Supporting Information

Hydrogen evolution at the *in-situ* MoO_3/MoS_2 heterojunctions created by non-thermal O_2 plasma treatment

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Table of Contents:

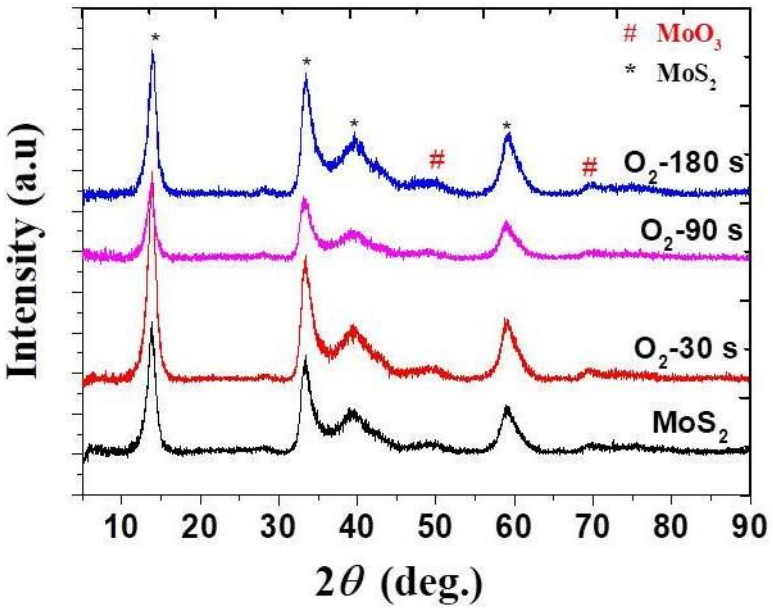

Fig. S1: PXRD of MoS_2 and oxygen plasma irradiated samples.

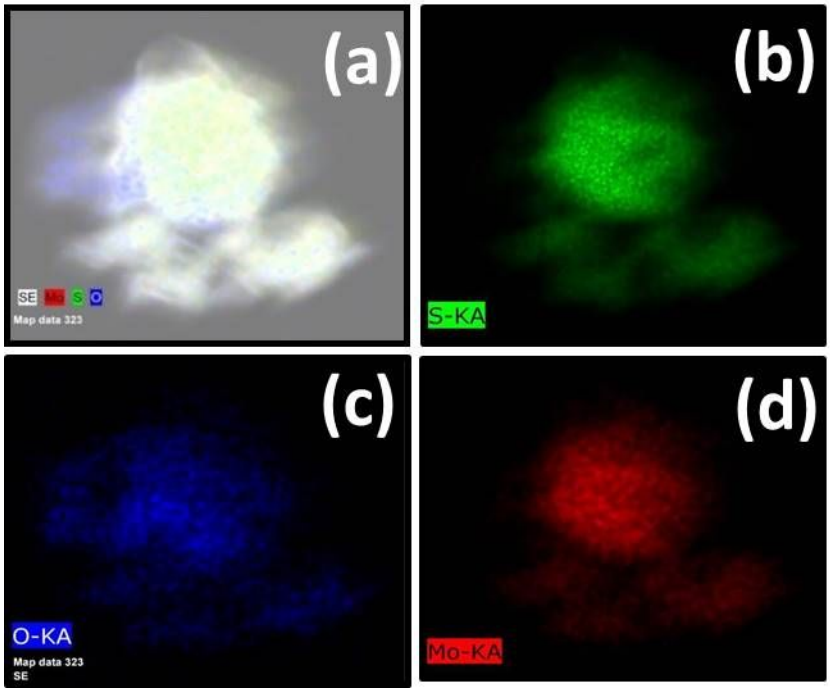

Fig. S2: (a) Overlay of STEM mapping of O_2-30 s and elements (b) S (c) O and (d) Mo confirms the uniformly distribution after irradiation of 30 sec of O_2 plasma .

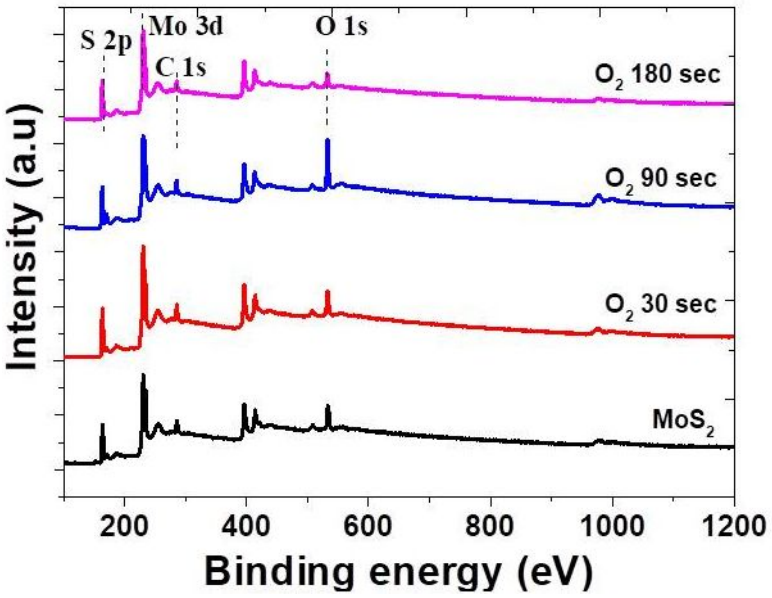

Fig. S3: Wide scan XPS spectra of MoS_2 along with O_2 plasma irradiated samples.

Table S1 XPS fitting parameters of Mo, S and O respectively

Position (eV)	Mo^{4+} $3d_{5/2}$	FWHM	Mo^{4+} $3d_{3/2}$	FWHM	S 2s	FWHM	Mo^{6+} $3d_{3/2}$	FWHM	Mo^{6+} $3d_{5/2}$	FWHM
MoS_2	229.85	0.95	232.95	1.21	227.01	2.36	-	-	-	-
O_2-30 sec	229.59	0.94	232.74	1.13	226.67	2.07	234.26	3.36	231.06	1.05
O_2-90 sec	229.22	0.99	232.39	1.31	226.46	2.38	233.59	1.13	230.39	1.45
O_2-180 sec	229.49	0.98	232.62	1.18	226.78	2.12	234.33	1.08	231.06	1.35

*In each case difference between peak position of Mo^{4+} $3d_{5/2}$ and Mo^{4+} $3d_{3/2}$ remains constant of 3.1 eV and in case of oxygen plasma irradiated samples difference between Mo^{6+} $3d_{5/2}$ and Mo^{6+} $3d_{3/2}$ is 3.2 eV respectively.

Position (eV)	S $2p_{3/2}$	FWHM	S $2p_{1/2}$	FWHM	SO_x^{y-}	FWHM
MoS_2	162.76	0.98	163.98	0.80	169.71	2.26
O_2-30 sec	162.24	0.92	163.47	0.82	169.38	2.65
O_2-90 sec	162.01	1.01	163.25	0.84	169.19	2.1
O_2-180 sec	162.28	1.04	163.52	0.80	168.94	1.78

*In each case difference between the binding energy of S $2p_{3/2}$ and S$2p_{1/2}$ remains 1.2 eV which is constant.

Sample	Position (eV)	FWHM	Position (eV)	FWHM	Position (eV)	FWHM
MoS_2	532.95	2.76	-	-	-	-
O_2-30 sec	531.60	2.19	533.08	2.26	530.55	1.28
O_2-90 sec	532.01	1.73	533.23	2.26	530.53	1.38
O_2-180 sec	531.43	1.43	533.43	1.56	530.63	1.21

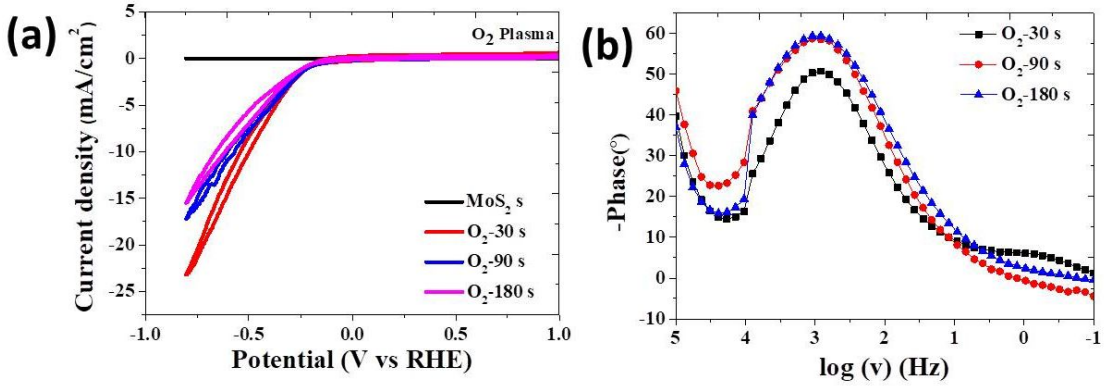

Fig. S4: CV curves of (a) O_2 plasma irradiated samples (b) Bode phase plot of O_2 plasma samples in 0.5 M H_2SO_4 electrolyte.

Table S2: Comparison of the HER activity of some reported transition chalcogenides

Sample	Tafel slope	Overpotential (η) ~ 10 mA /cm^2	Ref.
MoS_2	271 mV/dec	0.63 V vs RHE	6
SG/MoS_2	152 mV/dec	0.30 V vs RHE	6
MoO_3	138 mV/dec	-	7
MoO_3	130 mV/ dec	0.280 V vs RHE	8
MoS2-MoO3	125 mV/dec	0.250 V vs RHE	This work
Pt	30 mV/dec	0.070 V vs RHE	9

*SG = sulphur doped graphene

Table S3: All model structures investigated using DFT. We assume that H^+ energy is given by H_2 energy divided by 2.

Id	Structure	Total Energy [eV]	# Atoms
1	H_2	-31.7487	2
2	$Mo_{48}S_{96}$	-6383861.5910	144
3	$Mo_{48}S_{95}O_1$	-6375030.5416	144
4	$Mo_{48}S_{95}O_1$	-6385908.9130	145
6	$Mo_{48}S_{95}O_1$-H	-6375045.3923	145
7	$Mo_{48}S_{96}O_1$-H	-6385924.2961	146

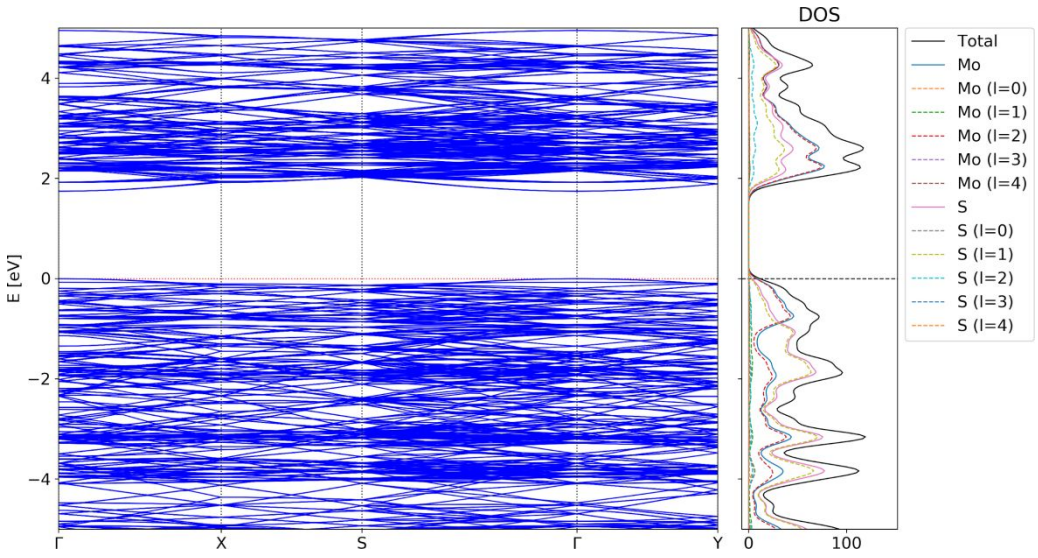

Fig. S5 Electronic band structure for model (i) MoS_2 (supercell $Mo_{48}S_{96}$), band gap 1.74 eV.

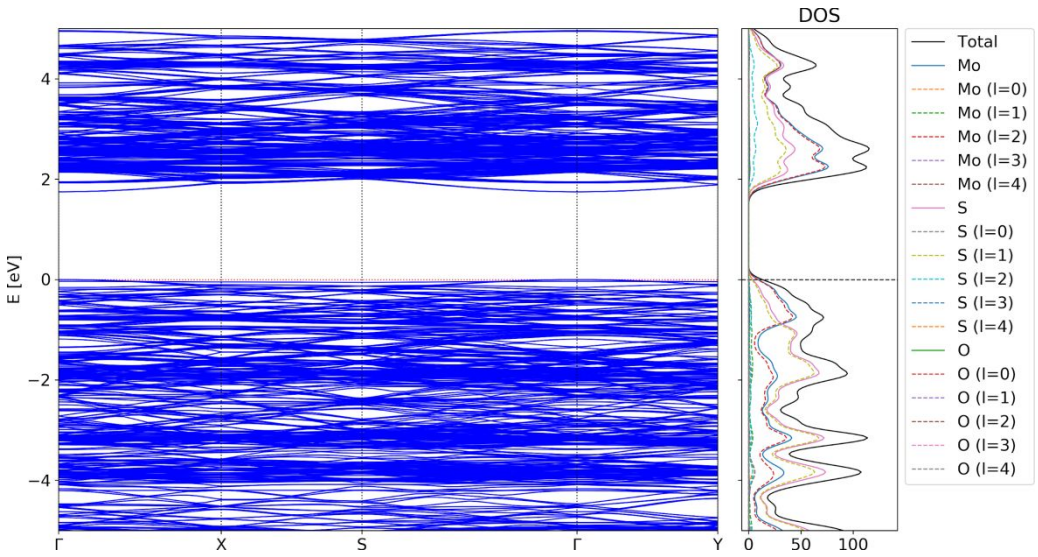

Fig. S6. Electronic band structure for model (ii) $Mo_{48}S_{95}O_1$, band gap 1.74 eV.

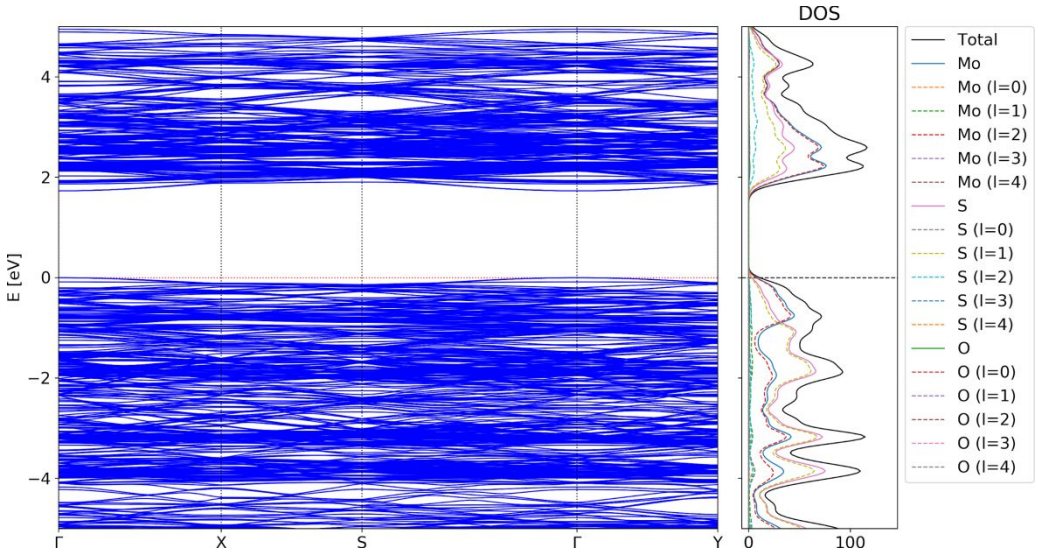

Fig. S7 Electronic band structure for model (iii) $\underline{Mo_{48}S_{96}O_1}$ band gap 1.72 eV