Multi-walled carbon nanotube supported Manganese Selenide as Highly Active Bifunctional OER and ORR electrocatalyst

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Electrodeposition of Pt and RuO_2

The platinum was electrochemically deposited from a solution of 5mM K_2PtCl_6 and 0.5M H_2SO_4 at a potential step from 0.8 V to -0.25 V for 5 s and immediately from -0.25 to 0.25 V for 25 s.

Electrodeposition of RuO_2 on GC substrate was carried out from a mixture of $RuCl_3$ (0.452 g) and KCl (2.952 g) in 40 ml of 0.01M HCl by using cyclic voltammetry from 0.015 to 0.915 V (vs. Ag|AgCl) for 100 cycles at a scan rate of 50 mV s^{-1}. Finally heated at 200 ^{o}C for 3 h in presence of Air.

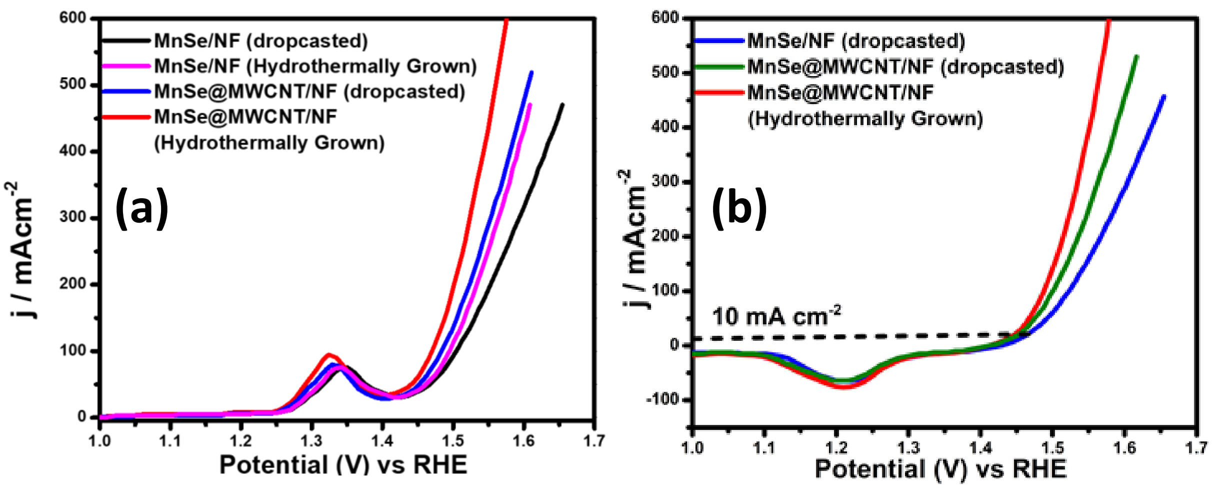

Figure S1. (a) Linear sweep voltammetry characterization showing the OER activity of MnSe and MnSe@MWCNT composite. (b) Estimation of overpotentials from reverse sweep of the CV plots.

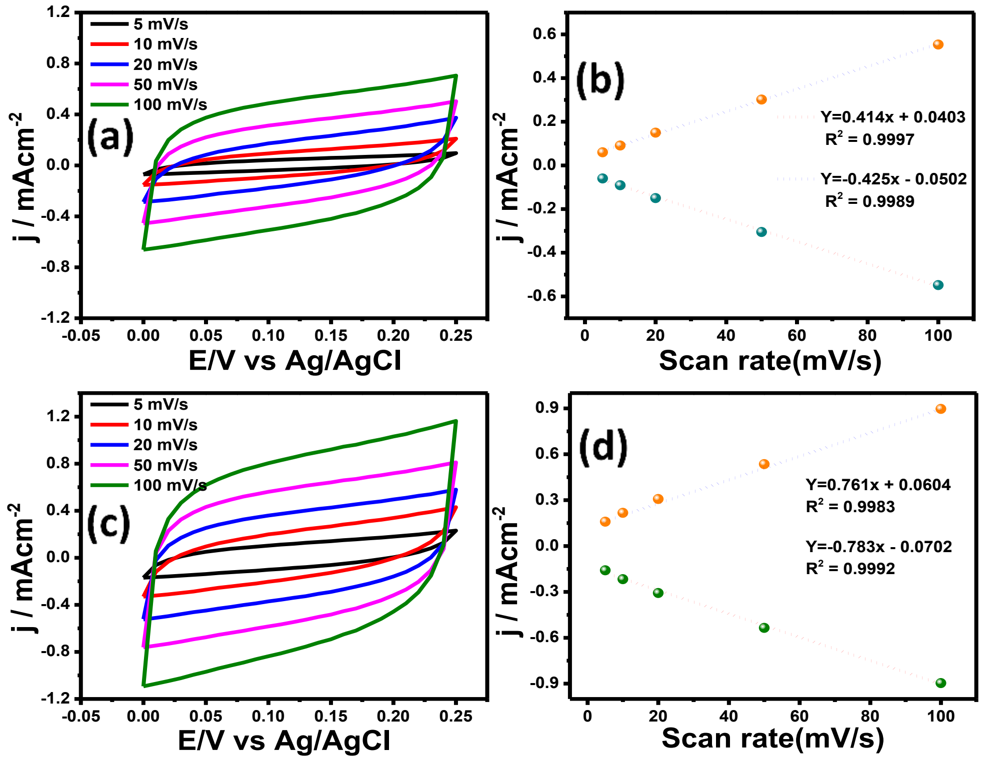

Figure S2. Cyclic voltammograms measured at different scan rates and corresponding plots of anodic and cathodic currents measured as a function of different scan rates for: (a,b) MnSe (c,d), MnSe@MWCNT .

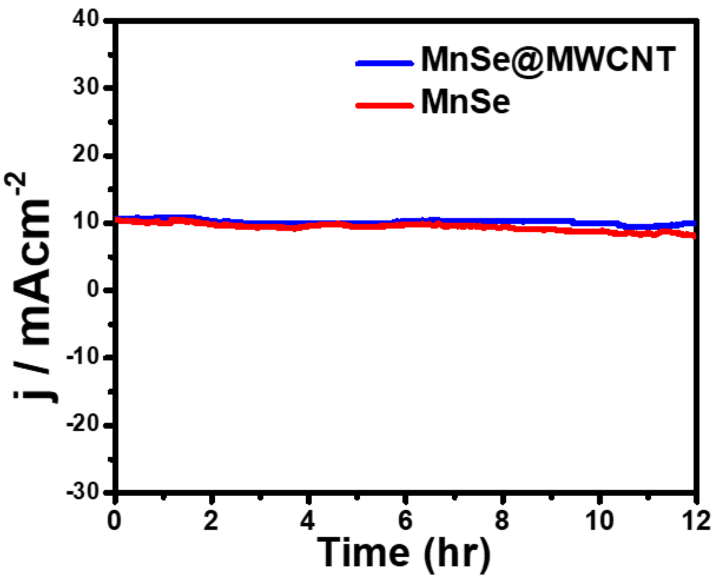

Figure S3. Chronoamperometry studies of the MnSe and MnSe@MWCNT electrodes at a constant applied potential of 1.55 V and 1.52 V respectively.

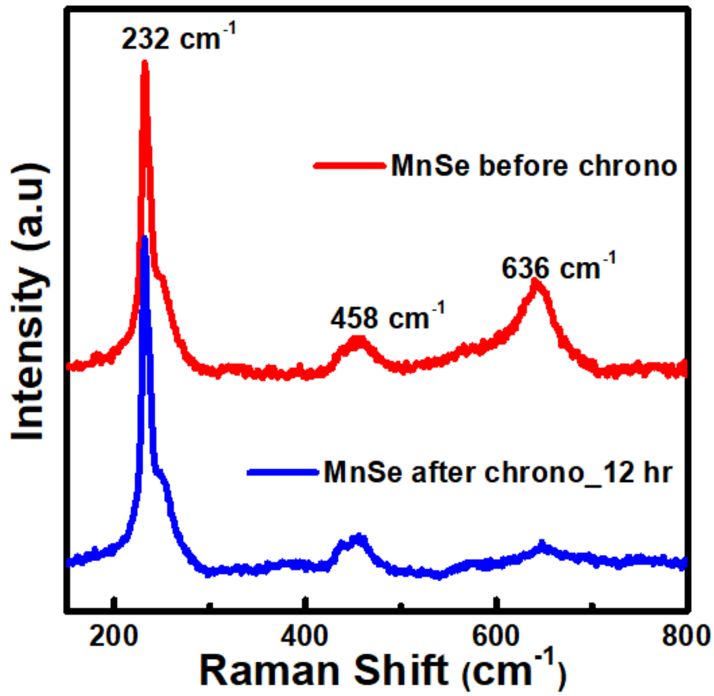

Figure S4. Raman spectra of MnSe before and after 12 hr of chronoamperometry studies.

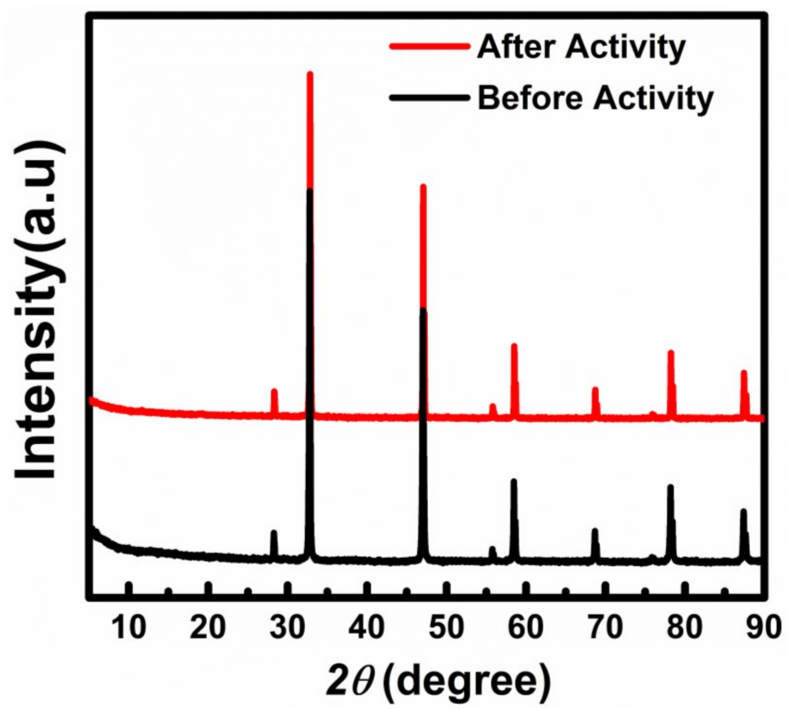

Figure S5. PXRD pattern of MnSe@MWCNT before and after 12 hr of chronoamperometry studies.

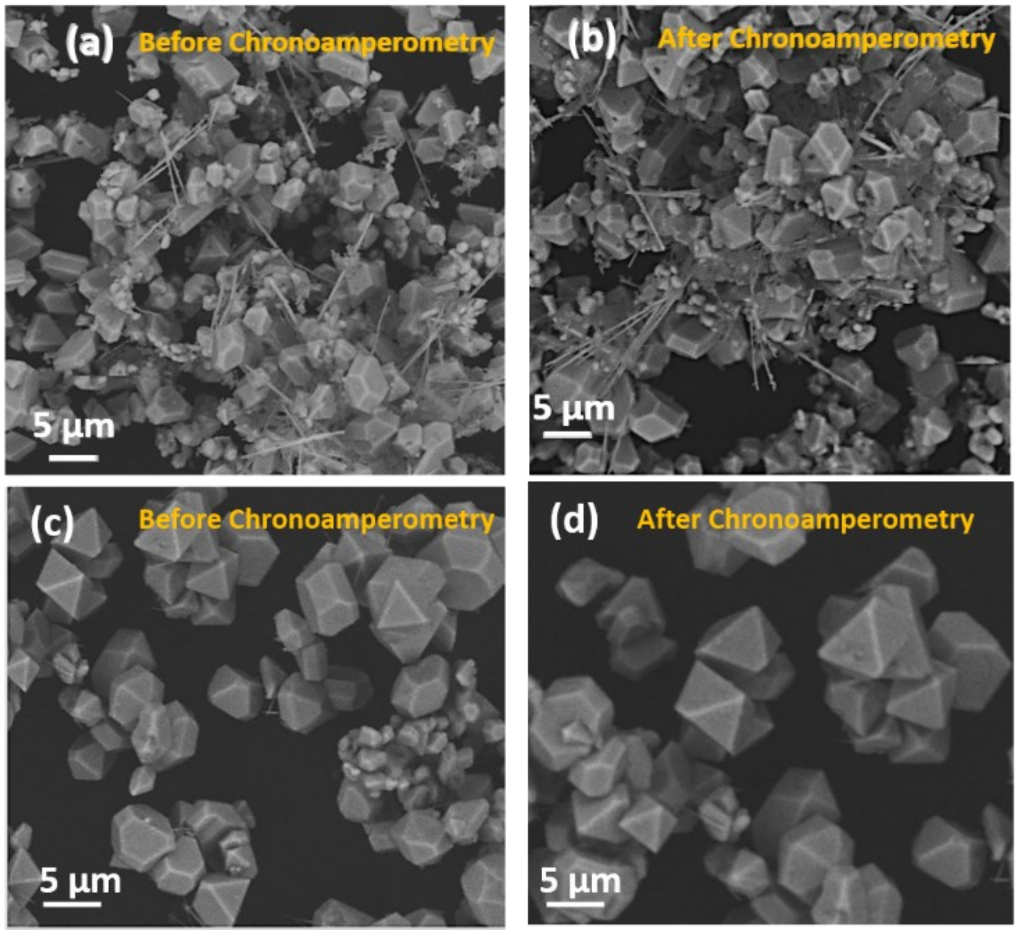

Figure S6. SEM images of (a,b) MnSe@MWCNT and (c,d) MnSe before and after 12 hr of chronoamperometry studies.

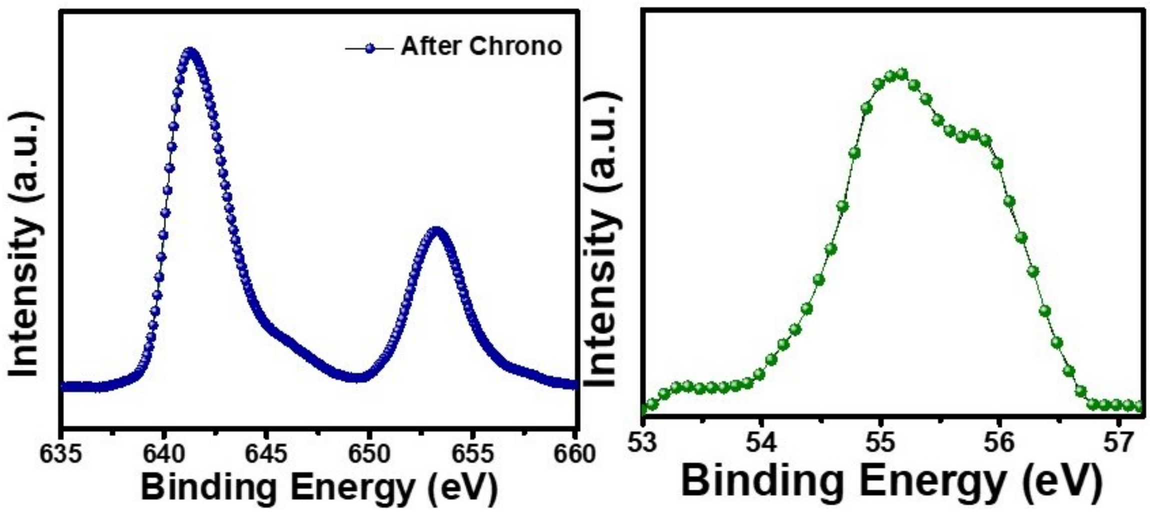

Figure S7. XPS spectra of MnSe@MWCNT (data collected at same spot where surface Raman spectra collected) after OER chronoamperometry.

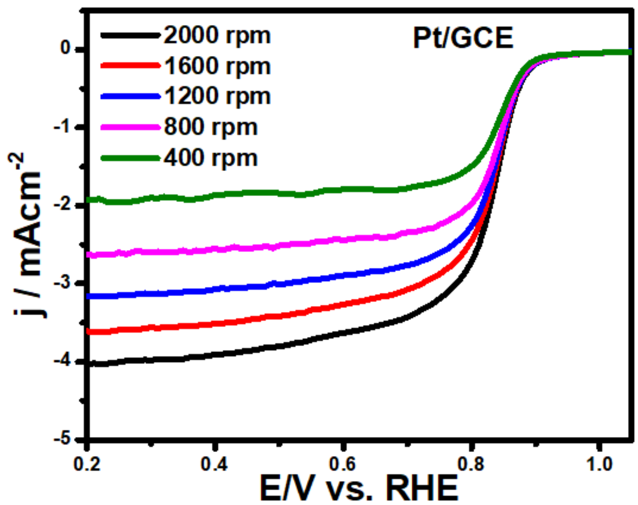

Figure S8. RDE linear sweep voltammograms of Pt/GCE catalysts at a different rotating speed.

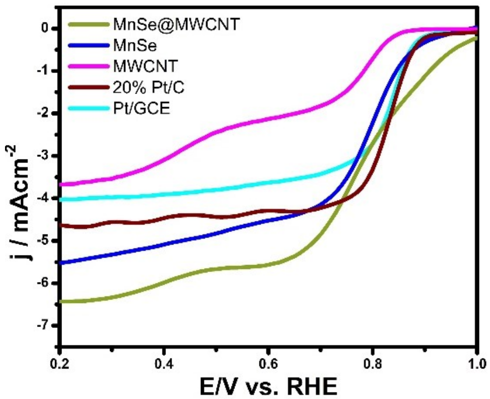

Figure S9. Comparison of ORR activity of MnSe and MnSe@MWCNT with Pt-based electrodes at rotating speed of 2000 rpm.

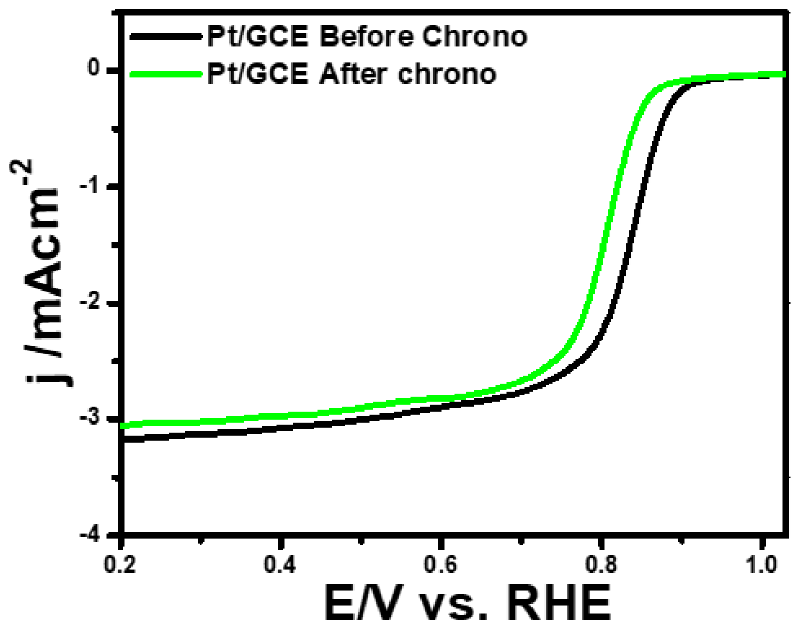

Figure S10. LSV before and after chronoamperometry studies of Pt/GCE.

Table S1. Comparison of electrocatalytic parameters of Manganese based catalysts for OER

OER Catalysts	Electrolytes	Onset potential/V	η @ 10 mA cm^{-2} (mV *vs* RHE)	Tafel slope mV dec^{-1}	Reference
α-MnO_2-H_2	0.1 M KOH	1.6	508	213.5	[1]
MnOx NWs	0.1 M KOH	-	519	106	[2]
Metal-doped MnO_2	1 M KOH	-	390	104.4	[3]
Ni–MnO_2	1 M KOH	-	330	23.7	[4]
MnO_2/CQD	1 M KOH	1.34	343	43.6	[5]
α-MnS	1 M KOH	-	292	70	[6]
α-MnO2/MnOOH	1 M KOH		302	51.3	[7]
$Mn_{0.6}Zn_{0.4}Co_2O_4$/rGO	1 M KOH	1.48	320	80.6	[8]
MnO_x/OCNT	0.1 M KOH	-	520	105	[9]
MnFeSe	1 M KOH	-	247	35	[10]
$Mn_{1.2}Fe_{0.8}O_3$	1 M KOH	-	245	38	[11]
Co_1Mn_1 NBs	1 M KOH	-	221	39.8	[12]
$Mn_{0.3}(Fe_{0.3}Ni_{0.7})_{0.5}O_X$/ MWCNTs-$O_x$	0.1 M KOH	-	330	-	[13]
Mn-Co-Se/NF	1 M KOH	-	243	62	[14]
MnSe/NF (drop casted)	**1 M KOH**	1.46	237*	-	**This Work**
MnSe/NF (Hydrothermally grown)	**1 M KOH**	1.45	230*	-	**This Work**
MnSe@MWCNT/NF (drop casted)	**1 M KOH**	1.42	223*	-	**This Work**
MnSe@MWCNT/NF (Hydrothermally grown)	**1 M KOH**	1.41	210*	-	**This Work**
MnSe/CC	**1 M KOH**	**1.49**	**310**	**61.43**	**This Work**
MnSe@MWCNT/CC	**1 M KOH**	**1.47**	**290**	**54.76**	**This Work**
RuO_2/CC	**1 M KOH**	**1.53**	**380**	**114.91**	**This Work**

* η @ 50 mA cm^{-2} (mV *vs* RHE); CC-Carbon Cloth; NF-Nickel Foam

Table S2. Comparison of overpotentials of MnSe-based composites and other reported systems at higher current densities.

OER Catalysts	η @ 10 mA cm^{-2} (mV *vs* RHE)	η @ 50 mA cm^{-2} (mV *vs* RHE	η @ 100 mA cm^{-2} (mV *vs* RHE	η @ 500 mA cm^{-2} (mV *vs* RHE	Reference
MnSe@MWCNT/NF (Hydrothermally grown)	**182**	**210**	**250**	**330**	**This Work**
MnSe/NF (Hydrothermally grown)	**220**	**230**	**290**	**380**	**This Work**
MnSe@MWCNT/NF (drop casted)	**208**	**223**	**270**		**This Work**
MnSe@MWCNT/CC	**290**	**390**	**-**	**-**	**This Work**
MnSe/CC	**310**	**340**	**-**	**-**	**This Work**
MnFeSe/NF	247	279	296	-	10
Co_1Mn_1 LDH/NF	285	350	390	-	15
Mn-Ni_2P-0.053/NF	-	299	330	-	16
CMS/NF	-	-	292	-	17
MnxNi_2–xP	196	270	370	-	18
Mn–F/$Ni(OH)_2$–NF	-	337	420	-	19
$MnGa_4$/NF	291	370	402	560	20
Mn_3O_4/NF	287	310	-	-	21
FeCo(Mn)−O/NF	235	250	280	-	22
Fe, Mn-Ni_3S_2/NF	-	230	260	-	23
Ni–Co_3O_4 NS\NF	310	-	390	-	24
MnCoP/CC	261	-	460	-	25
Ni_3Se_2/NF	-	-	315	-	26
$Co_{0.75}Ni_{0.25}Se$/NF	-	269	290	-	27
Fe–NiSe/NF	-	261	275	290	28
P-Ni_3S_2/$CoFe_2O_4$/NF	-	254	269	-	29
FeCoNiS_x/NF	231	250	280	-	30
$Fe_{7.4\%}$-NiSe/NF		231	245	-	31
Ni_3Se_2/NF	270	410	570	-	32

Table S3. Comparison of electrocatalytic parameters of Manganese based catalysts for ORR

ORR Catalysts	Electrolytes	E onset vs. RHE(V)	E 1/2 [V vs RHE]	J_L (mA cm^{-2})	Reference
α-MnO_2-H_2	0.1 M KOH	0.93	0.73	4.70	[1]
α-MnO_2 NWs	0.1 M KOH	0.94	0.72	5.48	[33]
α-MnO_2 NRs	0.1 M KOH	0.86	0.67	4.40	[33]
β-MnO2	0.1 M KOH	0.89	0.76	5.75	[34]
MnO_2/NRGO_ Urea	0.1 M KOH	0.94	0.8	5.1	[35]
MnO_2/C	0.1 M KOH	0.88	0.67	4.52	[35]
α-MnO_2-80	0.1 M KOH	0.92	0.79	5.67	[36]
MnO	0.1 M KOH	0.82	-	42.8	[37]
MnS	0.1 M KOH	0.86	-	4.66	[37]
MnSe	0.1 M KOH	0.91	-	5.82	[37]
MnS/G	0.1 M KOH	0.83	0.71	3.79	[38]
Defected Mn_3O_4	0.1 M KOH	0.87	0.65	5	[39]
$Mn_{0.5}(Fe_{0.3}Ni_{0.7})_{0.5}O_X$/MWCNTs-$O_x$	0.1 M KOH	0.84	0.81	-	[13]
MnSe	**1 M KOH**	**0.91**	**0.82**	**5.1**	**This Work**
MNSe@MWCNT	**1 M KOH**	**0.94**	**0.86**	**6.03**	**This Work**
Pt/GCE	**1 M KOH**	**0.92**	**0.81**	**3.92**	**This Work**

Table S4. Equivalent Circuit Parameters Obtained from Fitting of EIS Experimental Data

Parameter	**MnSe@MWCNT**	**MnSe**
R_f/Ω	6.4	8.5
R_{ct}/Ω	18.6	28.4
CPE $_{catalyst}$/F	0.8	1.4
Z_W	0.76	1.48

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