Supporting Information

A Synergistic Na-Mn-O Composite Cathodes for High-Capacity Na-Ion Storage

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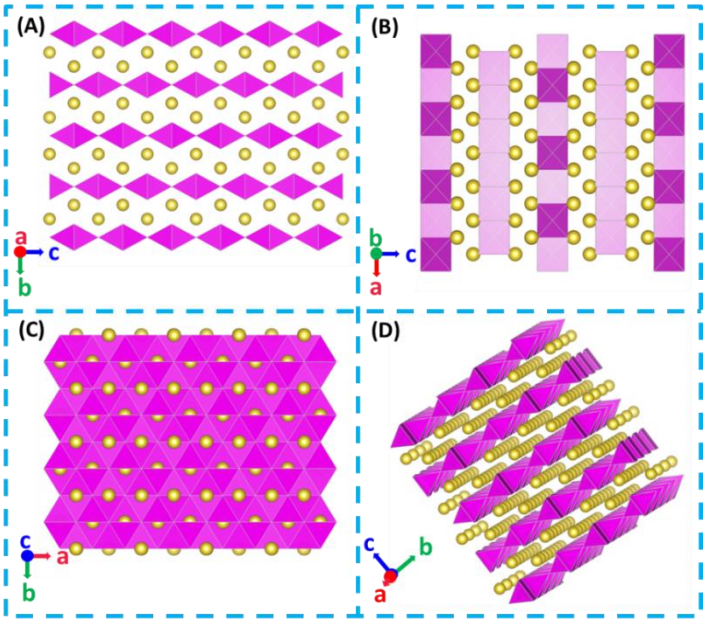

Figure S1. The crystal structure of orthorhombic $Na_4Mn_2O_5$.

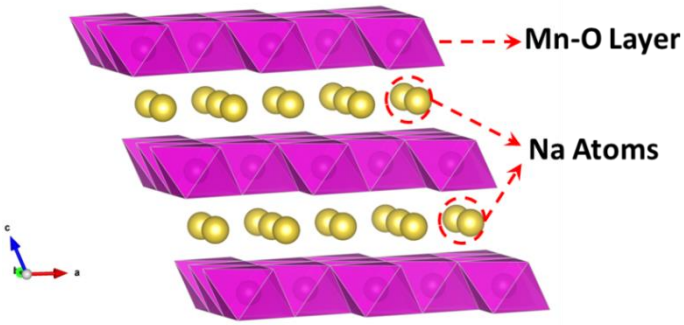

Figure S2. The crystal structure of layered $Na_{0.7}MnO_2$.

Table S1. The relation table of the Na:Mn ratio in initial state and final product.

Ratio of Na:Mn in precursor	**Ratio of Na:Mn in final products**	**Ratio of $Na_4Mn_2O_5$:$Na_{0.7}MnO_2$**
6:2	**2.91:2.00**	**0.58:0.42**
4:2	**2.54:2.00**	**0.44:0.56**
2:2	**2.42:2.00**	**0.39:0.61**

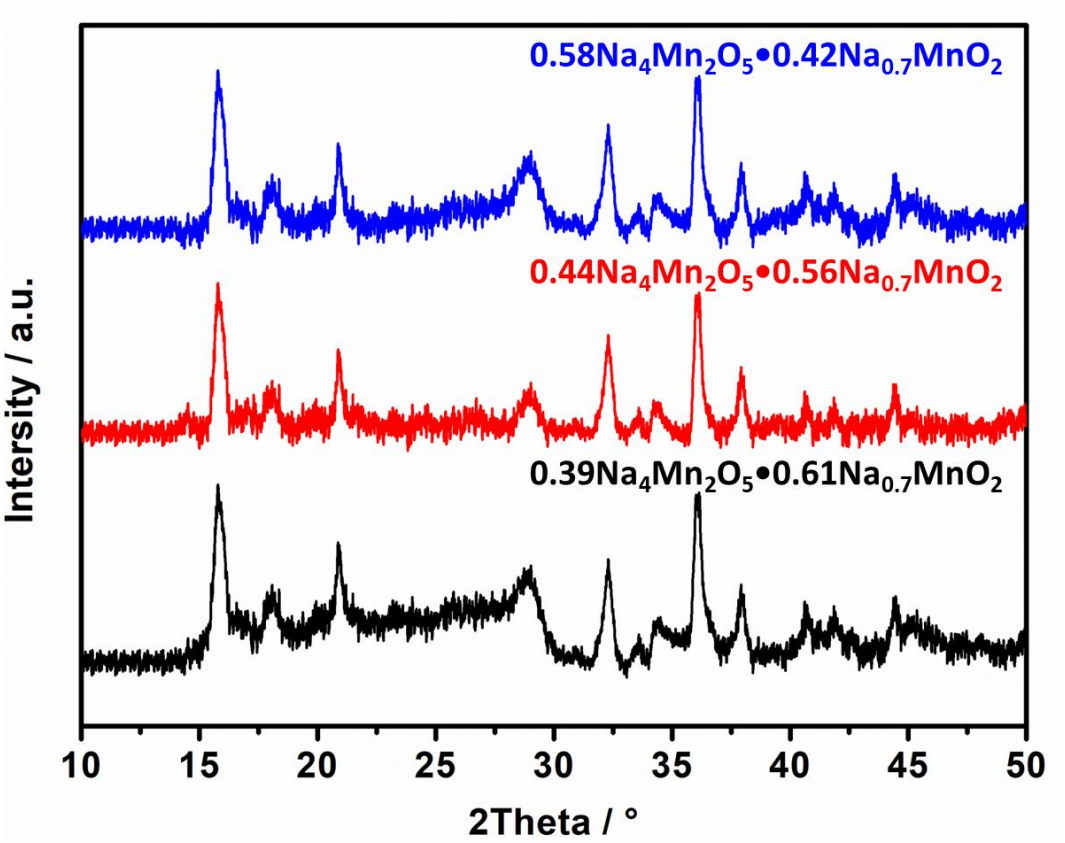

Figure S3. XRD patterns of the $0.58Na_4Mn_2O_5•0.42Na_{0.7}MnO_2$, $0.44Na_4Mn_2O_5•0.56Na_{0.7}MnO_2$ and $0.39Na_4Mn_2O_5•0.61Na_{0.7}MnO_2$, respectively.

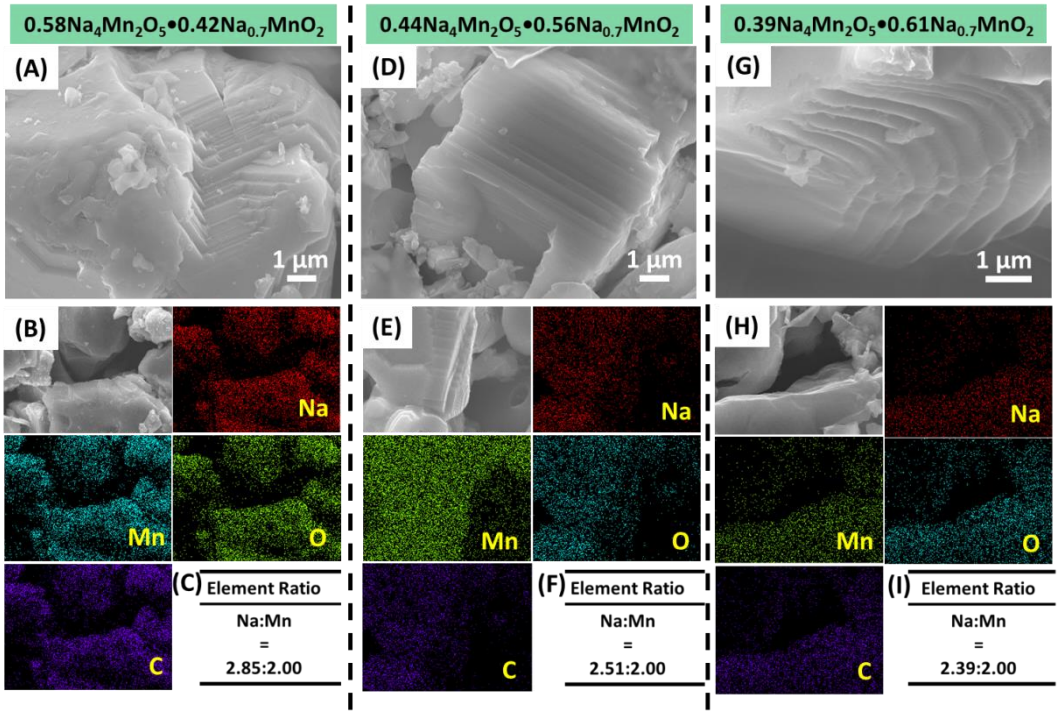

Figure S4. The SEM(A), EDS(B) and Na:Mn ratio (C) of $0.58Na_4Mn_2O_5•0.42Na_{0.7}MnO_2$. The SEM(D), EDS(E) and Na:Mn ratio (F) of $0.44Na_4Mn_2O_5•0.56Na_{0.7}MnO_2$. The SEM(G), EDS(H) and Na:Mn ratio (I) of $0.39Na_4Mn_2O_5•0.61Na_{0.7}MnO_2$.

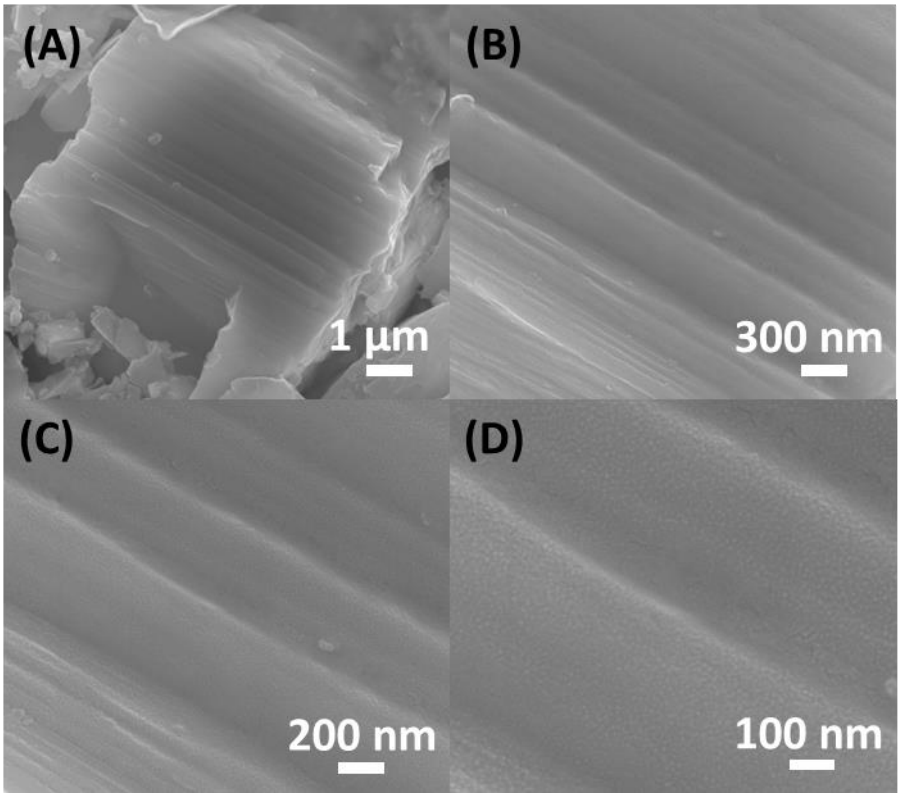

Figure S5. SEM images of the $0.44Na_4Mn_2O_5 \bullet 0.56Na_{0.7}MnO_2$.

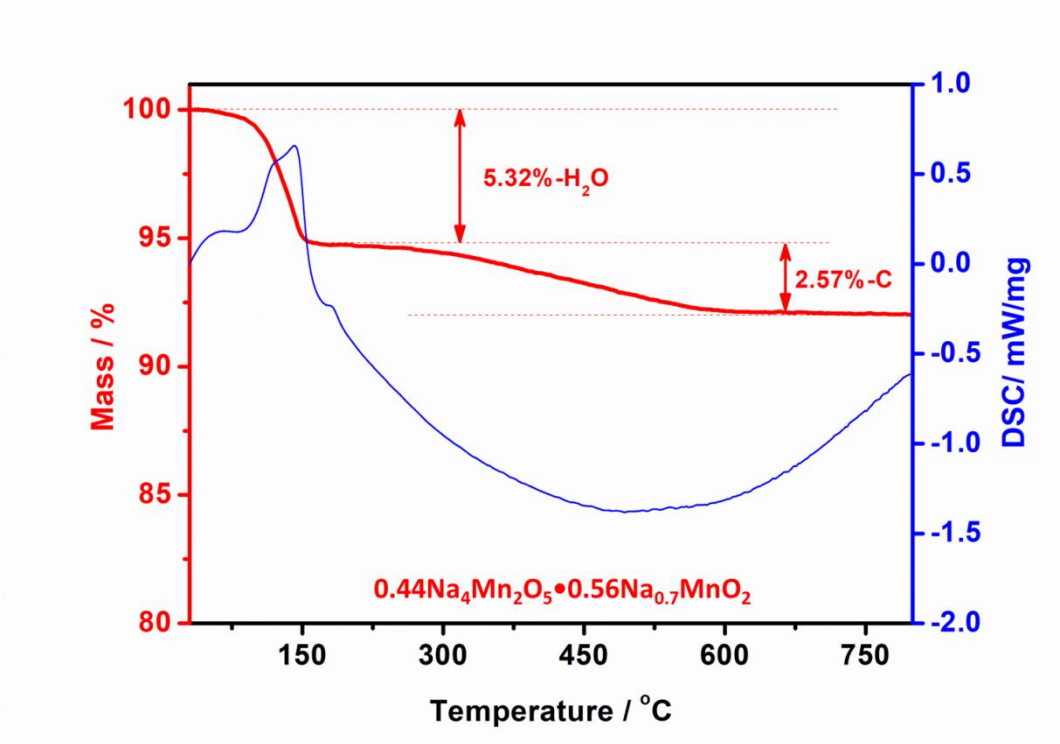

Figure S6. TG curves of the $0.44Na_4Mn_2O_5 \bullet 0.56Na_{0.7}MnO_2$.

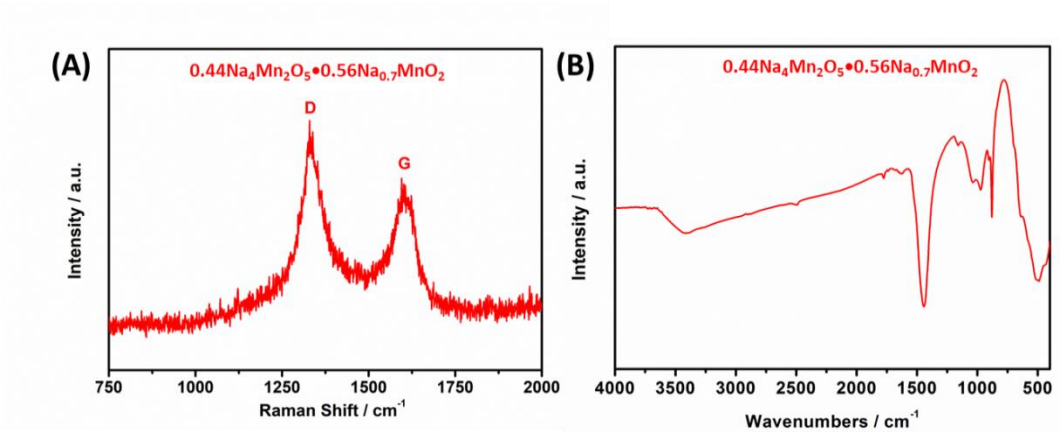

Figure S7. Raman spectra (A) and FT-IR (B) of the $0.44Na_4Mn_2O_5•0.56Na_{0.7}MnO_2$.

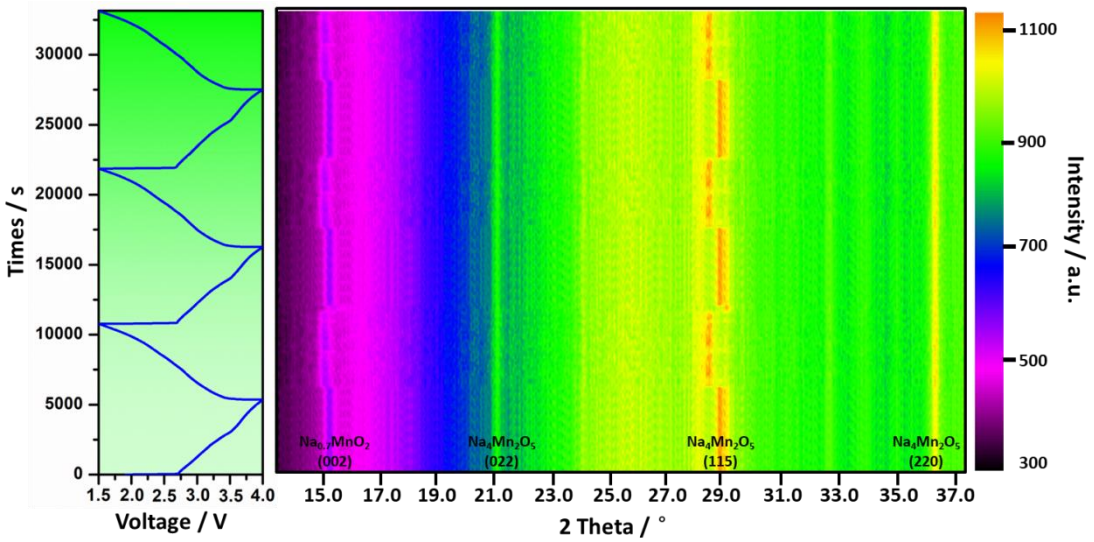

Figure S8. *In-situ* XRD patterns of $0.44Na_4Mn_2O_5•0.56Na_{0.7}MnO_2$ during galvanostatic charge/discharge at 150 mA g^{-1}. The image plot of the XRD patterns at 13.5–37.2 ° during the first three cycles.

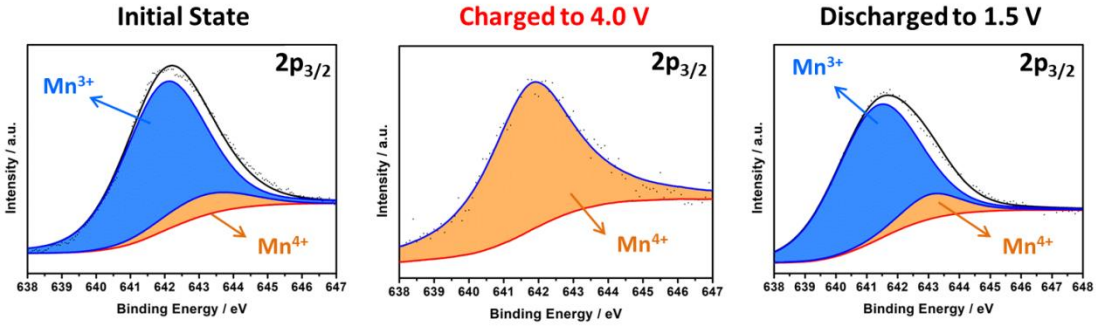

Figure S9. Charge/discharge curves of the $0.44Na_4Mn_2O_5•0.56Na_{0.7}MnO_2$ at different current densities.

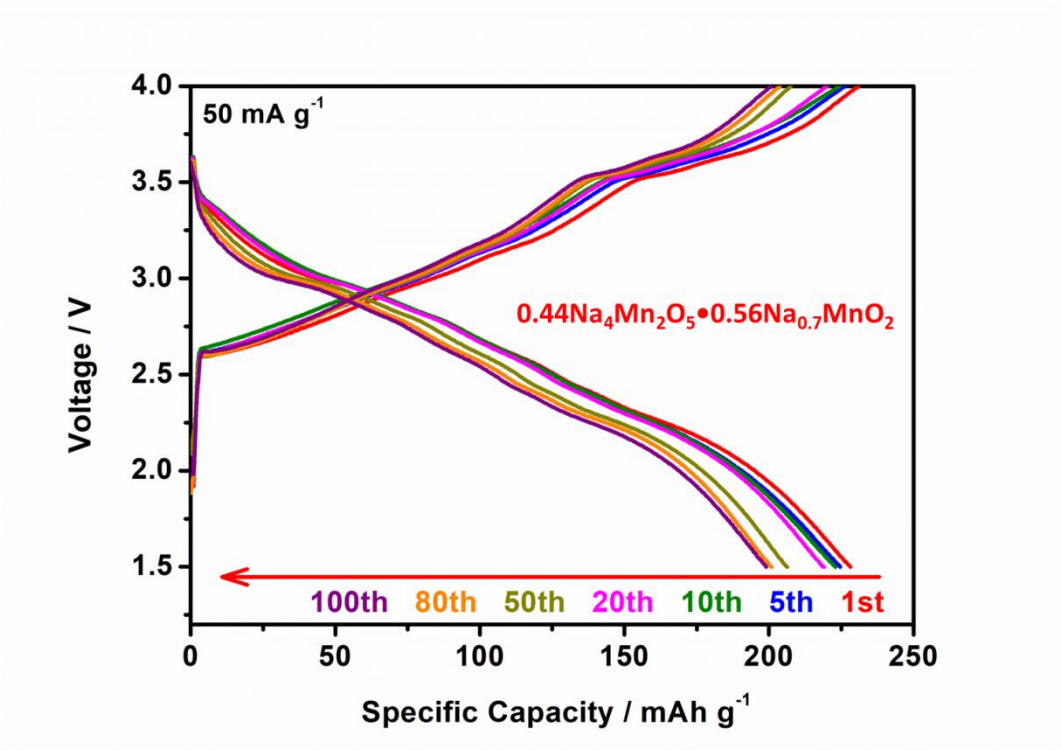

Figure S10. Charge/discharge curves of the $0.44Na_4Mn_2O_5•0.56Na_{0.7}MnO_2$ at different cycles.

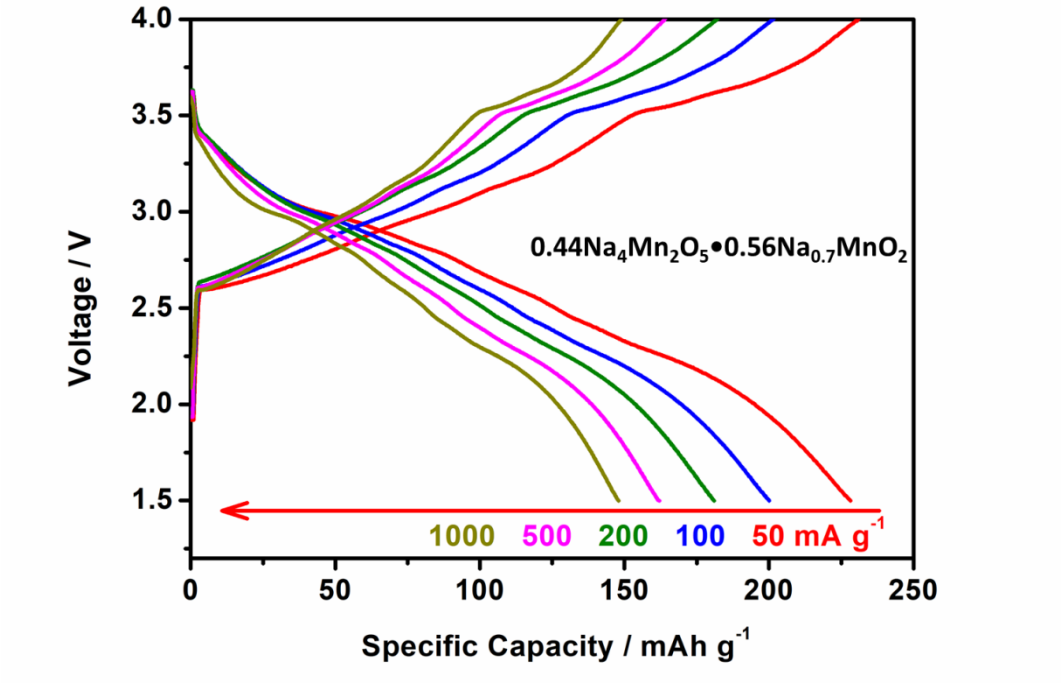

Figure S11. Charge/discharge curves of the $0.44Na_4Mn_2O_5•0.56Na_{0.7}MnO_2$ at different current densities.

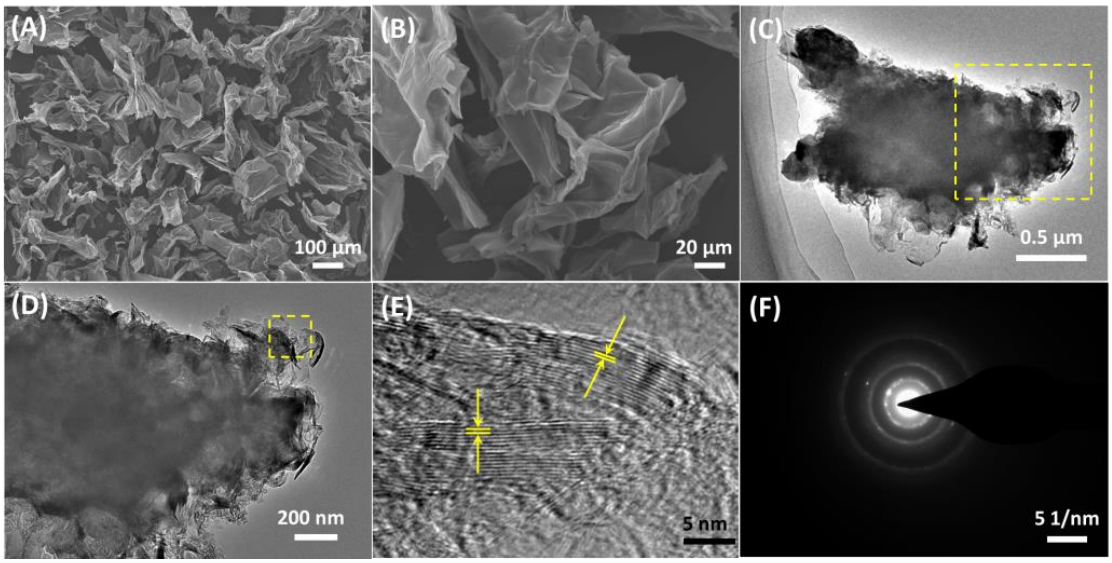

Figure S12. SEM images (A, B), TEM images (C, D), HR-TEM image (E) and SAED (F) of the hard carbon sintering at 1200 ^{o}C.

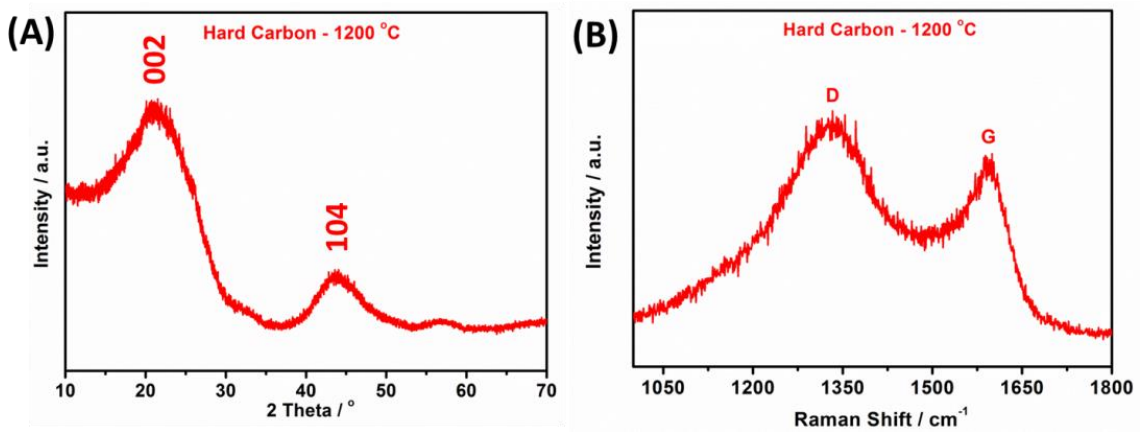

Figure S13. XRD spectrum (A) and Raman spectra (B) of the hard carbon sintering at 1200 ^{o}C.

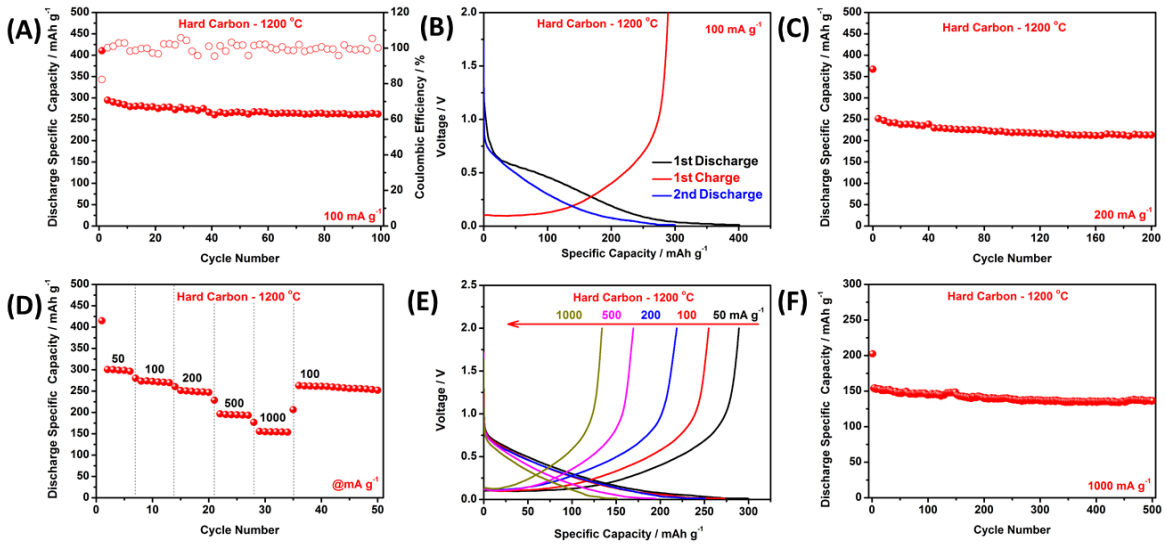

Figure S14. Characterization of electrochemical performance for hard carbon sintering at 1200 ^{o}C in NIBs. (A) Cyclic performance tested at 100 mA g^{-1}. (B) Charge/diacharge curves tested at 100 mA g^{-1}. (C) Cycling performance measured at 200 mA g^{-1}. (D) Rate performance. (E) Charge/diacharge curves tested different current densities. (F) Long-life cycling performance measured at 1000 mA g^{-1}.

Table S2. Comparison of the electrochemical performance of manganese-based cathode materials in LIBs and NIBs.

	Materials	Current Density ($mA\ g^{-1}$)	Initial Capacity ($mAh\ g^{-1}$)	Cycle Numbers	Capacity Retention	References
1	$0.44Na_4Mn_2O_5•0.56Na_{0.7}MnO_2$/Na Half Cells	50	228	100	87%	Our work
		100	208	400	89%	
		1000	157	500	90%	
	$0.44Na_4Mn_2O_5•0.56Na_{0.7}MnO_2$/Hard Carbon Full Cells	50	151	100	86%	
		500	101	200	84%	
2	$Li_4Mn_2O_5$-LIBs	24.6	355	8	69%	[23]
3	$Na_{0.6}(Li_{0.2}Mn_{0.8})O_2$-NIBs	15	120	50	118%	[9]
4	$Na_{0.66}Li_{0.18}Mn_{0.71}Ni0.21Co_{0.08}O_{2+\delta}$-NIBs	50	150	150	75%	[24]
5	$Na_{0.61}[Mn_{0.27}Fe_{0.34}Ti_{0.39}]O_2$-NIBs	88	71	100	90%	[34]
6	β-$NaMnO_2$-NIBs	10	187	100	65%	[8]
7	$Na_{0.7}Fe_{0.5}Mn_{0.5}O_2$-NIBs	13	190	30	78%	[14]
8	$K_{0.7}Fe_{0.5}Mn_{0.5}O_2$-NIBs	100	181	100	93%	[19]
9	$Na[Ni_{0.58}Co_{0.06}Mn_{0.36}]O_2$-NIBs	75	140.9	300	86%	[26]