Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels.

Supporting Information

Effect of anionic substitution in molybdenum oxysulfide supported on reduced graphene oxide sheets for hydrogen evolution reaction and supercapacitor application

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Table S1: Table of I_D/I_G ratio of RGO in MoS_2/RGO before and after oxygen plasma irradiation.

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Figure S8: Nyquist plot of MoS_2/RGO and all oxygen plasma irradiated samples in frequency range from 12068 Hz to 1 Hz.

Figure S9: Electrochemical supercapacitor behaviour of MoS_2/RGO.

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Figure S11: Nyquist plot observed at OCP after performing 3000 stability cycles for MoS_2/RGO with O_2 plasma irradiation of 0 sec and 180 sec respectively.

Table S5: Specific capacitance calculated from CV.

Table S6: Specific capacitance calculated from GCD.

Table S1: Table of I_D/I_G ratio of RGO in MoS_2/RGO before and after oxygen plasma irradiation.

Sample Id	**I_D**	**I_G**	**I_D/I_G**
MoS_2/RGO-0 sec	722.8	556.1	1.29
MoS_2/RGO -30 sec	3247.5	2921.5	1.11
MoS_2/RGO -60 sec	4592.0	4233.8	1.08
MoS_2/RGO -90 sec	7241.4	6762.6	1.07
MoS_2/RGO -150 sec	12052.9	10822	1.12
MoS_2/RGO -180 sec	17037.5	14150	1.23

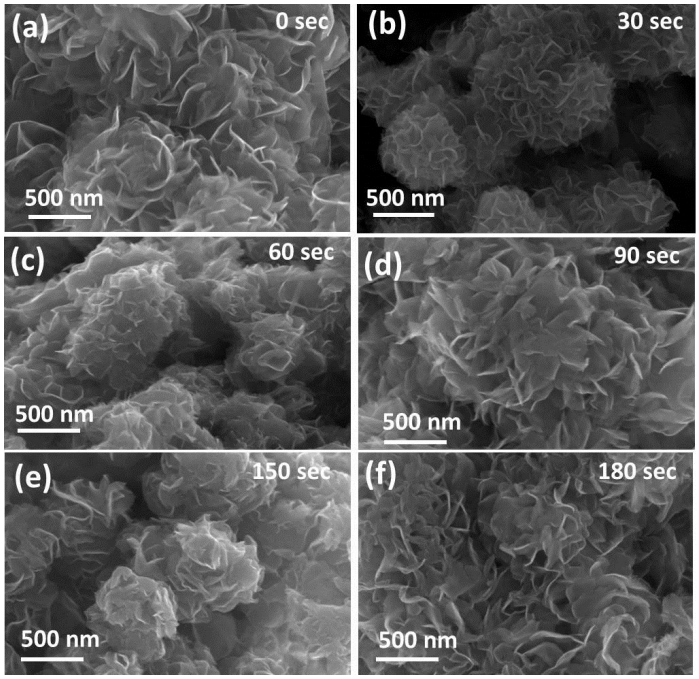

Figure S1: FESEM micrographs of MoS_2/RGO without and with irradiation of O_2 plasma for different fractions of time.

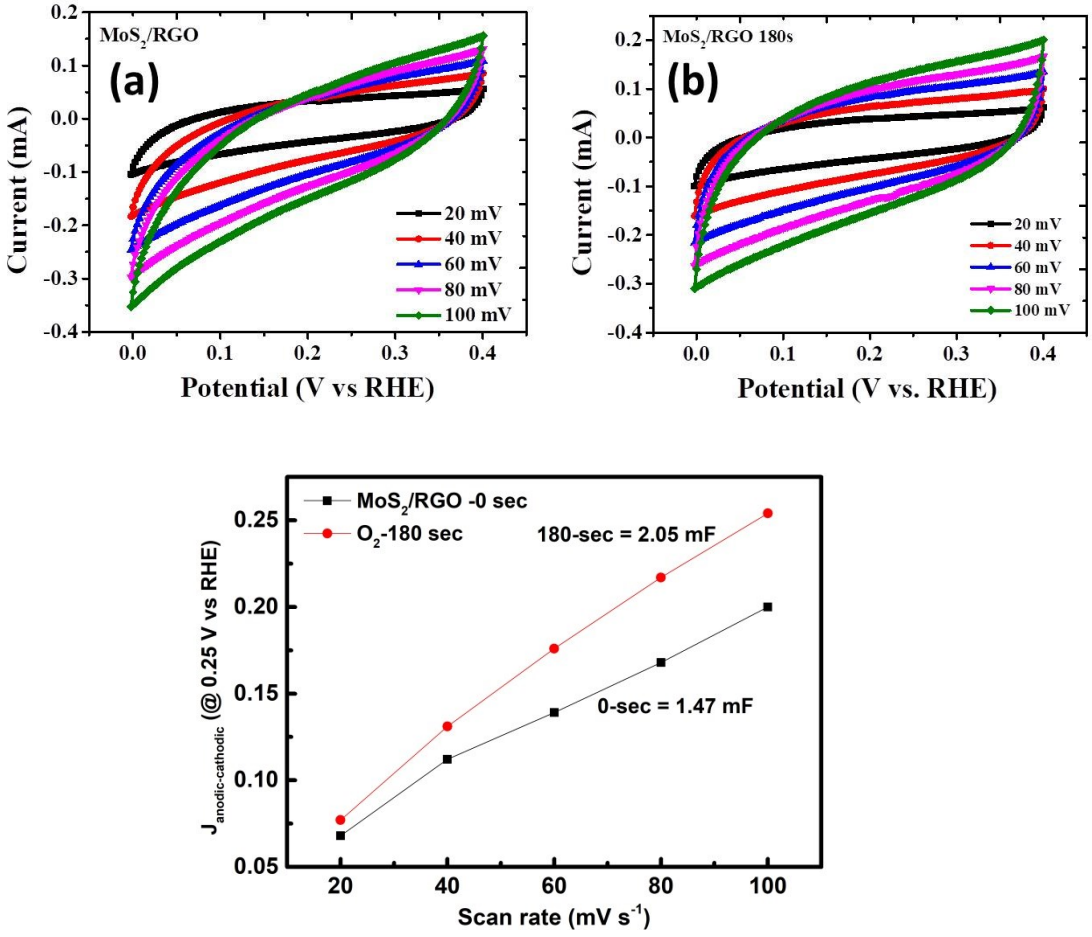

Figure S2: Cyclic voltammetry curves obtained with different scan rates for (a) MoS_2/RGO 0- sec (b) MoS_2/RGO –O_2-180 sec and (c) Electrochemical surface area (ECSA) analysis of MoS_2/RGO at 0 sec and after irradiation of 180 sec of oxygen plasma.

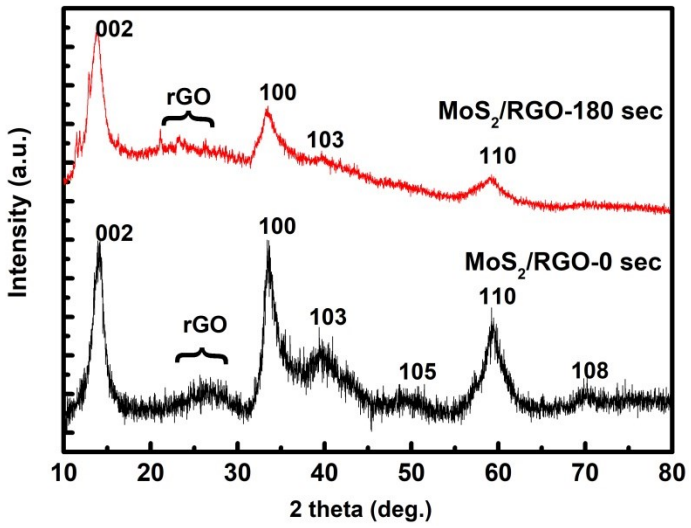

Figure S3: PXRD pattern of MoS_2/RGO without and with irradiation of 180 sec of O_2 plasma.

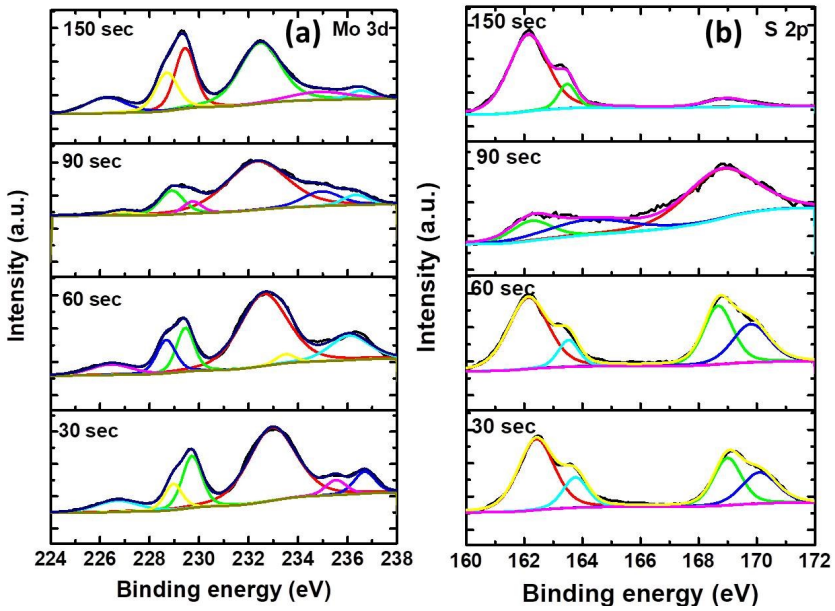

Figure S4: High resolution XPS spectra of (a) Mo 3d (b) S 2p after O2 plasma irradiation of 30 sec, 60 sec, 90 sec and 150 sec respectively.

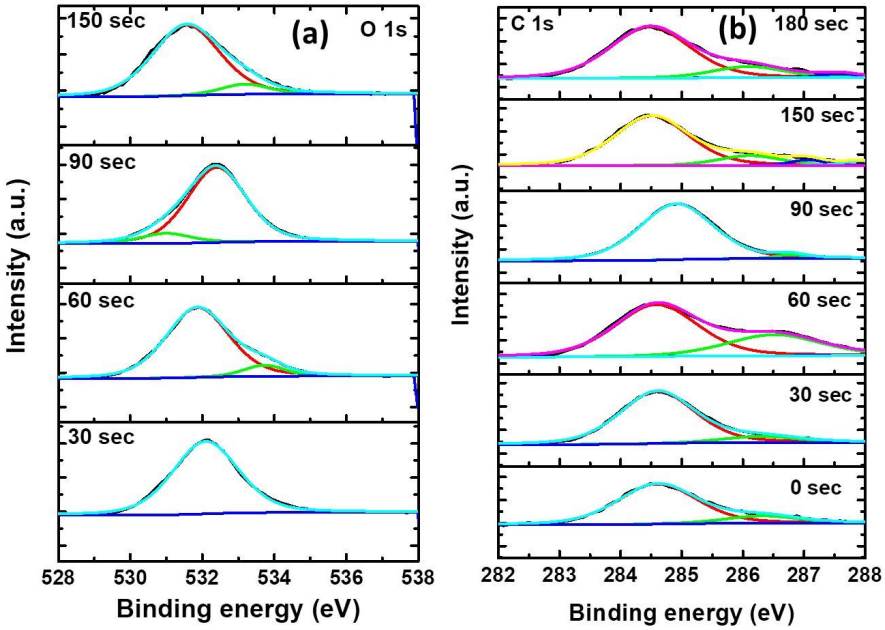

Figure S5: High resolution spectra of (a) O 1s after irradiation of 30 sec, 60 sec, 90 sec and 150 sec (b) C 1s spectra of untreated and treated samples after 30 sec, 60 sec, 90 sec, 150 sec and 180 sec respectively.

Table S2: XPS interpretation of Mo 3d in case of MoS_2/RGO and after oxygen plasma irradiation of 30 sec, 60 sec, 90 sec, 150 sec and 180 sec respectively.

Mo 3d	S				Mo^{4+}		Mo^{4+}		Mo^{6+}		Mo^{6+}	
	2s	FWHM		FWHM	$3d_{5/2}$	FWHM	$3d_{3/2}$	FWHM	$3d_{5/2}$	FWHM	$3d_{3/2}$	FWHM
MoS_2-0 sec	226.39	1.95	228.65	0.81	229.45	1.03	232.47	1.72	233.96	1.86	236.49	1.74
MoS_2-30 sec	226.68	2.05	228.96	0.85	229.72	0.94	232.96	2.26	235.53	0.98	236.70	1.02
MoS_2-60 sec	226.43	2.0	228.68	0.92	229.44	0.84	232.61	2.30	233.49	0.90	236.09	1.9
MoS_2 – 90 sec	226.86	1.20	228.89	1.14	229.74	0.88	232.34	2.94	234.95	1.77	236.34	1.20
MoS_2 – 150 sec	226.24	1.90	228.69	1.07	229.43	0.98	232.46	1.98	234.89	2.76	236.55	1.11
MoS_2 -180 sec	226.28	1.97	228.55	0.84	229.36	1.04	232.38	1.92	234.39	3.07	236.58	1.22

Table S3: XPS interpretation of high resolution spectra of S 2p of MoS_2/RGO at different time fractions of oxygen plasma involving 0 sec, 30 sec, 60 sec, 90 sec, 150 sec and 180 sec respectively.

S 2p								
		FWHM		FWHM		FWHM		
MoS_2-0 sec	162.19	1.46	163.50	0.75	169.37	2.03	-	-
MoS_2-30 sec	162.41	1.47	163.76	1.01	168.99	1.14	170.09	1.42
MoS_2-60 sec	162.14	1.62	163.52	0.84	168.67	1.19	169.8	1.48
MoS_2 – 90 sec	162.24	1.67	164.24	3.48	168.76	2.87	-	-
MoS_2 – 150 sec	162.14	1.59	163.48	0.71	168.97	1.71	-	-
MoS_2 -180 sec	162.13	1.55	163.41	0.78	169.4	2.07		

Table S4: XPS interpretation of high resolution spectra of O 1s of MoS_2/RGO at different time fractions of oxygen plasma involving 0 sec, 30 sec, 60 sec, 90 sec, 150 sec and 180 sec respectively.

O 1s					C 1s			
		FWHM		FWHM				
MoS_2-0 sec	532.02	2.36	-	-	284.6	1.53	286.32	1.41
MoS_2-30 sec	532.09	2.16	-	-	284.6	1.46	286.29	1.43
MoS_2-60 sec	531.87	2.07	533.73	1.34	284.59	1.61	286.51	1.83
MoS_2-90 sec	532.40	1.93	530.99	1.66	284.91	1.43	286.78	0.55
MoS_2-150 sec	531.55	2.21	533.19	1.56	284.51	1.44	286.12	1.21
MoS_2-180 sec	532	2.42	530.55	0.94	284.48	1.55	286.10	1.40

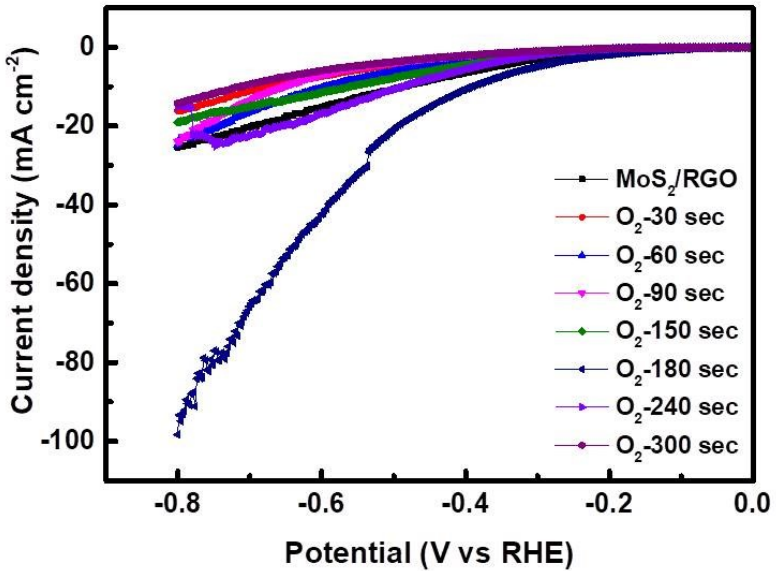

Figure S6: Linear scan voltammetry curves of MoS_2/RGO without treatment and after O_2 plasma irradiation of 30 sec, 60 sec, 90 sec, 150 sec, 180 sec, 240 sec and 300 sec respectively with graphite rod as counter electrode and Ag/AgCl as reference electrode in 0.5 M H_2SO_4 electrolyte.

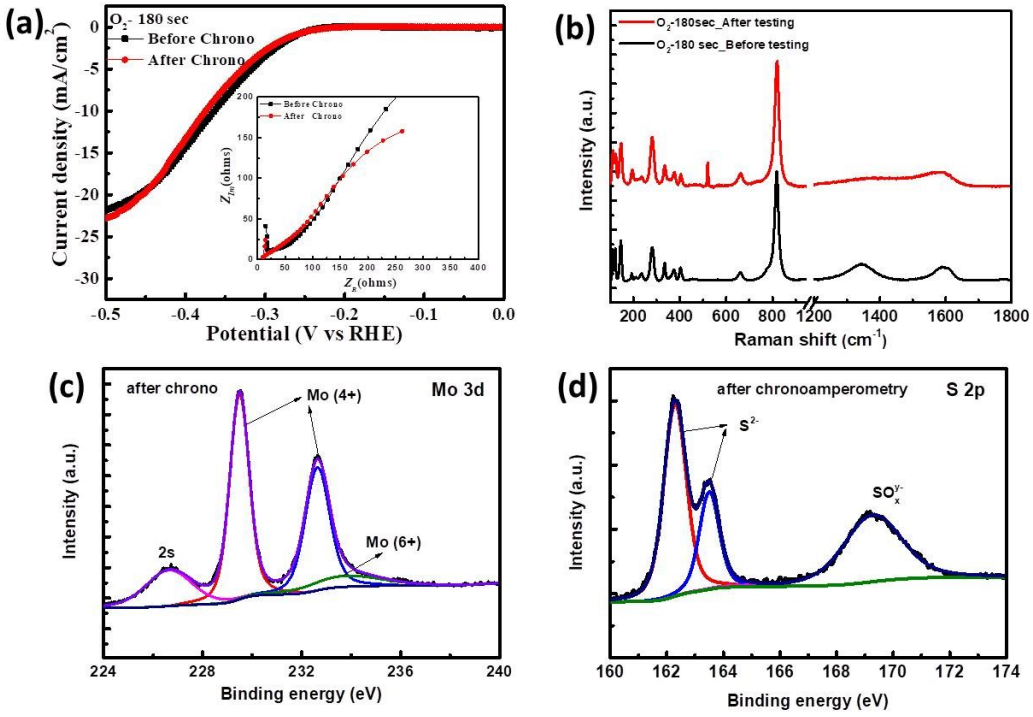

Figure S7: (a) LSV curves before and after chronoamperometry of 12 hrs for O_2-180 sec sample with Pt wire as counter electrode and Ag/AgCl electrode as reference electrode (inset- Nyquist plot for O_2-180 sec before and after long term stability testing) **(b)** Raman spectra and High resolution XPS spectra of **(c)** Mo 3d **(d)** S 2p. respectively.

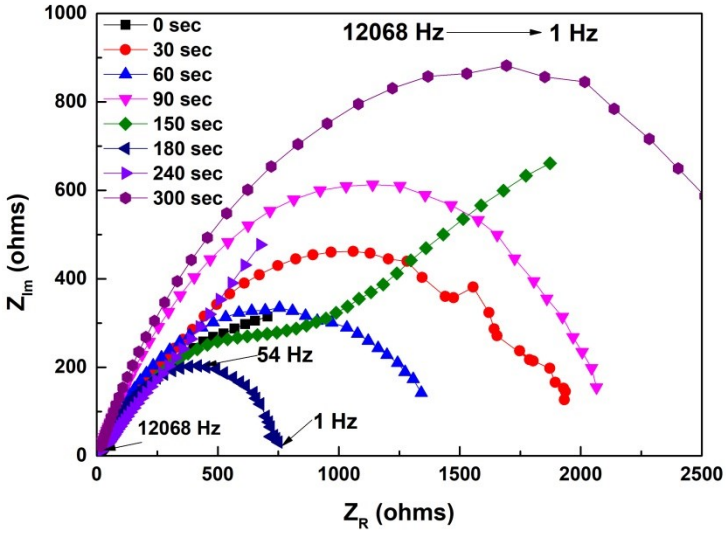

Figure S8: Nyquist plot of MoS_2/RGO and all oxygen plasma irradiated samples in frequency range from 12068 Hz to 1 Hz.

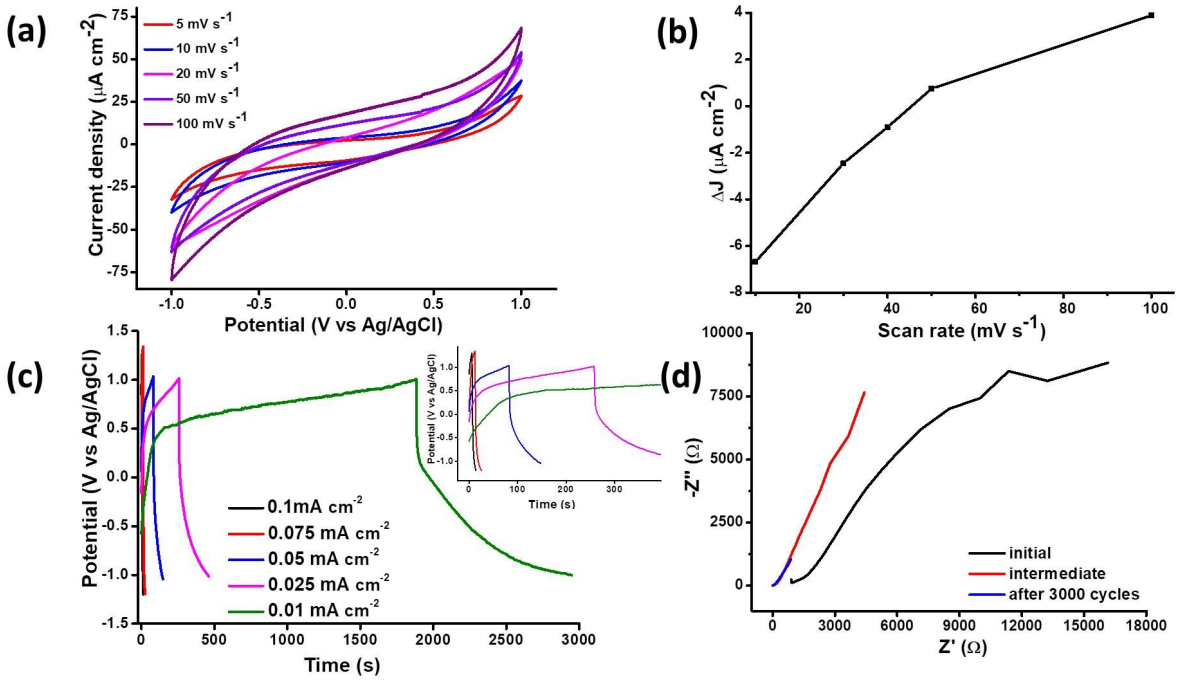

Figure S9: Electrochemical supercapacitor behaviour of MoS_2/RGO in a three electrode setup: **(a)** CV plots drawn by varying scan rate from 5 to 100 mV/s; **(b)** Current density vs Scan rate plot to determine the type of storage of supercapacitor; **(c)** GCD at varying current density from 0.01 mA cm^{-2} to 0.1 mA cm^{-2}; **(d)** EIS taken at different points during the long term GCD.

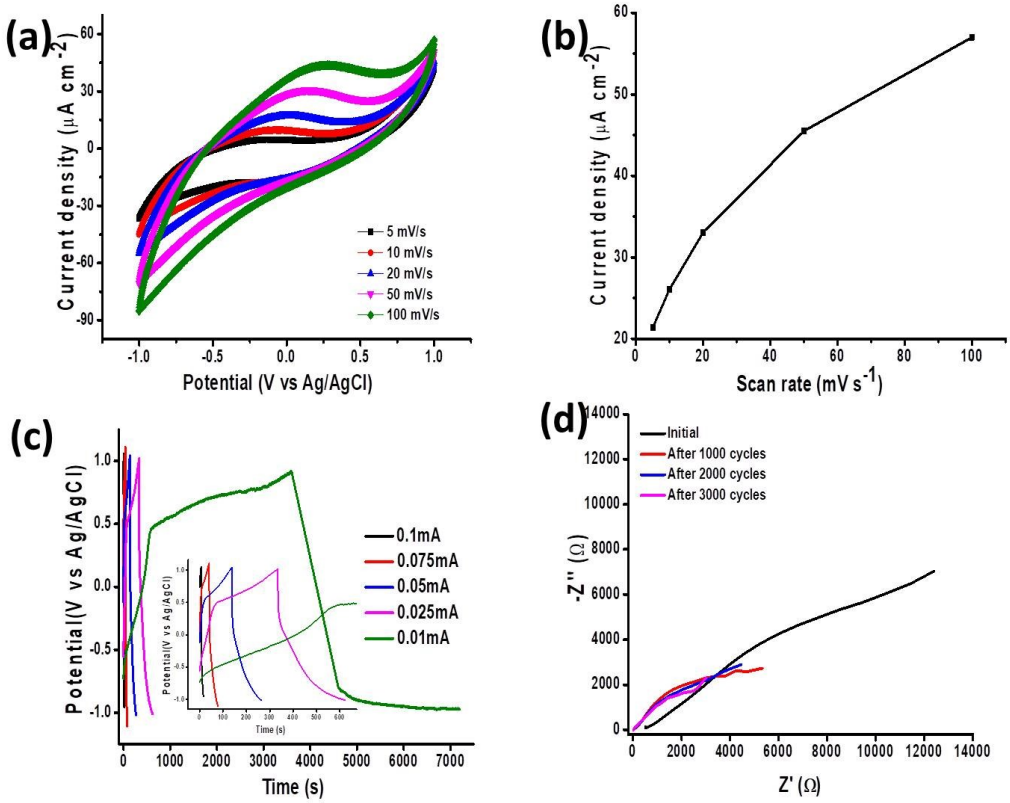

Figure S10. Electrochemical supercapacitor behaviour of O_2-180 sec in a three electrode setup: **(a)** CV plots drawn by varying scan rate from 5 to 100 mV/s; **(b)** Current density vs Scan rate plot to determine the type of storage of supercapacitor; **(c)** GCD at varying current density from 0.01 mA cm^{-2} to 0.1 mA cm^{-2}; **(d)** EIS taken at different points during the long term GCD

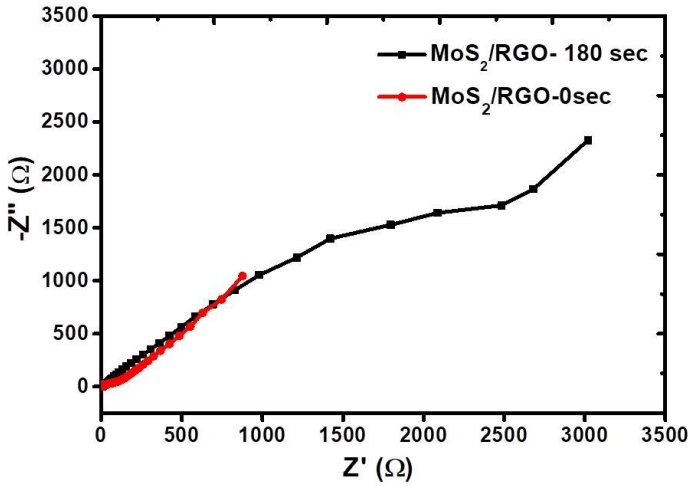

Figure S11. Nyquist plot observed at OCP after performing 3000 stability cycles for MoS_2/RGO with O_2 plasma irradiation of 0 sec and 180 sec respectively.

Table S5. Specific capacitance calculated from CV

	MoS_2/ RGO (O_2-180 sec)	MoS_2/ RGO (O_2-0sec)
Scan rate	C_{sp} (mF/cm^2)	
5	1.4926	0.9375
10	0.8705	0.5653
20	0.5378	0.4076
50	0.3075	0.2039
100	0.2079	0.1453

Table S6. Specific capacitance calculated from GCD

	MoS_2/ RGO (O_2-180 sec)	MoS_2/ RGO (O_2-0sec)
Current density (mA/cm^2)	C_{sp} (mF/cm^2)	
0.01	14.57	5.27
0.025	3.25	2.36
0.05	3.01	1.60
0.075	1.17	0.166
0.1	0.48	0.159