## **Electronic supplementary information**

## Self-Template Synthesis of Hollow Shell-Controlled Li<sub>3</sub>VO<sub>4</sub> as a

## **High-Performance Anode for Lithium-Ion Batteries**

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## **Experimental Section**

Synthesis of Li<sub>3</sub>VO<sub>4</sub>/rGO hollow shell: In a typical synthesis, moderate ethylene glycol (EG) and DI water were mixed first, then 5 mL graphene oxide (GO) dispersion (1 g  $L^{-1}$ ) was added into the mixed solvent to make the mixed solution volume to 80 mL in total. The graphene oxide is "graphene oxide dispersion liquid" (chemical pure) purchased from Nanjing XFNANO Materials Tech Co., Ltd. After magnetic stirring for a few minutes, 0.351 g NH<sub>4</sub>VO<sub>3</sub> and 2.94 g LiOH·H<sub>2</sub>O were added in the solution and stirred for another 1 h. After that, the solution was transferred to a oil bath pan and kept the temperature at 120 °C for 0.5 h. The obtained production was centrifuged and washed with ethanol several times. Then the precipitate was added into 30 mL DI water and stirred for 5 min to remove the core to get the Li<sub>3</sub>VO<sub>4</sub>/rGO hollow shell (denoted as LVO/rGO HS). The obtained LVO/rGO HS was centrifuged and washed with ethanol several times. To improve the crystallinity, the final products were annealed under Ar atmosphere at 400 °C for 2 h. LVO/rGO HS prepared with the volume ratio of DI water and EG range from 3:1, 1:1, 1:3, and 1:7 are denoted as LVO/rGO HS-1/2/3/4, respectively. The LVO-H, LVO-EG and LVO-M are prepared with the same process in pure H<sub>2</sub>O, EG and mixed solvent without GO, respectively. Material Characterizations: The XRD patterns of the products were measured using a Bruker D8 Advance X-ray diffractometer non-monochromated Cu Ka X-ray source. SEM images were collected by a JEOL-7100F SEM, and TEM images were recorded by a JEM-2100F microscope. C content analysis was performed by Vario EL cube CHNSO elemental analyzer.

*Electrochemical measurements*: The electrochemical performances were evaluated by assembly of 2016 coin cells in an argon-filled glove box. The anode electrodes were composed of 70% active material, 25% acetylene black and 5% carboxyl methyl cellulose (CMC) binder. Galvanostatic charge/discharge measurements were performed by using a multichannel battery testing system (LAND CT2001A) under 25 and 60 °C. Cycling voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were collected with an Autolab potentiostat/galvanostat under 25

and 60 °C.

The calculation of the capacitive and diffusion-controlled intercalation processes: According to power law relationship,  $i = k_1v$  for non diffusion limited processes and  $i = k_1v^{1/2}$  for diffusion limited processes. Thus, total current  $i = k_1v + k_2v^{1/2}$  and  $i(V)/v^{1/2} = k_1v^{1/2} + k_2$ . Current values at different potentials were calculated from cyclic voltammogram at different scan rates of 0.2 to 10 mV s<sup>-1</sup>. Plots of  $i/v^{1/2} vs$ .  $v^{1/2}$  have been drawn at different potentials and from the straight line obtained value of  $k_1$ (slope) and  $k_2$  (intercept) are calculated.<sup>23</sup>



Fig. S1 XPS spectra of LVO-H and LVO-EG.



Fig. S2 XRD patterns of LVO-H, LVO-EG and LVO-M.



Fig. S3 TEM image of LVO-M/rGO.



**Fig. S4** SEM images of the LVO/rGO HS-4 sample before (a) and after (b) removing of the core. Scale bar 200 nm.



Fig. S5 The typical charge-discharge profiles of LVO/rGO-HS-3 sample.

References	Anode	Rate capability
Nanoscale, 2014, 6 11072	LVO/CNT	240 mAh g <sup>-1</sup> at 40 C
Chem. Commun. 2015, 51, 229	LVO@GNS	133 mAh g <sup>-1</sup> at 50 C
Nano Lett. 2013, 13, 4715	LVO/G	233 mAh g <sup>-1</sup> at 20 C
Adv. Funct. Mater. 2015. 25, 3497	LVO/C	106 mAh g <sup>-1</sup> at 80 C
Nano Energy 2015, 12, 709	LVO/G	88.4 mAh g <sup>-1</sup> at 50 C
J. Power Sources 2015, 274, 345	LVO/C	100 mAh g <sup>-1</sup> at 30 C
Our present work	LVO/rGO-HS-3	253 mAh g <sup>-1</sup> at 80 C 201 mAh g <sup>-1</sup> at 125 C

Table S1 The comparison of the electrochemical performances with precious works.



Fig. S6 Rate performances of the solid LVO/rGO, LVO-HS-3 and solid LVO.