Supplementary Information for the article

Anion-exchange phase control of manganese sulfide for oxygen evolution reactions

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Table S1: PF calculations for rhombohedral $MnCO_3$ and all polymorphs of manganese sulfide prepared in the present study.

Sr. no.	Material	Crystal structure	Lattice constant (Å) a	b	c	Volume of unit cell (Å^3)	Ionic radii (Å)	Number of ions per unit cell	Total volume occupied by ions in unit cell (Å^3)	PF
1.	$MnCO_3$	Rhombohedral $\alpha = \beta = \gamma = 47.77°$	5.84	5.84	5.84	99.99	$Mn^{+2} = 0.81$ $C^{+4} = 0.3$ $O^{-2} = 1.26$	$Mn^{+2} = 2$ $C^{+4} = 2$ $O^{-2} = 6$	54.92	0.55
2.	MnS_2	Cubic $\alpha = \beta = \gamma = 90°$	6.11	6.11	6.11	227.98	$Mn^{+4} = 0.67$, $S^{-2} = 1.7$	$Mn^{+4} = 4$ $S^{-2} = 8$	169.58	0.74
3.	γ-MnS	Wurtzite $\alpha = \beta = 90°$, $\gamma = 120°$	3.97	3.97	3.97	88.05	$Mn^{+2} = 0.81$, $S^{-2} = 1.7$	$Mn^{+2} = 3$ $S^{-2} = 3$	68.38	0.77
4.	α-MnS	Rock salt $\alpha = \beta = \gamma = 90°$	5.24	5.24	5.24	143.87	$Mn^{+2} = 0.81$, $S^{-2} = 1.7$	$Mn^{+2} = 4$ $S^{-2} = 4$	91.17	0.63

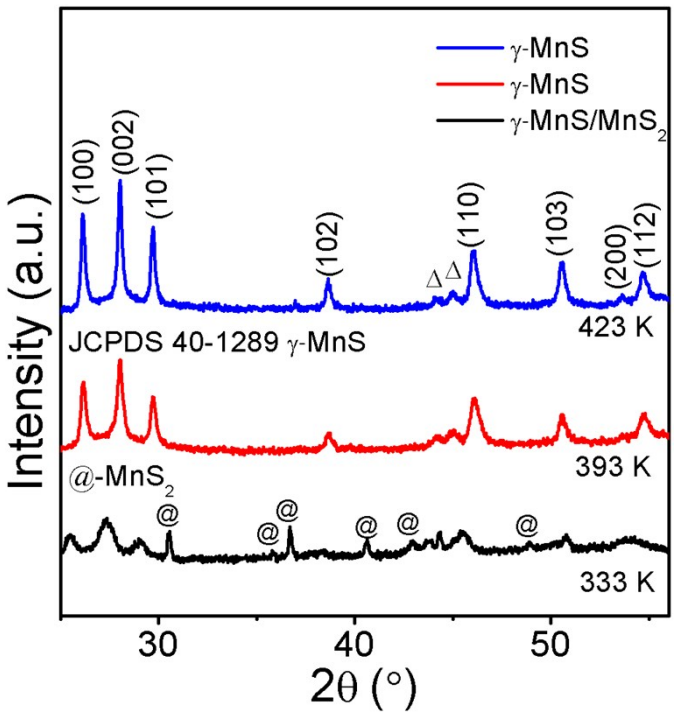

Figure S1: XRD patterns of manganese sulfide thin films prepared at different temperatures via anion exchange of $MnCO_3$ with the same mass ratio (1:1) of $MnCO_3$ to Na_2S.

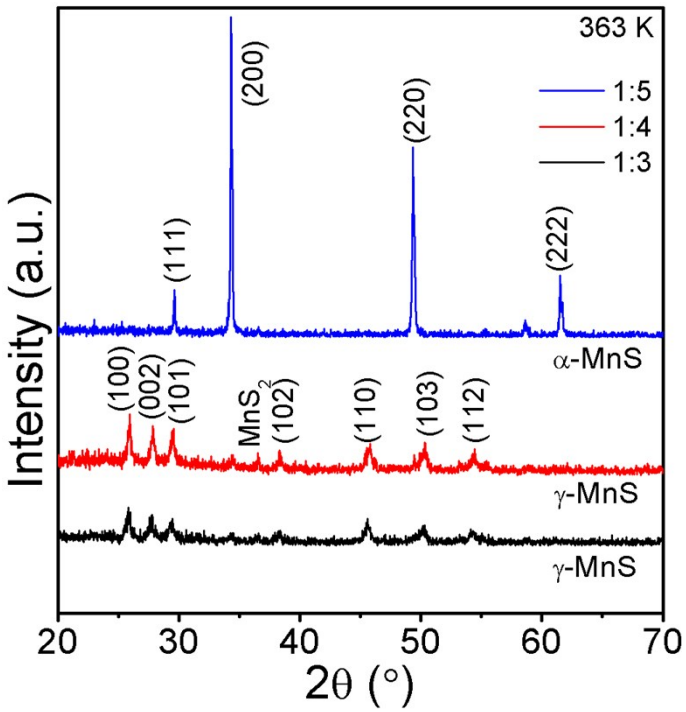

Figure S2: XRD patterns of manganese sulfide samples prepared via the anion-exchange chemical reaction between $MnCO_3$ and Na_2S precursors with different mass ratios at a hydrothermal temperature of 363 K.

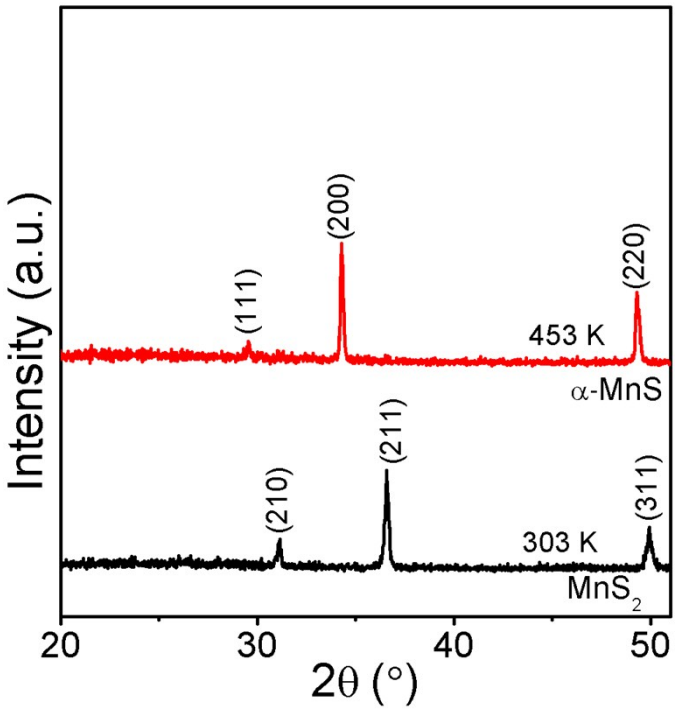

Figure S3: XRD patterns of manganese sulfide prepared at 303 and 453 K via the anion-exchange reaction with $MnCO_3$:Na_2S mass ratio of 1:5.

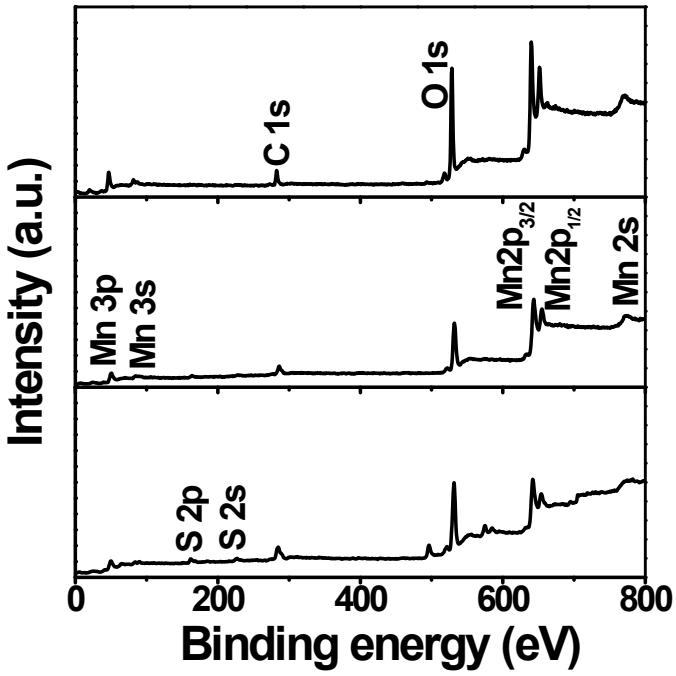

Figure S4: Comparative XPS survey profiles of the MnS_2, γ-MnS, and α-MnS phases of manganese sulfide.

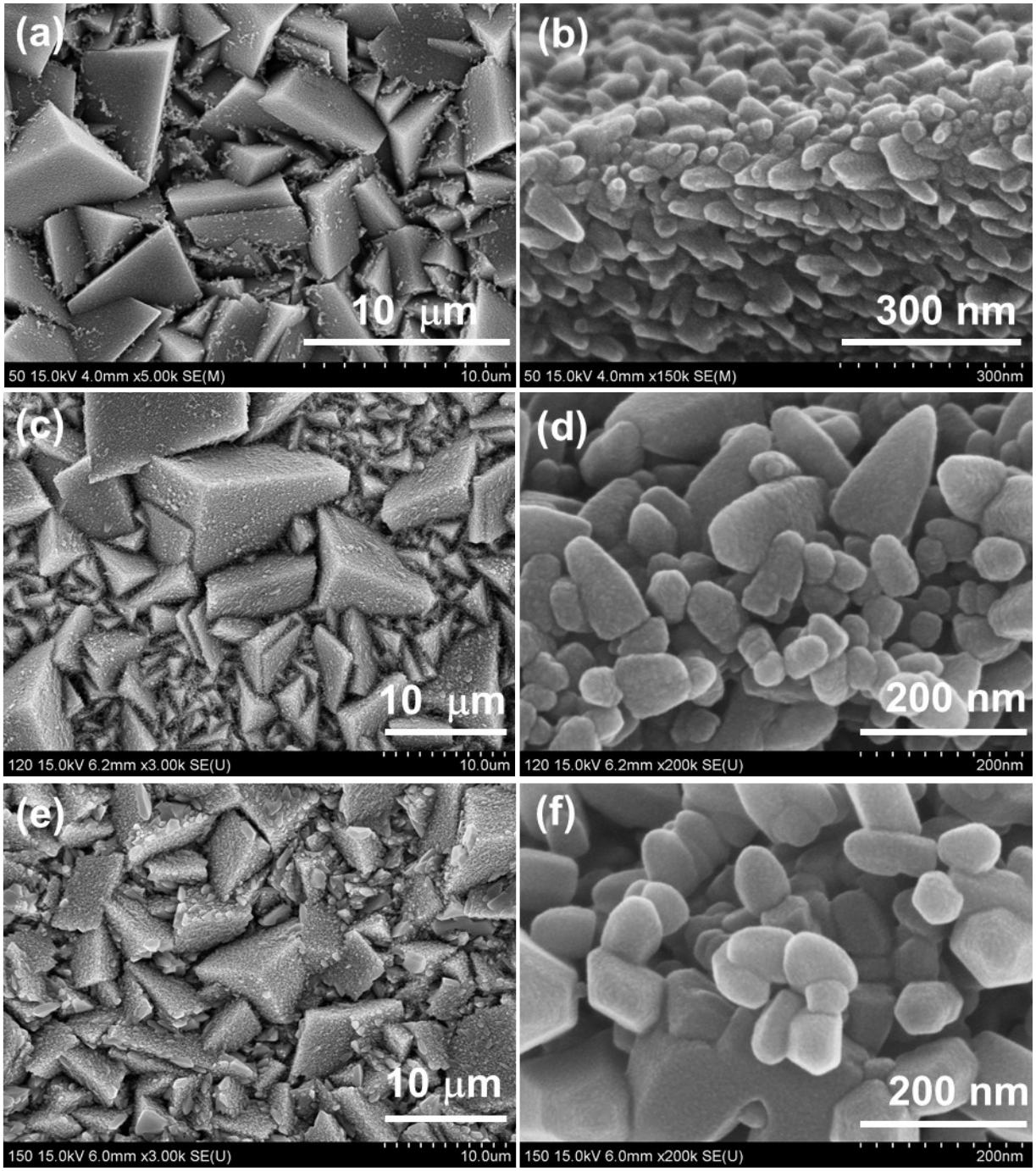

Figure S5: FE-SEM images of manganese sulfide thin films prepared via the anion-exchange reaction with $MnCO_3$:Na_2S mass ratio of 1:1 at different temperatures: **(a, b)** 333 K, **(c, d)** 393 K, and **(e, f)** 423 K.

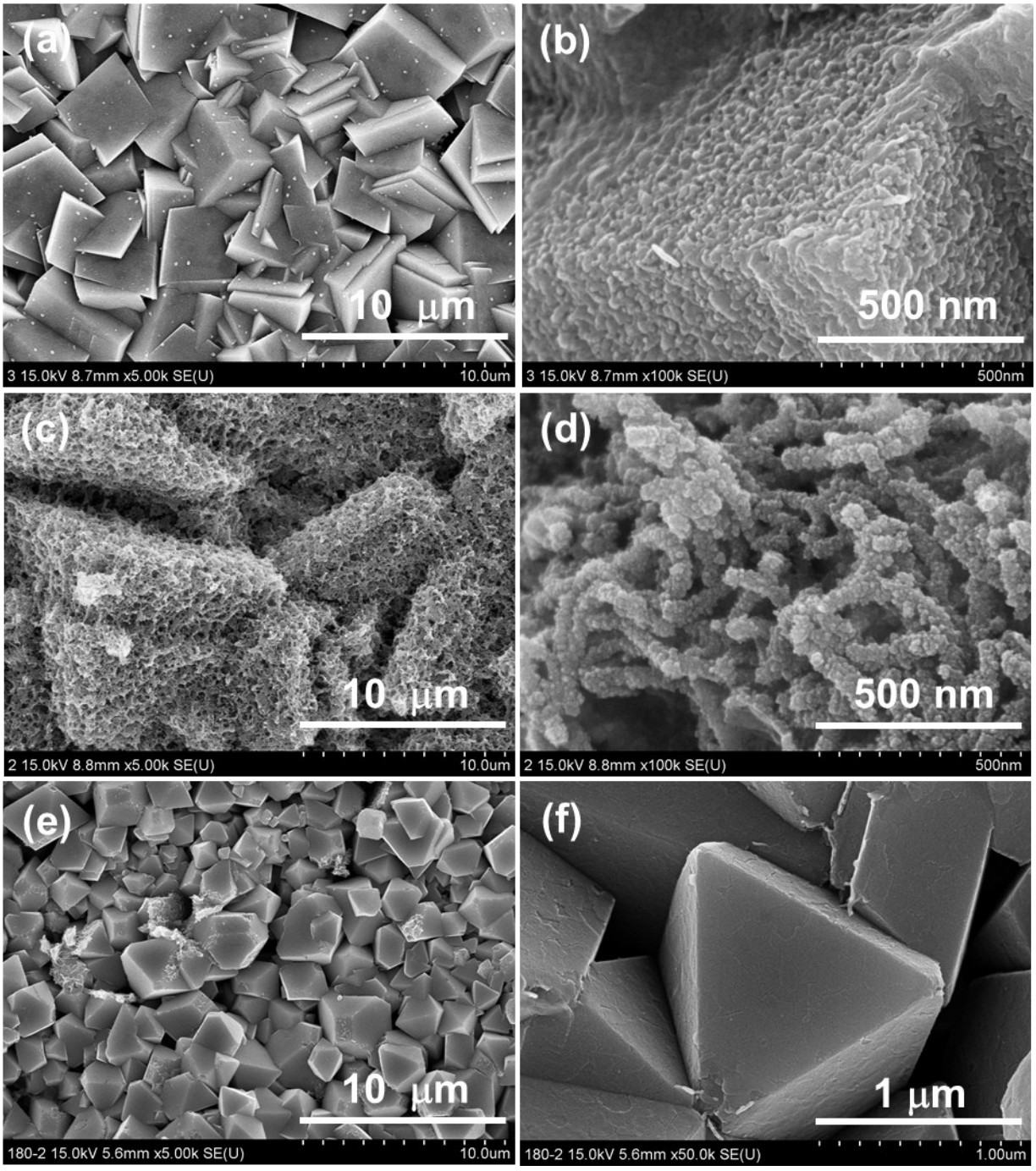

Figure S6: FE-SEM images of manganese sulfide thin films prepared via the anion-exchange reaction with $MnCO_3$:Na_2S mass ratio of 1:5 at different temperatures: **(a, b)** 303 K **(c, d)** 363 K, and **(e, f)** 453 K.

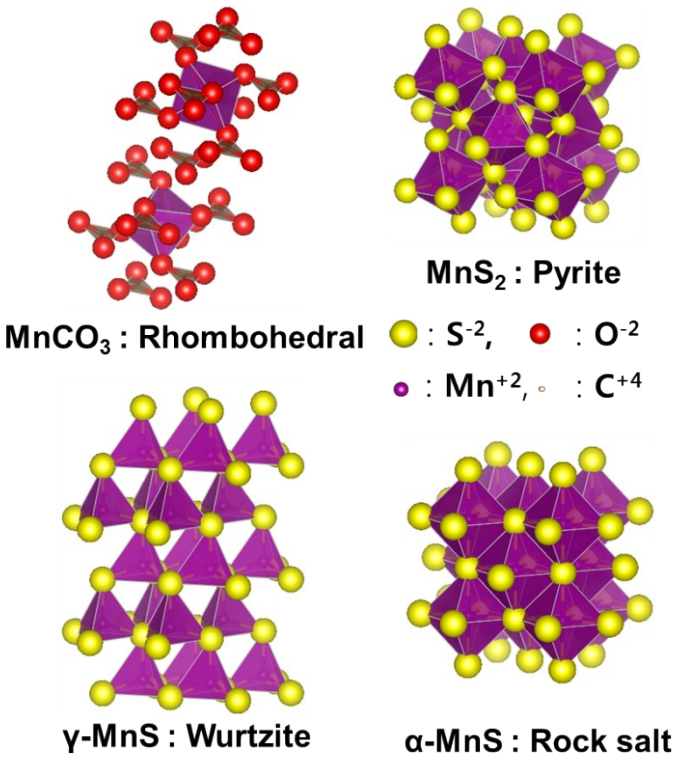

Figure S7: Crystal structure models of $MnCO_3$ and different phases of manganese sulfide.

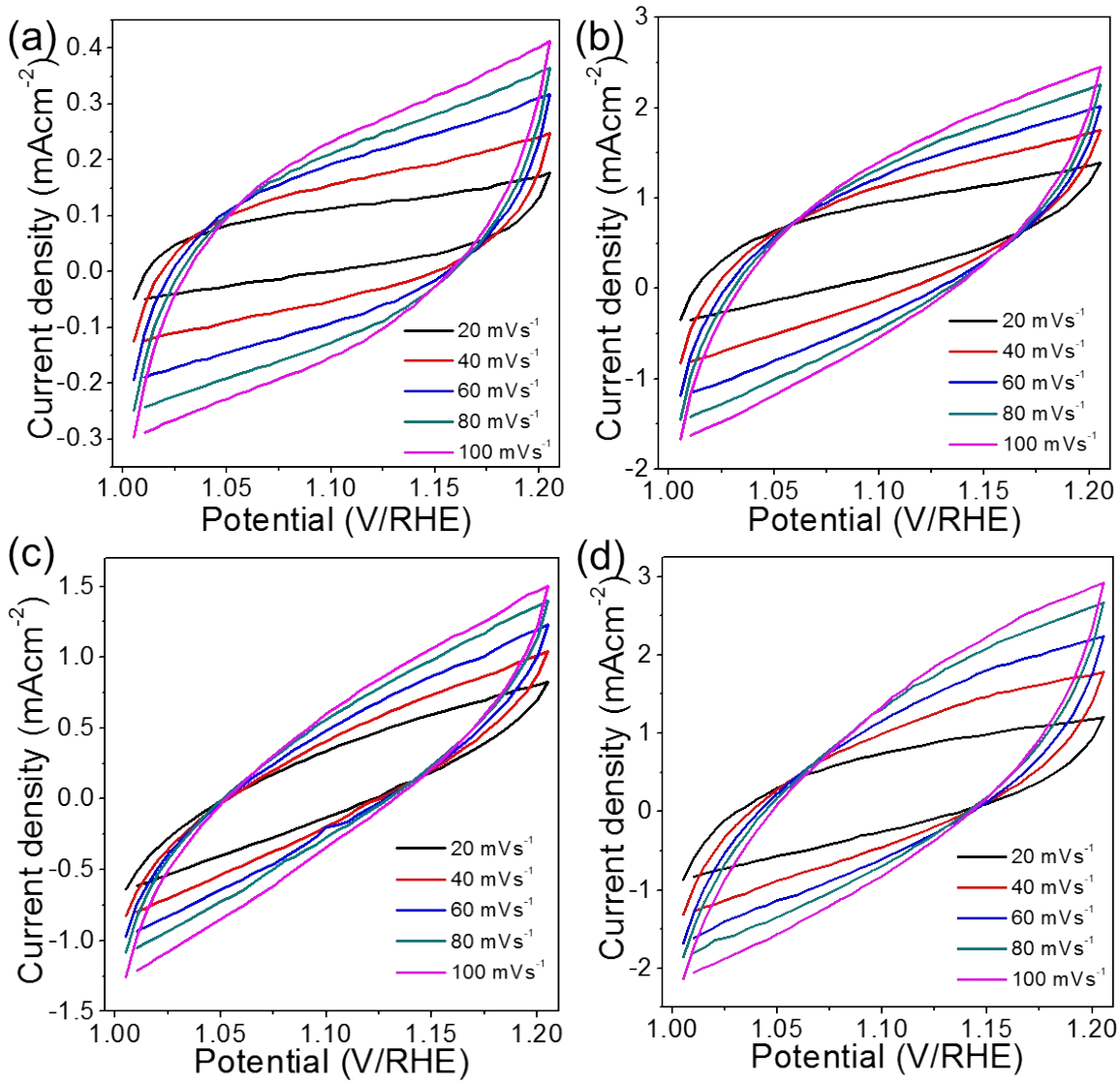

Figure S8: Cyclic voltammetry curves of (a) $MnCO_3$ (b) MnS_2 (c) γ-MnS, and (d) α-MnS catalysts obtained within non-faradaic region of 1.00 to 1.20 V/RHE in 1 M KOH.

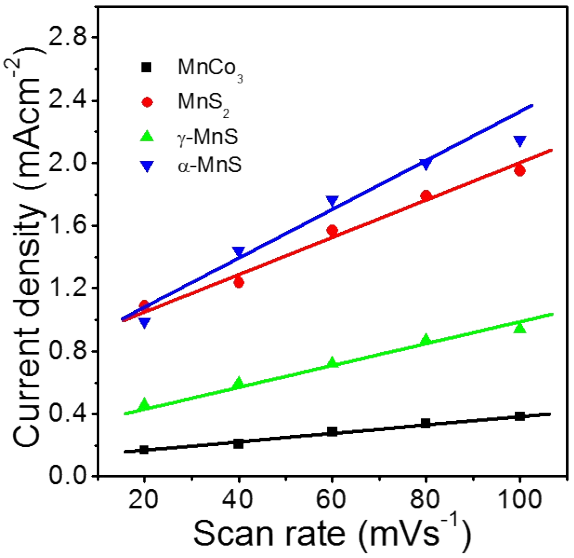

Figure S9: Current density versus scan rate plots of different electrodes for measurement of electrochemical active surface area.