

In situ synthesis of LiV₃O₈ nanorods on graphene as high Rate-Performance cathode materials for rechargeable lithium batteries

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Experimental Section

Synthesis of graphene oxide (GO)

GO was prepared from graphite flakes by a modified Hummersmethod.^{1,2} 1.0 g of graphite flakes, 1.0 g of NaNO₃ and 46 mL of concentrated H₂SO₄ were mixed together in an ice bath for 4 h. Then 6.0 g of KMnO₄ was added slowly into the solution. Afterwards, the ice bath was removed and the suspension was stirred for another 4 days. Then the suspension was further treated with 200 mL of warm water (~60 °C) and 10 mL of H₂O₂ (30%). The mixture was centrifuged at 4000 rpm and washed with diluted HCl and water to neutral. Finally, a homogeneous GO aqueous dispersion (1 mg mL⁻¹) was obtained for further use.

Synthesis of G-LVO NRs composites

The composites of LiV₃O₈ nanorods on rmGO were synthesized simply by two-step solution-phase reaction. In the first step of synthesis, 160 mg of V₂O₅ and oxalic acid 240 mg were dissolved into 30 mL of 1 mg mL⁻¹ GO aqueous dispersion and was vigorously stirred for 1 h. After that, the as-made composite was collected by centrifuge. In the second step of synthesis, the as-made composite from the first step of synthesis was dispersed in 30 ml of aqueous, to which a stoichiometric amount of LiOH aqueous solution(260 mg LiOH·H₂O) was added. The mixture was then sealed in a 40 ml Teflon lined stainless steel autoclave for hydrothermal reaction at 160 °C for 12 hours. The resulted product was washed with water and then centrifuged at 5000 g for 1 min, which was repeated for 6 times to remove side products. Pure LiV₃O₈ nanorods were also prepared by the similar procedure without any GNs.

Material Characterizations

The resulting sample was characterized by means of X-ray diffraction (XRD, Rigaku D/max- γ B) with monochromated Cu K α radiation at a scanning rate of 2° min⁻¹ in the range of 10-50°. morphology of products was characterized by scanning electron microscopy (SEM, Hitachi S4800) and high resolution transmission electron microscopy (HRTEM, JEM-2100) with an accelerating voltage of 200 KV. TG analysis was carried out with a TG/DTA6200 instrument. Additionally, Raman spectra were recorded at room temperature by employing an InVia Raman spectrometer using 633 nm red laser with 10% intensity to determine the extent of graphitic disorder.

Electrochemical measurements

The LiV₃O₈/rmGO active material powder (~120mg) was annealed at 450°C in Ar for 1h and mixed with Super P carbon black and polyvinylidifluoride (PVDF, Kynar HSV 900), with weight ratio of 80:10:10, in N-Methylpyrrolidone (NMP) solvent to produce an electrode slurry. The mass of active materials was calculated at ca.3.8 mg and integrated into two-electrode CR2025-type coin cells for electrochemical measurements, with G-LVO NRs composite electrode as cathode, metallic lithium foil as anode, two porous polypropylene films as separator; electrolyte was 1.0 M LiPF₆ dissolved in ethylene carbonate (EC) and dimethyl carbonate (DMC) and diethyl carbonate (DEC) at a volumetric ratio of 1:1:1. The discharge-charge tests were conducted at various rates within a voltage window from 1.5 V to 4.0 V (vs. Li⁺/Li) on the BTS battery testing system (Neware, Shenzhen, China). Electrical impedance spectroscopy (EIS) experiments were carried out on a Parstat 2273 advanced electrochemical systems in the frequency range mainly from 100 kHz to 10 mHz with the a.c. signal amplitude of 5 mV.

	R_s (Ω)	R_f (Ω)	R_{ct} (Ω)
LVO NRs	7	94	33
G-LVO NRs	5	32	24

Table S1. Impedance parameters calculated from equivalent circuit

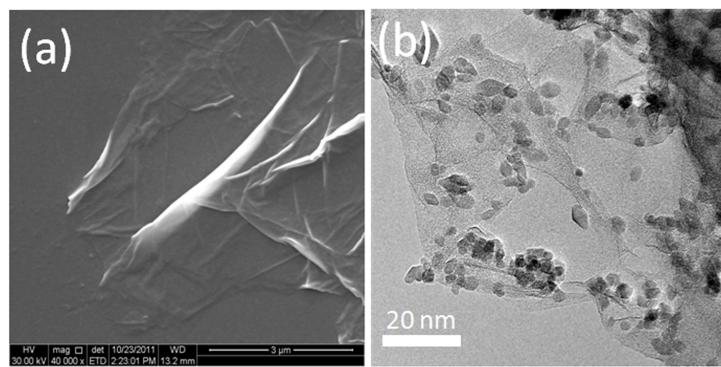


Figure S1. (a) SEM image of GO. (b) TEM images of vandyl oxalate hydrate nanoparticles on GO.

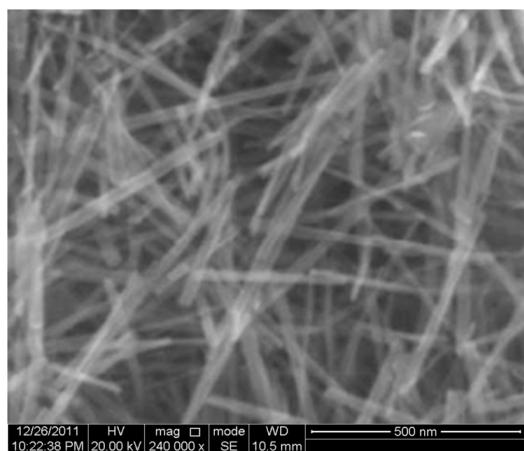


Figure S2. SEM images of LiV_3O_8 nanorods synthesized without the addition of GO.

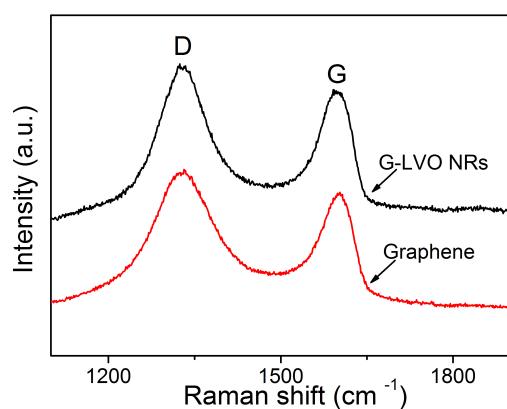


Figure S3. Raman spectra of Graphene and G-LVO NRs in the wave length range of 1100-2000 cm⁻¹.

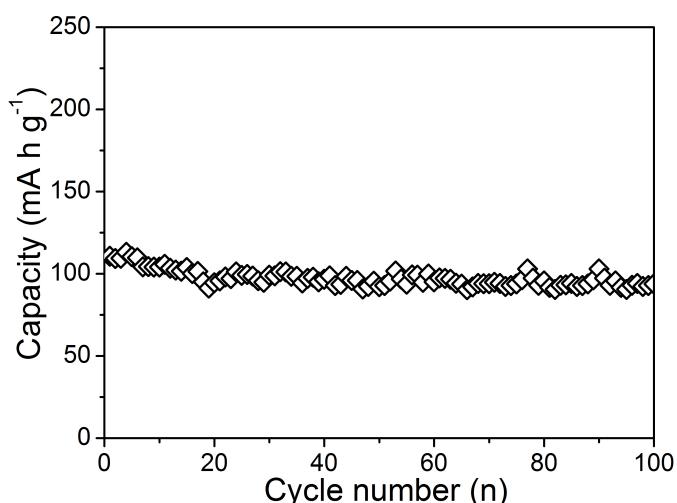


Figure S4. Cycling stability of G-LVO NRs cathode at 1500 mA g⁻¹ at room temperature.

Reference

- 1 Y. Chen, X. Zhang, P. Yu and Y. W. Ma, *Chem. Commun.*, 2009, 4527.
- 2 C. H. Xu, J. Sun and L. Gao, *J. Mater. Chem.*, 2011, **21**, 11253.