

# Electronic Supplementary Information

## Controllable Synthesis and *In-situ* TEM Study of Lithiation

### Mechanism of High Performance $\text{NaV}_3\text{O}_8$ Cathodes

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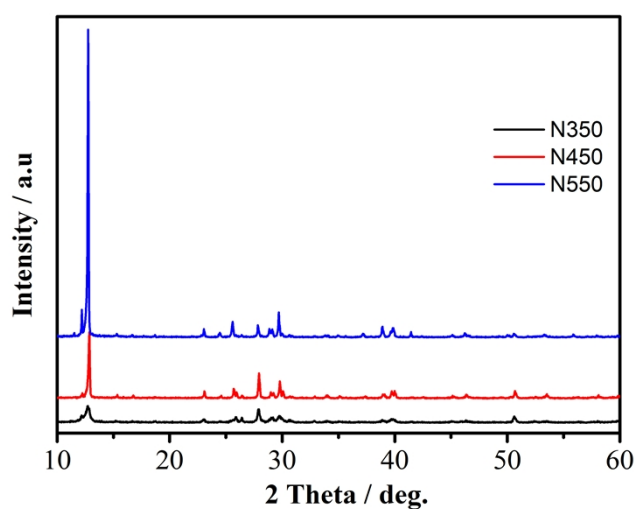


Figure S1. XRD patterns of  $\text{NaV}_3\text{O}_8$  products synthesized at different temperatures (350 °C, 450 °C, and 550 °C) for 12 h, which are designated as samples N350, N450 and N550, respectively.

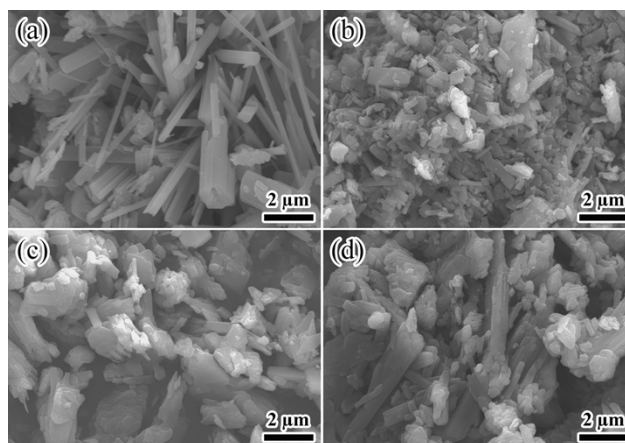


Figure S2. SEM images of  $\text{NaV}_3\text{O}_8$  products synthesized by (a)  $\text{NaCl}$ , (b)  $\text{NaOH}$ , (c)  $\text{NaNO}_3$  and (d)  $\text{Na}_2\text{SO}_4$ , the calcination condition is same as the synthesis of the N450 sample.

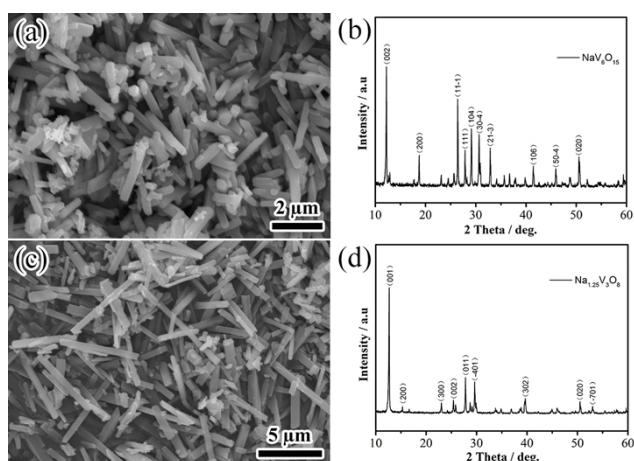


Figure S3. SEM image (a) and XRD pattern (b) of  $\text{NaV}_6\text{O}_{15}$  nanorods calcined at  $450\text{ }^\circ\text{C}$ ; SEM image (c) and XRD pattern (d) of  $\text{Na}_{1.25}\text{V}_3\text{O}_8$  nanorods calcined at  $450\text{ }^\circ\text{C}$ .

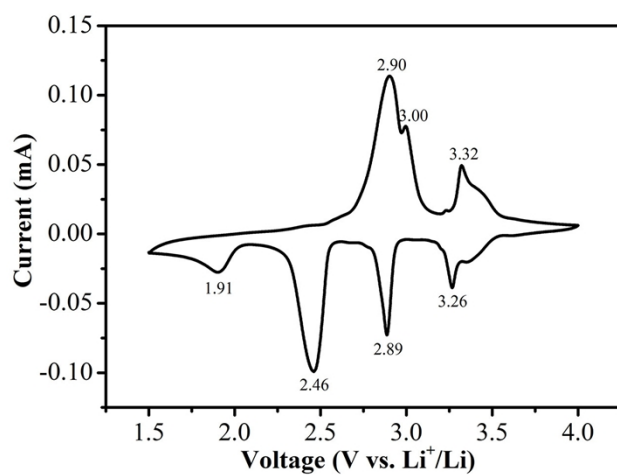


Figure S4. Cyclic voltammetry (CV) curves of  $\text{NaV}_6\text{O}_{15}$  calcined at  $450\text{ }^\circ\text{C}$  at a scan rate of  $0.1\text{ mV s}^{-1}$  from 1.5 to 4.0 V.

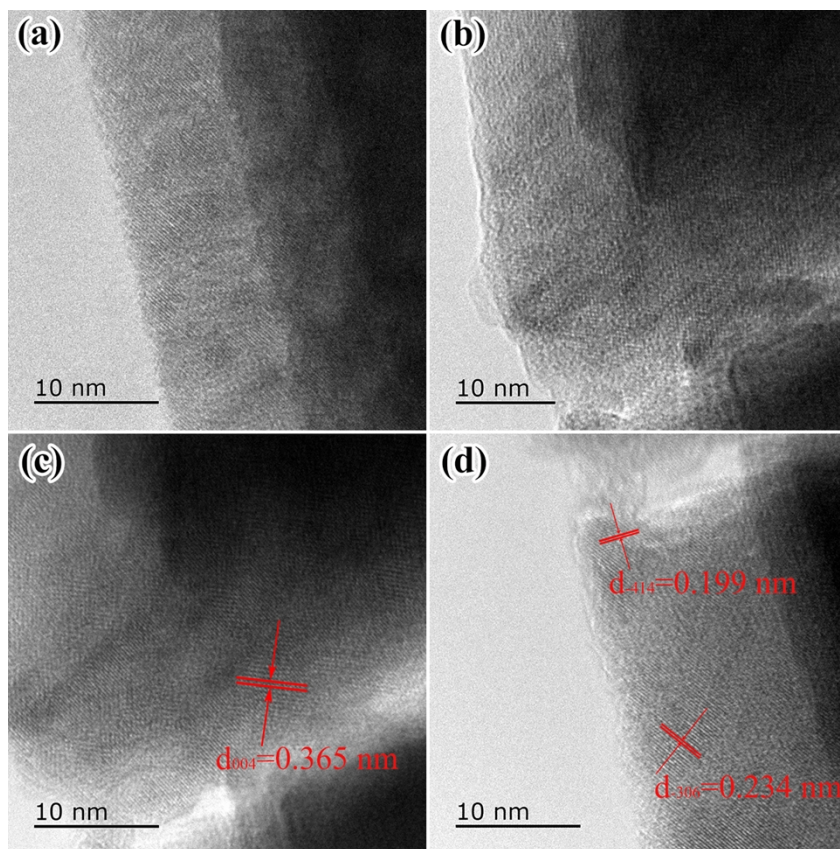


Figure S5. The HRTEM images of microstructure evolution during lithiation of the  $\text{NaV}_3\text{O}_8$  nanorod.

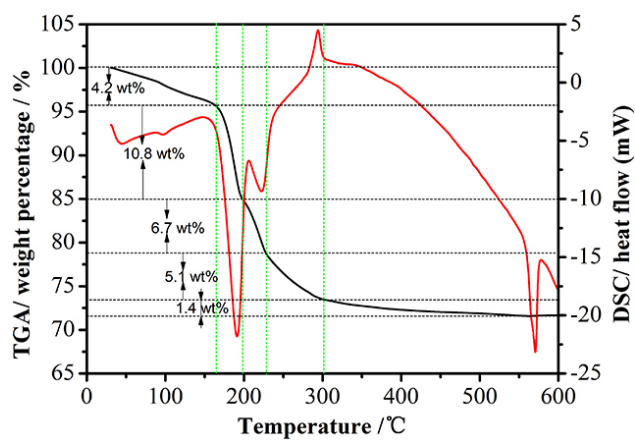


Figure S6. TG-DTA curves of the formation process of  $\text{NaV}_3\text{O}_8$  products.

(Thermogravimetric/Differential Thermal Analyzer analysis was performed using a TG-DTA instrument: Diamond TG/DTA, PerkinElmer, under an air flow of  $100 \text{ ml min}^{-1}$  with a heating rate of  $10 \text{ K min}^{-1}$  from room temperature to  $600 \text{ }^\circ\text{C}$ .)