Synthesis of graphene wrapped porous CoMoO₄ nanospheres as high-performance anodes for rechargeable lithium-ion batteries†

Donghao Lyu, Lingling Zhang, Huaxin Wei, Hongbo Geng and Hongwei Gu

Herein, we described a facile method to synthesise porous CoMoO₄ nanospheres wrapped with graphene (CoMoO₄@G). The porous CoMoO₄@G composites were generated from the calcination treatment of CoMo precursors, followed by a graphene-coating process. Compared with pristine CoMoO₄ porous spheres, the graphene sheets endowed the CoMoO₄@G with higher electrical conductivity and structural stability. When used as an anode materials for lithium-ion batteries (LIBs), the CoMoO₄@G electrode delivers a high initial specific capacity (1355.8 mA h g⁻¹ at 100 mA g⁻¹), good cycling stability (783 mA h g⁻¹ over 150 cycles at 500 mA g⁻¹) and excellent rate capacity (697.7 mA h g⁻¹ at 2000 mA g⁻¹). In view of this, the combination of the graphene sheets with CoMoO₄ nanospheres serve as potential anode materials for application in the new generation of LIBs.

Introduction

It has been several years since high power density and environmentally friendly energy systems, such as fuel cells, solar cells, lithium-ion batteries (LIBs), etc., came into public applications. Among them, LIBs, as a remarkable alternative and clean energy conversion, have attracted crucial attention, because of their high energy and power density, lack of memory effect, eco-friendliness as well as universal availability. With the development of electronic devices and power-driven machines, traditional LIBs using a graphite anode (whose specific capacity is about 372 mA h g⁻¹) cannot meet the expanding energy demand.

Recently, many researchers have focused on exploring high-performance electrode materials for LIBs. Among the anode materials investigated, metal molybdates (XMoO₄, X = transition metal) have received extensive attention. As a representative, CoMoO₄ with a high theoretical capacity (980 mA h g⁻¹) has attracted great attention due to its high electrochemical activity. Unfortunately, the low conductivity and strong aggregation tendency of CoMoO₄ compromise its electrochemical properties and hinder its practical application to a great extent. To address these problems, it is proposed and reported that coating CoMoO₄ nanostructure with conductive carbon could remedy the disadvantages mentioned above. Graphene with a huge specific surface area (2630 m² g⁻¹), high electrical conductivity and unique mechanical strength, is a promising candidate to improve the electrochemical properties of CoMoO₄. Two-dimensional (2D) graphene layer can effectively suppress the structural pulverization and large volumetric expansion in the cycling process, so as to maintain the stability of electrode material. For example, Yang et al. have successfully synthesized CoMoO₄/rGO composite via a simple green wet chemical method, and it delivers a discharge specific capacity of 628 mA h g⁻¹ after 100 cycles at a current density of 100 mA g⁻¹. Xu and his co-workers also prepared lotus root-like CoMoO₄@graphene nanofibers by electrospinning and subsequent heat treatment which displayed high reversible capacity of 735 mA h g⁻¹ at 100 mA g⁻¹. However, the relatively low specific capacities reported in the above literatures can not still satisfy the commercial applications of CoMoO₄ electrode materials.

In this work, we have synthesized the graphene wrapped CoMoO₄ structures (referred as CoMoO₄@G) via a facile method. When used as a anode for LIBs, the CoMoO₄@G composites demonstrated splendid electrochemical capacity, e.g. stable cycling performance (783.0 mA h g⁻¹ after 150 cycles at a current density of 500 mA g⁻¹), high coulombic efficiency and excellent rate performance (1103.0, 990.0, 909.3, 829.2 and 697.7 mA h g⁻¹ at 100, 200, 500, 1000 m and 2000 mA g⁻¹).
Experimental section

Materials
All reagents used in the experiment were of analytical purity and were used without further purification.

Synthesis of porous CoMoO₄ nanospheres
The CoMoO₄ nanospheres were synthesized via a controllable hydrothermal method as followed: 1.5 mmol Co(NO₃)₂·6H₂O and 1.5 mmol molybdenum(α) acetylacetonate were dissolved in 200 mL isopropyl alcohol and 40 mL glycerol. After stirred overnight at room temperature, the above mixed solution was transferred and uniformly distributed to four 100 mL hydrothermal reactor and reacted at 180 °C for 12 h. The light brown precipitate was collected by centrifugation and washed with ethanol and water for three times. After calcined at 600 °C in air for 2 h with a rate of 1 °C min⁻¹ and maintained at the temperature for 3 h in a muffle, a black powder was finally obtained (CoMoO₄ nanospheres).

Synthesis of the CoMoO₄@G complex
Typically, 80 mg as-prepared CoMoO₄ nanospheres were redispersed into 30 mL deionized water and then 40 mg graphene oxide (GO) aqueous suspension (0.5 mg mL⁻¹) was added into the above solution under stirring for 2 h to form a homogeneous solution. Next, the mixture was transferred into a 100 mL Teflon-lined stainless steel autoclave and kept at 180 °C for 12 h. After cooled to room temperature, the product was collected and washed with distilled water and absolute alcohol for three times. The final product was sintered under Ar atmosphere at 600 °C for 2 h with a rate of 1 °C min⁻¹.

Materials characterization
The morphologies of the materials were visualized by scanning electron microscopy (SEM Hitachi S-4700), transmission electron microscopy (TEM TecnaiG220, FEI, American) and high-resolution TEM (HRTEM) recorded on a Tecnai G2 F20 S-TWIN microscope with an accelerating voltage of 200 kV. The element contents were tested by energy dispersive X-ray spectroscopy (EDS) was also given to measure the element composition of the CoMo precursor and the porous CoMoO₄ nanospheres. As shown in Fig. S1a,† the CoMo precursor consist of Co, Mo, C, N, O element, of which the mass fraction are 15.24%, 22.51%, 29.77%, 3.91%, 28.56%, respectively. In Fig. S1b,† The atomic ratio of Co, Mo and O identifies with the stoichiometric ratio of CoMoO₄.

Electrochemical measurements
To prepare the electrode, active materials (CoMoO₄@G), acetylene black as well as polyvinylidene fluoride (PVDF) (7 : 2 : 1 in weight ratio) were dispersed in 1-methyl-2-pyrrolidone (NMP) to form a homogeneous slurry. The slurry was casted onto a copper foil and dried overnight at 110 °C in a vacuum oven. In the system, the as-prepared electrode was used as the working electrode, a metallic lithium foil (15 mm in diameter) was employed as the counter and reference electrode and Celgard 2400 membrane was applied as the separator. The electrolyte was 1 M LiPF₆ in the mixture of ethylene carbonate and diethyl carbonate (EC/DEC, 1/1 by volume). The charge/discharge measurement was performed using a LAND CT2001 test system with huge current ranging of 0.01–3.0 V (vs. Li/Li⁺). Cyclic voltammetry (CV) tests were carried out at a scanning rate of 0.1 mV s⁻¹ in the range of 0.01–3.0 V. Electrochemical Impedance Spectroscopy (EIS) was measured by a using a CS350 electrochemical workstation with the frequency changing from 100 kHz to 0.01 mHz.

Results and discussion
The preparation process of the CoMoO₄@G composites is illustrated in Scheme 1. Briefly, the CoMo precursors were obtained by a facile hydrothermal method using cobalt nitrate and molybdenyl acetylacetonate as the starting materials, followed by a calcination procedure, and the porous CoMoO₄ nanospheres were obtained. Afterwards, the CoMoO₄ nanospheres were wrapped with graphene oxide sheets though further hydrothermal and calcining approach to form the CoMoO₄@G composites.

From the SEM image (Fig. 1a), we can see that the precursor has smooth surface, with the diameter between 300 and 400 nm, which can be clearly observed via the corresponding TEM image (Fig. 1c). After the heat treatment, a large number of pores form on the surface of nanospheres (Fig. 1b). From the TEM images (Fig. 1d), the porous structure of the nanospheres is clearly presented. Besides, the result of energy dispersive X-ray spectroscopy (EDS) was also given to measure the element composition of the CoMo precursor and the porous CoMoO₄ nanospheres. As shown in Fig. S1a,† the CoMo precursor consist of Co, Mo, C, N, O element, of which the mass fraction are 15.24%, 22.51%, 29.77%, 3.91%, 28.56%, respectively. In the corresponding TEM image (Fig. 1c), the CoMoO₄@G complex is clearly presented. Besides, the result of energy dispersive X-ray spectroscopy (EDS) was also given to measure the element composition of the CoMoO₄@G complex, which can be lightweightly fabricated from the TEM images (Fig. 1d). From the SEM image, the high-resolution TEM (HRTEM) image reveals the crystallinity of the CoMoO₄@G.
lattice fringes possessing a spacing distance of 0.336 nm, in correspondence with the (002) lattice plane of CoMoO₄. The selective area electron diffraction (SAED) further supports the result (Fig. 2f). As displayed in Fig. 2g, the corresponding element mapping images further confirm the nanospheres consist of Co, Mo, O, which have uniform distribution. The element composition of the CoMoO₄@G was exhibited in Fig. S1c† as well.

Thermogravimetric metric analysis (TGA) was utilized to estimate the optimal calcination temperature to form the CoMoO₄ nanospheres. In Fig. 3a, it was carried out in definite air flow from 0–800 °C, with a heating rate of 10 °C min⁻¹ and the weight loss is about 52.07% ascribed to the thermal decomposition of precursors. With the temperature rising, the weight is reduced uniformity and stabilized at 600 °C. Powder X-ray diffraction (XRD) was used to analyze the crystallographic structure and purity of the CoMoO₄@G composites. As shown in Fig. 3b, it can be found that the XRD pattern of CoMoO₄@G is similar to pure CoMoO₄ nanospheres and all the diffraction peaks are indexed to the standard XRD data card (JCPDS no. 21-0868). In addition, the XRD pattern of pure CoMoO₄ was also displayed in Fig. S2,† which further confirm the high purity of the obtained products. The CoMoO₄ content in the CoMoO₄@G sample was also measured by the thermogravimetric analysis (TGA) carried out at same condition (Fig. S3†). It is implied based on the TGA result that the CoMoO₄ content was about 57.5%. Moreover, we took advantage of Raman spectrum to further investigate the graphitic sp² carbon in the CoMoO₄@G composite. The two broad peaks located at 1334 and 1579 cm⁻¹ could be attributable to typical D- and G-bands of graphene, respectively, confirming the presence of carbon (Fig. S4†).

The elemental composition and relevant electronic states was indicated evidently by X-ray photoelectron spectroscopy (XPS). Fig. 4a shows the survey spectrum of the CoMoO₄@G complex, revealing that the product is comprised of Co, Mo, O and C elements. In which, the peaks of Co, Mo and O can be attributed to CoMoO₄, while the C peak originate from...
graphene. Moreover, the Co 2p core level spectrum was presented in Fig. 4b, two peaks located at 796.5 and 779.5 eV are attributed to Co 2p1/2 and Co 2p3/2. The XPS spectra for Mo 3d was shown in Fig. 4c, it displays two peaks at 235.7 and 232.5 eV are attributed to Mo 3d3/2 and Mo 3d5/2, demonstrating the Mo6+ oxidation state is the main existence form of Mo element.35,36 In Fig. 4d, the peak with binding energies at 284.6 eV corresponds to sp2 hybridized carbon. Nitrogen adsorption–desorption isotherms was also given in Fig. S5.† As the result, The Brunauer–Emmett–Teller (BET) surface area of CoMoO4@G is calculated to be 15.5 m2 g−1 (Fig. S5a†). The pore-size distribution analyzed using the Barrett–Joyner–Halenda (BJH) method was display in Fig. S5b.† The dominant pore size distribution of CoMoO4@G is about 11.5 nm, revealing the porous structure of the CoMoO4@G composites.

Fig. 5a presents the charge/discharge profiles of the CoMoO4@G electrode in the first three cycles at a current density of 100 mA g−1. In the initial discharge process, the voltage dropping from 2.5 V to a plateau at 0.01 V can be attributed to the reduction of CoMoO4 and the irreversible reaction with the electrolyte.29,30 The first discharge and charge capacities of CoMoO4@G electrode at 100 mA g−1 is 1355.8 and 893.0 mAh g−1, respectively. The initial coulombic efficiency is 65.9%. Fig. 5b displays the cyclic voltammograms (CVs) of the as-prepared CoMoO4@G electrode in a potential voltage between 0.01 and 3.0 V at a scan rate of 0.1 mV s−1. In the initial cathodic scan, three peaks located at 0.08, 0.7 and 1.6 V are relevant to the structural change caused by the reduction reaction of Co and Mo oxide, together with the formation of solid electrolyte interface (SEI), expressed by eqn (1). In the anodic process, two peaks at 1.4 and 1.8 V can be obviously observed in correspondence with the lithium extraction from graphene and the formation of Co and Mo oxide. In which, the peak at 1.4 V might be ascribed to the oxidation of Mo0 to Mo4+, and the peak at 1.8 V could indicate the oxidation of Co to Co2+ and Mo4+ to Mo6+, expressed by eqn (2) and (3). In the subsequent cycles, two cathodic peaks at 0.6 and 1.55 V and two anodic peaks at 1.4 and 1.8 V can be surveyed, respectively. The difference between the first cycle curves and the followings might be caused by the inevitable formation of a solid electrolyte interphase (SEI). But the high overlap of the following cycles still implies the great cycling performance of the CoMoO4@G electrode material.32,35,38,41 Based on the charge–discharge profile, CV curves, the Li+ insertion/extraction behaviour of the CoMoO4@G electrode can be suggested as follows:

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\begin{align*}
    \text{CoMoO}_4 + 8\text{Li}^+ + 8\text{e}^- & \rightarrow \text{Co} + \text{Mo} + 4\text{Li}_2\text{O} \quad (1) \\
    \text{Co} + \text{Li}_2\text{O} & \rightarrow \text{CoO} + 2\text{Li} \quad (2) \\
    \text{Mo} + 3\text{Li}_2\text{O} & \rightarrow \text{MoO}_3 + 6\text{Li} \quad (3)
\end{align*}
\]

Fig. 5c displayed the cycling performance and coulombic efficiency of CoMoO4 and CoMoO4@G electrodes at a current density of 500 mA g−1. The CoMoO4@G electrode can deliver a specific capacity of 783.0 mA h g−1 after 150 cycles at a density of 500 mA g−1, which is higher than that of pure CoMoO4. It can be concluded that the presence of graphene layer plays an important role on the improvement of cycling stability.29 The CoMoO4@G electrode was tested at different current densities in order to survey the rate performance of CoMoO4@G material. As shown in Fig. 5d, the sample delivers specific capacities of 1103.0, 990.0, 909.3, 829.2 and 697.7 mA h g−1 at 100, 200, 500, 1000 m and 2000 mA g−1, superior to pure CoMoO4 nanospheres. When the current density reduced to 100 mA g−1, the capacity can return to be 1132.7 mA h g−1.

Electrochemical impedance spectroscopy (EIS) of pure CoMoO4@G nanospheres and CoMoO4@G composites fitted using an equivalent circuit was also carried out to examine the improved electrochemical performance. As we all know, every plot consists of a semicircle in the high-frequency region and a straight sloping line in the low-frequency. As seen in Fig. 6, the
high-frequency semicircle diameter of CoMoO$_4$@G is smaller than that of pure CoMoO$_4$. As a result, the CoMoO$_4$@G electrode possess enhanced electrochemical properties, the presence of graphene can improve the electrical conductivity as well.

**Conclusion**

In summary, porous CoMoO$_4$ nanospheres (about 400 nm in diameter) embedded in graphene sheets were successfully synthesized via a facile hydrothermal, calcination and graphene-coating approach. When tested as an anode for LIBs, the CoMoO$_4$@G electrode exhibited outstanding cycling performance (783 mA h g$^{-1}$ over 150 cycles at a current density of 500 mA g$^{-1}$), and rate capacity (1103.0, 990.0, 909.3, 829.2 and 697.7 mA h g$^{-1}$ at 100, 200, 500, 1000 m and 2000 mA g$^{-1}$). The good electrochemical performance can be attributed to the synergistic effect of porous structure and well-defined graphene-coating design. The utilization of porous architecture can shorten the lithium ion diffusion distance and restrain the volume change, enhancing the space for both Li$^+$ and electron transport. In addition, the graphene layer can effectively maintain the stability of CoMoO$_4$ nanospheres and improve the electric conductivity, which can improve the cycling and rate performances.

**Conflicts of interest**

There are no conflicts to declare.

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