Electronic Supporting Information (ESI)

Li_3VO_4 Anchored on Graphene Nanosheets for Long-Life and High-Rate Lithium-Ion Batteries†

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Synthesis

Graphite oxide (GO) was prepared from natural graphite powders (universal grade, 99.985%) via a modified Hummers method. Dried GO was thermally exfoliated at 300 ºC for 3 min in air. The sample was then treated at 900 °C for 3 h in Ar at a heating rate of 2 ºC/min. The obtained product was denoted as GNS. V_2O_5 was first dissolved in a LiOH solution in deionized water and ethanol (3:1 v/v), into which GNS was added. And then, the mixture was sonicated for 10 min and stirred for 10 h. After deionized water and ethanol were evaporated, the black sediment was collected and treated at 40 °C for 24 h in a blast drying oven. The dried sediment composite was subsequently treated at 600 °C for 2 h. The obtained product was denoted as Li_3VO_4@GNS. Pristine Li_3VO_4 was prepared by the same method without adding GNS.

Characterization

Pristine Li_3VO_4 and Li_3VO_4@GNS were structurally characterized by XRD using a Rigaku diffractometer using Cu Kα radiation (1.5405 Å). The morphology characterization was investigated using a scanning electron microscope (SEM, LEO Gemini 1525) and a transmission electron microscope (TEM, JEOL 2100F) operated at 200 keV. Raman spectra were obtained on a Micro Raman Spectrophotometer. Carbon content result was obtained using a thermogravimetric analysis (TGA).

A slurry containing 90 wt.% of Li_3VO_4@GNS composite and 10 wt.% of polyvinylidenefluofide (PVdF) was cast on an Cu foil and dried in vacuum at 100 °C for 10 hours. The coin cells were assembled with Li metal as counter electrode with 1 M $LiPF_6$ in EC: DEC (1:1) as electrolyte in an argon-filled glove box. Electrochemical measurements were performed using a MTI battery cycler. For pristine Li_3VO_4, GNS (26 wt.%, the same content in Li_3VO_4@GNS) was added as conductive additive. The electrochemical characterization for the pristine Li_3VO_4 and Li_3VO_4@GNS samples were performed in the voltage range of 0.2–3V vs Li/Li^+. For the electrochemical impedance spectroscopy measurement, the amplitude of the AC signal was 5 mV and the frequencies were swept from 1 MHz to 10 mHz using a Bio-logic VMP3. Before cycling, the open-circuit voltages for the cells based on pristine Li_3VO_4 and Li_3VO_4@GNS were 3.00 and 2.82 V vs Li/Li^+, respectively. After the first cycle, the cells were left rest for 30 min prior to the EIS measurements.

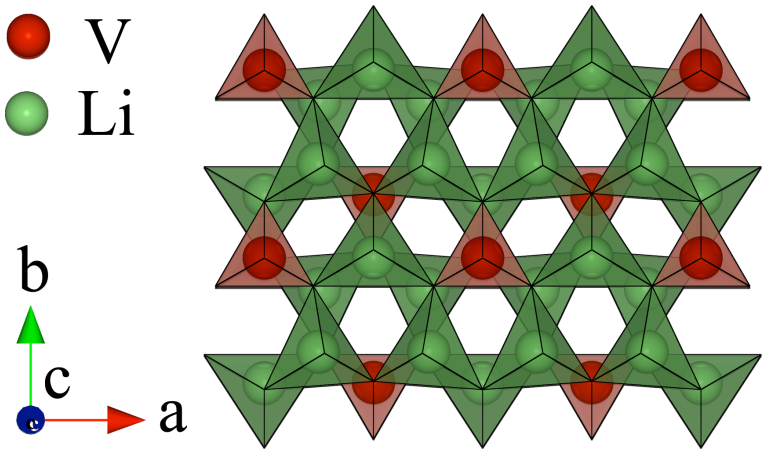

Figure S1 Schematic structure diagram of Li_3VO_4.

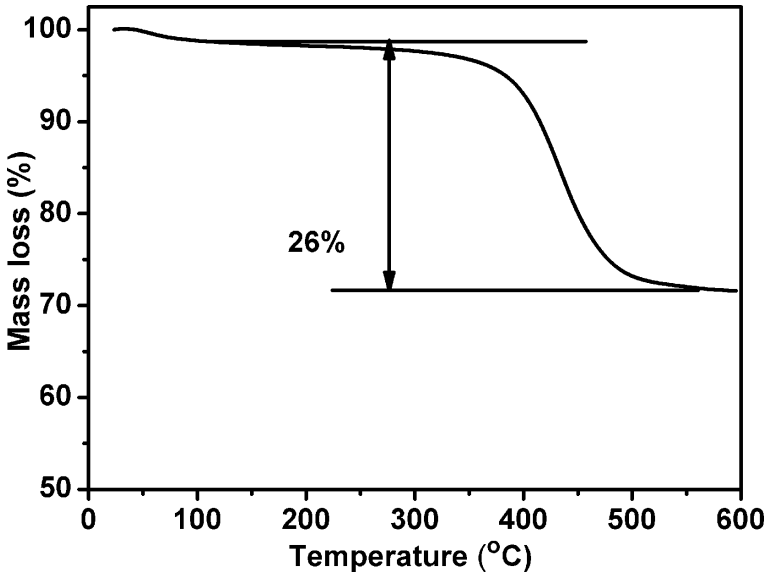

Figure S2 TGA curves of Li_3VO_4@GNS in air.

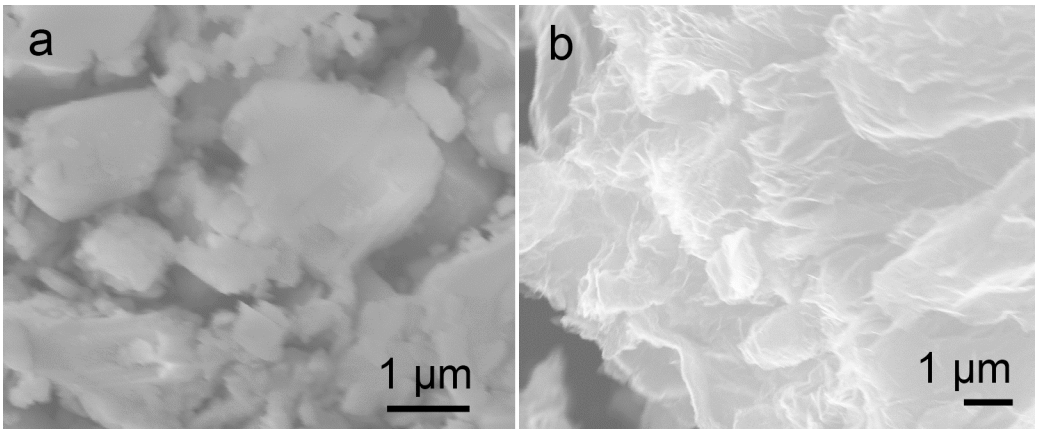

Figure S3 SEM images of the (a) pristine Li_3VO_4 and (b) Li_3VO_4@GNS composite.

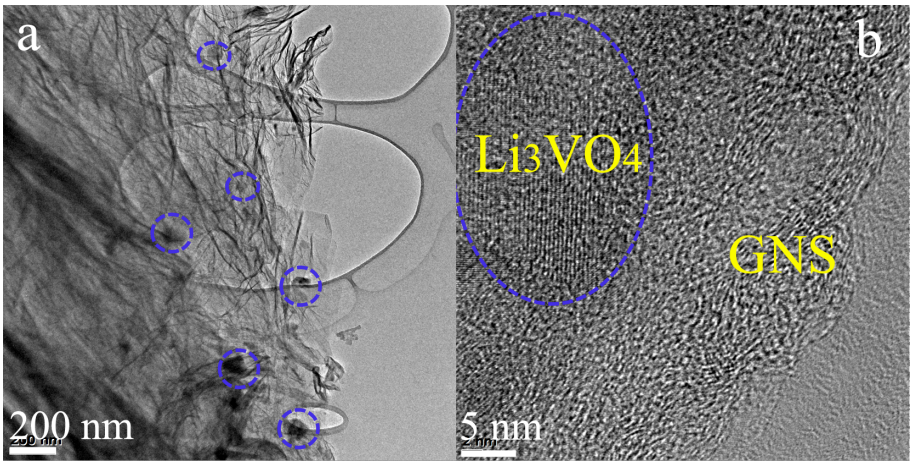

Figure S4 TEM images of the Li_3VO_4@GNS composite revealing smaller Li_3VO_4 particles with size around 10-30 nm.

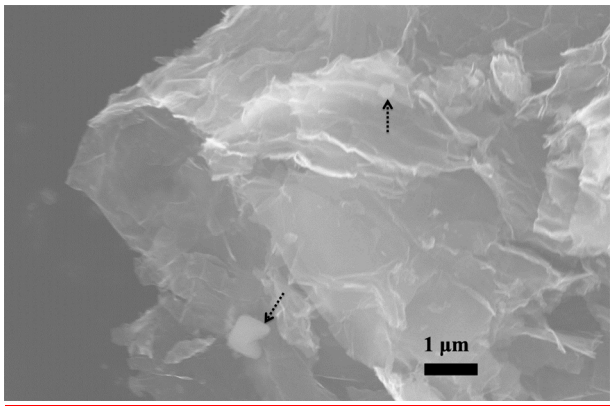

Figure S5 SEM image of the Li_3VO_4@GNS composite revealing larger Li_3VO_4 particles with size around 500 nm.

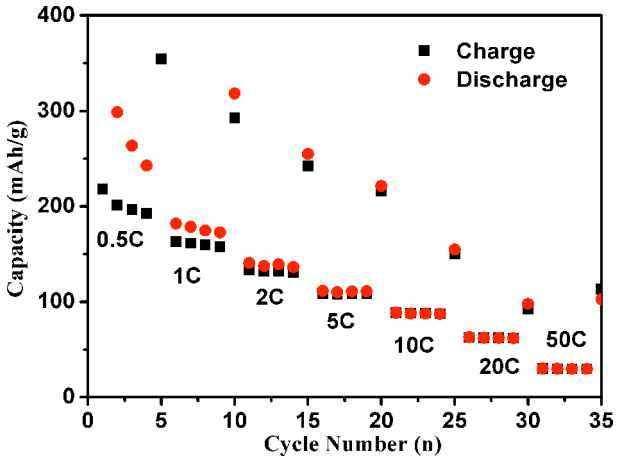

Figure S6 Discharge and charge capacities of the pristine Li_3VO_4 and Li_3VO_4@GNS composite at different C-rates. The C rates indicate the same current used for measuring Li_3VO_4/GNS at the same rate. The capacities of graphene nanosheets are measured to be ~200 mAh/g at 0.5 C and ~100 mAh/g at 5C. When we consider the GNS content (26 wt.%) in the Li_3VO_4@GNS composite, GNS contributes capacities of ~ 50 mAh/g at 0.5 C and 25 mAh/g at 5C. At a high rate of 50C, its contribution is only 8 mAh/g. Therefore, the majority of capacity (~90%) of the Li_3VO_4@GNS composite comes from Li_3VO_4.

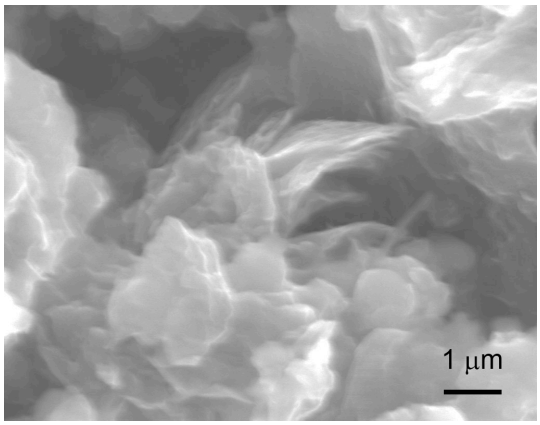

Figure S7 SEM image of the Li_3VO_4@GNS composite after 500 cycles at 5C rate. The composite has retained the original morphology as shown in Figure S3b, demonstrating excellent structure stability of this composite materials.