

Supporting Information for

Li₃V₂(PO₄)₃/graphene nanocomposites as Cathode Material for Power Lithium Ion Batteries

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Graphene Oxide (GO) making

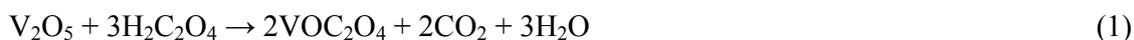
Graphite oxide (GiO) was prepared by a modified Hummers method (ref.7 in main text). 100 ml of concentrated H₂SO₄ (98 %) were added slowly into the mixture of 2.0 g of KNO₃ and 4.0 g of natural graphite (300 mesh) below 0 °C. The mixture was stirred for 30 minutes before slow addition of 15 g KMnO₄ in an hour. Then, the mixture was heated to 35 ± 3 °C and stirred for 2 hours. Subsequently, 180 ml of water was dropwise added under vigorous stirring, causing a quick rise in temperature to near 100 °C. The slurry was stirred at this temperature for another 30 minutes. Afterwards, 14 ml of H₂O₂ solution (30 wt%) and 120 ml of water were added sequentially to dissolve insoluble manganese species. The resulting graphite oxide suspension was filtrated and washed using 300 ml dilute HCl (3%) solution. After dispersing the collected precipitate into 1200 ml water, the solution was centrifuged and washed twice with water. The colloidal GiO was obtained and dried under vacuum at 80 °C for two days. The resulting product was ground into powder (100 mesh).

50 mg GiO powder was dispersed into 500 ml H_2O , and a brown homogeneous suspension was obtained after ultrasonicated for 4 hours.

Synthesis of LVP/graphene

50mg VC was added into GO suspension and followed by ultrasonic treatment for 2 hours. The suspension kept for 20 hours to form partly reduced graphene oxide due to the reduced reagent (VC) was lower than the mass of stoichiometric ratio.

LVP nanoparticles precursors were synthesized using a sol-gel method reported in our previous papers (ref.8 in main text). Typically, V_2O_5 (0.9186g) and oxalic acid (1.9006g) in a stoichiometric ratio of 1:3 were dissolved in deionized water under magnetic stirring at 80 °C until a clear blue solution was formed (eq 1). Then a mixture of stoichiometric $\text{NH}_4\text{H}_2\text{PO}_4$ (1.7428g) and Li_2CO_3 (0.5636g) was added to the solution, and this batch was vigorously stirred for 10minutes at 80 °C. The precursor LVP solution was poured into the partly reduced graphene suspension. The mixed precursor was vigorously stirred and being ultrasonicated for 4 hours to form a slurry at 80 °C. Thereafter, the slurry was dried at 100 °C, after ground the dried precursor was decomposed at 350 °C under nitrogen atmosphere for 4 hours. The pre-heat treated precursor was ground and reacted at 800 °C for 8 hours under nitrogen (eq 2). The formation process of the LVP/graphene nanocomposite was represented in Scheme 1.



Materials characterization

X-ray studies were done on a Rigaku diffractometer (Dmax-2200) with Cu K α radiation. The diffraction data are collected for 4s at each 0.02° step width from 10 to 70°. The crystal structure parameters of the sample LVP and LVP/graphene were refined by Reitveld analysis by using the General Structure Analysis System (GSAS). The morphology was characterized by using scanning electron microscope (SEM, Hitachi-X650 microscope, 20kV), transmission electron microscope (TEM, JEOL-2000CX, 200kV) and high resolution transmission electron microscope (HRTEM, JEOL-2010F, 200kV). The amount of carbon element in the product was measured by elemental analyzer (Elementar VarioEL III, Germany). The average size distributions were measured by a Zetasizer 3000HSA particle size analytical instrument (Malvern, England).

Electrochemical measurements

For the preparation of the electrodes, the active materials (60 wt%), Super P (30 wt%) and poly(vinylidene fluoride) (10 wt%) were mixed in N-methyl-2-pyrrolidone and stirred overnight. The slurry was cast onto Al foil by using a doctor blade, and dried at 120 °C for 12 h under vacuum. The electrode area was 0.95 cm² and the loading density was about 2~4 mg/cm². The coin cells (CR2016) were assembled in an argon-filled glove box using lithium metal as the negative electrode, Celgard 2500 as the separator, and 1 M LiPF₆ (dissolved in ethylene carbonate, dimethyl carbonate and ethyl-methyl carbonate with a

1:1:1 volume ratio) as the electrolyte. The galvanostatic charge and discharge experiments were made at room temperature by using LAND CT2001A (Wuhan, China) within the voltage range of 3.0-4.3 V (1 C=133 mAh/g) and 3.0-4.8V (1 C=197 mAh/g) (vs. Li^+/Li), respectively. Cyclic voltammetry (CV) was conducted on a LK2500 electrochemical workstation at a scanning rate of 0.1 mV/s in a potential range of 3.0-4.3V (vs Li^+/Li). A lithium foil acted as both the counter electrode and reference electrode. Electrochemical impedance spectroscopy (EIS) measures were carried out at the fresh state on a PARSTAT2273 electrochemical workstation with sinusoidal signal of 5 mV over a frequency range from 100 kHz to 10 mHz.

Supplementary Tables and Figures

Table S1. Atomic sites and fractional coordinates of LVP and LVP/graphene.

Atom	<i>x</i>		<i>y</i>		<i>z</i>	
	LVP*	LVP/graphene**	LVP	LVP/graphene	LVP	LVP/graphene
Li1(4e)	0.3024(7)	0.2083(3)	0.4325(3)	0.3025(5)	0.2710(4)	0.2534 (8)
Li2(4e)	0.5949(2)	0.7553(6)	0.4325(3)	0.1474(7)	0.4029(8)	0.4554(0)
Li3(4e)	0.9213(2)	0.9906(2)	0.4325(3)	0.2668(2)	0.3156(3)	0.3692(2)
V1(4e)	0.2485(5)	0.2457(1)	0.1088(6)	0.1080(2)	0.4620(4)	0.4613(0)
V2(4e)	0.7513(8)	0.7580(1)	0.3889(6)	0.3859(8)	0.4714(6)	0.4688(9)
P1(4e)	0.1046(4)	0.1217(3)	0.1474(7)	0.1438(8)	0.1020(7)	0.0993(5)
P2(4e)	0.6064(1)	0.6022(7)	0.3542(0)	0.3508(8)	0.1129(6)	0.1163(9)
P3(4e)	0.0397(9)	0.0387(3)	0.4930(9)	0.4930(7)	0.2569(0)	0.2550(1)
O1(4e)	0.4257(8)	0.4698(4)	0.3299(7)	0.3169(5)	0.0843(9)	0.1007(8)
O2(4e)	0.9317(2)	0.9122(8)	0.1567(0)	0.1447(0)	0.1147(4)	0.1001(5)
O3(4e)	0.3471(0)	0.3335(4)	0.2651(4)	0.2672(5)	0.4802(2)	0.4714(8)
O4(4e)	0.8049(6)	0.7955(9)	0.2158(2)	0.2256(4)	0.4903(7)	0.4917(9)
O5(4e)	0.1763(3)	0.1727(4)	0.0383(0)	0.0406(2)	0.0574(4)	0.0330(1)
O6(4e)	0.6489(1)	0.6447(8)	0.4742(5)	0.4633(0)	0.0800(7)	0.1047(5)
O7(4e)	0.4596(5)	0.4374(6)	0.0710(8)	0.0605(8)	0.3678(7)	0.3744(2)
O8(4e)	0.9297(5)	0.9177(5)	0.4086(0)	0.4173(1)	0.3274(7)	0.3251(5)
O9(4e)	0.1640(3)	0.1924(8)	0.4325(3)	0.4377(7)	0.1687(1)	0.1727(4)
O10(4e)	0.6193(1)	0.6113(7)	0.4325(3)	0.0666(2)	0.1365(9)	0.1390(3)
O11(4e)	0.1659(5)	0.1608(6)	0.4325(3)	0.1806(3)	0.2602(2)	0.2595(2)
O12(4e)	0.6451(9)	0.6030(9)	0.4325(3)	0.3146(8)	0.2823(5)	0.2855(1)

* For pure LVP, lattice constants $a=8.6115(3)$ Å, $b=12.0461(9)$ Å, $c=8.5993(0)$ Å, and $\gamma = 90.554(0)^\circ$, $V = 892.02$ Å³. The reliable factors are $wRp\% = 4.62\%$, $Rp = 3.29\%$, $\chi^2 = 1.007$, and $R_f = 1.43\%$.

** For LVP/graphene, lattice constants $a=8.6445(9)$ Å, $b=12.0889(9)$ Å, $c=8.6284(9)$ Å, and $\gamma = 90.573(1)^\circ$, $V = 901.67$ Å³. The reliable factors are $wRp\% = 5.57\%$, $Rp = 4.21\%$, $\chi^2 = 1.006$, and $R_f = 2.77\%$.

Table S2. The results of elemental analysis for LVP/graphene and pure LVP materials.

	C%	H%	N%
LVP/graphene	1.137	0.003	0.559
LVP	0.000	0.256	0.003

Table S3. Potential differences between the anodic and cathodic peaks for LVP and LVP/graphene electrodes in the first cycle of CV profiles.

	ΔE_{O1-R1} (V)	ΔE_{O2-R2} (V)	ΔE_{O3-R3} (V)
LVP/graphene	0.129	0.129	0.174
LVP	0.139	0.157	0.196

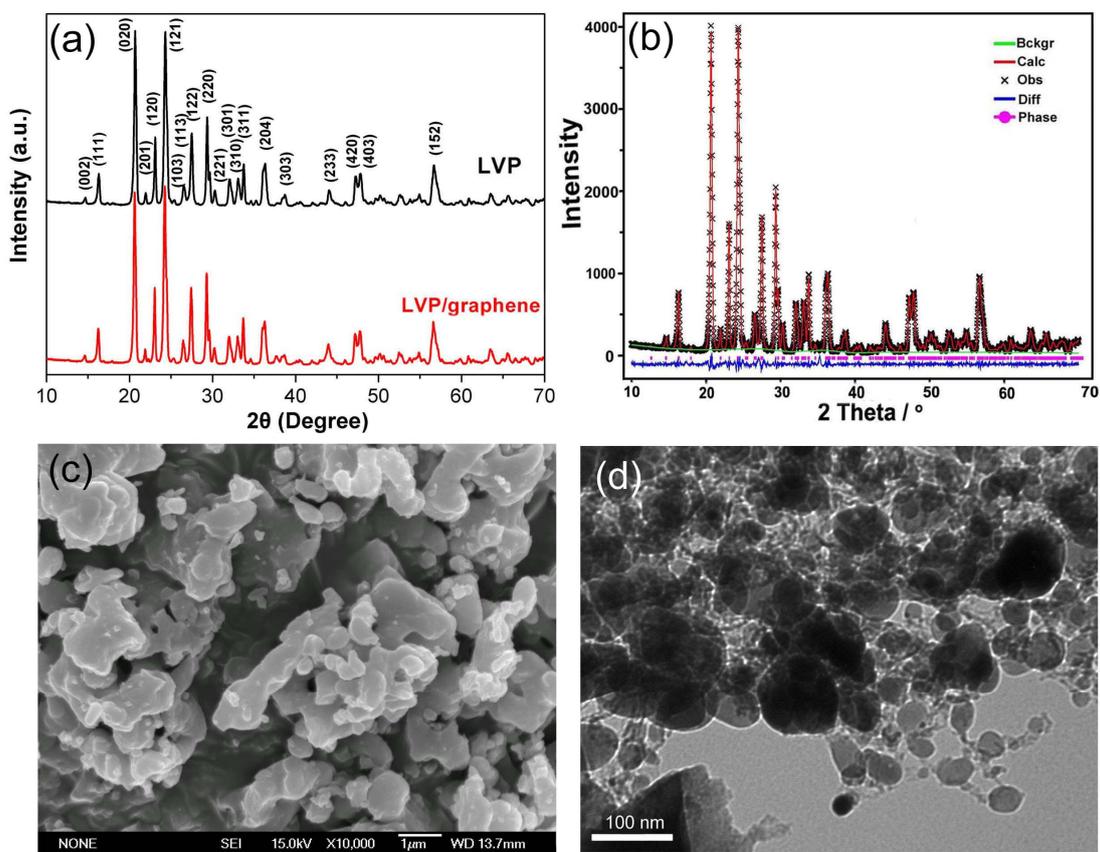


Figure S1. (a) XRD profiles of pure LVP and LVP/graphene nanocomposite. (b) Rietveld refinement of pure LVP. The observed and calculated intensity are indicated by crosses and red continuous lines respectively, the bottom blue line represents the fitting residual difference. (c) and (d) SEM and TEM image of pure LVP nanoparticles.

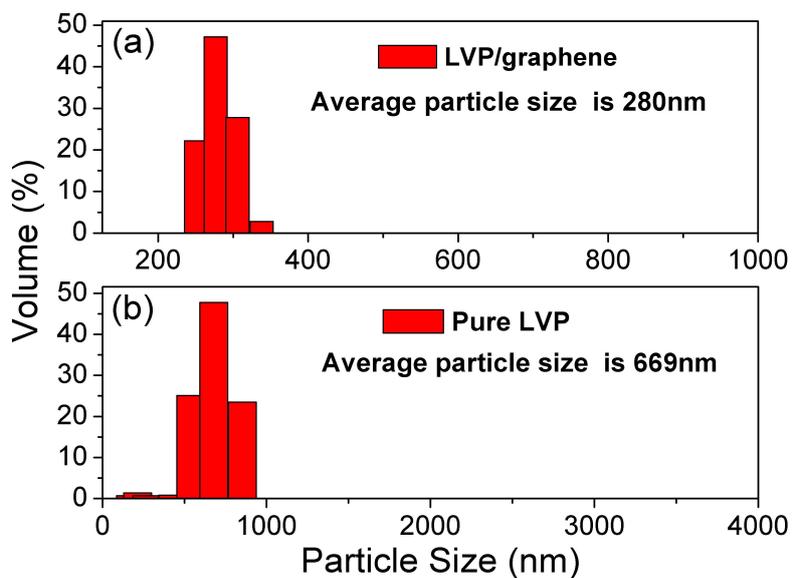


Figure S2. Particle size distributions of pure LVP and LVP/graphene materials.

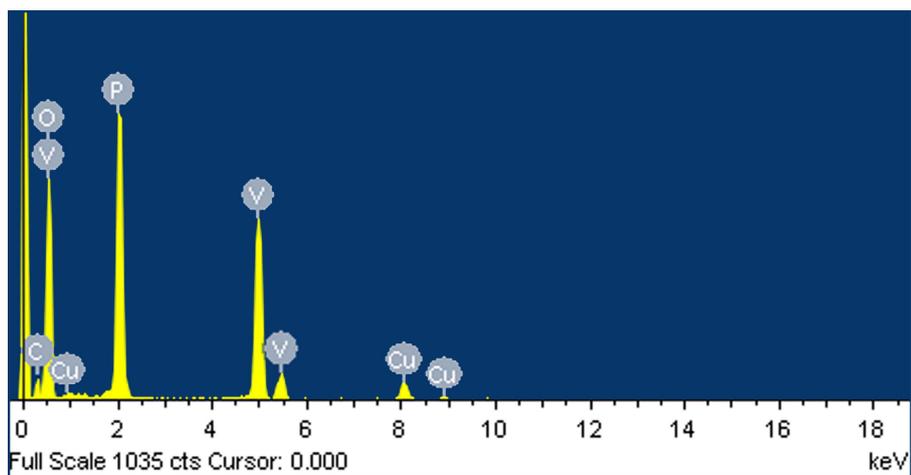


Figure S3. Energy dispersive X-ray spectrum of LVP/graphene.

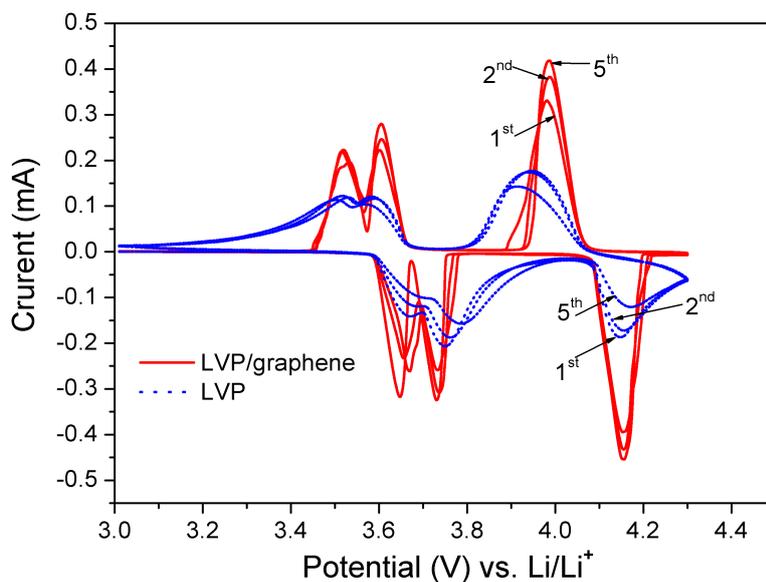


Figure S4. Cyclic voltammetry profiles of LVP/graphene nanocomposite (solid line) and pure LVP (dotted line) at a scanning rate of 0.1 mV/s between 3.0 and 4.3 V at room temperature.

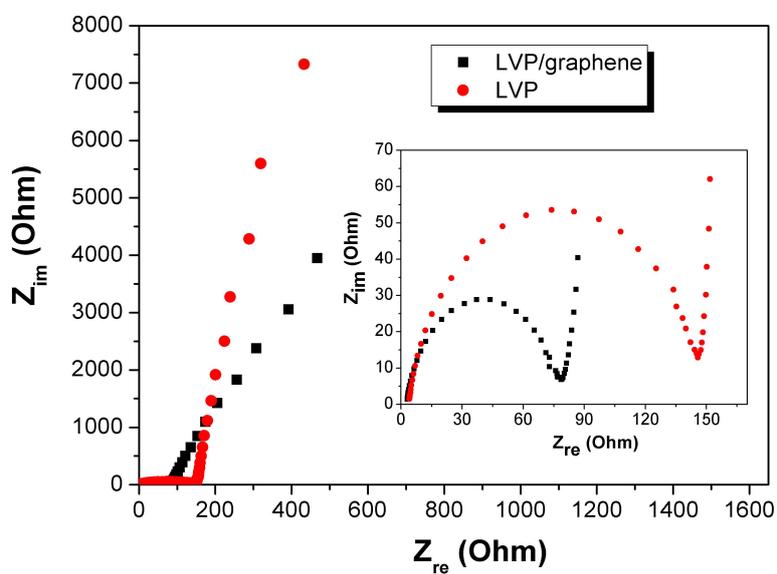


Figure S5. Nyquist plots of LVP/graphene hybrid and pure LVP electrode in freshly assembled test cells.

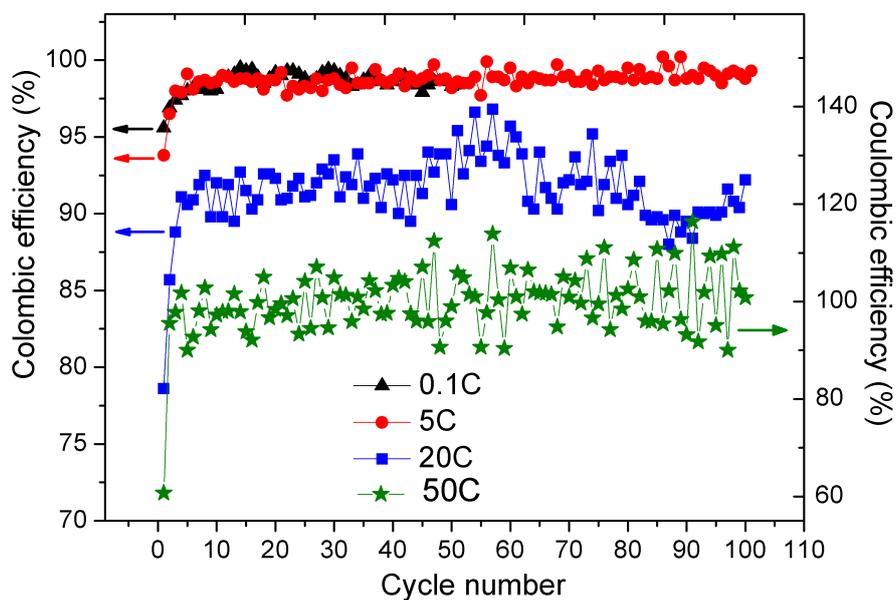


Figure S6. Coulombic efficiency of LVP/graphene at different discharge rates with constant charge at 0.1 C between the cut-off voltage 3 and 4.3V.