Supplementary Information

Nanostructured alkali cations incorporated δ-MnO₂ as cathode materials for aqueous sodium-ion batteries

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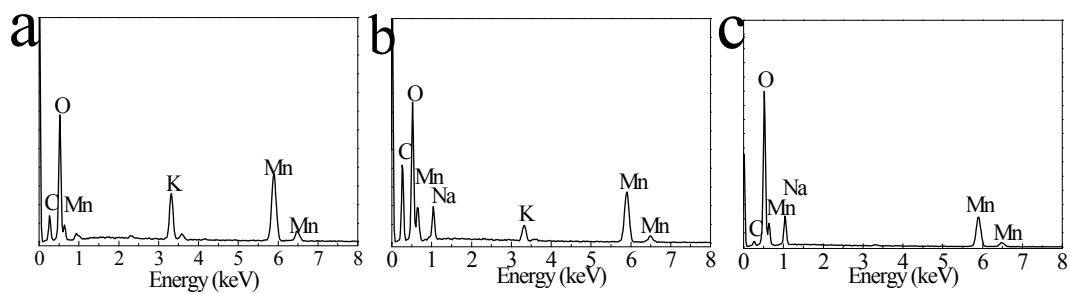
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Figure S1. EDS spectra of (a) K-δ-MnO₂ (KMO), (b) K, Na-δ-MnO₂ (KNMO), and
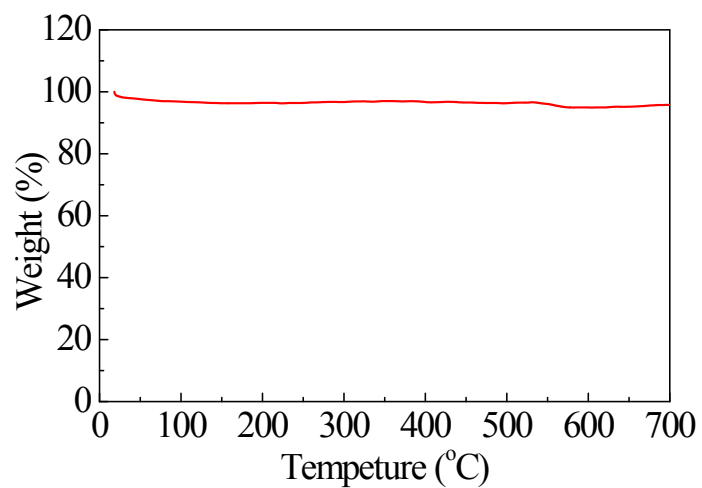
(c) Na-δ-MnO₂ (NMO).

Figure S2. The TG curve of NMO from room temperature to 700 °C at a rate of
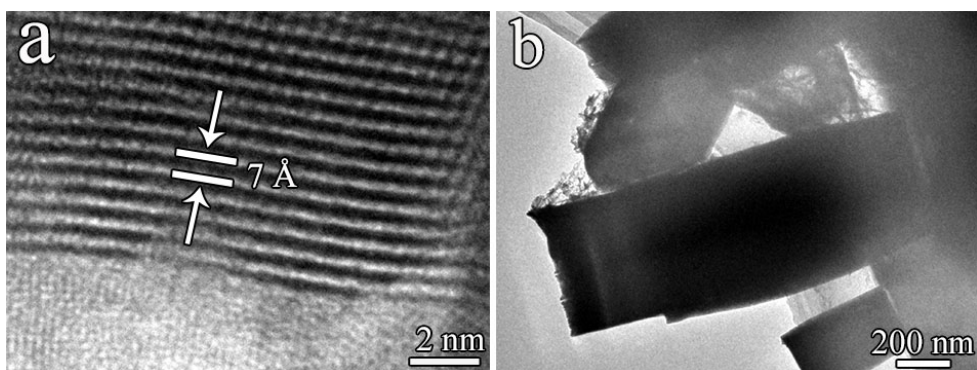
10 °C min⁻¹ in a flowing air.

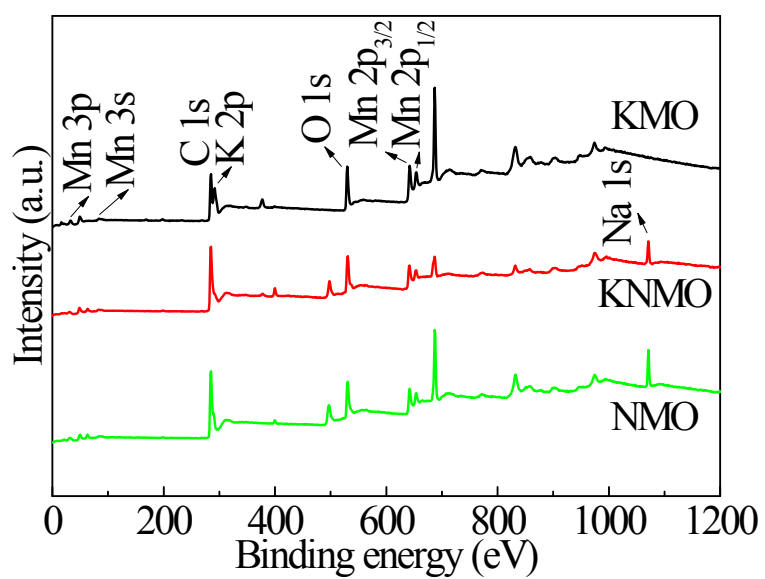**Figure S3.** HRTEM, TEM images of (a) KNMO, (b) NMO.

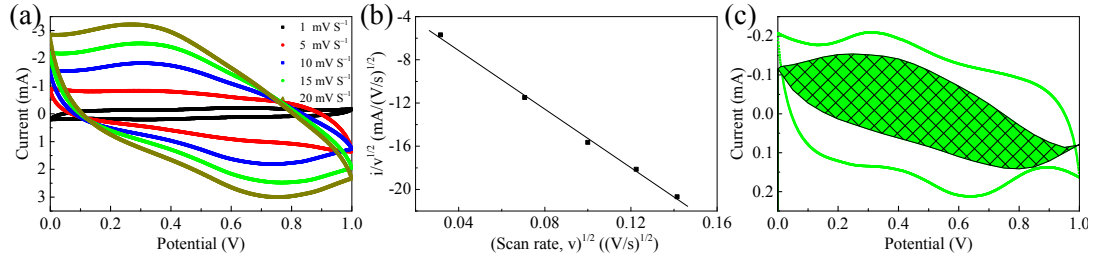**Figure S4.** Survey XPS spectra for pristine samples.

Figure S5. (a) CV curves of KNMO at different scan rates from 1 to 20 mV s^{-1}; (b) the linear dependence of $i/v^{1/2}$ on $v^{1/2}$ (i: current; v: scan rate); (c) CV curve of KNMO at a scan rate of 1 mV s^{-1} and the estimated capacitive contribution (shaded region).

The layered δ-MnO$_2$ was investigated as supercapacitor electrode. The capacitive contribution was evaluated by using KNMO as SIB electrode. Figure S5a shows the CV curves of KNMO at different scan rates from 1 to 20 mV s^{-1}. At a fixed potential, the overall current response is assumed to contain two contributions: surface capacitive effect and diffusion controlled insertion process, which is calculated as below [1, 2]:

$$i(V) = k_1 v + k_2 v^{1/2} \tag{1-1}$$

It can be written as

$$i(V)/v^{1/2} = k_1 v^{1/2} + k_2 \tag{1-2}$$

where $k_1 v$ is the current contribution from surface capacitive effect, and $k_2 v^{1/2}$ is from the diffusion controlled insertion process. As shown in Figure S5b and equation (1-2), the linear dependence of $i/v^{1/2}$ on the scan rate of $v^{1/2}$ is used to determine the slope (k_1) and the intercept (k_2) at each fixed potential. This means that the capacitive effect can

be estimated at a certain voltage. Figure S5c clearly demonstrates the estimated

capacitive contribution in the shaded region at a scan rate of 1 mV s^{-1}. On the basis of

the enclosed area, the capactive charge storage accounts for 49% of the overall charge
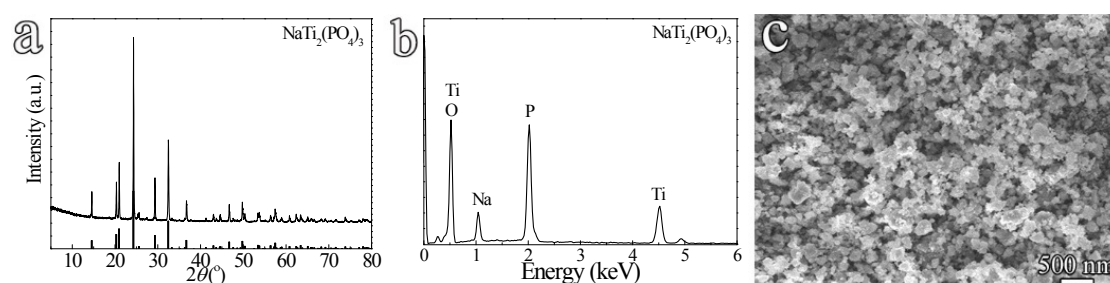
storage.

Figure S6. (a) XRD pattern, (b) EDS spectrum, and (c) FE-SEM image of

$NaTi_2(PO_4)_3$.

As shown in Figure S6a, the XRD pattern reveals that it is well-defined

NASICON structure (JCPDS 85-2265). The EDS result proves the coexistence of Na,

Ti, P and O elements in the sample (Figure S6b). FE-SEM observation reflects that

the $NaTi_2(PO_4)_3$ sample is consisted with a large number of aggregated particles.
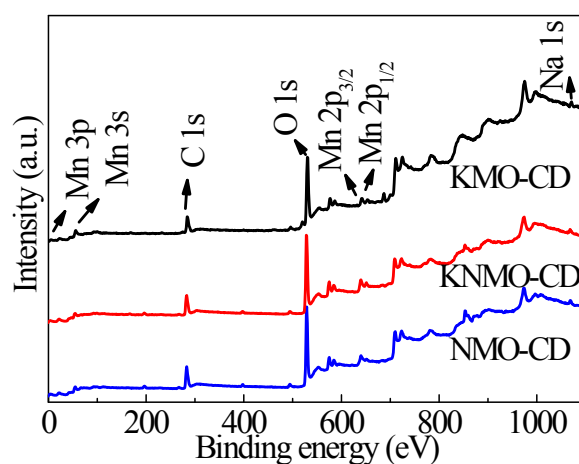
Figure S7. (a) XPS spectra for the three electrodes after charge/discharge cycle.
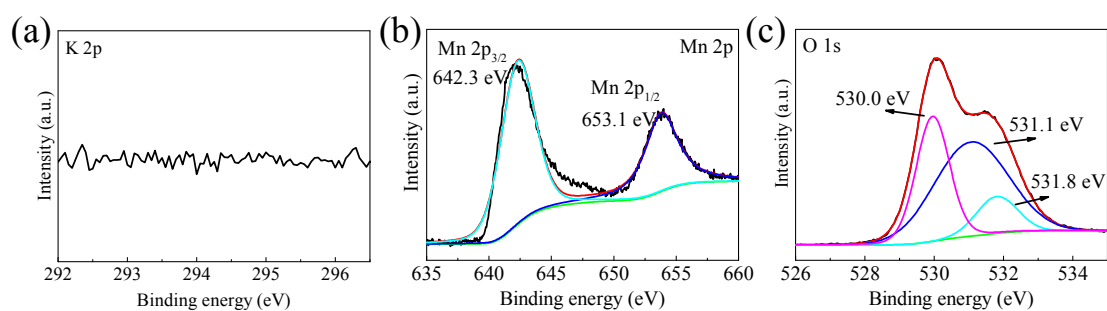

Figure S8. XPS spectra for etched electrode: high-resolution spectra of (a) K 2p, (b)

Mn 2p and (c) O 1s.

References

1   J. Wang, J. Polleux, J. Lim and B. Dunn, *J. Phys. Chem. C*, 2007, **111**, 14925-14931.

2   T. Brezesinski, J. Wang, J. Polleux, B. Dunn and S. H. Tolbert, *J. Am. Chem. Soc.*, 2009, **131**, 1802-1809.