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Ultrathin Li_3VO_4 Nanoribbon/Graphene Sandwich-Like Nanostructures with Ultrahigh Lithium ion Storage Properties

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Abstract: Two-dimensional (2D) "graphene-like" inorganic materials, because of the short lithium ion diffusion path and unique 2D carrier pathways, become a new research focus of the lithium storages. Some "graphene-like" binary compounds, such as, MnO_2 , MoS_2 and VO_2 ultrathin nanosheets, have been synthesized by a peeling method, which also exhibit enhanced lithium storage performances. However, it still remains a great challenge to synthesize widely-used lithium-containing ternary oxides with "graphene-like" nanostructures, because the lithium-containing ternary oxides, unlike ternary layered double hydroxides (LDH), are very hard to be directly peeled. Herein, we successfully synthesized ultrathin Li_3VO_4 nanoribbons with a thickness of about 3 nm by transformation from ultrathin $\text{V}_2\text{O}_5 \cdot x\text{H}_2\text{O}$ nanoribbons, moreover, we achieved the preparation of ultrathin Li_3VO_4 nanoribbon@graphene sandwich-like nanostructures (LVO/G) through a layer-by-layer

assembly method. The unique sandwich-like nanostructures shows not only a high specific reversible capacitance (up to $452.5 \text{ mA h}\cdot\text{g}^{-1}$ after 200 cycles) but also an excellent cycling performance (with more than $299.2 \text{ mA h}\cdot\text{g}^{-1}$ of the capacity at 10 C after 1000 cycles) as well as very high rate capability. Such template strategy, using "graphene-like" binary inorganic nanosheets as templates to synthesize lithium-containing ternary oxide nanosheets, may be extended to prepare other ternary oxides with "graphene-like" nanostructures.

1. Introduction

Two-dimensional (2D) "graphene-like" nanosheets or nanoribbons, especially those with a thickness of $<5 \text{ nm}$ and lateral dimension of submicron to micrometers, can be considered as a new class of inorganic macromolecules with exotic electronic properties and high specific surface areas that are important for sensing [1], catalysis [2], and energy storage applications [3-9]. In particular, 2D "graphene-like" nanosheets are ideal structures for fast lithium storage, which provide short lithium ion diffusion paths, two-dimensional carrier pathways, high active surface areas and good resistance to volume expansion capacity compared with bulk materials [6]. Recently, investigations of graphene, a 2D "aromatic" monolayer of carbon atoms, have demonstrated exceptional physical properties, including ultrahigh electron mobility [10], ballistic charge carrier transport [11], and other properties [12]. These studies have triggered wide interest in 2D "graphene-like" nanosheets other than carbon, such as BN [13], MoS_2 [14], VO_2 [15], and MnO_2 [16] nanosheets or nanoribbons. Unfortunately, in most cases, the above nanosheets have been generated from delamination of their materials with layered structures, and thus the product yields are extremely low owing to the limitations of the fabrication method adopted. This constitutes a major obstacle for exploiting other materials, especially the materials without layer crystal structures. Compared to the binary inorganic materials, lithium-containing ternary oxides (such as, LiCoO_2 , $\text{Li}_4\text{Ti}_5\text{O}_{12}$, Li_3VO_4 , LiV_3O_8 , etc.) are widely used in practice as active electrode materials for lithium ion batteries.

However, unlike ternary layered double hydroxides (LDH), the lithium-containing ternary oxides are very hard to be directly peeled. Therefore, it still remains a great challenge to synthesize lithium-containing ternary oxides with "graphene-like" structures, especially, the lithium-containing ternary oxides without layered crystal structures, such as, β - Li_3VO_4 with orthorhombic structure.

There are three main anode materials: the alloy-type anodes materials such as Si and Sn based alloys and their composites [17], the conversion reaction type ones such as transition metal oxides [18, 19], and the intercalation/deintercalation type one such as graphite, Ti-based oxides [20, 21], layered V-based oxides [22, 23], and Mo-based oxides [24, 25]. Although work on the alternatives to intercalation type anode materials has made important progress, graphite still remains the dominant commercial anode material. However, graphite has a small lithium diffusion coefficient and experiences a large volume variation of 9% during the lithium intercalation/deintercalation process. In addition, it has severe safety issues of dendritic lithium growth, due to its low potential (only about 0.2 V versus Li^+/Li). Especially at high rates, polarization would considerably lower its potential further, causing the birth of lithium dendrites and the consequent safety issues. Furthermore, the thick solid electrolyte interphase (SEI) layer on its surface could also introduce kinetic problems for fast charge and discharge.[26] $\text{Li}_4\text{Ti}_5\text{O}_{12}$ has been found to change its structure negligibly during the discharge/charge process and possesses good lithium ion mobility, a long and stable voltage plateau, together with low cost, environmental friendliness, and enhanced safety.[26-28] Nevertheless, its potential is still relatively higher, about 1.6 V (versus Li^+/Li), thus halving the overall cell voltage and negating the benefits. The estimated energy density of lithium ion batteries based on the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ anode (regarding both potential and capacity) does not exceed one third of that on graphite if they are coupled with a typical 4 V cathode.[21] It was recently reported that Li^+ can be intercalated into the layered transition metal oxide LiVO_2 , [22] but its major difficulty for application as an anode lies in the fast deterioration of the material.[29-

31] So, it would be of great interest to find a new intercalation anode with large capacity and appropriate intercalation potential.[19] Li_3VO_4 have been studied as attractive optic materials and ionic conduction materials for many years, however, its properties as a major electrode active material for lithium batteries have not been broadly investigated up to now.[32] Li_3VO_4 is reported to have several polymorphs in which the β form is stable in low temperature (LT) and the γ form is generally stable in high temperature (HT). Scheme.1 gives the schematic structure of $\beta\text{-Li}_3\text{VO}_4$. It is built up of oxygen atoms in approximately hexagonal close packing; the cations occupy ordered tetrahedral sites. All the tetrahedra point towards the up orientation along the c axis and connect with each other by corner-sharing only. [33] In the structure, Li^+ ions occupy two different tetrahedral sites, V^{5+} ions occupy a third tetrahedral site, there are still many empty cationic sites which might be capable of further insertion of Li^+ ions.[32, 33]

Recently, it was reported that Li_3VO_4^+ intercalates Li ions mainly in the voltage range between 0.5 and 1.0 V vs Li/Li^+ , lower than the potential of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and higher than that of graphite. Its theoretical capacity is 400 mA h g^{-1} , in accordance with $x = 2$ in $\text{Li}_{3+x}\text{VO}_4$. [34] Combined with the low and safe voltage, Li_3VO_4 features a large specific capacity and low cost. It might act as a new intercalation anode for the lithium ion battery. Despite these advantages, the practical use of this material still faces some barriers. Li_3VO_4 requires further modifications to overcome certain limitations, such as low electronic conductivity, which is quite lower than its ionic conductivity, and this may cause large resistance polarization and poor rate capability. Thus, reducing the particle size and hybridization with electronically conductive materials are necessary for this material to be suitable for future use. On the one hand, so as to enhance electronic conductivity of electrodes, hybridization with carbon materials is a practical and effective way.

Nanocomposites such as metal oxides-carbon, sulfide-carbon (graphene/CNTs/carbon), etc, are intensively studied for lithium ion batteries recently. In this regard,

SnO_2 @Carbon,[35] Sn-Co-CNT @ CNT,[36] Si/graphene,[37] Si@CNT,[38]
 SnO_2 /graphene,[39] LiFePO_4 @ CNT[40], TiO_2 /graphene,[41] Graphene/CNT @Porous
 Carbon-S[42] and Co_3O_4 /graphene[43] hybrids or composites, in which sulfur or metal oxides
 are distributed onto the surface of graphene or between the graphene layers, have been
 fabricated by restacking CNT or graphene sheets in the presence of guest nanoparticles or
 corresponding organometallic precursors. In particular, graphene, a new two-dimensional
 carbon material, exhibits superior electrical conductivity, large surface area, structural
 flexibility, and chemical stability, is greatly pursued by chemists and material scientists since
 it was proposed. [11, 12] On the other hand, reducing the particle size and synthesizing
 materials with particular morphology is also a practical method to improve the
 electrochemical performance. The properties of inorganic ultrathin structures can be well
 tuned by tailoring their morphology and crystalline.[4-9] So far, Scholars have paid much
 attention to the research of ultrathin two-dimensional materials and many achievements have
 been made in the synthesis of binary compound such as BN, TiO_2 , MoS_2 , VO_2 , MnO_2 , CoO ,
 VS_2 , TiS_2 , ect. Depending on the combination of chalcogen (typically O, Se, or Te) and
 transition metal (typically Co, Mo, W, Nb, Re, Ni, or V),^[1, 13-16, 44, 45] transition metal
 dichalcogenides occur in more than 40 different categories which are being studied or have
 been successfully prepared. However, the ternary compounds such as La_2CuO_4 ,[46]
 VOPO_4 [47] with ultrathin layered structure are rarely reported. Therefore, it is still a great
 challenge to develop feasible methods for synthesis of ternary compound nanosheets with
 well-defined ultrathin morphologies, especially, the lithium-containing ternary oxides (such as,
 LiCoO_2 , $\text{Li}_4\text{Ti}_5\text{O}_{12}$, Li_3VO_4 , LiV_3O_8 , etc.) which are widely used as electrode materials for
 lithium ion batteries. Here, we initially report a facile method to prepare a ternary compound
 of ultrathin Li_3VO_4 nanoribbons with a thickness of about 3 nm. Meanwhile, we achieved the
 preparation of ultrathin Li_3VO_4 nanoribbon @ graphene nanosheets nanocomposite (LVO/G)
 through a layer-by-layer assembly method. When the LVO/G nanocomposite is used as anode

material for lithium ion batteries, it offers excellent performances in capacity, rate capability, and cycling life compared to the reported vanadium based anode materials.[30] The present template strategy, which involves using inorganic nanosheets without containing lithium as templates to synthesize lithium-containing ternary oxide nanosheets, is facile but effective. It may be extended to prepare other lithium-containing ternary oxides with ultrathin nanosheet structures to enhance their lithium storage performances.

2. Experimental section

Preparation of graphene: Firstly, GO solution was made using a modified Hummers' method.[76, 77] Briefly, 1 g of raw graphite powder (SP-1), 0.5 g of $K_2S_2O_8$, and 0.5 g of P_2O_5 were stirred in 3 mL of H_2SO_4 at $80^\circ C$ for 4.5 h and copiously washed and dried in air overnight. Then 3 g of $KMnO_4$ was slowly added to the graphite powder solution with 23 mL of H_2SO_4 at $0^\circ C$. After vigorous stirring at $36^\circ C$ for 2 h, 46 mL of deionized water (DI water, $R \approx 18.2$ M) was added at $0^\circ C$ and the solution was stirred at $36^\circ C$ for additional 2h. The oxidation step was completed by the addition of 140 mL of DI water and 2.5 mL of H_2O_2 solution (35%). The GO solution (brown color) was washed, and filtrated with 250 mL of HCl (10 %). Before complete drying, the GO was dispersed in DI water (10 mg/mL) and dialyzed for 2 weeks, from which pH values attained ≈ 4 to 6. Secondly, 1g of Fe powder (average particle size: $1\mu m$, Shanghai CNPC Qifa Powder Material Co., Ltd.) and 20 mL of HCl (35 wt %) were directly added into 100 mL of GO (5mg/ml) suspension at ambient temperature. The mixture was stirred for 30 min and then maintained for a period of time. After reduction, 15 mL of HCl (35 wt %) was added into the above solution in order to fully remove excess Fe powder. Then, the resulting GNS was collected with filtration, washed with pure water and ethanol several times. Next, we disperse the GNS in aqueous solution of ethanol (the volume ratio of ethanol and water $\approx 3:1$) with ultrasonication for 30 minutes to prepare a uniform

dispersion of GNS (2mg/ml) for use. Finally, GNS nanosheets were modified by surface grafting of aminopropyltrimeth-oxysilane (APS) to render the oxide surface positively charged. More specifically, 30ml aqueous solution containing 2% (wt) APS (1.2 mg) were added into 30mL Graphene dispersions (2mg/ml) with a vigorous stirring for 30min.

Synthesis of ultrathin Li_3VO_4 nanoribbons precursor: Firstly, the precursor of ultrathin V_2O_5 nanoribbons were prepared as the following process: In a typical procedure, 0.364 g of V_2O_5 powder and 35 mL of de-ionized water were mixed under strong magnetic stirring, after that, 5 mL 35% H_2O_2 was added dropwise into the solution with continuous stirring. After 30 min, the mixture was poured into a 50 mL Teflon-lined autoclave at 180°C for 12 hours. Secondly, 0.8556g of LiNO_3 (Li: V in a stoichiometric ratio of 3.1: 1) were dissolved in actively stirred de-ionized water at room temperature until a clear solution was formed. Then, the LiNO_3 (aq) was added drop-by-drop into the sol-gel of V_2O_5 , and the mixture was vigorously stirred for 30 minutes.

Synthesis of graphene-based ultrathin Li_3VO_4 nanocomposites: 30 mL dispersion of APS modified GNS (2mg/mL) were added dropwise into the mixture solution above with a continuous stirring, and the resulting solution was heated overnight in an oven at 90°C for 12h to produce the dry solid material. The as-obtained material was loaded in central heating zone of a quartz tube in the furnace and calcined at 550°C in Ar/400 sccm for 2h. Once the annealing time was out, it was suddenly cooled by taking off the lid of the furnace and the sample obtained were designated LVO/G, with a comparison, the bare Li_3VO_4 ultrathin nanoribbon were prepared as the methods mentioned above and the sample obtained was designated LVO.

Characterization: Powder X-ray diffraction (XRD) measurements were collected from 10° to 80° (2θ) with a scanning step of 4° using Cu-K_α ($\lambda = 1.54178 \text{ \AA}$) incident radiation (40 kV, 50 mA) by a Rigaku D/max2500 XRD instrument. Raman spectrometers (LabRAM

Hr800) were used to obtain the structure information as well. The general size and morphology of the nanocomposites were characterized by a field-emission scanning electron microscope (FESEM, FEI Nova NanoSEM 230) and atomic force microscope (AFM, Picoplus). Transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM) and selected area electron diffraction (SAED) were carried on a JEOL-JEM-2100F transmission electron microscope (TEM) operating at a 200 kV accelerating voltage. Field emission scanning electron microscopy (FE-SEM) and energy dispersive spectroscopy (EDS) element mapping images were taken on FEI Nova NanoSEM 230 unit. Thermogravimetric analyses (TGA, Q500) were carried out in the temperature range of 30 to 800 °C under an air flow with a heating rate of 10 °C · min⁻¹.

Electrochemical measurements: The electrochemical tests were carried out via CR2032 coin type cells. The working electrodes were prepared by mixing the LVO/GNS nanocomposite, carbon black (Super P, MMM, Belgium), and poly (vinyl difluoride) (PVDF) at a weight ratio of 7:2:1. The resultant slurry was pasted on Cu foil and the electrodes were dried in a vacuum oven at 120 °C for 10 h. Coin cells were assembled in an argon-filled glove box (Mbraun, Unilab, Germany) by stacking a porous polypropylene separator containing liquid electrolyte between the LVO/G electrode and a lithium foil counter electrode. The electrolyte consisted of a solution of 1 M LiPF₆ in ethylene carbonate (EC)/dimethyl carbonate (DMC) (1:1, by volume). Cyclic voltammetry (CV) was tested on an electrochemical workstation (CHI604E, China) at a scan rate of 0.5 mV s⁻¹ in the voltage range of 0.2-3 V (vs. Li/Li⁺) and electrochemical impedance spectroscopy measurements were conducted on ZAHNER-IM6ex electrochemcial working station (Germany) in the frequency range of 100 kHz to 10 mHz on a cell in as-assembled condition. The discharge and charge measurements were conducted on an Arbin BT2000 tester with a cut off voltage of

0.2-3.0 V versus Li/Li⁺. The specific capacity for the LVO/G nanocomposites is calculated based on the total weight including Li₃VO₄ nanoribbon and graphene.

3. Results and discussion

In our work, the route we used to prepare LVO/G nano-composites was shown in scheme.2. There are main four steps to achieve the LVO/G nanocomposites: The synthesis of ultrathin V₂O₅·xH₂O nanoribbons; the synthesis of ultrathin Li₃VO₄ nanoribbons precursor; the preparation of graphene; preparation of graphene-based ultrathin Li₃VO₄ nanocomposite.

The specific procedures were introduced in the experiment section. The expected structure of the final LVO/G nanocomposites was schematically shown in scheme.2, which is stacked by the Li₃VO₄ nanoribbons and graphene alternatively through a layer-by-layer method. In this part, we used different characterization methods to confirm our expectation and the excellent performance of LVO/G as an anode material.

Raman spectroscopy was used to further investigate the structural features of the ultrathin Li₃VO₄ nanoribbon@GNS nanocomposites. The peak at 1358 cm⁻¹ (D band) is assigned to defects and disorder in the GNS. The distinctive peak at 1589 cm⁻¹ (G band) is related to the coplanar vibration of sp² bonded carbon atoms in GNS. The peak intensity ratio between the 1358 and 1589 cm⁻¹ peaks (I_D/I_G) generally provides a useful index about the degree of crystallinity of various carbon materials, that is, the smaller the I_D/I_G ratio, the higher the degree of ordering in the carbon material.[48] The intensity ratio I_D/I_G of ~1.2 indicates the size of the graphitic carbon (L_a) is about 5.3 nm according to the empirical equation L_a = 4.4 I_D/I_G (nm).[49] These results indicate that the carbon matrix is partially graphitized, which could benefit the electron transportation from/to the poorly conducting Li₃VO₄. The 2D band (2708 cm⁻¹) is the most prominent feature in the Raman spectrum of GNS in the ultrathin Li₃VO₄ nanoribbon@GNS nanocomposites, and its position and shape

are sensitive to the number of layers of graphene. The single, symmetrical 2D band exhibited at 2708 cm^{-1} corresponds to the graphene with a few layers. Bands associating with the stretching and bending vibration of VO_4^{3-} anions have been found to be active in Raman region. The band appearing at about 818 cm^{-1} can be attributed to symmetric stretching of (VO_4^{3-}), whereas the band at around 787 cm^{-1} can be attributed to asymmetric stretching of (VO_4^{3-}). Vibration of VO_4 tetrahedra that corresponds to a bending model has been observed at 324 cm^{-1} . [50, 51]

A combined differential scanning calorimetry (DSC)/TGA instrument (Mettler-Toledo, TGA/DSC STAR system) was used to study the decomposition and reaction of the precursors under flowing air with a temperature ramping rate of $5^\circ\text{C}/\text{min}$. The plot shows four main gradual weight-loss waves due to the release of adsorbed and chemically bound intercalated water molecules and the combustion of GNS in air and the decomposition of LiNO_3 and the volatilization of lithium. The first weight-loss between 30°C and 350°C shown in Fig. 2 can be attributed to the loss of physically and chemically bonded water, along with a large endothermic peak. The second wave of weight loss attributed to the combustion of graphene nanosheet extends to around 500°C , the weight of which may reached 10% or so in the nanocomposite, during this process, the exothermic peak of graphene combustion didn't appear owing to the amount of absorbed heat is greater than that of the heat release. The significant weight loss shown on the TG curve and the corresponding endothermic peak on the DTA curve between 500°C and 550°C are related to the pyrolysis of LiNO_3 , the weight loss resulted from the release of NO_2 which reached 22.02%. A weight loss happened around 600°C , corresponding to the volatilization of lithium under high synthetic temperature, only a little amount of lithium volatiled which reached 0.22% of the whole nanocomposites.

X-ray diffraction (XRD) patterns for the Li_3VO_4 ultrathin nanoribbon and the LVO/G nanocomposite (Fig.3) show that most diffraction lines can be indexed to the orthorhombic

Li₃VO₄ phase (JCPDS No. 38-1247) with the lattice parameters $a = 5.447 \text{ \AA}$, $b = 6.327 \text{ \AA}$, $c = 4.948 \text{ \AA}$, and $\alpha = \beta = \gamma = 90^\circ$. All peaks are sharp, suggesting that the sample is well-crystallized. From the X-ray diffraction spectrum, we can see that a small intensity peak of LiVO₃ (JCPDS NO.25-1100) appears in the Li₃VO₄ ultrathin nanoribbon and the LVO/G nanocomposite which was also reported in the other methods of preparation.[52, 53] But the intensity of LiVO₃ diffraction peak is very weak which shows that the amount of LiVO₃ is very small and moreover, it is an intercalation material which has a very small effect on the performance of a Li₃VO₄ electrode.[54] Meanwhile, we can see that the intensity of LiVO₃ diffraction peak in the LVO/G nanocomposite is weaker than that in the bare Li₃VO₄ nanoribbon which illustrates the addition of GNS can inhibit the growth of LiVO₃. In the X-ray diffraction spectrum of pure Li₃VO₄ nanoribbon, we find a little intensity peak of Li_{0.3}V₂O₅ but which disappeared in the LVO/G nanocomposite, which further proves that the graphite oxide in the nanocomposites can effectively suppress the generation of impure phase. As to the reasons, we sustain that it may relate to the interaction between Li₃VO₄ nanoribbon and graphene oxide nanosheet. For the Li₃VO₄ and the LVO/G nanocomposite, the intensity of (110) peak is stronger than that of the standards powder diffraction peaks of Li₃VO₄ which indicates the anisotropic growth of the nanostructure as well as the preferred orientation of the Li₃VO₄ nanoribbon on the substrate, i.e (110) plane of Li₃VO₄ is highly preferred. Diffraction peaks which might appear for graphene are absent, most likely because they are below the limits of detection by XRD, or the graphene (002) peak is eclipsed by the Li₃VO₄ (111) one. Another reason is that the layers of graphene nanosheets are too few, about 6 as the above-mentioned, and their diffraction intensity is very weak.

The morphology of LVO/G nanocomposite is characterized by field-emission scanning electron microscope (FESEM) and transmission electron microscope (TEM) as shown in Fig 4. The magnified FESEM image further reveals the detailed morphology of the LVO/G nanocomposite, which is composed of nanoribbons with different sizes (Fig 4a), moreover,

we can see that each nanoribbon is made of thinner layers, and the surface of the nanoribbons is very smooth.

In order to further characterized the specific nanostructure, we choose a side view of LVO/G nanoribbon as shown in Figure 4b, we can see that LVO/G nanocomposite is composed of Li_3VO_4 and GNS ultrathin layers which stacked layer-by-layer alternatively, but it does not clearly show any graphene sheets due to the penetration of electrons through the thin sheets, but the edges of some sheets can be distinguished because they are wrinkled. Meanwhile, we can see that there was plenty of interspace existing in the nanocomposite which can help the electrolyte make adequate contact with the LVO/G nanocomposite, which is expected to offer rapid routes for both Li^+ ion and electron transportation. Another indication of the presence of graphene nanosheets is the different contrast compared to Fig 4c. From the cross sectional view, it is easy to see the interstratified structure formed by graphene sheets where Li_3VO_4 nanoribbon are sandwiched between the sheets. This sandwich morphology ensures good contact between Li_3VO_4 and conductive graphene sheets, so that the graphene network can act as an electron pathway and the nanostructured Li_3VO_4 network acts as the Li^+ host during electrochemical cycling. With a higher magnified image in Fig 4c, we can see that the Li_3VO_4 nanoribbon structure consist of quantities of ultrathin Li_3VO_4 nanobelts, such a hierarchical structure gives rise to a relatively high surface area which is beneficial to the Li^+ storage capacity.

TEM analysis was used to study the morphology of the LVO/G nanocomposite which indicates that the sample comprises of Li_3VO_4 nanoribbon and graphene nanosheets. The representative image in Figure 4d clearly shows that graphene nanosheet exfoliates to form thin sheets with typical lateral dimensions of several micrometers. Wrinkles in the sheets manifest the flexibility of the GNS sheets. Any sp^3 hybridized carbon atoms present introduce defects into the 2D planes,[55] which could also contribute to the wrinkled morphology. On the wrinkeld graphene, a mass of ultrathin Li_3VO_4 nanoribbons distributed disorderly, which

is almost completely transparent to the electron beam i.e, the electron beam can transmit the Li_3VO_4 nanoribbons without too much resistance. This further illustrates the Li_3VO_4 nanoribbons have a ultrathin nanostructure which is consistent with the result of the Fig. 6. The average size of the Li_3VO_4 nanoribbons is around a few μm in length, 50-100 nm in width, and a few atomic layers in height. It should be emphasized that, even after a long period of sonication during the preparation of the TEM specimens, the Li_3VO_4 nanoribbons are still anchored on the surface of the graphene nanosheet, suggesting that their interaction is strong,[56] just these disorderly distributed Li_3VO_4 nanoribbons formed the hierarchical ultrathin Li_3VO_4 nanoribbons. The high-resolution (HR)TEM image shows clear lattice fringes of Li_3VO_4 nanobelts with an interfringe spacing of 0.413 nm, 0.247nm (Fig. 5c), corresponding to the d-spacing of (110), (200) planes of Li_3VO_4 , respectively. Moreover, the selected area electron diffraction (SAED) pattern (Fig. 2d) took from an layered nanoribbons exhibits well arranged polycrystal rings which stands for (110), (101), (200) crystal planes from inner to exterior, respectively, and the ring patterns and the corresponding lattice spacings are consistent with the XRD analysis shown in Fig. 3. The polycrystal rings sufficiently illustrates that the ultrathin Li_3VO_4 nanoribbons were made up of Li_3VO_4 nanobelts as shown in Fig. 6. Additionally, from Fig 4E, we can find the irregular lattice-fringe of graphene which distributed randomly on the carbon membrane and on the lattice-fringe of graphene, and there are lots of regular lattice fringes with different orientation that results from the Li_3VO_4 nanobelts. The clarity of lattice fringe of Li_3VO_4 nanobelts is very weak which obviously illustrates the ultrathin structure of Li_3VO_4 nanobelts. Thus, a unique nanoarchitecture of graphene-supported Li_3VO_4 nanoribbon can be readily identified.

In order to further illustrate that the multilayer structure is stacked layer-by-layer alternatively by Li_3VO_4 and GNS ultrathin layers, energy dispersive spectroscopy (EDS) were used to characterize the LVO/G nanocomposite. The EDX reveals that the nanocomposite of LVO/G consists of the elements V, O and C (shown in Fig 5), which is consistent with the

Raman, XRD and TEM results (Fig 1, 3 and 4). Moreover, from the SEM image and the corresponding elemental mapping of C, we can see that the C uniformly distributed among the layers which displays the graphene distributed uniformly in the layers. The graphene plays a very important role, which can : 1) suppress the aggregation of Li_3VO_4 nanoribbons, 2) accommodate the volume change during the cycle processes, 3) greatly improve the transportation efficiency of current carriers, 4) maintain a high electrical conductivity of the overall electrode. From the SEM image and the corresponding elemental mapping of V and O, the elements of V and O also uniformly distributed among the layers which illustrates the Li_3VO_4 nanoribbon distributed uniformly in the layers. Combined the layered structure as shown in Fig. 5a, we can conclude that the multilayer structure is stacked layer-by-layer alternatively by Li_3VO_4 and GNS ultrathin layers. Owing to the ultrathin structure of both graphene and Li_3VO_4 , we hardly find the obvious interface between graphene and Li_3VO_4 nanoribbon which further proves the uniform recombination between the different layers. Overall, we have successfully achieved the preparation of LVO/G nanocomposite with hierarchical structure.

AFM is considered to be a more powerful tool for identifying the ultrathin thickness of Li_3VO_4 nanoribbons. Before testing, the sample was first dispersed in ethanol under ultrasonication for 10 min. AFM testing (Fig. 6) gives a direct thickness of the Li_3VO_4 nanoribbons which is about 3 nm. The width of the Li_3VO_4 nanoribbons is about 50-100 nm, the length of the nanobelts is a few μm , in agreement with the FE-SEM results. Interestingly, the nanoribbon morphology is maintained well even after the calcination. To the best of our knowledge, no previous work involves such well-dispersed ultrathin Li_3VO_4 nanoribbons, as well as other vanadates including LiV_3O_8 and LiVO_3 .

Motivated by the unique ultrathin thickness of the Li_3VO_4 nanoribbons and graphene, the as-obtained LVO/G was tested for their lithium storage performance as a anode material. Coin

cells with a metallic Li counter electrode were assembled and a galvanostatic charge-discharge technique was employed to evaluate the electrochemical properties of LVO/G nanocomposites at room temperature. In order to make a comparison, bare Li_3VO_4 nanoribbon electrode was also tested at the same conditions.

Fig.7A indicates the Li^+ insertion/extraction capacities and the coulombic efficiency of the Li_3VO_4 nanoribbon@GNS nanocomposites. From the chart we can see that at the current density of $80 \text{ mA} \cdot \text{g}^{-1}$ between the voltage limits of 0.2 and 3.0 V (vs. Li^+/Li), and the LVO/G anode has a high specific capacity and a perfect cycle performance. The initial discharge capacity reached $567.6 \text{ mA h g}^{-1}$ and the second discharge capacity reached $406.1 \text{ mA h g}^{-1}$, the large capacity loss in the first two cycles may attributed to the irreversible intercalation of Li^+ ions into the crystal lattice and the formation of Li_2O , as well as other irreversible processes such as inevitable formation of solid-electrolyte interface (SEI) layer, as well as their irreversible reactions that include a reaction on the surface of ultrathin Li_3VO_4 nanoribbon and graphene, which are common for most interstitial transitional metal oxides anodes.[57, 58]The specific discharge and charge capacity of LVO/G anode experienced a sluggish increase at the primary dozens of cycles, and then almost sustained the same level (440 mA h g^{-1}) during the following cycles. Among the 200 cycles, the specific capacity has no decrease at all, instead there was a little increase, up to 453 mA h g^{-1} at 200th cycle, which is higher than the theoretical capacity of graphite (372 mA h g^{-1}). The reasons of the specific capacity increasing with the cycle numbers may be explained as the following: The nanostructure of LVO/G is constructed by the ultrathin Li_3VO_4 nanoribbons and the graphene nanosheets which stacked layer-by-layer alternately, so there were large numbers of capillary tubes existing in the nanocomposites. When the organic electrolyte soak through the inorganic Li_3VO_4 , according to the capillary theory, it is difficult for the organic electrolyte to infiltrate into the capillary tubes. But with continuous cycling of the anode, the organic EIS will form little by little on the surface of Li_3VO_4 which is beneficial for the infiltration process of

electrolyte. With the continuous infiltration of electrolyte, there will be more and more Li^+ inserting into the structure of Li_3VO_4 , which will lead to the capacity increase of LVO/G with the cycling process. However, when active materials have a full infiltration by the electrolyte, the capacity reached a limitation and then sustains the same level during the following cycles. The columbic efficiency was over 100% at the initial few cycles, which shows that the intercalation of some Li^+ ions into the crystal lattice is irreversible, and some other irreversible processes such as inevitable formation of solid-electrolyte interface (SEI) layer and irreversible reactions on the surface of ultrathin Li_3VO_4 nanoribbon and graphene, took place. But after several cycles, the columbic efficiency of the coin cell retain at the level of 100%, indicating the good reversibility of the interaction and extraction of Li^+ in the nanocomposite during the following cycles. This figure (Fig.7 B) shows the discharge/charge curves at the first, third, fiftieth, one hundredth, one hundred fiftieth and two hundredth cycles for the LVO/G electrode, the specific discharge capacities of which are $567.7 \text{ mA h g}^{-1}$, $396.8 \text{ mA h g}^{-1}$, $383.1 \text{ mA h g}^{-1}$, $440.1 \text{ mA h g}^{-1}$, $427.8 \text{ mA h g}^{-1}$, 453 mA h g^{-1} at the first, third, fiftieth, one hundredth, one hundred fiftieth, two hundredth cycles respectively. The corresponding specific charge capacities are $335.5 \text{ mA h g}^{-1}$, $361.2 \text{ mA h g}^{-1}$, $385.9 \text{ mA h g}^{-1}$, $440.6 \text{ mA h g}^{-1}$, $430.3 \text{ mA h g}^{-1}$, and $452.5 \text{ mA h g}^{-1}$, and the columbic efficiencies are 119.25 percent, 109.7 percent, 99.5 percent, 99.88 percent, 99.3 percent, 99.65 percent and 100 percent. We can see that, with the cycle numbers increasing, the cycling stability was increasing as well. The average potential for the discharge curves at 0.2 C rates is found to be around 1 V and this potential is lower than that of $\text{Li}_4\text{Ti}_5\text{O}_{12}$. [59, 60] The superior electrochemical performances of the materials described in this paper are attributed to the unique layer-by-layer stacked ultrathin nanoribbon structures.

Superior rate capability is highly desirable for high-power LIB applications such as hybrid electric vehicles (HEVs) and electric vehicles (EVs). The cycling responses of the LVO/G nanocomposites electrode at different C rates were evaluated and shown in Fig.7C.

To compare the rate capability, the C rate is based only on the Li_3VO_4 and 1 C is 400 mA g^{-1} . From the curves of rate performance we can see that the LVO/G nanocomposite exhibits an obviously much improved performance over the bare Li_3VO_4 ultrathin nanoribbon (Fig.7C). A high discharge capacity of 88.4 mA h g^{-1} was still obtained for the LVO/G nanocomposite at the current density of 50 C, whereas the bare Li_3VO_4 nanoribbons electrode is not able to show any electrochemical responses at 50 C. At 20 C, the LVO/G nanocomposite has 232 mA h g^{-1} but LVO nanoribbon only has a specific capacity of 103.2 mAhg^{-1} . Furthermore, when the rate go back to 0.2C after 10 cycles at high rate (50 C), the specific capacity of LVO/G anode electrode can still return to the initial level, while the LVO electrode can't restore to the original level which obviously illustrates the superior stability of LVO/G electrode. These results are also superior to the reported vanadium-based anode materials[29, 30, 61, 62] and superior to those of graphite.[63, 64]

The improvement in the electrochemical performance of the LVO/G nanocomposites electrode over the bare Li_3VO_4 nanoribbon and the reported vanadium-based anode materials can be due to several factors: First, the cavities or holes between the layers may provide extra space for the storage of lithium ions like in carbons,[65] which is beneficial for enhancing the specific capacity, and this is a main reason why the reversible capacities of the bare Li_3VO_4 ultrathin nanoribbon and the LVO/G nanocomposite are higher than the theoretical value of Li_3VO_4 . Second, the ultrathin structure is often associated with larger surface area, which provides more sites for lithium insertion-desertion, leading to good charge and discharge performance at large current densities.[66] Third, the nanometer (about 3 nm) thickness effectively reduces the diffusion distance for lithium ions, leading to better rate capabilities. Fourth, the graphene nanosheet distributed in the layers play a quite important role: On the one hand, GNS buffers the local volume change during lithium insertion/deinsertion and is able to alleviate the problem of pulverization and aggregation of the ultrathin Li_3VO_4 nanoribbon electrode , hence keeping structural stability during cycling.[67] On the other

hand, the GNS provides higher electronic conductivity leading to the reduced charge transference resistance.[68] Meanwhile, the high chemical diffusivity of Li^+ on a graphene plane favours the transportation of lithium ions.[69] Moreover, the graphene nanosheets have the open and flexible porous structure favouring the emission of the strain/stress, so the LVO/G nanocomposites electrode retained good structural stability during cycling.

The graph shows initial charge/discharge profiles for LVO/G nanocomposite and LVO anode at a current density of 80 mA g^{-1} (0.2 C) between 0.2 and 3.0 V . (Fig.7D) From the two curves of the charge and discharge, we can find that the discharge capacity is larger than the charge capacity, which may attribute to the side reactions such as formation of solid electrolyte interface (SEI) film between the electrode and electrolyte during the first discharge process. For the LVO/G nanocomposite electrode, the first discharge capacity achieves $567.7 \text{ mA h g}^{-1}$, corresponding to insertion of 2 Li^+ per formula. This value is much higher than the capacity of the commercial graphite anode (normally 372 mA h g^{-1}). In contrast, a lower initial discharge capacity of 401 mAhg^{-1} can only be achieved for the bare Li_3VO_4 ultrathin nanoribbon electrode with a large polarization, which is mainly related to the inferior transportation efficiency for Li ion and electron transportation. Additionally, there are a series voltage plateaus from 3 to 0.2 V in the discharge profile, which correspond to a series of phase transitions of crystalline Li_3VO_4 . The intercalation of Li^+ occurs at a voltage range below 1.0 V and above 0.2 V vs. Li/Li^+ , thus the potential problem of lithium deposition is avoided, rendering this material safer than graphite. Lithium intercalation into the interlayer space of Li_3VO_4 along the a-b plane follows the equation of $\text{Li}_3\text{VO}_4 + x\text{Li}^+ + xe^- \rightleftharpoons \text{Li}_{3+x}\text{VO}_4$ ($0 \leq x \leq 2$). [48] The plateaus in the discharge profile correspond to the phase transition of $\text{Li}_3\text{VO}_4 / \text{Li}_{3.5}\text{VO}_4 / \text{Li}_4\text{VO}_4 / \text{Li}_{4.5}\text{VO}_4 / \text{Li}_5\text{VO}_4$. The gentle slope in the charge/discharge curves of the LVO/G nanocomposite may be attributed to the graphene. Both of them show a great overlapping above 0.2 V in the charge/discharge curves. The charge (reversible) capacity of

the LVO/G composite is $372.8 \text{ mA h g}^{-1}$ (based on the weight of Li_3VO_4 in the nanocomposite) between 0.2 and 3.0 V, 68 mAhg^{-1} higher than that of the bare Li_3VO_4 ultrathin nanoribbon, and the main capacity is situated between 0.2 and 2.0 V. These data are much higher than those of the reported.[48, 70, 71] The main capacity is situated at about 1 V, which is consistent with their cyclic voltammograms.

To investigate the structural reversibility of Li_3VO_4 upon Li^+ insertion/de-insertion, we conducted the ex-situ XRD measurements on the electrodes at different charge/discharge states. All the electrodes were sealed with a Mylar thin film to prevent exposure to air and characterized immediately after the charge/discharge tests. As shown in Fig.8, all the main diffraction peaks of Li_3VO_4 can be observed in the XRD pattern of the electrode before discharge (at OCV). However, the peak intensity is much lower compared to that of the powder sample (Fig.3). This is attributed to the mixture nature of the nanocomposite electrode and the existence of Mylar film. The high background comes from the diffraction of Mylar film. The two intense peaks at 43.5° and 50.5° are the diffraction peaks of Cu current collector. When discharged to 1.2 V, XRD pattern of the electrode remains same to that obtained at OCV, showing maintenance of the Li_3VO_4 structure. Further discharged to 0.9 V, two new peaks at about 17.5° and 33.5° begin to appear in addition to the peaks of Li_3VO_4 , implying the generation of a second phase. When discharged to 0.2 V, the new peaks become more intense while the original Li_3VO_4 peaks become much weaker, which means the second phase is increasing and Li_3VO_4 phase is decreasing by discharging from 0.9 V to 0.2 V. According to the revolution of XRD patterns during discharge, the insertion of Li^+ into Li_3VO_4 can be interpreted by first a solid-solution step and then a two-phase mechanism. Upon charging, XRD patterns of the electrode undergo reversed changes to that of discharge: the new phase peaks decrease while the Li_3VO_4 peaks increase along the increase of cell voltage; after charged to 3.0 V, XRD pattern of the electrode turns back to what obtained at OCV. Although

three peaks including an intense peak at 17.5° and two weak peaks at 33.5° and 49° can be identified for the second phase, as denoted by asterisks in Fig.8, it is difficult to determine its detailed structure since these peaks cannot be indexed to any known phase in the standard crystallographic database. Besides, this unknown phase is not stable at ambient conditions as its peaks are detected at low voltage region. More work is left to clarify the phase structure of the discharge product. However, the recovery of XRD pattern by recharging the electrode to 3 V (close to OCV) indicates the structure changes of Li_3VO_4 are reversible upon Li^+ insertion/de-insertion. On the other hand, the diffraction peaks tend to broaden after charge/discharge, showing a decreased crystallization of the material. It is known that the insertion/deinsertion of Li^+ would generate a certain structure stress on the host material especially for insertion of large amount Li^+ . A large nanoribbon is unfavorable to relax such structure stress thus the large Li_3VO_4 nanoribbons may crack into several small nanoribbons after the inserting/deinsertion of Li^+ , which may account for the broadened peaks in XRD pattern. Together with the results of electrochemical performance and Ex-situ XRD, it is safe to say that Li_3VO_4 undergoes a reversible insertion/deinsertion mechanism during charge/discharge.

Cyclic voltammetry (CV) experiments were conducted to further evaluate the electrochemical performance of LVO@GNS nanocomposites at a scanning rate of $0.5 \text{ mV}\cdot\text{s}^{-1}$ over the voltage range 0.2 - 3.0 V. Fig. 9 shows the cyclic voltammetry (CV) curves for the 1st, 2nd, 3rd, 4th and 5th cycles of the LVO/G anode, which also shows the structural and electrochemical information during the Li^+ insertion/extraction process. From the CV curves, one pair of obvious reduction/oxide peaks is observed at 0.91/1.21 V. The irreversible reduction peak below 0.91V corresponds to the irreversible reduction of electrolyte and the formation of a passivating surface film, i.e. the formation of a solid electrolyte interface (SEI) layer, which disappeared in the following cycles. The peaks in the negative run can be attributed to the Li^+ insertion process. Then, the voltage plateau decrease slowly to 0.01 V,

associated with a conversion reaction of Li_3VO_4 with lithium. In the subsequent processes, all the peaks for the different oxidation–reduction pairs are reversible, due to Li^+ insertion/extraction with different site energies and the phase transition process of $\text{Li}_{3+x}\text{VO}_4$ ($0 \leq x \leq 2$). The major lithium extraction potential is close to 1.21 V vs. Li/Li^+ reference electrode. As shown in Scheme 1, the structure of Li_3VO_4 is composed of corner-shared VO_4 and LiO_4 tetrahedrons. Lithium ions are expected to reversibly intercalate into empty sites in the structure. Although further oxidation of V^{5+} in Li_3VO_4 is hard to achieve, reduction to V^{4+} by the insertion of lithium in the structure is possible through the charging process. The small reduction peak below 0.9V vs. Li in the first reduction cycle is related with the reduction of electrolyte. This peak corresponds to the small inflections (0.6-0.95 V) in the charge curve (Fig. 7B). A large reduction peak at 0.91 V vs. Li in the reduction cycle in Fig.9 corresponds to the plateaus in the discharge curves of Fig.7B. Meanwhile, the graph also shows us that the 5th cycle is almost identical to those of the 2nd cycle, which illustrates that the $\text{Li}_3\text{VO}_4@\text{GNS}$ nanocomposites anode is very stable and the de/intercalation of lithium is reversible. The properties illustrated in Fig. 9 are consistent with those displayed in Fig.7A and Fig.10.

To further confirm the function of GNS in the nanocomposite and the obvious advantages of this special structure, we have compared the LVO/G nanocomposite with LVO in cycling stability at high rates (10 C). The cycling performance of LVO/G compared with LVO is shown in Fig.10. As the LVO/G exhibits a better performance compared with the bare Li_3VO_4 nanoribbons, it was cycled for 1000 cycles at a current density of 10 C to investigate the long-life performance and high rate performance.(Fig. 10a) The initial discharge capacity of LVO/G is $264.1 \text{ mA h g}^{-1}$, but the capacity increased to $322.5 \text{ mA h g}^{-1}$ at the second cycle. After 1000 cycles, the specific capacity is still maintained at $299.2 \text{ mA h g}^{-1}$, 92.8% of the original capacity, indicating good reversibility of Li^+ insertion/deinsertion in the LVO/G anode. However, at the same conditions, the bare Li_3VO_4 electrode displays a quite inferior performance that the capacity of bare Li_3VO_4 nanoribbons experienced a fast attenuation. The

initial capacity of bare Li_3VO_4 nanoribbons is $328.1 \text{ mA h g}^{-1}$, after only 200 cycles, the capacity decreased to 100 mAhg^{-1} . The optimum performance of LVO/G demonstrates the successful fabrication of LVO/G nanocomposites by using a layer-by-layer construction method. The cycle life of 1000 cycles is longer than those of the reported anode electrode materials for power batteries such as $\text{Li}_4\text{Ti}_5\text{O}_{12}$ [60, 72], $\text{LiV}_{1+x}\text{O}_2$ [29], SnO_2 [73] and so on. Due to the synergetic effect of both increasing the cycling stability and rate capability, the impressive electrochemical performance of LVO/G can be achieved. In order to further confirm the perfect performance of LVO/G electrode, we compared the columbic efficiency of LVO/G with that of bare Li_3VO_4 . (Fig.10b) The columbic efficiency of LVO/G was very stable without large fluctuation and nearly sustained the same level of 100% at all the time, which also shows the perfect cycling stability of LVO/G and the excellent reversibility of the insertion and deinsertion of Li^+ in the ultrathin LVO/G nanocomposites. However, the columbic efficiency of Li_3VO_4 had a big fluctuation around the 100% which shows the stability of Li_3VO_4 nanoribbons without the GNS is inferior. The reasons of excellent cycling properties and high rate performance of LVO/G are considered as follows: (i) GNSs play a “flexible confinement” function to enwrap Li_3VO_4 , which can compensate for the volume change of Li_3VO_4 and prevent the detachment and agglomeration of ultrathin Li_3VO_4 nanobelts, thus extending the cycling life of the electrode; (ii) GNSs provide a large contact surface for individual dispersion of well-adhered Li_3VO_4 and act as an excellent conductive agent to provide a highway for electron transport, improving the accessible capacity; (iii) ultrathin Li_3VO_4 nanoribbons separate GNSs and prevent their restacking thus improving the adsorption and immersion of electrolyte on the surface of electroactive material; and (iv) the porosity formed by lateral GNSs and ultrathin Li_3VO_4 nanoribbons facilitates ion transportation.

After GNS mixing, however, both capacity retention and cycleability significantly improve, which implies that the GNS not only can enhance the electrochemical properties of

the compound, but also can effectively buffer the volume expansion and maintain the structural integrity. These improvements can be seen in the SEM images that are presented in Fig. 11(a) (before cycling) and Fig. 11(b) (after cycling). The images show that the LVO/G electrode is a tough film, which still adheres strongly to the copper substrate after cycling for over 1000 cycles. By contrast, the bare Li_3VO_4 nanoribbon electrode displays a continuous loss of capacity with cycling up to 200 cycles; this behaviour is due to damage to the integrity of the nanobelt after charge-discharge cycling and is supported by the SEM images shown in Fig. 6(c) (before cycling) and Fig. 6(d) (after cycling).

In summary, the introduction of GNS on the surfaces of Li_3VO_4 nanoribbons can clearly overcome the drawbacks of bare Li_3VO_4 nanoribbons to some extent. The GNS can not only improve the electrical conductivity of the electrodes but also serve as an effective buffering agent to absorb the volume expansion during Li insertion, thus maintaining the integrity of the electrode. In short, GNS can significantly enhance the electrochemical performance of Li_3VO_4 nanoribbons electrodes. LVO/G is therefore a quite promising anode material for future lithium-ion batteries, as they exhibit a high charge-discharge capacity, rate performance and excellent cycling performance compared to the current commercial graphite and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ anodes.[63, 72] It is surprising that we are not aware of such a good performance at these high rates in the literature. Especially, the performance at such high rates is much better than that of Li_3VO_4 nanoparticles,[70, 71, 74] hollow Li_3VO_4 microbox@ GNS,[48] (223 mA h g⁻¹ at 10 C after 50 cycles), Li_3VO_4 @C[61]. Based on the Table 1, it can be also seen that our sample shows greatly-enhanced high rate properties and stable cycling performance than those of Li_3VO_4 nanoparticles, hollow Li_3VO_4 microbox@GNS. Our sample shows such excellent performances as anode materials for LIBs mainly result from its unique structure which can: 1) suppress the aggregation of Li_3VO_4 nanoribbons, 2) accommodate the volume change during the cycle processes, 3) rise to a high chemical diffusivity of Li ions on the plane of graphene, 4) and maintain a high electrical conductivity of the overall electrode.

Table 1 Comparison on electrochemical properties of modified Li_3VO_4 as anode materials by different methods.

Sample ^{ref}	Methods	Current density (C)	Capacity ($\text{mA h}\cdot\text{g}^{-1}$) (cycle number)	Cycle life
Li_3VO_4 particles[70]	Solid-state reaction	0.05C	283(25)	25
Li_3VO_4 particles[71]	Solid-state reaction	1C	179.19 (100)	100
	Solution-based precipitation	1C	185.6 (100)	100
$\text{Li}_3\text{VO}_4@\text{C}$ [61]	Solid-state reaction	0.8C	365.9(40)	40
Li_3VO_4 particles[74]	Solid-state reaction	0.25C	396 (100)	100
Hollow Li_3VO_4 microbox @GNS[48]	Hydrothermal	0.05C	378(50)	50
		10C	223(50)	50
Presentwok ^{Fig7A, Fig10}	Hydrothermal +Solid-state reaction	0.2C	453(200)	200
		10C	299.2(1000)	1000

Electrochemical impedance spectroscopy (EIS) was conducted to further investigate the conductivity enhancement and to help us to further understand the reasons for the improved rate performances of the LVO/G nanocomposite anodes. Fig.12 shows the Nyquist plots of the LVO/G nanocomposite anodes and the bare LVO nanoribbon anodes. Each Nyquist plot seemed to have a similar shape with a semicircle in the high-frequency region and a straight line in the low-frequency region. The semicircle in the high-frequency region can be associated with the charge-transfer process and the properties of electrochemical reaction resistance, which reflects the resistance for Li^+ ions migration through the electrolyte/electrode interface,[75] and the low frequency straight lines relate to the properties of the diffusion process. Inset of Fig. 12 shows the equivalent circuit model for the impedance spectra. R_s is the combination of electrolyte resistance and ohmic resistances of cell components. R_f and R_{ct} are represented for the film resistance and charge-transfer resistance, respectively. QPE1, QPE2, and Z_w are the capacitance of the surface-passivating layer, double layer capacitance, and the Warburg impedance, respectively. Fig. 12 shows the primary simulation parameters of LVO/G nanocomposite and bare LVO nanoribbons. As can be

clearly seen in the chart, the R_{ct} (charge-transfer resistance) value of LVO/G nanocomposite ($R_{ct}=103\ \Omega$) is much smaller than that of bare LVO nanoribbons ($R_{ct}=200\ \Omega$).

This can be ascribed to the ultrathin nanoribbon structures of Li_3VO_4 and perfect electronic conductivity of GNS, which could reduce the lithium-ion diffusion and electron transportation distance, and greatly enhance the ions transportation efficiency. This point is consistent with the structure characteristic of LVO illustrated in Fig. 4C.

To further understand the electrode reaction kinetics of the nanocomposite, EIS measurements are carried out 3, 50, 100, 150 and 200 galvanostatic charge/discharge cycles are carried out and the different Nyquist plots of the LVO/G nanocomposite electrode are shown in Fig.13. It is seen that the charge-transfer resistance in the 3rd, 50th, 100th, 150th and 200th cycle has some increase compared to charge-transfer resistance before cycling (Fig. 12). It is because the formation of SEI film when a current was applied. During the following cycles, the charge-transfer resistance increases a little which is mainly because the continuous deposition of lithium ion in SEI film makes its thickness increase and then causes the increase of charge-transfer resistance, while the charge-transfer resistance only have a very little increase and nearly remain the same level which indicates the LVO/G has a perfect electron transport network and fast Li^+ diffusivity resulting from the incorporation of ultrathin GNS nanosheets and ultrathin Li_3VO_4 nanoribbons, and also illustrates the structure stability and perfect electron conductivity of LVO/G nanomoposite.

4. Conclusion

In summary, a nanocomposite of sandwich-like ternary compound Li_3VO_4 ultrathin nanoribbons/graphene has been initially synthesized by a novel facial hydrothermal combined with a post heat treatment method. The resultant nanocomposite reveals a unique morphology, in which homogeneous ultrathin ternary nanobelts Li_3VO_4 (thickness of about 3 nm) are

combined with ultrathin graphene nanosheets layer-by-layer alternatively. The hierarchical and sandwich-like structure could relax the stress/strain of Li^+ insertion/deinsertion, increase the surface area of the materials, provide extra space for the storage of lithium ions, and effectively reduce the effective diffusion distance for lithium ions. As a result, improved capacity (453 mA h g^{-1}), excellent rate capability (88.4 mA h g^{-1} at 50 C, 231 mA h g^{-1} at 20 C), and stable cycling performance ($299.2 \text{ mA h g}^{-1}$ after 1000 cycles at the current density of 10 C) have been achieved for the Li_3VO_4 ultrathin nanoribbons @GNS. Here, we, for the first time, focused on another vanadium oxide, Li_3VO_4 , and found that it intercalates Li ions at a voltage mainly between $0.5 \sim 1.0 \text{ V}$ vs. Li/Li^+ , lower than that of $\text{Li}_4\text{Ti}_5\text{O}_{12}$. Besides, it exhibited a capacity comparable to that of graphite. Combined with a low and safe voltage, a large specific capacity and an excellent cycling performance, therefore, the Li_3VO_4 /graphene nanosheets composite is a quite promising anode candidate for the development of high-performance advanced lithium batteries. The present template strategy, which involves using inorganic nanosheets without containing lithium as templates to synthesize lithium-containing ternary oxide nanosheets, is facile but effective. It may be extended to prepare other lithium-containing ternary oxides with ultrathin nanosheet or nanoribbon structures to enhance their lithium storage performances.

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Reference

- [1] J. Zhu, Z. Yin, H. Li, H. Tan, C.L. Chow, H. Zhang, H.H. Hng, J. Ma, Q. Yan, *Small*, 7 (2011) 3458-3464.
- [2] M. Choi, K. Na, J. Kim, Y. Sakamoto, O. Terasaki, R. Ryoo, *Nature*, 461 (2009) 246-249.
- [3] Z. Lu, J. Zhu, D. Sim, W. Zhou, W. Shi, H.H. Hng, Q. Yan, *Chemistry of Materials*, 23 (2011) 5293-5295.
- [4] X. Rui, Z. Lu, H. Yu, D. Yang, H.H. Hng, T.M. Lim, Q. Yan, *Nanoscale*, 5 (2013) 556-560.
- [5] C. Xu, Y. Zeng, X. Rui, N. Xiao, J. Zhu, W. Zhang, J. Chen, W. Liu, H. Tan, H.H. Hng, Q. Yan, *ACS Nano*, 6 (2012) 4713-4721.
- [6] X. Rui, Z. Lu, Z. Yin, D.H. Sim, N. Xiao, T.M. Lim, H.H. Hng, H. Zhang, Q. Yan, *Small*, 9 (2013) 716-721.
- [7] J. Liu, X.-W. Liu, *Advanced Materials*, 24 (2012) 4097-4111.
- [8] X. Rui, Z. Lu, Z. Yin, D.H. Sim, N. Xiao, T.M. Lim, H.H. Hng, H. Zhang, Q. Yan, *Small*, 9 (2013) 716-721.
- [9] C. Wu, X. Lu, L. Peng, K. Xu, X. Peng, J. Huang, G. Yu, Y. Xie, *Nat Commun*, 4 (2013).
- [10] H. Chang, H. Wu, *Energy & Environmental Science*, 6 (2013) 3483-3507.
- [11] C. Xu, B. Xu, Y. Gu, Z. Xiong, J. Sun, X.S. Zhao, *Energy & Environmental Science*, 6 (2013) 1388-1414.
- [12] V. Chabot, D. Higgins, A. Yu, X. Xiao, Z. Chen, J. Zhang, *Energy & Environmental Science*, 7 (2014) 1564-1596.
- [13] X. Wang, C. Zhi, L. Li, H. Zeng, C. Li, M. Mitome, D. Golberg, Y. Bando, *Advanced Materials*, 23 (2011) 4072-4076.
- [14] W. Zhou, Z. Yin, Y. Du, X. Huang, Z. Zeng, Z. Fan, H. Liu, J. Wang, H. Zhang, *Small*, 9 (2013) 140-147.
- [15] T. Yao, L. Liu, C. Xiao, X. Zhang, Q. Liu, S. Wei, Y. Xie, *Angewandte Chemie*, 125 (2013) 7702-7706.
- [16] Y. Huang, Y. Li, Z. Hu, G. Wei, J. Guo, J. Liu, *J. Mater. Chem. A*, 1 (2013) 9809-9813.
- [17] A. Manthiram, *The Journal of Physical Chemistry Letters*, 2 (2011) 176-184.
- [18] P.G. Bruce, B. Scrosati, J.M. Tarascon, *Angewandte Chemie International Edition*, 47 (2008) 2930-2946.
- [19] H. Li, X. Liu, T. Zhai, D. Li, H. Zhou, *Advanced Energy Materials*, 3 (2013) 428-432.
- [20] H. Ming, X. Li, Q. Zhou, M. Liu, L. Su, L. Bu, Z. Kang, J. Zheng, *New J. Chem.*, (2013).
- [21] W. Li, F. Wang, S. Feng, J. Wang, Z. Sun, B. Li, Y. Li, J. Yang, A.A. Elzatahry, Y. Xia, *Journal of the American Chemical Society*, (2013).
- [22] A.R. Armstrong, C. Lyness, P.M. Panchmatia, M.S. Islam, P.G. Bruce, *Nature Materials*, 10 (2011) 223-229.
- [23] R. Malini, U. Uma, T. Sheela, M. Ganesan, N. Renganathan, *Ionics*, 15 (2009) 301-307.
- [24] P. Lu, J. Liu, M. Lei, *CrystEngComm*, (2014).
- [25] J. Liu, S. Tang, Y. Lu, G. Cai, S. Liang, W. Wang, X. Chen, *Energy & Environmental Science*, 6 (2013) 2691-2697.
- [26] G. Wang, J. Gao, L. Fu, N. Zhao, Y. Wu, T. Takamura, *Journal of Power Sources*, 174 (2007) 1109-1112.
- [27] T. Ohzuku, A. Ueda, N. Yamamoto, *Journal of The Electrochemical Society*, 142 (1995) 1431-1435.
- [28] T. Ohzuku, A. Ueda, N. Yamamoto, *Journal of The Electrochemical Society*, 142 (1995) 1431-1435.
- [29] J.H. Song, H.J. Park, K.J. Kim, Y.N. Jo, J.-S. Kim, Y.U. Jeong, Y.J. Kim, *Journal of Power Sources*, 195 (2010) 6157-6161.

- [30] W.-T. Kim, Y.U. Jeong, H.C. Choi, Y.J. Kim, J.H. Song, H. Lee, Y.J. Lee, *Journal of Applied Electrochemistry*, 41 (2011) 803-808.
- [31] W.-T. Kim, Y.U. Jeong, Y.J. Lee, Y.J. Kim, J.H. Song, *Journal of Power Sources*, (2013).
- [32] A. West, F. Glasser, *Journal of Solid State Chemistry*, 4 (1972) 20-28.
- [33] M. Arroyo y de Dompablo, U. Amador, J. Gallardo-Amores, E. Moran, H. Ehrenberg, L. Dupont, R. Dominko, *Journal of Power Sources*, 189 (2009) 638-642.
- [34] Y. Shi, J.-Z. Wang, S.-L. Chou, D. Wexler, H.-J. Li, K. Ozawa, H.-K. Liu, Y.-P. Wu, *Nano letters*, 13 (2013) 4715-4720.
- [35] Y.-S. Lin, J.-G. Duh, M.-H. Hung, *The Journal of Physical Chemistry C*, 114 (2010) 13136-13141.
- [36] Y. Gu, F. Wu, Y. Wang, *Advanced Functional Materials*, 23 (2013) 893-899.
- [37] J. Ji, H. Ji, L.L. Zhang, X. Zhao, X. Bai, X. Fan, F. Zhang, R.S. Ruoff, *Advanced Materials*, 25 (2013) 4673-4677.
- [38] Q. Xiao, Y. Fan, X. Wang, R.A. Susantyoko, Q. Zhang, *Energy & Environmental Science*, 7 (2014) 655-661.
- [39] S.J.R. Prabakar, Y.-H. Hwang, E.-G. Bae, S. Shim, D. Kim, M.S. Lah, K.-S. Sohn, M. Pyo, *Advanced Materials*, 25 (2013) 3307-3312.
- [40] J. Yang, J. Wang, Y. Tang, D. Wang, B. Xiao, X. Li, R. Li, G. Liang, T.-K. Sham, X. Sun, *J. Mater. Chem. A*, 1 (2013) 7306-7311.
- [41] M. Zhen, L. Su, Z. Yuan, L. Liu, Z. Zhou, *RSC Advances*, 3 (2013) 13696.
- [42] H.J. Peng, J.Q. Huang, M.Q. Zhao, Q. Zhang, X.B. Cheng, X.Y. Liu, W.Z. Qian, F. Wei, *Advanced Functional Materials*, (2014).
- [43] J. Wang, J. Zhou, Y. Hu, T. Regier, *Energy & Environmental Science*, 6 (2013) 926-934.
- [44] J.A. Wilson, A.D. Yoffe, *Advances in Physics*, 18 (1969) 193-335.
- [45] M. Xu, T. Liang, M. Shi, H. Chen, *Chemical reviews*, 113 (2013) 3766-3798.
- [46] L. Hozoi, L. Siurakshina, P. Fulde, J. van den Brink, *Scientific reports*, 1 (2011).
- [47] C. Wu, X. Lu, L. Peng, K. Xu, X. Peng, J. Huang, G. Yu, Y. Xie, *Nature communications*, 4 (2013).
- [48] Y. Shi, J.-Z. Wang, S.-L. Chou, D. Wexler, H.-J. Li, K. Ozawa, H.-K. Liu, Y.-P. Wu, *Nano letters*, 13 (2013) 4715-4720.
- [49] K.S. Subrahmanyam, S.R.C. Vivekchand, A. Govindaraj, C.N.R. Rao, *Journal of Materials Chemistry*, 18 (2008) 1517-1523.
- [50] Y. Tao, D. Yi, J. Li, *Solid State Ionics*, 179 (2008) 2396-2398.
- [51] D. Capsoni, M. Bini, V. Massarotti, P. Mustarelli, F. Belotti, P. Galinetto, *The Journal of Physical Chemistry B*, 110 (2006) 5409-5415.
- [52] W.-T. Kim, Y.U. Jeong, Y.J. Lee, Y.J. Kim, J.H. Song, *Journal of Power Sources*, (2013).
- [53] V. Massarotti, D. Capsoni, M. Bini, P. Mustarelli, G. Chiodelli, C. Azzoni, P. Galinetto, M. Mozzati, *The Journal of Physical Chemistry B*, 109 (2005) 14845-14851.
- [54] X.M. Jian, H.Q. Wenren, S. Huang, S.J. Shi, X.L. Wang, C.D. Gu, J.P. Tu, *Journal of Power Sources*, 246 (2014) 417-422.
- [55] D.R. Dreyer, S. Park, C.W. Bielawski, R.S. Ruoff, *Chemical Society Reviews*, 39 (2010) 228-240.
- [56] Z.-S. Wu, W. Ren, L. Wen, L. Gao, J. Zhao, Z. Chen, G. Zhou, F. Li, H.-M. Cheng, *ACS Nano*, 4 (2010) 3187-3194.
- [57] Y. Gong, S. Yang, Z. Liu, L. Ma, R. Vajtai, P.M. Ajayan, *Advanced Materials*, 25 (2013) 3979-3984.
- [58] J. Jiang, Y. Li, J. Liu, X. Huang, C. Yuan, X.W. Lou, *Advanced Materials*, 24 (2012) 5166-5180.
- [59] L. Aldon, P. Kubiak, M. Womes, J. Jumas, J. Olivier-Fourcade, J. Tirado, J. Corredor, C. Pérez Vicente, *Chemistry of materials*, 16 (2004) 5721-5725.

- [60] A. Prakash, P. Manikandan, K. Ramesha, M. Sathiya, J. Tarascon, A. Shukla, *Chemistry of Materials*, 22 (2010) 2857-2863.
- [61] Z. Liang, Y. Zhao, L. Ouyang, Y. Dong, Q. Kuang, X. Lin, X. Liu, D. Yan, *Journal of Power Sources*, 252 (2014) 244-247.
- [62] W.-T. Kim, Y.U. Jeong, Y.J. Lee, Y.J. Kim, J.H. Song, *Journal of Power Sources*, 244 (2013) 557-560.
- [63] F. Ding, W. Xu, D. Choi, W. Wang, X. Li, M.H. Engelhard, X. Chen, Z. Yang, J.-G. Zhang, *J. Mater. Chem.*, 22 (2012) 12745-12751.
- [64] Y. Hu, W. Kong, H. Li, X. Huang, L. Chen, *Electrochemistry communications*, 6 (2004) 126-131.
- [65] Y.-P. Wu, C.-R. Wan, C.-Y. Jiang, S.-B. Fang, Y.-Y. Jiang, *Carbon*, 37 (1999) 1901-1908.
- [66] W. Tang, Y. Hou, F. Wang, L. Liu, Y. Wu, K. Zhu, *Nano letters*, 13 (2013) 2036-2040.
- [67] X.W. Lou, C.M. Li, L.A. Archer, *Advanced Materials*, 21 (2009) 2536-2539.
- [68] L. Wang, H. Wang, Z. Liu, C. Xiao, S. Dong, P. Han, Z. Zhang, X. Zhang, C. Bi, G. Cui, *Solid State Ionics*, 181 (2010) 1685-1689.
- [69] L. Noerochim, J.-Z. Wang, D. Wexler, Z. Chao, H.-K. Liu, *Journal of Power Sources*, (2012).
- [70] H. Li, X. Liu, T. Zhai, D. Li, H. Zhou, *Advanced Energy Materials*, (2012).
- [71] W.-T. Kim, Y.U. Jeong, Y.J. Lee, Y.J. Kim, J.H. Song, *Journal of Power Sources*, (2013).
- [72] Y. Tang, L. Yang, Z. Qiu, J.S. Huang, *Electrochemistry Communications*, 10 (2008) 1513-1516.
- [73] Y. Huang, D. Wu, J. Wang, S. Han, L. Lv, F. Zhang, X. Feng, *Small*, (2014).
- [74] S. Ni, X. Lv, J. Ma, X. Yang, L. Zhang, *Journal of Power Sources*, 248 (2014) 122-129.
- [75] S. Yoon, C. Jo, S.Y. Noh, C.W. Lee, J.H. Song, J. Lee, *Physical chemistry chemical physics : PCCP*, 13 (2011) 11060-11066.
- [76] Y. Xu, H. Bai, G. Lu, C. Li, G. Shi, *Journal of the American Chemical Society*, 130 (2008) 5856-5857.
- [77] Y. Xu, K. Sheng, C. Li, G. Shi, *Acs Nano*, 4 (2010) 4324-4330.

Figure Captions

Scheme 1. Structure of the orthorhombic β - Li_3VO_4 .

Scheme.2 Schematic illustration of formation process of sandwich-like graphene-based ternary compound Li_3VO_4 ultrathin nanoribbons anodes including: 1) the preparation of $\text{V}_2\text{O}_5 \cdot x\text{H}_2\text{O}$ nanobelts 2) preparation of Li_3VO_4 nanoribbons precursor 3) mixing of GNS with the precursor of Li_3VO_4 nanoribbons 4) heat treatment of Li_3VO_4 @GNS precursor.

Figure.1 Raman spectra of the ultrathin nanoribbon LVO/G composite.

Figure. 2 TG and DTA data for the precursor of ultrathin LVO/G nanocomposites.

Figure.3 XRD patterns of the prepared Li_3VO_4 ultrathin nanoribbon and the LVO/G nanocomposite.

Figure. 4 (a) SEM image of the LVO/G nanocomposite ground (b,c) SEM images of the LVO/G nanocomposite from side view with different magnification (d) TEM image of the LVO/G nanocomposite (e,f) HRTEM and SAED of the LVO/G nanocomposite.

Figure. 5 SEM image and the corresponding elemental mapping of V, O and C in the LVO/G nanocomposites.

Figure. 6 AFM image and the corresponding height profile for ultrathin Li_3VO_4 nanoribbons with heat treatment at 550°C for 2h.

Figure.7 (A) Cycling performance of LVO/G nanocomposites at the current density of 0.2 C (1C $\approx$ 400 mA g⁻¹) between the voltage range of 0.2 and 3 V. (B) The discharge/charge curves of LVO/G at different cycles. (C) Specific capacities of the LVO/G nanocomposites electrode for different charge/discharge cycles at various C rates. Here, 1 C is equal to 400 mA g⁻¹. (D) The initial charge/discharge profiles for LVO/G nanocomposite and LVO anode.

Figure. 8 Ex-situ XRD patterns of the LVO/G electrode at different insertion/de-insertion depth during the first discharge/charge process.

Figure. 9 CV curves of the initial five cycles of the ultrathin nanoribbon LVO/G nanocomposites anode.

Figure. 10 (a) Cycling performance of LVO/G and bare LVO electrodes in the voltage range of 0.2 - 3.0 V at the current density of 10C ($1C \approx 400 \text{ mA g}^{-1}$) and (b) the coulombic efficiency of the LVO/G and the LVO electrode. and perfect stability of LVO/G.

Figure. 11 Scanning electron microscope images at different magnifications of LVO/G nanocomposite (a) before and (b) after cycling, and bare Li_3VO_4 nanoribbons (c) before and (d) after cycling, respectively.

Figure. 12 Nyquist plots of LVO/G nanocomposite and bare LVO nanoribbon electrodes.

Figure. 13 Nyquist plots of LVO/G electrode before cycling and after 3, 50, 100, 150 and 200 galvanostatic charge/discharge cycles.

Highlights

“Graphene-like” ultrathin Li_3VO_4 nanoribbons with a thickness of about 3 nm have been synthesized by transformation from ultrathin $\text{V}_2\text{O}_5 \cdot x\text{H}_2\text{O}$ nanoribbons, and the ultrathin ternary nanoribbons Li_3VO_4 layer-by-layer combined with graphene nanosheets, show ultrahigh lithium ion storage properties.