Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic Supplementary Information

F-doping Effects on Carbon-Coated $Li_3V_2(PO_4)_3$ as a Cathode for High Performance Lithium Rechargeable Batteries: Combined Experimental and DFT Studies

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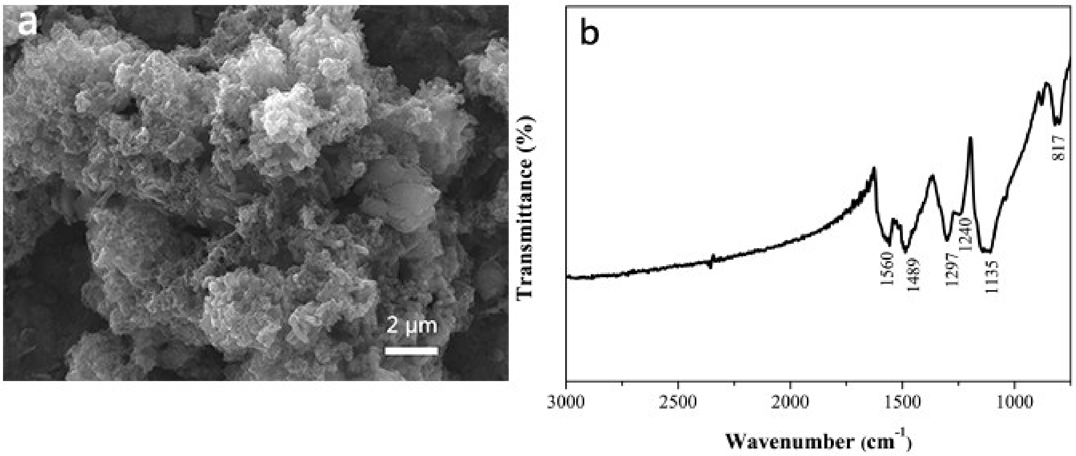

Fig. S1 (a) FESEM image of the as prepared polyaniline. (b) FTIR spectrum of the polyaniline coincides with that of the previously reported [1], confirming that it has been successfully synthesized.

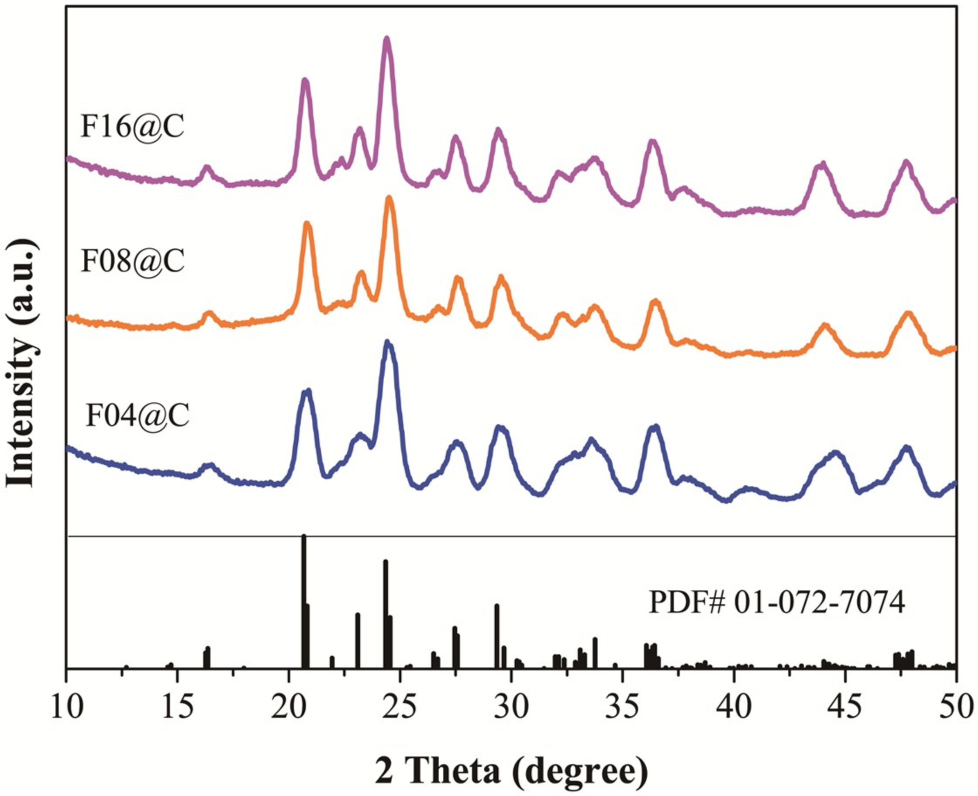

Fig. S2 X-ray diffraction patterns of as prepared $Li_3V_2(PO_4)_{3-x}F_x$@C (x= 0.04, 0.08 and 0.16).

Table S1 Structural parameters obtained from Rietveld refinement of XRD patterns.

Sample	a [Å]	b [Å]	c [Å]	β [°]	Volume [Å^3]	R factor [%]
F00@C	8.5893(8)	8.5893(3)	11.9945(2)	90.45(4)	881.7(6)	4.25
F04@C	8.6624(5)	8.5245(4)	12.0101(6)	90.26(3)	886.9(8)	3.98
F08@C	8.5988(5)	8.6049(9)	12.0138(5)	90.58(1)	888.9(2)	6.80
F12@C	8.6157(2)	8.5906(6)	12.0435(2)	90.43(7)	891.4(1)	3.18
F16@C	8.6823(8)	8.5413(8)	12.0333(7)	90.49(5)	892.3(7)	3.30

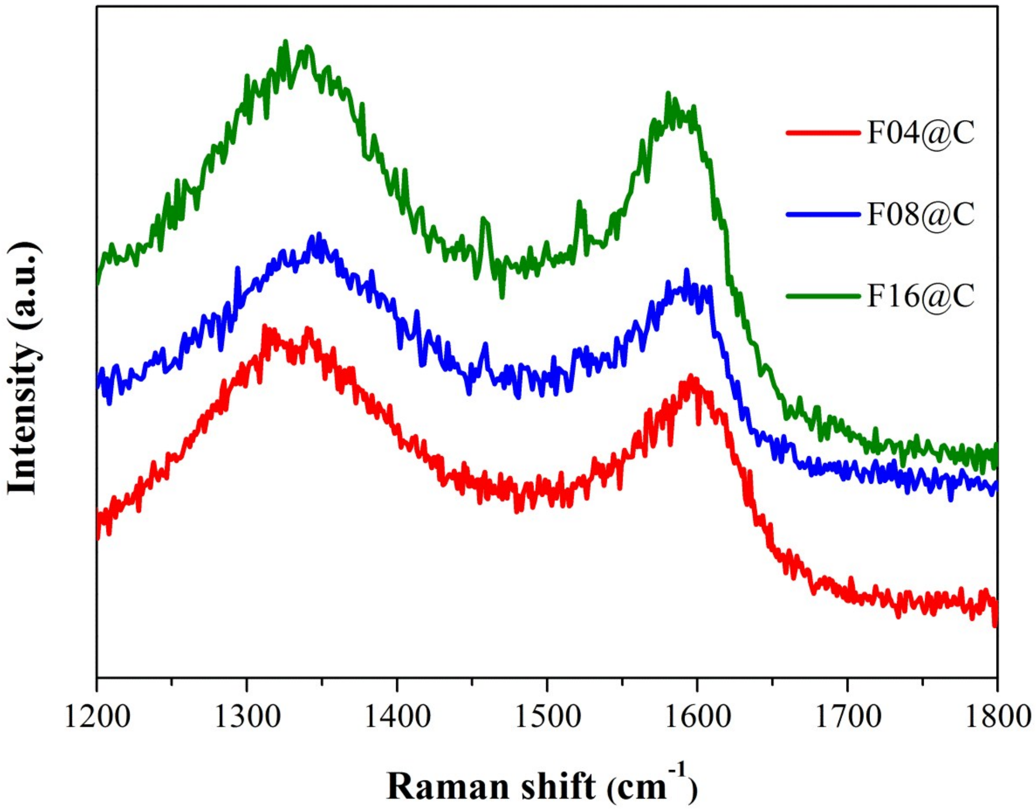

Fig. S3 Characterization of graphitization by Raman spectra of $Li_3V_2(PO_4)_{3-x}F_x$@C (x= 0.04, 0.08 and 0.16).

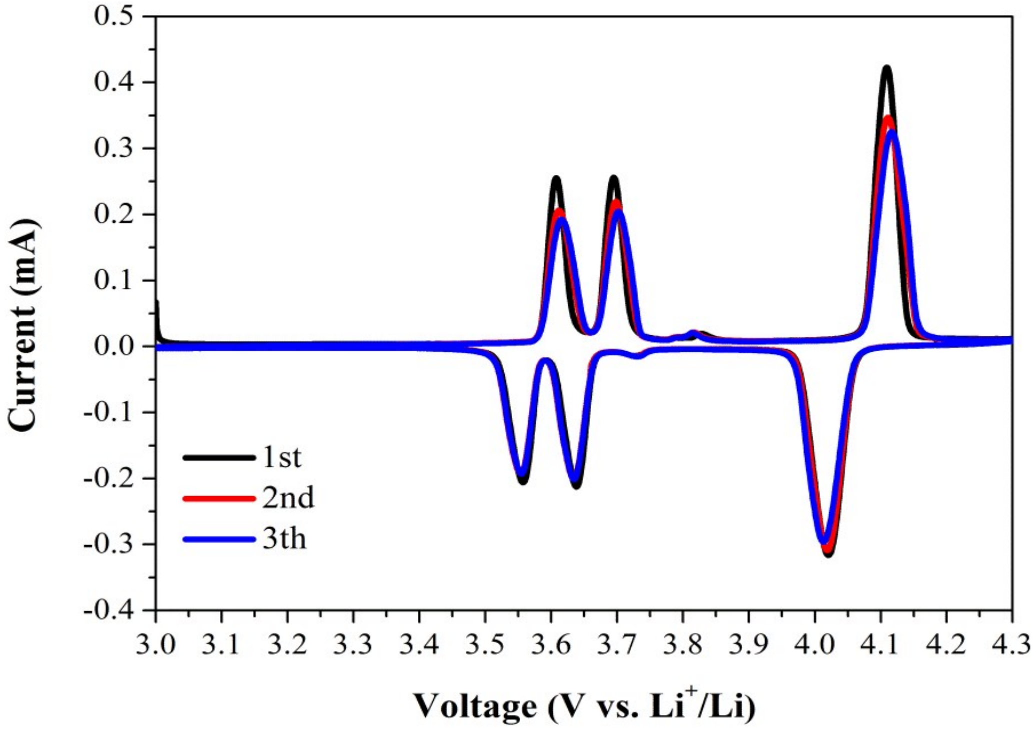

Fig. S4 The first three successive cyclic voltammogram curves of F00@C electrode at a scan rate of 0.2 mV s^{-1} in a voltage window of 3.0-4.3 V.

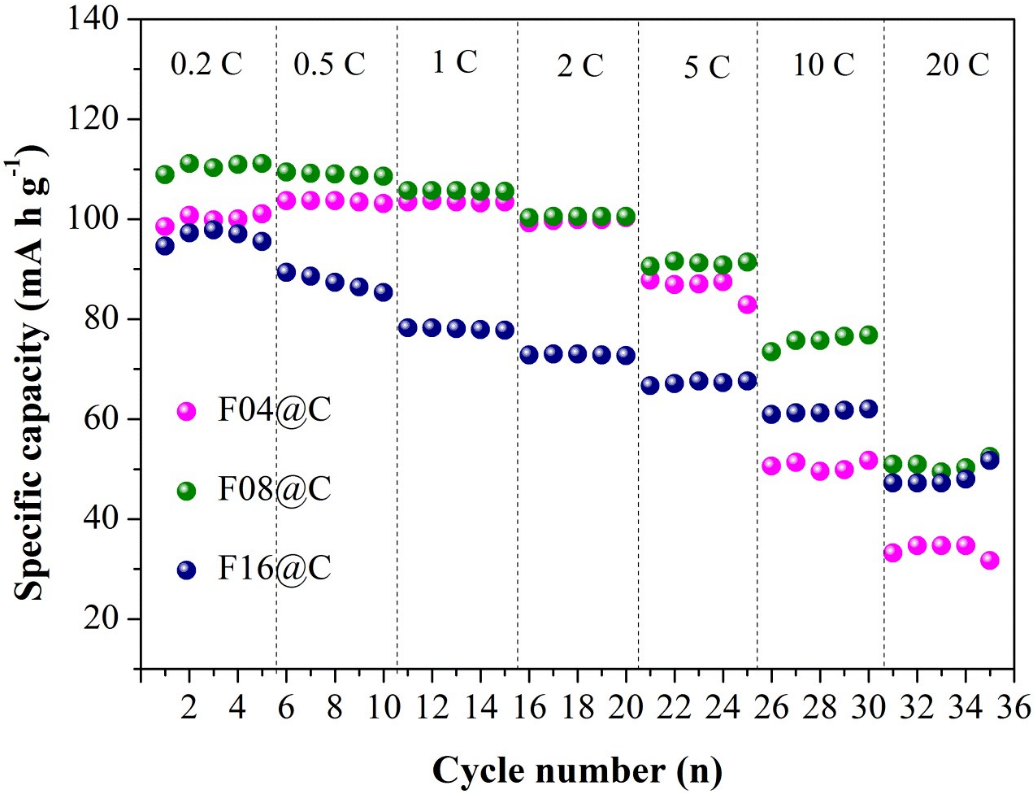

Fig. S5 Rate properties at various rates between the voltage range of 3.0-4.3 V of $Li_3V_2(PO_4)_{3-x}F_x$@C (x= 0.04, 0.08 and 0.16).

Table S2 Specific capacity (mAh g^{-1}) data of $Li_3V_2(PO_4)_{3-x}F_x$@C.

Sample	**0.2 C**	**0.5 C**	**1 C**	**2 C**	**5 C**	**10 C**	**20 C**
F00@C	96.34	94.93	90.44	87.97	79.25	62.74	35.50
F04@C	101.04	103.72	103.72	100.30	87.05	87.05	34.67
F08@C	111.11	109.44	105.69	100.56	91.39	76.81	52.50
F12@C	112.76	123.42	125.53	123.16	112.11	91.84	65.00
F16@C	97.84	89.35	78.24	72.80	67.60	62.04	51.70

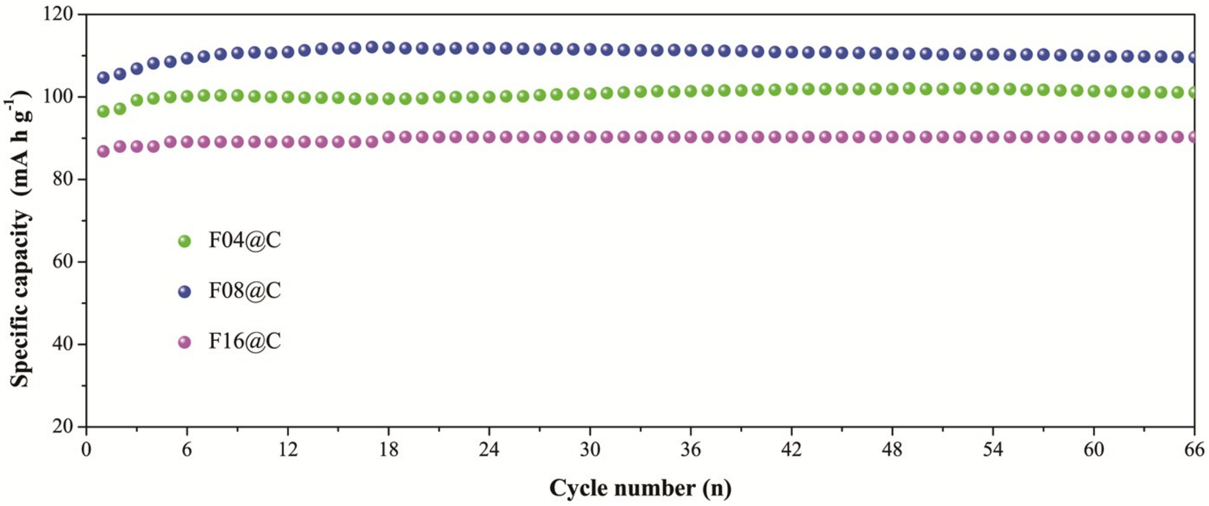

Fig. S6 Cycling performance at the current density of 1 C between the voltage range of 3.0-4.3 V of $Li_3V_2(PO_4)_{3-x}F_x$@C (x= 0.04, 0.08 and 0.16).

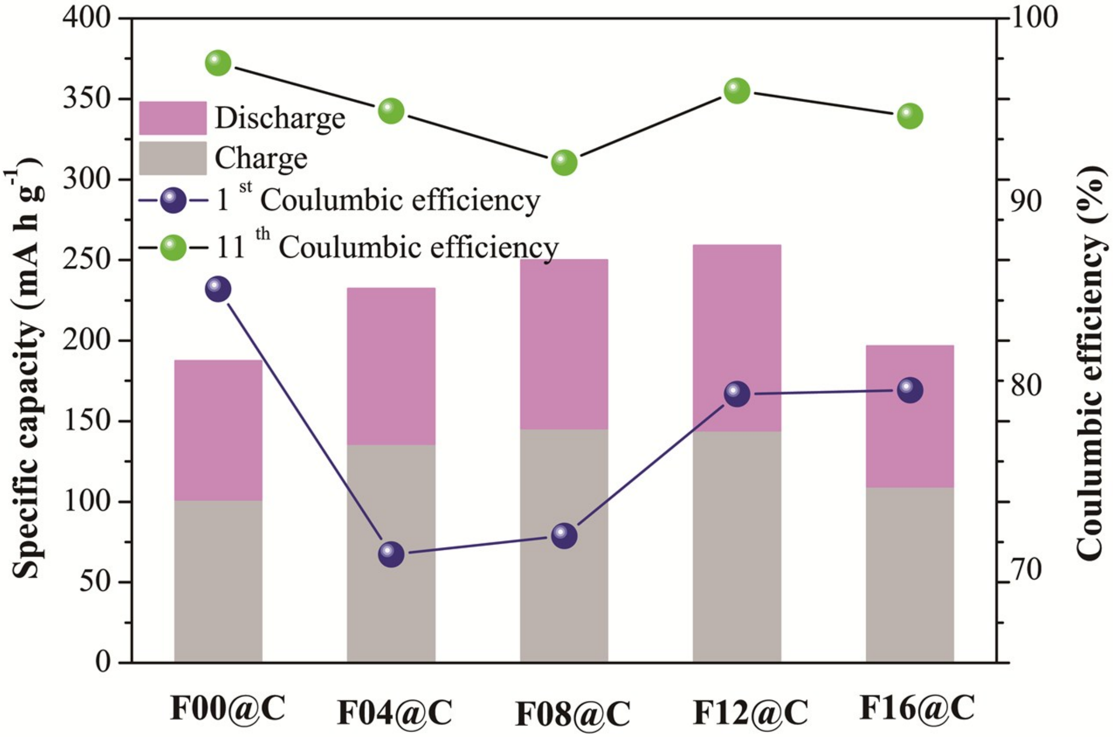

Fig. S7 The electrochemical data of the first cycle at 1 C between the voltage range of 3.0-4.3 V of $Li_3V_2(PO4)_{3-x}F_x$@C. For comparison, the Coulomb efficiency of cycle 11th is also given .

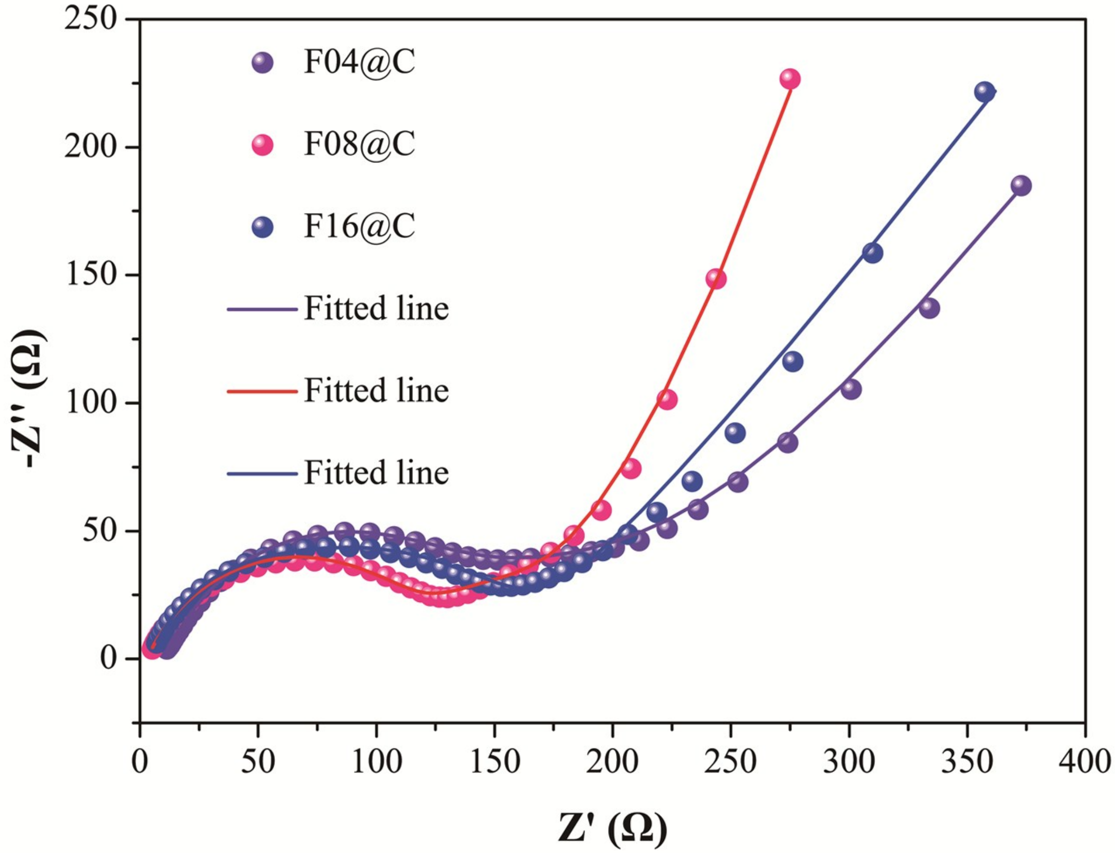

Fig. S8 EIS after 40 cycles from 0.2 to 20 C at full discharge state of $Li_3V_2(PO_4)_{3-x}F_x$@C (x= 0.04, 0.08 and 0.16).

Table S3 Kinetic parameters of $Li_3V_2(PO_4)_{3-x}F_x$ samples calculated from EIS.

Sample	R_e **(Ω)**	R_s **(Ω)**	R_{ct} **(Ω)**	δ_ω **(Ω·cm^2 s$^{-0.5}$)**	i_0 **(mA·cm^{-2})**	D_{Li^+} **(cm^2·s^{-1})**
F00@C	2.60	31.98	147.40	114.84	8.71×10^{-5}	4.28×10^{-16}
F04@C	8.47	94.85	118.30	133.28	1.09×10^{-4}	3.18×10^{-16}
F08@C	2.95	33.98	116.60	104.93	1.10×10^{-4}	5.12×10^{-16}
F12@C	2.74	21.43	98.12	45.09	1.31×10^{-4}	2.78×10^{-15}
F16@C	3.61	28.90	127.20	151.06	1.01×10^{-4}	2.47×10^{-16}

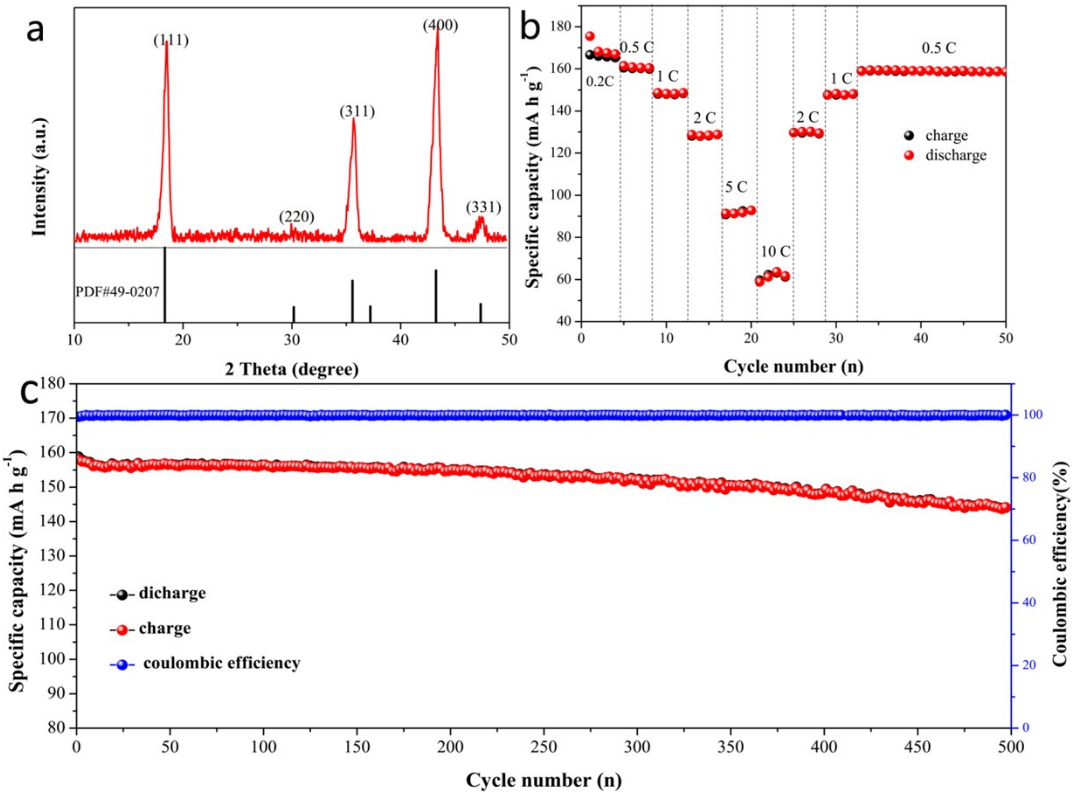

Fig. S9 (a) XRD pattern of as prepared $Li_4Ti_5O_{12}$@C sample (Cubic, Fd-3m (227), PDF#49-0207)[2]. (b) Rate capability at various discharge rates. (c) The cycle performance at 1 C (1 C = 175 mA h g^{-1}) charge and discharge for 500 cycles of $Li_4Ti_5O_{12}$@C sample. The cutoff voltage was 1.0-2.5 V (vs. Li^+/Li).

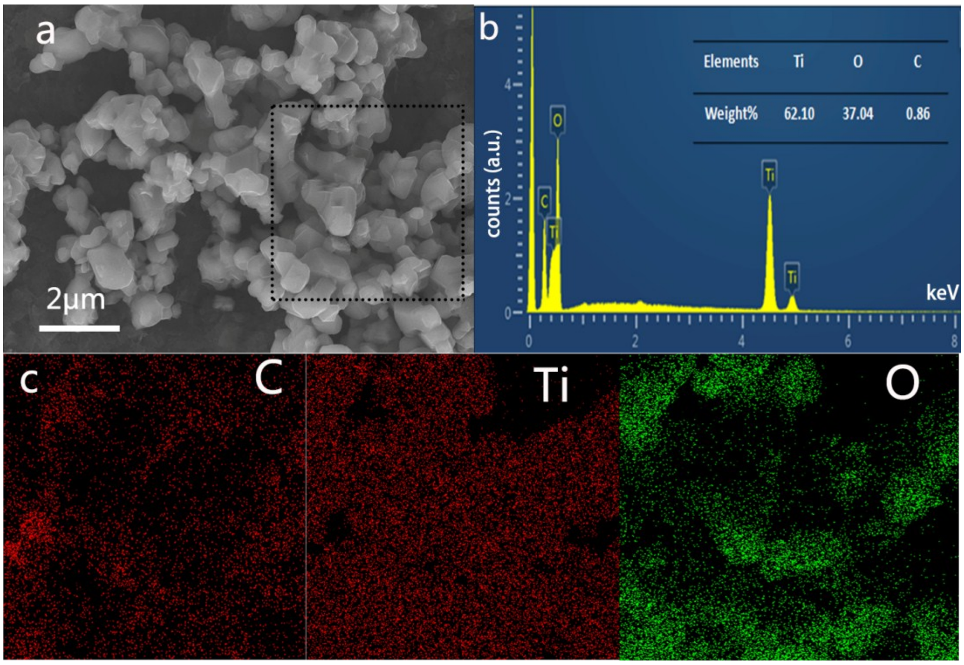

Fig. S10 (a) FESEM micrograph. (b) EDS spectrum. (c) EDS mappings of Ti, O and C elements of the as synthesized $Li_4Ti_5O_{12}$@C sample.

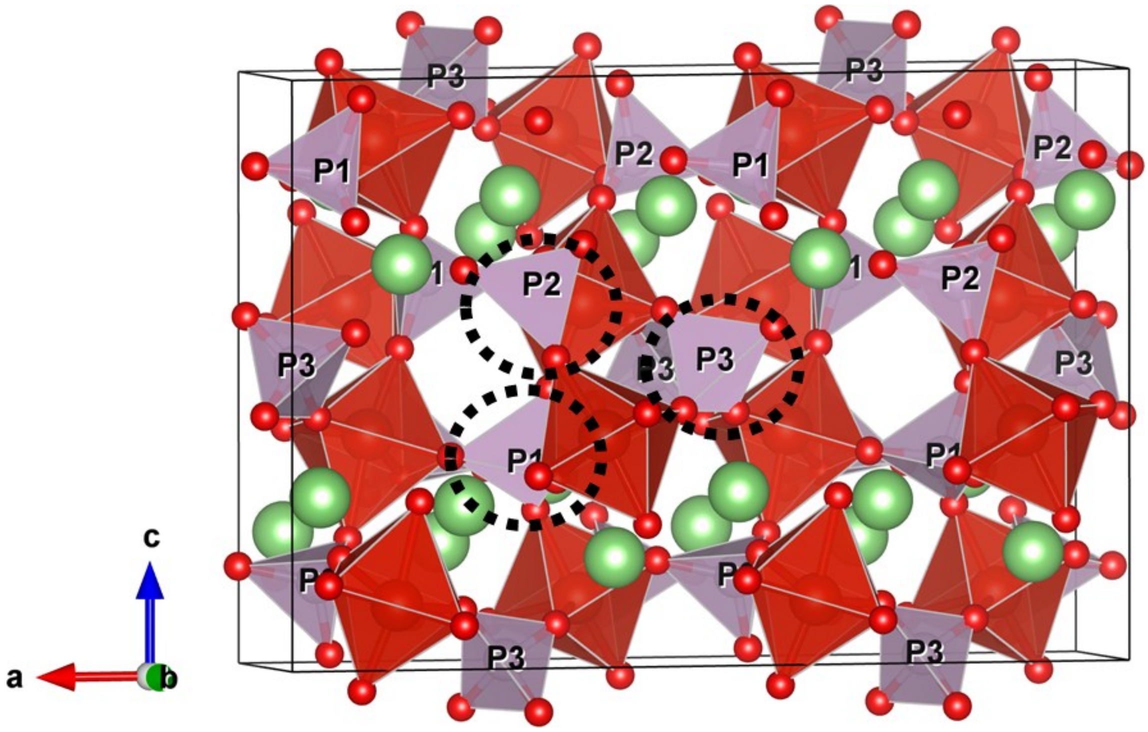

Fig. S11 Schematic illustration of the all three possible substitution sites of one F^- exchanged with one PO_4^{3-} of $Li_3V_2(PO_4)_{2.88}F_{0.12}$. As in $Li_3V_2(PO_4)_3$ 2×1×1 supercell, the all P atoms site at 8e position. Taking into account the symmetry of PO_4^{3-} in the supercell, F^- has three possibilities of substitution, which named P1, P2 and P3 respectively, as shown by the black dotted circle in the figure. Then all these substitutional configurations were relaxed. to the of their total energies. The total energies of P1, P2 and P3 site configuration are calculated to be -1109.75783, -1110.3133 and -1110.05315 eV, respectively, so that the F^- site ate P2 site is the most possible substitution configuration. (The P1, P2 and P3 site configuration see P1.cif, P2.cif and P3.cif.)

Table S4 $Li_3V_2(PO_4)_{2.88}F_{0.12}$: magnetization (x).

ion	s	p	d	totol
V1	0.014	0.021	2.001	2.035
V2	-0.013	-0.021	-1.989	-2.023
V3	0.014	0.020	2.005	2.039
V4	0.026	0.029	2.867	2.922
V5	0.029	0.029	2.869	2.927
V6	0.013	0.021	1.995	2.029
V7	0.013	0.021	1.998	2.032
V8	0.013	0.021	1.995	2.029
V9	0.014	0.021	2.001	2.036
V10	0.013	0.020	1.994	2.027
V11	0.014	0.021	2.002	2.037
V12	0.017	0.019	2.016	2.051
V13	0.014	0.021	2.007	2.041
V14	0.013	0.021	1.999	2.033
V15	0.013	0.021	1.998	2.032
V16	0.013	0.021	1.994	2.028

Table S5 $Li_3V_2(PO_4)_3$: magnetization (x).

ion	s	p	d	total
V1	0.013	0.021	1.997	2.031
V2	0.013	0.021	1.997	2.031
V3	0.013	0.021	1.997	2.031
V4	0.013	0.021	1.997	2.031
V5	0.013	0.021	1.997	2.031
V6	0.013	0.021	1.997	2.031
V7	0.013	0.021	1.997	2.031
V8	0.013	0.021	1.997	2.031
V9	0.013	0.021	1.994	2.028
V10	0.013	0.021	1.994	2.028
V11	0.013	0.021	1.994	2.028
V12	0.013	0.021	1.994	2.028
V13	0.013	0.021	1.994	2.028
V14	0.013	0.021	1.994	2.028
V15	0.013	0.021	1.994	2.028
V16	0.013	0.021	1.994	2.028

References

1. J. Zhang, Y. Xu, L. Fan, Y. Zhu, J. Liang and Y. Qian, *Nano Energy*, 2015, **13**, 592-600.
2. P. He, H. Li and H. Zhou, *Physical Chemistry Chemical Physics*, 2012, **14**, 9086-9091.