Electronic Supplementary Material (ESI) for RSC Advances.

Supporting information

Fabrication of inverse opal molybdenum sulfide and its use as catalyst for H_2 evolution

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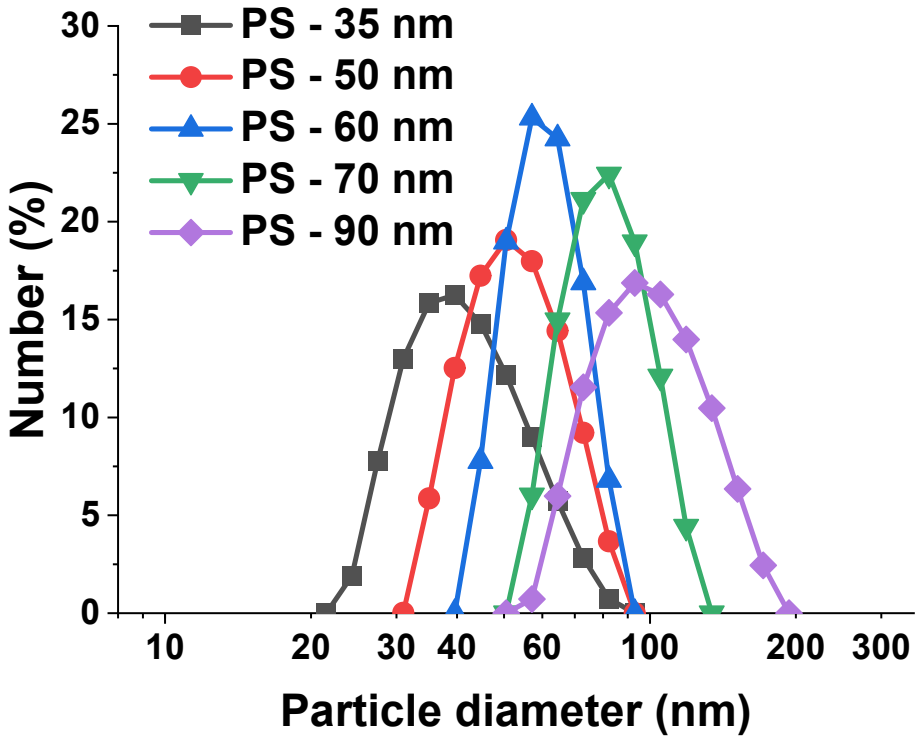

***Figure S1**. Size distribution of synthetic spherical polystyrene nanoparticles*

Table S1. Polystyrene particles parameters extracted from SEM and DLS analyses

No.	Styrene (mL)	MeOH/H_2O (mL)	KPS (%w/Sty)	SDS (%w/Sty)	Av. Size (nm) (SEM)	Av. Size (nm) (DLS)	PDI (DLS)
1	**1.55**	0/70	2.5	6	**35**	39.4	0.133
2	**1.55**	0/70	2.5	4.5	**50**	50.4	0.063
3	**1.55**	0/70	2.5	3	**60**	56.0	0.113
4	**1.55**	0/70	2.5	2	**70**	75.5	0.077
5	**1.55**	0/70	2.5	1.2	**90**	89.2	0.087

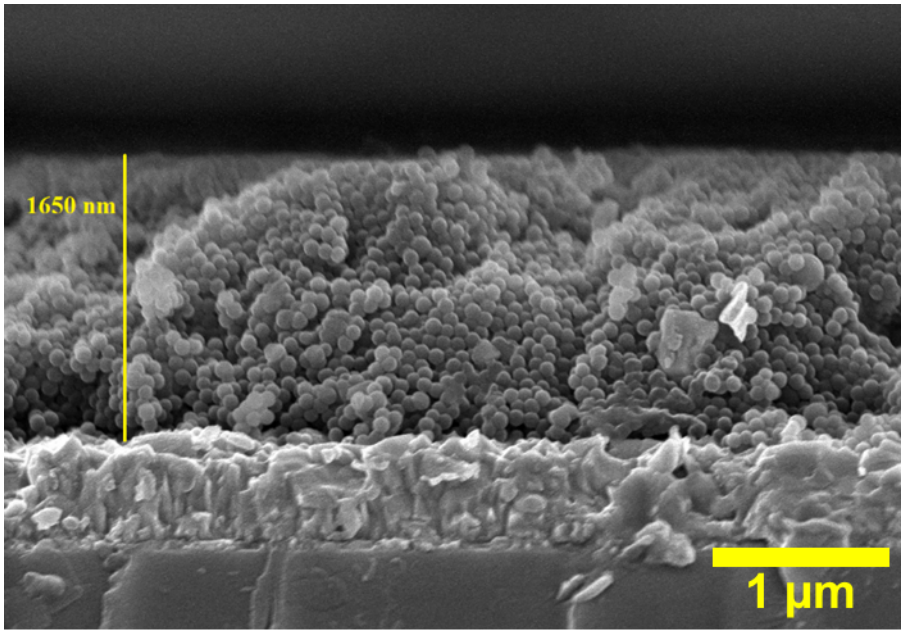

Figure S2. *SEM cross-section image of PS-90nm beads coated FTO electrode*

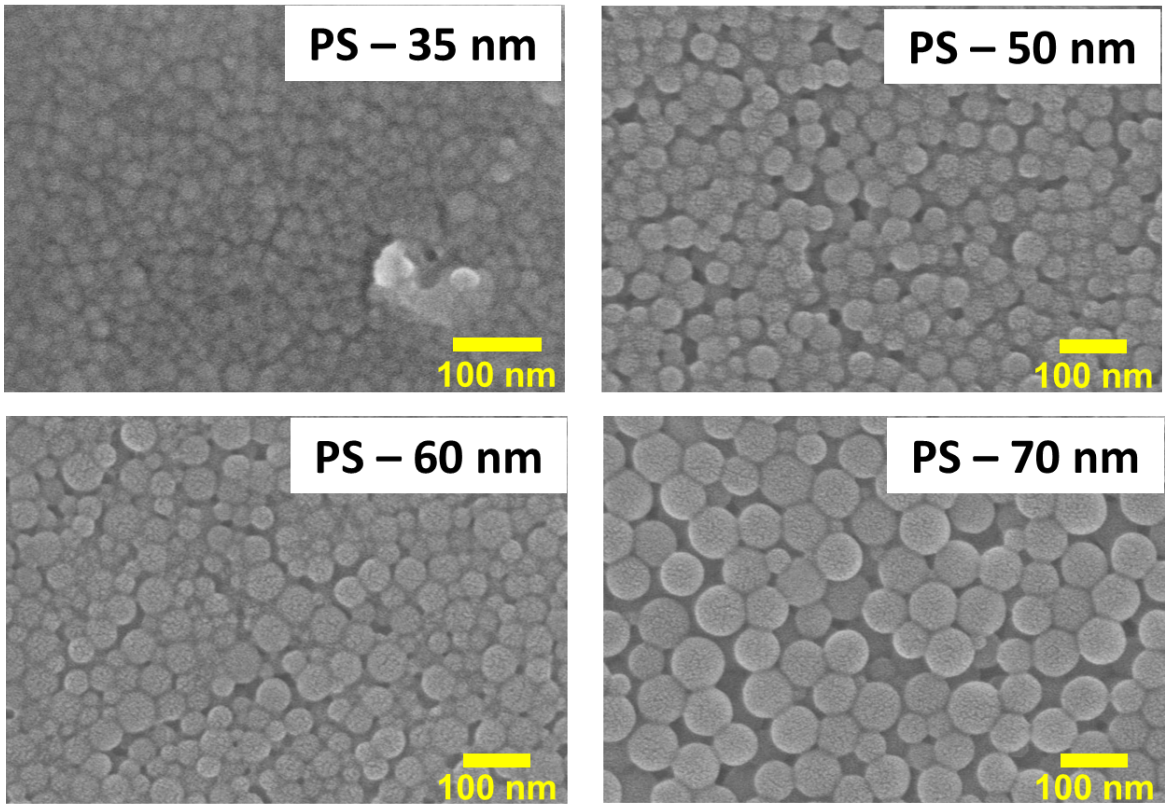

Figure S3. *Surface SEM images of PS-FTO electrodes (using PS particles with different size)*

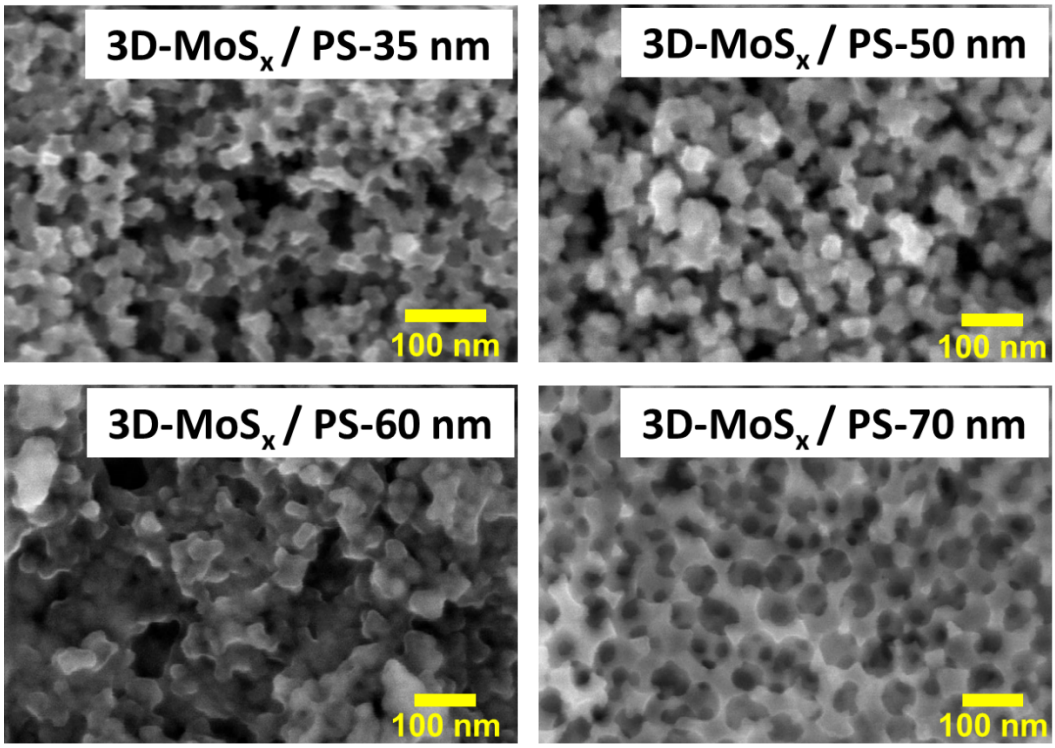

Figure S4. *Surface SEM images of 3D-MoS_x films obtained by using 3.53 mC/cm^2 deposition charge and different PS-FTO electrodes (different PS particle size)*

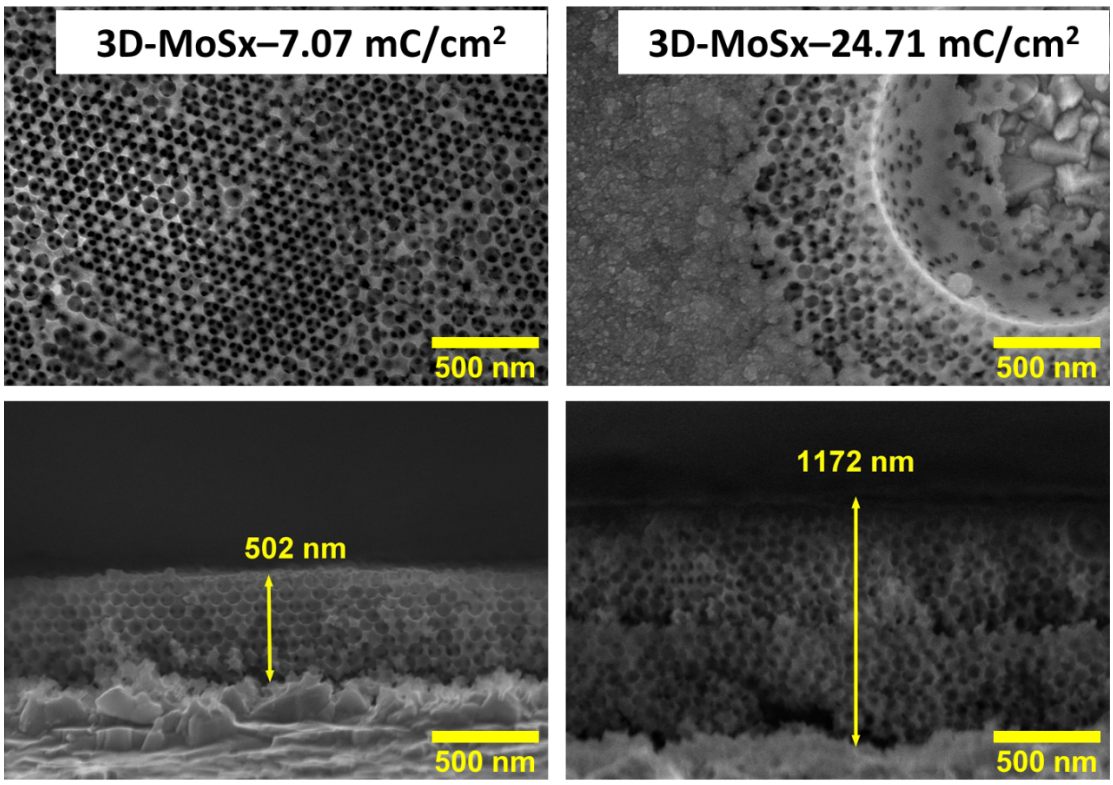

Figure S5. *Surface and cross-section SEM images collected on 3D-MoS_x-7.07 mC/cm^2 and 3D-MoS_x-24.71 mC/cm^2*

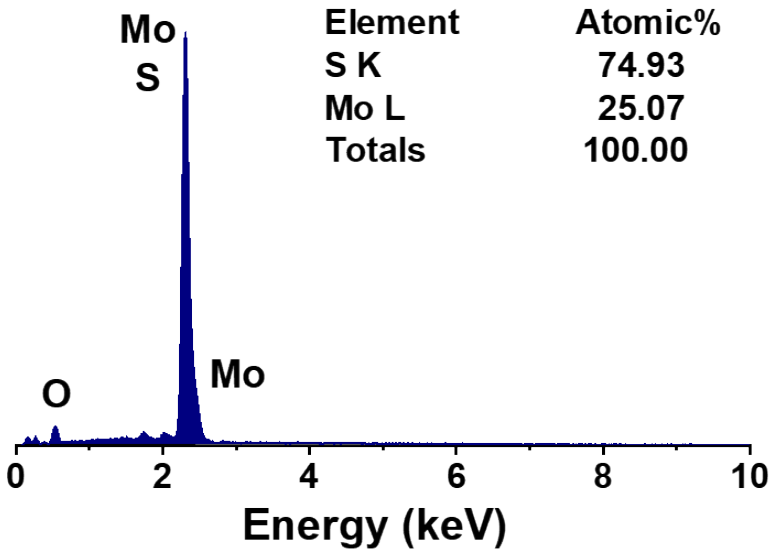

***Figure S6**. EDX analysis of an as-prepared 3D-MoS_x film*

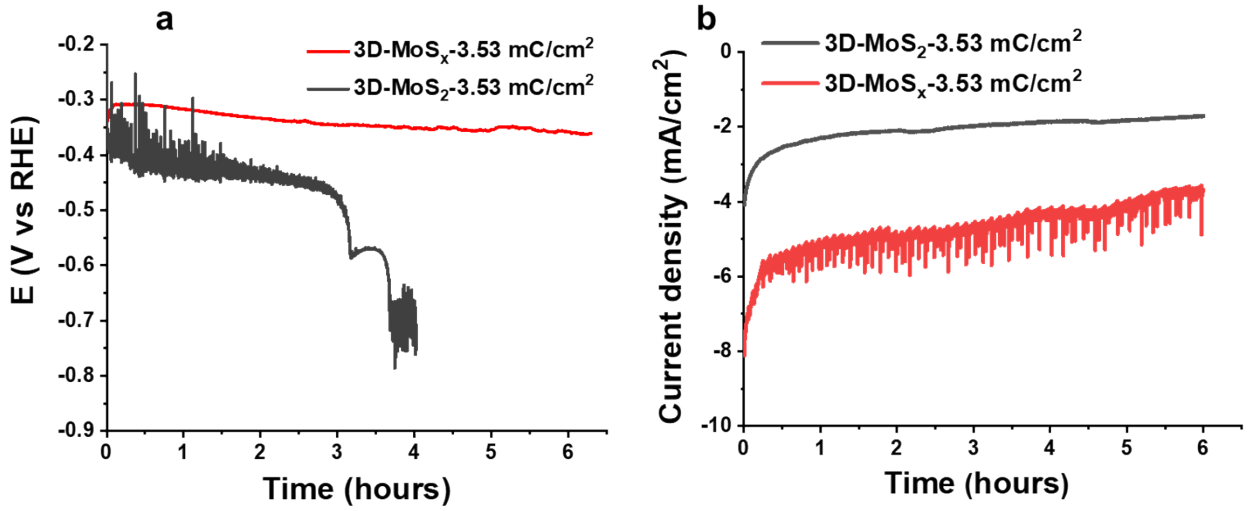

***Figure S7**. (a) Stability of 3D-MoS_x and 3D-MoS_2 catalyst electrode assayed by (a) applying a constant catalytic current density of 10 mA/cm^2 and (b) applying a constant cathodic potential of -0.3 V vs RHE for 6 hours. Electrolyte was a 0.5M H_2SO_4 solution (pH 0.3)*

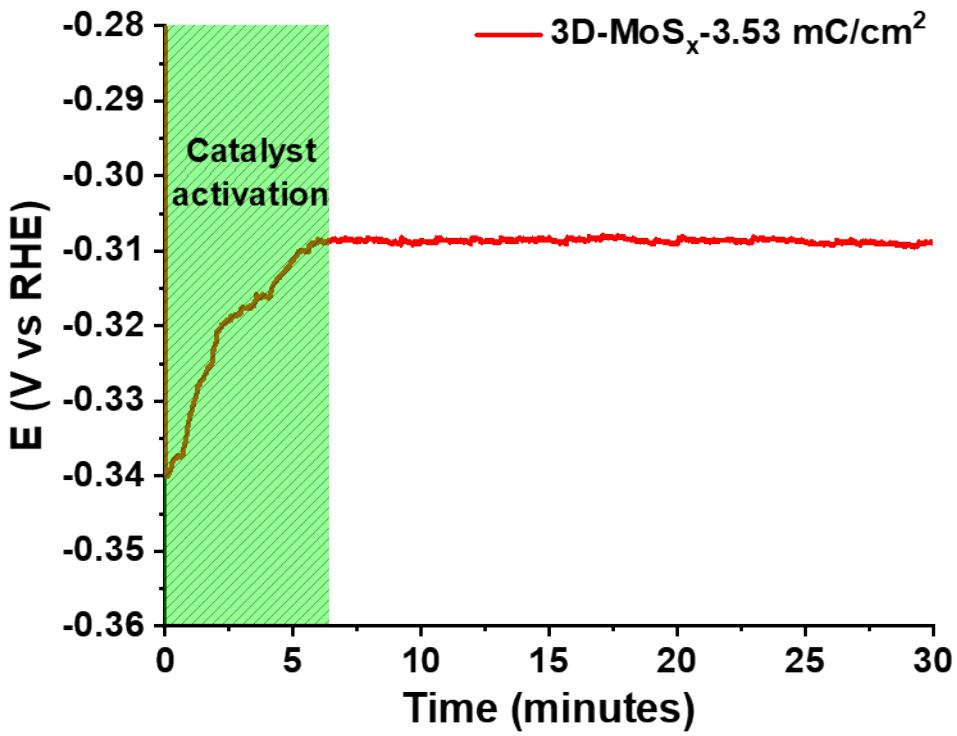

Figure S8. *E-t curve recorded on the 3D-MoS_x-3.53mC/cm^2 electrode conditioned at a constant catalytic current density of 10 mA/cm^2 in a 0.5M H_2SO_4 (pH 0.3) electrolyte solution*

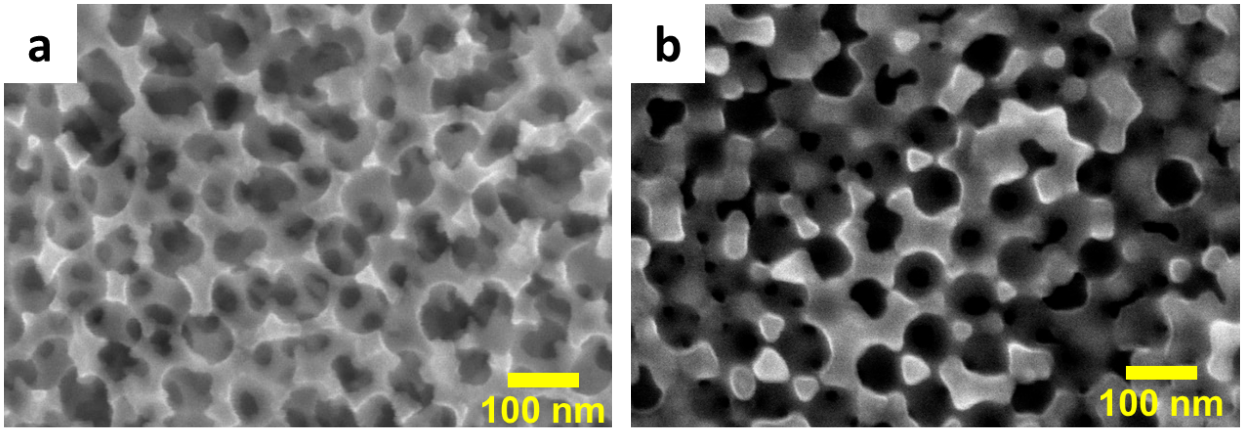

Figure S9. *Surface SEM images recorded on a (a) 3D-MoS_2 and (b) 3D-MoS_x film after 6 hours of bulk electrolysis at -0.3V vs. RHE. Electrolyte was a 0.5M H_2SO_4 solution (pH 0.3)*

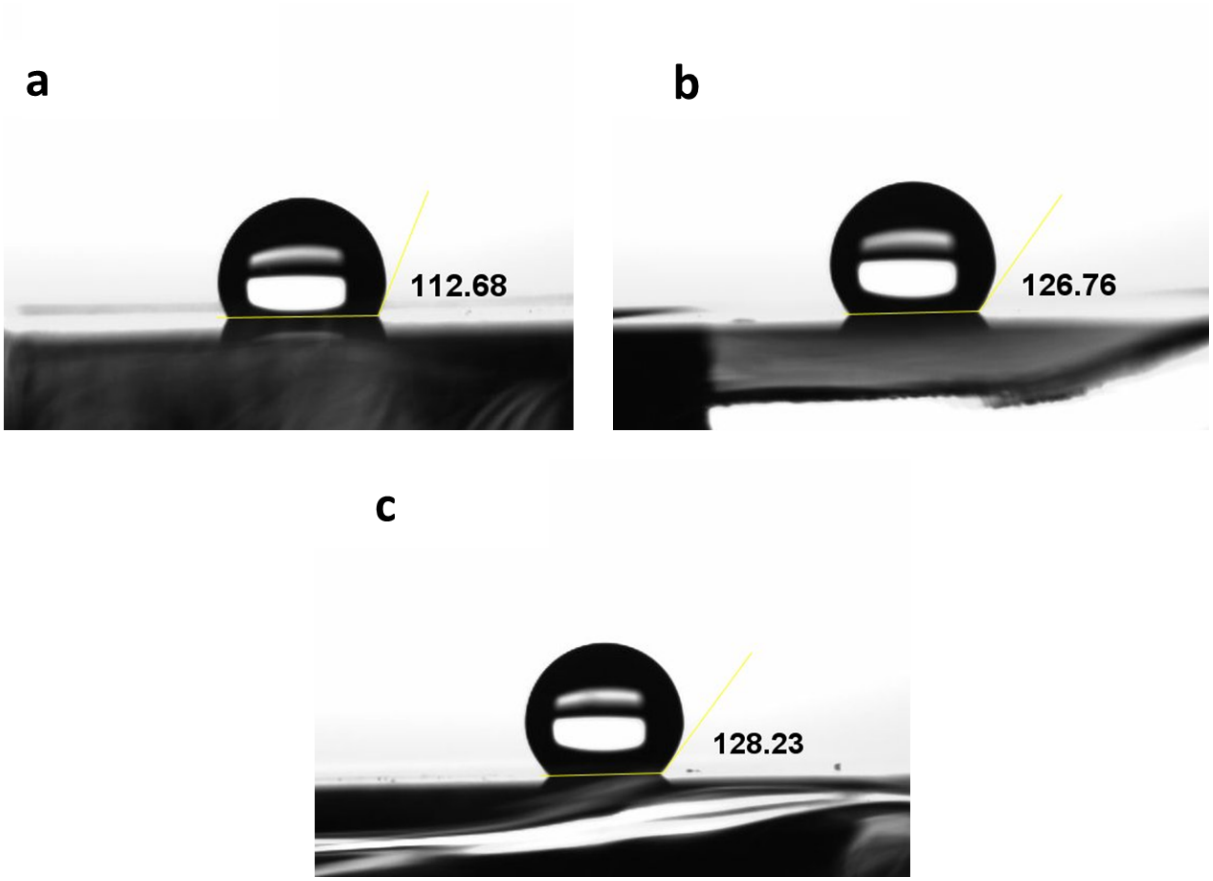

Figure S10. *Water contact angles determined for (a) a bulk MoS_x, (b) a 3D-MoS_x, and a (c) a MoS_2 film*

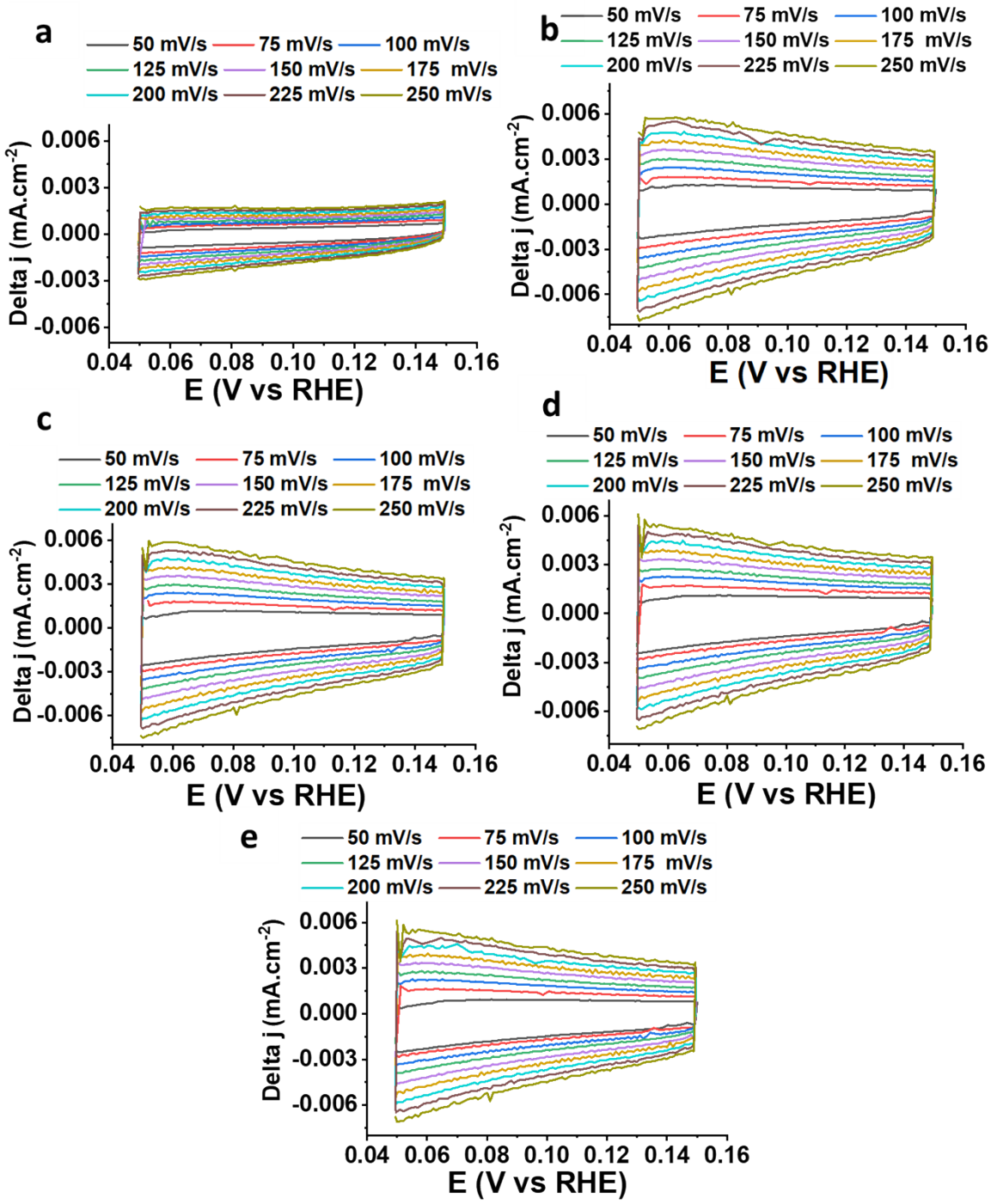

Figure S11. *Cyclic voltammograms recorded at different potential scan rates in the capacitive current region on: (a) the bulk-MoS_x-3.53 mC/cm^2, (b) 3D-MoS_x-3.53 mC/cm^2, (c) 3D-MoS_x-10.59 mC/cm^2, (d) 3D-MoS_x-17.75 mC/cm^2, (e) 3D-MoS_x-24.71 mC/cm^2. Electrolyte was a 0.5M H_2SO_4 solution (pH 0.3)*

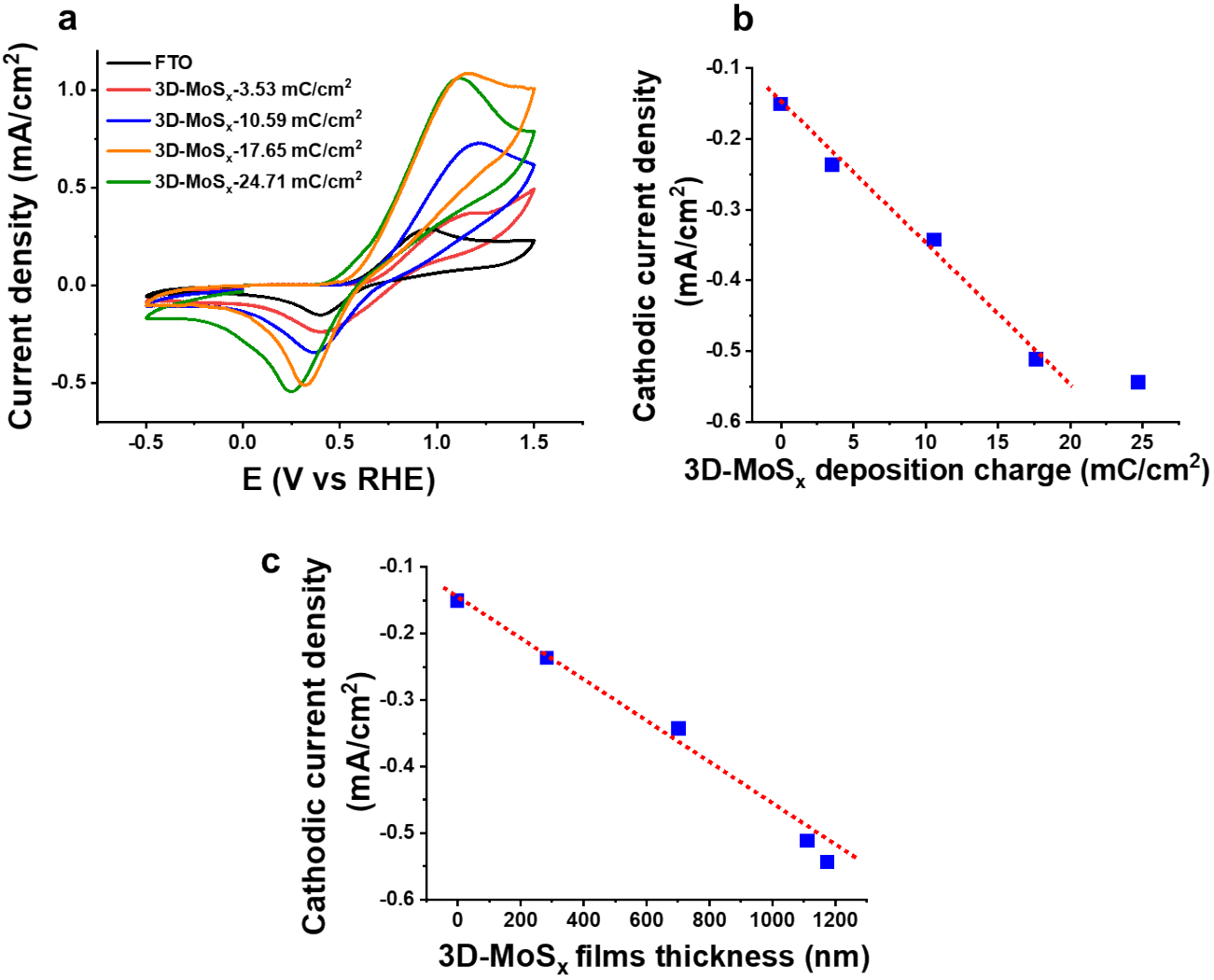

Figure S12. *(a) Cyclic voltammograms recorded for 1mM ferrocene in DCM (with 0.1M TBATFB electrolyte support) on 3D-MoS_x with different thickness. Potential scan rate was 50 mV/s. (b) Plotting the cathodic current density of the Fc^+/Fc couple in function of the 3D-MoS_x deposition charge density. (c) Plotting the cathodic current density of the Fc^+/Fc couple in function of the 3D-MoS_x films thickness*

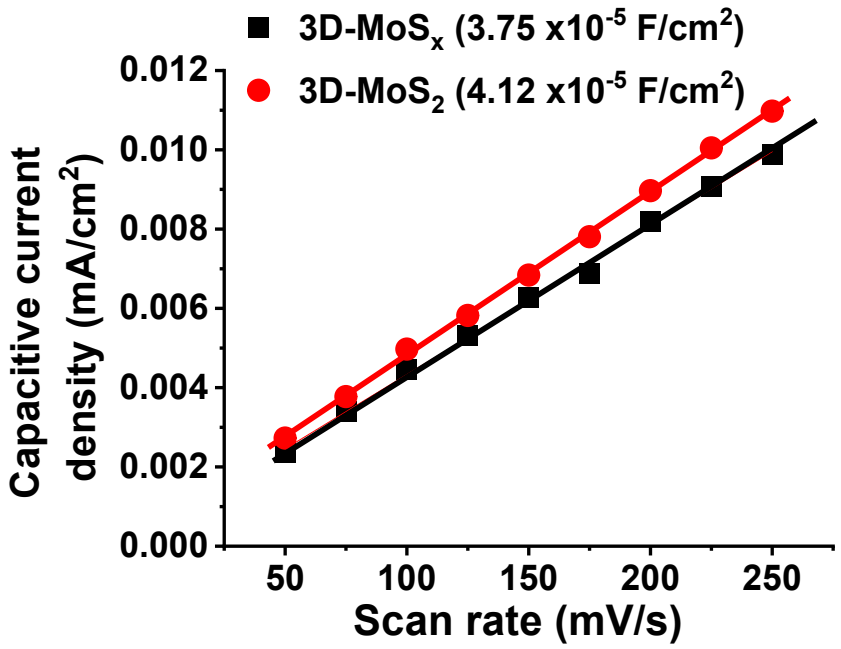

Figure S13. *Plotting capacitive current density obtained at 0.1 V vs. RHE in function of potential scan rate for 3D-MoS_2-3.53 mC/cm² and 3D-MoS_x-3.53 mC/cm² electrodes*

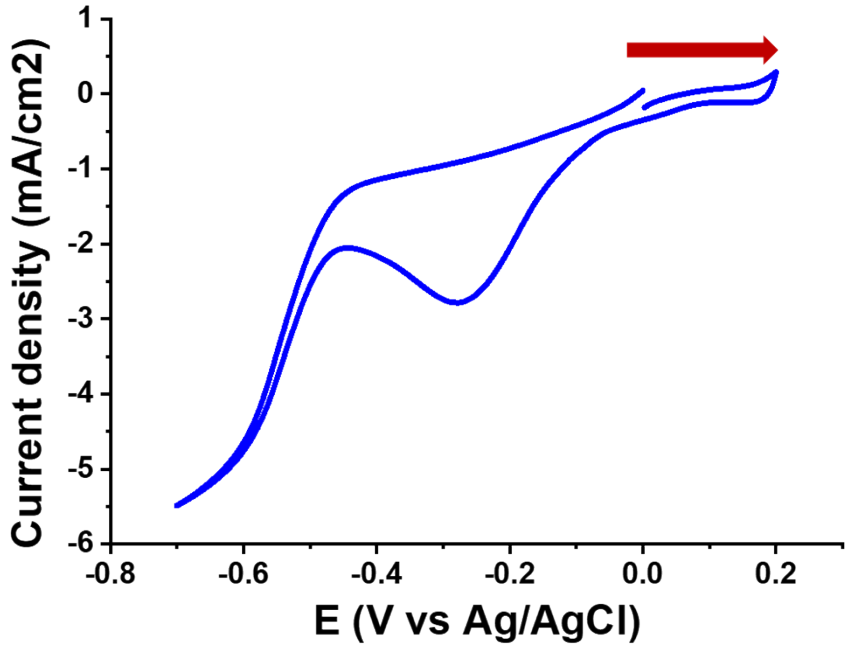

Figure S14. *Cyclic voltammogram recorded for a solution constituted of 1mM Cu_2SO_4 and 0.5M H_2SO_4 employing the 3D-MoS_x-10.59 mC/cm² electrode. Potential scan rate was 50 mV/s toward the anodic direction.*

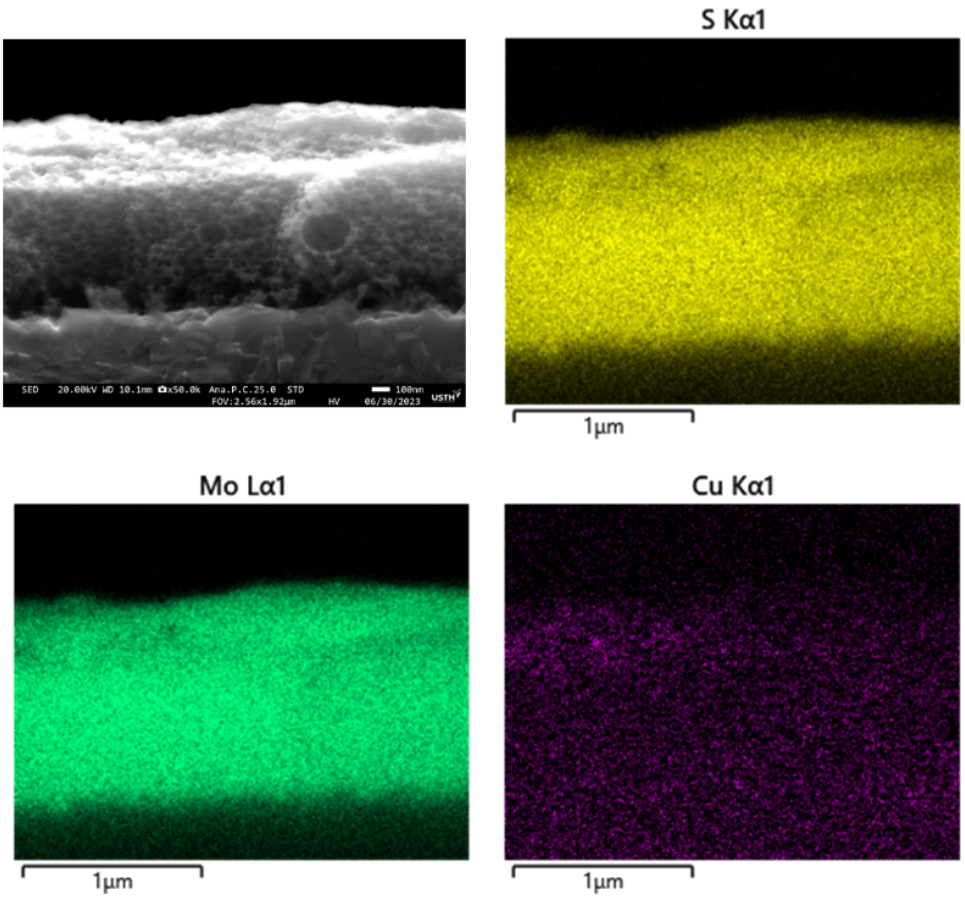

***Figure S15**. EDS elemental mapping (Mo, S and Cu element) on the cross-section of 3D-MoS_x-10.59 mC/cm^2 film after being conditioned by cycling potential between -0.7 V to 0.2 V vs. Ag/AgCl with a potential scan rate of 50 mV/s. Electrolyte was constituted of 1mM $CuSO_4$ and 0.5M H_2SO_4*

Calculation of theoretical surface area of 3D-MoS_x

Assume that the polystyrene particles are homogeneous perfect spheres and the arrangement of PS particles on FTO electrodes forms a hexagonal close-packed lattice structure (Figure S12). Each crystal unit cell contains 6 polystyrene particles.

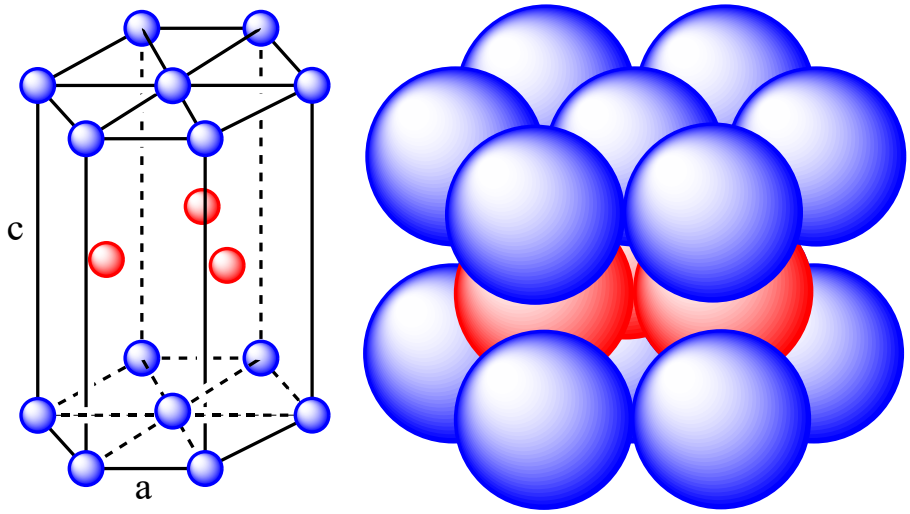

Figure S16. The hexagonal close-packed lattice structural arrangement of PS particles

+ The volume of unit cells is calculated as following: $V_{unit\ cell} = 24\sqrt{2}.R^3\ (nm^3)$

+ Assume that the working electrode was prepared with a working area of 1 cm^2. The 3D-MoS_x was electrochemically deposited to the d (nm) of thickness.

The volume of 3D-MoS_x films will be calculated as: $V_{(3D\text{-}MoSx)} = (1x10^{14}).\ d\ (nm^3)$

We then calculate the number of polystyrene particles in the deposited volume of 3D-MoS_x electrodes:

Number of polystyrene particles: $N = 6\ \frac{V(3D-MoSx)}{V(unit\ cell)}$

+ After removal of PS particles template, we can assume that the surface area of each polystyrene particle is equal to the remain surface area of each MoS_x inverse opal pore. Then the theoretical surface area of 3D-MoS_x can be defined:

$$S_{theo.} = N \times \frac{4}{3} \pi R^3$$

The theoretical calculated surface values are presented in the table 2.

Table 2. Theoretical calculation of surface area on 3D-MoS_x samples with geometrical area of 1.0 cm^2

Run	Sample	Diameter of PS (cm)	Volume of unit cell ($cm^{3)}$	Thickness of deposited film (cm)	Volume of deposited film (cm^3)	Number of PS particles in film	Surface area of a PS particle (cm^2)	Theoretical surface area (cm^2)
1	Bulk MoS_x*	0	0	-	-	-	-	**1.000**
2	3D-MoS_x-35nm	$3.5x10^{-6}$	$14.553x10^{-15}$	$3.0x10^{-5}$	$3.0x10^{-5}$	$12.369x10^{10}$	$1.539x10^{-10}$	**19.041**
3	3D-MoS_x-50 nm	$5.0x10^{-6}$	$42.427x10^{-15}$	$3.0x10^{-5}$	$3.0x10^{-5}$	$4.243x10^{10}$	$3.142x10^{-10}$	**13.328**
4	3D-MoS_x-60 nm	$6.0x10^{-6}$	$73.314x10^{-15}$	$3.0x10^{-5}$	$3.0x10^{-5}$	$2.455x10^{10}$	$4.524x10^{-10}$	**11.107**
5	3D-MoS_x-70 nm	$7.0x10^{-6}$	$11.642x10^{-14}$	$3.0x10^{-5}$	$3.0x10^{-5}$	$1.546x10^{10}$	$6.158x10^{-10}$	**9.520**
6	3D-MoS_x-90 nm	$9.0x10^{-6}$	$24.743x10^{-14}$	$3.0x10^{-5}$	$3.0x10^{-5}$	$7.275x10^{9}$	$10.179x10^{-9}$	**7.405**
7	3D-MoS_x-90 nm	$9.0x10^{-6}$	$24.743x10^{-14}$	$5.0x10^{-5}$	$5.0x10^{-5}$	$1.212x10^{10}$	$10.179x10^{-9}$	**12.341**
8	3D-MoS_x-90 nm	$9.0x10^{-6}$	$24.743x10^{-14}$	$7.0x10^{-5}$	$7.0x10^{-5}$	1.697x1010	$10.179x10^{-9}$	**17.278**
9	3D-MoS_x-90 nm	$9.0x10^{-6}$	$24.743x10^{-14}$	$11.0x10^{-5}$	$11.0x10^{-5}$	$2.667x10^{10}$	$10.179x10^{-9}$	**27.151**

*The surface area of bulk MoS_x is considered as geometrical working electrodes area of 1 cm^2