographs (A-C) of MoS_2 dried films overlaid with mapping of C, O, S and Mo elements. D) Average EDX spectrum of MoS_2 sheets. E) TEM image of MoS_2 sheets. Inset: SEAD. F) Particle lateral size distribution measured by DLS from MoS_2 sheet suspended in DMF.

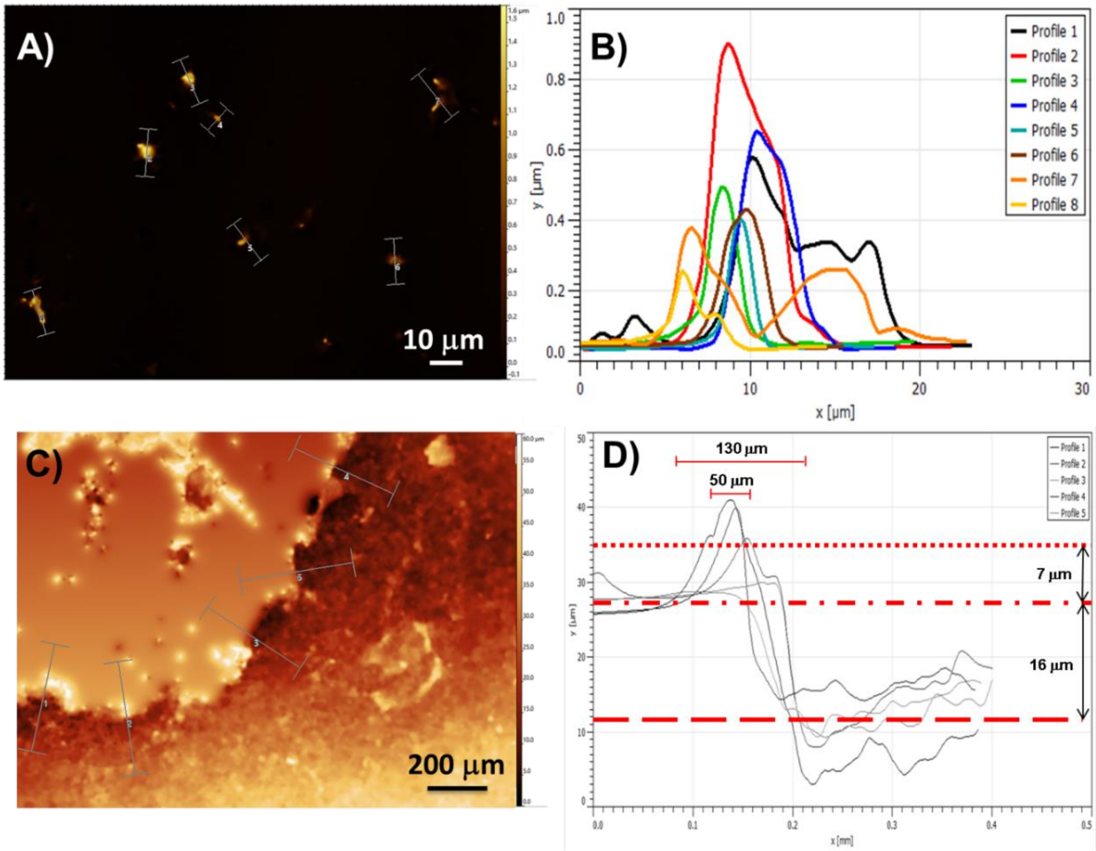


Figure S2. Topographical image MoS_2 in ITO acquired by optical profilometer (A), with respective height profiles for measurement of sheet thickness (B). Topographical image of an SPE sprayed with commercial MoS_2 with the 1.5 µm diameter mask acquired by optical profilometer (C), with respective height profiles for measurement of the MoS2 layer thickness (D).

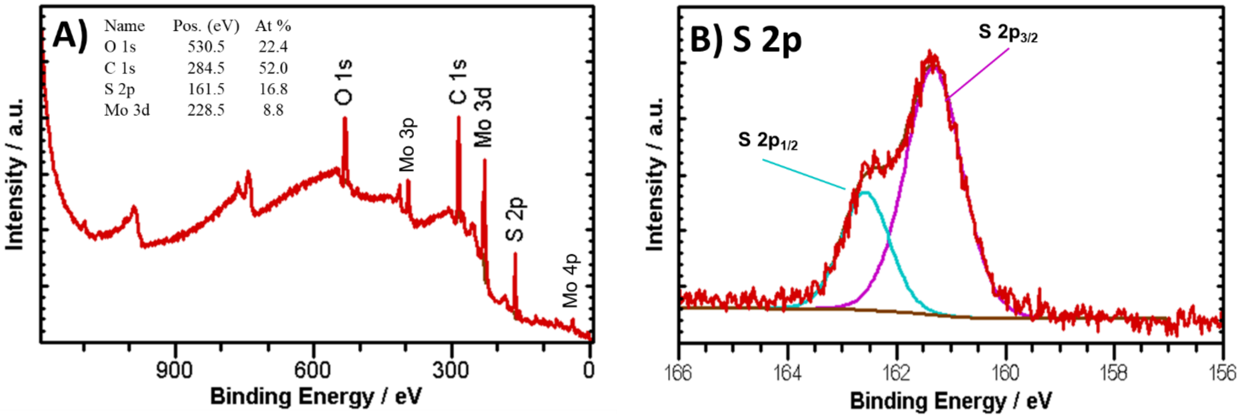


Figure S3. Wide XPS spectrum of dried MoS_2 from commercial spray (A) and high resolution S 2pcore level with peak deconvolution (B).

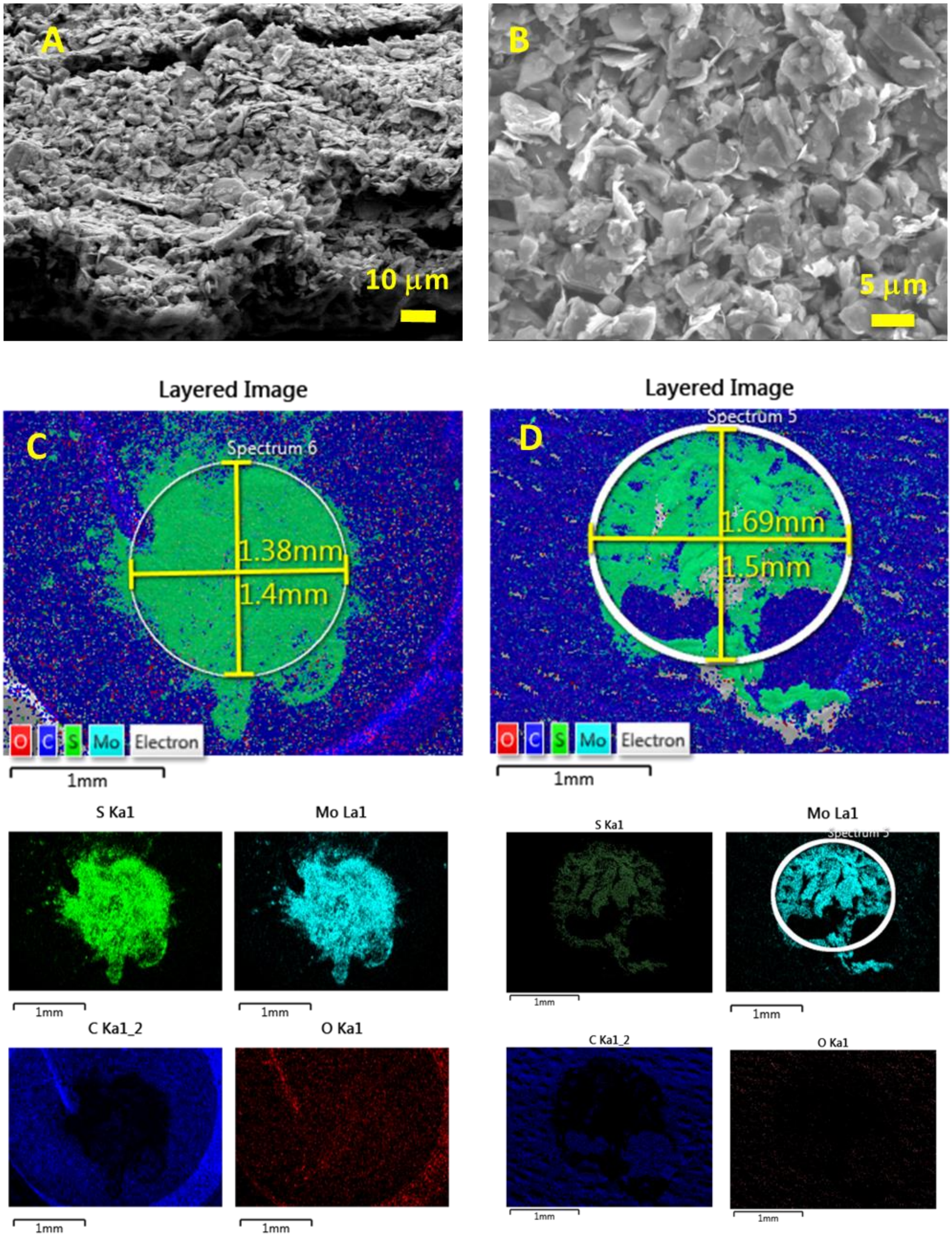
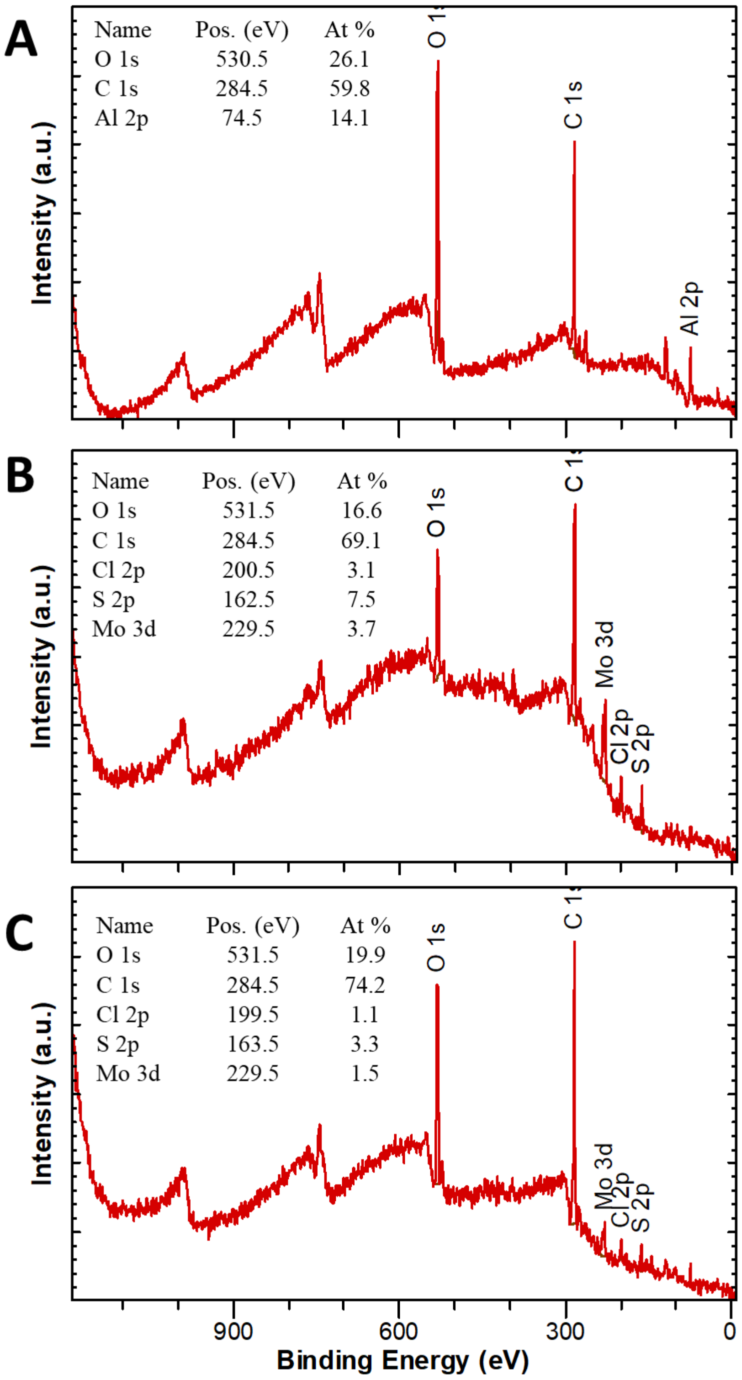


Figure S4. SEM micrographs at different magnifications of SPE modified by spray coating using commercial MoS_2 (A and B). Layered images of SEM micrograph and mapping of elements C, O, Mo and S of MoS_2 modified SPEs (C and D).



A

Name	Pos. (eV)	At %
O 1s	530.5	26.1
C 1s	284.5	59.8
Al 2p	74.5	14.1

B

Name	Pos. (eV)	At %
O 1s	531.5	16.6
C 1s	284.5	69.1
Cl 2p	200.5	3.1
S 2p	162.5	7.5
Mo 3d	229.5	3.7

C

Name	Pos. (eV)	At %
O 1s	531.5	19.9
C 1s	284.5	74.2
Cl 2p	199.5	1.1
S 2p	163.5	3.3
Mo 3d	229.5	1.5

Figure S5. Wide XPS spectrum of bare SPE (A), spray coated MoS_2 SPE before (B) and after (C) being used in hydrogen evolution reaction in both acidic and alkali conditions. Inset includes information on the core levels, peak position (eV) and atomic percentage for each sample.

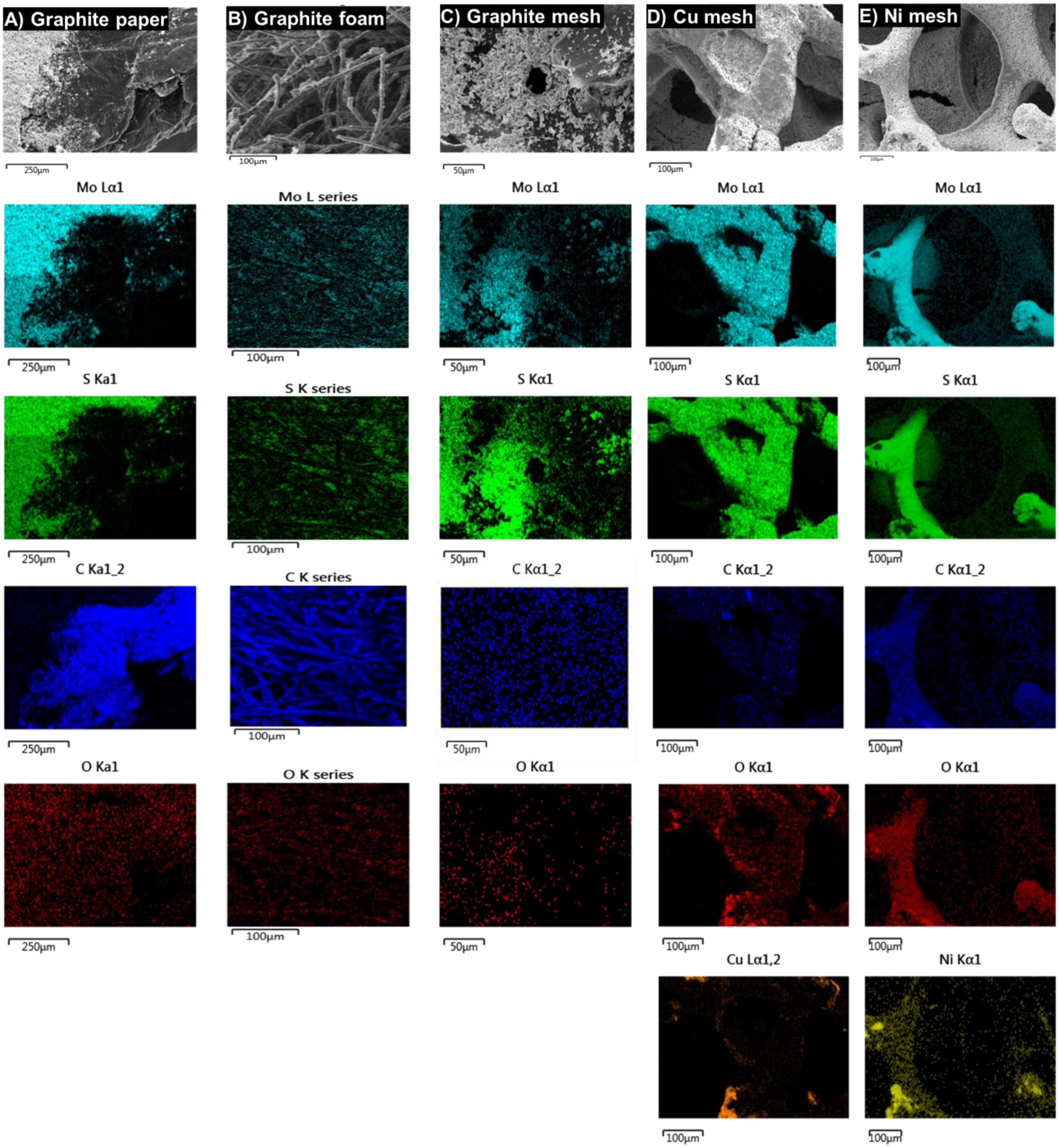


Figure S6. SEM micrographs of different surfaces modified by spray coating using commercial MoS_2 with respective mapping of elements: A) Graphite paper, B) Graphite foam, C) Graphite mesh, D) Cu mesh and E) Ni mesh.

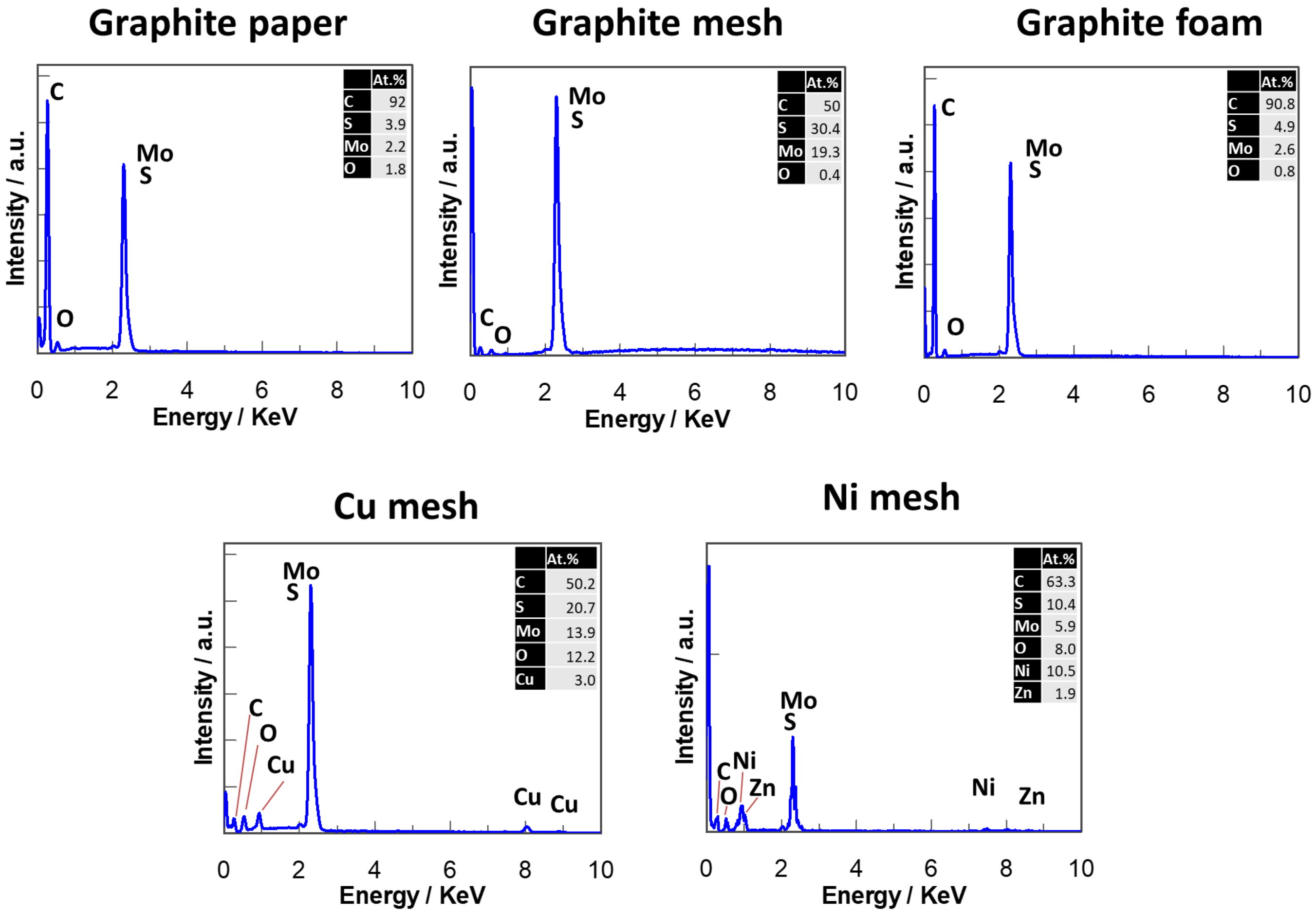


Figure S7. EDX spectra different surfaces modified by spray coating using commercial MoS_2 acquired from areas shown in Figure S5.

Table S1. MoS_2 loading on the sprayed coated surfaces.

Coated surface	MoS_2 loading (mg/cm^2)
SPE	4.7 ± 1.1
G paper	2.2 ± 0.8
G foam	19.8 ± 2.8
G mesh	4.9 ± 1.6
Cu mesh	17.1 ± 5.8
Ni mesh	16.7 ± 2.3
3D printed electrode	2.4 ± 0.9

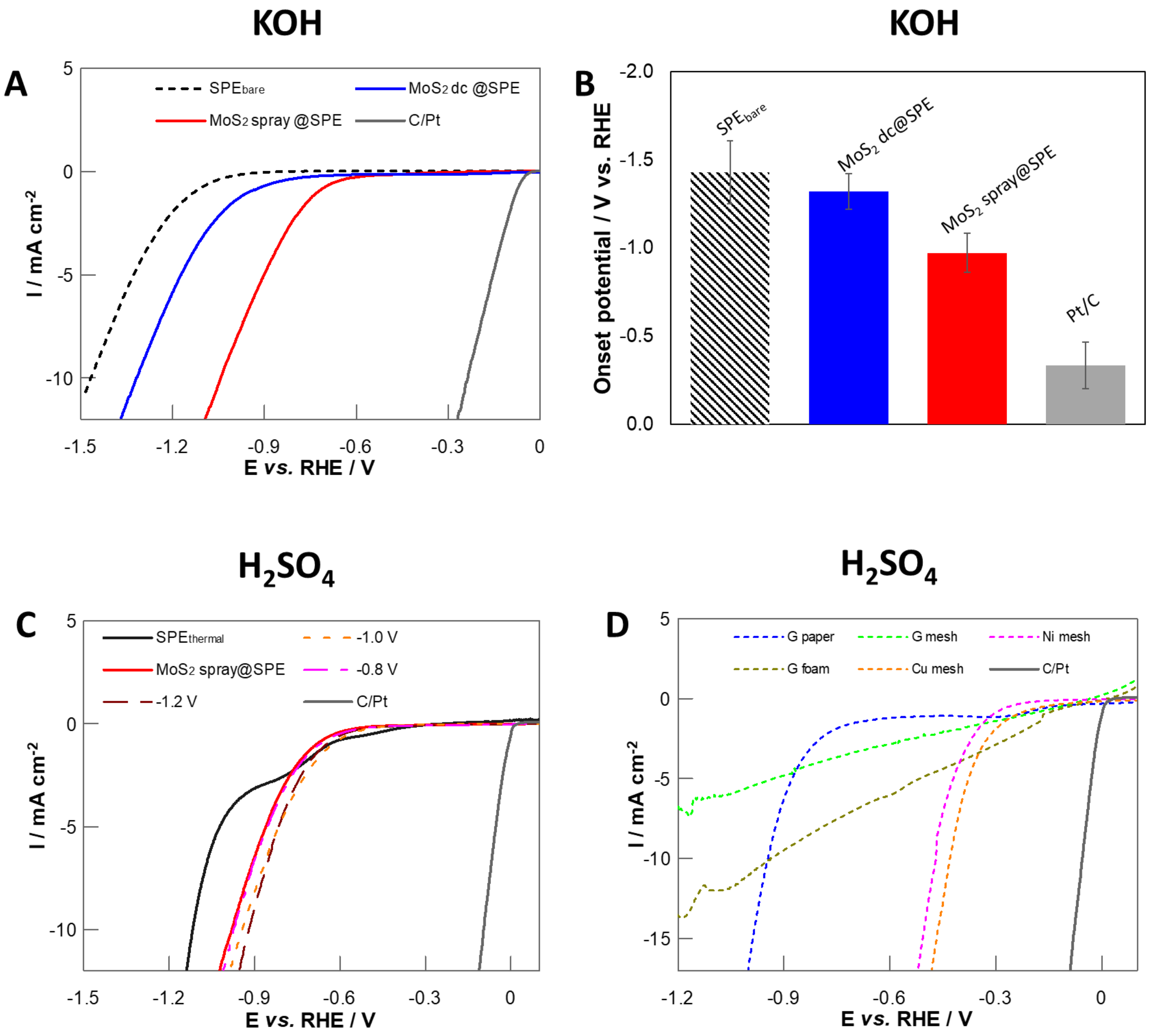


Figure S8. MoS_2 modified surfaces applied for HER. A) Polarization curves of MoS_2 materials in 1.0 M KOH. B) Corresponding average of the onset potentials at -10 mA cm^{-2}. C) Influence of cathodic pre-treatment on electrocatalytic properties of MoS_2 modified SPEs. D) HER performance of bare G-, Cu- and Ni-mesh, G paper and G foam. LSV for the set of MoS_2 modified SPE and bare surfaces in 0.5 M H_2SO_4 (C and D). Scan rate in all voltammograms: 5 mV s^{-1}.

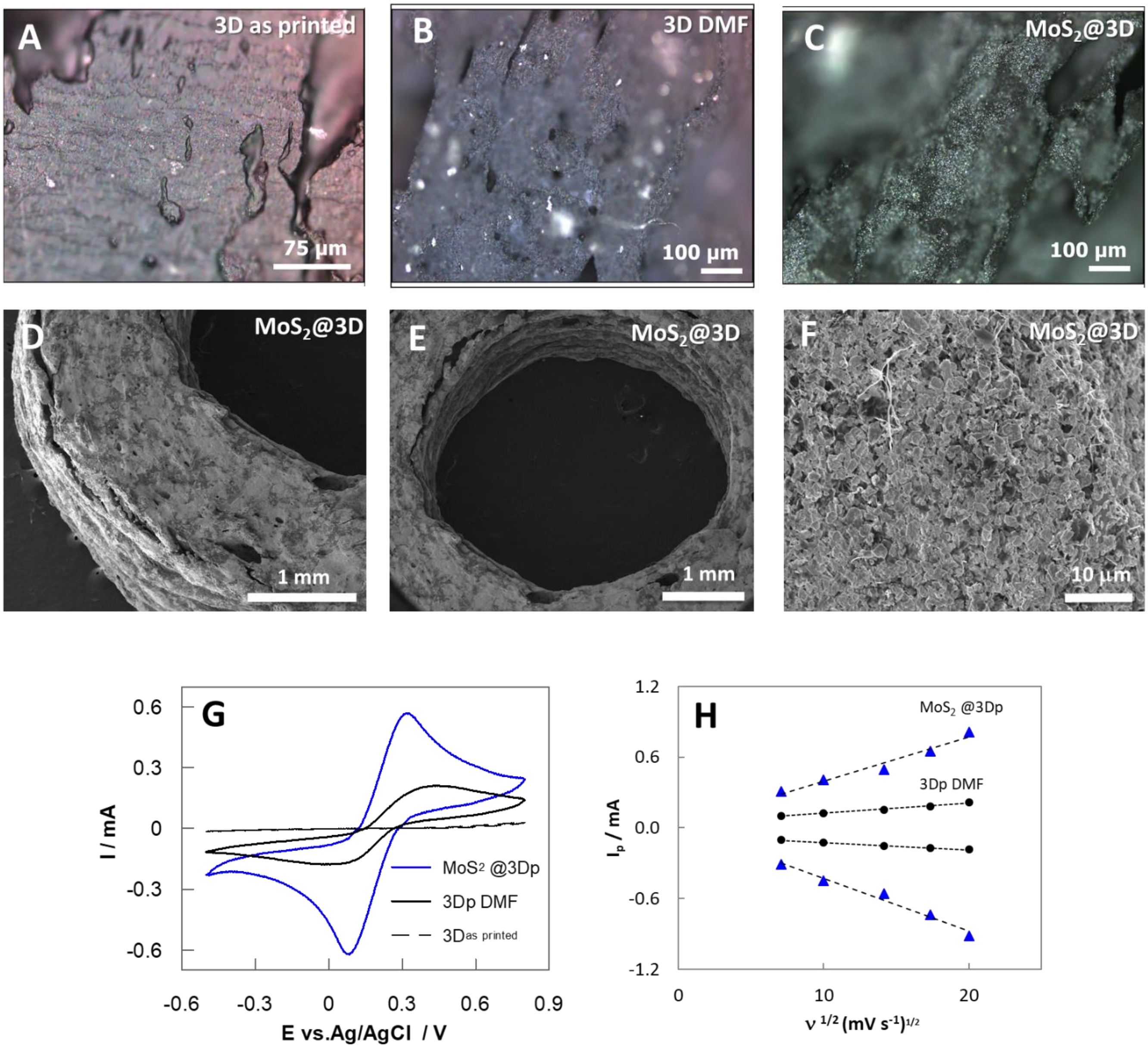


Figure S9. Optical images of 3D printed electrodes: as printed (A), activated with DMF (B) and, modified with commercial MoS_2 by spray coating technique (MoS_2@3D, C). SEM micrograph of MoS_2@3D showing the coating external periphery (D) and internal perimeter (E) of the 3D electrode. Detail of the top surface of the MoS_2@3D electrode (F). Effect of MoS_2 spray coating on ΔE using the $Fe(CN)_6^{4-/3-}$ redox probe . Conditions: Scan rate: 0.1 V s^{-1}, 5 mM $Fe(CN)_6^{4-/3-}$, 0.1 M KCl (G). Linear dependence of peaks currents on the square root scan rate ($50<\upsilon<400$ mV s^{-1}) for 3D DMF and MoS_2 @ 3D in 5 mM $Fe(CN)_6^{4-/3-}$, 0.1 M KCl (H).

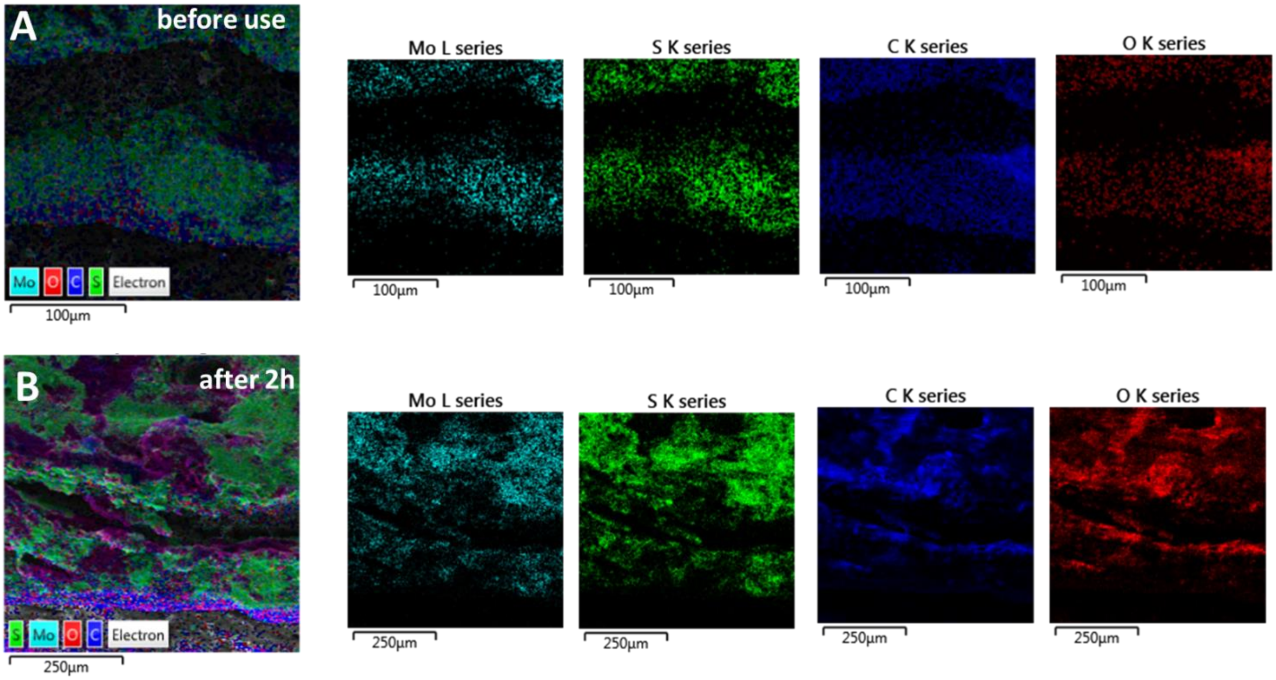


Figure S10. Layered images of SEM micrograph and mapping of elements C, O, Mo and S of the external perimeter of the MoS_2@3D before being used (A) and after being applied to hydrogen evolution reaction for 2 hour at a potential of -500 mV (B).

Equations

The values of the HET constant, k^0_{obs}, were determined by the Nicholson method through the use of the following equation: $\psi = k^0_{obs}[\pi DnvF/(RT)]^{-1/2}$ where ψ is the kinetic parameter, D is the diffusion coefficient, n is the number of electrons involved in the process, F is the Faraday constant, R is the universal gas constant and T is the temperature. The kinetic parameter, ψ, is tabulated as a function of ΔE_P at a set temperature (298 K) for a one-step, one electron process with a transfer coefficient, α, equal to 0.5.

To evaluate the effective electrochemical area, A_{eff}, given that for a co-planar macro electrode in the electrochemically quasi-reversible case, the Randles–Ševčík equation (at 298 K): $I_p = 2.65 \times 10^5 n^{3/2} D^{1/2} v^{1/2} C\, A_{\mathrm{eff}}$, where the notation is the same as above and C is the concentration of electroactive substance $Fe(CN_6)^{4-/3-}$.