Ultrathin Two-Dimensional Metal Oxides for Advanced Electrochemical Energy Storage

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Ultrathin Two-Dimensional Metal Oxides for Advanced Electrochemical Energy Storage

This thesis is presented as part of the requirements for the Award of the Degree of

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by

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APRIL 2018
I, Yang Zheng, declare that this thesis, submitted in fulfilment of the requirements for the award of Doctor of Philosophy, in the Institute for Superconducting and Electronic Materials, School of Mechanical, Materials and Mechatronic Engineering, Faculty of Engineering and Information Sciences, University of Wollongong, is wholly my own work unless otherwise referenced or acknowledged. This document has not been submitted for qualifications at any other academic institution.

Yang Zheng

17/04/2018
DEDICATION

To my family and friends who always stand by me.
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Rechargeable batteries have been recognized as one of the most promising energy storage systems for the wide applications ranging from consumer electronics to electric transport. The great success achieved in the mature market of commercialized Li-ion batteries motivates us to explore advanced energy storage techniques to meet the ever-increasing energy demand of our society, especially in the areas require high-energy density. The traditional battery technology could not provide reliable high energy density and satisfied cycle life, limited by the current electrode materials and preparation process, however, severely impede its large-scale practical application. Therefore, exploring novel electrode materials with high capacity to break the bottleneck of development next-generation battery technology is urgently needed. It is well established that 2D structures could be fantastic candidate materials for energy-related applications, due to the distinctive properties, such as large surface areas, rapid ion/electron diffusion kinetics, abundant active sites and good mechanical strength, which may greatly enhance the electrochemical properties, especially the high-rate capability and long-term cycling stability. Furthermore, the conversion/alloying-based anode materials, such as metal oxides typically have much higher theoretical specific capacity, thus leading to higher energy density than commercial graphite electrodes. Hence, this doctoral work will mainly focus on the rational design and controllable synthesis of novel 2D metal oxide materials and their hierarchical structure assembled by 2D building blocks for energy storage applications. More specifically, by employing the facile moderate “bottom-up” approach, a series of metal oxides, including the 3D hierarchical
ultrathin $\delta$-Bi$_2$O$_3$ nanosheets, atomically thin Bi$_2$MoO$_6$ nanosheets and the hierarchical porous NiO/$\beta$-NiMoO$_4$ heterostructured microspheres have been successfully synthesized and used as anode materials towards lithium ion batteries. Impressively, those as-prepared 2D electrode materials exhibited superior reversible capacity, excellent high-rate capability and good long cycling stability, which are much better than those of corresponding bulk counterparts. In addition, to further deeply understand the mechanism of enhancement Li-ion storage properties, the DFT calculation and the in-situ synchrotron XRPD techniques have been applied to analyse the reaction dynamics and the evolution of crystal structure during the charging/discharging processes. It is believed that the excellent electrochemical performance benefits from the strong interface effect, the unique 2D ultrathin configuration, and the superior structural stability of the crystal.
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<tr>
<th>Abbreviation</th>
<th>Full name</th>
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<tbody>
<tr>
<td>a.u.</td>
<td>Arbitrary unit</td>
</tr>
<tr>
<td>2D</td>
<td>Two-dimensional</td>
</tr>
<tr>
<td>3D</td>
<td>Three-dimensional</td>
</tr>
<tr>
<td>BET</td>
<td>Brunauer-Emmett-Teller</td>
</tr>
<tr>
<td>CMC</td>
<td>Carboxymethyl cellulose</td>
</tr>
<tr>
<td>CNTs</td>
<td>Carbon nanotube</td>
</tr>
<tr>
<td>CV</td>
<td>Cyclic voltammogram</td>
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<tr>
<td>DEC</td>
<td>Diethyl carbonate</td>
</tr>
<tr>
<td>EC</td>
<td>Ethylene carbonate</td>
</tr>
<tr>
<td>EDS</td>
<td>Energy dispersive X-ray spectroscopy</td>
</tr>
<tr>
<td>EES</td>
<td>Electrical energy storage</td>
</tr>
<tr>
<td>EIS</td>
<td>Electrochemical impedance spectroscopy</td>
</tr>
<tr>
<td>EV</td>
<td>Electric vehicle</td>
</tr>
<tr>
<td>FEC</td>
<td>Fluoroethylene carbonate</td>
</tr>
<tr>
<td>FESEM</td>
<td>Field-emission scanning electron microscopy</td>
</tr>
<tr>
<td>HRTEM</td>
<td>High-resolution transmission electron microscopy</td>
</tr>
<tr>
<td>JCPDS</td>
<td>Joint Committee on Powder Diffraction Standards</td>
</tr>
<tr>
<td>LIBs</td>
<td>Lithium ion batteries</td>
</tr>
<tr>
<td>MWCNTs</td>
<td>Multi-walled carbon nanotubes</td>
</tr>
<tr>
<td>NMP</td>
<td>1-methyl-2-pyrrolidinone</td>
</tr>
<tr>
<td>PAA</td>
<td>Polyacrylic acid</td>
</tr>
<tr>
<td>PC</td>
<td>Propylene carbonate</td>
</tr>
<tr>
<td>PVDF</td>
<td>Polyvinylidene fluoride</td>
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<tr>
<td>GO</td>
<td>Graphene oxide</td>
</tr>
<tr>
<td>RGO</td>
<td>Reduced graphene oxide</td>
</tr>
<tr>
<td>Acronym</td>
<td>Description</td>
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<tr>
<td>---------</td>
<td>-------------</td>
</tr>
<tr>
<td>SAED</td>
<td>Selected area electron diffraction</td>
</tr>
<tr>
<td>SEI</td>
<td>Solid electrolyte interphase</td>
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<td>Scanning electron microscopy</td>
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<tr>
<td>STEM</td>
<td>Scanning transmission electron microscopy</td>
</tr>
<tr>
<td>HAADF</td>
<td>High-angle annular dark-field</td>
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<tr>
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<td>Transmission electron microscopy</td>
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<td>X-ray photoelectron</td>
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<td>X-ray diffraction</td>
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<td>Electron paramagnetic resonance</td>
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<td>ESR</td>
<td>Electron spin resonance</td>
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List of Symbols

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<th>Unit</th>
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<tr>
<td>θ</td>
<td>Peak position of XRD</td>
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</tr>
<tr>
<td>C</td>
<td>Charge or discharge rate</td>
<td>C</td>
</tr>
<tr>
<td>d</td>
<td>Lattice spacing</td>
<td>nm</td>
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<tr>
<td>I</td>
<td>Current</td>
<td>mA</td>
</tr>
<tr>
<td>m</td>
<td>Active material weight</td>
<td>g</td>
</tr>
<tr>
<td>N</td>
<td>Avogadro's number = 6.022 × 10^{-23}</td>
<td>mol^{-1}</td>
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<tr>
<td>P/P₀</td>
<td>Relative pressure</td>
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<tr>
<td>PD</td>
<td>Power density</td>
<td>W L⁻¹</td>
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<tr>
<td>Q</td>
<td>Specific capacity</td>
<td>mA h g⁻¹</td>
</tr>
<tr>
<td>R</td>
<td>Resistance</td>
<td>Ω</td>
</tr>
<tr>
<td>SBET</td>
<td>Specific BET surface area</td>
<td>m² g⁻¹</td>
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<tr>
<td>SE</td>
<td>Specific energy</td>
<td>Wh kg⁻¹</td>
</tr>
<tr>
<td>SP</td>
<td>Specific power</td>
<td>W kg⁻¹</td>
</tr>
<tr>
<td>t</td>
<td>Time</td>
<td>s</td>
</tr>
<tr>
<td>T</td>
<td>Temperature</td>
<td>K or °C</td>
</tr>
<tr>
<td>V</td>
<td>Voltage</td>
<td>volt</td>
</tr>
<tr>
<td>η</td>
<td>Coulombic efficiency</td>
<td>%</td>
</tr>
<tr>
<td>λ</td>
<td>X-ray wavelength</td>
<td>Å</td>
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CHAPTER 1 INTRODUCTION

1.1 General background

Energy shortage and environmental pollution are still regarded as the two major challenges to our world.\textsuperscript{[1]} With the growing demand for energy consumption, clean and renewable energy sources are critically important to realize the energy requirement and sustainable development of our society. Therefore, high-performance energy storage systems are urgent needed to enable efficient, versatile, and environmentally friendly uses of renewable energy.\textsuperscript{[2]} Among various energy storage devices, rechargeable batteries have been considered as one of the most promising technologies to store and utilize electricity.\textsuperscript{[3–5]} Lithium-ion batteries, since the first successful commercialization in 1991, have become the most popular electrochemical energy storage devices, which have overwhelmingly dominated the power source markets of advanced consumer electronics, electric vehicles and even the grid-scale energy storage, owing to its high energy density, no memory effect and light weight.\textsuperscript{[6–8]} Over the past decades, the development of advanced lithium-ion batteries experienced a bottleneck, because the existing commercial graphite anodes are approaching their limits in terms of the theoretical specific capacity and cycling stability, which extremely impedes the practical applications in the markets of electric vehicles and large-scale energy storage.\textsuperscript{[9–11]} Hence, rational design and preparation of novel electrode materials with high energy density and superior cycling stability are important for the battery research.
Ultrathin two-dimensional materials will offer numerous advantages for electrochemical energy storage and conversion due to the fast charge transfer kinetics, highly accessible surface area, and tunable electronic and optical properties. Since the pioneering work on graphene preparation, some advancement has been achieved in exploring other 2D ultrathin materials.\textsuperscript{[12–14]} Nonetheless, such materials and endeavour are basically confined in the fabrication of ultrathin 2D crystals by mechanical exfoliation or chemical vapour deposition processes, with low yield and redundant procedure.\textsuperscript{[15–18]} It is still a great challenge to fabricate the 2D ultrathin nanosheets with a non-layered structure. Furthermore, the electrochemical reaction mechanism and the relationships between the 2D ultrathin materials and their crystal structure/electronic structure are not clear.

\textbf{1.2 Objectives of the research} 

Herein, this doctoral work focuses on achieving high performance electrode materials for high-energy rechargeable batteries via the interface engineering of novel 2D ultrathin materials. In this doctoral thesis, a series of ultrathin 2D metal oxides nanosheets have been fabricated through the general and feasible wet-chemical synthesis strategy (bottom-up approach). When employed as anode materials for rechargeable batteries, these as-prepared anode materials exhibited enhanced electrochemical performance, in terms of superior reversible capacity, good cycling stability and excellent high-rate capability, which can be attributed to the superior structural properties of 2D materials, such as the high specific surface area, short diffusion path of ions, abundant chemically active sites and stable crystal structure. Moreover, the DFT calculations have been conducted to investigate the changer transfer dynamics during the electrochemical reactions, such as the
migration energy barrier of lithium ions in the ultrathin nanosheets and the *in-situ* techniques, including the operando synchrotron X-ray powder diffraction (PD) have been applied to deeply study the charge transfer mechanism in the 2D materials for rechargeable batteries.

### 1.3 Thesis structure

Chapter 2 briefly introduces some general background knowledge on electrochemical energy storage systems, such as the historical development, prospects and challenges of rechargeable batteries. The important battery components, including electrode materials, electrolyte, binders and additives also have been discussed. Moreover, the recent research progress on exploring advanced anode materials for next-generation rechargeable batteries has been summarized, and the future outlook on high-energy conversion/alloying-type anodes for advanced energy storage systems also been proposed.

Chapter 3 shows the employed experimental and characterization methods in this thesis, including the details of used chemicals, synthesis strategies, materials characterization techniques, and electrochemical performance evaluation methods.

In Chapter 4, the 3D hierarchical ultrathin δ-Bi₂O₃ nanosheets have been synthesised through a facile hydrothermal synthesis approach. When used as anode material for lithium ion batteries, the as-prepared ultrathin δ-Bi₂O₃ nanosheets exhibited much higher reversible capacity, rate capability and cycling stability than the corresponding Bi₂O₃ bulk electrode. The significantly enhanced electrochemical Li storage properties can be ascribed to impressive structural features of 3D hierarchical structures assembled from the ultrathin 2D nanosheets, which can not only retain the
intrinsic properties of 2D atomic-thin nanosheets, but also provide other structural advantages at different size scales, such as large dimensions, accessible porous systems, large void spaces and high surface area, thus showing promising prospects for energy-related applications.

In Chapter 5, we developed a powerful multiscale coordinated strategy to design and synthesize advanced electrode materials for electrochemical energy storage, including synergistic modulation of the dimensionality, composition, atomic arrangement, and interfaces. By employing the bottom-up approach, the atomically thin Bi$_2$MoO$_6$ nanosheets have been acquired and achieved outstanding high-rate cycling performance toward Li-ion batteries. To further understand the mechanism of the enhancement of lithium storage, DFT calculations and in-situ synchrotron XRPD analysis have been carried out. It has been found that the excellent electrochemical performance could benefit from the strong electric-field effect within the crystal, the unique 2D ultrathin configuration, and the superior structural stability.

In Chapter 6, porous hierarchical NiO/β-NiMoO$_4$ heterostructured microspheres have been fabricated via a simple hydrothermal method followed by a calcination process. In such heterostructure, the two phases of NiO and β-NiMoO$_4$ were homogeneously dispersed at the nanoscale in the hybrid NiO/β-NiMoO$_4$ electrode. During the electrochemical evaluation, the prepared NiO/β-NiMoO$_4$ heterostructured microspheres presents much better lithium ion storage performance than those of pure phase of NiMoO$_4$ and NiO. Benefiting from the synergetic effect of complex components and the special porous hierarchical architecture, which can not only accelerate the Li$^+$ ion diffusion, but also maintain the structural integrity, the
constructed hierarchical NiO/β-NiMoO₄ heterostructure shows good capacity retention and outstanding long-term cyclability for Li-ion batteries.

Chapter 7 systematically summarizes the conducted work in this doctoral thesis and provides some prospects for the development of novel 2D materials and the applications in energy-related areas.

1.4 References


CHAPTER 2 LITERATURE REVIEW

2.1 General background

Nowadays, sustainable electrochemical energy storage system (SEES) plays an important role in many fields relevant to our daily lives ranging from portable electronics, to electrical transportation, and the renewable energy storage sector. After the first successful commercialization of the rechargeable carbon/LiCoO$_2$ cell by Sony in 1991, lithium-ion batteries (LIBs)$^{[1]}$, consisting of cathode, anode, lithium-ion conducting electrolyte, and separator have become the most popular electrochemical energy storage devices, which have overwhelmingly dominated the power source markets of advanced consumer electronics including laptop computers, digital cameras, smart phones, and even electric vehicles, by taking those significant advantages of LIBs, including high electrochemical energy density (high voltage and large capacity), no memory effect, light weight, and good safety. Meanwhile, in the 21$^{\text{st}}$ century, with the problems of increasing greenhouse effect and environmental pollution from the excessive use of ever-decreasing resources of fossil fuels, there is a growing interest in utilizing renewable energy resources such as solar energy, wind, biomass, geothermal power, as well as others for a more sustainable society. Nevertheless, because of the intermittent and variable nature of these renewable energy sources, a large-scale sustainable energy storage system is highly needed to collect, transmit, and distribute this energy effectively. Among above mentioned various energy storage technologies, electrochemical energy storage system based on rechargeable batteries has considerable advantages because of their high efficiency.
During charge-discharge trips, flexible power output, long and stable cycle life, and low maintenance. LIBs have also been applied to realize smart grids over the past several years. Many large-scale LIBs with energy storage at the megawatt-hour (MWh) level have been constructed or are planned for construction for EES\textsuperscript{[2]}.

During the past several decades, tremendous efforts have been conducted into improving the performance of LIBs by optimizing the electrode structure and the electrolyte composition, however, the development of high energy LIBs has encountered a bottleneck.\textsuperscript{[3–5]} Particularly, considering its ever-growing energy consumption in the fields of electric transport and grid-scale energy storage, current commercialized LIBs based on the traditional graphite anode cannot satisfy the increasing high energy needs, since the existing commercial graphite anodes are approaching their limits of energy density and power density. Hence, developing desirable electrode materials for high energy LIBs is still an urgent need for their practical application. Generally, there are three different kinds of electrochemical reaction mechanisms for traditional anode materials in LIBs, as shown in Figure 2.1.\textsuperscript{[6]} Unlike the intercalation-type carbonaceous and Ti-based materials, Li ions storage based on the conversion reaction mechanism or alloying reaction mechanism can be regarded as the main research fields in many potential anode materials, with theoretical capacities two or three times higher than for intercalation-type anodes, making them highly promising for application in high-energy LIBs. Considerable research has recently been conducted on high-rate capacity anode materials based on the alloying or conversion reactions progresses, as shown in Figure 2.2.\textsuperscript{[7]}
Figure 2.1 Schematic representation of the different reaction mechanisms observed in various electrode materials for lithium batteries. Black circles: voids in the crystal structure, blue circles: metal, yellow circles: lithium.\textsuperscript{[6]}

Figure 2.2 Schematic illustration of advanced anode materials for the next-generation lithium batteries.\textsuperscript{[7]}
Generally, huge volume variation that occurs during the charging/discharging processes, which can reach higher than 300%, could be the main challenge associated with the conversion and alloying-based anode materials for LIBs. By comparison, the intercalation-type anodes usually possess a much lower volume change of less than 120%. Such large volume change during the electrochemical reaction process could easily cause the pulverization of electrode materials, thus inducing the exfoliation of electrodes from the current collector and loss of electrical connectivity between the active materials. As a result, quick capacity decay during cycling will take place for such conversion or alloying-type electrodes in LIBs. Low coulombic efficiency may be another obvious drawback for such types of electrodes, which also seriously hampers their use in practical LIBs. Under working potentials lower than 1.0 V, is the main cause of low coulombic efficiency can be concluded as two main reasons, i) electrochemical reactions would take place between two fresh electrode materials, ii) the organic electrolyte leading to the formation of the solid-electrolyte interphase (SEI) film. Normally, the contact between two electrode materials and the liquid electrolyte can be prevented by the formed SEI film, and an improved coulombic efficiency may then appear during the following galvanostatic charge-discharge processes. Nevertheless, the large volume variation in the conversion or alloying-type electrode materials during cycling could dynamically cause damage to the SEI film, leading to the unveiling of new fresh surface of electrode to the electrolyte. This would induce the electrode-electrolyte interface reactions to take place all over again, thus lowering the coulombic efficiency during the subsequent cycling process. Hence, considerable research has recently been conducted in order to solve these issues, including the design of innovative electrode architectures and the development of new electrode binders and conductive additives,
in order to reduce the ions diffusion distance, provide sufficient buffer space, and suppress electrode pulverization. For instance, a useful and effective strategy to improve the specific capacity and rate performance is nanostructure design by providing more active sites and reducing the diffusion distance for ions. Nano-designing also can help to release the structural stress and overcome the volume changes of the electrodes. On the other hand, nanomaterials will lead to higher inter-particle resistance and decrease the electrical connection among the particles. It was also observed that the electrolyte has a major impact on the electrochemical performance of conversion or alloying-type anodes for batteries.

In this literature review, the recent advances in the progress of high-capacity anode materials (metals, metal oxides and metal sulfides) for high-energy rechargeable batteries, in terms of materials composition, the fabrication of nanostructures, the relationship between the materials composition and morphology and the electrochemical performance, as well as the reaction mechanism during the charging/discharging progresses will be elaborately summarized. The current progress in the development of advanced anodes for high-energy rechargeable batteries through the optimization of anode additives, including the binder and conductive additives, and the electrolyte is also described. In addition, the future outlook on advanced conversion/alloying type anodes for next-generation energy storage systems will also be addressed, and potential research directions are proposed.

2.2 Metals and alloys

Alloying materials in IVA and VA group of periodic table (such as Si, Ge, Sn, Sb) have received tremendous attention as anode materials for rechargeable batteries,
because those alloying type electrodes can react with lithium to develop various Li-metal-alloy phases, thus generating superior capacities compared to those of carbon-based (372 mA h g\(^{-1}\)) and Ti-based materials (< 340 mA h g\(^{-1}\)).\(^{[8-13]}\) However, significant volume change of the electrode can be regarded as the main issue for alloying type of electrode materials, resulting in the destruction of the structure and loss of conductivity.\(^{[14-16]}\) The aim of current research on such alloy-type anodes is to design the nano-architecture of the metal electrode by tailoring the particle size or forming a composite to suppress the volume changes during electrochemical reactions, while further optimization by the formation of an intermetallic alloy and sensitive characterization of the structural evolution during the reaction with Li will offer another approach to improve the expression in electrochemical batteries, especially its long-term cycling life.

2.2.1 Si-based anode materials

Silicon (Si) has been regarded as the most hopeful and potential anode candidate for LIBs, because of it owns ten times higher theoretical capacity than commercial graphite (about 4200 mA h g\(^{-1}\)), low discharge potential (< 0.5 V versus Li/Li\(^+\)) and low manufacturing cost.\(^{[17,18]}\) Nevertheless, the further practical and industrial application of Si-based electrode materials is seriously limited by its significant volume change (~300%) during the lithiation/delithiation cycles, resulted in the pulverization failure and rapid capacity fading.\(^{[19,20]}\) Many attractive strategies have been suggested to optimise the macroscale structures and enhance the performance of Si-based electrodes to address the inherent structural degradation problems.\(^{[21,22]}\) It has been proved that nanostructure engineering is a promising method to improve performance of Si-based anodes for LIBs.\(^{[23-25]}\) In the constructed Si-based
nanomaterials electrodes, the lithiation-induced mechanical stresses could be easily relaxed because of the available surrounding free space/voids combined with the small particles size, thus minimizing the pulverization of the structural integrity of the electrode materials and improving its cycling stability.\textsuperscript{[26]} On the other hand, surface coatings are shown to be an effective way to address the issues of unstable and fragile SEI layers and low electrical conductivity of Si-based electrodes for dramatically enhancing the cycling ability for lithium-ion batteries.\textsuperscript{[27]} As shown in Figure 2.3, Cheng \textit{et al.} investigated the structural variation of the individual Si nanoparticles and the confinement effect of the carbon nanotubes (CNTs) during the lithiation/de-lithiation processes via the in situ transmission electron microscope.\textsuperscript{[28]} As can be seen from the results, the multiwall of CNTs can effectively restrict the volume expansion (\textasciitilde 180\%) of the lithiated Si NPs and the CNTs can well accommodate this volume expansion without breaking its pristine tubular structure. The Si NP-filled CNTs structure showed an enhanced reversible lithium storage capacity and desirable high rate capability during the charge/discharge processes, since the pulverization and exfoliation of the Si NPs confined in CNTs have been efficiently prevented. Based on the “double-shell” concept, Yu \textit{et al.} prepared a novel structure that consists a double carbon shells coated Si single nanoparticles anode, exhibiting a good electrochemical capacity of 1802 mA h g\textsuperscript{−1} at a current rate density of 0.2 C, superior rate capability and excellent cycling performance up to 1000 cycles.\textsuperscript{[29]} Yang \textit{et al.} found that encapsulated commercial Si nanoparticles with the amorphous titanium oxide shell (\textasciitilde 3 nm) can greatly improve the cyclability of LIBs, since the TiO\textsubscript{2} coated shells is amorphous state and will offer superior volume buffering properties compared to crystalline TiO\textsubscript{2} layers.\textsuperscript{[30]} In order to enhance the volumetric capacity and degrade the cost of Si-based electrodes in industrial scale,
Cui and co-workers fabricated a novel nonfilling carbon-coated porous silicon micro-particle, which shown improved cycling stability with high reversible specific capacity (~1500 mA h g\(^{-1}\), 1000 cycles) at the high rate of C/4. The areal capacity can reach above 3 mA h cm\(^{-2}\) without obvious capacity decay after hundreds cycles.\(^{[31]}\) Recently, our group also demonstrated an all-integrated silicon anode with high capacity, good rate capability and super long-term cycling performance via synergistic effects between the double shelled-yolk-structured silicon and the robust binder system (Figure 2.4).\(^{[32]}\) The silicene flowers constructed by intrinsically interconnected silicene nanoplates with different spatial orientations could exhibit enhanced gravimetric capacity (2000 mA h g\(^{-1}\) at a much higher current density of 0.8 A g\(^{-1}\)), high volumetric capacity (about 1800 mA h cm\(^{-3}\)), excellent rate capability (950 mA h g\(^{-1}\) at 8 A g\(^{-1}\)), and remarkable cycling stability performance for LIBs (1100 mA h g\(^{-1}\) at 2 A g\(^{-1}\) over 600 cycles).\(^{[33]}\)
Figure 2.3 Possible dynamic structural transformations of single Si NP-filled CNT under electrochemical lithiation/delithiation. (a–d) Lithiation process of a Si NP-filled CNT material. The arrows in those images: (b)–(d) indicate the Li$^+$ transport pathways and the site where Li$_x$Si begins to form during lithiation process. (e–h) delithiation of the same Si NP-filled CNT. The arrow in image (f) shows the Li$^+$ transport direction during delithiation process. (i) illustrates the lithiation/delithiation process of Si NP-filled CNTs.\textsuperscript{[28]}
Figure 2.4 Proposed working mechanism of the all-integrated electrode and binding-energy calculation based on silicon/binder interaction. (a) The as-prepared double-shelled–yolk-structured silicon (CVSS) electrode with c-CMC-CA as binder, in which the chemical bonding between CVSS and the binder, and the cross-linking between CMC and CA are graphically presented. (b) Calculation of binding energy based on the relaxed models b1 (CO-OCH₃), b2 (SiO-OCH₃), and b3 (SiOH-H₃COOCH₃), representing the ester linkage between the carbon shell of CVSS and the c-CMC-CA binder, the covalent attachment between Si and the binder, and the hydrogen bonding between Si and the binder, respectively.\[32\]
2.2.2 Ge-based anode materials

During the past decade, another kind of promising electrode material-Ge-based materials have been tremendously studied as anodes for lithium-ion batteries, owning to its excellent electrical conductivity (100 times higher than silicon), fast Li\(^+\) diffusivity (400 times faster than in silicon) and excellent theoretical specific capacity (~1600 mA h g\(^{-1}\)) of Ge.\[^{34}\] However, obstacles including the pronounced volume changes, resulting in structural deterioration and capacity decay, and the aggregation of the Ge particles during cycling progresses in LIBs, leading to increased electrochemical impedance and longer Li ion diffusion paths for lithium-ions caused the inferior electrochemical performance of Ge-based materials for practical applications.\[^{35}\] To alleviate the adverse challenges, some strategies have been applied to optimize the electrochemical properties, such as structural modification,\[^{36,37}\] modification by surface coating,\[^{38,39}\] forming Ge-based alloys,\[^{40}\] and forming binary\[^{41}\] or ternary\[^{42}\] Ge-based composites.

As displayed in Figure 2.5, the fabricated novel Ge anode materials exhibited excellent lithium storage performance in half-type and full-type cells, by employing the nanostructured current collector (such as cobalt oxide nanowire array fabricated on general nickel foam) and setting an appropriate voltage cut-off window technic.\[^{43}\] Wang et al. designed an unique Ge nanowires-in-graphite tubes via the facile liquid assisted Ge/C synergetic confined growth method and achieved excellent LIBs performance in terms of both cyclic stability and rate performance, as shown in Figure 2.6.\[^{44}\] Li et al. developed the Ge@carbon cubes electrode by embedding germanium nanoparticles into nanoboxes-like carbon, which shown an impressive tap density and enhanced conductivity when compared to general carbon-
coated germanium bulks.\textsuperscript{[45]} The novel 3D nanostructure Ge coated with carbon materials can be obtained through a facile carbonthermal reduction method in an art atmosphere, which recently reported by Park’s group (Figure 2.7).\textsuperscript{[46]} The superior LIBs performance of 3D-Ge/C nanostructure is attributed to 3D nanoarchitecture of Ge/C, which exhibits a short solid-phase lithium diffusion distance, full Li\textsuperscript{+} accessibility, fast lithium ion transfer, and a high specific area for facilitating reactivity. In addition, Yang and co-workers reported a stable structure that contains a 3D interconnected porous nitrogen-doped graphene foam with encapsulated Ge nanoparticles@N-doped graphene yolk-shell materials (Ge-QD@NG/NGF) with high reversible specific capacity (1220 mA h g\textsuperscript{-1}). The material can hold a very ultra-high rate capability (over 800 mA h g\textsuperscript{-1} at 40 C) and long cycling capability for flexible LIBs (Figure 2.8).\textsuperscript{[47]} Recently, Prof. Guo \textit{et al.} designed a novel double-carbon shell strategy for synthesizing a Sn/Ge carbonaceous composites to relieve the volume changes of tin and germanium.\textsuperscript{[48]} The obtained Sn@C@Ge@C architecture presents outstanding electrochemical properties due to the unique double-shell structure.

\textbf{Figure 2.5} (a) Schematic of the assembled Ge/LiCoO\textsubscript{2} full-cell. (b) Optical image of a light-emitting diode (LED) lighted by the Ge/LCO full-cell.\textsuperscript{[43]}
Figure 2.6 (a) The dark-field TEM image of several nanowires under low-magnification. (b) LIB cyclic stability test of the obtained composite after 100 cycle’s measurement.[44]

Figure 2.7 Schematic diagram image illustrates the whole procedure to fabricate novel 3D-Ge/C nanostructure.[46]
2.2.3 Tin-based anode materials

Metallic tin-based anode materials have drawn much attentions as potential alternative anode materials for high performance Li-ion batteries, due to its high specific reversible theoretical capacity (992 mA h/g for Li$_{4.4}$Sn) and good electronic conductivity property. Nevertheless, the practical or industrial application of Sn-based anodes has been hindered by their poor electrochemical performance resulting...
from the lithiation-induced severe electrode fracture and rapid capacity decay. Furthermore, the thickness of formed solid electrolyte interphase (SEI) on the electrode surface is very large and the serious aggregation of Sn nanoparticles will lead to the sluggish reaction kinetics.\cite{49} In recent years, to further improve the performance under very high current and cycle lifespan of the Sn-based materials, substantial efforts have been made, especially the structural design and surface modification.\cite{50} For instance, Wang introduced the aerosol spray pyrolysis method to design the nano-Sn/C composites (about 10 nm Sn nanoparticles dispersed within a spherical-like carbon shell) for traditional Li-ion battery anodes.\cite{51} It was found that the obtained Sn/C nanoparticles anodes can provide exceeded 600 mA h/g even at an extremely high rate of 20 C, which seems much higher than those of previously reported results for Sn-based anodes. Chen et al. prepared the tin/carbon composites with ultrasmall tin particles (about 5 nm) delicately dispersed in the N-doped porous carbon network via the pyrolysis of organic-based material of Sn(Salen). When the obtained materials evaluated in Li-ion batteries as anode material, the ultrasmall Sn/C (5 nm) electrode presents excellent electrochemical performance, due to the synergistic effect of the ultra-small Sn nanoparticles and the native porous carbon network.\cite{52} Interesting, the composite anode of 3.5 nm Sn nanoparticles dispersed in the N-doped carbon was achieved through the hydrolysing, following pyrolyzing processes as well.\cite{53} Furthermore, Qin et al. constructed the 3D porous graphene networks anchored with Sn nanoparticles encapsulated with graphene shells of about 1 nm (Sn@G-PGNWs) through the traditional in situ chemical vapor deposition (CVD) growth technique (Figure 2.9). When this kind of material used as the anode for Li-ion battery, the obtained stable architecture exhibited superior rate performance under high current density and extremely stable long cycling life even
at high rates.\textsuperscript{[54]} The authors claimed that the unique 3D architecture is responsible for the outstanding electrochemical performance, since the graphene shells can retain the whole structure stability of the electrode and relieve the mechanical stress during cycling, while the interwoven 3D porous graphene networks can enhance the electron conductivity and maintain the whole mechanical flexibility. By optimizing the organic type of electrolytes used for Li-ion batteries, Eom and co-workers investigated the effect of a novel fluorine based additive-fluoroethylene carbonate (FEC) on the electrochemical properties and morphology of the prepared nano- and micro-sized bare Sn electrodes for Li-ion batteries (Figure 2.10). It was found that after adding the FEC into the electrolyte, an unsatisfactory protective and less-resistant SEI formed on tin nanoparticles during the \textit{in-situ} electrochemical SEI formation cycle. Moreover, according to the result, FEC can be regarded as a good oxidizing agent which can help to remove the highly oxidized carbon compounds, thus making a SEI thinner during the delithiation process. Interestingly, the high-quality SEI only can improve the rate-capability and capacity of nano-sized bare Sn electrodes, but not for the micro-sized Sn electrode, because the micro-sized materials with long lithium-ion diffusion distance are susceptible to decrepitation during repeated volume changes.\textsuperscript{[55]}
Figure 2.9 (a) Schematic illustration of the 3D Sn@G-PGNWs. (b) SEM image of 3D Sn@G-PGNWs. (c) HRTEM image of 3D Sn@G-PGNWs. (d) High rate cycle performance of the obtained electrodes of 3D Sn@G-PGNWs and Sn/C composites.
at different charge/discharge rates (0.2 to 10 C (1 C = 1 A/g) ) for about 340 stable cycles. (e) The cycling property of the 3D Sn@G-PGNW electrode at current densities of 0.2, 0.5, and 1 A/g for the initial six cycles and then 2 A/g for the following thousand cycles.\(^{[54]}\)

![Figure 2.10 Schematic of the formation and degradation mechanisms of micro-/nano-scaled Sn particles with high/low-quality SEI, showing the two dimensional cross-sectional images of 1\(^{st}\) lithiated, 1st delithiated, and cycled micro-/nano-Sn particles with/without FEC electrolyte additive.\(^{[55]}\)](image)

2.2.4 Sb-based anode materials

In addition to Sn, Sb-based electrode was also investigated as an alloying-type anode for rechargeable batteries. Similar to other alloy-type anode materials, the main problem of poor capacity retention during cycling hampered its commercial
Current approaches focus on the rational design of the materials to maximize the advantages of Sb anode, such as high capacity and appropriate voltage plateaus, while minimizing the volume expansion. The effect of particle size on the electrochemical performance of antimony-based anodes was also systematically investigated by Kovalenko et al. in both Li-ion and Na-ion batteries (Figure 2.11).[58] It has been found that the as-synthesized Sb nanocrystals with small particle size between 10 nm and 20 nm both show enhanced rate-capability and higher cycling stability when compared with the microcrystalline Sb anode. Particularly, the rate capacities of obtained 20 nm Sb particles are much better than both acquired 10 nm and bulk Sb anodes when tested under all C-rates (0.5–20 C), indicating that faster kinetics and more stable operation at higher current densities can be achieved with decreasing the primary Sb size to 20 nm, while further reducing to 10 nm or below may in fact be detrimental, as shown from the lowering of charge storage capacity by ca. 5% for Li-ions. Yang et al. confirmed the enhancement effect of TiO$_{2-x}$ to the Sb-based material in Li-ion batteries by constructing the double-walled Sb@TiO$_{2-x}$ nanotubes electrode (Figure 2.12).[59] In the obtained Sb@TiO$_{2-x}$ nanotubes electrode, the huge volume changes during cycling can be well accommodated, thus retaining the whole structural stable. Meanwhile, the oxygen vacancies generated during the calcination process under the Ar/H$_2$ environment could promote the charge-transfer dynamic, particularly at the interface area. In addition, Yu et al. designed and fabricated a novel hollow Sb@C yolk-shell spheres to greatly enhance the electrochemical performance of the Sb-based electrode materials towards Li-ion batteries (Figure 2.13).[60] Thanks for such superior yolk-shell microstructure, the additional obtained void space produced in these novel Sb@C yolk-shell particles could accommodate the volume change of inner Sb while retaining the structure of
the Sb@C material and forming a stable SEI film on the outside carbon layer, therefore, excellent lithium ion storage properties, including the high specific capacity, superior rate capability as well as long cycling performance have been achieved.

Figure 2.11 (a) A novel one-pot synthesis of monodisperse Sb nanocrystals with original TEM images showing narrow size distributions of below 11% and range from 10 to 20 nm. (b) Rate-capability tests under high current density of half-cells employing Sb anodes made from colloidal Sb NCs and from microcrystalline powders.\textsuperscript{[58]}
Figure 2.12 (a) The whole synthesis process of original double-walled Sb@TiO$_{2-x}$ nanotubes under facile method. Electrochemical performance, include (b) cycling performances and (c) high current density properties of the electrodes based on three materials: Sb@TiO$_{2-x}$, Sb, and TiO$_2$.$^{[59]}$
Figure 2.13 Dark-field TEM images (a) and EFTEM element mapping images (b–d) of hollow Sb@C yolk-shell spheres. (e) Super-long cycling performances of hollow-like Sb@C yolk-shell structured anode at 1 A g$^{-1}$.[60]

2.2.5 Bi-based anode materials

Although metallic Bi could storage lithium via the alloying reactions (formed Li$_3$Bi), there are quite few reports about the Bi-based anode materials for rechargeable ion batteries. This may be due to the relative lower theoretical gravimetric capacity (385 mA h g$^{-1}$) compared with other alloying-based anode materials, such as Sn and Sb. On the other hand, the high volumetric capacity (ca. 3800 mA h cm$^{-3}$) of Bi will highlight its potential as a promising anode material in practical applications of LIBs for electronic mobile devices.[61] By employing a facile synthetic strategy involving the hydrothermal growth of Bi$_2$S$_3$ NWs followed by thermal decomposition, Zheng et al. prepared the mesoporous carbon-coated Bi (Bi@C core–shell) nanowires. The obtained Bi@C core–shell nanowires exhibited much enhanced reversible Li$^+$ storage capacity and cycling performance, which could be ascribed to the increased
specific surface area and pore volume of the nanowires and the carbon shell, allowing accommodation of more lithium ions and retaining the structural stability.\cite{62} The sphere-like Bi@C nanocomposites have been fabricated via the aerosol spray pyrolysis procedure and used as anode materials for both Li and Na-ion batteries by Lai’s group. In such microspheres, Bi nanoparticles (with a size of 10–20 nm) were evenly distributed in the carbon matrix and achieved high specific capacity and good rate performance.\cite{63} Furthermore, since Bi and Sb have similar physiochemical properties and could form alloys at any molar ratio, Manthiram et al. designed the homogeneous alloys consisting of Bi and Sb via a facile high-energy mechanical milling with carbon. More specifically, the developed Bi$_{0.57}$Sb$_{0.43}$-C and Bi$_{0.36}$Sb$_{0.64}$-C anode materials exhibited electrochemical properties superior to those of their counterparts Bi-C and Sb-C in both LIBs and SIBs.\cite{64}

### 2.3 Metal oxides

Metal oxides have been one of the most studied types of anode material in LIBs for decades, since they could generate higher capacities compared with intercalation compounds and generally more satisfactory cycling performance compared with metal alloys. According to the potential electrochemical reaction mechanism, metal oxides can be generally classified into two types:\cite{65}

1. **Conversion reaction-type of transition metal oxides**

   Generally, transition metals, such as iron, cobalt, nickel, Copper, molybdenum and manganese are electrochemically inactive in the oxide, so metal oxides maybe react with Li$^+$ through a simple one-step conversion reaction.\cite{66-71}

   The conversion reaction mechanism is as follows:
\[
M_xO_y + 2ye^- + 2yLi^+ \leftrightarrow x [M]^0 + yLi_2O
\]

After the electrochemical reaction, the product consists of a uniform distribution of metal nanoparticles embedded in the Li_2O matrix. Although owning higher theoretical capacity than those of intercalation-type anodes (graphite and Ti-based anodes), these conversion-type metal oxides suffer from the unsatisfactory rate capability and insufficient cycling performance due to the poor electronic conductivity and massive volume change during the lithiation reaction. Generally, designing nanostructures of electrodes could greatly improve the electrochemical performance while combing with conductive materials will enhance their rate capability.

Iron oxides (Fe_2O_3 and Fe_3O_4) have been intensively investigated as potential electrode for rechargeable batteries due to their earth abundance and environmental friendliness.\(^{[72,73]}\) To improve the properties in LIBs, Kang et al. designed the bubble-nanorods-like Fe_2O_3-carbon nanofibers (Fe_2O_3-CNF) by combining the Kirkendall effect with the useful electrospinning method. The unique structure, in which the nanosized Fe_2O_3 spheres uniformly dispersed in the amorphous carbon substance, can not only inhibit the aggregation of Fe_2O_3 nanoparticles and retain the structural/electrical integrity of the composite during repeated cycling processes, but also accommodate the mechanical stress via the void spaces between the Fe_2O_3 bubbles and carbon matrix, thus exhibiting superior electrochemical performance (Figure 2.14).\(^{[74]}\) Yan et al. compared the electrochemical performance of amorphous and crystalline Fe_2O_3 anodes and observed a unique electrochemical behaviour and enhanced capacitive storage in the amorphous Fe_2O_3 electrode. Impressively, the amorphous Fe_2O_3 electrode exhibited excellent Li-ion storage properties, in terms of
the high-rate capacity, superior cycling stability and narrow voltage hysteresis. This work shows the significant potential of amorphous materials for the applications of energy storage.$^{[75]}$ To further improve the rate capability, Jiao et al. constructed the binder-free electrodes by growing the 3D hierarchical porous $\alpha$-Fe$_2$O$_3$ nanosheets on commercial copper foil used for Li-ion batteries.$^{[76]}$ The large contact area of electrode-electrolyte, short Li-ion transport distance and the capability to accommodate large volume changes contribute to the high stable capacity outstanding rate capability as well as excellent cycling stabilities. In addition, after combined with graphene, the as-prepared sandwiched composite of graphene-wrapped Fe$_3$O$_4$-graphene nanoribbons shown enhanced reversible cycling performance, high capacity and good rate capability.$^{[77]}$
Figure 2.14 (a) Schematic formation mechanism of bubble-nanorods-like Fe$_2$O$_3$-C composite nanofiber by Kirkendall-type diffusion. (b) Cycling performances of the bare Fe$_2$O$_3$ hollownanofibers and bubble-nanorod-structured Fe$_2$O$_3$-C composite nanofibers.$^{[74]}$

CuO is also a promising anode candidate due to its abundance, chemical stability, and nontoxic nature, and recent studies on cupric oxides have made great progress.$^{[78]}$ Fan et al. successfully designed and synthesized the novel CuO/Cu/GQD (graphene quantum dots) triaxial nanowires electrode for Li-ion batteries. The as-prepared electrodes present significantly fast and stable Li-ion storage properties, with higher reversible capacities and improved rate and cycling
stability than the nanowires without GQDs because of the unique Cu and GQD double layer enhancement. Additionally, the uniform hollow CuO octahedral doped with FeOOH has been used as anode in Li-ion batteries and demonstrated good performance (Figure 2.15).\textsuperscript{[79]} Moreover, in recent years, Ni-based anodes have received increasing research interests as well. For example, by anchoring NiO nanosheets on flat carbon hollow particles, the bowl-like hybrid structures have been designed and fabricated, which exhibited superior Li-ion storage performance in terms of high capacity, long term cycling stability and excellent rate capability (Figure 2.16).\textsuperscript{[80]} The ultrathin NiO nanosheets also achieved superior electrochemical properties when evaluated as anodes for Li- and Na ion batteries.\textsuperscript{[81]}

\textbf{Figure 2.15} (a) Typical field emission scanning electron microscopy (FESEM) image of F-CuO hollow octahedral. (b,c) Generally transmission electron microscopy (TEM) pictures of F-CuO hollow octahedral. (d) Cycling performance of F-CuO hollow octahedral like at a high current density of 1 A g\textsuperscript{-1}.\textsuperscript{[79]}
Figure 2.16 (a) Representative SEM and (b) Low-magnification TEM images of Ni-precursor@SPS nanoparticles; (c) FESEM and (d) TEM image of bowl-like NiO NSs@C nanoparticles; (e–g) elemental mapping (EDS) images of an individual bowl-like NiO NSs@C particle shown in (d).[^80] (h) SEM and (i) TEM images of the Nickel oxide nanosheets obtained from Ni(OH)$_2$ synthesized at 140 °C for 4 h.[^81]

Recently, orthorhombic Co$_3$O$_4$ demonstrated outstanding high-rate capability and good cycling performance for lithium storage. Yu et al. developed a facile template-directed strategy for the controlled synthesis of 2D assembly of Co$_3$O$_4$ nanoparticles (ACN) with unique holey architecture and changeable hole sizes (Figure 2.17).[^82] When used as anode for lithium and sodium ion batteries, the as-prepared holey ACN with 10 nm holes shown much better performance than the counterpart of ACN with 5 nm or 20 nm holes and conventional Co$_3$O$_4$ particles, which can be attributed
to the unique interconnected holey architecture promoting the fast charge/mass transport and maintaining the structural integrity. Atomically thin mesoporous Co$_3$O$_4$ nanosheets/graphene composite (ATMCNs-G) has been successfully obtained and evaluated as anode materials for LIBs.$^{[83]}$ Benefiting from the unique layer-by-layer structure in atomic scale of Co$_3$O$_4$/graphene, offering highly accessible surface areas, short lithium diffusion path, high electronic conductivity, stable electrode structure and pseudocapacitive interfacial storage, the prepared ATMCNs-G exhibited excellent specific retention, superior rate capability and ultra-long cycle life. Furthermore, the Co$_3$O$_4$ nanosheets with the in-plane nanopores and highly active exposed facets ($\{112\}$) also delivered good Li-ion storage properties, due to its unique morphological structures.$^{[84]}$

Figure 2.17 (a−c) STEM images of representative Co$_3$O$_4$ HACN (5 nanometer holes), HACN-10 (10 nanometer holes), and HACN (20 nanometer holes), respectively. (d) Cycling performance of the holey ACN with different pores distribution at 1000 mA/g.$^{[82]}$

(2) Alloy reaction-based metal oxides
When the metal element is electrochemically active, such as germanium, tin, antimony and bismuth, metal oxides can further react with Li\(^+\) via a electrochemical conversion reaction and a subsequent alloying reaction.\(^{[85–88]}\) The Li-alloy reaction mechanism is always as follows:

$$M_xO_y + 2ye^- + 2yLi^+ \rightarrow x[M]^0 + yLi_2O$$

$$M + ze^- + zLi^+ \leftrightarrow 2Li_xM$$

Among all of the active metal oxide anodes, tin oxides has been one of the most intensively investigated materials in rechargeable batteries due to its capability for facile nanostructured design, high theoretical capacity, and low potential.\(^{[89]}\) Previous works have shown that the anodic reaction of SnO\(_2\) proceeds in the following two steps:

$$SnO_2 + 4Li^+ + 4e^- \rightarrow Sn + 2Li_2O \quad (1)$$

$$Sn + xLi^+ + xe^- \leftrightarrow Li_xSn \quad (0 \leq x \geq 4.4) \quad (2)$$

However, similar to other kinds of alloy-type anode materials, SnO\(_2\) also suffers from huge volume expansion during repeated cycles with low capacity retention, while the irreversible conversion reaction leads to low columbic efficiency in first cycle (about 30–40%). Significant works have been conducted to improving the cycling stability and preventing capacity fading for SnO\(_2\)-based anode materials. The double-shelled yolk-shell-structured SnO\(_2\) anode material was synthesized by the scalable spray pyrolysis process and exhibited superior lithium storage capacities.\(^{[90]}\)

The freestanding web of SnSiO\(_{x+2}\)@G-250 nanocables have been rationally designed to achieve high-performance anode materials for Li-ion batteries. In such structure,
ultrafine SnO$_x$ evenly dispersed in the SiO$_2$ matrix and then ultrathin graphitic carbon grown ion the surface of SnSiO$_{x+2}$ nanofibers, hence, the issues of volumetric expansion and the Sn nanoparticles aggregation could be effectively suppressed.$^{[91]}$ Zhu et al. constructed a series of metal-tin oxide-Graphite (SnO$_2$-M-Graphite (M = Fe, Mn, Co)) ternary nanocomposites via two-step ball milling method and found that these composites can deliver high stable reversible capacities and superior high-rate capability (Figure 2.18).$^{[92]}$ Interesting, the obtained SnO$_2$-Fe-Graphite nanocomposite achieved the superior initial columbic efficiency of 88.6%, almost the highest values among reported works in SnO$_2$-based powder anodes. The authors claimed that the nanosized M grains can not only act as barriers to prevent the Sn coarsening, but also promote the decomposition of Li$_2$O since the reversion of M/Li$_2$O to MO needs the override of a much lower energy barrier than that of Sn/Li$_2$O to SnO$_2$, leading to an enhanced reversibility of conversion reactions in the SnO$_2$-M electrodes. Despite some achievements on improving the reversible capacity and cycling performance, boosting the power density is still great challenge for the practical applications of SnO$_2$-based electrodes. Considering this problem, Yan et al. developed the Sn-based alloying anodes with highly reversible, high-rate and cycle-stable Li-ion storage properties by combining the pseudocapacitive Li-ion storage and spatially confining electrochemical reactions in the electrode materials. Specifically, thanks for the rational design of SnO$_2$-Fe$_2$O$_3$-Li$_2$O nanocomposites and the optimal cut-off potential (0.005–1.2V), a high fraction of interfaces of Fe/Sn/Li$_2$O has been achieved, resulting in fast electron/Li ion transport among the large number of interface active sites of Sn (Figure 2.19).$^{[93]}$ To resolve the phase aggregation and cracking issues associated with the lithiation/delithiation processes in SnO$_2$–based anode materials, the highly conducting black SnO$_{2-x}$ have been
employed for Li-ion batteries (Figure 2.20). The as-prepared black SnO$_{2-x}$ with rich oxygen vacancies and enhanced electrical conductivity can allow tiny metal Sn particles to uniformly form in the Li$_2$O matrix during discharging, followed by metal particle oxidation during charging. These fine Sn precipitates are too small to crack and their intimate contact with Li$_2$O makes redox reaction facile in both directions.

**Figure 2.18** (a) Schematic for the high reversibility reactions in ternary SnO$_2$-M-graphite hybrids. Due to the thermally induced recrystallization and the driving force from repeated electrochemical stress, the nanosized Sn phases tend to coarsen to form larger grains. The Fe nanograins can act as barriers to impede the Sn coarsening during delithiation. (b) Cycling performance of the SnO$_2$-Fe-G, SnO$_2$-Mn-G nanocomposite in comparison with that of the SnO$_2$ milled-20 h at 0.2 and 2 A g$^{-1}$. \[92\]
Figure 2.19 Electrochemical properties of as-prepared SnO$_2$-Fe$_2$O$_3$-Li$_2$O films. (a) Rate cycling capacities of SnO$_2$-Fe$_2$O$_3$-Li$_2$O at various rate current densities. (b) Charge–discharge curves of SnO$_2$-Fe$_2$O$_3$-Li$_2$O at various specific currents. (c) Cycling performance of SnO$_2$-Fe$_2$O$_3$-Li$_2$O, SnO$_2$-Li$_2$O, and SnO$_2$-Fe$_2$O$_3$ at a current density of 1000 mA g$^{-1}$. (d) Charge-discharge profiles of SnO$_2$-Fe$_2$O$_3$-Li$_2$O at 1000 mA g$^{-1}$. (e) Cycling performance at high rate densities of 5000, 10000 mA g$^{-1}$ of SnO$_2$-Fe$_2$O$_3$-Li$_2$O.$^{[93]}$

Some attempts also have been made to explore other metal oxide anodes for rechargeable batteries. For instance, tube-like Sb$_2$O$_4$ submicron-structures and Sb$_2$O$_4$/rGO composite have been employed in LIBs,$^{[95,96]}$ however, the electrochemical properties are not satisfied, especially the high-rate capability and long-term cycling stability. Facile and universal strategies for rational design and
controllable synthesis of novel structures of Sb-based materials are still needed. Through a spray-pyrolysis process, Kang et al. fabricated a kind of amorphous GeO$_x$-anchored into reduced graphene oxide balls with a novel of sandwich structure, which shown superior reversible capacity and high charge capacity retention even after 1600 cycles.\textsuperscript{[97]} Interestingly, Cho et al. believed that the Li ions storage performance of GeO$_2$ nanoparticles can be attributed to the quantum confinement and the related effects during lithiation and delithiation. The authors further studied the size influence of the GeO$_2$ nanoparticles (\~2, \~6, \~10, and \~35 nm) by controlling the condition and compared their electrochemical properties for LIBs. It was observed that the GeO$_2$ nanoparticles with the size of \~6 nm exhibited the best electrochemical performance, while the smallest sized GeO$_2$ (about 2 nm) showed the worse electrochemical performance compared to the counterpart of the bigger sized one (about 6 nm). The unexpected result was ascribed to the smaller GeO$_2$ (\~2 nm) nanoparticles may hold inferior electrical conductivity resulting from its quantum confinement effect, which is also related to the increase in the resistance in charge transfer process (Figure 2.21).\textsuperscript{[98]}

As another kind of alloy reaction-based metal oxide, Bi$_2$O$_3$ anode materials also have received some research interests due to the high gravimetric (690 mA h g$^{-1}$) and volumetric capacities (6280 mA h cm$^{-3}$). For example, Luo et al. firstly prepared the binder-free p-Bi$_2$O$_3$/Ni foam by a facile polymer-assisted solution approach and investigated its electrochemical properties towards LIBs.\textsuperscript{[99]} The electrochemical properties for the obtained p-Bi$_2$O$_3$/Ni exceed those of the commercial Bi$_2$O$_3$ powder and the p-Bi$_2$O$_3$ (fabricated via the polymer-assisted solution method), due to the higher volumetric utilization efficiency, better connection between the active
materials and current collector, and shorter Li ion diffusion path. In order to reduce the issues of rapid capacity fading and large irreversible capacity loss resulting from the huge volume changes in Bi-based materials, three-dimensionally ordered macroporous (3DOM) β-Bi₂O₃ has been designed through a modified colloidal crystal templating method and exhibited higher specific capacities and better capacity retention than conventional β-Bi₂O₃ nanoparticles as anode materials for LIBs. More interestingly, a hierarchical Bi₂O₃-Bi₂S₃ heterostructure has been constructed by sulfurization of Bi₂O₃ nanosheets. Owning to the high surface areas, rich porosity, and unique heterogeneous phase, the fabricated Bi₂O₃-Bi₂S₃ nanostructure exhibited a high Coulombic efficiency, stable capacity delivery and remarkable rate capability, notably outperforming reported bismuth based materials. Apart from creating the heterostructure consisting of the metal oxide/metal sulphide, other design concept and strategy also has been developed to fabricate novel electrode materials, such as introducing alloying-type metals with a high conductivity and high capacity into the conversion-type transition-metal oxides, thus significantly optimizing the electrochemical performance. For instance, the hierarchical Sb₂MoO₆ architectures assembled from nanobelts have been prepared through a facile microwave-hydrothermal method and achieved superior electrochemical properties, which has been attributed to the synergistic interaction between both the active Sb- and Mo-species, based on the combination mechanism of alloying/dealloying and conversion reaction. Moreover, the in-situ generated MoOₓ and Li₂O matrix during the electrochemical reactions could efficiently accommodate the volume changes of the Li−Sb alloying/dealloying upon cycling, demonstrating the synergistic enhancement effect on Li storage performance. Recently, the 3D hierarchical porous Bi₂MoO₆ microspheres have been fabricated
and evaluated as anode for LIBs. Due to the unique structural advantages, the as-prepared anode exhibited superior lithium storage performance.\[^{103}\]

**Figure 2.20** Microstructural evolution. Schematic microstructure evolves during charging/discharging process of (a) SnO\(_2\) and (b) SnO\(_{2-x}\) electrodes. Processes (1–5) correspond to the (1–5) peaks in Figure 3d, and processes (2–5) constitute the reversible Sn → Li\(_x\)Sn → Sn → SnO\(_2\)/SnO\(_{2-x}\) cycle during charging/discharging.\[^{94}\]
Figure 2.21 (a) XRD patterns of the GeO$_2$ nanoparticles with different size range from $\sim$2, to $\sim$35 nm. (b) The UV spectra results show the calculated band gap value. (c) Cycle performances of the different sized GeO$_2$ nanoparticles at rates of 1 C.$^{[98]}$

Above all, most transition metal oxides with an electrochemically inactive metal element presented reversible capacities of less than 600 mA h/g and poor long-term cycling life. For alloy reaction-based metal oxides, although these metal oxides showed higher reversible capacity due to the activity of the metal elements towards alkali metal ions, pulverization of the electrode and loss of contact with the current collector induced by huge volume expansion would hinder their practical development. Tailoring the size down to below 10 nm or embedding the active electrode material in a 2D or 3D matrix may be effective, based on previous reports, for improving the reversible charge capacity and the cycling stability performance. Further understanding the interface behaviour between the electrode and electrolyte
during the charge/discharge processes may offer new insights for the design of nanostructures.

2.4 Metal sulfides

Recently, metal sulfides have attracted tremendous interests from researchers owing to their impressive electrochemical reactivity, as shown by such characteristics as long cycling life, and high power/energy density.\textsuperscript{[104,105]} Like the metal oxides, the Li-ion storage mechanisms in metal sulfides can be classified into three types: intercalation reactions, conversion reaction and alloying reaction. Especially, some layered metal sulfides of MS\textsubscript{x} (M = V, Mo, Sn, W, Zr, etc.) have been extensively studied due to their structure peculiarities and redox variabilities (Figure 2.22).\textsuperscript{[106–109]} Such layered metal sulphides, similar to graphite but with a much larger interlayer spacing, enables reversible Li ions intercalation/extraction without any significant volume change, thus maintaining stable structure and exhibiting superior electrochemical performance than other metal sulfides. Hence, recent advancement on these promising layered metal sulphides used as anode materials for rechargeable batteries will be summarized.
Figure 2.22 Structure of some typical layered transition metal sulfides (TMSs): (a) MoS$_2$ or WS$_2$, (b) ZrS$_2$ or VS$_2$, (c) VS$_4$ and (d) SnS$_2$.\[106\]

MoS$_2$ is a typical intercalation host for rechargeable batteries, which is composed of layers of molybdenum atoms coordinated to six sulfur atoms and has an interlayer spacing of approximately 6.2 Å, nearly double that of graphite (3.35 Å). Due to its laminar nature and weak van der Waals forces between adjacent layers, MoS$_2$ is inherently able to accommodate other larger metal cations such as Na$^+$ and Mg$^{2+}$ in addition to Li$^+$.\[110-112\] As a potential anode material for LIBs, MoS$_2$ has high theoretical capacity (about two times higher than graphite, 670 mA h g$^{-1}$). However, the low intrinsic electric conductivity between two adjacent layers leading to insufficient rate capability, while the shuttling effect of the intermediate polysulfide would cause poor cycling stability due to the electrochemical degradation of the electrode.\[113\] To circumvent these obstacles, Li et al. constructed the 2D MoS$_2$ and
mesoporous carbon (MoS$_2$/m-C) hybrid nanosheet superstructure with ideal MoS$_2$/m-C atomic interface. Interesting, benefiting from the ideal atomic interface contact between single-layer MoS$_2$ and mesoporous carbon, which can maximize the interface synergistic interaction between the MoS$_2$ and carbon sheets, the as-prepared MoS$_2$/m-C nanosheet shown excellent specific capacity (1113 mA h g$^{-1}$ at 400 mA g$^{-1}$) and outstanding high-rate capability (943 mA h g$^{-1}$ at 6400 mA g$^{-1}$). Furthermore, even after 500 cycles under the current density of 400 mA g$^{-1}$, it can be maintained at 1023 mA h g$^{-1}$ (Figure 2.23).\cite{114} Lou et al. designed the hierarchical MoS$_2$ tubular structures internally wired by carbon nanotubes to address these mentioned problems (Figure 2.24).\cite{115} Owning to its unique structural and compositional characteristics, the obtained CNT-wired MoS$_2$ tubular structures presents exceptional electrochemical properties. Recently, through an in situ sulfidation process, the 2D MoS$_2$-on-MXene heterostructures were synthesized. The introduced MXene could enhance the adsorption of Li and Li$_2$S during the intercalation and conversion reactions.\cite{116} In addition, flexible free-standing MoS$_2$/reduced graphene oxide composite (MoS$_2$-rGO) also has been fabricated to optimise the electrode structure and improve the electrochemical properties.\cite{117} To further advance the development of the MoS$_2$ materials as promising materials for LIBs, Guo and co-workers systematically studied the electrochemical reaction mechanism of MoS$_2$ based on experimental and theoretical combined methods, including the in situ and ex situ X-ray absorption spectroscopy techniques and density functional theory (DFT) calculations. It has been found that the conversion reaction of MoS$_2$ electrode is irreversible and the generated Li$_2$S can be converted to sulfur in the initial charge process. In the following cycles, Li$_2$S/sulfur becomes the main redox couple and contributes major reversible capacity. Additionally, because
of the insulating nature of the intermediate product (Li$_2$S and sulphur), a strong relaxation effect is observed during the cycling process (Figure 2.25).\textsuperscript{[118]}

**Figure 2.23** (a–c) Lithium ion storage at MoS$_2$/carbon atomic interface. The concept of rational design of the MoS$_2$/m-C nanosheet superstructure for creating idea MoS$_2$/C atomic interface to promote Li-ion storage. (d) The electrochemical performance of the obtained MoS$_2$/m-C nanosheet composite, MoS$_2$/G, exfoliated graphene nanosheets, and the traditional annealed MoS$_2$ materials at various current densities from 0.2 to 6.4 A g$^{-1}$. (e) Generally cyclability of the MoS$_2$/m-C hybrid nanosheet superstructure at 0.4 A g$^{-1}$ for hundreds cycles.\textsuperscript{[114]}
Figure 2.24 Schematic picture of the synthesis process by using tubular structures constructed from ultrathin nanosheets of the CNT-wired hierarchical MoS$_2$ (CNT/MoS$_2$ nanohybrid). (a) Illustration of the preparation procedure of the CNT/PAN tube-in-fiber structure via electrospinning method. (b) Schematic of the synthesis process for the CNT-in-tube structure. (I) A protective layer of CoS$_x$ growth on the CNT-in-fiber composite. (II) Formation of MoS$_2$ nanosheets on the composite accompanied by the removal of PAN, yielding a similar tubular structure. (III) Heating treatment of the hybrid to reduce the CoS$_x$ to Co nanoparticles. (IV) Acid treatment to remove Co particles to obtain a CNT/MoS$_2$ tubular structure. (c) Cycling performance of the CNT/MoS$_2$ tubular nanohybrid at 5000 mA g$^{-1}$ for 1000 cycles.$^{[115]}$
Figure 2.25 The proposed mechanism of the MoS$_2$ electrode during electrochemical reaction process. The intercalation reaction of MoS$_2$ is reversible, accompanied by an obvious phase transformation between 2H and distorted 1T phases.$^{[118]}$

Two-dimensional nanostructures of SnS$_2$ or SnS were also recognized as promising anode materials for rechargeable batteries. For instance, Yu et al. developed an electrostatic spray deposition technique to prepare the 3D porous interconnected SnS/carbon nanocomposite.$^{[119]}$ In such obtained structure, small nanorods of SnS (size from 10 to 20 nm) are embedded in amorphous carbon structure and further self-assembled into a 3D porous interconnected nanocomposite, then directly grown on titanium foil and used as the binder-free electrode for rechargeable batteries, exhibiting a high reversible capacity, rate capability, and long cycling stability for both lithium and sodium storage. By constructing a unique yolk-
shell-structured SnS powders with a distinctive SnS@void@SnS configuration, Kang et al. obtained superior electrochemical properties when used the SnS anode for Li-ion batteries.\cite{120} To understand the origin of the structural stability of SnS$_2$ electrode during electrochemical reaction, Chi’s group investigated the microstructural evolution of SnS$_2$ upon lithiation by using \textit{in situ} STEM/TEM imaging and EELS spectrum. It has been observed that, the crystalline SnS$_2$ can possess the initial lithium intercalation process, and after that, the following two-step reaction would undergo as follows: (1) irreversible formation of metallic tin phase and amorphous Li$_2$S phase; (2) the rate-determining step of reversible transformation of metallic Sn to Li–Sn alloys. Interestingly, a self-assembled composite framework formed during the irreversible conversion reaction was firstly observed. In this self-assembled framework, crystalline Sn nanoparticles are homogeneously embedded within the amorphous Li$_2$S “matrix”, which can greatly suppress the agglomeration of Sn nanoparticles upon cycling, thus offering desired structural tolerance and ensuring a sufficient electron pathway (Figure 2.26).\cite{121}
Figure 2.26 (a–d) Initial lithium ion intercalation process of SnS$_2$. Time-series showing the volume change of SnS$_2$ nanoplates (marked by the red dashed lines) supported on a Gr-coated lacey carbon film. (e) Schematic representation of the lithiation reaction for SnS$_2$ nanocrystals. Pink, Sn; red, S; green, Li; blue matrix, Li$_x$S; purple, Li$_x$Sn.$^{[121]}$
In addition, VS$_4$-based anodes also have been studied for rechargeable batteries. Cho et al. investigated the Li reaction mechanism of prepared VS$_4$–reduced graphene electrode and proposed a conversion reaction mechanism with an irreversible phase change during the initial discharge/charge progresses.$^{[122]}$ The VS$_4$ nanoparticles rooted by a-C coated MWCNTs structure have been designed for rechargeable batteries and shown outstanding lithium ion storage properties, in terms of both cycling stability and rate capability.$^{[123]}$ Interesting, through a CVD process, the structure of ultrauniformly distributed ReS$_2$ nanowalls on 3D graphene foam has been synthesized and exhibits a good cycling performance and high-rate capability because the extremely weak vdW between the ReS$_2$ layers is beneficial to boosting electrode performance (Figure 2.27).$^{[124]}

Figure 2.27 Schematic illustration of the weak interlayer interaction of ReS$_2$, compared with MoS$_2$ and graphite.$^{[124]}$
The majority of metal sulfide electrodes can offer higher capacity, higher energy density, and more stable cycling performance than their metal oxide counterparts in rechargeable batteries, in virtue of the greater stability of the Li$_2$S compared with Li$_2$O in the LIBs, and there are lower reaction voltage plateaus for metal sulfides compared with metal oxides. Nevertheless, the large volume expansion of metal sulfides occurring during insertion/de-insertion processes and their inherent low conductivity still degrade their activity. Therefore, a variety of available methods, for example, design of nanostructures and optimization of the working voltage window and electrolytes are required to develop high-performance metal sulfide electrodes for rechargeable batteries.

In this literature review, the recent research progress on high performance anodes for rechargeable batteries have been summarized, including the metals/alloys, metal oxides, and metal sulphides. Since these anode materials can store alkali metal ions via the conversion, alloying, or combined reactions, they typically have much higher theoretical capacity compared with the insertion-type materials and thus showing great potential for the commercialization of rechargeable batteries for applications in large-scale energy storage. The concerns associated with those potential anodes, such as low capacity utilization, inferior rate capability, poor cycling life resulting from the great volume changes, and sluggish ion diffusion dynamics also have been discussed, while the effective approaches, ranging from electrode material structural design, and electrolyte optimization to voltage window control, to further improve the electrochemical properties have been reviewed. Specifically: 1) electrode material structural design, such as nanocrystallization, surface modification and forming hybrids with other materials can effectively accommodate and restrict the
large volume changes during the insertion/de-insertion progresses, improve the initial reversible capacity, and shorten the ion/electron diffusion distance, and thus improving the energy density, power density and cycling lifespan; 2) Choosing proper electrolytes, for example, high-quality SEI films formed in the optimised electrolytes with FEC additive will normally provide a much higher initial coulombic efficiency and ultralong cycling life for metal sulphides anodes; 3) Controlling the voltage range can limit the insertion/de-insertion reactions to within the conversion step and inhibit the alloy step, which will reduce the volume change and contribute capacity, thus extensively improving the high-rate and long-term cycling performance. Although such impressive progress has been achieved on the anode materials for rechargeable batteries, there are still huge challenges. Generally, the nanostructured anode materials have low tap density, which leads to poor volumetric capacity, while most of current reported high performance of those materials were obtained at a quite low mass loading in laboratory. In addition, the severe agglomeration of nanomaterials will badly affect their lithium storage properties, but the developed carbon coating strategies, including the hydrothermal method and CVD are timing-consuming or low yield, which is not beneficial to large-scale application. Thirdly, the most widely used electrolytes in current rechargeable batteries are the carbonate-based electrolytes, which will result in irreversible initial capacity loss due to the formation of unstable SEI films, whereas the ether-based electrolytes will sacrifice the capacity contributed in the alloying reaction. Furthermore, this voltage range also leads to low voltage and energy density when applied in the full cells. From the perspective of practical applications, in order to fully utilize the potential of rechargeable batteries, further work needs to be
conducted on electrode design, electrolyte composition, in-depth studies on the interfaces between electrodes and electrolytes.

2.5 Reference


CHAPTER 3 EXPERIMENTAL METHODS

3.1 Experimental procedures

To develop high performance electrode materials for advanced rechargeable batteries, in this research work, a series of two dimensional (2D) metal oxides with few-layer thickness and adjustable components have been rationally designed and controllably synthesized via facile and versatile wet-chemical synthesis strategy. The research work in this thesis follows the procedures described in Figure 3.1. The physical and chemical properties of these as-prepared materials have been systematically characterized. Specifically, the crystal structure and phase composition were investigated by the X-ray diffraction (XRD), while the molecular structure and chemical bond would be analyzed based on the room temperature Raman spectra. Scanning Electron Microscope (SEM) and Transmission electron microscope (TEM) can be used to observe the sample's surface topography and composition, fine structure, crystal orientation and electronic structure. The detailed chemical information including the elemental composition, chemical and electronic states of the contained elements in the materials could be obtained from the X-ray photoelectron spectroscopy (XPS) technique and the thermal stability and composition of the materials were measured thermogravimetric analysis (TGA) method. In addition, the local oxygen vacancies/defects generated on the exposed surface of the 2D ultrathin materials were studied via the Electron paramagnetic resonance (EPR). Furthermore, the electrochemical properties would be well investigated by the electrochemical impedance spectroscopy, cyclic voltammetry and
galvanostatical cycling tests. The electrochemical reaction mechanism during alkali metal ions insertion/de-insertion processes were also deeply studied based on the in-situ synchrotron X-ray powder diffraction (SXRPD). The SXRPD experiments were conducted on the Powder Diffraction beamline at the Australian Synchrotron. More importantly, to understand the fundamental relationship between the electronic properties of materials and their exhibited electrochemical performance, theoretical calculations were conducted as well. All the theoretical calculations were performed by employing the first-principles projector augmented wave (PAW) method based on density functional theory (DFT) with the Perdew-Burke-Ernzehof (PBE) functional as implemented in the Vienna ab initio simulation package.
Figure 3.1 Outline of experimental procedures and techniques conducted in this thesis.
3.2 Chemicals

The chemicals used in this thesis for the materials synthesis, characterization, and electrochemical tests are summarized in details in Table 3.1.

**Table 3.1 List of chemicals used in this thesis**

<table>
<thead>
<tr>
<th>Chemicals</th>
<th>Formula</th>
<th>Purity (%)</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon black</td>
<td>C</td>
<td>Super P</td>
<td>Timcal, Belgium</td>
</tr>
<tr>
<td>Acetone</td>
<td>(CH₃)₂CO</td>
<td>99</td>
<td>Ajax Finechem</td>
</tr>
<tr>
<td>Copper foil</td>
<td>Cu</td>
<td>N/A</td>
<td>Vanlead Tech</td>
</tr>
<tr>
<td>CR2032 coin cells</td>
<td>N/A</td>
<td>N/A</td>
<td>China ChemsT</td>
</tr>
<tr>
<td>Diethyl carbonate (DEC)</td>
<td>C₅H₁₀O₃</td>
<td>99+</td>
<td>Sigma Aldrich, Australia</td>
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<td>Ethanol</td>
<td>C₂H₅OH</td>
<td>Reagent</td>
<td>Q-store, Australia</td>
</tr>
<tr>
<td>Ethylene carbonate (EC)</td>
<td></td>
<td>99</td>
<td>Sigma Aldrich, Australia</td>
</tr>
<tr>
<td>Fluoroethylene carbonate (FEC)</td>
<td></td>
<td>N/A</td>
<td>Sigma Aldrich, Australia</td>
</tr>
<tr>
<td>Single-wall carbon nanotubes (SWCNTs)</td>
<td>C</td>
<td>98</td>
<td>NanoAmor</td>
</tr>
<tr>
<td>Multi-wall carbon nanotubes (MWCNTs)</td>
<td>C</td>
<td>95</td>
<td>NanoAmor</td>
</tr>
<tr>
<td>N-methyl-2-pyrrolidone (NMP)</td>
<td></td>
<td>99.5</td>
<td>Sigma Aldrich, Australia</td>
</tr>
<tr>
<td>Poly (acrylic acid) (MW=130,000)</td>
<td></td>
<td>N/A</td>
<td>Sigma Aldrich, Australia</td>
</tr>
<tr>
<td>Polyvinylidene difluoride (MW=543,000)</td>
<td></td>
<td>N/A</td>
<td>Sigma Aldrich, Australia</td>
</tr>
<tr>
<td>Substance</td>
<td>Formula</td>
<td>Purity</td>
<td>Supplier</td>
</tr>
<tr>
<td>---------------------------------</td>
<td>------------------</td>
<td>--------</td>
<td>-------------------</td>
</tr>
<tr>
<td>Propylene carbonate (PC)</td>
<td><img src="image" alt="Propylene carbonate structure" /></td>
<td>99.7%</td>
<td>Sigma Aldrich, Australia</td>
</tr>
<tr>
<td>Sodium carbonate</td>
<td>Na$_2$CO$_3$</td>
<td>99%</td>
<td>Sigma Aldrich, Australia</td>
</tr>
<tr>
<td>Sodium carboxymethyl cellulose</td>
<td><img src="image" alt="Sodium carboxymethyl cellulose structure" /></td>
<td>N/A</td>
<td>Sigma Aldrich, Australia</td>
</tr>
<tr>
<td>(MW = 90,000)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sodium cubes (stored in mineral</td>
<td>Na</td>
<td>99.9%</td>
<td>Sigma Aldrich, Australia</td>
</tr>
<tr>
<td>oil)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sodium perchlorate</td>
<td>NaClO$_4$</td>
<td>98%</td>
<td>Sigma Aldrich, Australia</td>
</tr>
<tr>
<td>DI Milli-Q Water</td>
<td>H$_2$O</td>
<td>5 ppb</td>
<td>Millipore, USA Q-store, Australia</td>
</tr>
<tr>
<td>Ethanol</td>
<td>C$_2$H$_5$OH</td>
<td>Reagent</td>
<td>Sigma Aldrich, Australia</td>
</tr>
<tr>
<td>High pure ethanol</td>
<td>C$_2$H$_5$OH</td>
<td>99.95%</td>
<td>Sigma Aldrich, Australia</td>
</tr>
<tr>
<td>Polypropylene separator</td>
<td>(C$_3$H$_6$)$_n$</td>
<td>Celgard</td>
<td>Hoechst Celanese Corporation, USA</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2500</td>
<td></td>
</tr>
<tr>
<td>Lithium foil</td>
<td>Li</td>
<td>99.9%</td>
<td>Sigma Aldrich, Australia</td>
</tr>
<tr>
<td>Bismuth (III) nitrate pentahydrate</td>
<td>Bi(NO$_3$)$_3$ \cdot 5H$_2$O</td>
<td>98%</td>
<td>Sigma Aldrich, Australia</td>
</tr>
<tr>
<td>Sodium molybdate dihydrate</td>
<td>Na$_2$MoO$_4$ \cdot 2H$_2$O</td>
<td>99%</td>
<td>Sigma Aldrich, Australia</td>
</tr>
<tr>
<td>Nitric acid</td>
<td>HNO$_3$</td>
<td>69%</td>
<td>Sigma Aldrich, Australia</td>
</tr>
<tr>
<td>Ammonium vanadate</td>
<td>NH$_4$VO$_3$</td>
<td>99%</td>
<td>Fluka, Australia Sigma Aldrich, Australia</td>
</tr>
<tr>
<td>Sodium hydroxide</td>
<td>NaOH</td>
<td>98%</td>
<td>Sigma Aldrich, Australia</td>
</tr>
<tr>
<td>tert-Dodecanethiol</td>
<td>C$<em>{12}$H$</em>{25}$SH</td>
<td>98.5%</td>
<td>Sigma Aldrich</td>
</tr>
<tr>
<td>Molybdenic acid</td>
<td>H$_2$MoO$_4$</td>
<td>85%</td>
<td>Sigma</td>
</tr>
<tr>
<td>Substance</td>
<td>Formula</td>
<td>Purity</td>
<td>Supplier</td>
</tr>
<tr>
<td>-----------------------------------------------------</td>
<td>--------------------------</td>
<td>--------</td>
<td>-------------------</td>
</tr>
<tr>
<td>Nickel(II) acetate tetrahydrate</td>
<td>Ni(OCOCH₃)₂ · 4H₂O</td>
<td>99</td>
<td>Sigma Aldrich</td>
</tr>
<tr>
<td>Nickel(II) chloride hexahydrate</td>
<td>NiCl₂ · 6H₂O</td>
<td>98</td>
<td>Sigma Aldrich,</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Australia</td>
</tr>
<tr>
<td>Lithium hexafluorophosphate</td>
<td>LiPF₆</td>
<td>99.99</td>
<td>Sigma Aldrich,</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Australia</td>
</tr>
<tr>
<td>Dimethyl carbonate (DMC)</td>
<td>C₃H₆O₃</td>
<td>99+</td>
<td>Sigma Australia</td>
</tr>
<tr>
<td>Hydrochloric acid</td>
<td>HCl</td>
<td>36.5</td>
<td>Sigma Aldrich</td>
</tr>
<tr>
<td>Cetyltrimethylammonium bromide (CTAB)</td>
<td>CH₃(CH₂)₁₅N(Br)(CH₃)₃</td>
<td>99</td>
<td>Sigma Aldrich,</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Australia</td>
</tr>
</tbody>
</table>
3.3 Methodology and theory of experiments

Inspired by the discovery of mechanically exfoliated graphene in 2004,[11] ultrathin two-dimensional (2D) nanomaterials have attracted considerable attention owning to their fascinating physical, chemical, electronic, and optical properties and potential applications including catalysis, energy storage/conversion, sensing platforms and electronics/optoelectronics.[2–5] Typically, there are two categories of methods to synthesize ultrathin 2D nanomaterials: the top-down and bottom-up methods.[6]

Specifically, the top-down methods mainly include the mechanical cleavage and liquid exfoliation (such as mechanical exfoliation, electrochemical exfoliation and intercalation-assisted liquid exfoliation), which is a process of exfoliating layered materials into mono-/few-layers by chemical reaction or intercalation (Figure 3.2).[7–10] However, all these employed methods heavily rely on the exfoliation of thin layer 2D crystals from their corresponding layered bulk materials, which means that only those materials whose bulk crystals are layered compounds can be prepared through the top-down methods.[11] When considered those non-layered materials, it is difficult to obtain the desired thin layer 2D materials by the top-down strategy owning to the strong atomic bonding in three dimensions.[12,13]

For the bottom-up methods, which are based on the chemical reactions of certain precursors at different experimental environment, contain the chemical vapor deposition (CVD) and wet-chemical synthesis.[14,15] Compared to the limitation of the top-down approaches, the bottom-up methods are more versatile and controllable, particularly the thickness and mass of the produced materials.[13,16] CVD method has been widely applied to prepare ultrathin 2D nanosheets, particularly the layered transition metal dichalcogenides (TMDs),[17–19] such as MoS$_2$, MoSe$_2$, WS$_2$, WSe$_2$, etc.
etc. To achieve high quality and very thin 2D nanosheets, it usually needs the high temperature but low throughput during the CVD progress, which will severely limit its practical application. Considered abovementioned problems, the wet-chemical synthesis strategy might be more promising for the exploring novel ultrathin 2D materials for the applications in the energy storage.

**Figure 3.2** Schematic illustration of the top-down methods for layered material production.[7–10]

3.3.1 Hydrothermal method

Hydrothermal synthesis is a technique of crystallizing substances by chemical reactions in a sealed heated solution above ambient temperature and pressure.[20] Generally, the reaction mechanism of hydrothermal method follows a liquid nucleation model,[21] which is different from that of solid-state reactions, mainly involving diffusion of atoms or ions at the interface between reactants. The hydrothermal method has been extensively used to the synthesis of advanced inorganic materials, which are difficult or impossible to fabricate by a traditional high-temperature solid-state reaction. Figure 3.3 shows the used autoclave in this
thesis, containing an acid digestion vessel and a polytetrafluoroethylene (PTFE) cup with a cover. When the reaction is conducted in an organic or non-aqueous solvent, it can be referred to as solvothermal synthesis.

To control the composition, morphology and structure of the target product, the reaction parameters and conditions need to be adjusted systematically. Normally, the concentration of the precursors, solvents (including the species, volumes and the ratio of different solvents), reaction temperature, reaction time, pressure, pH value, and surfactants will significantly affect the crystal phase, morphology, and particle size of final products. In order to obtain desired materials, the reaction parameters and conditions should be considered and regulated carefully.
3.4 Characterization and measurement methods

3.4.1 X-ray diffraction

Powder X-ray diffraction (XRD) technique has been widely applied to study the structure of crystalline materials based on the X-ray diffraction effects with the crystal. X-rays can be considered waves of electromagnetic radiation, while atoms can scatter X-ray waves through the atoms' electrons. Furthermore, the periodically arranged atoms in a crystal cause a beam of incident X-rays to diffract into many specific directions, thus producing a regular array of spherical waves (Figure 3.4). The patterns of the scattered X-ray waves have a characteristic relationship with the given crystal materials and can be determined by the Bragg's law.

\[ 2dsin\theta = n\lambda \]
Here $d$ is the spacing between diffracting planes, $\theta$ is the incident angle, $n$ is any integer, and $\lambda$ is the wavelength of the beam.

The XRD device used in this thesis was a GBC MMA diffractometer (Figure 3.5) in ISEM, UOW. All the XRD device use Cu K\textalpha radiation, $\lambda = 1.54056$ Å.

![Figure 3.4](image1.png) The basic principles of X-ray diffraction.

![Figure 3.5](image2.png) The GBC MMA equipment in ISEM of UOW.
3.4.2 Scanning electron microscopy

The scanning electron microscope (SEM) is a type of electron microscope which can scan the surface of samples with a focused electron beam and create images. The high-energy electrons interact with atoms in the sample, generating various signals and offering information about the surface topographical feature and composition of the sample. The electron beam is typically scanned in a raster scan pattern and the position of the light beam is combined with the detected signal to produce an image. Generally SEM can attain a resolution of better than 1 nm. The morphology and structure of prepared samples in this research work were characterized with a field-emission scanning electron microscope (FESEM; JEOL 7500FA (Figure 3.6) in EMC, UOW).

Figure 3.6 The JEOL 7500FA facility.
3.4.3 Transmission electron microscopy

Transmission electron microscopy (TEM) is an important microscopy technique to observe the morphology and fine structure (such as the crystal orientation, lattice spacing and electronic structure) of the sample. It operates on the same fundamental principles as the light microscope but can achieve a resolution a thousand times better than with a light microscope owning to the smaller de Broglie wavelength of used electrons. In TEM, a beam of accelerated electrons penetrate through the thin specimen and simultaneously interact with the specimen, determining the contrast of the image. The image is magnified and focused onto an imaging device, such as a fluorescent screen, on a layer of photographic film, or to be detected by a sensor such as a charge-coupled device. Selected area electron diffraction (SAED) can be conducted by a TEM and offer the crystallographic information about the sample. The used TEM facilities in this thesis were JEOL 2011 and JEOL JEM-ARM200F (Figure 3.7). Elemental mapping was carried out on the X-ray spectrometer attached to the JEM-200F instrument.

![Figure 3.7](image)

*Figure 3.7* The (left) JEOL 2011 and (right) JEOL JEM-ARM200F facility.
3.4.4 Energy-dispersive X-ray spectroscopy

Energy-dispersive X-ray spectroscopy (EDS) is a useful analytic technique applied for the elemental analysis or chemical characterization of a specimen. It mainly relies on the interaction between the excitation source of X-rays and a specimen. A high-energy beam, such as electrons or X-rays is generally used to stimulate the emission of characteristic X-rays from a specimen. In this thesis, the EDS mapping analysis was conducted in the TEM and SEM.

3.4.5 Brunauer-Emmett-Teller measurements

Brunauer-Emmett-Teller (BET) is an important analysis method, which has been extensively used to investigate the physical adsorption of inert gas molecules (such as N\textsubscript{2}) on a solid sample’s surface, and thus measure the specific surface area, pore volume and the pore size distribution of the material. The BET measurement is normally performed at liquid nitrogen temperature (77 K) over different relative pressures. The BET specific surface area can be calculated by a multipoint BET method using the adsorption data in the relative pressure \( P/P_0 \) range of 0.05–0.30. The desorption isotherm can be used to determine the pore size distribution by using the Barret–Joyner–Halenda (BJH) method. In this thesis, nitrogen adsorption was conducted by the Quanta Chrome Nova 1000 facility in ISEM of UOW.

3.4.6 Raman spectroscopy

Raman spectroscopy is a vibrational spectroscopic technique employed to study the vibrations of chemical bonds and symmetry of molecules, providing the information about molecular vibrations and crystal structures of materials. The technique utilizes a laser beam to illuminate a sample, and produce an infinitesimal amount of Raman
scattered light, which can be detected as a Raman spectrum by using a CCD camera. The obtained characteristic fingerprinting pattern in a Raman spectrum can help to identify materials. In this thesis, JOBIN Yvon Horiba Raman Spectrometer model HR800 (Figure 3.8), with a 10 mW helium/neon laser at 632.8 nm, was used to collect Raman spectra.

Figure 3.8 The JOBIN Yvon Horiba Raman Spectrometer model HR800 equipment.

3.4.7 X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) is a commonly used surface-sensitive quantitative spectroscopic technique for the measurement of the elemental composition, chemical state and electronic state of the elements in a sample. When a material is irradiated by a beam of X-rays, while the numbers of electrons escaping from the top 0–10 nm of the material are counted and the kinetic energy are simultaneously measured, the XPS spectra can be obtained. From XPS spectra, the valence states of elements can be identified and the ratio of each valence state can be estimated. In this thesis, XPS was conducted on VG Scientific ESCALAB 2201XL (Figure 3.9) in ISEM of UOW, with a Thermo Scientific Sigma Probe instrument in
KETI using Al Kα X-ray radiation and a fixed analyser transmission mode.

Figure 3.9 The VG Scientific ESCALAB 2201XL facility.

3.4.8 Electron paramagnetic resonance

Electron paramagnetic resonance (EPR) is an effective magnetic resonance technique to characterize materials containing unpaired electrons and also can be called electron spin resonance (ESR). The fundamental principle of EPR is similar to that of nuclear magnetic resonance (NMR); however, instead of measuring the nuclear transitions in NMR, it mainly detects the transitions of unpaired electrons in an applied magnetic field. EPR technique is specifically useful for detecting the properties of unpaired electrons such as free radicals, transition metal ions, biradicals, triplet-state systems and point defects in solids. Continuous-wave EPR experiments were conducted on a Bruker ELEXSYS E580 spectrometer operating in the X-band (9.4 GHz) mode, with an Oxford CF935 helium flow cryostat and an ITC-5025 temperature controller. For accuracy and homogeneity, a coal standard (g = 2.00285 ± 0.00005) was used to calibrate the g tensors. The receiver acquisition and scans number were adapted to make every sample spectrum comparable at a rational
signal-to-noise ratio.

3.5 Electrode preparation and coin cell assembly

3.5.1 Electrode fabrication

The working electrode was fabricated by mixing the synthesized active materials, conductive materials, and binders in a specific ratio. After completely mixing these materials, some solvents were dropped into the mixture to form uniform slurry. Then, the slurry was homogeneously coated onto a current collector by a blade, and was dried in a vacuum drying oven to get the final working electrode. The obtained electrode was punched into small discs, which would be placed into an inert gas filled glove box and ready to be assembled into a coin cell.

3.5.2 Coin cell assembly

The battery assembly procedure was conducted in an Argon-filled glove box with a 2032-type coin cells. As shown in Figure 3.10, the Li metal foil was firstly placed in the negative cap with adding 2-3 drops of prepared electrolyte; then the separator was completely immersed in the electrolyte by adding extra 1-2 drops of the electrolyte. After that, the working electrode disc was placed onto the separator and was progressively covered by stainless steel spacer, spring, and positive cap. After tightly sealed, the coin cell was rested for overnight before the electrochemical test, ensuring the electrolyte completely penetrated into the electrode and separator.
Figure 3.10 Schematic diagram and order assembly of 2032-type coin cells.

3.6 Electrochemical measurements

3.6.1 Cyclic voltammetry

Cyclic voltammetry (CV) is a useful potentiodynamic electrochemical measurement that can be used to study the electrochemical properties of an electrode. The method is mainly performed by applying a cyclic potential on the working electrode at a fixed rate from a starting potential to an endpoint potential, and then changing back to the initial potential at the same rate. When a redox reaction occurred, both anodic and cathodic peaks could be observed from the CV cure. For the coin cell testing, it is based on a two-electrode model and the Li foil will act as both reference electrode and counter electrode. In this work, the CV data were obtained on a Biologic VMP-3 electrochemical workstation (Figure 3.11).
3.6.2 Galvanostatic electrochemical testing

Galvanostatic testing technique is used to evaluate the electrochemical performance of assembled coin cells. During the test, the battery can be charged and discharged in a given cut-off voltage at a constant current. The capacity of charge and discharge process can be counted from the used current and the cumulative time for the whole process. Moreover, the testing method also can be used to measure rate capability by employing different current densities for a certain number of cycles. The Land battery tester (Figure 3.13) was applied to carry out the Galvanostatic electrochemical testing.
3.6.3 Electrochemical impedance spectroscopy

Electrochemical impedance spectroscopy (EIS) is a perturbative characterization of the dynamics of an electrochemical process and can be applied to the surfaces of various electrochemical systems, such as batteries, photovoltaic systems, and fuel cells. This technique is based on introducing a perturbation in the target system by using a sine wave current or small amplitude potential, while the instrument can record the resulting changes in the form of an impedance diagram and provide data expressed graphically in a Bode plot or a Nyquist plot. Basically, electrochemical impedance is the response of an electrochemical system to an applied potential and the response of the system as a function of the perturbation frequency can reveal internal dynamics. In battery system, the impedance spectrum usually contains a high-frequency semicircle together with a low-frequency linear tail. The high-frequency semicircle is related to the kinetics processes indicating the charge transfer resistance and a double layer capacitance, whereas the linear tail reflects the solid-state diffusion of ions (such as Li$^+$ or Na$^+$) into the bulk of the active materials. In this work, a Biologic VMP-3 electrochemical workstation was used to obtain the EIS data.

3.6.4 Synchrotron in-situ X-ray powder diffraction

In order to understand the electrochemical reaction mechanisms of the electrode materials during the discharging/charging progress, a customized CR2032 coin cell for use in-situ synchrotron X-ray powder diffraction (SXRPD) experiments (Figure 3.13) was made and the SXRPD experiments were conducted on the Powder Diffraction beamline at the Australian Synchrotron, where the SXRPD patterns from the cell were collected every 3.4 minutes during charge and discharge using a
MYTHEN microstrip detector. The wavelength used was determined to be 0.6899(3) Å using a LaB₆ NIST SRM 660b.

**Figure 3.13** The coin cell sample stage with a sample mounted. The hole, sealed using polyimide film, permits the diffracted X-rays to leave the cell.

### 3.7 Reference


CHAPTER 4 HIERARCHICAL Bi$_2$O$_3$ NANOSHEET ASSEMBLIES: A SUPERIOR ANODE MATERIAL FOR LI-ION BATTERIES

4.1 Introduction

Lithium ion batteries have dominated the consumer electronics market and shown great promising in the electric traffic and grid-scale energy storage.[1–3] The low energy density due to the intrinsic gravimetric capacity limitation of commercial graphite anodes, however, makes it difficult to meet the ever-growing energy demands on these areas.[4,5] To achieve high performance anode materials for next generation rechargeable batteries, great efforts have been devoted to exploring novel electrode materials with large theoretical capacity, including the alloying and conversion-based anodes and further improve the electrochemical properties by nanocrystallization.[6–8] On the other hand, volumetric capacity is another important factor for practical application of batteries needs to be considered, particularly when applied in the electric vehicles.[9,10] Thus, the ideal anode candidate material for high-energy LIBs should have both gravimetric capacity and volumetric capacity.

Among various metal oxides, bismuth oxides (Bi$_2$O$_3$) have received considerable attention for its wide applications ranging from the electronics, photonics, catalysis, sensors to energy due to its excellent properties.[11–13] More importantly, the intriguing properties, in terms of the non-toxicity, thermal stability and low cost make it a quite promising candidate for energy storage application.[14,15] Particularly, the large gravimetric capacity (690 mA h g$^{-1}$) and pretty high volumetric capacity (6280 mA h cm$^{-3}$) enables it to offer desired electrochemical performance for next
generation LIBs.\textsuperscript{[16]} Till to now, there are few studies focused on the bismuth oxide electrodes for LIBs. For example, three-dimensionally ordered macroporous (3DOM) b-Bi\textsubscript{2}O\textsubscript{3}, Bi\textsubscript{2}O\textsubscript{3}/rGO nanocomposite, Bi\textsubscript{2}O\textsubscript{3}@CMK-3 nanocomposite, Bi\textsubscript{2}O\textsubscript{3}@N-G, p-Bi\textsubscript{2}O\textsubscript{3}/Ni, Bi\textsubscript{2}O\textsubscript{3}microribbons have been prepared for LIBs.\textsuperscript{[16-21]} Although combined with Ni form, graphene or carbon, those reported Bi\textsubscript{2}O\textsubscript{3} anode materials still show unsatisfactory electrochemical performance in Li-ion batteries. Similar to other high-energy alloying metal oxides, Bi\textsubscript{2}O\textsubscript{3} also suffer from inferior structural stability due to huge volume expansion during lithiation/de-lithiation process, which result in the rapid capacity decay, thus severely hinder its practical application. To address the issue of stress-induced structural degradation, rational design and controllable synthesis of novel architecture is urgently needed.

Ultrathin two dimensional (2D) materials have been considered as competitive materials in energy storage application owning to their unprecedented properties and great diversities.\textsuperscript{[22-25]} It is well established that different-dimensional structures exhibit their unique performances based on surface and structural characteristics. Compared to other structured materials, such as 0D nanoparticles, 1D micro ribbons, the 2D ultrathin materials can offer promising opportunities for exploring advanced energy storage systems with satisfactory electrochemical performance.\textsuperscript{[26]} Firstly, the large interlayer spacing between adjacent layers is favourable for the fast ion and electron transfer. Secondly, the high surface area provides more electrochemical active sites for the alkali metal ions storage. Thirdly, the atomic defects induced by oxygen vacancies/ dangling bonds typically trigger unexpected changes in electronic states, consequently affording higher charge mobility. Lastly, the good structural stability and mechanical flexibility endowed by the atomic thickness make them
suitable for applications of next-generation flexible energy storage devices.\textsuperscript{[27,28]} Nevertheless, the serious aggregation or re-stacking of atomically thin 2D nanomaterials significantly impedes the full utilization of their high surface area, even blocks electrolyte access.\textsuperscript{[29]} Notably, constructing hierarchical structures assembled from the ultrathin 2D nanosheets could be an effective way to resolve the problem, since the hierarchical nanosheet assemblies will not only preserve the intrinsic properties of 2D nanostructures, but also exhibit other structural features at different size scales, such as large dimensions, accessible porous systems, large void spaces and high surface area, thus showing promising prospects for energy-related applications.\textsuperscript{[30]}

It is worth noting that among the five polymorphic phases of Bi\textsubscript{2}O\textsubscript{3}, only the $\alpha$-Bi\textsubscript{2}O\textsubscript{3} (monoclinic) and the $\delta$-Bi\textsubscript{2}O\textsubscript{3} (face centered cubic) are stable at low-temperature and high temperature, respectively, while the others $\beta$, $\gamma$, $\omega$ phases are high temperature metastable phases and usually transform into the stable monoclinic $\alpha$-Bi\textsubscript{2}O\textsubscript{3}.\textsuperscript{[31]} Interestingly, the $\delta$-Bi\textsubscript{2}O\textsubscript{3} is a typical cubic phase and has the layered structure, which could be a promising 2D anode candidate for high performance energy storage. However, there is not any report about the ultrathin $\delta$-Bi\textsubscript{2}O\textsubscript{3} anode materials for rechargeable batteries. Hence, we report the facile preparation of ultrathin $\delta$-Bi\textsubscript{2}O\textsubscript{3} self-assembled hierarchical structure via a facile and general wet-chemical synthesis approach and employed as anode materials for lithium ion batteries. Due to its unique hierarchical structure composed of the atomically thin $\delta$-Bi\textsubscript{2}O\textsubscript{3} nanosheets, which can provide extremely short diffusion paths and maintain the structural integrity, the obtained Bi\textsubscript{2}O\textsubscript{3} anode exhibits superior Li storage properties.
4.2 Experimental methods

4.2.1 Sample preparation

4.2.1.1 Synthesis of ultrathin Bi$_2$O$_3$ nanosheets

Firstly, 0.5 mmol bismuth (III) nitrate pentahydrate and 88 mg ammonium vanadate were added into 5 mL HNO$_3$ solution (4 mol L$^{-1}$). Then, 20 mL deionized water was added into the solution. After stirring for 30 minutes, the pH of the solution was adjusted to 12 by adding NaOH solution. The resultant yellow suspension was transferred to an autoclave, which was kept in an oven at 60 °C for 24 h. The obtained product was separated by centrifugation and washed many times with de-ionized water and ethanol, and finally dried at 60 °C for 12 h in vacuum.

4.2.1.2 Synthesis of Bi$_2$O$_3$ bulk sample

The bulk Bi$_2$O$_3$ was prepared via a solid state reaction process. Typically, a certain amount of bismuth (III) nitrate pentahydrate was placed on the magnetic boat and transferred to the tube furnace. The reaction was carried out at 500 °C for 4 h.

4.2.2 Materials characterization

The morphologies of the as-prepared products were observed by field emission scanning electron microscopy (FESEM, JEOL JSM-7500FA). The details of the crystal structure and EDS mapping were further examined by scanning transmission electron microscope (STEM, JEOL JEM-ARM200F), which was conducted at 200 kV. The crystalline structure of the obtained materials was checked by X-ray diffraction (XRD, GBC MMA diffractometer) with Cu Kα radiation at a scanning rate of 1° min$^{-1}$. X-ray photoelectron spectroscopy (XPS) was performed on a VG
Multilab 2000 (VG Inc.) photoelectron spectrometer using monochromatic Al Kα radiation under vacuum at $2 \times 10^{-6}$ Pa. All of the binding energies were referenced to the C 1s peak at 284.8 eV of the surface adventitious carbon. Raman analysis was performed with a JobinYvon HR800 Raman spectrometer. Continuous-wave electron paramagnetic resonance (EPR) experiments were conducted by a Bruker ELEXSYS E580 spectrometer operating in the X-band (9.4 GHz) mode and equipped with an Oxford CF935 helium flow cryostat with an ITC-5025 temperature controller.

4.2.3 Electrochemical measurements

The electrochemical tests were conducted through the CR2032 coin-type cells. The working electrodes were prepared by mixing the obtained materials, Super P, and poly(acrylic acid)/sodium carboxymethyl cellulose (1:1) in a weight ratio of 70:20:10. The resultant slurry was pasted on Cu foil and dried at 80 °C for 12 h in vacuum, followed by pressing at 300 kg/cm². Electrochemical measurements were carried out using two-electrode coin cells with Li metal as counter and reference electrode and Celgard (product 2400) film as the separator. The electrolyte consisted of a solution of 1 M LiPF₆ in ethylene carbonate/diethyl carbonate (1/1; v/v) with 5 wt% fluoroethylene carbonate. Electrochemical impedance spectroscopy and cyclic voltammetry were conducted on a VMP-3 electrochemical workstation at a scan rate of 0.1 mV s⁻¹. The cells were galvanostatically charged/discharged in a voltage range of 0.01–3.0 V versus Li/Li⁺ at different current densities on a Land CT2001A battery tester.

4.3 Results and discussion

The crystal structure and phase purity of as-prepared samples were firstly
investigated by the powder X-ray diffraction (XRD). As shown in Figure 4.1, all the diffraction peaks of the obtained Bi$_2$O$_3$ sheet can be well assigned to the cubic phase δ-Bi$_2$O$_3$ (JCPDS No. 27-0052, a = 5.525 Å). No other peak appeared confirms the high purity of the prepared Bi$_2$O$_3$ sample. In comparison, the diffraction peaks of the fabricated Bi$_2$O$_3$ bulk could be indexed to the monoclinic α-Bi$_2$O$_3$ (JCPDS No. 65-2366). Furthermore, the as-prepared Bi$_2$O$_3$ sheet exhibited the relatively weak intensity and broadened peaks when compared to the Bi$_2$O$_3$ bulk, demonstrating the small particle size of the Bi$_2$O$_3$ sheet sample.

![Figure 4.1 XRD patterns of the prepared ultrathin Bi$_2$O$_3$ nanosheets and Bi$_2$O$_3$ bulk samples.](image)

Figure 4.1 XRD patterns of the prepared ultrathin Bi$_2$O$_3$ nanosheets and Bi$_2$O$_3$ bulk samples.

The morphology and microstructure of the as-synthesized samples were studied by scanning electron microscope (SEM). As present in Figure 4.2a, the low-magnification SEM image of the Bi$_2$O$_3$ sheet sample indicates that the product
consists of large amount of uniform flower-like sphere with a size about 1 μm. Further magnified observation reveals that the micro-sized sphere with a hierarchical structure was assembled by many thin nanosheets that were oriented to different angles (Figure 4.2b). Such assembled hierarchical structure can not only minimize the restacking of 2D nanosheets, but also offer a facile access even to the deep inside of the assembly, thus maintaining the structural stability and providing more active sites for Li ions and electrolyte access. More interestingly, the highly curved sheet demonstrates that the 2D ultrathin nature of the obtained Bi₂O₃ nanosheets units (Figure 4.2c). As present in Figure 4.2d, the Bi₂O₃ bulk samples show the block structure with sizes about 1–6 μm.

Figure 4.2 SEM images of as-prepared (a–c) ultrathin Bi₂O₃ nanosheets and (d) Bi₂O₃ bulk samples.
The detailed structure of the Bi$_2$O$_3$ nanosheets was further investigated by the transmission electron microscope (TEM). The typical low-magnification of STEM-high angle annular dark-field (STEM-HAADF) image and bright field TEM image (Figure 4.3a,b) confirm the uniform assembled hierarchical structure of Bi$_2$O$_3$ nanosheets, while the enlarged TEM image of a single flower-like sphere (Figure 4.3c,d) clearly shows the wrinkled and transparent structural characteristic on the loose edge of the nanosheets, revealing the flexible and 2D ultrathin property, which is consistent with the SEM results. Furthermore, Figure 4.3e shows a representative TEM image with a lateral view of the nanosheet and reveals the well-defined layer-like architecture with a thickness of about 1.68 nm, corresponding to 3 layers of cubic Bi$_2$O$_3$ unit cell along the c-axis. Meanwhile, the high-resolution TEM (HRTEM) image (Figure 4.3f) demonstrates that the Bi$_2$O$_3$ sheets grow along the [001] direction. The lattice spacings of about 0.275 and 0.276 nm, respectively, correspond to the (200) and (020) planes of cubic Bi$_2$O$_3$, indicating that the Bi$_2$O$_3$ sheets preferentially expose the {001} facets. The elemental mapping (Figure 4.3g-i) result indicates that Bi and O elements coexist and are distributed uniformly in the assembled hierarchical structure of Bi$_2$O$_3$ nanosheets.
Figure 4.3 Morphology of obtained ultrathin Bi$_2$O$_3$ nanosheets. (a,c) STEM-high angle annular dark-field (STEM-HAADF) images and (b,d) bright field TEM images. (e) Lateral HAADF-STEM image. (f) HRTEM image. (g–i) Corresponding EDS elemental mappings.

The surface electronic states and chemical compositions of the as-prepared samples were studied by X-ray photoelectron spectroscopy (XPS). Figure 4.4a presents the XPS survey spectra of the Bi$_2$O$_3$ sheets, which exhibits the characteristic bands for Bi, O and C elements in the samples, respectively. Furthermore, the high-
resolution Bi 4f and O 1s XPS spectra of the Bi$_2$O$_3$ sheets were displayed in Figure 4.4b,c. The binding energy located at 159.1 and 164.2 eV can be ascribed to the Bi 4f$_{5/2}$ and Bi 4f$_{7/2}$, respectively, which is in agreement with the previous report.\cite{33} In addition, two O 1s peaks located at 529.7 and 533.2 eV are observed, which are attributed to the lattice oxygen and near surface oxygen, respectively.\cite{34,35} More importantly, a new peak that appeared at 531.7 eV can be assigned to the oxygen vacancies,\cite{34,35} which is due to the rearranged and unsaturated states of the surface Bi and O atoms of ultrathin nanosheets, typically resulting in an imbalanced charge distribution and enhance the interaction between Li ions and electrode materials, thus boosting the electrochemical reactions.

![XPS spectra of ultrathin Bi$_2$O$_3$ nanosheets. (a) Survey XPS spectra. High-resolution XPS spectra: (b) Bi 4f and (c) O 1s.](image)

**Figure 4.4** XPS spectra of ultrathin Bi$_2$O$_3$ nanosheets. (a) Survey XPS spectra. High-resolution XPS spectra: (b) Bi 4f and (c) O 1s.
The Li-ion storage properties of the synthesized Bi$_2$O$_3$ sheets were studied through cyclic voltammetry (CV). Figure 4.5a shows the typical CV curves for the 1$^{\text{st}}$, 2$^{\text{nd}}$, and 5$^{\text{th}}$ cycles at a scanning rate of 0.1 mV s$^{-1}$ in the voltage range of 0.01–2.5 V. The CV curves exhibits multipeak features, indicating that the electrochemical reactions of the Bi$_2$O$_3$ sheets with Li via multiple steps. In the first negative scan, two cathodic peaks located at about 1.75 V and 1.36 V could be assigned to the reduction reaction of Bi$_2$O$_3$ to Bi,$^{[36]}$ which is believed as the irreversible reaction, resulting in the large initial capacity loss in the first cycling. The obvious reductive peak centred at 0.56 V results from the alloying reactions of Bi with Li to form Li$_3$Bi and the formation of solid electrolyte interface (SEI).$^{[16]}$ The increased resistance of the electrode due to the formation of SEI make it difficult to distinguish the two-step alloying reactions between Bi with Li (formation of LiBi and Li$_3$Bi, respectively), thus leading to a broaden peak between 0.25 V and 1.0 V.$^{[33]}$ However, it can be clearly seen that the broad reduction peak is split into two small peaks at around 0.73 and 0.60 V in the subsequent cycles, demonstrating that the two-step electrochemical alloying reactions of Bi with Li occurred. Moreover, the strong oxidation peak localized at about 0.98 V is associated with the de-alloying process of Li$_3$Bi, while the small anodic peak at about 1.73 V might be attributed to the oxidation of Bi with Li$_2$O to regenerate the Bi$_2$O$_3$.$^{[37]}$ It is notable that from the second cycle onward, both the reduction and oxidation peaks in the CV curves overlap very well, revealing that the Bi$_2$O$_3$ anode has high reversibility and stability during the electrochemical cycling process. In comparison, the Bi$_2$O$_3$ bulk electrode experienced a large irreversible capacity loss during the first cycle (Figure 4.6), which is due to the huge volume expansion after the Li-ions insertion process caused the electrode
pulverisation and the SEI layers broken, thus resulting in a much lower initial
coulombic efficiency and inferior cycling stability.

![Graph](image)

**Figure 4.5** Electrochemical performance of prepared Bi$_2$O$_3$ samples for Li storage.

(a) Cyclic voltammograms for the 1$^{st}$, 2$^{nd}$, and 5$^{th}$ cycles of the Bi$_2$O$_3$ sheets at a
scanning rate of 0.1 mV s$^{-1}$. (b) Galvanostatic discharge-charge profiles for selected
cycles of the Bi$_2$O$_3$ sheets at 100 mA g$^{-1}$. (c) Cycling performance of Bi$_2$O$_3$ sheets
and Bi$_2$O$_3$ bulk at 100 mA g$^{-1}$. (d) Rate capabilities of Bi$_2$O$_3$ sheets and Bi$_2$O$_3$ bulk at
various current densities.

In addition, galvanostatic discharge/charge measurements were carried out to
evaluate the electrochemical performance of the Bi$_2$O$_3$ electrodes. As can be seen
from Figure 4.5b,c, the Bi$_2$O$_3$ sheet exhibits high reversible capacity and good
cycling stability. After 80 cycles at a current density of 100 mA g$^{-1}$, it still can
deliver a stable capacity of 950 mA h g$^{-1}$. In comparison, the corresponding Bi$_2$O$_3$
bulk sample suffered from fast capacity decay and only a quite low capacity of 150 mA h g\(^{-1}\) can be maintained after 80 cycles. Such significantly enhanced electrochemical properties can be attributed to the unique 2D structural feature, which could provide more electrochemical active sites to store Li-ions, while the large interlayer space could greatly facilitate the reversible insertion/deinsertion process. Furthermore, the good cycling stability of the Bi\(_2\)O\(_3\) sheet demonstrates the superior structural stability during the repeated electrochemical lithiation/delithiation reactions. As expected, the distinctive hierarchical structure assembled by the atomically thin nanosheets could effectively relieve the induced-stress during huge volume changes of electrodes and maintain the structure integrity.

**Figure 4.6** Cyclic voltammograms for the 1\(^{\text{st}}\), 2\(^{\text{nd}}\), and 5\(^{\text{th}}\) cycles of the Bi\(_2\)O\(_3\) bulk at a scanning rate of 0.1 mV s\(^{-1}\).

Furthermore, the Bi\(_2\)O\(_3\) sheet achieved superior rate capability at varied current rates. In Figure 4.5d, the Bi\(_2\)O\(_3\) sheet delivered a reversible capacity of 500 mA h g\(^{-1}\) at a current density of 1000 mA g\(^{-1}\). Even when cycled at a high current density of
2000 mA g$^{-1}$, a specific capacity of 400 mA h g$^{-1}$ could be attained, which is much higher than for the Bi$_2$O$_3$ bulk sample. The excellent high-rate capability benefits from the fast electron/ions transfer dynamics, which can be attributed to the good structural properties. Specifically, the open surfaces potentially offer additional shortened paths for electrons/ions transfer process, whereas the rich surface defects induced by oxygen vacancies or dangling bonds usually induce unexpected changes in electronic states, consequently providing higher charge mobility. In addition, electrochemical impedance spectroscopy (EIS) measurements were further conducted to investigate the kinetic differences on the Bi$_2$O$_3$ sheet and bulk electrodes. It is observed that the diameter of the semicircle in the high–medium–frequency region for the Bi$_2$O$_3$ sheet electrode is smaller than that for the bulk electrode (Figure 4.7), which indicates the significantly reduced charge-transfer impedance at the electrode/electrolyte interface,$^{[38]}$ thus contributing to the enhanced electron/Li$^+$ transfer kinetics.
Figure 4.7 Nyquist plots of the Bi$_2$O$_3$ sheets and Bi$_2$O$_3$ bulk electrodes. Spectra were obtained by applying a sine wave with an amplitude of 5.0 mV over the frequency range of 100 kHz–0.01 Hz. The Bi$_2$O$_3$ sheets show much lower charge transfer impedance compared to the Bi$_2$O$_3$ bulk electrode, indicating the enhanced electron- and Li-ion transport dynamics.

4.4 Conclusions

In summary, by integrated the structural advantages of 2D ultrathin configuration and 3D hierarchical structure, the hierarchical Bi$_2$O$_3$ nanosheet assemblies have been successfully fabricated via a facile and general wet-chemical synthesis approach and employed as anode materials for lithium ion batteries. Benefiting from its unique hierarchical structure composed of the atomically thin δ-Bi$_2$O$_3$ nanosheets, which can provide abundant electrochemical active sites, extremely short diffusion paths, fast reaction dynamics and superior structural integrity, the obtained Bi$_2$O$_3$ nanosheets anode exhibits high reversible capacity, excellent high-rate capability and good cycling stability.
4.5 References


5.1 Introduction

High performance lithium-ion batteries (LIBs) are currently the most promising energy storage technology to satisfy the ever-growing demands for portable electronics and electrical transportation. Since existing commercial graphite anodes are approaching their limits, novel electrode materials with excellent high-rate capability and ultra-long lifespan are highly desirable, which is the key step toward enabling LIBs integration into large-scale energy storage systems. It is widely recognized that dimensionality, composition, and atomic arrangement play important roles in determining the intrinsic properties of materials, markedly influencing their electrochemical activity in energy storage. Therefore, ingenious designs that synergistically optimize these characteristics may allow for the creation of electrodes with the desired properties, which is desperately needed, although significant challenges still remain to date.

Atomically-thick two-dimensional (2D) materials have been receiving great attention due to their intriguing properties and potential applications. In particular, their open surfaces potentially provide additional shortened paths for ionic/electronic transport, while the atomic defects induced by oxygen vacancies or dangling bonds typically trigger unexpected changes in electronic states, consequently affording higher charge mobility. Despite some progress in realizing 2D materials with atomic thickness, current approaches mostly rely on
chemical vapor deposition\textsuperscript{[15,16]} or mechanical exfoliation\textsuperscript{[17,18]} techniques via exfoliating bulk compounds, particularly, liquid exfoliation of van der Waals layered crystals, for example, phosphorene.\textsuperscript{[19]} Unfortunately, such poor scalability and complicated processes make it difficult to scale up to a practical level. Furthermore, exfoliating other materials, especially complex oxides stacked with ionically bonded layers, is exceedingly challenging. Nevertheless, it is well established that ternary metal oxides generally show higher electrochemical activities than binary metal oxides, owning to the complex composition and synergistic effects of multiple metal species.\textsuperscript{[20]}

Besides the aforementioned factors, the interface interplay among materials could effectively tailor their physicochemical properties as well,\textsuperscript{[21,22]} considering that the charge/mass transfer process and most chemical reactions are occurring at the interface. More importantly, coupling of 2D materials to create heterogeneous interfaces can further alter their performance in electrochemical applications, since charge redistribution and structural distortion might occur.\textsuperscript{[23,24]} For example, a 2D MoS\textsubscript{2}/C nanosheet superstructure exhibited superior Li storage performance, which was attributed to the ideal atomic interface contact between the monolayer MoS\textsubscript{2} and carbon, contributing to a strong interface synergistic effect.\textsuperscript{[25]} Ultra-fast charge transfer occurred very efficiently in atomically thin MoS\textsubscript{2}/WS\textsubscript{2} heterolayers.\textsuperscript{[26]} Unlike conventional heterogeneous interfaces constructed by assembling disparate crystals together, the inherent atomic interfaces formed in an individual ultrathin 2D ternary material may possess better electrochemical properties because of the strong chemical bonds and perfect lattice match between neighboring layers, thus tuning the electron distribution and maximizing the interaction at the interface. Of particular
note is that sufficient hybridization of atomic orbitals at an interface with strong ionic bonds allows carrier delocalization, which promotes charge transfer across the interface, leading to band bending and the formation of a built-in potential.\textsuperscript{[27]} Interestingly, recent work has revealed that such a built-in electric field within the heterointerfaces could boost interfacial charge transfer and accelerate reaction kinetics.\textsuperscript{[28]} Herein, rational construction of well-defined ternary metal oxide nanosheets with atomic thickness might be an effective approach to optimize the electrochemical performance by coupling unique structural features in terms of atomic interface interactions and the electric-field effect.

Here, a facile and scalable wet-chemical synthesis approach has been introduced for fabrication of atomically thin Bi\textsubscript{2}MoO\textsubscript{6} nanosheets (BMO sheets), consisting of alternate stacking of [Bi\textsubscript{2}O\textsubscript{2}] and [MoO\textsubscript{4}] layers, with large interlayer channels. Interestingly, the self-adaptive oxygen vacancies produced on the open surfaces of BMO sheets is explicitly confirmed by X-ray photoelectron spectroscopy (XPS) and electron paramagnetic resonance (EPR) spectra. More intriguingly, the density functional theory (DFT) calculations demonstrate that an unbalanced charge distribution could occur between the stacked layers as well as around the oxygen vacancies, which induces an interfacial electric field within the interface and local in-panel electric field on the open surfaces, thus accelerating Li ion diffusion kinetics and promoting high-rate capability. In addition, extra migration paths formed on the open interfaces would facilitate charge transport, thereby further enhancing the Li storage performance. Benefiting from the unique structure ensured by the coupling effect of the atomic interfaces, the present atomically thin BMO sheets exhibit good high-rate capability and ultra-long cycling stability, showing enormous potential for
next-generation LIB anode. More importantly, this work demonstrates a powerful multi-scale coordinated strategy for designing advanced electrode materials for electrochemical energy storage, including synergistic modulation of the dimensionality, composition, atomic arrangement, and interfaces.

5.2 Experimental methods

5.2.1 Materials synthesis

5.2.1.1 Synthesis of ultrathin Bi$_2$MoO$_6$ nanosheets (BMO sheets)

In a typical process, 0.225 g cetyltrimethylammonium bromide, 0.5 mmol sodium molybdate dihydrate, and 1 mmol bismuth (III) nitrate pentahydrate were added to 20 mL de-ionized water and 20 mL ethylene glycol solution under magnetic stirring for 30 minutes. The resultant solution was then transferred to an autoclave, which was kept in an oven at 120 °C for 24 h. The obtained product was separated by centrifugation and washed many times with de-ionized water and ethanol after the autoclave was cooled down naturally. The resultant composite was dried at 60 °C under vacuum conditions for 12 h.

5.2.1.2 Synthesis of bulk Bi$_2$MoO$_6$ (BMO bulk)

In a typical procedure, 5 mmol bismuth (III) nitrate pentahydrate and 2.5 mmol sodium molybdate dihydrate were added into 20 mL de-ionized water under magnetic stirring. The resultant solution was then transferred to an autoclave, which was kept in an oven at 200 °C for 24 h. The obtained product was separated by centrifugation and washed many times with de-ionized water and ethanol after the autoclave was cooled down naturally. The collected composite was dried at 60 °C
under vacuum conditions for 12 h and then annealed in a tube furnace at 500 °C for 2 h under flowing argon.

5.2.1.3 Synthesis of ultrathin Bi$_2$O$_3$ nanosheets (BO sheets)

Firstly, 0.5 mmol bismuth (III) nitrate pentahydrate and 88 mg ammonium vanadate were added into 5 mL HNO$_3$ solution (4 mol L$^{-1}$). Then, 20 mL deionized water was added into the solution. After stirring for 30 minutes, the pH of the solution was adjusted to 12 by adding NaOH solution (2 mol L$^{-1}$). The resultant yellow suspension was transferred to an autoclave, which was kept in an oven at 60 °C for 24 h. The obtained product was separated by centrifugation and washed many times with de-ionized water and ethanol, and finally dried at 60 °C for 12 h in vacuum.

5.2.1.4 Synthesis of ultrathin MoO$_3$ nanosheets (MO sheets)

Ultrathin MoO$_3$ nanosheets were prepared according to the literature.$^{[29]}$ Firstly, 0.3 g molybdenic acid was added into 15 mL deionized water with continuous stirring. Then, 3 ml t-dodecanethiol was added and agitated by sonication for 30 minutes. The obtained solution was transferred to an autoclave, which was kept in an oven at 190 °C for 12 h. The resultant dark precipitate was then collected, washed, and dried at 60 °C for 12 h in vacuum.

5.2.1.5 Synthesis of Bi$_2$O$_3$ + MoO$_3$ nanosheets (BO+MO sheets):

The mixture of Bi$_2$O$_3$ and MoO$_3$ nanosheets was obtained by mechanical mixing of the as-prepared Bi$_2$O$_3$ nanosheets and MoO$_3$ nanosheets according to the molar ratio of 1:1.
5.2.2 Materials characterization

The morphologies of the as-prepared products were observed by field emission scanning electron microscopy (FESEM, JEOL JSM-7500FA). The details of the crystal structure and EDS mapping were further examined by scanning transmission electron microscope (STEM, JEOL JEM-ARM200F), which was conducted at 200 kV. The crystalline structure of the obtained materials was checked by X-ray diffraction (XRD, GBC MMA diffractometer) with Cu Kα radiation at a scanning rate of 1° min⁻¹. X-ray photoelectron spectroscopy (XPS) was performed on a VG Multilab 2000 (VG Inc.) photoelectron spectrometer using monochromatic Al Kα radiation under vacuum at 2 × 10⁻⁶ Pa. All of the binding energies were referenced to the C 1s peak at 284.8 eV of the surface adventitious carbon. Raman analysis was performed with a JobinYvon HR800 Raman spectrometer. Continuous-wave electron paramagnetic resonance (EPR) experiments were conducted by a Bruker ELEXSYS E580 spectrometer operating in the X-band (9.4 GHz) mode and equipped with an Oxford CF935 helium flow cryostat with an ITC-5025 temperature controller.

5.2.3 Electrochemical measurements

The electrochemical tests were conducted through the CR2032 coin-type cells. The working electrodes were prepared by mixing the obtained materials, Super P, and poly(acrylic acid)/sodium carboxymethyl cellulose (1:1) in a weight ratio of 70:20:10. The resultant slurry was pasted on Cu foil and dried at 80 °C for 12 h in vacuum, followed by pressing at 300 kg/cm². Electrochemical measurements were carried out using two-electrode coin cells with Li metal as counter and reference electrode and Celgard (product 2400) film as the separator. The electrolyte consisted of a solution of 1 M LiPF₆ in ethylene carbonate/diethyl carbonate (1/1; v/v) with 5 wt%
fluoroethylene carbonate. Electrochemical impedance spectroscopy and cyclic voltammetry were conducted on a VMP-3 electrochemical workstation at a scan rate of 0.1 mV s\(^{-1}\). The cells were galvanostatically charged/discharged in a voltage range of 0.01–3.0 V versus Li/Li\(^+\) at different current densities on a Land CT2001A battery tester.

5.2.4 \textit{In-situ} synchrotron X-ray powder diffraction (SRXRD)

A customized CR2032 coin cell for use in \textit{in-situ} SRXRD experiments was made, and the assembly details can be found elsewhere.\textsuperscript{[30]} Similar to the coin cells used in electrochemical testing, the cell contained the working Bi\(_2\)MoO\(_6\) electrode and a counter/reference Li metal electrode, with Celgard (product 2400) film as the separator. The cell was galvanostatically charged and discharged over 0.1–3.0 V (vs. Li) at constant current of 0.3038 mA (equivalent to \(~200\) mA/g) for the first 2 cycles and 0.1519 mA for another 2 cycles during data collection. SRXRD experiments were conducted on the Powder Diffraction beamline at the Australian Synchrotron, where the SRXRD patterns from the cell were collected every 3.4 minutes during charge and discharge using a MYTHEN microstrip detector. The wavelength used was determined to be 0.6899(3) Å using a LaB6 NIST SRM 660b. The lattice evolution of Bi\(_2\)MoO\(_6\) upon lithium insertion and extraction was extracted and examined using single -peak-fitting analysis with the Large-Array Manipulation Program (LAMP)\textsuperscript{[31]} to track the variations in peak position, intensity, and width of the (131), (002)/(200), and (060) reflections of Bi\(_2\)MoO\(_6\).
5.2.5 DFT calculation

All theoretical calculations are performed by employing the first-principles projector augmented wave (PAW) method\textsuperscript{32} based on density functional theory (DFT) with the Perdew-Burke-Ernzehof (PBE) functional\textsuperscript{33} as implemented in the Vienna \textit{ab initio} simulation package.\textsuperscript{34} The kinetic cut-off and Monkhorst-Pack scheme \textit{k}-point mesh were set to 520 eV and (6×6×2) respectively, with a (6×6×1) \textit{k}-point mesh for monolayer Bi\textsubscript{2}MoO\textsubscript{6} (BMO). The convergence energy threshold for the electronic self-consistent loop was set to 10\textsuperscript{-4} eV. A periodic slab model was utilized to simulate different monolayer BMO phases, and a void region of 15 Å separating the layers was set along the \textit{c}-axis. During the structure optimizations, both the atoms’ positions and the parameters of the lattice were allowed to relax. The van der Waals (vdW)-inclusive DFT-D3 method with Becke-Jonson damping\textsuperscript{35} was employed, and the migration paths and corresponding energy barriers of Li in BMO were computed by adopting the climbing image nudged elastic band method (CINEB).\textsuperscript{36}

The optimized bulk structure of BMO is orthorhombic crystal, and its lattice parameters are $a = 5.58$ Å, $b = 16.31$ Å, and $c = 5.57$ Å. Bulk BMO possesses a rather complicated structure and consists of Bi\textsubscript{2}O\textsubscript{2} and MoO\textsubscript{4} layers, which are arranged alternately along the \textit{b}-axis, as illustrated in Figure 5.20 Within the MoO\textsubscript{4} layers, Mo atoms are six-coordinated in the centers of the distorted MoO\textsubscript{6} octahedra, and Bi atoms are distributed on both sides of the Bi\textsubscript{2}O\textsubscript{2} layer with O atoms placed in the middle. Considering the charge distribution, it should be noted that the charges are mainly concentrated in the MoO\textsubscript{4} layer. Meanwhile, the results based on Bader charge analysis\textsuperscript{37–39} show that the MoO\textsubscript{4} and Bi\textsubscript{2}O\textsubscript{2} layers are charged at -2.89 e and +2.89 e, respectively.
To simulate the BMO {010} surface, a 2×1×2 slab was adopted, while the other condition is the same with the former calculations.

The difference of charge density is defined as:

\[ \Delta \rho = \rho_{OV} - \rho_{\text{perfect}} \]

where \( \rho_{OV} \) and \( \rho_{\text{perfect}} \) are the charge densities of monolayer BMO with O vacancy and perfect monolayer BMO, respectively. The yellow and blue indicate the increase and decrease of the charge density, respectively.

5.3 Results and discussion

The typical scanning electron microscope (SEM) and transmission electron microscope (TEM) images in Figure 5.1a,b visually confirm the sheet-like morphology of the obtained ultrathin BMO. Figure 5.1c shows a representative TEM image, which is a lateral view of the marked nanosheet in Figure 5.1b and reveals the well-defined layer-like architecture with a thickness of about 2.45 nm, corresponding to 1.5 layers of orthorhombic Bi\(_2\)MoO\(_6\) unit cell along the b axis. Meanwhile, the high-resolution TEM (HRTEM) image (Figure 5.1d) demonstrates that the BMO sheets grow along the [010] direction. The lattice spacings of about 0.275 nm and 0.274 nm respectively correspond to the (002) and (200) planes of orthorhombic Bi\(_2\)MoO\(_6\),\(^{[40]}\) indicating that the BMO sheets preferentially expose the {010} facets. What is interesting is that some structural defects/disorder are generated around the exposed surface, which might affect the electronic structure of the material, thus, in turn, tailoring its electrochemical properties.\(^{[41]}\) More importantly, the lateral high-angle annular dark-field-scanning transmission electron microscope (HAADF-STEM)
imaging further clearly reveals the crystal structure of the BMO sheets (Figure 5.1e). In principle, the signal intensity in the HAADF image is proportional to the atomic number, while the O atoms are invisible. Hence, the brighter spots stand for Bi atoms, and the spots with lower brightness represent Mo atoms, demonstrating that the arrangement of Bi and Mo atoms in the ultrathin sheets is highly consistent with the schematic diagram of the Bi$_2$MoO$_6$ crystal structure (Figure 5.1f). Elemental mapping (Figure 5.1g–j) indicates that Bi, Mo, and O coexist and are distributed uniformly in the ultrathin sheets. The acquired BMO sheets have an average sheet thickness of 1.61 nm, as determined by atomic force microscopy (Figure 5.1k,l), close to the 1.62 nm thickness of a BMO along the [010] direction, which is in good agreement with the TEM results. In addition, the morphologies of the obtained micro-sized BMO (BMO bulk), ultrathin sheets of Bi$_2$O$_3$ (BO sheets) and MoO$_3$ (MO sheets), and their mixture (BO+MO sheets) can be verified by the SEM and TEM results (Figures 5.2–5.6).
**Figure 5.1** Morphology of obtained BMO sheets. (a) FESEM image. (b) TEM image. (c) Enlarged high resolution TEM image. In c, the red line marks the thickness of 2.45 nm, corresponding to 1.5 layers of orthorhombic Bi$_2$MoO$_6$ unit cell along the b axis. (d) HRTEM image. In d, the lattice spacings of 0.274 nm and 0.275 nm are shown, with a dihedral angle of 90°, indicating the {010} exposed lattice plane of BMO sheets. (e) Lateral HAADF-STEM image. (f) Schematic diagram of orthorhombic Bi$_2$MoO$_6$ crystal structure. (g–j) Corresponding EDS elemental mappings. (k,l) Atomic force microscope (AFM) image and corresponding height profiles.
Figure 5.2 Electron microscope characterization of the BMO bulk. (a) SEM image. (b) High-angle annular dark-field-scanning TEM (HAADF-STEM) image. (c) Corresponding bright-field TEM image. (d–g) Corresponding element mapping images.

Figure 5.3 Electron microscope characterization of the BO sheets. (a) SEM image. (b) TEM image. (c–e) Corresponding element mapping images.
Figure 5.4 Electron microscope characterization of the MO sheets. (a) SEM image. (b) TEM image. (c–e) Corresponding element mapping images.

Figure 5.5 Electron microscope characterization of the BO+MO sheets. (a) SEM image. (b) HAADF-STEM image. (c) Bright field TEM image. (d–g) Corresponding element mapping images.
Figure 5.6 (a) HAADF-STEM image of the as-prepared ultrathin BO sheets. (b) High-resolution TEM image of the obtained ultrathin MO sheets.

The crystalline nature and purity of the resultant samples were examined by powder X-ray diffraction (XRD). As shown in Figure 5.7a, all the diffraction peaks of BMO sheets can be readily indexed to the orthorhombic Bi$_2$MoO$_6$ (JCPDS No. 77-1246), indicating the highly purity of prepared nanosheets. Compared to the bulk sample, however, only four broadened and weak diffraction peaks emerged, demonstrating the ultrathin thickness and small particle size of the BMO sheets. Interestingly, the intensity ratio I(060)/I(131) of the BMO sheets represents a dramatic enhancement relative to their bulk counterpart, suggesting that the BMO sheets preferentially grow along the [010] direction, which is in agreement with the TEM results (Figure 5.1d). The structures of the acquired BMO products were characterized by Raman spectroscopy. As can be seen from Figure 5.7b, well-defined phonon modes were observed in the 200–1000 cm$^{-1}$ wavenumber range, corresponding to the vibrational modes of orthorhombic Bi$_2$MoO$_6$ and confirming the formation of pure Bi$_2$MoO$_6$.[42] Specifically, the Raman bands at 700–850 cm$^{-1}$ correspond to the stretching vibrations of MoO$_6$ octahedra, while the presence of the
modes in the 230–460 cm\(^{-1}\) range can be assigned to the bending motions of the MoO\(_6\) octahedra and BiO\(_3\) tetrahedra. It is notable that the Raman peaks of BMO sheets showed broadening and slightly shifted towards lower wave number compared to those of the bulk, further revealing the ultrathin nature of the BMO sheets.\(^{[43]}\) The XRD and Raman results (Figures 5.8 and 5.9) demonstrate the preparation of pure Bi\(_2\)O\(_3\) and MoO\(_3\) samples.

The chemical compositions and surface electronic states of the fabricated products were investigated by X-ray photoelectron spectroscopy (XPS). Figure 5.7c,d displays the high-resolution Bi 4f and O 1s XPS spectra of the BMO products. In contrast to the spectra of the bulk sample, two asymmetric peaks of Bi 4f can be found in the BMO sheets (Figure 5.7c), signifying the different electronic state of Bi atoms in the ultrathin sheets. Moreover, the deconvolved shoulder peaks associated with Bi 4f\(_{5/2}\) (167.3 eV) and Bi4f\(_{7/2}\) (161.6 eV) emerge at higher binding energies, revealing that the Bi atoms in the BMO sheets are more electropositive,\(^{[44]}\) due to the rearranged and unsaturated states of the surface Bi and O atoms, resulting in an imbalance in the charge distribution. This would strengthen the interaction between Li ions and electrode materials, and improve the electrochemical activity. In addition, two O 1s peaks located at 529.7 eV and 533.2 eV are observed for both samples, which are attributed to the lattice oxygen and near-surface oxygen, respectively.\(^{[45,46]}\) In particular, a new peak that appeared at 531.7 eV can be assigned to oxygen vacancies.\(^{[45]}\) Furthermore, the Mo 3d peaks of the BMO sheets slightly shifted towards lower binding energy, which is likely due to the bond distortion between the Mo-O atoms in the nanosheets, accompanying with the redistribution of electron density.\(^{[47]}\) The chemical compositions of BO sheets and MO sheets were confirmed
by XPS results (Figure 5.10). It has been demonstrated that atomic defects, especially oxygen vacancies not only can promote faster charge transport kinetics, but also help to retain the integrity of the electrode structure, thus enhancing the electrochemical activity.\textsuperscript{14,48} Therefore, it is desirable to introduce oxygen vacancies into the target electrode material to improve its electrochemical performance. Here, electron paramagnetic resonance (EPR) measurements were conducted to offer fingerprint evidence for probing oxygen vacancies.\textsuperscript{46} Figure 5.7c clearly shows their characteristic EPR signal, revealing the presence of isolated oxygen vacancies in the BMO sheets.

**Figure 5.7** Structural and compositional characterization of the BMO sheets and bulk sample. (a) XRD patterns. (b) Raman spectra. (c–e) Corresponding high-resolution XPS spectra of Bi 4f, O 1s, and Mo 3d. (f) EPR spectra. In d, the new peak at 531.7 eV can be attributed to oxygen vacancies generated on the surface of the BMO sheets. In f, a clear oxygen vacancy signal could be observed in the EPR spectrum of the BMO sheets, indicating the existence of oxygen vacancies in the BMO sheets.
Figure 5.8 XRD patterns of the obtained BO sheets and MO sheets. The XRD results confirmed the purity of as-prepared of pure Bi$_2$O$_3$ and MoO$_3$.

Figure 5.9 Raman spectra of the prepared BO sheets, MO sheets, and BO+MO sheets. The Raman spectra further verify the formation of the pure Bi$_2$O$_3$ and MoO$_3$. The much stronger peaks of the mixture (BO+MO sheets) resulted from the superposition of peaks associated with the BO sheets and MO sheets.
Figure 5.10 XPS spectra of BO sheets and MO sheets. (a) Survey XPS spectra. High-resolution XPS spectra: (b) Bi 4f of BO sheets; and (c) Mo 3d of MO sheets. The XPS results confirmed the formation of Bi$_2$O$_3$ and MoO$_3$.

The Li-ion storage behavior of the BMO sheets was initially investigated using cyclic voltammetry (CV). Figure 5.11a displays representative CV curves for the 1st, 2nd, and 5th cycles at a scan rate of 0.1 mV s$^{-1}$ in the voltage range of 0.01–2.5 V. The CV curves show multi-peak features, demonstrating that the reaction of the BMO sheets with Li proceeds in multiple steps. During the first negative scan, the cathodic peak at ~1.60 V might be assigned to the insertion of Li-ion into the layered structure of BMO crystal, whereas the small peak at 1.24 V is associated with the reduction of BMO to Bi and Mo metal.$^{49,50}$ An obvious cathodic peak appearing at 0.52 V can be attributed to the formation of the solid electrolyte interphase (SEI) film.
and the alloying reaction of Bi with Li to form Li$_3$Bi. Furthermore, the broad reduction peak is divided into two peaks at ~0.74 and 0.61 V in the subsequent cycles, suggesting that the electrochemical lithiation reaction of Bi takes place via two steps (formation of LiBi and Li$_3$Bi, respectively).[50] The strong oxidation peak localized at around 0.98 V corresponds to the de-alloying process of Li$_3$Bi, while the small anodic peaks at about 1.40 V and 1.74 V might be attributed to the oxidation of Mo and Bi, respectively.[49-51] It is noteworthy that from the second cycle onwards, both the reduction and the oxidation peaks in the CV curves overlap very well, proving that the electrode exhibits good reversibility and stability during the electrochemical reactions. Based on the above analysis, the possible electrochemical reactions of the ultrathin BMO anode are believed to proceed as follows [Reactions 5.1–5.4]:

\[
\text{Bi}_2\text{MoO}_6 + x\text{Li}^+ + x\text{e}^- \rightarrow \text{Li}_x\text{Bi}_2\text{MoO}_6 \quad (5.1)
\]

\[
\text{Li}_x\text{Bi}_2\text{MoO}_6 + (12-x)\text{Li}^+ + (12-x)\text{e}^- \rightarrow 2\text{Bi} + \text{Mo} + 6\text{Li}_2\text{O} \quad (5.2)
\]

\[
\text{Bi} + \text{Li}^+ + \text{e}^- \leftrightarrow \text{LiBi} \quad (5.3)
\]

\[
\text{LiBi} + 2\text{Li}^+ + 2\text{e}^- \leftrightarrow \text{Li}_3\text{Bi} \quad (5.4)
\]

Similarly, the BMO bulk presents CV curves with almost the same shape as those of the BMO sheets, but with poor reversibility during the 1st cycle. The CV curves of the BO+MO sheets show the combination of the redox peaks of the BO sheets and the MO sheets, (Figure 5.12).
Figure 5.11 Electrochemical performance of various electrodes for Li storage. (a) Cyclic voltammograms for the 1st, 2nd, and 5th cycles of the BMO sheets at a scanning rate of 0.1 mV s\(^{-1}\). (b) Galvanostatic discharge-charge profiles for selected cycles of the BMO sheets at 50 mA g\(^{-1}\). (c) Cycling performance of BMO sheets, BMO bulk, and BO+MO sheets at 50 mA g\(^{-1}\). (d) Rate capabilities of BMO sheets, BMO bulk, and BO+MO sheets at various current densities. (e) Long-term cycling performance of the BMO sheets at 2000 mA g\(^{-1}\) and the corresponding coulombic efficiency.
Galvanostatic discharge/charge measurements were conducted to evaluate the electrochemical performance of the BMO anodes. Remarkably, the BMO sheets achieved a high reversible capacity of 903 mAh g\(^{-1}\) at a current density of 50 mA g\(^{-1}\), with an initial coulombic efficiency (CE) of 78\% (Figure 5.11b,c). In contrast, the BMO bulk exhibited a much lower first-cycle reversible capacity of 770 mA h g\(^{-1}\), corresponding to an initial CE of 70.3\% (Figure 5.11c,d), while the BO+MO sheets showed a CE of 74\%, with a specific capacity of 810 mA h g\(^{-1}\). As expected, the BMO sheets or BO+MO sheets showed higher specific capacity and coulombic efficiency compared to the BMO bulk, due to their 2D ultrathin structures, which can provide more transport paths to give access to ions and electrons, accompanied by enhanced energetics for ionic/electronic transfer kinetics. On the other hand, the BMO sheets demonstrate better performance in Li\(^+\) storage than the BO+MO sheets, which should be attributed to the effects of interlayer coupling in the ultrathin BMO. Importantly, the specific capacity of the BMO sheets was stabilized at 832 mA h g\(^{-1}\) after 80 cycles, (~ 92\% capacity retention), manifesting its superior cycling stability.

In addition, the BMO sheets exhibited remarkable rate capability at varied current rates. As shown in Figure 5.11d, the BMO sheets delivered a reversible capacity of 580 mA h g\(^{-1}\) at a current density of 1000 mA g\(^{-1}\). Even when cycled at a high current density of 2000 mA g\(^{-1}\), a specific capacity of 490 mA h g\(^{-1}\) could be attained, which is higher than for the BMO bulk and BO+MO sheets. It is well known that long-term cycling stability, especially for charging/discharging at high rate is an important performance for practical application of high-energy LIBs. To further evaluate the high-rate cycling performance, the BMO sheet anode was subjected to prolonged cycling at 1000 mA g\(^{-1}\) and 2000 mA g\(^{-1}\), respectively (Figure
5.12 and Figure 5.11e). The BMO sheets attained an initial charge capacity of 673 mA h g$^{-1}$ at 1000 mA g$^{-1}$ and retained a large charge capacity of 587 mA h g$^{-1}$ after 1000 cycles, which is much higher than the corresponding values for the bulk BMO, BO sheets, MO sheets, and BO+MO sheets (Figures 5.13–5.16), demonstrating the superior high-rate cycling stability. Encouragingly, even after 1500 cycles at 2000 mA g$^{-1}$, a high reversible capacity of 478 mA h g$^{-1}$ was still obtainable with an average coulombic efficiency approaching 100% (Figure 3e), suggesting the great promise of 2D BMO for next-generation high-power LIBs. The significantly enhanced high-rate capacity accompanied by exceptional cycling performance for Li storage should be closely related to the unique structure of the BMO sheets. More importantly, the high-rate cycling performance of the present BMO sheets is significantly superior to those of most reported mixed-metal-oxide-based anodes for Li-ion batteries (Table 5.1).
Figure 5.12 Cyclic voltammograms for the 1\textsuperscript{st}, 2\textsuperscript{nd}, and 5\textsuperscript{th} cycles of various electrodes at a scanning rate of 0.1 mVs\(^{-1}\). (a) BMO bulk. (b) BO+MO sheets. (c) BO sheets. (d) MO sheets. In a, the BMO bulk presents similar CV curves to the BMO sheets, indicating the same electrochemical reactions during the cycling process. In b, the different redox peaks appear in the CV curves of the BO+MO sheets when compared to the BMO bulk, owing to the different chemical composition and reaction mechanism in the mixture.
Figure 5.13 The long-term cycling performance of BMO sheets at 1000 mA g\textsuperscript{-1}.

Figure 5.14 The long-term cycling performance of BMO bulk at 1000 mA g\textsuperscript{-1}.

Figure 5.15 The long-term cycling performance of BO sheets at 1000 mA g\textsuperscript{-1}.
To study the structural superiority of BMO material, in-situ synchrotron X-ray powder diffraction (SXRPD) was utilized to reveal the structural changes in the electrode material during the charge/discharge cycling. The variations of the (131), (200)/(002), and (060) reflections were extracted using the single-peak fitting approach, with these being correlated to lattice parameters $a$, $b$, and $c$. The single-peak fitting results suggest that the positions of the (131), (200)/(002), and (060) reflections did not move significantly during the cycling process (Figures 5.18 and 5.19), indicating that the lattice parameters remained nearly unchanged during the electrochemical reactions. The results revealed that the distorted edge-sharing MoO$_6$ octahedral network and the trigonal-bi-planar BiO$_3$ are strongly bonded, offering...
excellent structural stability against the lithiation and delithiation processes, which explains the outstanding prolonged cycling performance of the Bi$_2$MoO$_6$ when used as anode in LIBs. On the other hand, one can also see that the intensities of these reflections are gradually dropping as cycling progresses, despite the charging and discharging, suggesting that pulverization occurs during cycling, as a result of the conversion reaction.

**Figure 5.18** Contour plots using operando synchrotron X-ray powder diffraction data collected during electrochemical cycling. The variation of (131) and (200)/(002) diffraction peaks of BMO bulk. The positions of the (131) and (200)/(002) reflections did not move significantly during the cycling process, suggesting that the lattice parameters remained nearly unchanged during the electrochemical reactions.
Figure 5.19 The variation in integrated intensity, peak width, and peak position of the (131), (200)/(002), and (060) reflections of Bi$_2$MoO$_6$ phase during discharge and charge.

In order to deeply understand the properties of the crystal structure that are responsible for the enhanced lithium storage performance, DFT calculations were performed to investigate the migration barriers to Li$^+$ along different paths in the BMO bulk and nanosheets. In bulk BMO, three typical lithium diffusion paths were considered (Figure 5.20a), and the migration paths between the three kinds of binding sites and the corresponding barriers are shown in Figure 5.20b. Among them, “A” and “B” site are equivalent symmetrically and arranged along the b-axis, while “C” site is in the middle of MoO$_4$ layer. Along the c-axis in bulk BMO, the crystal can form natural transmission channels with large interlayer spaces between the [MoO$_4$] and [Bi$_2$O$_2$] layers, making them very suitable for Li ion migration. As a result, the barrier from the A to the B sites is only 0.40 eV, whereas the barriers from A and B to C are 1.14 eV and 1.24 eV, respectively, which indicates that Li ions mainly diffuse through the interlayer channels along the c-axis in bulk BMO. For the BMO sheets, the following four kinds of intercalation sites are considered: on the surface O atoms above Bi and Mo, denoted as “A1(B1)” and “A2(B2)”, respectively,
and in the interior of the sheets, denoted as “A3(B3)” and “A4(B4)”. It should be noted that, although the transmission channels are distorted to some extent, the BMO sheets show similar or even lower migration barriers of 0.44 and 0.35 eV in these interlayer channels. More importantly, compared to the BMO bulk, the barriers to the migration of Li ions between different binding sites are quite low. As can be seen from Figure 5.20e, the barrier from the A1 to the A2 site is only 0.76 eV, which is much lower than in BMO bulk (1.14 eV or 1.24 eV). Thus, in the BMO sheets, Li ions could be transferred along both the ab-plane and the c-axis, thereby forming interconnected migration paths on the open surfaces, which is superior to the unidirectional migration in bulk BMO. In addition, the interlayer electron-electron coupling in the atomically thin BMO was further analyzed (Figure 5.20f–h). The calculated results signified that the imbalance in the charge distribution occurred between the [MoO₄] and [Bi₂O₂] layers, which could induce a built-in electric field within the atomic interface, thus boosting the Li ion diffusion kinetics and improving the high-rate performance. Furthermore, the charge density distribution around the oxygen vacancies area is calculated theoretically by first principles. As expected, charge redistribution can be observed in the BMO with O-vacancies and an imbalance in charge distribution occurs (Figure 5.21), which might induce the formation of a local electric field in plane, contributing to faster charge transfer kinetics.
Figure 5.20 Crystal structure, Li$^+$ diffusion paths, corresponding migration energy barriers, and charge density distribution calculated by DFT. (a) Crystal structure of BMO bulk with three Li ions intercalated at A, B, and C sites. (b) Calculated migration energy barriers to Li$^+$ diffusion through different paths in BMO bulk. (c,d) Crystal structure of BMO sheets and four kinds of intercalation sites. (e) Migration energy barriers to Li$^+$ diffusion along different paths in BMO sheets. (f) Crystal structure of the BMO viewed along the [001] direction. (g) Charge density distribution of the BMO in the initial state. (h) Charge density distribution of the BMO in the charged state ($\text{Li}_2\text{Bi}_2\text{MoO}_6$). In g, the calculated result indicates that the charges are mainly concentrated in the [MoO$_4$] layer. Meanwhile, the results based on Bader charge analysis show that the [MoO$_4$] and [Bi$_2$O$_2$] layers are charged at -
2.89 e and +2.89 e, respectively. In h, it shown that the imbalance in the charge distribution occurs during the charging state, indicating the presence of the built-in electric field.

![Figure 5.21](image)

**Figure 5.21** The charge distribution around the oxygen vacancy area simulated based on the first principle. (a) The top view of monolayer Bi$_2$MoO$_6$. (b,c) The difference of charge density of monolayer Bi$_2$MoO$_6$ with two different O vacancy sites (isosurface level is set to 0.055). The yellow and blue in Figure 5.21b,c indicate the increase and decrease of the charge density, respectively.

By combining the *in-situ* synchrotron XRPD and DFT analysis, a possible mechanism for the enhancement of lithium storage in the atomically thin BMO nanosheets could be proposed (Figure 5.22). The unbalanced charge distribution between [Bi$_2$O$_2$]$_{2+}$ and [MoO$_4$]$_{2-}$ layers induces an interfacial electric-field within the interfaces, while lopsided charge distribution around oxygen vacancies resulted in a local in-plane electric-field, thus promoting ion diffusion/electron transport, which can be confirmed by the much lower charge-transfer impedance (Figure 5.23) and the high-rate performance (Figure 5.11d). Meanwhile, benefiting from the structural advantages of the 2D ultrathin construction, interconnected charge migration paths were formed on the open surfaces, which could facilitate the charge transfer process.
in the BMO sheets, as evidenced by the higher diffusion coefficient of Li$^+$ (Figure 5.24). Therefore, profiting from the strong interlayer coupling effect and atomic defects, which induces built-in electric-field within the crystal and promotes charge transfer dynamics, the superior configuration of the ultrathin sheets, resulting in additional transport paths, as well as the good structural stability ensured by the edge-sharing MoO$_6$ octahedral network and the trigonal-bi-planar BiO$_3$ architecture, the BMO sheets exhibit remarkable high-rate capability and outstanding cycling stability for Li-ion storage.

**Figure 5.22** Summary of the enhanced high-rate capacity mechanism of the BMO sheets for LIB. (a) The schematic diagram of the induced in-panel electric field and the interface electric field within the BMO sheets viewed along different directions.
(b) The electric field distribution and the corresponding crystal structure of the BMO sheets in a. (c) The relationship between the electric field, migration paths and the Li transfer kinetic in BMO sheets and BMO bulk.

Figure 5.23 Nyquist plots of electrodes containing BMO sheets, BMO bulk, and BO+MO sheets. Spectra were obtained by applying a sine wave with an amplitude of 5.0 mV over the frequency range of 100 kHz–0.01 Hz. The BMO sheets displayed the lowest charge transfer impedance compared to the BMO bulk or BO+MO sheets, indicating the enhanced electron- and Li-ion transport dynamics.
Figure 5.24 CV curves at different scan rates for LIB cells with (a) BMO sheets, and (b) BMO bulk electrodes. (c) The linear relationship between the peak current ($i_p$) and the square root of the scan rate ($v^{1/2}$) for BMO sheets and BMO bulk electrodes.

The lithium-ion diffusion coefficient ($D_{Li^+}$) can be calculated based on the Randles-Sevcik Equation:

$$i_p = (2.69 \times 10^5) n^{3/2} SD^{1/2} C v^{1/2} \quad (5.5)$$

Where $i_p$ is the peak current (A), $n$ is the number of transferred electrons, $D$ is the diffusion coefficient of Li$^+$ (cm$^2$ s$^{-1}$), $S$ is the surface area of the electrode, $C$ is the concentration of Li ions in the electrolyte, and $v$ is the potential scan rate (Vs$^{-1}$).
Since the two electrodes were prepared and tested by the same procedure, the Randles-Sevchik equation can be further simplified as:

\[ i_p = AD^{1/2} \nu^{1/2} \quad (5.6) \]

Where \( A \) is supposed to be constant for the two cells and \( AD^{1/2} \) is defined as the apparent diffusion coefficient of Li\(^+\) in the cells, which can be calculated by fitting the linear curves shown in Figure 5.24c. According to the fitting results, the BMO sheets exhibited a much higher apparent diffusion coefficient of Li\(^+\) compared to the bulk sample.
Table 5.1: Comparison of the high-rate cycling performance of various mixed metal oxide-based anodes. The high-rate cycling performance of our obtained Bi$_2$MoO$_6$ nanosheets was found to be much better than those of most reported anode materials for Li-ion batteries.

<table>
<thead>
<tr>
<th>Materials</th>
<th>High-rate cycling performance (mA h g$^{-1}$)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi$_2$MoO$_6$ nanosheets</td>
<td>587 (after 1000 cycles) 1000 mA g$^{-1}$ 478 (after 1500 cycles) 2000 mA g$^{-1}$</td>
<td>This work</td>
</tr>
<tr>
<td>ZnMn$_2$O$_4$ hollow microspheres$^{[52]}$</td>
<td>750 (after 120 cycles) 400 mA g$^{-1}$</td>
<td>NA</td>
</tr>
<tr>
<td>CoSnO$_2$@C nanoboxes$^{[53]}$</td>
<td>450 (after 400 cycles) 200 mA g$^{-1}$</td>
<td>NA</td>
</tr>
<tr>
<td>ZnCo$_2$O$_4$ microspheres$^{[54]}$</td>
<td>421.6 (after 100 cycles) 90 mA g$^{-1}$</td>
<td>NA</td>
</tr>
<tr>
<td>Fe$_2$GeO$_4$ NPs/RGO$^{[55]}$</td>
<td>720 (after 130 cycles) 900 mA g$^{-1}$ 560 (after 130 cycles) 1500 mA g$^{-1}$</td>
<td>NA</td>
</tr>
<tr>
<td>NiCo$_2$O$_4$ microspheres$^{[56]}$</td>
<td>-400 (after 100 cycles) 500 mA g$^{-1}$</td>
<td>NA</td>
</tr>
<tr>
<td>CoMn$_2$O$_4$ triple-shelled hollow spheres$^{[57]}$</td>
<td>726.7 (after 200 cycles) 200 mA g$^{-1}$</td>
<td>NA</td>
</tr>
<tr>
<td>ZnFe$_2$O$_4$ sub-microcubes$^{[58]}$</td>
<td>-487 (after 200 cycles) 1000 mA g$^{-1}$ -453 (after 200 cycles) 2000 mA g$^{-1}$</td>
<td>NA</td>
</tr>
<tr>
<td>NiFe$_2$O$_4$ nanotubes$^{[59]}$</td>
<td>-1349 (after 200 cycles) 100 mA g$^{-1}$</td>
<td>NA</td>
</tr>
<tr>
<td>Co$_3$V$_2$O$_8$·n H$_2$O$^{[60]}$</td>
<td>847 (after 255 cycles) 500 mA g$^{-1}$</td>
<td>NA</td>
</tr>
<tr>
<td>Flake-like MnCo$_2$O$_4$ $^{[61]}$</td>
<td>952 (after 100 cycles) 100 mA g$^{-1}$</td>
<td>NA</td>
</tr>
<tr>
<td>FeWO$_4$/graphene nanospheres$^{[62]}$</td>
<td>441 (after 100 cycles) 500 mA g$^{-1}$</td>
<td>NA</td>
</tr>
<tr>
<td>ZnSnO$_3$ $^{[63]}$</td>
<td>440 (after 100 cycles) 200 mA g$^{-1}$</td>
<td>NA</td>
</tr>
<tr>
<td>Zn$_2$Co$_3$O$_4$ polyhedra$^{[64]}$</td>
<td>990 (after 50 cycles) 100 mA g$^{-1}$</td>
<td>NA</td>
</tr>
<tr>
<td>Zn$_2$SnO$_4$ nanowires$^{[65]}$</td>
<td>983 (after 100 cycles) 54.7 mA g$^{-1}$</td>
<td>NA</td>
</tr>
<tr>
<td>Material</td>
<td>Capacity (after cycles)</td>
<td>Current Density</td>
</tr>
<tr>
<td>----------------------------------</td>
<td>-------------------------</td>
<td>-----------------</td>
</tr>
<tr>
<td>Ca$_2$Ge$<em>7$O$</em>{16}$ hollow microspheres$^{[66]}$</td>
<td>804.6 mA g$^{-1}$ (after 100 cycles)</td>
<td>NA</td>
</tr>
<tr>
<td>CoFe$_2$O$_4$/rGO aerogel$^{[67]}$</td>
<td>330 mA g$^{-1}$ (after 1000 cycles)</td>
<td>4500 mA g$^{-1}$</td>
</tr>
</tbody>
</table>

### 5.4 Conclusions

In summary, by means of synergistically modulating their structural configuration and electronic interactions, the atomically-thin BMO nanosheets acquired through a facile wet-chemical synthesis procedure achieved outstanding high-rate cycling performance towards Li-ion batteries. By a combined approach involving DFT calculations and in-situ synchrotron XRPD analysis, the mechanism for the enhancement of lithium storage was investigated in depth. The excellent electrochemical performance can be attributed to the strong electric-field effect within the crystal, the unique 2D ultrathin configuration, and the superior structural stability. The good high-rate cycling performance, along with the simple and scalable synthetic approach for ultrathin 2D materials, makes this material design strategy a promising approach to exploit novel 2D materials with remarkable performance in advanced energy technologies.

### 5.5 References


CHAPTER 6 HIERARCHICAL POROUS NiO/β-NiMoO₄ HETEROSTRUCTURE AS SUPERIOR ANODE MATERIAL FOR LITHIUM STORAGE

6.1 Introduction

High-performance rechargeable lithium-ion batteries (LIBs) are gradually becoming indispensable units in portable commercialized electronics, electric vehicles, and renewable energy storage. Nevertheless, the conventional LIBs based on the prevailing carbon-based intercalation materials are already reaching their energy capacity limits. Hence, tremendous efforts have been devoted to exploring novel anode materials with higher energy density, sustainable lifespan, cost-effectiveness, and safe working potential to make these materials applicable for the advanced LIBs to meet the ever-growing demands for electrical applications.

Ternary transition metal oxides (TTMOs) are emerging as promising candidate electrode materials for high-energy LIBs due to their distinctive properties. It is widely demonstrated that TTMOs generally exhibit superior reversible capacity, good structural stability, and high electronic conductivity. Specifically, the synergetic effects associated with their complex chemical compositions typically contribute to remarkable electrochemical activities and high specific capacity, while the multiple valences of the cations are beneficial to achieve more versatile redox reactions. More importantly, because of the lower activation energy for electron transfer between different cations, it normally possess higher electrical conductivity than their corresponding binary metal oxide counterparts. Among various
potential TTMOs, spinel structure nickel molybdate (NiMoO$_4$) has been regarded as an attractive material in view of its high theoretical capacity (about 984 mA h g$^{-1}$), good electrical conductivity, environmental friendliness, and low cost.$^{[11,12]}$ At atmospheric pressure, there are two phases of NiMoO$_4$ both with monoclinic structure: the $\alpha$-NiMoO$_4$ (low temperature stable phase) and $\beta$-NiMoO$_4$ (high temperature stable phase). The most obvious difference between those two polymorphs is the coordination of the Mo$^{6+}$ ions, with pseudo-octahedral coordination in the $\alpha$-NiMoO$_4$ phase and distorted tetrahedral coordination in the $\beta$-NiMoO$_4$ phase.$^{[13]}$ Generally, $\beta$-NiMoO$_4$ has higher intrinsic conductivity and reactivity than that of $\alpha$-NiMoO$_4$,$^{[14]}$ but it is very difficult to be prepared and maintained. In addition, NiMoO$_4$ electrode materials suffer from some drawbacks, such as the huge volume change, low electrochemical reversibility, leading to inferior electrochemical performance.$^{[15,16]}$ Therefore, rational design and facile synthesis of $\beta$-NiMoO$_4$ materials for high energy LIBs still remains a significant challenge.

Constructing heterostructure by combining active materials with metal oxides or sulfides has proven to be an effective way to conquer above-mentioned obstacles.$^{[17,18]}$ It is believed that such constructed heterostructure usually enables abundant electrochemical active sites, short ion diffusion path, and good structural stability originating from the synergistic effect of different components, thus exhibiting better electrochemical performance.$^{[19]}$ For example, Yuan et.al, developed the hierarchical mesoporous ZnO/ZnFe$_2$O$_4$ sub-microcubes which exhibited better electrochemical Li-storage properties than the single-phase ZnFe$_2$O$_4$, owning to the striking synergistic effect between the bi-component active, well-
dispersed ZnO and ZFO phases at the nanoscale.\cite{20} Mai et al. found that hierarchical MnMoO$_4$/CoMoO$_4$ heterostructured nanowires shown enhanced specific capacitance and reversibility when compared to the MnMoO$_4$ and CoMoO$_4$ electrodes.\cite{21} Similarity, other hybrid heterostructures such as the ZnCo$_2$O$_4$/NiO core/shell nanowires,\cite{22} NiO-Co$_3$O$_4$ nanoplates,\cite{23} CoO/CoFe$_2$O$_4$ nanocomposites,\cite{24} and CoMoO$_4$/Co$_3$O$_4$ composites,\cite{25} have been employed as LIB electrodes and demonstrated improved reversible capacity and cycling performance.

Besides the favorable component, the structure also plays important roles in determining the electrochemical property of the developed electrode materials. It is considered that the hierarchical architecture constructed from 2D building blocks possess superior structural characteristics featuring in large specific surface area, more accessible pores, high structural stability, endowing them promising prospects for energy-related applications.\cite{26} Undoubtedly, the large specific surface would provide rich Li storage active sites, while the generated numerous pores may offer additional space to accommodate the volume expansion, consequently maintaining the structural stability and electrode integrity. Lou et al, synthesized the hierarchical tubular structure of Co-Mn mixed metal oxides manifesting excellent electrochemical properties when employed as electrodes in Li-ion batteries and hybrid supercapacitors.\cite{27} A hierarchical fascicular structure of Zn$_2$GeO$_4$ anode obtained through a wet chemistry method also exhibited remarkable Li-ion storage performance, since the hierarchical structure could alleviate the volume changes and retain the whole configuration, while the small building units will enlarge the contact area for electrode/electrolyte and construct the integrated interlaced conductive network.\cite{28}
Herein, we have designed and constructed a novel hierarchical porous NiO/β-NiMoO₄ (NNMO) heterostructure via a facile hydrothermal technique followed by a calcination process. Interestingly, the NiO phases in the NNMO heterostructure could be regarded as a multifunctional layer, which can not only contribute to high theoretical capacity, but also function as the mechanical buffer to alleviate the huge volume changes of NiMoO₄ matrix, thus offering high capacity and good structural stability. Furthermore, the generated metallic nickel (Ni) nanoparticles from the lithiation reaction of NiO nanosheets with Li are able to promote the reversibly decompose of Li₂O during delithiation process, leading to high initial columbic efficiency and enhanced reversible capacity of the NiMoO₄, while the abundant pores produced from the surface interconnected nanosheets and the self-assembled microspheres with hierarchical structure will provide more space to relieve the induced-stress during lithiation/delithiation processes and preserve the structural integrity. As expected, the as-prepared NiO/β-NiMoO₄ heterostructured anode exhibited much better electrochemical Li storage properties than those of single-phase NiO or NiMoO₄ counterparts. Such significantly enhanced electrochemical performance can be attributed to its superior structural characteristics achieved by rational structure engineering of the electrode.

6.2 Experimental methods

6.2.1 Materials synthesis

6.2.1.1 Synthesis of hierarchical porous NiO/β-NiMoO₄ heterostructure

In a typical synthesis process, 2 mmol nickel acetate tetrahydrate (0.4978 g) and 1 mmol sodium molybdate dehydrate (0.3629 g) with a Ni/Mo molar ratio of 2:1 were
slowly added into 30 mL deionized water under magnetic stirring for 30 min to form a transparent solution. The above resultant solution was then transferred to a 50 mL Teflon-lined autoclave, and then it was kept in an oven at 180 °C for 12 h. After the hydrothermal reaction, the obtained green product was separated by centrifugation and washed several times with de-ionized water and ethanol. The resultant composite was then dried at 80 °C overnight, followed by heating in a tube furnace under oxygen atmosphere at 550 °C for 2 h with a ramp rate of 2 °C min⁻¹, yielding the hierarchical NNMO electrode with a Ni : Mo ratio of 2.3:1, as determined by inductively coupled plasma (ICP) (Table 6.1).

6.2.1.2 Synthesis of single-phase NiO (NO) materials

The synthesis process is similar to that for NNMO. First, 1.2 mmol nickel chloride hexahydrate (0.2852 g), 3 mmol urea (0.1802 g), and 0.33 mmol cetyltrimethyl ammonium bromide (CTAB, 0.12 g) were added into 30 ml deionized water under magnetic stirring for 30 minutes to form a transparent solution. Then, the above solution was transferred to a 50 mL Teflon-lined autoclave and kept in an oven at 180 °C for 12 h. The obtained slurry was centrifuged, washed with deionized water, and then dried at 80 °C for 24 h. After thermal oxidation at 550 °C for 2 h with a ramp rate of 2 °C min⁻¹, the single phase NiO material was obtained.

6.2.1.3 Synthesis of single-phase α-NiMoO₄ (NMO) materials

In a typical procedure, 1.3 mmol nickel chloride hexahydrate (0.3090 g) and 1.3 mmol sodium molybdate dehydrate (0.3527 g) with a Ni/Mo molar ratio of 1:1 were added into a given amount (30 mL) of distilled water. The resulting solution was then transferred into a Teflon-lined stainless-steel autoclave and maintained at 180 °C for
12 h. After cooling to room temperature, the slurry was washed several times with
deionized water and dried at 80 °C for 24 h in an oven. Finally, the dried material,
which had a green color, was thermally treated at 550 °C for 2 h in a tube furnace
under oxygen atmosphere to yield the α-NiMoO₄.

6.2.2 Material characterization

The crystalline structure of the materials was investigated by X-ray diffraction
(XRD, Bruker AXS, D8 diffractometer) with Cu Kα radiation at a scanning rate of 1°
min⁻¹. The morphology and energy dispersive spectroscopy (EDS) mapping of the
as-prepared products were observed by scanning electron microscopy (SEM; JEOL
JSM, 6510V), and the details of the crystal structure were further examined by
transmission electron microscopy (TEM; FEI TF20). X-ray photoelectron
spectroscopy (XPS) was then conducted on an ESCALAB 250XI photoelectron
spectrometer using monochromatic Al Kα radiation under vacuum at 2 × 10⁻⁶ Pa. All
of the binding energies are referenced to the C 1s peak at 284.8 eV of the surface
adventitious carbon. The actual contents of the Ni and Mo elements were measured
by inductively coupled plasma (ICP) emission spectroscopy using a Perkin Elmer
Optimal 8000 instrument (detection limit: 0.01 ppm for Ni, 0.01 ppm for Mo).
Specific surface areas and pore size distributions were also obtained from N₂
adsorption/desorption isotherms recorded at 77 K with a Micromeritics ASAP 2020
porosimeter. Prior to surface area measurements, the sample was dried under vacuum
at 393 K for 8 h. The surface area was computed using the Brunauer–Emmett–Teller
(BET) method, whereas the pore size distribution was calculated in accordance with
the Barrett–Joyner–Halenda (BJH) method.
6.2.3 Electrochemical measurements

Electrochemical tests were further conducted on CR 2025 coin-type cells that were assembled in an argon-filled glove box. The working electrodes were prepared by mixing the active materials, Super P, and Na-carboxymethyl cellulose (CMC) in a weight ratio of 60:30:10 then pasted on Cu foil and dried at 80 °C for 12 h in a vacuum oven, which was followed by pressing at 300 kg/cm². The mass loading of the materials on individual electrodes was about 1.15 mg cm⁻². Electrochemical measurements were further carried out using two-electrode coin cells with Li metal as the counter and reference electrode and Celgard (product 2300) film as the separator. The electrolyte consisted of a solution of 1 M LiPF₆ in ethylene carbonate/diethyl carbonate/ethyl methyl carbonate (1:1:1; v/v/v). Electrochemical impedance spectroscopy and cyclic voltammetry were conducted on a CHI 660E electrochemical workstation at different scan rates. The cells were galvanostatically charged/discharged in the voltage range of 0.01–3.00 V versus Li/Li⁺ at different current densities on a Land CT2001A battery tester.

The lithium-ion diffusion coefficient \( D_{\text{Li}^+} \) was further calculated based on the Randles-Sevcik Equation, as in previously reported methods:\(^{[3]}\)

\[
i_p = (2.69 \times 10^5) n^{3/2} S D_{\text{Li}^+}^{1/2} C^{1/2} \nu^{1/2}
\]

(6.1)

Where \( i_p \) is the peak current (A), \( n \) is the number of transferred electrons, \( D_{\text{Li}^+} \) is the diffusion coefficient of Li ions (cm² s⁻¹), \( S \) is the electrode surface area, \( C \) is the concentration of Li⁺ in the electrolyte, and \( \nu \) is the potential scan rate (V s⁻¹). Since the electrodes were prepared and tested by the same procedure, the Randles-Sevcik equation can be further simplified as follows:
\[ i_p = AD^{1/2}v^{1/2} \quad (6.2) \]

Where \( A \) is supposed to be a constant and \( AD^{1/2} \) is defined as the apparent diffusion coefficient of \( \text{Li}^+ \) in the coin cells, which can be calculated by fitting the linear curves.

6.3 Results and discussion

The synthesis of hierarchical porous NiO/\( \beta \)-NiMoO\(_4\) (NNMO) heterostructure by a novel and facile strategy is schematically illustrated in Figure 6.1. First, appropriate proportions of \( \text{Ni}^{2+} \) and \( \text{MoO}_4^{2-} \) precursors were homogeneously mixed into deionized water under magnetic stirring for certain time, so that the acetate could be adsorbed on the surface of \( \text{MoO}_4^{2-} \) by electrostatic interaction, and after that, the NNMO was obtained by oxidation of the as-prepared precursor mixture at 550 °C under oxygen atmosphere. For further comparison, single phase NiO (NO) and NiMoO\(_4\) (NMO) were also fabricated by similar processes, with the exception of the different precursors that were chosen.
Figure 6.1 Schematic illustration of the novel hierarchical porous NiO/β-NiMoO$_4$ (NNMO) heterostructure prepared via a facile hydrothermal method followed by a calcination process.

The purity and crystal structure of fabricated samples were analysed by powder X-ray diffraction (XRD). The XRD patterns in Figure 6.2a confirm that the as-prepared NNMO materials are composed of pure β-phase NiMoO$_4$ (JCPDS Card No. 12-0348) and cubic bunsenite NiO (JCPDS Card No. 47-1049), indicating the coexistence of pure β-NiMoO$_4$ and NiO phase in the obtained NNMO composite. Furthermore, the formation of cubic NiO phase in the hybrid heterostructure is revealed by the diffraction peaks centered at 37.25°, 43.28°, and 62.89°, corresponding to the (111), (200), and (220) crystal planes, respectively. The remarkable diffraction peak at the value of 26.65° can be indexed to the characteristic (220) planes of β-NiMoO$_4$, suggesting the high purity of the β-phase NiMoO$_4$, without any trace/residual of the α-phase.$^{[29]}$ As shown in Figure 6.3a, the diffraction patterns of prepared single-phase NO are well matched with pure NiO (JCPDS Card No. 47-1049), while all the diffraction peaks in Figure 6.3b can be
assigned to the pure monoclinic α-NiMoO₄ (JCPDS Card No. 33-0948). Notably, no diffraction peaks can be indexed to β-phase NiMoO₄.

N₂ adsorption/desorption measurement were carried out to analyze the physical properties of the obtained samples (Figure 6.2b,c). As presented in Figure 6.2b, the isotherm curves of all three samples show distinct type IV adsorption isotherm with H1-type hysteresis loops within a relative pressure $P/P₀$ range from 0.05 to 0.95 in the desorption isotherm, implying the existence of numerous pores. Based on the BET method analysis, it was found that the NNMO has a much larger specific surface area of 23.20 m² g⁻¹ with a total pore volume of 2.4 cm³ g⁻¹, compared to the single-phase NO (10.45 m² g⁻¹) and NMO (18.40 m² g⁻¹) (Inset in Figure 6.2b). Accordingly, the BJH pore size distribution profiles derived from the adsorption branches of isotherms were also calculated and are shown in Figure 6.2c. The pore size distribution curves for NNMO reveal that most of the pores range between 20 and 50 nm, markedly confirming the existence of a kind of mesoporous nanostructure. In addition, the narrow pore size distributions of NO and NMO show that the numerous pores are mainly macropores. Impressively, the unique structural features including the high specific surface area and abundant porous structure of NNMO heterostructure will not only provide many electroactive sites, large electrode/electrolyte contact area as well as easy access of electrolyte, but also accommodate the huge volume changes of the electrode during repeated lithiation/delithiation processes,[8,30,31] thus making it extremely beneficial to high-rate performance and long-cycle stability for Li ions storage.
Figure 6.2 (a) General XRD pattern of as-prepared NNMO; (b) N$_2$ adsorption/desorption isotherms (inset: comparison of the specific surface areas of NO, NMO, and NNMO) and (d) pore size distributions of those three samples.

Figure 6.3 General XRD patterns of (a) NO electrode and (b) NMO electrode.

The chemical states and elemental composition of the as-synthesized sample were further characterized by the X-ray photoelectron spectroscopy (XPS) technique. As displayed in Figure 6.4a, the whole survey scan of the NNMO primarily demonstrates the presence of the elements Ni, Mo, and O. The high-resolution spectrum of Ni 2p (Figure 6.4b) can be deconvoluted into two main peaks by using the Gaussian fitting method, with the binding energies centered at 855.9 eV and 873.8 eV, corresponding to two spin-orbit doublets (Ni 2p$_{3/2}$ and Ni 2p$_{1/2}$) and two weak shake-up satellite peaks of nickel located at 861.5 eV and 880.1 eV,
The spin-energy separation of 17.9 eV is characteristic of the presence of Ni$^{2+}$.\textsuperscript{34} On the other hand, the binding energies of Mo 3d$_{5/2}$ and Mo 3d$_{3/2}$ (Figure 6.4c) are located at 232.0 eV and 235.1 eV, respectively. The binding energies and the energy separation (3.1 eV) are characteristics of the Mo$^{6+}$ oxidation state in NiMoO$_4$.\textsuperscript{35} Figure 6.4d clearly shows the high-resolution spectrum in the O 1s region, which consists of a main peak located at 531.7 eV coupled with a shoulder at 532.7 eV. Therefore, the XPS results indicate the presence of Ni$^{2+}$ and Mo$^{6+}$ both in the composite. Based on the XRD results (Figure 6.2a), the Ni$^{2+}$ and Mo$^{6+}$ can be ascribed to the NiO and NiMoO$_4$ phases in the material.

Figure 6.4 (a) XPS survey spectrum, (b) high resolution Ni 2p spectrum, (c) Mo 3d spectrum, and (d) O 1s region of the obtained NNMO material.
The detailed morphology and microstructure of the as-prepared hierarchical porous NiO/β-NiMoO₄ heterostructure were investigated by the scanning electron microscopy (SEM) and high-resolution transmission electron microscopy (HRTEM). Figure 6.5a,b shows the representative SEM images of the NNMO at low and high magnification, respectively. It can be seen that the NNMO shows typical hierarchical porous microspheres, constructed from large amount of nanosheets with a thickness of 10~20 nm. Moreover, close observation can reveal that there are numerous nanopores generated on the nanosheets (Figure 6.5b) and the assembled nanosheets also formed abundant large pores, which is also consistent with the BET results. The TEM images further confirm the hierarchical porous structure of the NNMO sample. (Figure 6.5c,d) These pores could promote the electrolyte to access the interior portion of material and offer enough additional space to accommodate the volume changes of the electrodes, thus improving electrochemical performance for Li-ion storage. Furthermore, the marked interplanar distances in the high resolution TEM image are 0.336 and 0.241 nm (Figure 6.5e), corresponding to the (220) and (111) lattice planes of β-NiMoO₄ and NiO, respectively, certifying the presence of the two phases in the composite. More interestingly, the β-NiMoO₄ and the NiO nanosheets are in tight contact with each other and form the heterostructure, which may promote rapid ion/electron transfer. In addition, the introduced NiO phase could function as the buffer layer to accommodate the volume expansion and effectively maintain the structural integrity and stability. In the selected area electron diffraction (SAED) pattern of the NNMO (Figure 6.5f), the diffraction rings can be assigned to the (111), (200), (220), and (222) planes of NiO phase, as well as to the (220) planes of β-NiMoO₄, respectively, which also indicates the coexistence of the two phases in the NNMO composite. This novel architecture and its composition were further
researched by the corresponding energy dispersive X-ray spectroscopy (EDX) elemental mapping images (Figure 6.5g-5j), which confirm the presence of Ni, Mo, and O elements in the NNMO. Moreover, the Ni, Mo and O elements are homogeneously distributed in the entire microsphere, indicating the intimate contact between the two components and the formation of heterostructures. On the contrary, the SEM images of the NO (Figure 6.6a,b) show networks constructed from many disordered and aggregated rods. The length of the rods is between one and tens of micrometers. Figure 6.6c,d further reveal the general microsphere architecture of α-phase NiMoO₄ with several micrometers in average diameters. Although the morphology of α-phase and β-phase NiMoO₄ are quite similar, without the introduced NiO phase, the nanosheets of NMO microsphere aggregated severely, resulting in less pores and inferior structural stability.

**Figure 6.5** (a,b) Representative SEM images at different magnifications of NNMO; (c–e) TEM and HRTEM images of as-prepared NNMO; (f) SAED pattern and (g–j) Corresponding EDS elemental mapping images of the NNMO material.
Figure 6.6 Representative SEM images of (a,b) NO and (c,d) NMO at different magnifications.

To further investigate the electrochemical behavior of the synthesized materials for Li-ion batteries, cyclic voltammetry (CV) measurements were conducted. Figure 6.7a shows the first five consecutive CV curves of NNMO electrode recorded at a scan rate of 0.1 mV/s in the potential range of 0.01–3.00 V versus Li/Li⁺. It is evidently observed that from the second to fifth cycles, these CV profiles overlap well, implying the good reversibility and cycling stability of the NNMO electrode during electrochemical reactions. In the first cycle, two intense reduction peaks in the cathodic scan occurred at around 0.59 V and 0.42 V, corresponding to the initial reduction of β-NiMoO₄ to Ni and Mo (NiMoO₄ + 8Li⁺ + 8e⁻ → Ni + Mo + 4Li₂O) and NiO to Ni (NiO + 2Li⁺ + 2e⁻ → Ni + Li₂O), combined with the formation of
amorphous Li$_2$O and SEI layers.$^{[16,36,37]}$ Meanwhile, the broad peaks in the voltage range from 1.4 V to 1.8 V can be further ascribed to the oxidation process of Mo to Mo$^{6+}$ (Mo + 3Li$_2$O $\rightarrow$ MoO$_3$ + 6Li$^+$ + 6e$^-$),$^{[38]}$ whereas the oxidation of metallic Ni to NiO$_x$ contributes to the anodic peak located at approximately 1.83 V.$^{[39]}$ In the following cycles, the different reduction/oxidation peak pairs of 0.75/1.45 V and 1.42/1.79 V are reversible because of the lithium insertion/extraction process with MoO$_3$.$^{[39,40]}$ Notably, an anodic peak near 2.25 V is observed in the NNMO electrode, owing to the conversion reaction of Ni to NiO (Ni + Li$_2$O $\rightarrow$ NiO + 2Li$^+$ + 2e$^-$).$^{[36]}$ On the other hand, the CV curves of NO and NMO electrodes show different behavior in comparison with that of the NNMO. In the first cathodic process of NO electrode, a sharp peak is clearly observed at 0.437 V, because of the reduction reactions of NiO and the formation of amorphous Li$_2$O, as well as a partially irreversible SEI layer. The oxidation of metallic Ni to NiO contributes to the anodic peak located at approximately 2.26 V, whereas the anodic peaks located at about 1.805 V are attributed to the formation of Mo. (Figure 6.8).
Figure 6.7 Electrochemical evaluation of NNMO, showing (a) cyclic voltammograms for the first 5 cycles from 0.01 V to 3.00 V; (b) galvanostatic charge/discharge voltage profiles versus capacity of NNMO electrode from for selected cycles at a current rate of 0.2 A g\(^{-1}\); (c) cycling performances of the obtained NO, NMO, and NNMO electrodes at 0.2 A g\(^{-1}\) and coulombic efficiency of the NNMO electrode at 0.2 A g\(^{-1}\); (d) rate performances of those three electrodes at varying current rates of 0.2, 0.5, 1, 2, 5, and 0.2 A g\(^{-1}\); (e) ultra-long cycling performance at 1 A g\(^{-1}\) of the obtained NNMO electrode and the corresponding coulombic efficiency.
Figure 6.7b shows the typical galvanostatic discharge/charge voltage profiles of NNMO anode from 0.01 to 3.0 V at a current density of 0.2 A g\(^{-1}\). In the first cycle, the NNMO electrode delivered an initial discharge capacity of 1538 mA h g\(^{-1}\) and charge capacity of 1282 mA h g\(^{-1}\), corresponding to an initial coulombic efficiency (ICE) of 83%, which is higher than those of the NO (80%) and NMO electrodes (78%) (Figure 6.9), demonstrating the high reversibility and good stability of the NNMO electrode during the electrochemical reactions. The higher reversible capacity of the NNMO can be explained by the further delithiation reaction observed above 2.0 V (Figure 6.7a), which is attributed to the catalytic behavior of the metallic nickel nanocrystals and its unique porous hierarchical structure that can shorten ion diffusion pathways.\(^{[41]}\) Furthermore, the NNMO anode exhibited excellent cycling stability. As shown in Figure 6.7c, the NNMO electrode delivered an initial reversible capacity of 1282 mA h g\(^{-1}\), which then gradually increased to 1314 mA h g\(^{-1}\), with the coulombic efficiency nearly 100% after 100 cycles. The feature of increased capacity after the initial cycle is not surprising for a metal oxide-based material, as it always ascribed to the reversible growth of polymeric gel-like layers and capacitive interface storage including electric double layer capacitance, as well as an activation process in the nanostructures.\(^{[37]}\) On the contrary, rapid capacity fading and inferior capacity retention are clearly observed in the NO and NMO materials. The high electrochemical reversibility and good cycling stability of the NNMO material may be attributed to the following factors: 1) the in-situ generated Ni nanocrystals from the NiO phase could function as a direct catalyst for the reversible decomposition of intermediate Li\(_2\)O and the oxidation of metallic Ni and Mo from \(\beta\)-NiMoO\(_4\); 2) the NiO nanosheets can act as the mechanical buffer to effectively stabilize the NiMoO\(_4\) phase, thus reducing the self-agglomeration of
NiMoO$_4$ nanosheets and maintaining good structural stability; 3) the unique hierarchical porous architecture constructed from the small nanosheets will provide more active sites for Li$^+$ storage, short ion diffusion pathways, as well as abundant additional space to release the internal stress induced by volume changes during discharge/charge process.

**Figure 6.8** Comparison of CV curves of NO, NMO, and NNMO with the potential window from 0.01 V to 3.00 V: (a) first cycle and (b) third cycle.

**Figure 6.9** Galvanostatic charge–discharge curves of (c) NO and (d) NMO materials.

Additionally, the NNMO electrode also exhibited remarkable rate capability at different current densities. As can be seen from Figure 6.7d, the NNMO electrode is
capable of delivering the specific capacities of 1360, 1003, 631, 469, and 308 mA h g\(^{-1}\) at the current densities of 0.2, 0.5, 1.0, 3.0, and 5.0 A g\(^{-1}\), respectively. More importantly, the capacity can recover to the initial value (about 1339 mA h g\(^{-1}\)) when the current rate is set back to 0.2 A g\(^{-1}\) after 60 cycles, indicating the excellent rate capability and good reversibility of the NNMO electrode. On the contrary, both the NO and the NMO electrodes show much inferior capacity retention and severe capacity decay between the current densities of 1 and 5 A g\(^{-1}\). The excellent rate capability can be attributed to the synergistic effects of the binary composition and the short lithium diffusion distance in the porous hierarchical NNMO heterostructure.

The long cycling performance is also an important parameter of batteries in practical applications. Hence, we further examined the long-term cycling property of the NNMO electrode at a high current density of 1 A g\(^{-1}\) (Figure 6.7e). After 400 cycles, the NNMO anode still retained a high reversible capacity around 500 mA h g\(^{-1}\), and the average coulombic efficiency is close to 100%. More importantly, the NNMO electrode can maintain the hierarchical porous structure after long-term cycles, demonstrating its good structural stability. The superior structural characteristics, such as the 2D building blocks, large surface area and abundant pores enable its good structural integrity (Figure 6.10).
Figure 6.10 Typical SEM images of the NNMO electrode before (a) and after (b) 100 cycles at the current density of 1000 mA g⁻¹.

To reveal the boosted charge transfer behavior in the NNMO heterostructure, the kinetic differences of lithium ion diffusion in these anodes have been investigated as well. As shown in Figure 6.11a,b, the NNMO sample exhibits larger peak intensities and smaller polarization at all scan rates, indicating the greatly enhanced electrochemical kinetics in the NNMO electrode, which are favorable for achieving better rate capability. Furthermore, the significantly promoted charge transfer process in the NNMO heterostructure also can be proved by the higher diffusion coefficient of Li⁺ compared to the NMO sample (Figure 6.11c). Meanwhile, the electrochemical impedance spectroscopy (EIS) measurements have been conducted to research the kinetic differences between various electrodes (Figure 6.12). It is noticed that the diameter of the semicircle in the high–medium–frequency region for the NNMO electrode is much smaller than for the NMO and NO electrodes, demonstrating the highly improved electron/ion transport dynamic in the heterostructure of the NNMO sample.⁴²,⁴³
Figure 6.11 CV curves at different scan rates for LIB cells with (a) NNMO and (b) NMO materials, and (c) the linear relationship between the peak current \( (i_p) \) and the square root of the scan rate \( (\nu^{1/2}) \) for NNMO electrode.
Figure 6.12 Electrochemical impedance spectroscopy (EIS) spectra of the obtained NO, NMO, and NNMO electrodes.

Table 6.1 Inductive coupled plasma (ICP) results for the NNMO material.

<table>
<thead>
<tr>
<th>Results</th>
<th>Concentration</th>
<th>Ni$^{2+}$ (mol)</th>
<th>Mo$^{6+}$ (mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.751</td>
<td>0.319</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>0.725</td>
<td>0.325</td>
<td></td>
</tr>
<tr>
<td>Average</td>
<td>0.738</td>
<td>0.322</td>
<td></td>
</tr>
</tbody>
</table>
6.4 Conclusions

In summary, we have developed a facile strategy to synthesize the novel hierarchical porous NiO/β- NiMoO₄ heterostructure constructed from small nanosheets, featuring in large surface area, short ions diffusion paths, and good structural stability. By means of synergistically active ternary metal oxides, boosted charge transfer dynamic, and enhanced electrochemical reversibility, the NNMO heterostructure achieved high reversible capacity, good rate capability and superior long-term cyclability for Li-ion batteries. Our material design strategy presented here could be a promising approach for designing novel heterostructure nanomaterials for high-performance rechargeable batteries.

6.5 References


CHAPTER 7 CONCLUSIONS AND OUTLOOK

7.1 General conclusions

To achieve high performance, in terms of high reversible capacity, high-rate capacity and long cycling life for advanced rechargeable batteries, enormous attempts have been made to explore novel candidate materials and optimise currently established battery components for energy storage systems. It has been clearly demonstrated that the intrinsic properties of materials, including the dimension, composition, crystal structure and interface interaction play important roles in determining the inherent physical and chemical properties. The great success on graphene motivates researchers to design and synthesize novel 2D nanomaterials for energy-related applications owning to the fascinating properties. The large surface area, shorten ion/electron diffusion path, abundant active sites, good mechanical strength and exposed surface defects can effectively offer more Li-ion storage sites and accelerate the ion/electron diffusion dynamic process, resulting in enhanced electrochemical performance for rechargeable batteries. Moreover, porous hierarchical architectures assembled by 2D nanosheets building blocks will not only retain the unique properties of the 2D units, but also offer other structural features at different size scales, such as large dimensions, accessible porous systems, large void spaces and high surface area, thus showing promising prospects for energy storage applications.

Despite some progress, the preparation of 2D nanomaterials mainly depends on the “top-down” approach, which greatly limited the practical applications. Therefore,
facile and gentle “bottom-up” strategies have been developed to fabricate 2D metal oxides materials and exhibited impressive electrochemical properties towards Li-ion batteries. Despite this, there are still various tough challenges to conquer before next-generation electrochemical energy storage systems based on rechargeable batteries can be implemented in the future.

In the first work, porous hierarchical Bi$_2$O$_3$ microflowers self-assembled from atomic-thin nanosheets have been designed and prepared via a facile hydrothermal procedure. By combining the structural advantages of 2D ultrathin nanosheets and the 3D hierarchical structure, the porous hierarchical Bi$_2$O$_3$ architecture will effectively provide more Li-ion storage sites, boost the ion/electron diffusion kinetics as well as enhance the cycling stability, benefiting from the synergistic function of the 2D ultrathin building blocks and the porous 3D hierarchical assemblies. As a result, the constructed porous hierarchical structures exhibited much higher reversible capacity and high-rate capability than the corresponding bulk counterpart.

Second, in order to systematically optimize the electrochemical performance, a powerful multiscale coordinated strategy for designing advanced electrode materials for electrochemical energy storage, including synergistic modulation of the dimensionality, composition, atomic arrangement, and interfaces. In this work, by coupling the unique structural features in terms of atomic interface interactions and the electric-field effect, novel well-defined ternary metal oxide nanosheets with atomic thickness have been synthesized by a facile wet-chemical synthesis route. The as-prepared Bi$_2$MoO$_6$ nanosheets achieved outstanding high-rate cycling performance toward Li-ion batteries. More impressively, even after 1500 cycles at a high current density of 2000 mA g$^{-1}$, a high reversible capacity of 478 mA h g$^{-1}$ was
still retained with an average coulombic efficiency approaching 100%, demonstrating the great promise of 2D Bi₂MoO₆ for next-generation high-power LIBs. Furthermore, the mechanism for the enhancement of electrochemical performance was deeply studied by the DFT calculations and in situ synchrotron XRPD analysis. The excellent electrochemical property can be ascribed to the strong electric-field effect within the crystal, the unique 2D ultrathin configuration, and the superior structural stability. The good high-rate cycling performance, along with the simple and scalable synthetic approach for ultrathin 2D materials, makes this material design strategy a promising approach to exploit novel 2D materials with remarkable performance in advanced energy technologies.

In the last work, the novel hierarchical porous NiO/β-NiMoO₄ heterostructure has been fabricated and exhibited high reversible capacity, superior rate capability, and good cycling stability towards LIBs, which is much better than the corresponding single phase NiMoO₄ and NiO materials. The significantly enhanced electrochemical properties can be attributed to its superior structural characteristics, including the large surface area, abundant pores, fast charge transfer, and catalytic effect of the intermediate product of metallic nickel. The NiO/β-NiMoO₄ heterostructure delivered a high capacity of 1314 mA h g⁻¹ at 0.2 A g⁻¹ after 100 cycles. Furthermore, even after 400 cycles at 1 A g⁻¹, the reversible capacity still remained at around 500 mA h g⁻¹. These results indicate that the NiO/β-NiMoO₄ heterostructure shows great potential as anode materials for high-performance LIBs.
7.2 Outlook

Despite some advances have been achieved on the preparation and application of 2D nanomaterials over the past few years, there are still great challenges, while the research of 2D functional materials for the energy-related application is still in its early stage.

First of all, currently established strategies to prepare 2D functional nanomaterials are mostly based on the “top-down” methods, which mainly contain the mechanical cleavage or liquid exfoliation approach. It is a typical procedure that exfoliates layered crystal into mono-/few-layers via chemical reaction or intercalation progress. However, all those involved methods heavily rely upon the exfoliation of ultrathin 2D crystals from their corresponding layered bulk materials, thus only those 2D materials with layered bulk crystals can be prepared by the top-down methods, whereas it is difficult to obtain the desired 2D nanomaterials from those non-layered materials through the process. The other commonly used “bottom-up” method is the chemical vapor deposition. Nevertheless, the poor scalability and complicated processes make it difficult to scale up to a practical level. From the perspective of practical application, facile and versatile approaches need to be developed for the large-scale production of novel 2D nanomaterials with high quality.

Secondly, the growth mechanisms of those ultrathin 2D nanomaterials and the derived 3D hierarchical structures are still unclear. Profound understanding the formation mechanisms will be beneficial for researchers to rationally design and controllably synthesize novel 2D nanomaterials, thus provide us opportunities to regulate the intrinsic structural properties, such as the layer numbers, electronic
states, atomic interface, and surface defects, which undoubtedly play important roles in determining the physical and chemical properties and electrochemical reactivity in energy storage applications. In addition, constructing ideal 2D heterostructures by integrating different 2D atomically thin nanomaterials are tough issues to be addressed, due to the lattice mismatch, interface stress and weak interaction forces.

Thirdly, the detailed electrochemical reaction mechanisms of 2D nanomaterials involved in rechargeable batteries are not fully understood. Because of the large interlayer channels, it is normally believed that the alkali metal ions insertion reaction will firstly occur in 2D nanomaterials, which is similar to the reaction progress proceed in carbon-based materials. Therefore, some transition metal sulfides, such as FeS₂, CoSe₂ will show pseudocapacitive storage behaviors during redox processes. Other 2D metal sulfides, like the SnS, SnS₂-based anode materials can store alkali metal ions by conversion and allying reactions, thus exhibiting much higher theoretical capacity. By rationally tailoring the voltage window or optimize the electrolyte systems, the electrochemical reaction can be effectively confined within the allying step, thus achieving ultrahigh rata capability and outstanding cycling stability based on the pseudocapacitive storage. Deeply understanding the reaction mechanisms will provide people the chance to integrate the superior properties of high reversible capacity, high-rate capability and ultra-long cycling stability in 2D electrode materials.

Finally, it should be noted that all the electrode components including active materials, binders, conductive materials, electrolytes, and additives will significantly influence the electrochemical performance of the electrode materials. Except the active materials, other components are needed to be further studied and promoted as
well. After systematically optimised all the above-mentioned compositions, it is expected that advanced energy storage devices based on the novel 2D materials with high performance will be commercialized in the future.
APPENDIX A: LIST OF PUBLICATIONS

From 2014.11-2018.4


APPENDIX B: AWARDS RECEIVED

1  ISEM Postgraduate Student Excellence Award, 2016, University of Wollongong.

2  International Postgraduate Research Scholarships, 2014.12-2018.4, Faculty of Engineering & Information Sciences, University of Wollongong.

3  International Postgraduate Tuition Award (IPTA), 2014.12-2018.4, University of Wollongong.