

## Supporting information

### Synthesis of Uniform Hierarchical $\text{Na}_3\text{V}_{1.95}\text{Mn}_{0.05}(\text{PO}_4)_2\text{F}_3$ @C Hollow

### Microspheres as a Cathode Material for Sodium Ion Batteries

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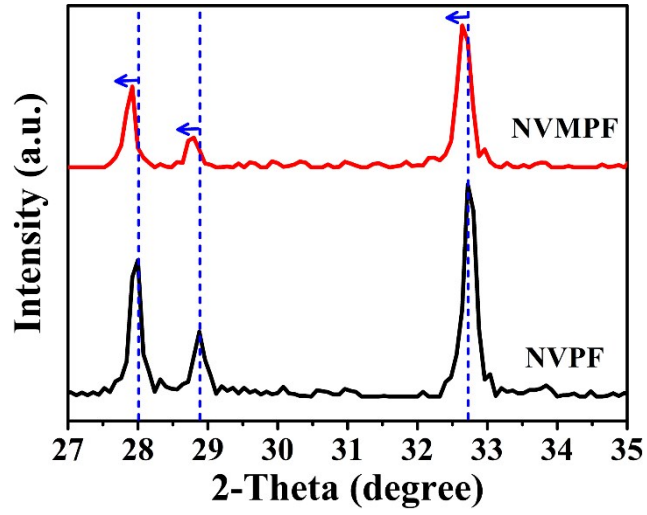


Fig. S1 Partial magnified view of XRD patterns of the NVPF and NVMPF.

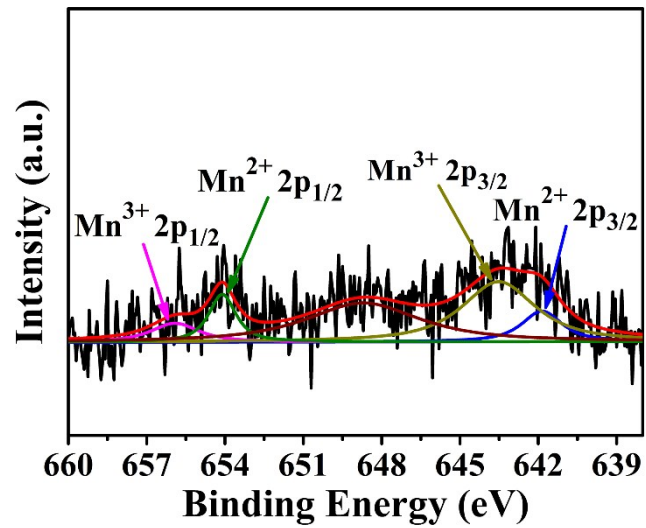
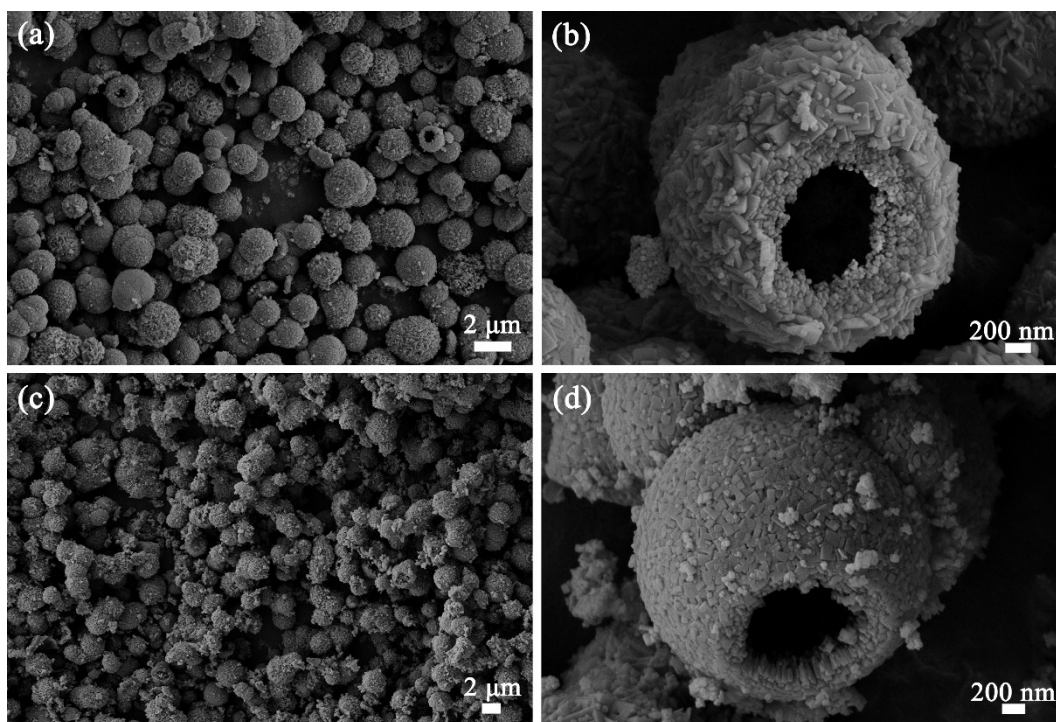


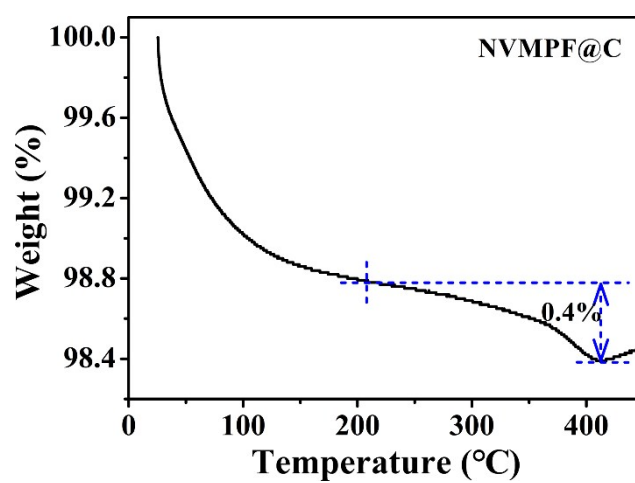
Fig. S2 XPS spectra of Mn 2p of NVMPF.



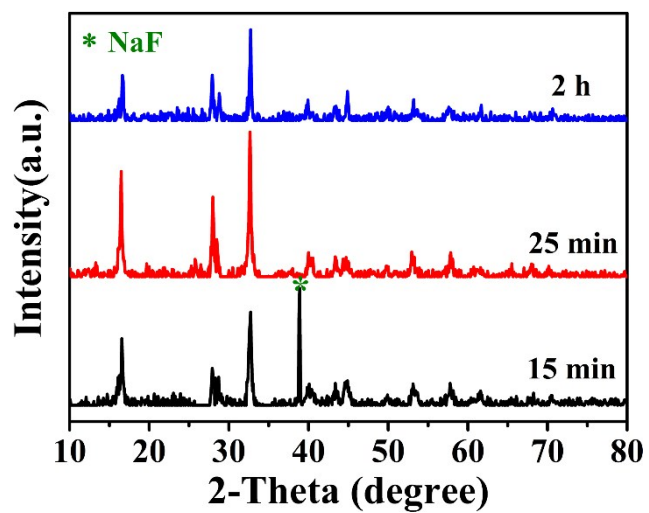
Fig. S3 Low magnification SEM image of NVPF.



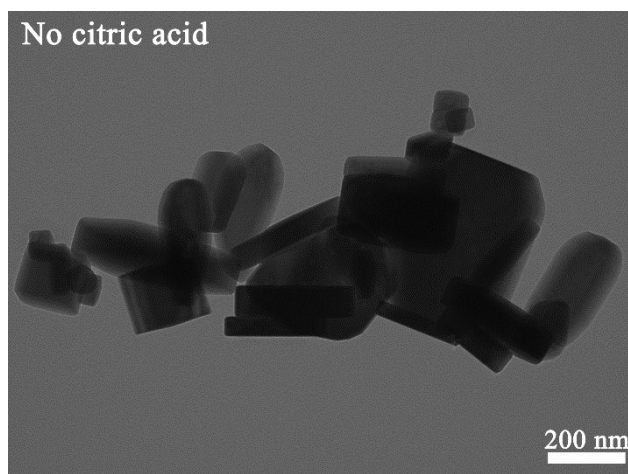
**Fig. S4** SEM images of (a-b) NVMPF and (c-d) NVPF@C; low magnification SEM images (a, c) and enlarged images (b, d) of broken NVMPF and NVPF@C.



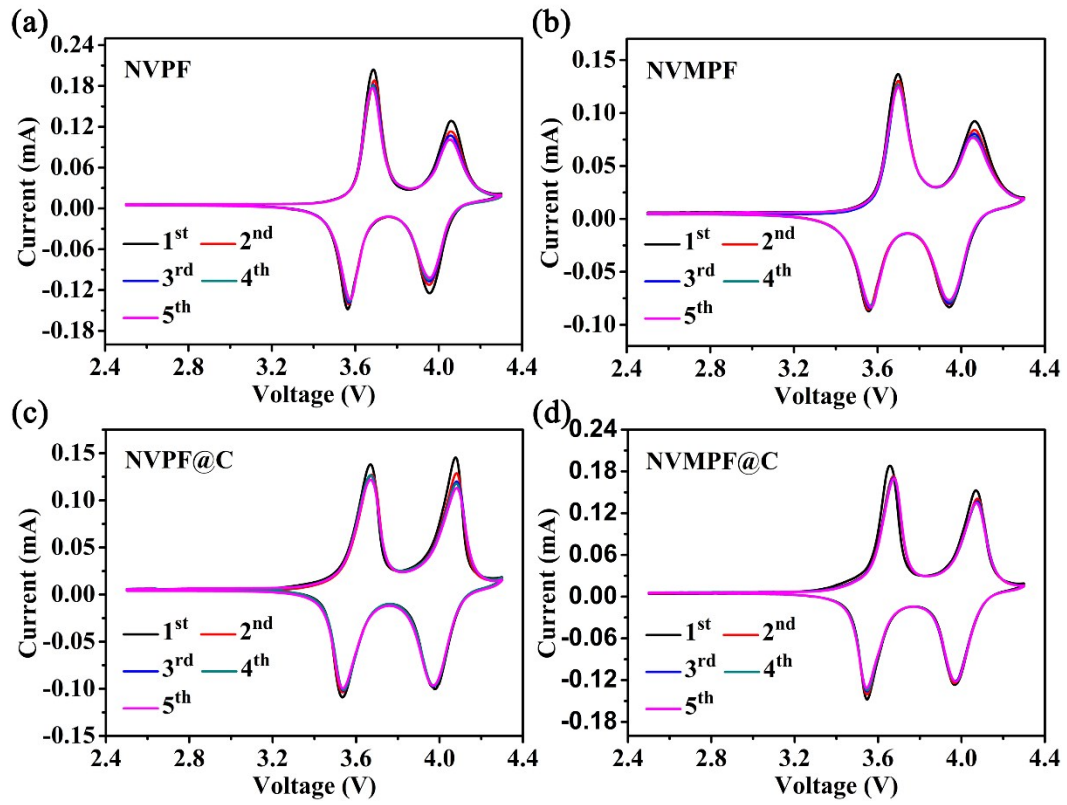
**Fig. S5** TG curve of NVMPF@C.



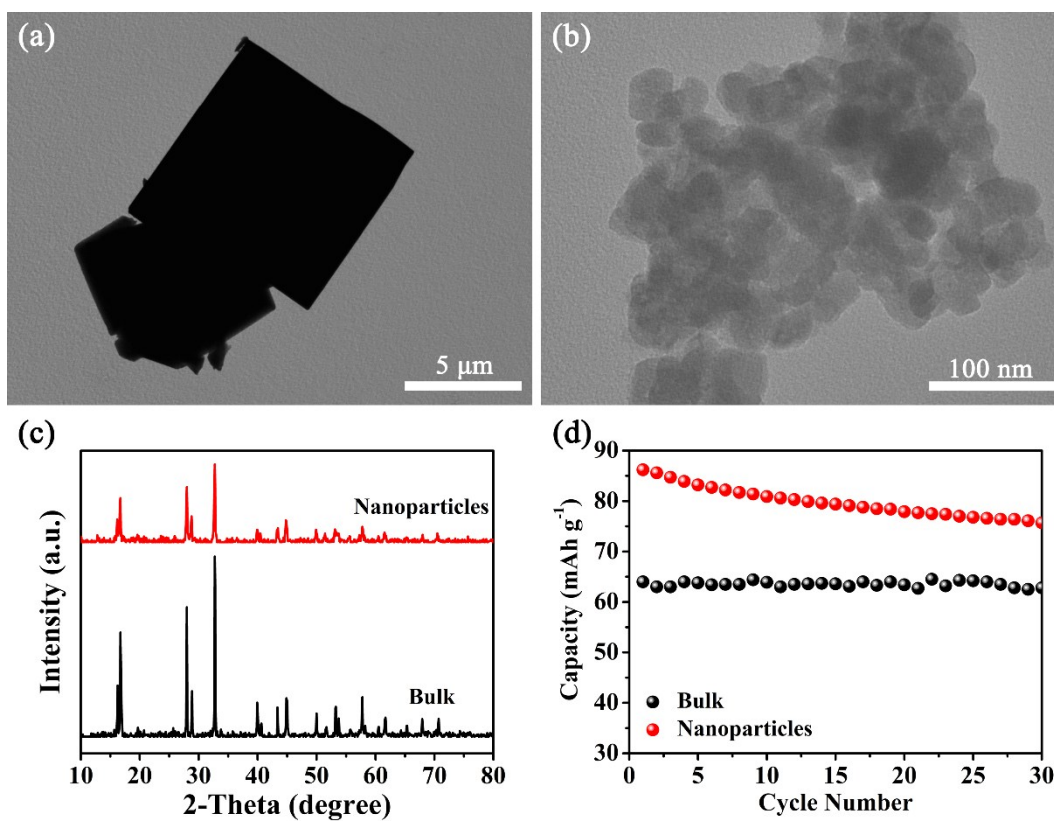
**Fig. S6** XRD patterns of NVPF with different hydrothermal time.



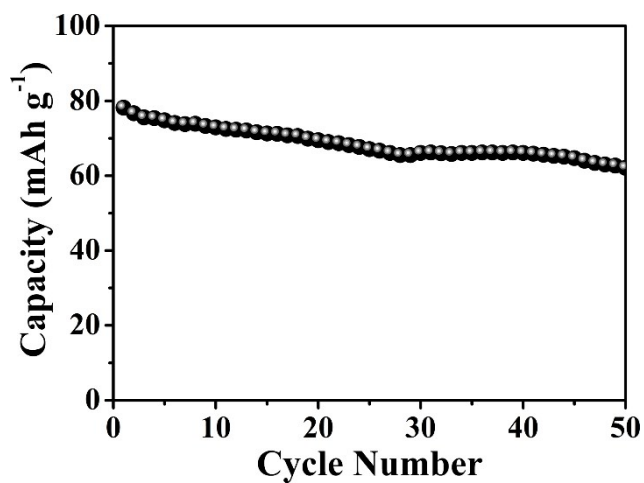
**Fig. S7** TEM image of NVPF obtained with no citric acid.



**Fig. S8** CV curves of (a) NVPF, (b) NVMPF, (c) NVPF@C and (d) NVMPF@C for the anterior five cycles.

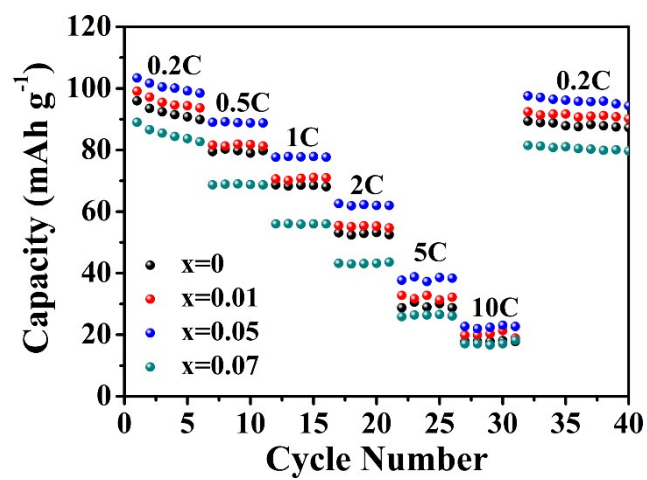


**Fig. S9** TEM images of (a) bulk and (b) nanoparticles NVPF samples; XRD patterns (c) and cycling performance (d) of bulk and nanoparticles NVPF samples at 0.2 C for 30 cycles.

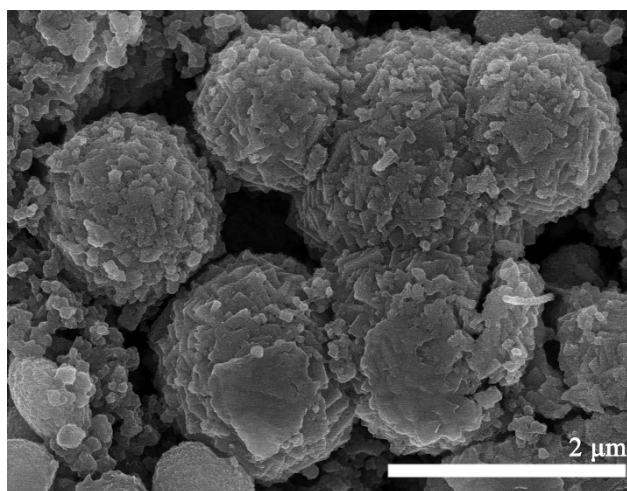


**Fig. S10** Cycling performance of NVPF obtained at 2 h.





**Fig. S11** Rate performance of  $\text{Na}_3\text{V}_{2-x}\text{Mn}_x(\text{PO}_4)_2\text{F}_3$  ( $x=0, 0.01, 0.05, 0.07$ ) at different rates.



**Fig. S12** SEM image of NVMPF@C electrode after 500 cycles at 0.2C.