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Graphene nanosheets encapsulated α-MoO₃ nanoribbons with ultrahigh lithium ion storage properties

Pei-Jie Lu a, b, Ming Lei c, Jun Liu * a, b

A facile and effective way has been reported to synthesize of graphene-encapsulated α-MoO₃ nanoribbons by self-assembly between negatively charged graphene oxide and positively charged MoO₃ nanoribbons. Compared to those structures of MoO₃ nanobelts grown on graphene or other hybrids of MoO₃ composited with carbon or non-carbon, this unique hybrid architecture of graphene-encapsulated MoO₃ nanoribbons exhibits not only a high specific capacity (up to 823 mAh•g⁻¹ after 70 cycles at 200mA•g⁻¹), but also an excellent cycling performance (with more than 754 mAh•g⁻¹ after 200 cycles at 1000mA•g⁻¹) as well as a greatly-enhanced high-rate capability (displaying a high discharge capacity of 710 mAh•g⁻¹ after 30 cycles at 3000 mA•g⁻¹), thus holding a great potential as an anode material for lithium ion batteries.

I Introduction

Looking forward to the energy future of humanity, renewable energy will definitely be the most sustainable way to solve many social and environmental problems. How to store the variable renewable energy in an efficient and cheap way would be a great challenge. The most promising energy storage systems should combine the features of relatively high energy density, good power capability, environmental friendliness, and low cost. Lithium ion batteries (LIBs) are considered among the most practical and effective technologies for electrochemical energy storage. LIBs can be widely used in electric vehicles, multifunctional electronic devices, communication equipment, and renewable energy integration. Therefore, developing LIBs with high energy density, power density, and excellent cycling performance becomes critical. Numerous efforts have been devoted to develop the new electrode materials to meet these demands of LIBs. Electrochemically active transition metal oxides (MxOy), such as Fe₂O₃, Fe₃O₄, SnO₂, Co₃O₄, and TiO₂ may be used as promising candidates for anode materials in the future owing to their high theoretical capacity and natural abundance. Among the metal oxide, molybdenum trioxide (MoO₃) has recently received much attention as an electrode material for LIBs owing to its good chemical stability and high charge storage capability. MoO₃ is a well-known Li⁺ insertion compound and has been investigated during the early years of lithium battery research. As an anode material, MoO₃ not only has a superior theoretical specific capacity of nearly 1111 mAh•g⁻¹, which is nearly three times than that of graphite (372 mAh•g⁻¹), but also has a very stable layered structure (as show in scheme 2a). This layered structure is able to act as a temporary host for intercalated Li⁺. However, the poor conductivity and poor kinetics of Li⁺ diffusion in bulk layered MoO₃ limits its electrochemical performances.

One way to enhance the kinetics for lithium storage in MoO₃ is to prepare nanostructured MoO₃, which can enlarge the surface area of active material and lessen the diffusion dimension of charges. Another way is to synthesize MoO₃-carbon composite, which not only prevents the exfoliation of active material from current collector but also improves the conductivity of MoO₃. In this regard, Sn-Co-CNT@CNT, Si/graphene, Si@CNT, SnO₂/graphene, LiFePO₄@CNT, Graphene/CNT@Porous Carbon-S, and CoO/graphene hybrids or composites, in which metals 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 materials scientists since it was proposed. Therefore, graphene is regarded as a promising substitute for graphite to prepare high performance MoO₃-carbon composite. MoO₃ nanobelts grown on reduced graphene oxide or graphene have been reported by hydrothermal methods however, as far as we known, the graphene-encapsulated MoO₃ nanoribbon has not been reported. Although these reported MoO₃ nanomaterials or MoO₃-graphene composites have shown improved performances, achieving MoO₃ with good rate performances and stable cycling properties still remains a great challenge until now.

In this work, we initially come up with the idea that the α-MoO₃ nanoribbon can be modified by APS to achieve the fabrication of graphene-encapsulated α-MoO₃ nanoribbon by
self-assembly between negatively charged graphene oxide and positively charged MoO3 nanoribbons. The strategy mainly includes three steps. Firstly, APS were used to modify the α-MoO3 nanoribbon so as to make the α-MoO3 nanoribbon positively charged. Secondly, we mix the positively charged MoO3 nanoribbons and the negatively charged graphene oxide. Last, graphene oxide-encapsulated α-MoO3 nanoribbon by the mutual electrostatic interactions of the two species is followed by chemical reduction in H2/Ar atmosphere and high temperature pyrolysis of GO (as shown in scheme 1a, b). As a result, we achieved the fabrication of graphene-encapsulated α-MoO3 nanoribbon by self-assembly between negatively charged graphene oxide and positively charged MoO3 nanoribbons. The resulting α-MoO3@GNS nanocomposite possesses flexible and ultrathin graphene shells that effectively wrap the α-MoO3 nanoribbons. Compared to those structures of MoO3 nanobelts grown on reduced graphene oxide or graphene, this unique hybrid architecture of graphene-encapsulated MoO3 nanoribbon can take several advantages: 1) suppress the aggregation of α-MoO3 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 (as shown in scheme 1c). Most importantly, the α-MoO3@GNS exhibits not only a high specific capacitance (up to 823 mAhg⁻¹ after 70 cycles at 200mA·g⁻¹), but also an excellent cycling performance (with more than 754 mAhg⁻¹ after 200 cycles at 1000mA·g⁻¹ ) as well as a greatly-enhanced high-rate capability (displaying a high discharge capacity of 710 mAhg⁻¹ after 30 cycles at 3000mA·g⁻¹), thus holding a great potential as an anode material for lithium ion batteries.

2 Experimental section

2.1 Preparation of the α-MoO3@ Graphene nanohybrids

Synthesis of materials: All chemicals were of analytical purity and were used as received without further purification.

GO Synthesis: GO solution was made using a modified Hummers’method.39-41 Briefly, 1 g of raw graphite powder (SP-1), 0.5 g of K₂S₂O₈, and 0.5 g of P₂O₅ were stirred in 3 mL of H₂SO₄ at 80°C for 4.5 h and copiously washed and dried in air overnight. Then 3 g of KMnO₄ was slowly added to the graphite powder solution with 23 mL of H₂SO₄ at 0°C. After vigorous stirring at 36°C for 2 h, 46 mL of deionized water was added at 0°C and the solution was stirred at 36°C for additional 2 h. The oxidation step was completed by the addition of 140 mL of DI water and 2.5 mL of H₂O₂ solution (35%). The GO solution (brown color) was washed, and filtered with 250 mL of HCl (10%). Before complete drying, the GO was dispersed in DI water (10 mg·mL⁻¹) and dialyzed for 2 weeks, from which pH values attained ≈ 6 to 7.

α-MoO3 nanoribbons synthesis: The α-MoO3 nanoribbons were synthesized by hydrothermal treatment of a peroxomolybdc acid solution. The peroxomolybdc acid precursor solution was prepared as follows: 80 mL of 30 wt % H₂O₂ aqueous solutions were slowly added to a round bottle flask containing of 9.6 g of Mo metal powder in an icy water bath with violent magnetic stirring. A transparent yellow solution was obtained, and it was further diluted to 0.10 mol/L. In a typical synthesis of α-MoO3 nanoribbon, 30 mL of precursor solution was sealed in a 50 mL autoclave and hydrothermally treated at 180 °C for 24 h.42 A white colloidal suspension was obtained, and then, the α-MoO3 paper was prepared by vacuum filtration and washed thoroughly with distilled water. After dried, the α-MoO3 paper was grounded for use.

**Scheme.1** Schematic illustration of (a) formation process of graphene-encapsulated α-MoO3 nanoribbon nanocomposite, including: 1) modification of the α-MoO3 nanoribbon by grafting aminopropylmethoxysilane (APS) to render the oxide surface positively charged; 2) hybrid assembly between positively charged α-MoO3 nanoribbon and negatively charged graphene oxide by electrostatic interactions; and 3) chemical reduction of α-MoO3 nanoribbon. (b) sketched morphological features, and (c) proposed cross-sectional Li⁺/e⁻ transfer mechanism in graphene-encapsulated α-MoO3 nanocomposite.

Assembly of α-MoO3 nanoribbons@GO hybrids and Heat-Treatment: MoO3 nanoribbons were firstly modified by surface grafting of aminopropylmethoxysilane (APS) to render the oxide surface positively charged. More specifically, 0.432 g α-MoO3 were dropped into 30 mL aqueous solution containing 2% wt APS with a vigorous stirring for 30 min, meanwhile 10 mL GO solution (10 mg/mL) were added into the former with vigorous stirring for another 30 minutes, after that the mixture were vacuum filtration. The as-formed product was subsequently treated at 450 °C (ramp rate: 10 °C·min⁻¹) in a atmosphere of 800 sccm (standard cubic centimeter) gas mixture (95% Ar and 5% H₂) for 20 minutes. Once the annealing time was out, it was suddenly cooled by taking off
the lid of the furnace. Finally, the black-coloured product of MoO$_3$@GNS was collected for further characterizations.

The process used to prepare the anode is described below. The Li/ MoO$_3$@GNS coin cells are assembled in a glove box (Mbraun, Germany) using metallic lithium as anode, polypropylene separator, and 1M solution of LiPF$_6$ in ethylene carbonate/dimethyl carbonate (EC/DMC) (1:1, v/v) as electrolyte. The galvanostatic charge/discharge performances of the electrodes were evaluated at room temperature using a Land Battery Tester (Land CT 2001A, Wuhan, China) within the voltage range of 0.01 V-3V (vs. Li/Li$^+$). The loading of the α-MoO$_3$@GNS anode material for coin cell test is about 1-2mg. Cyclic voltammetry (CV) was tested on an electrochemical workstation (CHI660C, China) at a scan rate of 0.05 mV·s$^{-1}$ in the voltage range of 0.01-3V (vs. Li/Li$^+$). The electrochemical impedance spectrometry (EIS) was performed on a ZAHNER-IM6ex electrochemical workstation (ZAHNER Co.Germany) in the frequency range of 100 kHz to 10 mHz on a cell in as-assembled condition.

3 Result and discussion

3.1 Structural characterization

A combined Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA) instrument (SDT,Q600) was used to study the evolution of the precursor in air at a heating rate of 5°C·min$^{-1}$. The phases of the as-prepared products were studied by X-ray power diffraction (XRD, Rigaku D/max 2500 XRD with Cu-Kα radiation, λ=1.54178 Å). The morphologies and sizes of the as-prepared products were characterized by scanning electron microscopy (SEM, FEI Nova Nano SEM 230) and transmission electron microscopy (TEM, JEOLJEM-2100F).

![Fig. 1 TG and DTA data for the nanocomposites of α-MoO$_3$ nanoribbon@GNS.](image)

Fig. 1 shows the TG and DTA results of the composite of α-MoO$_3$ nanoribbons @GNS under flowing air with a temperature ramping rate of 5°C /min. The slow weight-loss between 30°C and 450°C shown in Fig. 1 can be attributed to the loss of physically and chemically bonded water and partial decomposition of GO in the composite. The significant weight loss shown on the TG curve and a corresponding exothermal peak on the DTA curve between 450°C and 550°C are related to the combustion of graphene nanosheets (GNS), the weight of which reached 6.90% in the nanohybrids.

![Fig. 2 XRD patterns for the sample fabricated at 450°C under 800 sccm gas mixtures (95%Ar and 5%H$_2$).](image)

XRD measurement was used to study the phase and lattice modification of the α-MoO$_3$ nanoribbons@GNS. The diffraction peaks of the XRD pattern for the sample can be readily indexed to be orthorhombic MoO$_3$ i.e. α-MoO$_3$, whose lattice parameters is $a=0.3966$ nm, $b=1.388$ nm, and $c=0.3703$ nm, and of which space group is Pbnm (Joint Committee on Powder Diffraction Standards, JCPDS No.05-0507). No peaks of any other molybdenum oxide phases were detected, indicating the high purity of the α-MoO$_3$ nanoribbons. For the α-MoO$_3$ nanoribbons, the intensities of (020), (040) and (060) peaks are stronger than those of the bulk MoO$_3$ which indicates the anisotropic growth of the nanostructure as well as the preferred orientation of the nanoribbons. From partial enlarged detail of the XRD pattern, we can see that the stronger intensity peak (040) at 2θ=25.879° of pure α-MoO$_3$ nanoribbon become a broader one when GNS combined with MoO$_3$ nanoribbon. The characteristic (002) diffraction peak of the graphene nanosheets appear at about 22 - 26° as well. The defect and few layers deteriorate the integrity of graphite crystal structure which make GNS a amorphous-like material, so the intensity peak (002) become a broader one, as shown in the Supporting information Fig. S1. Due to the superposition of the two peaks, the stronger intensity peak (040) at 2θ=25.879° of α-MoO$_3$ nanoribbon@GNS becomes a broader one. Meanwhile, from partial enlarged detail of the XRD pattern, we can’t see that the characteristic diffraction peak of the graphene oxides (GO) between 10 - 15° in XRD pattern of the annealed sample. Therefore, it can be confirmed that the GO had been reduced to the ultrathin defective GNS after annealing treatment. The similar experiment is also reported by Müllen and Zhang.

Raman spectroscopy was used to further investigate the structural features of MoO$_3$@GNS and the carbon matrix GNS in the MoO$_3$@GNS composite (Fig. 3a). The peak at ~1350 cm$^{-1}$ (D band) is assigned to defects and disorder in the GNS. The distinctive peak at ~1580 cm$^{-1}$ (G band) is related to the
coplanar vibration of sp²-bonded carbon atoms in GNS. According to the Raman spectra comparison between GO and GNS (shown in Fig. S2), the Fig. 3a indicates that our sample is the MoO₃@GNS composite, not MoO₃@GO composite, since the intensity of D peak is higher than that of G peak. Moreover, the peak intensity ratio between the 1350 and 1580 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.⁴⁷ The intensity ratio of 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).⁴¹ These results indicate that the carbon matrix is partially graphitized, which could benefit the electron transportation from/to the poorly conducting MoO₃. The 2D band (2708 cm⁻¹) is the most prominent feature in the Raman spectrum of GNS in the MoO₃@GNS composite, 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. Fig. 3a showed the Raman spectra of the MoO₃@GNS composite. The Mo-O stretching (ν) and bending (δ) vibrations usually appear in the 1000-600 cm⁻¹ and 600-150 cm⁻¹ range, respectively. The Raman spectra of the MoO₃@GNS composite showed the characteristic Raman bands of MoO₃ at 993 (A_g, ν_M=O stretch), 817 (A_g, ν_M=O stretch), 665 (B_{2g}, B_{3g}, ν_M O-M-O stretch), 473 (A_g, ν_α O-M-O stretch and bend), 380 (B_{1g}, δ O-M-O scissor), 376 (B_{1g}), 366 (A_{1g}, δ O-M-O scissor), 334 (A_g, B_{1g}, O-M-O bend), 293 (B_{1g}, δ O-M-O wagging), 285 (B_{2g}, δ O=Mo-O wagging), 247 (B_{1g}, τ O=Mo-O twist), 216 (A_g, rotational rigid MoO₄ chain mode, R_c), 197 (B_{2g}, τ O=Mo-O twist), 159 (A_g/B_{1g}, translational rigid MoO₄ chain mode, T_c), 116(B_{2g}, translational rigid MoO₄ chain mode, T_c), 100 (B_{2g}, translational rigid MoO₄ chain mode, T_c) and 89 cm⁻¹ (A_g, translational rigid MoO₄ chain mode, T_c). The observed bands are assigned according to the single crystal study of Py et al.⁴⁸ The Mo=O bond distances along the a- and b-axes (167 and 173 pm) are shorter than the Mo-O bond distance along the c axis (195 pm). The high stretching frequency at 993 and 817 cm⁻¹ can be assigned to the stretching vibration of the terminal Mo=O bonds along the a- and b-axes.⁴⁹ The high intensity of 993 and 817 cm⁻¹ bands may indicate that the high oxygen vacancy concentration in MoO₃@GNS composite,⁴⁸ which may result from the sample annealing in an atmosphere of 800 sccm gas mixtures (95% Ar and 5% H₂).
The morphology and structure of the α-MoO₃@GNS nanocomposite were characterized by SEM and TEM. Figure 4A and B present the top-view SEM images of pure α-MoO₃ nanoribbons and α-MoO₃@GNS composite, respectively. Uniform α-MoO₃ nanoribbons with width of 300-600 nm and lengths of 4-10 µm can be observed clearly from image A. However, the thicknesses of the nanoribbons are hard to determine from the SEM images. From Figure 4B, we can found that the α-MoO₃ nanoribbons were not that uniform and smooth comparing with image A, which resulted from the GNS adhering to α-MoO₃ nanoribbons. To further understand the morphology and structure characteristics of α-MoO₃@GNS composite, TEM and corresponding selected area electron diffraction (SAED) and HRTEM pattern are shown in panels C, D and E of Figure 4, respectively. Figure 4C shows a typical TEM image which further confirms special structure of graphene nanosheets encapsulated α-MoO₃ nanoribbons, and the overall belt-like morphology of as-prepared products, the bottom (a), side (b, d), and upper side (c) of α-MoO₃ nanoribbons all were wrapped up by the ultrathin graphene which can enormously increase the electric conductivity of the nanocomposites and buffer the strain from the change in volume of α-MoO₃ nanoribbons during the cycling process. Moreover, the TEM image in Figure 4C reveals that the α-MoO₃ nanoribbon is firmly attached to the GNS even after long time ultrasonic treatment, suggesting strong interaction between α-MoO₃ nanoribbon and GNS, which could contribute to effective electrostatic interaction caused by APS between the two materials. This special structure characteristic can well-explain the perfect cycling performance and rate performance illustrated in Figure 6. From the contrast along the width of the nanoribbons (refer to Figure 4F), it is obvious that the observed nanoribbons are actually composed of two parallel and closely stacked single nanoribbons. It is of interest to note that, although the observed nanoribbons are composed of two single nanoribbons, only one set of electron diffraction spots can be detected, indicating that two parallel nanoribbons have identical crystallographic orientation. The most possible reason for this phenomenon is "oriented attachment". The SAED pattern shown in Figure 4E can be attributed to the [010] zone axis of orthorhombic α-MoO₃. It should be mentioned that, besides the allowed diffraction spots such as 200* and 002*, some forbidden diffraction spots can also be observable (such as 100* and 001* indicated by white arrows), which can be explained as the double diffraction caused by the dynamic scattering of the strong electron beam. On comparison of the TEM image and its corresponding SAED pattern, it is confirmed that the α-MoO₃ nanoribbons grow along the [001] direction and along the (010) plane (as shown in scheme 2a, b). Two sets of crystal lattice fringes, corresponding to the {100} (0.40 nm) and {001} (0.37nm) atomic spacings (as shown in scheme 2c, d), can be clearly distinguished in the top-view high-resolution HRTEM image of the α-MoO₃ (Figure 4D).

**Scheme 2.** Schematic of stable layered α-MoO₃ structures and lithiated MoO₃.

Energy dispersive spectroscopy (EDS) reveals that the nanocomposite of nanoribbon α-MoO₃@GNS consists of the elements Mo, O and C (shown in Figure 5), which is consistent with the XRD, Raman and TEM results (Figures 2, 3 and 4). Moreover, from the SEM image (Fig.5a) and the corresponding elemental mapping of C (Fig.5d), we can see that the nanoribbon α-MoO₃ is uniformly wrapped up by the GNS which illustrates we have successfully achieved the preparation of graphene nanosheets encapsulated α-MoO₃ nanoribbons.

**Fig. 5** SEM image and the corresponding elemental mapping of Mo, O and C in the graphene nanosheets encapsulated α-MoO₃ nanoribbons nanostructures.
3.2 Electrochemical performance

To address the effect of nanocoating layer (GNS) on the electrochemical performance of the \( \alpha \)-MoO\(_3\) nanoribbon, we have studied the electrochemical performance of \( \alpha \)-MoO\(_3@GNS\) nanocomposites and pure \( \alpha \)-MoO\(_3\) nanoribbon on the same time.

Fig. 6a indicates the Li\(^+\) insertion/extraction capacities and the coulombic efficiency of the \( \alpha \)-MoO\(_3@GNS\) and the \( \alpha \)-MoO\(_3\) nanoribbon. From the chart we can see that under a current density of 200 mA\(\cdot\)g\(^{-1}\) between the voltage limits of 0.01 and 3.0V (vs. Li\(^+\)/Li), the \( \alpha \)-MoO\(_3@GNS\) anode has a high specific capacity and a perfect cycle performance. The initial discharge capacity reached 1321 mAh\(\cdot\)g\(^{-1}\), the large capacity loss in the first two cycles is mainly attributed to the irreversible intercalation of Li\(^+\) ions into the crystal lattice which results in the structural change of MoO\(_3\) and the formation of Li\(_2\)O. The structural change of MoO\(_3\) at the end of the first recharge can’t be fully recovered after the initial discharge which plays an important role in the large capacity loss. The similar results are reported by T.Tsumura, Minoru Inaba, etc.\(^{50, 51}\) Meanwhile some other irreversible processes such as inevitable formation of solid-electrolyte interface (SEI) layer also may result in the capacity loss as well, which are common for most interstitial-free transitional metal oxides anodes. The specific discharge and charge capacity of \( \alpha \)-MoO\(_3@GNS\) anodes experienced a sluggish increase firstly, and then almost sustain the same level and even after 70 cycles, there was still 833 mAh\(\cdot\)g\(^{-1}\) remained to the nanoribbon \( \alpha \)-MoO\(_3@GNS\) anodes, which is 2.2 times more than the theoretical capacity of graphite (372 mAh\(\cdot\)g\(^{-1}\)). The coulombic efficiency increases at the initial few cycles and after several conditioning cycles, the coulombic efficiency of the coin cell increased to higher than 99% (Figure 2b, c), indicating good reversibility of the interaction and extraction of Li\(^+\) in the nanocomposite.

To further understand the cyclic performance of nanoribbon \( \alpha \)-MoO\(_3@GNS\) electrodes, the voltage-capacity curves of the nanoribbon \( \alpha \)-MoO\(_3@GNS\) sample in the 1st, 20th, 30th, 40th, 60th and 70th cycles at 0.2C (200mA\(\cdot\)g\(^{-1}\)) discharge rate are shown in Fig. 6b. The charge and discharge platform were 1.3V and 0.6V, respectively. The discharge capacity of 1st, 20th, 40th, 60th and 70th cycle are 1321, 984, 980, 900 and 843 mAh\(\cdot\)g\(^{-1}\), respectively. From 2nd to 70th, there was only 14.3% attenuation of capacity, which means only a 0.2% capacity decrease per cycle. Moreover, we can see that the discharge plateaus in the 1st are higher and the charge plateaus are lower compared to consequent cycles. This was due to irreversible reactions between Li\(^+\) and GNS and decomposition of the electrolyte solvent, forming a solid electrolyte interphase (SEI) when a current was applied and the SEI film form gradually in the first few cycles. After that, the charge plateaus voltage rises and discharge plateaus voltage decreases synchronously with cycling,

![Fig. 6](image-url)
indicating that the reversible capacity decreases gradually. At this time, the second deposition of lithium ions occurs on SEI surface, leading to the increase of SEI thickness and the decrease of reversible capacity. The charge–discharge plateaus of α-MoO$_3$@GNS are very close with the increase of the cycles, suggesting the reversible capacity of α-MoO$_3$@GNS decreases slowly which is probably due to its small electrode polarization. The charge and discharge capacities of the α-MoO$_3$@GNS electrode for the 2nd and 70th cycles are 926 mAhg$^{-1}$ and 843 mAhg$^{-1}$, respectively, which illustrate the GNS in the nanocomposites greatly improve the capacity and cycling properties. The reasons of excellent cycling properties and high capacity are considered as follows: (i) GNS plays a “flexible confinement” function to enwrap α-MoO$_3$, which can compensate for the volume change of α-MoO$_3$ and prevent the detachment and agglomeration of pulverized α-MoO$_3$, thus extending the cycling life of the electrode; (ii) GNS provides a large contact surface for individual dispersion of well-adhered α-MoO$_3$ and act as an excellent conductive agent to provide a highway for electron transport, improving the accessible capacity; (iii) α-MoO$_3$ separate GNS 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 GNS and α-MoO$_3$ facilitates ion transportation.

The excellent cycling performance of the α-MoO$_3$@GNS nanocomposite is presented in Figure 6c. The generally overlapping profiles indicate the good reversibility of the electrochemical processes upon cycling. With a voltage window of 0.01–3.0 V and the high charge and discharge current density (1000 mA/g$^{-1}$), the α-MoO$_3$@GNS nanocomposites retain a remarkable reversible capacity of 754.6 mAhg$^{-1}$ at the end of the 200th cycle, which corresponds to a capacity fading rate of only 0.1 % per cycle. For the voltage windows (0.01–3.0 V), the Coulombic efficiency remains close to 100 % during the cycling tests, suggesting the excellent reversibility of the electrodes and stable cycling performance.

The most significantly improved property of the α-MoO$_3$@GNS anode is the excellent rate performance, as shown in Figure 6d. The α-MoO$_3$@GNS still displays a reversible capacity of 820 and 710 mAhg$^{-1}$ after 30 cycles when the current density increases to 1500 mAhg$^{-1}$ and 3000 mAhg$^{-1}$, respectively, which are higher than the capacity of 493 mAhg$^{-1}$ of α-MoO$_3$ nanoribbon anode after 30 cycles at discharge current of 200 mAhg$^{-1}$. When the current density increases to 1500 mAhg$^{-1}$, the capacity of the pure α-MoO$_3$ nanoribbon electrode experienced a quick loss, from the initial 693 mAhg$^{-1}$ decreasing to 150 mAhg$^{-1}$ only after 30 cycles. The high-rate performances of the α-MoO$_3$@GNS anode also show obvious improvement compared with the previous α-MoO$_3$ anode materials.18, 32, 33 The superior rate performance of the α-MoO$_3$ can be attributed to the better Li$^+$ diffusion kinetics in the α-MoO$_3$ nanoribbon than in the pristine MoO$_3$ powder. What’s more, the GNS wrapping up the α-MoO$_3$ plays a very important role. Firstly, the ultrathin GNS has a perfect electronic conductivity which enormously improves the conductive ability of the insulating MoO$_3$. Secondly, the ultrathin GNS wrapped up the MoO$_3$ nanoribbons which can restrain the volume expansion and even the pulverization of crystal MoO$_3$ nanoribbons when charging and discharging. The results of electrochemical impedance spectroscopy (EIS in Fig 8) can verify the important role of GNS in improving the conductivity of the nanocomposites. The special structure characteristic as shown in Figure 4-5 can also illustrate these points.49

Fig. 7 CV curves of the initial six cycles of the α-MoO$_3$@GNS anode.

Cyclic voltammetry (CV) experiments were conducted to evaluate the electrochemical performance of α-MoO$_3$@GNS at a scanning rate of 0.05 mV•s$^{-1}$ over the voltage range 0.01–3.00V. Figure 7 shows the CV curves for the 1st, 2nd, 3rd, 4th, 5th and 6th cycles of the α-MoO$_3$@GNS anodes, which also shows the structural and electrochemical information during the Li$^+$ insertion/extraction process. In the 1st Li$^+$ insertion process, four peaks are observed at 2.748, 2.315, 1.235 and 0.27 V. The irreversible reduction peak at ~2.748 and 0.27 V in the 1st negative run is mainly attributed to the irreversible intercalation of Li$^+$ ions into the crystal lattice which results in the structural change of MoO$_3$ and the formation of Li$_2$O. The structural change of MoO$_3$ at the end of the first recharge can’t be fully recovered after the initial discharge. The similar results are reported by T. Tsunemura, Minoru Inaba, etc.51, 54 Meanwhile some other irreversible processes lead to the reduction peak as well, such as inevitable formation of solid-electrolyte interface (SEI) layer, which are common for most interstitial-free transitional metal oxides anodes. The irreversible reduction of electrolyte and the formation of a passivating surface film, i.e. the formation of a solid electrolyte interface (SEI) layer, disappeared in the following cycles. The other two peaks in the 1st negative run may be also attributed to the Li$^+$ insertion process. Then, the voltage plateau decrease slowly to 0.01 V, associated with a conversion reaction of MoO$_3$ with lithium. In the subsequent processes, all the peaks for the different oxidation–reduction pairs of 0.253/0.563, 1.261/1.312, and 1.404/1.924 V are reversible, due to Li$^+$ insertion/extraction with different site energies and the phase transition process of Li$_2$Mo alloy and α-MoO$_3$. The major lithium extraction potential is close to 1.302 V vs. Li/Li$^+$ reference electrode. The peaks (0.253, 0.421, 1.261, 1.404 V) in the continue cycles may be from Li$_2$Mo alloys in the subsequent steps. The lithium in MoO$_3$ is believed to take place in two stages: Stage-I occurs up to a potential of 1.5 V. During this stage, Li$^+$ intercalates with MoO$_3$ as follows:55

$$\text{MoO}_3 + x\text{Li}^+ + xe^- \leftrightarrow \text{Li}_x\text{MoO}_3 \quad (1)$$

The lithium content in this solid solution ranges between 1 and 1.5V, up to a potential of 1.5 V. The high lithium content is accommodated in the interlayer spacing between octahedral Mo–O layers and interlayers. Most of the Li ions intercalated at the potentials (1.261 and 1.404 V) can subsequently be extracted from the material leading to reversibility of the
reaction. Lithium ion intercalation during stage-II corresponds to potentials below 0.7 V and occurs by the following mechanism:

$$\text{Li}_x\text{MoO}_3 + x\text{Li}^+ + xe^- \rightarrow \text{Mo} + 3\text{Li}_2\text{O} \ (2)$$

In the lower voltage range, lithium reacts with the solid solution to consequently form metal and Li$_2$O. However, Li$_2$O is primarily irreversible, but the presence of nanoscale α-MoO$_3$ nanoribbon leads to the reversibility of Li$_2$O, which has been reported earlier. From the CV curves shown in Fig 7 we can see that, two reduction peaks (0.253 and 0.421 V) associated with the insertion reaction appeared below 0.7 V and other two reduction peaks (1.261 and 1.404 V) appeared between 1 and 1.5 V, which shows Stage-I and stage-II took place simultaneously. Moreover, both the processes are reversible. The curves of the 6th cycle are almost identical to those of the 2nd cycle which show the MoO$_3$@GNS anode is very stable and the deintercalation of lithium is reversible which can explain the excellent cycling performance of α-MoO$_3$ nanoribbon@GNS essentially. The properties illustrated in Fig. 7 are consistent with those displayed in Fig. 6b.

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 MoO$_3$ nanoparticles, carbon-coated MoO$_3$, MoO$_3$ nanowires and MoO$_3$ nanowire/Si coaxial-cable (ca. 780 mAh g$^{-1}$ at 100 mA g$^{-1}$). 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 MoO$_3$ nanoparticles, carbon coated MoO$_3$, MoO$_3$ nanowires and MoO$_3$ nanowire/Si coaxial cable. Our sample shows such excellent performances as anode materials for LIBs may result from its unique structure which can: 1) suppress the aggregation of α-MoO$_3$ nanoribbons, 2) accommodate the volume change during the cycle processes, 3) rise to a high α-MoO$_3$ in the composite (up to 93.1% by weight), 4) maintain a high electrical conductivity of the overall electrode (as shown in scheme 1).

The EIS tests were applied to help us to further understand the reasons for the improved rate performances of the α-MoO$_3$@GNS anodes. Fig. 8 shows the Nyquist plots of the MoO$_3$@GNS anodes and the pure MoO$_3$ 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, and the low frequency straight lines relate to the properties of the diffusion process. Inset of Fig. 8 shows the equivalent circuit model for the impedance spectra. R$_e$ is the combination of electrolyte resistance and ohmic resistances of cell components. R$_f$ and R$_dt$ are represented for the film resistance and charge-transfer resistance, respectively. QPE1, QPE2, and CPE are the capacitance of the surface-passivating layer, double layer capacitance, and the Warburg impedance, respectively. Fig. 8 shows the primary simulation parameters of α-MoO$_3$@GNS and pure MoO$_3$ nanoribbon anodes. As can be clearly seen in the chart, the R$_e$ (charge-transfer resistance) value of α-MoO$_3$@GNS ($R_{e}=230 \ \Omega$) is much smaller than that of pure MoO$_3$ nanoribbons ($R_{e}=400 \ \Omega$). This can be ascribed to the ultrathin nanoribbon structures of MoO$_3$ 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 α-MoO$_3$@GNS illustrated in Figure 4C.

**Table 1 Comparison on electrochemical properties of modified MoO$_3$ as anode materials by different methods.**

<table>
<thead>
<tr>
<th>Sample$^{18}$</th>
<th>Methods</th>
<th>Current density (mA g$^{-1}$)</th>
<th>Capacity (mAh g$^{-1}$) (cycle number)</th>
<th>Cycle life</th>
</tr>
</thead>
<tbody>
<tr>
<td>MoO$_3$ @Carbon$^{18}$</td>
<td>Hydrothermal</td>
<td>100</td>
<td>1064 (50)</td>
<td>50</td>
</tr>
<tr>
<td>MoO$_3$ nanowire$^{18}$</td>
<td>CVD</td>
<td>50</td>
<td>630 (20)</td>
<td>20</td>
</tr>
<tr>
<td>MoO$_3$ nanowire @Si$^{52}$</td>
<td>CVD</td>
<td>100</td>
<td>590 (10)</td>
<td>10</td>
</tr>
<tr>
<td>MoO$_3$ nanoparticle$^{88}$</td>
<td>Electrostatic Selfassembly</td>
<td>400</td>
<td>780 (15)</td>
<td>15</td>
</tr>
<tr>
<td>Present work$^{64,65}$</td>
<td>Electrostatic</td>
<td>1500</td>
<td>820 (30)</td>
<td>30</td>
</tr>
</tbody>
</table>

Fig. 8 Nyquist plots of nanoribbon α-MoO$_3$@GNS and pure MoO$_3$ nanoribbon.
To further understand the electrode reaction kinetics of the nanocomposite, EIS measurements were carried out before cycling and after 1, 20, 40, 50, 60 and 70 galvanostatic charge/discharge cycles.

Fig. 9 Nyquist plots of nanoribbon α-MoO3@GNS before cycling and after 1, 20, 40, 50, 60 and 70 galvanostatic charge/discharge cycles.

5 Conclusions

A facile and effective way has been reported to synthesize α-MoO3 nanoribbon@graphene nanosheet nanocomposites through an electrostatic self-assembly method. The characterizations of Raman, FT-IR, XRD, FESEM, TEM, SAED and HRTEM demonstrate that graphene nanosheets wrapped up the MoO3 nanoribbon tightly and homogeneously and formed a robust composite structure. Compared to those structures of MoO3 nanobelts grown on reduced graphene oxide or graphene, this unique hybrid architecture of graphene-encapsulated MoO3 nanoribbon can take several advantages: 1) suppress the aggregation of α-MoO3 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. Most importantly, the α-MoO3@GNS nanocomposites exhibit not only a high reversible capacitance (up to 823 mAh g\(^{-1}\) after 70 cycles) but also an excellent cycling stability (with more than 754 mAh g\(^{-1}\) after 200 cycles at 1000 mAh g\(^{-1}\)) as well as a greatly-enhanced rate capability (displaying a high discharge capacity of 710 mAh g\(^{-1}\) after 30 cycles at 3000 mAh g\(^{-1}\)). We attributed the superior electrochemical performances of the α-MoO3@GNS nanocomposites to their robust composite structure and the synergistic effect between MoO3 nanoribbon and graphene nanosheet. EIS analysis confirms that the incorporation of graphene preserves the high conductivity and greatly enhances the transportation efficiency of Li\(^+\) in the MoO3@GNS nanocomposites during the electrochemical reaction. Therefore, the present results suggest that this kind of the α-MoO3@GNS nanocomposites hold a great potential as anode materials for high performance LIBs.

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Notes and references


