## Supporting information

## Electrospinning Hierarchical LiV<sub>3</sub>O<sub>8</sub> Nanowire-in-Network

## for High-Rate and Long-Life Lithium Batteries

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**Fig. S1** Related photographs of the synthesis processes for the LVO-PVA (a), LVO-PVA/PEO (b) and LVO-PEO (c), respectively.



Fig. S2 FTIR spectra of electrospun LVO-PVA and LVO-PEO composite before annealing.



Fig. S3 TEM image (a), HRTEM image (b) and SAED patterns (c) of hierarchical LVO-PVA/PEO nanowire.



Fig. S4 SEM images of the electrospun LVO-PVA/PEO nanofibers after annealing at (a) 300 °C and (b) 350 °C for 2h. It indicates that the nucleary of original  $LiV_3O_8$  grain and the decomposition of polymer components occur simultaneously so that hierarchical nanowires are formed.



Fig. S5 SEM images of the electrospun LVO-PVA/PEO nanofibers after annealing at 450 °C. The size of  $LiV_3O_8$  nanorods grow much bigger and it consumes a large number of connected materials so that the hierarchical network structure cannot be maintained.



**Fig. S6** FESEM images of the electrospun LVO-PVA/PEO nanofibers after annealing at 400  $^{\circ}$ C. The weight ratio of PVA and PEO is 3:1 (a), 2:1 (b), 1:2 (c) and 1:3 (d) for the starting materials.



Fig. S7 TG images of the electrospun LVO-PVA and LVO-PEO nanofibers.



Fig. S8 Charge–discharge curves (a) and differential capacity vs. voltage curves (b) of

LVO-PVA/PEO sample at different cycles.



Fig. S9 Electrospinning process with four working injectors

Table S1. Comparison of the electrochemical performance of  $LiV_3O_8$  based cathode materials for

lithium batteries.							
	Material	Current density (mA g <sup>-1</sup> )	Maximum capacity (mAh g <sup>-1</sup> )	Cycle numbers	Capacity after cycle (mAh g <sup>-1</sup> )	Decay per cycle (%)	Reference
		100	320	100	272	0.153	
1	LiV <sub>3</sub> O <sub>8</sub>	1000	254	500	129	0.098	Our work
		2000	202	500	103	0.099	
2	Mo- LiV <sub>3</sub> O <sub>8</sub>	300	269	100	206	0.235	S1
3	$Li_xV_2O_5/LiV_3O_8$	300	195	420	161	0.042	S2
4	G-LiV <sub>3</sub> O <sub>8</sub>	300	226	100	197	0.129	S3
5	LiV <sub>3</sub> O <sub>8</sub>	1000	240	100	194	0.190	S4
6	LiV <sub>3</sub> O <sub>8</sub>	300	200	200	191	0.023	S5
7	LiV <sub>3</sub> O <sub>8</sub> /PTh	300	250	50	217	0.264	S6

## Reference

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