## **Supporting Information**



**Fig. S1.** 3D packing diagram of  $KNaV_{10}$  with a spacefill style along *a* axis.



**Fig. S2.** The TGA curve of  $MgV_{10}$ .



Fig. S3. The experimental and simulated XRD patterns of  $\mathsf{KNaV}_{10}.$ 



Fig. S4. The experimental and simulated XRD patterns of  $MgV_{10}$ .



Fig. S5. TEM images of  ${\rm MgV}_{10}$  collected at different amplifications.



Fig. S6. Cyclic voltammograms of  $KNaV_{10}$  with a scan rate of 0.1 mV s<sup>-1</sup> at the potential range of 3.8 -1.0 V.



**Fig. S7.** SEM images of  $KNaV_{10}$  in the stage of (a) pristine, (b) discharged, (c) charged and  $MgV_{10}$  in the stage of (d) pristine, (e) discharged, (f) charged.



Fig. S8. FTIR spectra of  $KNaV_{10}$  in the stage of pristine, discharged and charged.



Fig. S9. FTIR spectra of  $MgV_{10}$  in the stage of pristine, discharged and charged.



Fig. S10. Cycling performance of  $KNaV_{10}$  at 50 mA g<sup>-1</sup>.



Fig. S11. Rate capability of  $MgV_{10}$  and  $KNaV_{10.}$ 



Fig. S12. The evolutions of the electron number of  $\mathsf{MgV}_{10}$  and  $\mathsf{KNAV}_{10}$  upon on

battery cycling.