Graphene network scaffolded flexible electrodes : from lithium to sodium ion batteries

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**NANYANG
TECHNOLOGICAL
UNIVERSITY**

GRAPHENE-BASED FLEXIBLE ELECTRODES:
FROM LI TO NA-ION BATTERIES

**GRAPHENE NETWORK SCAFFOLDED FLEXIBLE
ELECTRODES
-----FROM LITHIUM TO SODIUM ION BATTERIES**

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SCHOOL OF PHYSICAL AND MATHEMATICAL SCIENCES

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ELECTRODES**

-----FROM LITHIUM TO SODIUM ION BATTERIES

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School of Physical and Mathematical Sciences

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Selected Publications (1st and co-1st authors)

1. **D. Chao**, C. Zhu, P. Yang, X. Xia, J. Liu, J. Wang, X. Fan, S. Savilov, J. Lin, H. Fan, Z. X. Shen, Array of Nanosheets Render Ultrafast and High Capacity Na-ion Storage by Tunable Pseudocapacitance, *Nat. Commun.*, **12122** (2016).
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Abstract

Research on deformable and wearable electronics has promoted an increasing demand for next-generation power sources with high energy/power density, low cost, light weight, as well as thin and flexible features. One key challenge in flexible electrochemical energy storage devices lies in the development of reliable electrodes with open-framework material, robust structure, and high performance. In this thesis 3D array electrode using graphene network as scaffold was fabricated and studied as the cathode or anode for lithium and sodium ion batteries. These include: graphene foam (GF) supported V_2O_5 @PEDOT nanobelt array for cathode of Li-ion battery in Chapter 2, which exhibited superior plateau performance than reported results and ultra-stable cycling performance even after 1000 cycles; VO_2 @GQD ultrathin array for cathode of Na-ion battery (SIB) in Chapter 3, where VO_2 was first applied as cathode for SIB with capacity more than 300 mAh g^{-1} and high-rate at even 60°C ; In Chapter 4, $\text{Na}_3(\text{VO})_2(\text{PO}_4)_2\text{F}$ nanoarray was first successfully synthesized as 3D array Na-containing cathode for batteries application, where *in-situ* XRD was used to detect the structure evolution during sodiation/desodiation. Various SnS nanoarray architectures were fabricated as anodes for SIB in Chapter 5, the electrode showed highest ever reported reversible capacity more than 1000 mAh g^{-1} and unexpected rate performance at 30 A g^{-1} with the help of proposed pseudocapacitance-dominated capacity contribution mechanism. All in all, by smart design and facile synthesis approach 3D array electrode can be fabricated on flexible graphene foam, which can achieve high performance due to its ultrathin, porous and robust structure, favorable electrolyte affinity, ions/electrons transportation, etc.

Chapter 1 General Introduction

1.1 Lithium and sodium ion batteries

1.1.1 Background

Fig. 1.1 (a) Energy storage systems and typical applications. *Source: Gyuk 2002.* (b) Ragone plot of existing electrochemical energy storage systems.¹

Energy is the lifeblood of modern society and plays a vital role in the advancement of human civilization. Over the past decades, substantial effort has been placed on developing sustainable energy sources (such as tidal energy, mechanical vibration, wind, and solar radiation) to meet ever-increasing global energy demand and reduce environmental pollution.²⁻⁴ However, due to the intermittent and/or diffuse nature of these renewable energy sources, there is a pressing need to design and fabricate

high-performance energy storage systems to make full use of the sustainable energy (see Fig. 1.1a).

Among various energy storage systems, electrochemical energy storage (EES) (such as Li- and Na-ion batteries) has been extensively studied and considered as one of the most fascinating and green energy storage systems for realizing the renewable energy future of the mankind due to its high efficiency, versatility, and flexibility.^{1,5-11} As can be seen in Fig. 1.1b by comparing kinds of energy storage devices, supercapacitors and fuel cells possess high energy density and power density, respectively, while lithium ion battery (LIB) holds potential for both high energy and power densities.¹ Notably, LIBs are the most important and popular rechargeable devices with high capacity, high working potential, low toxicity and long-term stability.^{12,13} With such attractive performances, LIBs products have conquered the portable power source markets. Nevertheless, formidable issues still block the way to develop high performance LIBs, such as poor electronic conduction of cathode/anode materials, relatively inferior ion transport kinetics, which dominate both energy and power density of LIBs.¹⁴⁻¹⁷ Hence, high-performance LIB with high energy and power densities is still highly desirable and becoming one of the most important challenges of modern electrochemistry.

Because of the limitation of Li resources, alternative batteries based on earth-abundant and cheaper metal ions are drawing our attentions.¹⁸ In the 1970's, sodium ion battery (SIB)s were actually proposed earlier than LIBs.¹⁹ Compared to LIBs, SIBs showed inferior electrochemical performances, so it was laid aside for years.²⁰ There are many references which have listed detailed differences and similarities between LIBs and SIBs.^{18,21-24} Although Na ion shows bigger size, higher redox potential (0.3 V higher), and lower capacity density, sodium resource is around two orders of magnitude cheaper than that of lithium. Recently, with more and more achievements in the field of SIBs, it seems optimistic that Na-based electrode is potentially competitive to Li one.^{25,26}

1.1.2 Working principle of rechargeable battery

Fig. 1.2 Schematic illustration of working principles of lithium or sodium ion batteries. A denotes Li⁺ or Na⁺.

The working principle of lithium and sodium ion batteries is schematically illustrated in Fig. 1.2. The inner components of a traditional LIB cell are composed of anode, separator, cathode, electrolyte, and current collector. My research has been mainly focused onto the electrode materials which are Li or Na storage compounds capable of reversible Li⁺/Na⁺ insertion and extraction. The working principle of lithium ion and sodium ion batteries is similar. As illustrated in Fig. 1.2, the materials permit the A⁺ (Li⁺ or Na⁺) shuttling between the cathode and anode during the charge/discharge process. During discharging, A⁺ migrates from the anode to the cathode through the separator and electrolyte, and the electrons from the anode to the cathode through the external circuit. In this process, there are decreasing of cathode potential and increasing of anode potential, leading to a smaller cell voltage and release of electrochemical energy. During charging, the migration of ions and electrons are reversed. The whole processes are known as rocking-chair mechanism.

1.2 Graphene network boosted battery performance

1.2.1 Graphene as an excellent electrode material

Fig. 1.3 Graphene, and its hybrids and their applications in energy storage devices.

Graphene is an advanced carbon material with extraordinary electrical conductivity (64 mS cm^{-1}), mechanical, optic and thermal properties, making graphene a promising material in many fields, such as sensor, nanoelectronics, catalysis, drug delivery and energy storage and conversion.¹⁴¹⁻¹⁴³ And it can also be used as anode material for LIBs with excellent charge conductivity and specific capacity ($\sim 600 \text{ mAh g}^{-1}$)¹⁴⁴. Graphene does not experience significant volume change when it forms a composite with other materials and undergoes ions insertion/extraction. Therefore, it can serve as a conductive flexible current collector, effective buffer network to fasten the electron transportation, mitigate volume pulverization of the active materials, and to maintain the structural integrity of the whole electrode. Hence, we can develop graphene scaffold supported metal oxides or sulfides for cathode or anode of the batteries, in order to obtain high energy and power densities.

Fig. 1.4 Graphene foam supported array of Fe_3O_4 , VO_x , MoS_2 , CNT, CNT- MnO_2 , CNT- Fe_2O_3 and etc. electrodes.

It has been demonstrated in literatures (Fig. 1.4) that creating aligned arrays by coupling nanoflakes/nanowires with backbone could facilitate charge transport and enhance the surface reaction kinetics owing to sufficient electrode/electrolyte contact of ion pathways, large structural separation for volume change of ion insertion, and strong grip with the current collector, i.e. low contact resistance.¹⁴⁵⁻¹⁴⁷ It thus seems that the nanoarray architecture can be an excellent strategy for seeking of high capacity and rate capability. However, most of the current reports in batteries are in the form of pure or composite powders, and most of the nanoarray materials in literature were grown with relatively high temperature and long reaction time in template-assisted multistep processes, or, in particular, on the heavy inactivating metal Cu foil, stainless steel sheet, carbon cloth, nickel foam ($10\text{-}30 \text{ mg cm}^{-2}$). Herein, we realized unique 3D nanoarray cathode/anode on flexible light-weight graphene foam backbone ($\sim 0.6 \text{ mg cm}^{-2}$). The special architecture possesses significantly increased rate capability together with the high long-term high-rate durability for batteries.

As one of the most promising carbon materials, graphene has attracted much attention in various fields because of its good flexibility, large surface area, extraordinary mechanical/chemical/thermal stability, superior electrical and

thermal properties. One of the most important applications of graphene in energy storage is to form composites with active electrode materials and improve their performance for LIBs/SIBs. In this section, graphene supported electrode materials will be reviewed, for both cathodes and anodes.

Research on deformable and flexible electronics has promoted an increasing demand for next-generation power sources with high energy/power density, low cost, light weight, as well as thin and flexible features. One key challenge in flexible electrochemical energy storage devices lies in the development of reliable electrodes with open-framework material, robust structure, and high performance. Graphene foam as a flexible light-weight backbone support demonstrates many advantages including high electron and ion conductivity and long-term rate durability. By smart design and facile synthesis approach 3D array electrode can be fabricated via the growth of 2D active materials on robust graphene foam, which can achieve high performance due to its high porous structure, favorable electrolyte affinity and ions/electrons transportation. Below I summarize what have been reported in literature on the graphene network scaffolded cathode and anode systems.

1.2.2 Graphene network scaffolded cathode materials

Nowadays, the positive electrode materials including LiCoO_2 , LiFePO_4 , LiMn_2O_4 , $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$, and V_2O_5 for LIBs and $\text{Na}_3\text{V}_2(\text{PO}_4)_3$, $\text{Na}_3\text{V}_2\text{O}_2(\text{PO}_4)_2\text{F}$, NaFePO_4 , $\text{Na}_2\text{FePO}_4\text{F}$, NaFeSO_4F for SIBs have been well-studied, while graphene can make them performing better.²⁷

Taking LiFePO_4 (LFP) for example, it has been widely used and largely investigated as a positive electrode for LIBs due to the proper potential, high theoretical specific capacity 170 mAh g^{-1} , low cost and toxicity. But its poor electronic conductivity ($\sim 10^{-9} \text{ S cm}^{-1}$) significantly restrict the performance of LIBs. Therefore, graphene was introduced in 2010 by Ding and coworkers.²⁸ The LFP/Graphene composite, which was prepared by coprecipitation method, shows an improved capacity of $\sim 160 \text{ mAh g}^{-1}$ compared to that of bare LFP ($\sim 113 \text{ mAh g}^{-1}$). As shown in Fig. 1.5, spray drying is an effective way to prepare

LiFePO₄-graphene composites.²⁹ This secondary spherical microstructure exhibits a high capacity $\sim 70 \text{ mAh g}^{-1}$ at a discharge rate of 60C.

Fig. 1.5 Schematics of the fabrication process of microstructure LiFePO₄-graphene composites.²⁹

In addition to LFP, Li₃V₂(PO₄)₃ and LiMnPO₄ are other attractive cathode materials for LIBs due to their higher Li ion intercalation potential $> 4.0 \text{ V}$, corresponding to improved energy density $\sim 20\%$ vs. that of LFP. Coincidentally, their intrinsic ultralow electrical conductivity ($\sim 240 \text{ nS cm}^{-1}$ and $\sim 10^{-14} \text{ S cm}^{-1}$, respectively) limit their rate capacity. Therefore, Li₃V₂(PO₄)₃-graphene and LiMn_{1-x}Fe_xPO₄-graphene composites were prepared to enhance the electrochemical performances.^{30,31}

LiMn₂O₄ (LMO) has been widely used and largely investigated as a positive electrode for LIBs with advantages of low cost, abundance storage and proper potential, but poor electronic conductivity and corresponding low-rate capacity. LiMn₂O₄-graphene composite was prepared by a simple microwave-assisted hydrothermal method, which shows good rate capacity 117 and 101 mAh g⁻¹ at 50C and 100C, respectively.³² Published paper demonstrated that graphene was also an effective agent to improve the conductivity and rate performance of LiNi_{1/3}Mn_{1/3}Co_{1/3}O₂.³³

Normally, the capacities of cathode electrode materials (such as 150 mAh g⁻¹ for Spinel LMO and 170 mAh g⁻¹ for Olivine LFP) are much lower than that of anode materials (such as 370 mAh g⁻¹ for graphite and 4200 mAh g⁻¹ for Silicon).

Therefore, it has been a limiting factor to enhance the energy density of the whole LIBs, because of the capacity limitation from cathode materials. Sulfur, the cathode material for lithium-sulfur batteries, possesses a ultrahigh capacity $\sim 1675 \text{ mAh g}^{-1}$. Nevertheless, it undergoes rapid capacity fading during charge/discharge cycles due to the poor electrical conductivity of sulfur and dissolution of polysulfides in electrolyte. It has been demonstrated that sulfur-graphene composite is one effective way to alleviate the problems of sulfur in LIBs. It can be seen in Fig. 1.6 that S particles are wrapped by graphene sheets, which can not only render high electrical conductivity but also trap the polysulfides.³⁴

Fig. 1.6 Schematics of the fabrication process of microstructure S-graphene composites.³⁴

V_2O_5 , as one of the most promising candidates for cathodes of LIBs, involves multi-electron insertion/extraction reactions with high theoretical capacity $\sim 294 \text{ mAh g}^{-1}$ in the voltage window of 2.0 to 4.0 V (vs. Li/Li^+). Moreover, V_2O_5 has advantages of low cost, high energy density and abundant resources. A layer structured $\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ -graphene composite was fabricated via a cost effective and energy saving technique. The initial discharge capacities of the composite is $\sim 299 \text{ mAh g}^{-1}$, and the capacity decrease to 174 mAh g^{-1} after 50 cycles.³⁵ By a simple solvothermal method, V_2O_5 -graphene nanosheets composite was composed for the first time.³⁶ The composite exhibits a discharge capacity ca. 412 mAh g^{-1} @ 50 mA g^{-1} , and remains $\sim 316 \text{ mAh g}^{-1}$ at discharge current 1600 mA g^{-1} . An extremely stable V_2O_5 nanowire-graphene paper composite was prepared with

improved cycle life (a perserved capacity even after 100 000 cycles).³⁷ Recently, a simple solvothermal method was used to fabricate V₂O₅ nanosheets-reduced graphene oxiede nanocomposite with efficient electronic/ion conducting path and high surface area.³⁸ This composite can give a capacitay ~138 mAh g⁻¹ at even 10C, and a capacity of ~102 mAh g⁻¹ after 160 cycles at 2C. The enhanced performance can be ascribed to improved electron/Li⁺ transport, resulting from the special nanostructure. A comprehensive list of vanadium pentoxide as cathode of Li-ion bateries is summarized in below Table 1.1, where graphene-V₂O₅ composite shows superior electrochemical performances.

Fig. 1.7 Schematics of the fabrication process of 3D V₂O₅ nanosheets-RGO composites.³⁸

Table 1.1 A comprehensive summary of electrochemical properties of V₂O₅ and its hybrid composites published in the literature.

Electrode description	Specific capacity ^a (mAh g ⁻¹)	High potential percentage ^b (%)	Cycling stability ^c (%)
Graphene supported V ₂ O ₅ /PEDOT array	297 at 300 mA g ⁻¹ 265 at 1500 mA g ⁻¹	62 % at 300 mA g ⁻¹ 60 % at 1500 mA g ⁻¹	98 % after 1000 cycles at 18 A g ⁻¹
yolk-shell V ₂ O ₅ powders ³⁹	271 mAh g ⁻¹ at 1000 mA g ⁻¹	39% at 1000 mA g ⁻¹	75% after 100 cycles at 1000 mA g ⁻¹
V ₂ O ₅ /PEDOT&MnO ₂ nanowire ⁴⁰	185 mAh g ⁻¹ at 50 mA g ⁻¹	37% at 50 mA g ⁻¹	93% after 40 cycles at 50 mA g ⁻¹
V ₂ O ₅ /PPY composite ⁴¹	235 mAh g ⁻¹ at 30 mA g ⁻¹	46% at 30 mA g ⁻¹	75% after 50 cycles at 30 mA g ⁻¹
V ₂ O ₅ /TiO ₂ nanocomposite ⁴²	175 mAh g ⁻¹ at 300 mA g ⁻¹	37% at 300 mA g ⁻¹	79% after 25 cycles at 300 mA g ⁻¹

Carbon-Coated Nanocrystals ⁴³	V ₂ O ₅	297 mAh g ⁻¹ at 1000 mA g ⁻¹	47% at 1000 mA g ⁻¹	97% after 50 cycles at 1000 mA g ⁻¹
Combustion synthesized V ₂ O ₅ ⁴⁴		240 mAh g ⁻¹ at 15 mA g ⁻¹	38% at 15 mA g ⁻¹	---
Coral-like nanowhiskers ⁴⁵	V ₂ O ₅	310 mAh g ⁻¹ at 44 mA g ⁻¹	36% at 44 mA g ⁻¹	---
Cu doped V ₂ O ₅ flowers ⁴⁶		259 mAh g ⁻¹ at 59 mA g ⁻¹	44% at 59 mA g ⁻¹	85% after 50 cycles at 59 mA g ⁻¹
V ₂ O ₅ /rGO ⁴⁷		220 mAh g ⁻¹ at 190 mA g ⁻¹	---	60% after 200 cycles at 5700 mA g ⁻¹
V ₂ O ₅ nanobelt ⁴⁸		240 mAh g ⁻¹ at 400 mA g ⁻¹	26% at 1000 mA g ⁻¹	94% after 50 cycles at 4000 mA g ⁻¹
V ₂ O ₅ nanospike ⁴⁹		280 mAh g ⁻¹ at 50 mA g ⁻¹	45% at 50 mA g ⁻¹	63% after 50 cycles at 50 mA g ⁻¹
V ₂ O ₅ particles by urea combustion ⁵⁰		240 mAh g ⁻¹ at 35 mA g ⁻¹	26% at 35 mA g ⁻¹	82% after 50 cycles at 35 mA g ⁻¹
V ₂ O ₅ /PANI composite ⁵¹		260 mAh g ⁻¹ at 295 mA g ⁻¹	42% at 295 mA g ⁻¹	97% after 50 cycles at 295 mA g ⁻¹
Electrospun nano-V ₂ O ₅ ⁵²		270 mAh g ⁻¹ at 0.1 mA cm ⁻²	46% at 0.1 mA cm ⁻²	78% after 25 cycles at 0.1 mA cm ⁻²
Ultrathin V ₂ O ₅ nanosheet ⁵³		235 mAh g ⁻¹ at 100 mA g ⁻¹	43% at 100 mA g ⁻¹	96% after 50 cycles at 147 mA g ⁻¹
V ₂ O ₅ nanowire-GO composite ³⁷		220 mAh g ⁻¹ at 100 mA g ⁻¹	12% at 100 mA g ⁻¹	90% after 200 cycles at 100 mA g ⁻¹
V ₂ O ₅ Nanosheet ⁵⁴		290 mAh g ⁻¹ at 100 mA g ⁻¹	48% at 100 mA g ⁻¹	67% after 50 cycles at 300 mA g ⁻¹
V ₂ O ₅ ·0.44H ₂ O bulky paper ⁵⁵		297 mAh g ⁻¹ at 50 mA g ⁻¹	17% at 50 mA g ⁻¹	78% after 20 cycles at 50 mA g ⁻¹
nanorod structured V ₂ O ₅ ⁵⁶		274 mAh g ⁻¹ at 15 mA g ⁻¹	37% at 15 mA g ⁻¹	82% after 30 cycles at 15 mA g ⁻¹
Graphene-V ₂ O ₅ ·nH ₂ O xerogel composite ³⁵		227 mAh g ⁻¹ at 30 mA g ⁻¹	22% at 30 mA g ⁻¹	69% after 50 cycles at 30 mA g ⁻¹
Al-intercalated electrospun nanofiber ⁵⁷	V ₂ O ₅	290 mAh g ⁻¹ at 35 mA g ⁻¹	18% at 35 mA g ⁻¹	66% after 50 cycles at 35 mA g ⁻¹
PPY/V ₂ O ₅ hybrid with PSA additive ⁵⁸		160 mAh g ⁻¹ at 10 mA g ⁻¹	31% at 10 mA g ⁻¹	82% after 30 cycles at 10 mA g ⁻¹
Carbon nanotubes/V ₂ O ₅ nanoribbon ⁵⁹		250 mAh g ⁻¹ at 30 mA g ⁻¹	25% at 30 mA g ⁻¹	90% after 30 cycles at 30 mA g ⁻¹
Hierarchical V ₂ O ₅ microsphere ⁶⁰		266 mAh g ⁻¹ at 300 mA g ⁻¹	38% at 300 mA g ⁻¹	75% after 100 cycles at 300 mA g ⁻¹
Electrospun nanofiber ⁶¹	V ₂ O ₅	308 mAh g ⁻¹ at 35 mA g ⁻¹	33% at 35 mA g ⁻¹	74% after 50 cycles at 35 mA g ⁻¹
Centimeter-long nanowire ⁶²	V ₂ O ₅	250 mAh g ⁻¹ at 50 mA g ⁻¹	46% at 50 mA g ⁻¹	50% after 20 cycles at 50 mA g ⁻¹

Multiwalled CNT-V ₂ O ₅ composite	260 mAh g ⁻¹ at 50 mA g ⁻¹	39% at 50 mA g ⁻¹	56% after 50 cycles at 100 mA g ⁻¹
V ₂ O ₅ nanorod ⁶³	235 mAh g ⁻¹ at 10 mA g ⁻¹	17% at 10 mA g ⁻¹	---
V ₂ O ₅ nanobelt membrane ⁶⁴	290 mAh g ⁻¹ at 500 mA g ⁻¹	18% at 500 mA g ⁻¹	83% after 50 cycles at 500 mA g ⁻¹
Porous V ₂ O ₅ microspheres ⁶⁵	276 mAh g ⁻¹ at 54 mA g ⁻¹	47% at 54 mA g ⁻¹	92% after 20 cycles at 54 mA g ⁻¹
Mesoporous V ₂ O ₅ ⁶⁶	200 mAh g ⁻¹ at 147 mA g ⁻¹	33% at 147 mA g ⁻¹	100% after 800 cycles at 7350 mA g ⁻¹
rGO supported porous V ₂ O ₅ spheres ⁶⁷	238 mAh g ⁻¹ at 90 mA g ⁻¹	36% at 90 mA g ⁻¹	85% after 50 cycles at 90 mA g ⁻¹
V ₂ O ₅ nanosheet/RGO nanocomposite ³⁸	271 mAh g ⁻¹ at 60 mA g ⁻¹	45% at 60 mA g ⁻¹	52 after 120 cycles at 600 mA g ⁻¹
V ₂ O ₅ hollow microsphere ⁶⁸	287 mAh g ⁻¹ at 60 mA g ⁻¹	46% at 60 mA g ⁻¹	---
FeF ₃ /V ₂ O ₅ composite ⁶⁹	219 mAh g ⁻¹ at 24 mA g ⁻¹	35% at 24 mA g ⁻¹	88% after 30 cycles at 24 mA g ⁻¹
V ₂ O ₅ nanostructure by precipitation ⁷⁰	275 mAh g ⁻¹ at 50 mA g ⁻¹	19% at 24 mA g ⁻¹	73% after 20 cycles at 24 mA g ⁻¹
3D V ₂ O ₅ microstructures ⁷¹	267 mAh g ⁻¹ at 300 mA g ⁻¹	45% at 300 mA g ⁻¹	82% after 50 cycles at 300 mA g ⁻¹
yolk-shell V ₂ O ₅ microsphere ⁷²	280 mAh g ⁻¹ at 30 mA g ⁻¹	49% at 30 mA g ⁻¹	79% after 30 cycles at 30 mA g ⁻¹
yolk-shelled V ₂ O ₅ microsphere ⁷³	256 mAh g ⁻¹ at 300 mA g ⁻¹	33% at 300 mA g ⁻¹	89% after 50 cycles at 300 mA g ⁻¹
V ₂ O ₅ nanowire/graphene composite ³⁶	275 mAh g ⁻¹ at 50 mA g ⁻¹	44% at 50 mA g ⁻¹	69% after 50 cycles at 400 mA g ⁻¹
Ultrathin V ₂ O ₅ nanosheet ⁷⁴	290 mAh g ⁻¹ at 59 mA g ⁻¹	44% at 59 mA g ⁻¹	94% after 50 cycles at 59 mA g ⁻¹
V ₂ O ₅ hollow microflower ⁷⁵	284 mAh g ⁻¹ at 300 mA g ⁻¹	48% at 300 mA g ⁻¹	74% after 100 cycles at 300 mA g ⁻¹
V ₂ O ₅ nanoflower by electrochemical reaction ⁷⁶	275 mAh g ⁻¹ at 50 mA g ⁻¹	40% at 50 mA g ⁻¹	87% after 50 cycles at 50 mA g ⁻¹
V ₃ O ₇ nanowire templated graphene scroll ⁷⁷	260 mAh g ⁻¹ at 100 mA g ⁻¹	21% at 100 mA g ⁻¹	88% after 400 cycles at 2 A g ⁻¹
V ₂ O ₅ /graphene composite ⁷⁸	270 mAh g ⁻¹ at 300 mA g ⁻¹	41% at 300 mA g ⁻¹	77% after 100 cycles at 2 A g ⁻¹
V ₂ O ₅ hollow microsphere ⁷⁹	250 mAh g ⁻¹ at 300 mA g ⁻¹	---	80% after 50 cycles at 300 mA g ⁻¹
V ₂ O ₅ ·0.86H ₂ O/RGO composite film ⁸⁰	189 mAh g ⁻¹ at 70 mA g ⁻¹	8% at 70 mA g ⁻¹	83% after 200 cycles at 70 mA g ⁻¹
Rattle-type V ₂ O ₅ microsphere ⁸¹	294 mAh g ⁻¹ at 300 mA g ⁻¹	40% at 300 mA g ⁻¹	64% after 100 cycles at 300 mA g ⁻¹

Nanostructured V ₂ O ₅ hollow microspheres ⁸²		241 mAh g ⁻¹ at 300 mA g ⁻¹	47% at 300 mA g ⁻¹	75% after 110 cycles at 300 mA g ⁻¹
Coral-like V ₂ O ₅ nanowhisker ⁸³		300 mAh g ⁻¹ at 44 mA g ⁻¹	37% at 44 mA g ⁻¹	74% after 50 cycles at 44 mA g ⁻¹
Leaf-like V ₂ O ₅ Nanosheets ⁸⁴		303 mAh g ⁻¹ at 50 mA g ⁻¹	47% at 50 mA g ⁻¹	78% after 100 cycles at 500 mA g ⁻¹
Template-free V ₂ O ₅ ⁸⁵	yolk-shell	275 mAh g ⁻¹ at 300 mA g ⁻¹	18% at 300 mA g ⁻¹	79% after 100 cycles at 300 mA g ⁻¹

^a Estimated value of specific capacity at different discharge current (the calculated potential range from 2.0~4.0 V vs. Li/Li⁺)

^b Estimated value of high voltage percentage at corresponding discharge current (the calculated potential range from 3.0~4.0 V vs. Li/Li⁺). Generally, the higher the discharge current sets, the larger discharge polarization shows in the discharge curve, and correspondingly the less discharge capacity.

^c The cycling stability is calculated by $C_n/C_{max} \times 100\%$, where C_n is the discharge capacity at the n cycle, C_{max} is the maximum discharge capacity during n cycles.

Graphene (G) and its hybrids electrode materials are widely studied as protecting layer or 3D substrate in SIBs. Regarding connection tightness, Capsule like wrapping using G⁸⁶ and reduced graphene oxide (rGO)⁸⁷ were reported to form three dimensional contact between active material particles. The existence of π - π bonds in graphene is proved to be beneficial in increasing the rGO adhesion to Na_{2/3}Ni_{1/3}Mn_{2/3}O₂.⁸⁷ Resultantly, Na_{2/3}Ni_{1/3}Mn_{2/3}O₂-rGO cathode reaches high capacity retention (200 cycles, ~ 99 %) at 1 C even though the capacity of ca. 83 mAh g⁻¹ is not high among various SIB cathode materials due to material intrinsic property. The coating/doping method discussed above has the limitation to tune the materials mass loading and the mass ratio between the active material and enhancing additives. By introducing the vacuum filtering method, Zhu⁸⁶ increased the mass loading of Na_{2/3}Fe_{1/2}Mn_{1/2}O₂ and tuned the mass loading between graphene and Na_{2/3}Fe_{1/2}Mn_{1/2}O₂. The as synthesized Na_{2/3}Fe_{1/2}Mn_{1/2}O₂@rGO electrode showing stable plateau at ~4.1 V is proven to be a proper cathode material.

1.2.3 Graphene network scaffolded anode materials

The electrochemical performance of anode material is also very important for the

improvement of full cell. Conventional graphite anode is still insufficient to meet the demands in energy and power densities due to its low theoretical specific capacity (372 mAh g^{-1}). Although graphene, as an anode material for LIBs, shows a high initial specific capacity (670 mAh g^{-1}), the large irreversible capacity and low initial coulombic efficiency limit its direct application as the electrode of LIBs. But it exhibits synergetic effect when forming composite with other anode active materials. Transition metal oxides (TMO), tin and silicon have been proved effective as active anode materials due to their high specific capacities (usually ranging from 600 to 1000 mAh g^{-1}). Nevertheless, these materials undergo severe volume change during charge/discharge cycles, which leads to the poor cycling stability of the batteries. To alleviate this problem, graphene has been employed as a buffer matrix (to mitigate the pulverization and aggregation) for these active materials.

TMO was introduced into the anode of LIBs for the first time by Poizot et al. in 2000.⁸⁸ During lithiation, the TMOs are converted into their metallic phase state. Conversely, the metal particles are oxidized to TMO during delithiation process. It should be noted that this oxidation process can only happen at a nano scale. Generally, almost all TMOs show low electrical conductivity and possess a typical insulator or semiconductor behavior with a band gaps $3 \sim 4 \text{ eV}$.

Manganese oxides are attractive because of abundance Mn resource, lower oxidation potential (1.2 to $1.3 \text{ V vs. Li/Li}^+$) compared to that of other TMOs, but show a low electrical conductivity ($\sim 10^{-7} \text{ S cm}^{-1}$). Graphene has been added to improve the performance of various kinds of manganese oxides, such as Mn_3O_4 and MnO_2 .^{89,90} Mn_3O_4 needles-RGO composite demonstrates a capacity of $\sim 675 \text{ mAh g}^{-1}$ and no obvious decay after 100 cycles at 75 mA g^{-1} .⁸⁹

Iron oxides are also of the most interesting TMOs, with an abundant storage and theoretical capacities $\sim 1000 \text{ mAh g}^{-1}$, but suffering huge volume expansion upon cycling. Several graphene supported Fe_2O_3 , Fe_3O_4 have been reported.^{91,92} A three-dimensional graphene foam supported Fe_3O_4 nanoparticles electrode was prepared by a bottom-up strategy (see Fig. 1.8).⁹¹ The composite exhibits a high capacity $\sim 785 \text{ mAh g}^{-1}$ at 1C rate, and shows no capacity decay after 500 cycles at

10C.

Fig. 1.8 Schematics of the 3D graphene supported Fe_3O_4 composites and its cycling performance.⁹¹

As shown in equation (1.1), tin is a metalloid element which could intercalate/de-intercalate lithium via alloying/de-alloying reaction. It has a theoretic discharge capacity $\sim 993 \text{ mAh g}^{-1}$ with a maximum x value ($x = 4.4$). However, it suffers from large volume expansion $\sim 260\%$. Tin dioxide is also an effective anode of LIBs. The lithiation process of SnO_2 can be divided into two steps. First, SnO_2 is irreversibly reduced to Sn with Li_2O by-product (see equation (1.2)). Even though the Li_2O matrix may prevent the expansion and keep Sn in its nano form, the degradation of electrode cannot be controlled. Furthermore, the first reduction process in equation (1.2) should lead to a significant irreversible capacity (almost half of the capacity of the electrode). Hence, graphene was introduced into Sn/ SnO_2 to mitigate these problems.

One interesting work on graphene nanosheets supported SnO_2 was performed by Wang et al. showing a stable capacity $\sim 515 \text{ mAh g}^{-1}$ at 130 mA g^{-1} , and a capacity of $\sim 100 \text{ mAh g}^{-1}$ at 8000 mA g^{-1} .⁹³ Another graphene/Sn composite anode material was fabricated by reduction of carbon-coated SnO_2 on graphene (see Fig. 1.9).⁹⁴ The composite exhibits a capacity $\sim 600 \text{ mAh g}^{-1}$ at 100 mA g^{-1} after 100 cycles.

Fig. 1.9 Left: TEM figure of carbon-coated Sn nanoparticles on graphene; Right: the rate capacity of the previous composite.⁹⁴

Silicon has been intensively pursued as the most promising anode materials for LIBs due to its high theoretical capacity ($\sim 4200 \text{ mA h g}^{-1}$, see equation (1.3)).

Like Sn, silicon uptakes lithium via alloying/dealloying process. However, Si suffers from severe capacity decay, caused by dramatic volume expansion (300% - 400%) during lithiation/de-lithiation processes. An effective way to save the capacity and cycling stability is to adopt nano-sized Si (nSi) or Si-based composites. To form graphene-silicon nanocomposites might be a better way to alleviate these problems.

Graphene shells wrapped Si nanoparticles with a submicrometer-sized capsules were fabricated by a rapid, one-step aerosol-assisted capillary (see in Fig. 1.10).⁹⁵ The highly crumpled graphene network can accommodate the expansion of the inside Si nanoparticles, and protect the nSi from SEI deposition. The composite shows greatly improved electrochemical performance (940 mAh g^{-1} after 250 cycles at 1 A g^{-1}). One facile synthesis of graphene sheets wrapped silicon nanoparticles is called freeze-drying. The composite fabricated by Guo's group shows remarkably improved cycling and rate performance (1153 mAh g^{-1} after 100 cycles).⁹⁶

Another kind of positively charged (by PDDA) Si was mixed with graphene oxide (GO) aqueous suspension. The GO encapsulated Si water solution was then drop-casted on the ultrathin graphite foam (UGF, also known as graphene foam), and followed by a thermal annealing process. The composite (Si/graphene/UGF) shows a

first discharge capacity $\sim 983 \text{ mAh g}^{-1}$ and then retained 370 mAh g^{-1} after 100 cycles.⁹⁷

Fig. 1.10 Schematics of the fabrication process of crumpled-graphene-wrapped Si nanoparticles.⁹⁵

Conventional graphite and silicon anodes used in LIBs are proved not suitable for sodium ion storage, because of the Na plating on the carbon surface before forming the graphite intercalation compounds, and limited sodiation of Si with Na (NaSi)^{98,99}. For other carbon based anode materials, hard carbons which show disordered structure surprisingly present good performance as SIB anode candidates because of its disordered “messy card” arrangement with large pores or spacing. Study presents that hard carbon anode in SIBs is able to give a capacity as high as 200 mAh g^{-1} after 100 cycles.¹⁰⁰ The alloying-mechanism-based anodes such as Na_3P (2560 mAh g^{-1}), Na_3Sb (600 mAh g^{-1}), $\text{Na}_{15}\text{Pb}_4$ (485 mAh g^{-1}), and $\text{Na}_{15}\text{Sn}_4$ (847 mAh g^{-1}) show high sodium ion capacities. But this process goes along with huge volume change (from $\sim 200\%$ to 520%), which lead to decay of the performance during cycles. Advanced nano architecture designs are thus becoming the key research interest to eliminate this problem. Moreover, the active materials are in the form of powder and pasted to flat metallic Al/Cu current collectors with additive binders and conductive agent in these studies, resulting in a limited capacity and energy density of the whole device.

Fig. 1.11 (a-c) SEM and electrochemical performances of the rGO@SnS₂ electrode.¹⁰¹ (d-f) SEM and electrochemical performances of SnS@G electrode.¹⁰²

When the active materials combines with graphene, a higher conductivity and electrochemical properties can be achieved.¹⁰³ A CdI₂-type layered SnS₂¹⁰¹ (Fig. 1.11a) was pointed out as a promising layered material with large interlayer spacing for Na-ion storage. With protection from the graphene, the particles aggregation during synthesis of SnS₂ and the volume expansion of Na_xSn products are released. The SnS₂@G composite results in reversible capacity as high as 630 mAh g⁻¹ at 200 mA g⁻¹ with high rate performance (Fig. 1.11b and c), and excellent cyclability (more than 90 % capacity retention even after 400 cycles at 1.0 A g⁻¹). Similar G@SnS₂ composite electrode^{104,105} was prepared which shows higher capacity ca. 1100 mAh g⁻¹ @ 100 mA g⁻¹.¹⁰⁵ The multi-phase transformation process from hexagonal-SnS₂ to tetragonal-Sn then to orthorhombic-Na_{3.75}Sn¹⁰² in the whole discharge process should be responsible for the short cycling life. To alleviate the phase transformation effect, SnS₂ was transferred to SnS (less structural phase change material) (Fig. 1.11d).¹⁰² Covered with graphene, the SnS@G electrode delivers a reversible capacity as high as 940 mAh g⁻¹ @ 30 mA g⁻¹ (Fig. 1.11e), moreover the electrode retains 30 % of that capacity even at 7.2 A g⁻¹ (Fig. 1.11f). A comprehensive list of SIB anodes is summarized in below Table 1.2, where tin sulfide @ graphene composite shows superior electrochemical performances.

Table 1.2 A comprehensive summary of electrochemical properties of anodes in SIBs.

Electrode description	Reversible capacity	Cycling stability ^a	coulombic efficiency	High rate capability
GF-SnS NH ^b (this work)	1100 mAh g ⁻¹ at 30 mA g ⁻¹	92 % after 200 cycles at 30 mA g ⁻¹	81 %	420 mAh g ⁻¹ at 30 A g ⁻¹
Porous			78 %	
γ -Fe ₂ O ₃ @C nanocomposite ¹ 06	750 mAh g ⁻¹ at 200 mA g ⁻¹	79 % after 200 cycles at 200 mA g ⁻¹		340 mAh g ⁻¹ at 8 A g ⁻¹
Hollow carbon nanowire ¹⁰⁷	250 mAh g ⁻¹ at 50 mA g ⁻¹	84 % after 400 cycles at 50 mA g ⁻¹	51 %	150 mAh g ⁻¹ at 0.5 A g ⁻¹
Se-C composite ¹⁰⁸	485 mAh g ⁻¹ at 170 mA g ⁻¹	70 % after 380 cycles at 170 mA g ⁻¹	45 %	168 mAh g ⁻¹ at 3.4 A g ⁻¹
Micrometric Sb ¹⁰⁹	600 mAh g ⁻¹ at 300 mA g ⁻¹	96 % after 160 cycles at 300 mA g ⁻¹	75 %	552 mAh g ⁻¹ at 2.4 A g ⁻¹
Na ₇ V ₄ (P ₂ O ₇) ₄ (P O ₄)-C nanorod ¹¹⁰	40 mAh g ⁻¹ at 320 mA g ⁻¹	80 % after 50 cycles at 320 mA g ⁻¹		37 mAh g ⁻¹ at 1 A g ⁻¹
Sn-Al ₂ O ₃ nanoparticle ¹¹¹	650 mAh g ⁻¹ at 85 mA g ⁻¹	93 % after 40 cycles at 85 mA g ⁻¹	65 %	
MoS ₂ nanoflower ¹¹²	350 mAh g ⁻¹ at 50 mA g ⁻¹	140 % after 1500 cycles at 1 A g ⁻¹		195 mAh g ⁻¹ at 10 A g ⁻¹
Pyrite FeS ₂ ¹¹³	200 mAh g ⁻¹ at 200 mA g ⁻¹	90 % after 20000 cycles at 1 A g ⁻¹	75 %	170 mAh g ⁻¹ at 20 A g ⁻¹
TiO ₂ -C Nanorods ¹¹⁴	90 mAh g ⁻¹ at 1.65 A g ⁻¹	90 % after 50 cycles at 1.65 A g ⁻¹		53 mAh g ⁻¹ at 33 A g ⁻¹
Li ₄ Ti ₅ O ₁₂ -C nanowire ¹¹⁵	168 mAh g ⁻¹ at 35 mA g ⁻¹	97 % after 50 cycles at 35 mA g ⁻¹		38 mAh g ⁻¹ at 17.5 A g ⁻¹
Li activated Ge nanowire ¹¹⁶	350 mAh g ⁻¹ at 55.4 mA g ⁻¹	97 % after 50 cycles at 55.4 mA g ⁻¹	79 %	169 mAh g ⁻¹ at 3.69 A g ⁻¹
MoS ₂ -G ¹¹⁷	250 mAh g ⁻¹ at 25 mA g ⁻¹	88 % after 20 cycles at 25 mA g ⁻¹	75 %	200 mAh g ⁻¹ at 0.2 A g ⁻¹
SnS ₂ -G ¹¹⁸	610 mAh g ⁻¹ at 200 mA g ⁻¹	63 % after 100 cycles at 200 mA g ⁻¹	67 %	300 mAh g ⁻¹ at 4 A g ⁻¹
SnS ₂ -GO ¹¹⁹	580 mAh g ⁻¹ at 50 mA g ⁻¹	95 % after 50 cycles at 50 mA g ⁻¹	67 %	350 mAh g ⁻¹ at 2 A g ⁻¹
Sb-C ¹²⁰	610 mAh g ⁻¹ at 100 mA g ⁻¹	94 % after 100 cycles at 100 mA g ⁻¹	85 %	309 mAh g ⁻¹ at 2 A g ⁻¹
SnS ₂ -rGO ¹²¹	550 mAh g ⁻¹ at 1 A g ⁻¹	91 % after 400 cycles at 1 A g ⁻¹	79 %	570 mAh g ⁻¹ at 2 A g ⁻¹
SnS-C ¹²²	490 mAh g ⁻¹ at 500 mA g ⁻¹	88 % after 50 cycles at 500 mA g ⁻¹	63 %	300 mAh g ⁻¹ at 5 A g ⁻¹

CoS ₂ -MWCNT ¹²³	650 mAh g ⁻¹ at 100 mA g ⁻¹	88 % after 100 cycles at 100 mA g ⁻¹	93 %	525 mAh g ⁻¹ at 0.8 A g ⁻¹
NiS-PEDOT ¹²⁴	450 mAh g ⁻¹ at 600 mA g ⁻¹	60 % after 50 cycles at 600 mA g ⁻¹	83 %	300 mAh g ⁻¹ at 1.2 A g ⁻¹
SnO ₂ -G ¹²⁵	650 mAh g ⁻¹ at 20 mA g ⁻¹	95 % after 100 cycles at 20 mA g ⁻¹	31 %	150 mAh g ⁻¹ at 0.64 A g ⁻¹
MoS ₂ nanosheet ¹²⁶	550 mAh g ⁻¹ at 80 mA g ⁻¹	64 % after 100 cycles at 80 mA g ⁻¹	42 %	300 mAh g ⁻¹ at 0.32 A g ⁻¹
MoS ₂ -C ¹²⁷	600 mAh g ⁻¹ at 67 mA g ⁻¹	87 % after 50 cycles at 67 mA g ⁻¹	45 %	380 mAh g ⁻¹ at 1.34 A g ⁻¹
Sn-SnS-C composite ¹²⁸	450 mAh g ⁻¹ at 100 mA g ⁻¹	87% after 150 cycles at 100 mA g ⁻¹	62 %	350 mAh g ⁻¹ at 0.8 A g ⁻¹
Sb-C ¹²⁹	635 mAh g ⁻¹ at 200 mA g ⁻¹	94% after 100 cycles at 200 mA g ⁻¹	64 %	310 mAh g ⁻¹ at 3 A g ⁻¹
SnS-rGO ¹³⁰	457 mAh g ⁻¹ at 20 mA g ⁻¹	94% after 100 cycles at 100 mA g ⁻¹	56 %	240 mAh g ⁻¹ at 0.4 A g ⁻¹
SnS-C ¹³¹	544 mAh g ⁻¹ at 100 mA g ⁻¹	98% after 80 cycles at 100 mA g ⁻¹	66 %	450 mAh g ⁻¹ at 0.8 A g ⁻¹
SnSb-C ¹³²	485 mAh g ⁻¹ at 100 mA g ⁻¹	81% after 50 cycles at 100 mA g ⁻¹	75 %	295 mAh g ⁻¹ at 1 A g ⁻¹
MoS ₂ -G ¹³³	440 mAh g ⁻¹ at 20 mA g ⁻¹	63% after 100 cycles at 20 mA g ⁻¹	41 %	352 mAh g ⁻¹ at 0.64 A g ⁻¹
Sn-CNT ¹³⁴	600 μ Ah cm ⁻² at 50 μ A cm ⁻²	92% after 100 cycles at 50 μ A cm ⁻²	81 %	300 mAh g ⁻¹ at 1 mA cm ⁻²
SnS ₂ -G ¹³⁵	725 mAh g ⁻¹ at 20 mA g ⁻¹	89% after 60 cycles at 20 mA g ⁻¹	52 %	463 mAh g ⁻¹ at 0.64 A g ⁻¹
Sn-C ¹³⁶	300 mAh g ⁻¹ at 20 mA g ⁻¹	60% after 15 cycles at 20 mA g ⁻¹	40 %	20 mAh g ⁻¹ at 1 A g ⁻¹
Sb ₂ S ₃ -rGO ¹³⁷	650 mAh g ⁻¹ at 50 mA g ⁻¹	97% after 50 cycles at 50 mA g ⁻¹	68 %	520 mAh g ⁻¹ at 3 A g ⁻¹
MoS ₂ -CNT ¹³⁸	496 mAh g ⁻¹ at 200 mA g ⁻¹	85% after 80 cycles at 200 mA g ⁻¹	67 %	300 mAh g ⁻¹ at 0.5 A g ⁻¹
SnS ₂ -rGO ¹³⁹	649 mAh g ⁻¹ at 100 mA g ⁻¹	89% after 400 cycles at 800 mA g ⁻¹	64 %	337 mAh g ⁻¹ at 12.8 A g ⁻¹
SnS-G ¹⁰²	500 mAh g ⁻¹ at 810 mA g ⁻¹	94% after 250 cycles at 810 mA g ⁻¹	70 %	308 mAh g ⁻¹ at 7.29 A g ⁻¹
Sb ₂ S ₃ ¹⁴⁰	835.3 mAh g ⁻¹ at 50 mA g ⁻¹	92% after 100 cycles at 200 mA g ⁻¹	73 %	553.1 mAh g ⁻¹ at 2 A g ⁻¹

^a The cycling stability is calculated by $C_n/C_{max} \times 100\%$, where C_n is the discharge capacity at the n cycle, C_{max} is the maximum discharge capacity after the first 3 cycles.

^b All the capacity values were all calculated based on the active material SnS only and include no weight of current collector (GF).

1.3 Target and outline of this dissertation

1.3.1 Motivation of this research

As discussed previously, design and optimization of high-performance graphene scaffold composites could be significantly important in developing high performance LIB and NIB. This thesis focuses on designing and controllable synthesis of high-performance oxides, sulfides using graphene sheets or graphene foam as the conducting network or scaffold support for both cathode and anode of LIBs/SIBs.

The experimental works are generally fall into the following three categories:

- a. Novel structure design: To fabricate a high-performance electrode the structure and morphology of the active materials are crucial. Ultrathin nanorods and nanoflakes with or without shell protection facilitate the electron and ion transportation. Hence advanced electrode material of ultrathin structures with graphene scaffold will be synthesized for LIBs/SIBs. The reaction parameters (concentration, temperature, time and etc.) will be optimized to get the best result and a better understanding of the structure.
- b. Electrochemical performance and electrochemical kinetics tests: Normal electrochemical tests, such as cyclic voltammetry (CV), charge/discharge profiles and electrochemical impedance spectroscopy will be performed to measure specific capacity, rate property, and cycling stability, in order to identify the best materials and structures, to quantitatively study the charge-transfer and mass-transport processes, and to determine the rate-determining step. For each composite electrode, the role of graphene scaffold will be the focus of the studies, including how it improves the electronic transportation and decreases the impedance. The correlation between the structures and the electrochemical properties will also be investigated in detail by tunable pseudocapacitive contributions.
- c. Characterization of the active materials as well as charge/discharge products: in-situ X-ray diffraction (XRD), in-situ Raman, X-ray photoelectron spectroscopy (XPS), High resolution Transmission Electron Microscope

(HRTEM) etc. are employed to explore the structure/phase evolution mechanism during electrochemical reactions.

1.3.2 Outline of this thesis

There are six chapters in this dissertation.

Chapter 1 is the general background introduction and mechanism of Li- and Na- ion batteries. Some traditional electrode materials for both cathode and anode are also reviewed for both LIBs and SIBs. The research motivation, targets and methods are also introduced.

In Chapter 2, novel V_2O_5 electrodes were successfully prepared by directly growing V_2O_5 nanobelts on graphene foam (GF). The V_2O_5 film was coated with a mesoporous thin layer of conducting polymer PEDOT. This is an “all-in-one” integrated electrode that outperforms all V_2O_5 -based LIB electrodes (see a comprehensive Table S3), with power density being even better than supercapacitors. This result will most likely push the promising V_2O_5 LIB nanoelectrode an important forward jump towards practical applications.

Chapter 3 presents the research on graphene foam supported bi-layer VO_2 nanoarrays for both LIB and NIB cathodes. This new electrode combines three new materials into one: graphene quantum dots (GQDs), VO_2 nanoarrays, and ultralight graphene foam (GF). VO_2 is a hot cathode material but suffers from poor stability. The GQDs layer has radically improved the performance of VO_2 both for LIB and NIB. Our new electrode exhibits Li and Na ion storage properties superior to any other ones reported to date.

In Chapter 4, an ingenious approach is adopted for fabrication of 3D sodium-containing cathode, i.e. sodium vanadium fluorophosphate (NVOPF) oriented arrays grown directly on flexible light-weight graphene foam backbone. This new electrode demonstrates high-rate capability and long-term rate durability. First principles computational investigation and *in situ* XRD observations reveal that the anisotropic growth of nanoarrays creates more intercalation sites along a- and b- axes

with short diffusion length, small migration barriers for Na^+ , and small volume changes during charge/discharge cycles.

Chapter 5 is focused on tunable SnS nanostructures grown directly on 3D graphene foam. Excitingly, this material demonstrates high-capacity and high-rate properties for SIB and the high-rate capability even outperforms its Li ion storage performance, which opened the pioneering cognition for the possibility of “SIB could be better than LIB”. Quantitative kinetics analysis has been performed, for the first time, showing a decisive maximized pseudocapacitive contribution to the rate capability of Na-ion storage in few-layered SnS nanosheet arrays. The encouraging result may accelerate further development of SIBs by smart nanoengineering of the electrode materials.

Chapter 6 indicates some limitation of our current work and proposes avenues for the future work of this research.

Chapter 2 Vanadium Pentoxide for Li-Ion Storage

2.1 Introduction and motivation

Energy is the lifeblood of modern society and plays an important role in the advancement of human civilization. Over the past decades, substantial effort has been placed on developing renewable energy sources (such as solar radiation, wind, and waves) to meet ever-increasing global energy demand and reduce environmental pollution.²⁻⁴ However, due to the intermittent and/or diffuse nature of these renewable energy sources, there is a pressing need to design and fabricate high-performance energy storage systems to make full use of the renewable energy.

It is noteworthy that the energy density is the core characteristics of LIBs. In compliance with the premise of high energy density, we have to find effective way to improve the power density (or high-rate performances) of the positive electrode materials as much as possible because the high-rate capability is extremely important for the hybrid electric vehicles (HEV) and electric vehicles (EV). The general approaches for enhancing the energy (or capacity) and power densities (or rate capability) of positive electrodes include constructing three-dimensional (3D) porous electrode with conductive 3D backbone,^{148,149} fabricating nanoscale architecture with short ion/electron transportation path,¹⁵⁰⁻¹⁵² coating conductive layer on active materials.³ These strategies are adopted alone or work together to fabricate V_2O_5 based positive electrodes with enhanced electrochemical activity and kinetic feature. So far, numerous V_2O_5 nanostructures (such as nanotubes,¹⁵³ nanofibers,^{52,57} nanospikes,⁴⁹ nanorods,¹⁵⁴ nanobelts,^{48,64,155} nanosheets,^{53,74,156,157} yolk-shell,³⁹ nanoflowers,^{75,158} nanoflakes,¹⁵⁹ and hollow spheres¹⁶⁰⁻¹⁶²) have been prepared and improved electrochemical performances are proven in these systems. Nevertheless, the single nanoscale design is not enough for constructing high-performance V_2O_5 electrodes because the electrical conductivity of pure nano-size V_2O_5 is still not satisfactory resulting in moderate power performances. To further improve the performance of V_2O_5 electrodes, scientific researchers combine the strategies of

nanoporous design and conductive composite design to prepare V₂O₅/carbon (porous carbon, carbon nanotube and reduced graphene oxide),^{37,43,67,163-167} and V₂O₅/conducting polymer (polypyrrol (PPY), Poly(3,4-ethylenedioxythiophene, PEDOT), and polyaniline (PANI))¹⁶⁸⁻¹⁷³ composite positive electrodes with improved electrochemical properties due to the introduction of conductive layers in the nanoporous structure. Despite this progress, almost all the efforts are focused on V₂O₅ powder products (whether V₂O₅ nanostructures or composites mentioned above), which need to be mixed with additives (such as carbon black), and polymer binders, and finally compressed on conductive substrates (Al foil). This comes with the risk of negating the benefits associated with the reduced particle size and introduces supplementary, undesirable interfaces. Furthermore, the extra weight of additives, polymer binders, and metal conductive substrates will decrease the energy and power density of the whole electrodes.

To overcome these problems and preserve the benefits of electrochemistry at the nanoscale, recently, a new electrode design strategy is proposed to fabricate high-performance positive electrodes of LIBs, namely bind-free integrated positive electrode without conventional binders, additives, and metal substrates. This strategy involves directly depositing active materials on the self-supported three-dimensional (3D) porous carbon materials forming an integrated, binder-free and light positive electrode.¹⁷⁴⁻¹⁸⁰ Though chemically-derived graphene (or called reduced graphene oxide) is a popular self-supported conductive scaffold for active materials, the electron transport in the reduced graphene oxide is not high enough leading to moderate rate performance.^{178,181} In a departure from the reduced graphene oxide, the chemical vapor deposition (CVD)-derived 3D graphene foam (GF) (or called ultrathin graphite foam, UGF) has been demonstrated to be an excellent backbone for constructing high-performance binder-free positive electrodes owing to its fast transport channel of charge carriers and light weight. The integrated design of positive electrodes based on 3D GF was pioneered by Ruoff's group,^{175,178} and Chen's group,^{177,181} and high-performance LiFePO₄/GF electrodes were prepared and excellent rate capability and high capacity were demonstrated. However, to date, there

is no report on integrated positive electrode by combining V_2O_5 and UGF as well as their applications for LIBs. Additionally, it should be pointed out that the single combination between nanoscale positive active materials with GF is still not a perfect approach to improve the kinetic feature of the electrode because the electron transportation around the positive active materials is not homogeneous and differ widely in this way. The positive active materials are always loaded on the surface of the GF. In such a configuration, the electron transfer at the bottom of positive active materials will be enhanced, while this effect will be great weakened for the upper part of positive active materials.

In view of this situation and based on the design considerations, in the present work, we report light bind-free integrated positive electrodes by combining 3D porous UGF, V_2O_5 nanoarrays and conducting polymers (Poly (3,4-ethylenedioxythiophene), PEDOT) together in one electrode. The research strategy of this work is highlighted as follows. (1) The CVD-UGF has been demonstrated with good electrical conductivity ($\sim 1,000 \text{ S m}^{-1}$), a high porosity of $\sim 99.7 \%$, a light weight ($\sim 0.6 \text{ mg cm}^{-2}$) and a large specific surface area ($\sim 850 \text{ m}^2 \text{ g}^{-1}$).^{177,181} The 3D porous CVD-UGF is acted as the light conductive scaffold for the growth of hierarchical V_2O_5 /PEDOT core/shell crossed nanobelt arrays (CNBA) to ensure fast conductive pathway for electrons and short ion diffusion length. (2) To our best knowledge, V_2O_5 nanoarrays are fabricated on kinds of substrates (including 3D UGF/GF, carbon cloth, ITO glass) for the first time, and require short synthesis times (solvothermal for 100 minutes) compared with some other methods (1~7 days)^{55,62,182,183}. (3) The conductive PEDOT layer is homogeneously coated on the surface of the hierarchical V_2O_5 CNBA without any help of additive surfactant (such as para-toluenesulfonic acid¹⁸⁴ (p-TSA)), to further provide fast electron transfer around the V_2O_5 . Furthermore, the PEDOT is also served as a structural stabilizer to keep the whole structure intact and stable during the long-term cycling. Furthermore, the introduction of PEDOT could decrease the polarization of electrodes and prolong the discharge plateau above 3.0 V resulting in increased proportion of high-voltage (3.0 V–4.0 V) capacity. (4) 3D free-standing thin core/shell nanobelt nanoarrays architecture may possess much more advantages

than other nanostructures, such as short Li^+ diffusion distance, efficient electron transport pathways and large contact area between electrolyte and active materials. Moreover, it can accommodate the strain caused by the Li ion insertion/extraction and alleviate the structural damage resulting in long cycle life. With these fascinating merits, as positive electrodes for LIBs, the as-developed 3D UGF- V_2O_5 /PEDOT core/shell CNBA exhibits superior high-rate capability (265 mAh g^{-1} at 5 C and 168 mAh g^{-1} at 60 C , respectively) and cycling stability with 98 % capacity retention after 1000 cycles at 60 C .

2.2 Preparation and materials characterization

2.2.1 Growth of 3D GF by CVD method

The growth of the 3D ultrathin graphite foams was achieved using nickel foams as the 3D templates by chemical vapor deposition (CVD). The Ni foams were put into a 5-inch quartz tube inside a horizontal tube furnace and heated to $1000 \text{ }^\circ\text{C}$ under the gas flow of Ar (280 sccm) and H_2 (20 sccm) for 15 min in order to clean the surfaces of Ni foams and reduce the oxide layer. After the annealing, ethanol was bubbled into the reaction tube by Ar (160 sccm) + H_2 (40 sccm) flow at $900 \text{ }^\circ\text{C}$ under ambient pressure to participate in the reaction. After reaction for 15 min, the tube was rapidly cooled down to room temperature at a rate about $100 \text{ }^\circ\text{C min}^{-1}$ under the protection of Ar (280 sccm) and H_2 (20 sccm). Free-standing UGF (0.6 mg cm^{-2}) was obtained via etching of nickel backbone in a mixture solution of 1 M FeCl_3 and 0.5 M HCl for 5 h at $80 \text{ }^\circ\text{C}$.

2.2.2 Preparation of V_2O_5 /PEDOT

The above 3D UGF was used as the backbone for the growth of V_2O_5 /PEDOT core/shell crossed nanobelt arrays by the combination of solvothermal synthesis and electro-deposition methods. Firstly, hierarchical V_2O_5 nanobelt arrays were prepared by a facile modified solvothermal synthesis method. The solvothermal solution was prepared by dissolving 2 mM V_2O_5 powder (Sigma-Aldrich) and 6 mM $\text{H}_2\text{C}_2\text{O}_4$

powder (Sigma-Aldrich) with 12 mL of distilled water at 75 °C for about 2 hours until VOCl_2 (a dark blue solution) was formed. 3 mL of 30 % H_2O_2 was added and kept continuously stirring for about 20 min to give a brown solution, and then 65 mL ethanol was added. The obtained solution was transferred into 100 mL Teflon-lined stainless steel autoclave liners. The 3D UGF was immersed into the reaction solution. The autoclave liners were kept at 180 °C for 100 minutes, and then the sample was collected and rinsed with distilled water and ethanol in turn for three times. Finally, the samples were annealed at 300 °C in air for 2 h to obtain V_2O_5 nanobelt arrays. The load weight of V_2O_5 nanobelt arrays is $\sim 0.7 \text{ mg cm}^{-2}$.

Then, the PEDOT layer was decorated on the V_2O_5 nanobelt arrays forming core/shell nanobelt arrays by a facile electro-deposition method. The electrolyte for electro-polymerization of PEDOT was obtained by dissolving 10 mM 3,4-ethylenedioxythiophene (EDOT) and 100 mM LiClO_4 in an acetonitrile solution. The PEDOT shell was deposited by applying constant anodic current density of 1 mA cm^{-2} for 300 s. The electro-polymerization was conducted by a two-electrode system together with above V_2O_5 nanobelt arrays as the working electrode and a Pt foil as the counter-electrode. As a comparison sample, PEDOT was electro-polymerized directly on UGF to form UGF/PEDOT composite with the same method mentioned above. The mass ratio of PEDOT/ V_2O_5 is about 10 %. In addition, to demonstrate the generality, the V_2O_5 /PEDOT core/shell nanobelt arrays were also grown on some other substrates (such as carbon cloth, ITO glass and 3D porous nickel film) as the same deposition parameters described above.

2.3 Results and discussion

2.3.1 Structure and morphology analysis

Fig. 2.1 (a-c) Schematic illustration of synthesis of UGF-V₂O₅/PEDOT core/shell CNBA. SEM images and photos of (d, e) UGF, (f, g) UGF-V₂O₅ CNBA and (h, i) UGF-V₂O₅/PEDOT core/shell CNBA. (Fine structures in upper-right inset).

Fig. 2.1a-c shows the fabrication process of the UGF-V₂O₅/PEDOT core/shell CNBA. The CVD-derived UGF is directly served as a 3D porous scaffold for the solvothermal synthesis (SS) growth of hierarchical V₂O₅ CNBA, which is further coated by PEDOT shell via a facile electro-deposition (ED) method, finally forming self-supported UGF-V₂O₅/PEDOT core/shell CNBA. The obtained UGF exhibits a continuous and interconnected 3D network with branches of 60–100 μm and macropores of 150–500 μm , and no cracks or failure is observed (Fig. 2.1d and S1a). The UGF shows a color of grey (Fig. 2.1e) and intact structure, and does not need structural supporting agent like polymethyl methacrylate (PMMA), which will reduce the electrical conductivity of the UGF.¹⁷⁸ In our case, the as-prepared UGF is very light, only $\sim 0.6 \text{ mg cm}^{-2}$, much lower than those of metal foams (e.g., 10–15 mg cm^{-2} for nickel and copper foams). After SS, the UGF is uniformly covered by hierarchical V₂O₅ nanobelts made up of ~ 4 secondary belts with thickness of $\sim 15 \text{ nm}$, which are

interconnected along the same axis (Fig. 2.1f and S1b). The sample exhibits a color of greenish yellow after loading of SS-V₂O₅ nanobelts (Fig. 2.1g). The diameter of the hierarchical V₂O₅ nanobelt is ~180 nm, about two times the size of secondary belt (Fig. 2.1f). The hierarchical V₂O₅ nanobelts grow vertically to the surface of the UGF, indicating that each nanobelt has its own contact with the UGF and could participate in the electrochemical reactions. After electro-deposition (ED) of PEDOT, the color of the sample changes into black (Fig. 2.i). Importantly, the PEDOT thin layer can be homogeneously deposited on the surface of hierarchical V₂O₅ nanobelts forming bind-free integrated UGF-V₂O₅/PEDOT core/shell CNBA electrode (Fig. 2.1h). The appearance of the V₂O₅/PEDOT core/shell nanobelt is much rougher than the single V₂O₅ nanobelt due to the decoration of PEDOT. The diameter of the V₂O₅/PEDOT core/shell nanobelts becomes a little bigger, ~210 nm. Noticeably, both UGF-V₂O₅ core/shell CNBA and UGF-V₂O₅/PEDOT core/shell CNBA have enough mechanical stability and good flexibility (Fig. 2.S2). The samples can be bent without any protective case and will not be broken, indicating that they are real self-supported bind-free integrated electrodes without conventional polymer binders, additives and metal substrates. In addition, no active materials are peeled off even repeated bending. Meanwhile, according to the application requirements, the V₂O₅/PEDOT core/shell CNBA can also be fabricated on other different conductive substrates such as ITO glass, carbon cloth, and 3D nickel film (Fig. 2.S3).

Fig. 2.S1 SEM images of the (a) UGF, (b) UGF-V₂O₅ nanobelts array and (c) UGF-V₂O₅/PEDOT core/shell nanobelts array.

Fig. 2.S2 Photos of self-supported (a) UGF-V₂O₅ nanobelts array and (b) UGF-V₂O₅/PEDOT core/shell nanobelts array electrodes.

Fig. 2.S3 SEM images of V_2O_5 /PEDOT core/shell nanobelts array grown on different substrates: (a) ITO glass; (b), (c) Photos of V_2O_5 nanobelts array, V_2O_5 /PEDOT core/shell nanobelts array respectively on ITO glass; (d) carbon cloth; (e) Photos of V_2O_5 /PEDOT core/shell nanobelts array on carbon cloth.

The detailed microstructure of products at different states is further analyzed by the TEM-HRTEM images. The UGF exhibits a rippled and crumpled structure. The reflection spots in the selected area electronic diffraction (SAED) pattern of the UGF are arranged in a typical hexagonal pattern characteristic of the graphitic nature (Fig. 2.2a).¹⁷⁶ Additionally, the lattice fringes with a lattice spacing of ~ 0.34 nm corresponds to the (002) planes of graphitic carbon (JCPDS 75-1621) (Fig. 2.2b). The hierarchical structure of the V_2O_5 nanobelts is clearly shown in Fig. 2.2c. The secondary belts are connected with each other forming the hierarchical V_2O_5 nanobelt with an average diameter of ~ 180 nm as well as a smooth texture and narrow tip. The measured lattice spacing of 0.57 nm in HRTEM image (Fig. 2.2d) is in good agreement with the (200) interplanar distance of the orthogonal V_2O_5 phase (JCPDS

41–1426). Furthermore, the HRTEM analysis plus the fast fourier transform (FFT) pattern reveal that the obtained V_2O_5 nanobelt is single crystalline in nature.

Fig. 2.2 TEM-HRTEM images of (a, b) the UGF (SAED pattern in inset), (c, d) V_2O_5 nanobelt (Insets: low magnification TEM and FFT pattern) and (e, f) V_2O_5 /PEDOT core/shell arrays (Insets: HRTEM images and FFT pattern).

After electro-deposition of the PEDOT, the hierarchical nanobelt architecture is well preserved, and a rougher appearance is demonstrated by the TEM image (Fig. 2.2e). The V_2O_5 nanobelt core is intimately wrapped by the PEDOT shell. From the HRTEM image in Fig. 2.2f, notice the fact that the PEDOT shell has a thickness of about 15 nm and is amorphous in nature, supported by the HRTEM result (upper-right inset in Fig. 2.2f), because no lattice fringes and no FFT pattern are observed in the

PEDOT region. In addition, similar to the pure V_2O_5 nanobelt above, typical FFT pattern and interplanar distance of 0.57 nm belonging to orthogonal V_2O_5 phase are noticed. This unique core/shell hetero-structure is also clearly verified by the energy dispersive X-ray spectroscopy (EDS) elemental mapping of C, S, V and O (Fig. 2.S4a). The elements of S and C come from the PEDOT. These elements are also verified by the EDS spectrum (Fig. 2.S4b).

Fig. 2.S4 (a) Dark field TEM image of V_2O_5 /PEDOT core/shell nanobelts array and corresponding EDS mapping of S, O, V, and C. (b) EDS spectrum of the UGF- V_2O_5 /PEDOT core/shell nanobelts array.

Table 2.S1 Typical Raman peaks of crystalline V_2O_5 ¹⁸⁵⁻¹⁸⁷

Peaks (cm^{-1})	Vibration modes
995	Stretching vibration of $\text{V}=\text{O}$
700	Stretching vibration of V_2-O
527	Stretching vibration of V_3-O
479	Bending vibration of $\text{V}-\text{O}-\text{V}$
320	Bending vibration of V_3-O
404 and 283	Bending vibration of $\text{V}=\text{O}$
145 and 197	Lattice vibration

Table 2.S2 Typical Raman peaks of PEDOT¹⁸⁸

Peaks (cm ⁻¹)	Vibration modes
1538	Asymmetric C _α =C _β stretching
1456	Symmetric C _α =C _β stretching
1372	C _α -C _α inter-ring stretching
1265	C _β -C _β inter-ring stretching
1538	Deformation of C-O-C
1456	Deformation of oxyethylene ring
1372	Symmetric O-S bending

Fig. 2.S5 (a) XRD patterns of the UGF, UGF-V₂O₅ nanobelts array and UGF-V₂O₅/PEDOT core/shell nanobelts array. (b) Wide range Raman spectra of the UGF, UGF-V₂O₅ nanobelts array and UGF-V₂O₅/PEDOT core/shell nanobelts array. (c, d) Narrow range Raman spectra of the UGF, UGF-V₂O₅ nanobelts array and UGF-V₂O₅/PEDOT core/shell nanobelts array.

Fig. 2.S6 XPS spectra of the UGF- V_2O_5 /PEDOT core/shell nanobelts array: (a) V 2p, (b) C 1s, (c) O 1s and (d) S 2p.

For the V 2p spectrum (Fig. 2.S6a), the binding energy separation between core levels V 2p_{1/2} (524.7 eV) and V 2p_{3/2} (517.3 eV) is ~7.4 eV, which matches with electronic states of V_2O_5 .¹⁸⁹ The peak fitting of core level C 1s spectra is shown in Fig. 2.S6b. The peaks at 284.7 eV, 285.8 eV, and 286.6 eV correspond to C-C, C-O, and C-S bonds of the PEDOT, respectively.^{190,191} In O 1s spectra (Fig. 2.S6c), the peaks at 530.1 eV, and 531.1 belong to V-O and V-OH bonds, respectively. The weak V-OH peak is probably due to the atmospheric contact. The peak at 533.1 eV is assigned to the (C-O-C) of the PEDOT.¹⁸⁸ In addition, the two typical characteristic peaks at 164.9 eV and 164.0 eV correspond to sulphur atoms in the thiophene units of the PEDOT (Fig. 2.S6d).^{190,191}

The phase and composition of products at different states are also monitored and confirmed by the XRD, Raman and XPS results. The 3D UGF show two typical

diffraction peaks at 26.4° and 54.5° attributed to the (002) and (004) reflections of graphitic carbon (JCPDS 75-1621), respectively (Fig. 2.S5a). For the UGF- V_2O_5 CNBA and UGF- V_2O_5 /PEDOT core/shell CNBA, except for the peaks of the UGF, the other diffraction peaks can be well indexed to the orthogonal α - V_2O_5 phase (JCPDS 41-1426) (Fig. 2.S5a). No diffraction peaks of the PEDOT are observed due to the amorphous nature, which is consistent with the TEM results. Fig. 2.S5b and c shows the Raman spectra of UGF, UGF- V_2O_5 CNBA and UGF- V_2O_5 /PEDOT core/shell CNBA. Raman spectrum is the direct evidence to check whether the existence of UGF. Two characteristic peaks at $\sim 1575\text{ cm}^{-1}$ (G band) and 2680 cm^{-1} (2D band) are identified for the UGF (Fig. 2.5b).¹⁷⁷ The defect-related D band in the UGF is not observed, implying the overall high quality of the UGF by chemical vapour deposition (CVD) method with little defects. For the UGF- V_2O_5 CNBA, in addition to the peaks of the UGF, the other Raman peaks can be well indexed to crystalline V_2O_5 (Fig. 2.5b and c).¹⁸⁵⁻¹⁸⁷ The relation between peaks and stretching modes of the V_2O_5 is listed in Table 2.S1. For the UGF- V_2O_5 /PEDOT core/shell CNBA, the PEDOT is also verified by the Raman spectrum. The main characteristic peaks of the PEDOT are located in the range from 1050 cm^{-1} to 1650 cm^{-1} (Fig. 2.5b and d).¹⁸⁸ The corresponding dependency between peaks and vibration modes of the PEDOT is shown in Table 2.S2. The compositions of the V_2O_5 /PEDOT core/shell CNBA is further confirmed by the XPS analysis (Fig. 2.S6). Based on the results above, it is concluded that the V_2O_5 /PEDOT core/shell CNBA is successfully fabricated on the UGF forming self-supported bind-free integrated electrode by the aid of SS and ED methods.

2.3.2 Electrochemical performance

Fig. 2.3 Electrochemical characterizations of UGF- V_2O_5 CNBA and UGF- V_2O_5 /PEDOT core/shell CNBA: (a) CV curves at the scanning rate of 0.2 mV s^{-1} at the 5th cycle; (b) Charge/discharge curves at 1 C; (c) Our data and results (summarized form Table 1.1) published in the literature; (4) Rate capability; (5) Nyquist plots at fully charge stage (Equivalent circuit in inset).

A series of electrochemical tests were conducted to investigate the lithium ion storage properties of the UGF- V_2O_5 /PEDOT core/shell CNBA. Fig. 2.3a shows the typical cyclic voltammograms (CV) curves of the UGF- V_2O_5 CNBA and UGF- V_2O_5 /PEDOT core/shell CNBA at a scanning rate of 0.2 mV s^{-1} at the 5th cycle in the voltage range from 4.0 to 2.0 V (vs. Li/Li^+). Notice that both positive electrodes exhibit three main redox couples, but the peak current densities of the

UGF-V₂O₅/PEDOT core/shell CNBA are much stronger than the UGF-V₂O₅ CNBA, meaning its better electrochemical reactivity and higher capacity can be anticipated. Taking the CV curve of the UGF-V₂O₅/PEDOT core/shell CNBA for example, the first reduction peak at ~3.36 V is due to the conversion from α -V₂O₅ into ϵ -Li_{0.5}V₂O₅. Further reductions take place at ~3.15 V and ~2.17 V corresponding to the formation of δ -LiV₂O₅ and γ -Li₂V₂O₅, respectively. These reactions are reversible and contribute large capacity during the cycling. The simplified electrochemical reactions are expressed as follows.^{40,44,192,193}

It is clearly shown in the CV curves that the introduction of PEDOT into the core/shell structure can effectively enhance the electrochemical reactivity of reactions in eqn. (1) and (2), indicating that the capacity above 3.0 V will be improved due to the enhanced active material utilization and conductivity of the electrode arising from the conductive PEDOT network, which has an electrical conductivity of ~400 S cm⁻¹ measured by four points probe technique. This capacity enhancement is confirmed by the charge/discharge curves measured between 2.0 V and 4.0 V at a current density of ~300 mA g⁻¹, namely 1C rate (300 mA g⁻¹ is equal to 1 C, which is defined as insertion/extraction of two lithium ions into/from per V₂O₅ in one hour) (Fig. 2.3b). Three discharge plateaus (~3.4 V, ~3.2 V and ~2.3 V) are noticed for both electrodes, which are consistent with the CV result. Apparently, the UGF-V₂O₅/PEDOT core/shell CNBA exhibits lower charge voltage plateaus and higher discharge voltage plateaus than the UGF-V₂O₅ CNBA. It is indicated that the UGF-V₂O₅/PEDOT core/shell CNBA has smaller polarization during the charge/discharge processes due to the homogenous PEDOT conductive network. It is known that high polarization always leads to low discharge voltage and high charge voltage. The integrated PEDOT conductive network helps to transfer the charge efficiently and diminish the polarization, which decreases the charge voltage plateau and improves the discharge

voltage. Higher discharge voltage plateau means more energy that the electrodes can release, and it is also favorable for the improvement of the power density of the batteries. The UGF- V_2O_5 /PEDOT core/shell CNBA delivers a specific capacity of 297 mAh g^{-1} at 1 C rate, comparable to those in the literature (Fig. 2.3c and Table 1.1), and higher than the UGF- V_2O_5 CNBA (264 mAh g^{-1} at 1 C rate). The specific capacity is calculated based on the mass of active materials. The UGF has little capacity in the voltage of 2–4 V, also reported in other works. Importantly, the discharge capacity at high voltage (3.0–4.0 V) is greatly improved in the core/shell CNBA system and accounts for ~62 % in all the capacity between 4.0–2.0 V (vs. Li/Li^+), larger than the UGF- V_2O_5 CNBA (44 %). This high-voltage capacity percentage is also higher than other V_2O_5 nanostructures and composites in the literature (Table 1.1 and Fig. 2.3c).

Fig. 2.S7 (a) Discharge curves of UGF- V_2O_5 /PEDOT core/shell nanobelts array and (b) UGF- V_2O_5 nanobelts array at different rates. (c) Photograph of 10 green LEDs that are powered by one coin cell based on the UGF- V_2O_5 /PEDOT electrode.

Fig. 2.4 Cycling performances of UGF- V_2O_5 CNBA and UGF- V_2O_5 /PEDOT core/shell CNBA (a) 5 C and (b) 60 C. (c, d) SEM-TEM images of V_2O_5 /PEDOT core/shell CNBA after 1000 cycles at 60 C. (e, f) SEM-TEM images of V_2O_5 CNBA after 1000 cycles at 60 C.

Excellent high-rate capability is essential and highly desirable for high-power LIBs applications such as hybrid electric vehicles (HEVs) and electric vehicles (EVs). The high-rate capability and typical discharge curves at different current densities are shown in Fig. 2.3d and Fig. 2.S7, respectively. Impressively, the UGF- V_2O_5 /PEDOT core/shell CNBA shows superior and stable high-rate performances with a specific capacity of 297 mAh g^{-1} at 1 C, 265 mAh g^{-1} at 5 C, 236 mAh g^{-1} at 10 C, 187 mAh g^{-1} at 30 C, 156 mAh g^{-1} at 60 C, and 115 mAh g^{-1} at 80 C, respectively (Fig. 2.3d and Fig. 2.S7), much higher than those of the UGF- V_2O_5 CNBA (264 mAh g^{-1} at 1 C,

218 mAh g⁻¹ at 5 C, 181 mAh g⁻¹ at 10 C, 122 mAh g⁻¹ at 30 C, 87 mAh g⁻¹ at 60 C, and 56 mAh g⁻¹ at 80 C) as well as other V₂O₅ nanosheets powders and composites with chemical-derived graphene. In addition, for the UGF-V₂O₅/PEDOT core/shell CNBA, the capacity retention of 38.7 % is maintained as the charge/discharge rate increases from 1 C to 80 C, and a high specific capacity of 295 mAh g⁻¹ is recovered when the rate changes back into 1 C, much better than the UGF-V₂O₅ CNBA (21.2 % for 80 C capacity/1 C capacity and 254 mAh g⁻¹ recovered at 1 C). The exciting high-rate capability of the UGF-V₂O₅/PEDOT core/shell CNBA is particularly attractive for high-performance LIBs with both large energy and high power densities. To take as an example, the UGF-V₂O₅/PEDOT core/shell CNBA shows a capacity of 156 mAh g⁻¹ at 60 C, meaning that the whole charge/discharge process is very fast and finished in about 31.5 s. Remarkably, the UGF-V₂O₅/PEDOT core/shell CNBA shows an energy density of ~238 Wh kg⁻¹ at a power rate of 23 kW kg⁻¹ based on the total mass of the positive electrode, higher than the UGF-V₂O₅ CNBA (~131 Wh kg⁻¹ at a power rate of 23 kW kg⁻¹). These high-rate values are even much higher than those of reported aqueous-system supercapacitors (usually lower than 60 Wh kg⁻¹ at 20 kW kg⁻¹),^{1,149,194-196} indicating the superior high energy and power characteristics of the UGF-V₂O₅/PEDOT core/shell CNBA. The above results are in agreement with the electrochemical impedance spectra (EIS) analysis. As demonstrated by the EIS, the kinetics of lithium insertion/extraction is significantly improved in the core/shell system (Fig. 2.3e). Both samples show a semicircle in high-medium frequency regions and an inclined line in low frequency regions, which corresponds to electrochemical reaction impedance (namely, charge transfer) and ion diffusion impedance, respectively. A simple equivalent circuit model is used to simulate the reaction systems (inset in Fig. 2.3e). The corresponding symbolic meaning is as follows: R_s—ohmic resistance of solution and electrodes; R_{ct}—charge transfer resistance; Q—double layer capacitance; Z_w—Warburg impedance. The simulated value of R_s and R_{ct} for the UGF-V₂O₅/PEDOT core/shell CNBA is 1.9 Ω and 91.5 Ω, respectively, lower than the those of the UGF-V₂O₅ CNBA (2.2 Ω and 190.2 Ω, respectively). It is indicated that the UGF-V₂O₅/PEDOT core/shell CNBA has smaller

charge transfer resistance due to the introduction of PEDOT, which constructs an integrated conductive network for the V_2O_5 providing fast electron transfer and favorable for the improvement of electrochemical reactivity resulting in enhanced reaction kinetics.

Fig. 2.S8 (a, b) SEM images of UGF-PEDOT. (c) Discharge curves of UGF-PEDOT at different rates and (d) cycling stability at 60 C.

The cycling stability is a very important indicator for the practical applications of LIBs. Inspiringly, the UGF- V_2O_5 /PEDOT core/shell CNBA exhibits superior high-rate cycling stability, no matter at 5 C or 60 C rate (Fig. 2.4a and b). Notice the fact that little capacity decay is observed for the UGF- V_2O_5 /PEDOT core/shell CNBA during the high-rate cycles. A specific capacity of 265 mAh g^{-1} is obtained at 5 C after 500 cycles. More excitingly, after 1000 cycles at 60 C, the UGF- V_2O_5 /PEDOT core/shell CNBA still delivers a specific capacity of 163 mAh g^{-1} and keeps the capacity retention of $\sim 98\%$ of the highest value. The excellent fast charge/discharge, high-power electrochemical properties are highly attractive for LIBs with applications

in HEVs and EVs. The assembled coin cell based on the UGF-V₂O₅/PEDOT core/shell CNBA can easily power and light 55 green LED lights (Fig. 2.S7c). In contrast, the UGF-V₂O₅ CNBA shows obvious capacity degradation with a specific capacity of 164 mAh g⁻¹ at 5 C after 500 cycles and 52 mAh g⁻¹ at 60 C after 1000 cycles with the capacity retention of ~60 %. To further check the reasons for the enhanced stability of the UGF-V₂O₅/PEDOT core/shell CNBA, SEM-TEM tests were conducted after cycling at 60 C for 1000 cycles. It is observed that the core/shell CNBA architecture is well preserved and does not show obvious deformation (Fig. 2.4c and d), while for the pure V₂O₅ CNBA, in which the nanobelt starts to aggregate and deform, and become thicker (Fig. 2.4e and f). Even breakage is noticed on the UGF branch. Through comparative results above, it is justified that the introduction of PEDOT in the core/shell structure not only provides a good integrated conductive network for the V₂O₅, but also acts as a soft “armor” to protect the V₂O₅ core material. As a flexible organic material, the PEDOT shell may accommodate the strain resulting from lithiation/delithiation cycles and keep the whole structure stable during high-rate cycles, leading to superior cycle life. Moreover, the results of the UGF-V₂O₅/PEDOT core/shell CNBA are also much better than those V₂O₅ nanostructures and composites with reduced graphene oxides and other conducting polymers in the literature (Table 1.1). Compared to the published V₂O₅ nanostructures and composites, the UGF-V₂O₅/PEDOT core/shell CNBA not only possesses the same advantages as other nanostructures with short ion/electron diffusion path and large reaction surface, but also has some unique merits. (1) Integrated bind-free light electrode based on light and highly conductive UGF substrate. Such design can eliminate the negative effect of conventional binders, additives and metal substrates and increase the energy and power densities. (2) Inorganic/organic core/shell nanoarray architecture. The organic shell (PEDOT) can modify the charge transfer and improve the electrical conductivity of the V₂O₅ electrode with better and faster reaction kinetics resulting in enhanced high-rate capability. (3) Enhanced structural stability from the “armor” effect of PEDOT. The PEDOT serves like a soft “armor” to keep the V₂O₅ electrode stable and prevents it from collapsing and breaking down

during high-rate cycling. It should be mentioned that the UGF does not show capacity in the voltage of 2.0–4.0 V, but the PEDOT on the UGF has small capacity for Li ion storage of 32 mAh g⁻¹ at 1 C and 15 mAh g⁻¹ at 60 C, respectively (Fig. 2.S8). Importantly, the UGF-PEDOT shows excellent cycling stability at 60 C with no capacity decay after 1000 cycles, implying that the PEDOT is an superior structural stabilizer for the V₂O₅. In a nutshell, the UGF-V₂O₅/PEDOT core/shell CNBA shows excellent lithium ion storage properties with high power density and energy density as well as superior high-rate cycling stability.

2.4 Conclusions

According to the requirements of high energy and power densities for LIBs, we have designed and fabricated self-supported integrated binder-free UGF-V₂O₅/PEDOT core/shell crossed nanobelt arrays (CNBA) for electrochemical energy storage application. As positive electrodes of LIBs, the UGF-V₂O₅/PEDOT core/shell CNBA exhibits excellent and fast Li ion storage performances with higher capacity than the UGF-V₂O₅ core/shell CNBA as well as improved rate capability and cycling ability. Impressively, high specific capacities of 265 mAh g⁻¹ at 5 C and 168 mAh g⁻¹ at 60 C are achieved for the the UGF-V₂O₅/PEDOT core/shell CNBA as well as a high capacity retention of 98 % is obtained during 60 C cycling. It is proposed that the introduction of PEDOT into the core/shell system can greatly improve the charge transfer resulting fast reaction kinetics and maintain the electrode structure stable after long-time high-rate cycling. Such design by combing UGF, V₂O₅ and PEDOT into one integrated binder-free electrode represents an effective way to improve energy and power densities, specific capacitance, rate capability and cycling stability of V₂O₅-based high-performance LIBs.

Chapter 3 Vanadium Dioxide for Li- and Na-Ion Storage

3.1 Introduction and motivation

Due to the exhausting of traditional non-renewable fossil resources, marvelous demand of energy by industrial development and serious environment pollution problems, finding sustainable and clean energy sources has becoming the hot research topic worldwide.¹⁹⁷⁻²⁰⁰ Among all the reproducible energy supplies, Li ion batteries (as referred LIBs) have been favored by electronics and electric vehicles because of their advantages such as high capacity, long cycle life and environmental friendly properties.²⁰¹⁻²⁰³ Although LIBs technology is quite mature and extensively used now, there remain questions regarding its safety, lifetime, and energy/power density performance. More seriously, when talking about the long-term development of Li ion batteries, the increasing demand for lithium commodity chemicals and its geographically-constrained Li mineral reserves attract world attention. So at this crucial juncture, ambient temperature Na ion batteries (as referred SIBs) rise resulting from its within-touch spread and low cost²⁰⁴. Recently, scientists reported a number of new materials such as layered transition metal oxides $\text{P2-Na}_x\text{CoO}_2$ ²⁰⁵, $\text{Na}_x[\text{Fe}_{1/2}\text{Mn}_{1/2}]\text{O}_2$ ²⁰⁶, cubic $\text{Na}_x\text{MnFe}(\text{CN})_6$ ²⁰⁷, NASICON-type $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ ²⁰⁸, Fluoride-based ReO_3 -type FeF_3 ²⁰⁹. These pioneer work in SIBs opened a new window for researchers although they still suffered from low specific capacity (less than 200 mAh g⁻¹), corresponding to suppressed energy density.

Vanadium oxide has been long regarded as a promising electrode material for LIBs owing to its high capacity, low cost and abundant sources^{77,210-212}. In particular, vanadium dioxide stands out because of its unique structure (VO_2 (B), bilayers formed from edge-sharing VO_6 octahedra), rapid lithium ion diffusion rate and higher capacity than other types vanadium oxides^{211,213}. So far, numerous VO_2 nanostructures have been prepared with decent electrochemical performance, such as VO_2 nanoparticles²¹⁴, VO_2 nanowires²¹⁵, VO_2 nanobelts²¹⁶, star-like VO_2 mesocrystals²¹⁷, VO_2 nanowires assembled hollow microspheres²¹³ (see a complete list in Table 3.S1).

Although VO₂-related materials are extensively studied as LIBs cathode, their application in SIB was still left as vacuum. But bilayered V₂O₅ nanoparticles²¹⁸ and V₂O₅ nanobelts²¹⁹ with larger d-spacing have been recently synthesized and demonstrated with a good SIBs performance. Worse still, these materials used in both LIBs and SIBs suffered from fast capacity fading and poor high-rate performance, due to their self-aggregation, dissolution and the increased charge transfer resistance during cycles. Therefore, tailored nanoarchitecture design and additional aided materials which can both secure high surface conductivity and sustain the structure integrity are urgently needed in structural architecturizing.

In this Communication, in order to improve the overall electrochemical properties of VO₂-based electrode both in LIBs and SIBs, strategies “from bottom to top” and “from inside to outside” are proposed as follows: (a) 3D porous graphene foam (GF, also known as ultrathin graphite foam) acts as both a lightweight scaffold for the growth of VO₂, and an efficient current collector, forming a flexible, free-standing and binder-free electrode directly. Compared to traditional electrode substrates (Ni foam, carbon cloth, metal (Ti, Ni, stainless steel...) foils), GF possesses not only high electric conductivity but 3D, “inside and outside backbone” active material loading. On the other hand, the existence of binder (PTFE, PVDF, etc.), conductive additive (carbon black, active carbon, etc.) and current collector (Al/Cu foil) should decrease the effective mass of the electrode and lowers the energy density on a full cell level. Besides, kinds of conductive additive are proved to be capacity distributor during sodiation (50 mAh g⁻¹ to 150 mAh g⁻¹)^{220,221}, which in turn obstructs the intrinsic research of active materials. And the widely used binder PVDF has been found recently to accelerate the deterioration during sodiation^{222,223}. However, most of the current electrode materials used in SIBs was in the form of powders, where conductive additives and binders cannot be neglected. As a result, studies on free-standing and binder-free electrode seems particularly significant in SIBs; (b) Since the diffusion time of ions (t) is proportional to the square of the diffusion length (L): $t \approx L^2/D$ ²¹¹, another effective strategy to enhance rate performance is to reduce the characteristic dimensions and thickness of the active materials. Hence nanobelts

would be competitive to achieve fast ion diffusion. Compared to conventional forms of VO₂, nanoarrays architecture exhibits great advantages for its large surface area, reduced Li⁺ diffusion length, electrolyte mobility and expansion accommodation through the inter-array spacing. However, to our best knowledge, no report of VO₂ nanoarray electrode was found to date. So GF supported thin VO₂ nanobelt array architecture, which combines both nanobelts and nanoarrays, should be an attractive choice to boost the rate performance both in Li and Na ion batteries; (c) VO₂-based composites with graphene have also been reported with good electrochemical performance, for example, VO₂/graphene ribbons²¹¹, VO₂ nanotube/graphene²²⁴, VO₂/CNT nanowires²²⁵, but it remains to be hard to achieve a homogeneous continuous graphene covering on VO₂ architecture. Graphene quantum dots (GQDs, small graphene ribbons (usually smaller than 100 nm in size and less than 10 layers in thickness)), as an emerging attractive carbon material²²⁶, have been extensively applied in LEDs²²⁷, supercapacitors²²⁸, solar cells,^{229,230} oxygen reduction reaction²³¹, and sensors²³² owing to its unusual and interesting optical and electronic properties (tunable bandgap by controlling the size and surface chemistry). Application of GQDs in LIBs and SIBs were scarcely reported to date. Herein, we anchor functionalized GQDs onto VO₂ nanobelts array by applying electrophoresis deposition. The homogeneously GQDs covering can not only separate the VO₂ nanoarrays thus avoiding agglomeration but limit dissolution of the active materials, especially for the long-term cycling. With these merits, our 3D GF supported GQDs anchored VO₂ nanoarrays architecture exhibits superior high-rate capability and cycling stability both in LIBs and SIBs. Our results push the promising VO₂-based sodium ion battery an important step forward into practical applications.

3.2 Preparation and materials characterization

3.2.1 Growth of bilayered VO₂ arrays

Vanadium oxide was synthesized according to our previously reported method with

modification²¹². Firstly, 1.2 g V_2O_5 powder (Sigma-Aldrich) and 1.8 g $\text{H}_2\text{C}_2\text{O}_4$ powder (Sigma-Aldrich) were dissolved with 40 mL of distilled water at 75 °C until a dark blue solution was formed. 5 mL of the above solution was transferred into a 30 mL Teflon-lined stainless steel autoclave. Then 1 mL of 30 % H_2O_2 and 20 mL ethanol was added and kept continuously stirring for about 20 min. And then, one piece of 3D graphene foam (GF, 2×5 cm, ca. 0.6 mg cm⁻², prepared by CVD method according to our previously results^{233,234}) was immersed into the reaction solution. The autoclave liners were kept at 180 °C for 3 h, and then the sample was collected and rinsed with ethanol and distilled water in turn for three times. Finally, the samples were dried at 120 °C in vacuum to obtain bilayered VO_2 array (0.6 mg cm⁻²).

3.2.2 Preparation of $\text{VO}_2@\text{GQD}$ arrays.

150 mg graphene oxide (GO, by a modified Hummers method) was dispersed in 20 mL DMF (under ultrasonication for 30 minutes). The solution was transferred into a 30 mL Teflon-lined stainless steel autoclave and heated at 200 °C for 8 h. After being cooled down naturally, the mixture was filtered using a 0.22 μm microporous membrane and the obtained brown solution was functional GQDs dispersion in DMF. The solvent of suspension was removed with the aid of a rotary evaporator at 80 °C under reduced pressure. $\text{VO}_2@\text{GQD}$ arrays can be obtained in the help of a facile electrophoresis process by dispersing the functional GQD in DI water. The above GF supported VO_2 arrays were used as the substrate (working electrode) for the growth of $\text{VO}_2@\text{GQD}$ arrays, and Pt plate was used as counter electrode. And then a positive potential of 6 V for different time in the condition of ice-bath was applied to deposit functional GQDs onto the surface of VO_2 arrays. Finally, the samples were annealed at 400 °C in Ar for 2 h to obtain good structure stability. As a comparison, $\text{VO}_2@\text{GQD}$ arrays were also fabricated on transparent conductive fluorine-tin-oxide (FTO) substrates using the same methods as described above. The weight increase (measured by an analytical balance, RADWAG, MYA 21, d=1 μg) after GQDs deposition was ca. 30 μg (ca. 5 % weight of VO_2 arrays).

3.2.3 Characterization of GF supported VO₂@GQD arrays

The crystal structures of the samples were identified using X-ray diffraction (XRD, RigakuD/Max-2550 with Cu K α radiation). Raman spectra were obtained with a WITec-CRM200 Raman system (WITec, Germany) with a laser wavelength of 532 nm (2.33 eV). The Si peak at 520 cm⁻¹ was used as a reference to calibrate the wavenumber. The morphologies of the samples were characterized by field emission scanning electron microscopy. The structures of the samples were investigated by high-resolution transmission electron microscopy (HRTEM, JEOL JEM-2010F at 200 kV). The XPS measurements were performed by a VG ESCALAB 220i-XL system using a monochromatic Al K α 1 source (1486.6eV).

3.2.4 Battery fabrication and electrochemical measurements

Standard CR2032-type coin cells was assembled in an argon-filled glove box (Mbraun, Unilab, Germany) with the as-fabricated GF supported VO₂@GQD nanoarrays as the working electrode (with diameter of 12 mm , without any binder or additives). For lithium ion battery fabrication, the metallic lithium foil as the counter-electrode, 1 M LiPF₆ in ethylene carbonate (EC)–dimethyl carbonate (DME) (1:1 in volume) as the electrolyte, and a polypropylene (PP) film (Cellgard 2400) as the separator; For sodium ion battery fabrication, the metallic sodium foil as the counter-electrode, 1 M NaPF₆ in ethylene carbonate (EC)–diethyl carbonate (DEC)–fluoroethylene carbonate (FEC) (1:1:0.05 in volume) as the electrolyte, and glass fiber as the separator. The CV measurements were carried out using a Parstat-2273 electrochemical potentiostat at a scanning rate of 0.3 mV s⁻¹. For electrochemical impedance spectroscopy (EIS), the amplitude of the sine perturbation signal was 5 mV, and the frequency was scanned from the highest (10 kHz) to the lowest (5 mHz). Galvanostatic charge discharge cycles were tested by Neware battery tester at different current densities at room temperature.

3.3 Results and discussion

3.3.1 Structure fabrication and morphology

Fig. 3.1 Construction processes of GF supported GQDs-anchored VO₂ arrays: (a-c) the 3D yellow hollow foam represent the GF substrate. The green arrays represent VO₂ nanoarrays, and the blue cover represents the graphene quantum dots (GQDs); (d-f) SEM images of GF, GV, GVG, respectively (fine structure in inset).

The representative synthetic procedure of the 3D graphene foam (GF) supported graphene quantum dots (GQD)-anchored VO₂ arrays electrode (GVG) is illustrated in Fig. 3.1a-c. First, graphene foam skeleton (Fig. 3.1a,d, by CVD method) was employed as the substrate to grow VO₂ nanoarrays (GV) via a solvothermal process (Fig. 3.1b). As can be seen from Fig. 3.1e, the VO₂ nanoarrays exhibit a homogeneous size and shape distribution hierarchical structure with two intersected nanobelts (ca. 80 nm in width and ca. 15 nm in thickness). This similar structure (six-armed

microspindle particle) was also observed by Mai et. al^{213,217}. The simplified reactions during solvothermal reaction are proposed as follows:

Hence, the growth mechanism is pointed due to the “self-assembly” and “oriented crystallization” processes. During solvothermal reaction, the VOC_2O_4 nucleate onto the surface of GF, where bonding between the particles reduces overall energy. Then belts structure formed according to the strong crystal orientations crystallization of monoclinic VO_2 . Finally, two single belts coalesce together to form the intersected nanobelts architecture through the oriented attachment mechanism^{217,235}. There may be some degree of subsequent coarsening with the increase of the solvothermal time. Actually, as can be seen in Fig. 3.S1, the longer the solvothermal time last, the thicker and bigger of the nanobelts show. So as to the detailed crystal growth mechanism of the synthesized nanosheets and the overall architecture should be proposed in next part.

Fig. 3.S1. Time-control experiments to reveal the morphology evolution: (a-c) GF- VO_2 nanoarray after solvothermal growth of VO_2 for 3h, 6h, 12h, respectively; (d-f) GF- VO_2 @GQD nanoarrays after electrophoresis of GQDs for different times 100s, 200s, 300s, respectively; (g,h) GF- VO_2 -GQD composite by drop-dry GQD solution method for 5 times.

The interspaces between neighboring nanoarrays are believed to enable sufficient solution contact. Negatively charged GQDs (rich of negatively charged carboxyl groups) was further tightly immobilized onto the positively charged surface of VO₂ nanoarrays based on a facile positive bias potential electrophoresis deposition (EPD) (Fig. 3.1c). The SEM image of the resulting hierarchical structure shows a preserved nanobelts array structure, but making the nanobelts surface more wrinkled (Fig. 3.1f). As the increase of electrophoresis time, GQDs tend to fill up all corners of the intersected nanobelts (Fig. 3.S1f). Here, we prefer to choose thinner VO₂ nanobelts with thinner GQDs layer to assure a higher electrochemical kinetics. We can clearly see that the VO₂@GQD hierarchical structure can be grown on both the outer and inner sides of GF skeleton which can largely facilitate the utilization of the skeleton and enhance the active sites with electrolyte. Another GQD fabrication route, called vacuum-assisted drop-dry method, was also applied to assemble GQDs onto VO₂ nanoarrays in consideration of the hydrophilia and porous nature of GV nanoarrays (Fig. 3.S1g,h). Compared to EPD route, the drop-dry method generated VO₂-GQDs composite gives an aggregated morphology with GQDs densely piled up and blocked the interspace between nanoarrays in many areas. The optical images of GV and GVG nanoarray electrodes are shown in Fig. 3.S2d,f, and the severely bent GVG film demonstrates the flexibility and light weight of the electrode.

Fig. 3.S2. Photos of self-supported: (a) GF-VO₂@GQD nanoarrays that is bent by small force to demonstrate the flexibility and light weight of the electrode; (b) FTO glass supported VO₂@GQD nanoarrays; (c) battery electrodes of GF-VO₂ (left) and GF-VO₂@GQD (right) with diameter of 12 mm, without any binder or additives.

3.3.2 Structure characterization and growth mechanism

The X-ray diffraction (XRD) result in Fig. 3.S3a demonstrates the highly crystalline structure of GF (JCPDS 75-1621), GV (monoclinic VO₂ (B) with the lattice parameters of $a = 12.07 \text{ \AA}$, $b = 3.69 \text{ \AA}$, $c = 6.43 \text{ \AA}$, $\beta = 106.6^\circ$, C2/m space group, JCPDS 31-1438). The diffraction peaks of GF and VO₂ (B) can also be well indexed, demonstrating that the EPD process has negligible influence on the intrinsic crystallinity of the VO₂ (B). Fig. 3.S3b show the Raman spectra of GF, GV arrays and GVG nanoarrays. The characteristic peak at $\sim 1575 \text{ cm}^{-1}$ (G band) is identified for the GF. The defect-related D band in the UGF is not observed, implying the overall high quality of the UGF by the CVD method with little defects. In addition to the peaks of the GF, the other Raman peaks can be well indexed to crystalline VO₂^{211,236}. No more XRD diffraction peaks and Raman characteristic peaks are observed for the GQDs due to its overlap with GF. In order to avoid the interference of GF for GQDs detecting, VO₂ arrays and GQDs are also fabricated on transparent conductive fluorine-tin-oxide (FTO) substrates with the same method. For FTO-GQD sample, D (ca. 1350 cm^{-1}) and G (ca. 1580 cm^{-1}) bands are remarkably observed due to the existence of defects and functional groups of GQDs. Compared with GV arrays, these two characteristic peaks are also found after GQDs EPD (GVG), illustrating the successful fabrication of GQDs on VO₂ arrays.

The detailed crystal structures of the functional GQDs, bilayered VO₂, and GVG nanoarrays were characterized by TEM, high-resolution TEM, and corresponding FFT pattern analyses (Fig. 3.2). The typical TEM images of GQDs (Fig. 3.2a) exhibits that as-made GQDs are well-dispersed and have a typical lateral size ca. 5 nm (with a bandgap less than 0.5 eV according to density functional theory calculation^{237,238}). The representative HRTEM image of GQDs (Fig. 3.2b) shows that the resultant GQDs are highly ordered with an interlayer spacing of $2.5 \text{ \AA}$, corresponding to the hexagonal lattice plane spacing of (1120)²³⁹. GQDs dispersion appears a homogeneous light-brown phase under day light without any noticeable precipitation even after several weeks at room temperature. The solution excited by a 365 nm lamp

emits an intense blue-green fluorescence (Fig. 3.2c), which is likely attributable to the effect of size and surface functional groups. Fig. 3.2d identifies the hierarchical structure with one horizontal nanobelt and another near-vertically intersected nanobelt. The thickness of the nanobelts is also confirmed ca. 15 nm (Fig. 3.2d,e). Fig. 3.2e presents clear lattice fringes with spacing of 5.8 Å on the horizontal nanobelt, corresponding to the (200) lattice plane of monoclinic VO₂ (JCPDS 31-1438). The single crystalline nature of single nanobelt on the horizontal nanobelt is also confirmed by FFT pattern. All FFT spot patterns can be fully indexed along the [002] zone axis. It is also demonstrated from the (200) lattice plane of the horizontal nanobelt that the lattice distance is 6.1 Å, corresponding to the d₍₀₀₁₎ spacing of monoclinic VO₂. On the other hand, the preferred growth direction of the bilayered VO₂ structure is realized by considering the relative stacking rate of the “steplike” bilayered VO₆ octahedra at various crystal faces (inset in Fig. 3.2f), and the average shortest bond (relatively high stacking rate) in the bilayered VO₂ structure is along the [010] direction²⁴⁰. Hence, these findings corroborate that the single crystalline bilayered VO₂ nanobelts grow along the [010] direction, which is in agreement with previous literature results^{217,240} (as illustrated by the geometric model in Fig. 3.2f). As for the interface of VO₂, the longest bond between V and O is along [001] direction (inset in Fig. 3.2f), which makes [001] the slowest growth direction. As a result, (001) facets are the thinnest crystal planes of the VO₂ nanobelts and the predominantly exposed facets on which the large interlayers between the (200) crystal planes provide a facile channel for both Li and Na ion diffusion.

After EPD of GQDs, the VO₂ nanoarrays are closely wrapped by a uniform GQDs layers (ca. 2 nm) with a preserved nanoarrays structure but more jagged. The HRTEM and FFT results reveal the single crystal nature of GQDs (2.5 Å of (1120)) and bilayered VO₂ (5.8 Å of (200)) with the same lattice spacing described above (Fig. 3.2h and its enlarged Fig. 3.S4). (MD simulations) Energy dispersive X-ray spectrometry (EDS) mapping analysis of heterostructure VO₂@GQD nanoarrays (scratched from FTO-VO₂@GQD sample) unambiguously confirms the GQDs anchored VO₂ nanoarrays structure and the existence of V, O and C elements. The

mapping result is consistent with the EDS spectrum shown in Fig. 3.S3d. All in all, it can be concluded that we have successfully fabricated the integrated electrode, using the combination of solvothermal synthesis and electrophoresis deposition.

Fig. 3.2 TEM characterization. (a) TEM of GQDs with insets: the size distribution of GQDs; (b) HRTEM of GQDs with inset FFT pattern; (c) Photographs of the GQD aqueous solution taken under visible light (left) and 365 nm UV light (right), respectively; (d,e) TEM and HRTEM of VO₂ nanoarray with inset FFT pattern (white dashed circle in Fig 2d, on the (002) zone axis); (f) Geometrical model of as-prepared bilayered VO₂ nanobelt, in which enclosed colored crystal planes ((100)-red, (010)-green, and (001)-blue); (g,h) TEM and HRTEM of VO₂@GQD nanoarray with inset FFT pattern; (i) Dark field TEM image of VO₂@GQD nanoarray and corresponding EDS mapping of V, O and C.

Fig. 3.S3. (a) XRD patterns of the GF, GF-VO₂ and GF-VO₂@GQD nanoarray; (b) Raman spectra of the GF, GF-VO₂ and GF-VO₂@GQD nanoarray; (c) Raman spectra of the FTO-GQD, FTO-VO₂ and FTO-VO₂@GQD nanoarray; (d) EDS spectrum of VO₂@GQD powders scratched from FTO-VO₂@GQD sample.

Fig 3.S4. Enlarged image of HRTEM of VO₂@GQD nanoarray in Figure 2f.

3.3.3 Lithium storage performance

The approaches above enabled us to fabricate batteries with bicontinuous electron and lithium/sodium ion transfer channels in the electrode material, as shown in Fig. 3.3a. Herein, GF serve as both current collector (electron transfer) and backbone for structural stabilization. During lithiation, electrolyte can enter the interval between nanoarrays on both outside and inner surface of GF, so that the Li/Na ion and electrons can react with the nanoarrays directly. Meanwhile, the nanoarrays will twist and intertwine with each other to release the strain and then restore and shrink back during delithiation. The VO₂@GQD structure provides four more attractive features as an electrode material in comparison to pure VO₂ nanoarrays: (1) the outside GQDs covering, which contact directly with GF current collector, forms a whole continuous graphene network and provides fast electron transfer channels on the surface of bare VO₂ during charge/discharge process; (2) the nanocavity between functional GQDs (more lipophilic than bare VO₂ arrays) provide “gate” for entry, higher storage of electrolyte, and more ion transfer channels. (3) the homogeneously GQDs covering can separate the VO₂ nanoarrays avoiding the agglomeration among the nanoarrays; (4) the surface protection of GQDs can limit the gradually dissolution of VO₂⁷⁷. The last two points should particularly play roles during the long-term cycles.

The CV tests of GV, and GVG electrodes for cathodic/anodic process (Fig. 3.3b) were carried out at a sweep rate of 0.3 mV s⁻¹ in the voltage range of 3.5 to 1.5 V versus Li/Li⁺. As clearly shown in GV curves, a pair of distinctive redox peaks occurs around 2.40 and 2.73 V respectively, accompany with several small redox peaks which indicate a multistep lithium ion intercalation/deintercalation. The overall lithium insertion/extraction process occurring in the VO₂ electrode could be described as (where x is the mole fraction of inserted Li ions):

while GVG electrode deliver a positive cathodic peak (2.44 V) and a negative anodic peak (2.69 V) compared that of GV electrode. The difference in anodic and cathodic peaks is due to the increased surface electrochemical activity and the decreased polarization of the as-prepared GVG electrode. In order to evaluate the polarization

more accurately, the overpotential is calculated from the difference between charge and discharge potential ($\Delta V_{Q/2}$) at the half reversible capacity ($(Q/2)^{213}$). The overpotential of GVG electrode is only 70 mV, nearly half that of electrode without GQDs (135 mV), indicating higher electrical and ionic conductivity (Fig. 3.3c and Fig. 3.S5: 45, 20, 35 S cm⁻¹ for GF, GV and GVG, respectively). Electrochemical impedance spectroscopy (EIS) is employed to understand why the GVG electrode shows a better electrochemical activity (inset in Fig. 3.3d). The charge transfer resistance (R_{ct}) of GV is ca. 190 Ω , while the corresponding R_{ct} of GVG is only 120 Ω , suggesting its fast electronic mobility and improved electro-catalysis activity. As a result, the GVG electrode exhibits a higher specific capacity of 421 mAh g⁻¹ than that of VO₂@GQD electrode (391 mAh g⁻¹). A ca. 99% initial coulombic efficiency and 100% during the following cycles can be obtained for all of the electrodes, implying an excellent reversibility of the electrodes (Fig. 3.S6a,b).

Fig 3.S5. Electrochemical characterization of GF-VO₂ and GF-VO₂@GQD electrodes for Li ion batteries: (a, b) 1st, 2nd, 5th, 10th CV curves at the scanning rate of 0.3 mV s⁻¹ of GF-VO₂ and GF-VO₂@GQD nanoarrays electrode, respectively; (c, d) Charge/discharge curves at different rates of GF-VO₂ and GF-VO₂@GQD nanoarrays electrode, respectively.

To manifest the rate performance during the charge/discharge process, the specific discharge capacities at different discharge/charge rates ranging from 1/3 C to 120 C

were tested (Fig. 3.3d, Fig. 3.S6c,d). The GVG electrode delivers discharge capacities of 421, 390, 349, 331, 309, 251, 198 and 151 mAh g⁻¹ at the discharge/charge rate of 1/3 C, 1 C, 2 C, 5 C, 10 C, 30 C, 60 C and 120 C, respectively, which is also much higher than that of electrode without GQDs protection. It means the hierarchical nanostructure of GVG can better maintain the electrolyte contact for reaction even in fast charge/discharge processes. After this high rate measurement, the GVG electrode is able to provide nearly no capacity decay (389 mAh g⁻¹ at 1 C), manifesting good rate reversibility. Such a high specific capacity and rate performance can be comparable to or higher than those of previous VO₂-based cathode materials (see detailed comparison in Table 3.S1). This may be due to its unique features, such as thin nanobelts constituting nanoarrays, high surface area, and enhanced conductivity and charge transfer due to the presence of GQDs.

Fig. 3.S6. Electrode morphology of Li-ion batteries after cycles: (a, b) SEM and TEM images of GF-VO₂ nanoarrays electrode after 1500 cycles at 60 C. (c, d) SEM and TEM images of GF-VO₂@GQD electrode after 1500 cycles at 60 C.

Table 3.S1 A survey of electrochemical properties of VO₂ and its hybrid composites in lithium ion batteries.

Electrode description	Specific capacity ^a (mAh g ⁻¹)	High rate capability ^b (%)	Cycling stability ^c (%)
GF-VO ₂ @GQD nanoarrays ^d (this work)	421 mAh g ⁻¹ at 100 mA g ⁻¹ between 3.5~1.5 V	151 mAh g ⁻¹ at 36 A g ⁻¹	94 % after 1500 cycles at 18 A g ⁻¹
VO ₂ /graphene nanosheets ²⁴¹	418 mAh g ⁻¹ at 50 mA g ⁻¹ between 4.0~1.5 V	102 mAh g ⁻¹ at 5 A g ⁻¹	60 % after 50 cycles at 50 mA g ⁻¹
VO ₂ nanoparticles ²⁴²	300 mAh g ⁻¹ at 0.5 mA cm ⁻² between 3.5~1.5 V	---	Near no decay after 20 cycles at 0.5 mA cm ⁻²
VO ₂ nanoparticles ²¹⁴	300 mAh g ⁻¹ at 0.5 mA cm ⁻² between 4.0~1.5 V	---	84 % after 20 cycles at 0.5 mA cm ⁻²
VO ₂ nanowires ²¹⁵	186 mAh g ⁻¹ at 100 mA g ⁻¹ between 3.0~2.0 V	101 mAh g ⁻¹ at 1 A g ⁻¹	95 % after 100 cycles at 100 mA g ⁻¹
VO ₂ nanorods ²⁴³	306 mAh g ⁻¹ at 0.4 mA cm ⁻² between 3.6~1.5 V	---	80 % after 15 cycles at 0.4 mA cm ⁻²
VO ₂ hollow microsphere ²⁴⁴	195 mAh g ⁻¹ at 50 mA g ⁻¹ between 4.5~1.5 V	---	83 % after 50 cycles at 50 mA g ⁻¹
VO ₂ /graphene ribbons ²¹¹	415 mAh g ⁻¹ at 415 mA g ⁻¹ between 3.5~1.5 V	204 mAh g ⁻¹ at 37.2 A g ⁻¹	93 % after 1000 cycles at 37.2 A g ⁻¹
VO ₂ /CNT nanowires ²²⁵	200 mAh g ⁻¹ at 95 mA g ⁻¹ between 3.5~1.5 V	50 mAh g ⁻¹ at 1.9 A g ⁻¹	94 % after 100 cycles at 316 mA g ⁻¹
VO ₂ /carbon nanobelts ²⁴⁵	161 mAh g ⁻¹ at 100 mA g ⁻¹ between 4.0~2.0 V	100 mAh g ⁻¹ at 2 A g ⁻¹	80 % after 50 cycles at 100 mA g ⁻¹
VO ₂ /carbon microspheres ²⁴⁶	185 mAh g ⁻¹ at 0.15 mA g ⁻¹ between 4.0~1.5 V	---	51 % after 50 cycles at 0.15 mA g ⁻¹
VO ₂ /carbon nanobelts ²⁴⁷	219 mAh g ⁻¹ at 50 mA g ⁻¹ between 4.0~1.5 V	138 mAh g ⁻¹ at 1 A g ⁻¹	70 % after 100 cycles at 50 mA g ⁻¹
Star-like VO ₂ mesocrystals ²¹⁷	258 mAh g ⁻¹ at 150 mA g ⁻¹ between 3.8~2.0 V	158 mAh g ⁻¹ at 1.5 A g ⁻¹	76 % after 50 cycles at 150 mA g ⁻¹
VO ₂ nanowires assembled hollow microspheres ²¹³	203 mAh g ⁻¹ at 100 mA g ⁻¹ between 3.0~2.0 V	134 mAh g ⁻¹ at 2 A g ⁻¹	80 % after 1000 cycles at 2 A g ⁻¹
VO ₂ nanorods ²⁴⁸	171 mAh g ⁻¹ at 0.1 mA g ⁻¹ between 4.0~1.5 V	---	63 % after 47 cycles at 0.1 mA g ⁻¹
VO ₂ nanobelts ²¹⁶	195 mAh g ⁻¹ at 20 mA g ⁻¹ between 3.0~2.0 V	98 mAh g ⁻¹ at 2 A g ⁻¹	82 % after 1000 cycles at 1 A g ⁻¹
VO ₂ nanotube /graphene ²²⁴	450 mAh g ⁻¹ at 40 mA g ⁻¹ between 4.0~1.5 V	180 mAh g ⁻¹ at 100	89 % after 20 cycles at 100 mA g ⁻¹

^a Estimated value of specific capacity at different discharge current (the calculated potential range from 3.5~1.5 V vs. Li/Li⁺ for GF-VO₂@GQD electrode);

^b Estimated value of high rate capability at high charge/discharge current density;

^c The cycling stability is calculated by $C_n/C_{max} \times 100\%$, where C_n is the discharge capacity at the n cycle, C_{max} is the maximum discharge capacity during n cycles.

^d All the capacity values were all calculated based on the active material VO₂ only. Capacity of our GF-VO₂@GQD nanoarrays electrode was based on weight of VO₂ and GQDs covering.

The major bottleneck to VO₂ as the cathode material is its unsatisfactory cycleability (Table 3.S1). Star-like VO₂ mesocrystals²¹⁷, VO₂ hollow microsphere²⁴⁴ reported a capacity retentions of 76 % after 50 cycles and ca. 83 % after 50 cycles, respectively. The unsatisfying capacity retention may be due to their micro-size structure and poor electric conductivity. To further improve the cyclability, nano-size materials with kinds of conductive additives have been prepared by researchers to optimize the cycle performance of VO₂. However, VO₂/carbon nanobelts^{245,247}, VO₂/graphene nanosheets²⁴¹, and VO₂ nanotube/graphene²²⁴ still delivered a relatively poor capacity retentions of 70% after 100 cycles, 80% after 50 cycles, 60 % after 50 cycles, and 89 % after 20 cycles, respectively. The poor cyclability of the nanosized VO₂ may be caused by the aggregation and gradually dissolution of active materials during the cycling process. For our GVG electrode, 94 % of the original capacity is retained after 1500 cycles at 60 C (18 A g⁻¹), and even the GV electrode without GQDs protection also has a capacity retention of 85 %. The good cyclic performance of GVG nanoarrays may be due to its excellent electric conductivity (whole continuous graphene network of GF and GQDs) and proper shield of bare VO₂, which prevent the aggregation and dissolution of active material (shown in Fig. 3.S7).

Fig. 3.3. Electrochemical characterization of GV and GVG electrodes for Li ion batteries: (a) Schematic of the GVG nanoarchitecture with bicontinuous electron and Li/Na ion transfer channels; (b) CV curves at a scan rate of 0.3 mV s⁻¹; (c) Charge-discharge curves at 0.5 C (1 C = 300 mA g⁻¹); (d) Rate performance of GV and GVG electrodes (inset is AC impedance plots at the full-charged state after the 1st cycle. The resistance is simulated using equivalent circuit of $R_s(Q(R_{ct}ZW))$, where R_s is the ohmic resistance of solution and electrodes; R_{ct} is the charge transfer resistance; Q is the double layer capacitance and Z_W is the Warburg impedance.); (e) Long-term cycling performance at 60 C for 1500 cycles (1/3 C at first 5 cycles for activation).

3.3.4 Sodium storage performance

Growing body of knowledge suggests that materials suitable for application in Na ion batteries are recommended of both (i) tailored design of nanoarchitecture of materials offers unprecedented opportunities in exploration of their alternative properties²¹⁸, and (ii) more open framework and two-dimensional layered structure can accommodate large volume changes^{219,249}. Because the larger sodium ion and

higher ionization potential (compared to Li ion) require a more open framework for Na-ion intercalation and deintercalation. For these reasons, we thoroughly examined the sodium storage performance based on the as-designed single-crystalline bilayered VO₂ nanostructure for the first time. Given the advantage of GQDs coating demonstrated above, herein we will make our characterization and discussion only based on the GVG electrode, and data are presented in Fig. 3.4.

Table S2 A survey of electrochemical properties of VO_x and its hybrid composites in sodium ion batteries.

Electrode description	Specific capacity ^a (mAh g ⁻¹)	High rate capability ^b (%)	Cycling stability ^c (%)
GF-VO ₂ @GQD nanoarrays (this work)	306 mAh g ⁻¹ at 100 mA g ⁻¹ between 3.5~1.5 V	93 mAh g ⁻¹ at 36 A g ⁻¹	88 % after 1500 cycles at 18 A g ⁻¹ 91 % after 500 cycles at 1.5 A g ⁻¹
bilayered V ₂ O ₅ nanoparticles ²¹⁸	250 mAh g ⁻¹ at 20 mA g ⁻¹ between 3.8~1.5 V	150 mAh g ⁻¹ at 630 mA g ⁻¹	85 % after 320 cycles at different rate
bilayered V ₂ O ₅ nanobelts ²¹⁹	232 mAh g ⁻¹ at 80 mA g ⁻¹ between 4.0~1.0 V	134 mAh g ⁻¹ at 640 mA g ⁻¹	74 % after 100 cycles at 80 mA g ⁻¹
VO _x /Ni nanotubes ²⁵⁰	140 mAh g ⁻¹ at 0.1 C between 3.4~1.0 V	45 mAh g ⁻¹ at 1 C	29 % after 35 cycles at 0.1 C
FeF ₃ • 0.5H ₂ O/CNT composite ²⁰⁹	143 mAh g ⁻¹ at 0.1 C between 4.5~1.7 V	80 mAh g ⁻¹ at 1 C	80 % after 300 cycles at 0.1 C
Sodium manganese hexacyanoferrate ²⁰⁷	143 mAh g ⁻¹ at 0.05 C (6 mA g ⁻¹) between 4.2~2.0 V	45 mAh g ⁻¹ at 40 C	85 % after 50 cycles at 0.05 C
Na ₂ MnP ₂ O ₇ ²⁵¹	80 mAh g ⁻¹ at 0.05 C between 4.5~2.0 V	---	84 % after 15 cycles at 0.05 C
Na _x [Fe _{1/2} Mn _{1/2}]O ₂ ²⁰⁶	190 mAh g ⁻¹ at 0.05 C (12 mA g ⁻¹) between 4.3~1.5 V	57 mAh g ⁻¹ at 4 C	79 % after 30 cycles at 0.05 C
Na ₃ V ₂ (PO ₄) ₃ nanograins ²⁰⁸	118 mAh g ⁻¹ at 0.5 C (59 mA g ⁻¹) between 4.3~1.5 V	101 mAh g ⁻¹ at 5 C	96 % after 200 cycles at 5 C
Na _{0.67} [Mn _{0.65} Co _{0.2} Ni _{0.15}]O ₂ microflakes ²⁵²	141 mAh g ⁻¹ at 20 mA g ⁻¹ between 4.4~2.0 V	---	89 % after 50 cycles at 20 mA g ⁻¹

^a Estimated value of specific capacity at different discharge current;

^b Estimated value of high rate capability at high charge/discharge current density;

^c The cycling stability is calculated by $C_n/C_{max} \times 100\%$, where C_n is the discharge capacity at the n cycle, C_{max} is the maximum discharge capacity during n cycles.

The GVG electrode delivers a very high discharge capacity of 306 mAh g⁻¹ at 1/3 C (100 mA g⁻¹) in the voltage range of 3.5 to 1.5 V versus Na/Na⁺. It should be noted that the discharge profile shows no obvious plateau as a whole, but it can be divided into two diagonal stages (Stage 1: 2.7–2.4 V, and Stage 2: 1.9–1.6 V), indicating different sodium intercalation processes:

where x is the mole fraction of inserted Na ions. The CV curves in Fig. 3.4b exhibit only two convex protrusions during cathodic processes (Peak 1: 2.7–2.4 V, and Peak 2: 1.9–1.6 V), in accordance to the charge/discharge profiles. Reversible sodium deintercalation process is obtained by charge the electrode to 3.5 V (ca. 99 % initial coulombic efficiency and 100% in the following cycles), demonstrating a stable GVG nanoarchitecture electrode during Na⁺ insertion and extraction (Fig. 3.4b).

Fig. 3.S7. SEM (a) and TEM (b) images of GF-VO₂@GQD nanoarrays electrode after sodium insertion/extraction for 1500 cycles.

One of the most important characteristics of electrode materials to be used in energy storage systems is their rate tolerance capability. It was a pity that the rate performance of kinds of current electrode materials used in sodium ion batteries are focused in relatively low rate 0.1–5 C^{137,209,218,219,222,253,254} (Table 3.S2). The reason for this poor rate performance may be related to the instinct characterization of large Na⁺ ions and its sluggish electrochemical kinetics compared with that of Li⁺ ions. Obviously, it is still too far away to be used as a particle electrode material, such as

the grid-scale electricity storage and electric vehicle applications. In this work, we try to apply GVG electrode in really high charge/discharge current density from 1/3 C to 120 C based on our previous exploration in Li storage performance. When cycled at high rate: 1 C, 2 C, 5 C, 10 C, 30 C, 60 C and 120 C, it can achieve a remarkably stable and high capacity of 284, 265, 247, 201, 160, 127 and 93 mAh g⁻¹, respectively, and then recovers to 281 mAh g⁻¹ at 1 C (Fig. 3.4c). This is in sharp contrast to those reported VO_x electrode: bilayered V₂O₅ nanoparticles²¹⁸, bilayered V₂O₅ nanobelts²¹⁹, VO_x/Ni nanotubes²⁵⁰ (listed in Table 3.S2).

The sodium-ion devices based on the GVG electrode retained 91 % of the initial capacity after 500 cycles at a charge/discharge rate of 5 C (Fig. 3.4d). The superior cycle stability of the electrode for reversible Na⁺ storage was highly repeatable according to the different batches. To gain further insight into the electrode changes mechanism upon sodium ion insertion/extraction cycles, the EIS is recorded during 1st to 500th cycles. The fitted sodium charge transfer resistance (R_{ct}) data corresponding to the Nyquist plots is shown in inset of Fig. 3.4e. It should be noted that the R_{ct} values decrease steeply in the first 50 cycles and then increase slightly in the following cycles. We propose that electrolyte gradually penetrated on the surface of nanoarrays and diffused into the predominantly exposed (001) facets after the first few cycles which should facilitate the electrochemical reaction and lead to the decrease of R_{ct} . It is well-known that the lower increase of resistance during cycles means lower polarization. Hence, the subsequent mild R_{ct} increase perfectly illustrates the good cycling behavior of the electrode. More remarkably, the GVG architectures can also survive long-term ultrafast charge/discharge cycling. Even after 1500 cycles at the ultrahigh rate of 60 C, the discharge capacity can be stabilized at 111 mAh g⁻¹, delivering over 88 % capacity retention (Fig. 3.4f). To the best of our knowledge, such an excellent electrochemical performance surpasses any other SIB cathode reported in the literature to date (Table 3.S2). Furthermore, at the ultrahigh rate of 120 C, the power density based on mass of the whole GVG electrode is as high as 42 kW kg⁻¹ with an energy density of more than 100 Wh kg⁻¹ (Fig. 3.4g). Assuming that the cathode takes up ca. 40% of the total device weight, our power density is still 15 times

higher than those of the current Li-ion batteries (ca. 1 kW kg^{-1}).^{211,249} Overall, from the Ragone plot we can conclude that the energy and power performance of the Na-ion battery is highly competitive with that of Li-ion batteries²¹².

Fig. 3.4. Electrochemical characterization of GVG electrode for Na ion batteries: (a) Charge-discharge curves at different C rates ($1 \text{ C} = 300 \text{ mA g}^{-1}$); (b) CV curves at a scan rate of 0.3 mV s^{-1} ; (c) Rate tolerance performance of GVG electrode; (d) Cycling performance of three different batches at 5 C for 500 cycles; inset shows the regulation of R_{ct} as increase of cycle number. (e) AC impedance plots at full-charged state after different cycles, the resistance is simulated using the same equivalent circuit $R_s(Q(R_{ct}ZW))$ as used before in Li ion battery; (f) Long-term cycling performance of three different batches at 60 C for 1500 cycles ($1/3 \text{ C}$ at first 5 cycles for activation); (g) Ragone plot of energy and power densities based on the total mass of the whole electrode.

The superior electrochemical performance of VO_2 -based cathode material in

Na-ion batteries could be ascribed to the unique long-range order single-crystalline structure with thin nanobelt morphology (ca. 15 nm, short-path and unhindered Na ion diffusion), large interlayer spacing and exposed facets, providing open channels for facile sodiation/desodiation. Moreover, the GQDs protection layer also contributes much for the electric conductivity and the structure stability of the whole GVG architectures, especially for the long-term cycling (Fig. 3.S8). We believe that this ultrafast charging/discharging capability can significantly boost the development of high-rate and long lifespan Li and Na ion batteries.

3.4 Conclusions

In this study, we have demonstrated large capacity, fast and reversible lithium and sodium ion storage performance using single-crystalline long-range-ordered bilayered VO₂-based nanoarray architectures. It was also proved that GQDs EPD is a facile and effective method to further enhance the electrochemical performance both in Li and Na ion batteries. In lithiation, this unique GVG self-supported, binder-free positive electrode delivers a high capacity more than 420 mA h g⁻¹ and an ultrafast and stable cycling of 94 % after 1500 cycles at 18 A g⁻¹. During sodiation, It can also exhibit an ultrahigh capacity of 306 mA h g⁻¹ and superior rate and capacity retention (88 % after 1500 cycles at 18 A g⁻¹), with a power density of 42 kW kg⁻¹ at an energy density more than 100 Wh kg⁻¹. We believe that the results shown here will prove to be a milestone in the development of rechargeable sodium-ion batteries for large-scale applications with a comparable overall performance to the present large-scale lithium batteries, thus providing an attractive, cost-effective alternative for next-generation postlithium (e.g., Na and Mg) batteries.

Chapter 4 $\text{Na}_3(\text{VO})_2(\text{PO}_4)_2\text{F}$ Array for Cathode of Na-Ion Battery

4.1 Introduction and motivation

There is an on-going interest in new versatile and flexible power sources to meet the special needs for next-generation, high-performance, shape-conformable, and wearable electronics, including soft bendable mobile phones, roll-up displays, wearable sensors, and implantable medical devices²⁵⁵⁻²⁵⁹. To ameliorate and fulfill flexible energy-storage systems, such as flexible supercapacitors, lithium-ion and sodium-ion batteries (LIBs and SIBs), tremendous efforts have been made in recent years²⁶⁰. The fabrication of such an energy-storage device remains a great challenge owing to the lack of reliable electrodes that combine robust mechanical flexibility, excellent electrolyte corrosion resistance, superior structure stability, high electron and ion conductivity and mobility²⁶¹. Using nanosized active materials incorporated with flexible carbon materials such as carbon nanotubes, graphite and graphene papers as skeletons has been recently demonstrated one of the most promising routes toward flexible batteries²⁶². Ajayan et al. demonstrated that nanoporous cellulose paper embedded with aligned CNTs electrode exhibited reversible capacity of 110 mAh g^{-1} , however the flexibility of the full battery was limited due to the Li metal counter electrode²⁶³. By pasting the active materials particles onto conductive CNTs paper current collector, Cui et al. fabricated LTO-LCO paper battery with a discharge platform of 2.0–2.2 V. Even though no metal is used, conductive agent (super P) and less-conductive binder additive (PVDF) still cannot be avoided, which further decrease the energy and power densities of the device²⁶⁴.

For a thin-film flexible binder-free design with two-dimensional (2D) geometry, it inherently suffers a compromise between energy density (planar areal limitation) and power density (prolonged diffusion length with intractable loading). In recent years there has been the realization that improved battery performance can be achieved by reconfiguring the electrode materials currently employed in 2D geometry into 3D

architectures, comprising a 3D matrix of components (cathode, anode and electrolyte) arranged in either a periodic array or an aperiodic ensemble^{255,262}. A 3D matrix of electrode materials configured in complex geometries should benefit for both the power requirement by shortening transport lengths and energy demand by enhancing loading per unit area. Based on these strategies, a series of 3D nanowire/nanoflake arrays anode materials, such as ZnCo_2O_4 nanowire on carbon cloth²⁶⁵, $\text{MoC}_{0.654}$ @carbon nanosheets on Ni foam¹⁴⁵, SnS and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ nanosheets on graphene foam^{263,266}, have been successfully prepared, showing improved discharge capacities and rate capabilities compared with their planar counterparts. However, extremely rare reports on flexible 3D array cathode (*i.e.* LiFePO_4 , LiCoO_2 , $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ *etc.*) have been presented for both LIBs and SIBs, probably due to the specific multielements feature of the cathode materials and difficulty in nucleating onto substrates, poor ability of oriented crystallization, and indispensable high temperature annealing in air. A report of Xia et al.²⁶⁷ fabricated LiCoO_2 nanowire array with utilization of Au substrate to solve the high-temperature annealing issue and Co_3O_4 nanoarray precursor to overcome the problem of oriented growth of LiCoO_2 . However, the electrode is based on a complicated synthesis processes with costly heavy metals as current collector, which makes the electrode less flexible, and low energy density.

Herein, we realize a unique 3D sodium vanadium fluorophosphate $\text{Na}_3(\text{VO})_2(\text{PO}_4)_2\text{F}$ oriented arrays (NVOPF OA) cathode on flexible light-weight graphene foam backbone (0.6 mg cm^{-2}) by a two-step solvothermal method. The special architecture possesses significantly increased rate capability together with the highest reported long-term high-rate durability for SIBs (10,000 cycles at 50C), which are comparable to or even outperform reported Li-ion cathode function. Combining first principles computational investigation with *in situ* experimental observations, the unprecedented performances can be attributed to the uniform, robust and 3D array design with preferred growth along the (002) plane.

4.2 Preparation and materials characterization

4.2.1 Synthesis

3D VO₂ nanosheets were prepared by a facile solvothermal method. Hydrogen peroxide (0.5 mL, 30%) were added dropwise to vanadyl oxalate (2 mL, 6.6 mM) in a 30 mL Teflon-lined stainless steel autoclave. Then 25 mL ethanol and one piece of substrate (carbon cloth or graphene foam²¹²) was immersed into the solution. The autoclave was kept at 170 °C for 5 h. The resulting sample was collected by rinsing with DI water and ethanol in turn. Na₃(VO)₂(PO₄)₂F oriented arrays (NVOPF OA) were prepared in the help of VO₂ nanosheets (NS) precursor. In general, 8 mL aqueous solution was prepared at 90 °C with NH₄VO₃ (0.1 M), NH₄H₂PO₄ (0.1 M), NaF (0.05 M), Na₂CO₃ (0.05 M). The as-prepared VO₂ precursor was transferred into the autoclave with 8 mL previous solution and 20 mL N,N-dimethylformamide (DMF) with adjusted PH value 6 by H₃PO₄. The system was sealed and heated at 180 °C for 6 h. After washing with DI water and ethanol, the resulting product was coated by a thin layer of carbon by an express annealing process. Before annealing, an alumina boat with 1.5 mL ethylene glycol was loaded at the upstream zone of the quartz tube. NVOPF OA electrode was obtained after maintaining the furnace at 400 °C for 20 min (mass loading of NVOPF OA electrode 3.1 mg cm⁻² and graphene foam 0.6 mg cm⁻²). NVOPF random particles can also be prepared by similar method without immersing VO₂ film during the solvothermal reaction. The express carbon annealing was also applied to VO₂ NS precursor to forming VO₂ NS electrode (with mass loading 0.8 mg cm⁻²).

4.2.2 DFT and NEB calculation details

First-principles plane-wave calculations within density-function theory (DFT) using projector-augmented wave (PAW) potentials were performed using the Vienna *ab initio* simulation package (VASP)^{268,269}. The exchange and correlation potential was approximated by generalized gradient approximation (GGA). We considered the Perdew-Burke-Ernzerhof (PBE) exchange and correlation functional. After energy

convergence analysis, a plane-wave basis set with kinetic energy cutoff of 550 eV and Brillouin Zone (BZ) sampling with Monk horst–Pack (MP) method of $4 \times 4 \times 4$ k-points were chosen for the bulk phase calculations. While for the 0-dimension quantum dots calculations, Brillouin Zone (BZ) sampling was chosen with Gamma point of $1 \times 1 \times 1$ k-points. All the parameters including the exchange and correlation functional and the E_{cut} are checked to make sure our calculation was creditable. The supercells are large enough to ensure the vacuum space (at least 20 Å in any direction) in order to avoid the interaction. The convergence threshold was set as 10^{-5} eV in energy and 10^{-3} eV Å⁻¹ in force. The positions of all the atoms in the supercell were fully relaxed during the geometry optimizations. On the basis of the equilibrium structures, the formation energy was calculated and which was the critical parameter to determine the equilibrium structure of a NVPOF and the transition products (all possible structure are list in Fig. 4.2g). And formation energy is used to evaluate the chemical reaction difficulty. For $A + B = AB$ reaction, the formation energy can be expressed as: $E_f = E_{AB} - E_A - E_B$. Where, A and B denote different materials, and E_{AB} , E_A and E_B denote the total energy of the corresponding compounds. Fig. 4.2h shows the chemical reaction formation energies of each step.

The charging and circuit rate performance of the sodium-battery is mainly determined by the Na mobility on the electrode material. It is vital to quantify the diffusion of Na in NVOPF. Na ion may migration within the plane, or in the perpendicular direction. The structural anisotropy plays an important role in the migration of Na atom on a specific path. The temperature-dependent molecular transition rate can be evaluated by the Arrhenius equation^{270,271} from which the diffusion constant (D) of Na follows: $D = D_0 \exp(-E_a/(k_B T))$, where D_0 , E_a and k_B are the pre-exponential factor, the activation energy (diffusion barrier) and Boltzmann's constant, respectively, T is the environmental temperature. According to the equation, the diffusion mobility of Na in the ab plane of NVOPF is very fast (< 31 meV). However, the migration barrier along perpendicular direction is about 292 meV. Kang et al.²⁷² reported that the migration energy barrier of Na_{1.5}VPO_{4.8}F_{0.7} is about 30 meV in the plane and 310-330 meV along c axis, which are in agreement with our results.

As a comparison, NaFeSO₄F (600–910 meV), NaFePO₄ (320 meV), Na₂FePO₄F (300 meV) show much higher diffusion barriers²⁷³. Therefore, an extremely high-rate capability is expected for sodium vanadium fluorophosphates based Na-ion battery.

4.3 Results and discussion

Fig. 4.1 Synthesis strategies and the structure of GF supported NVOPF nanostructures. (a,d) Schematic illustrations for VO₂ precursor and NVOPF electrode. (b,e) Cross-section FESEM images of VO₂ precursor and NVOPF electrode. (c,f) XRD of VO₂ precursor, and Rietveld refinement of NVOPF electrode. The green, orange lines, black circles, and grey lines represent the observed intensities, background, calculated pattern, and difference, respectively. Short dashes and the tick marks indicate the position of standard Bragg reflections from graphene foam and NVOPF. $R_p = 2.08\%$, $R_{wp} = 3.00\%$.

4.3.1 Synthesis, structure, and growth mechanism

The synthesis of three-dimensional $\text{Na}_3(\text{VO})_2(\text{PO}_4)_2\text{F}$ oriented array (3D NVOPF OA) is achieved with the help of VO_2 nanosheet (NS) precursor, illustrated in Fig. 4.1a,c. Generally, VO_2 is first deposited onto 3D graphene foam (GF) via a solvothermal process. As can be seen from Fig. 4.1b, the VO_2 NS exhibit a mesoporous feature, homogeneous sheet size distribution (~ 100 nm) with deposition thickness ~ 100 nm. The XRD in Fig. 4.1c confirms the highly crystalline structure of GF substrate (JCPDS 75-1621) and monoclinic VO_2 (B) (JCPDS 31-1438, C2/m space group). After another solvothermal reaction, cuboid-shaped NVOPF OA is quasi-vertically aligned onto the top of GF substrate with width 80–100 nm and height ~ 400 nm (Fig. 4.1d,e, S1a,b). One can clearly see that a layer of NVOPF film grows between the arrays and the GF substrate on both the outer and inner sides of the hollow GF. The biface architecture renders robust structural stability and largely increased utilization of the skeleton and the active sites with electrolyte. Meanwhile, the resulting electrode presents favorable flexibility and foldability (Fig. 4.S1c,d). The growth of the NVOPF OA nanostructures is also substrate friendly to carbon cloth (Fig. 4.S1e-g). On the contrary, the NVOPF particles are keen to aggregate leading to big micro-size NVOPF random particle (RP) without the substrates (see Fig. 4.S2). Moreover, the VO_2 precursor is proved to play crucial roles in the growth of NVOPF OA. No layer deposition or growth of NVOPF OA is observed on the surface of substrates in the absence of VO_2 precursor (Fig. 4.S3). Further XRD refinement in Fig. 4.1f and Raman characterization in Fig. 4.S4 indicate the purity of NVOPF without peaks from VO_2 , suggesting that the VO_2 precursor was successfully transferred into NVOPF during the solvothermal reaction. The calculated lattice parameters a , c of NVOPF OA are 6.36 and 10.69 Å (JCPDS 76-3645), respectively, in corresponding with the reported results^{274,275}.

Fig. 4.2 Structure characterization and evolution of NVOPF OA nanostructures. (a,b) TEM and HRTEM images of VO₂ NS electrode. Inset a: high magnification TEM images. Inset b: fast Fourier transform (FFT) pattern in the [002] zone axis. (c) EDX mapping of NVOPF OA elements. (d-f) TEM and HRTEM images of NVOPF OA electrode. Inset e: FFT pattern. (g) Schematic illustration of the proposed structure evolution from VO₂ precursor to NVOPF seed layer. (h) Calculated formation energy in each transformation step.

Fig. 4.S1 FESEM images and digital photo of NVOPF array electrodes. (a,b,e,f) SEM images of NVOPF array nanostructures on the substrates of graphene foam a,b, and carbon cloth e,f. (c,g) Photographs of bent NVOPF array nanostructures on the substrate of graphene foam and carbon cloth, respectively. (d) unfolded NVOPF array electrode showing foldability and flexibility of the electrode after three times fold (up inset). Down inset: Photo of graphene foam substrate hangs below a plastic container with electrostatic force suggesting lightweight feature of the substrate.

Fig. 4.S2 FESEM images of the synthesized NVOPF random particle without substrates. (a,b) Low and high magnification FESEM images.

The detailed crystal structures were characterized by TEM and HRTEM in Fig. 4.2a-f. VO₂ NS presents intrinsic mesoporous feature with interlayer spacing 0.58 nm for the (200) planes of VO₂ (B). The inset fast Fourier transform spots also reveal the existence of (110) facets in the [002] zone axis, demonstrating that the layers of VO₂ are stacked along [002] direction. The NVOPF OA electrode displays a preserved nanocuboid structure with homogeneous elements distribution after the express carbon annealing (~2nm, Fig. 4.2c-f, S5). The HRTEM and FFT results unambiguously reveal the unique crystallographic orientation along [002] direction.

Compared with NVOPF RP, the short lengths in a-b plane and preferred growth along c direction of NVOPF OA are beneficial to the fast Na ions insertion/extraction between (002) facets. The structure evolution mechanism is proposed with calculated formation energy in each steps (shown in Fig. 4.2g,h). Firstly, the excess Na^+ and H_2O molecular in the solution promote the exfoliation of bilayered VO_2 in (002) facets in the first two steps, forming layered VO_5 pyramids chain in the condition of high energy and weak acid. Then a new group layer of alternatively stacked VO_5 pyramids and PO_4 tetrahedrons forms after insertion of negatively charged PO_4^- in step 3 (T3). Furthermore, strongly electronegative charged F^- would be spontaneously stable between the resulting group layers (T4) with negative formation energy (Fig. 4.2h). Finally, NVOPF bottom seed layer is successfully synthesized after the adsorption of Na^+ around F (T5) forming a more stable structure with high coordination. An implication can be found by the structure evolution during the solvothermal reactions in Fig. 4.S6. Pure phase of NVOPF bottom seed layer is revealed to have been *in situ* transferred from VO_2 precursor after only 2 h reaction. Specially, spot f in Fig. 4.1d lies at the bottom layer part of the aligned NVOPF array, where the same crystalline orientation with the body part (Fig. 4.2e) is disclosed in Fig. 4.2f. The results further imply that the NVOPF OA is epitaxially grown from the bottom NVOPF layer along [002] direction. All in all, it can be concluded that we have successfully achieved the integrated 3D nanoarrays cathode design.

Fig. 4.S3 FESEM images of the substrate after NVOPF synthesis without VO_2 precursor. (a,b) SEM images of graphene foam substrate. (c) SEM images of graphene foam substrate. The results indicate that NVOPF array cannot crystallize and grow on the top of substrates without the VO_2 precursor.

Fig. 4.S4 Raman spectra of the synthesized VO₂ precursor and NVOPF array. a) For the VO₂ NS: The peak at 991 cm⁻¹ is the in-phase stretching vibrational mode of V=O. The peak at 690 cm⁻¹ can be assigned to the doubly coordinated oxygen (V₂-O) stretching mode. The peak at 521 cm⁻¹ is attributed to the triply coordinated oxygen (V₃-O) stretching mode of edge-shared oxygen. 405 cm⁻¹ peak is the bending vibrations of the bridging V-O-O. Two frequency peaks at 280 and 190 cm⁻¹ result from the bending vibrations of the V=O bonds. The distinguished low-frequency peak at 138 cm⁻¹ is related to the lattice vibration.^{211,236} b) For the NVOPF array: the intense peaks at 1041, 938, and 375 correspond to antisymmetric stretching bands ν_3 of the tetrahedral PO₄³⁻ anion, and A_{1g} symmetric P-O stretching vibration band ν_1 , ν_2 (E) mode, respectively. The peaks of 650 and 533 cm⁻¹ attribute to ν_4 vibrations.²⁷⁶ Low-frequency peaks (265, 190 cm⁻¹) might be assigned to external modes of the [VO₅F] octahedral and/or [PO₄] tetrahedra.²⁷⁷

Fig. 4.S5 EDX spectrum of NVOPF array electrode. Elemental ratio of NVOPF array is about 3.01:2.01:2.02:1 for Na:V:P:F in corresponding with the target composition.

Fig. 4.S6 Synthetic procedure analysis of NVOPF film after 2 h solvothermal reaction. (a) FESEM image of NVOPF film after 2 h solvothermal reaction. (b) XRD pattern of pure phase NVOPF film suggesting successful in-situ transformation of NVOPF from VO_2 precursor after 2 h reaction. (c) EDX mapping of NVOPF film after 2 h reaction showing a homogeneous elements distribution.

4.3.2 Sodium storage performance

Fig. 4.S7 Electrochemical Na⁺ storage performance of NVOPF array electrode. (a) Galvanostatic profiles at 0.5C of NVOPF array electrode for activation between 4.3 and 2.0 V. A gradually increasing discharge capacity is shown in inset and then trends to stable after 4 cycles. Meanwhile, an initial coulombic efficiency ~92% is obtained for NVOPF array electrode, while nearly 100% is maintained after the first cycle. (b) Cycling stability of NVOPF array and particle electrodes showing similar cycling stability at relatively low charge/discharge rate of 2C.

Fig. 4.S8 Galvanostatic profiles of NVOPF particle electrode at rates from 0.5C to 40C. The capacity vanishes gradually at high charge/discharge rates.

Our designed robust 3D nanoarrays cathode electrode allow bicontinuous electron and ion transfer through the GF network without the necessity of extra conductive additives, binders, and heavy metal current collectors, which are deemed essential for increasing the overall energy/power densities of the full cell²⁶⁶. GF serves as both foldable/compressible backbone for grasping active materials and lightweight 3D current collector for electron transfer. Fig. 4.3a displays the galvanostatic profiles of NVOPF OA at rates from 0.5C to 60C after an activation of 5 charge/discharge cycles (Fig. 4.S7a), where 1C is defined as 130 mA g⁻¹ based on the theoretical capacity. At low charge/discharge rate of 0.5C, the 3D NVOPF OA cathode reaches a discharge capacity of 130 mAh g⁻¹, and similar value is found for the NVOPF RP electrode (Fig. 4.3b, S8). However, two times higher capacity (80 mAh g⁻¹ for OA vs 34 mAh g⁻¹ for RP) is observed when the rate increasing to 30C. More significantly, a discharge capacity of ~45 mAh g⁻¹ could still be retained at 60C (charge and discharge in 40 s). Electrochemical impedance spectroscopy (EIS) is employed to understand the charge transfer difference between OA and RP electrode (Fig. 4.3c). The charge transfer resistance value of OA is fitted ~137 Ω , which is much smaller than that of RP ~375 Ω , suggesting fast electronic mobility and electro-catalysis activity of OA. The GF-NVOPF OA array electrode demonstrates a remarkable long-term cycling stability after 10,000 cycles at high rate of 50C. On the basis of a comprehensive summary, such excellent rate capability and cycling tolerance are superior to previous SIBs cathode reported to date, and even comparable to the performance of present LIBs. Besides, benefiting from its robust structure and integrated electrode design, the areal capacity of NVOPF OA achieves as high as 1.6 mAh cm⁻² and shows negligible specific capacity decay after 2 times fold of the flexible OA electrode (Fig. 4.3e). The specific 3D array nano-architecture with extensively exposed (002) edges is believed to be essential to achieve the excellent cycling and rate ability. Detailed mechanism and electrochemical processes will be analyzed in the next part.

Fig. 4.3 Electrochemical Na⁺ storage performance of NVOPF OA electrodes and VO₂ NS electrode. (a) Galvanostatic profiles of NVOPF OA electrode between 4.5 and 2.0 V after 5 cycles activation. (b) Rate performances of NVOPF OA and RP electrodes at various current densities from 0.5 to 60 C. (c) Electrochemical AC impedance spectrum of NVOPF OA and RP electrodes at full-charged state after 5 cycles activation. The resistance is simulated using inset equivalent circuit of $R_b(Q_1R_1)(Q_2(R_2W))$. (d) High-rate long-term cycling stability of NVOPF OA electrodes at 50C. Inset: performance comparison with other reported congeneric materials^{275,276,278,279}. (e) Galvanostatic consistency showing foldability of NVOPF OA electrode with 0, 1, 2 times fold.

4.3.3 Mechanism discussion

Fig. 4.S9 *In situ* XRD patterns collected during galvanostatic discharge/charge at 0.5C of the NVOPF array electrode. Fixed peaks at ~ 38.7 and 41.5 are corresponds to beryllium window.

Fig. 4.S10 *In situ* XRD conducted during galvanostatic discharge/charge at 1C of the NVOPF array electrode. Contour plot (a) and corresponding patterns (b) of NVOPF array electrode.

To provide more insight about the charge storage mechanism in the 3D NVOPF OA

cathode, structure evolution during charge/discharge was recorded by *in situ* XRD. Clear contour plot of peak intensities versus operating states displays the phase transition process in Fig. 4.4a. Selected acquisition windows are chosen to *in situ* monitor the (200), (202), and (220) diffraction peaks during charge/discharge processes at 0.5C (see Fig. 4.S9). It can be seen that the peaks shift positively during charging, and return to original positions in the subsequent discharge process, suggesting that the process involves a simple single-phase solid solution reaction without any phase transition. As shown in Fig. 4.4b, the peak positions shift is closely related to the change in lattice parameters. A sustained decrease in lattice parameter a is shown while c increases with sodium extraction. This process reverses during sodium insertion. The overall lattice volume shrinks dramatically in the first sodium extraction ($Na1$ site, step I) and keeps relatively stable in the second extraction ($Na2$ site, step II), meaning that the structure distortion from $Na_3(VO)_2(PO_4)_2F$ to $Na_2(VO)_2(PO_4)_2F$ is larger than that of $Na_2(VO)_2(PO_4)_2F$ to $Na(VO)_2(PO_4)_2F$ upon Na ion deintercalation. The related total volume change is $\sim 2.4\%$ for our NVOPF OA electrode, which is smaller than that of reported powders: $Na_3V_2(PO_4)_3$ ($\sim 8.26\%$),²⁷⁷ $Na_3V_2O_2(PO_4)_2F$ ($\sim 2.79\%$),²⁷⁹ $NaFePO_4$ ($\sim 17\%$),²⁸⁰ Na_2FePO_4F ($\sim 3.7\%$),²⁸¹ $NaFeSO_4F$ ($\sim 14.3\%$),²⁷³ and even $LiFePO_4$ ($\sim 6.8\%$) used in LIBs. Hence, very promising electrochemical long-term cycling stability can be granted for NVOPF OA with low volume expansion.

Fig. 4.S11 First principles calculation of Na^+ migration barrier along c direction. The arrows indicate optimum diffusion path. IS and FS denote initial state and final state respectively.

Severe volume expansion induced strain and electrochemical “grinding” during sodium extraction/insertion results in fast capacity fade and also poor rate capability owing to the possible amorphization of the active material especially in long-term high-rate cycling.^{273,281} Similar phenomenon is also monitored by *in situ* XRD at a relatively higher charge/discharge rate (1C), indicating good structure reversibility and fast Na⁺ response under high rate (Fig. 4.S10). The calculated apparent diffusion coefficient of our NVOF OA electrode is $\sim 3.2 \times 10^{-10} \text{ cm}^2 \text{ s}^{-1}$ based on Randles-Sevcik equation, which is higher than reported SIB cathode materials and near 3 times larger than that of NVOF RP electrode ($\sim 1.1 \times 10^{-10} \text{ cm}^2 \text{ s}^{-1}$). The results were further proved by Na⁺ migration barriers calculation by first principles (Fig. 4.4d,e and Fig. 4.S11). A smallest activation barriers value $\sim 18 \text{ meV}$ could be estimated along *ab*-plane from *Na1* site to a neighboring *Na2* site (Fig. 4.4e), which is much smaller than that of reported cathode materials for SIBs.²⁷³ Favorable in-plane Na⁺ mobility ($< 31 \text{ meV}$) can also be detected compared with the perpendicular migration (292 meV), indicating a two-dimensional diffusion feature in (002) planes. Consequently, the preferred orientation growth of NVOF along (002) direction, which is perpendicular to the diffusion paths, is favorable to the fast Na⁺ migration and electrochemical high-rate capability.

Fig. 4.4 Electrochemical process analysis and mechanism of fast kinetics. (a) *In situ* XRD contour plot collected during galvanostatic discharge/charge at 0.5C of the NVOPF OA electrode. (b) Parameters a , c , and V change rates during Na^+ deintercalation/intercalation. Inset: illustration of the structure evolution. (c) The relationship of the anodic peak current (i_p) and the square root of scan rate ($v_{1/2}$) for NVOPF RP and NVOPF OA electrodes. (d,e) First principles calculation of the in-plane (ab) diffusion pathways and corresponding energy barriers of Na-ion migration. The arrows indicate optimum diffusion paths. IS and FS denote initial state and final state respectively.

4.4 Conclusions

In summary, a novel strategy was developed to fabricate a promising flexible 3D oriented $\text{Na}_3(\text{VO})_2(\text{PO}_4)_2\text{F}$ nanoarrays structure as cathode for batteries application. The electrode architecture provides, to the best of our knowledge, the unprecedented high-rate durability of 10,000 cycles at 50C, which can be ascribed to (i) fast 2D ions migration feature with small barrier; (ii) open and immobile NASICON-type structure with small and reversible volume variation; (iii) a decisive 3D oriented array anchored on conductive substrate design maximizes the ions/electrons transfer and structure stability. The hybrid device (intercalation NVOPF array // pseudocapacitive VO_2 nanosheet) enables high-rate charge/discharge (20C) with energy density as high as 215 Wh kg^{-1} . The findings redefine the scope of new 3D array framework for cathode

materials, and offer an original clue to make all-flexible 3D device possible. We strongly believe that 3D array design of cathode will not only open up a new sub-group for advanced open framework cathodes, but also inspire future success in commercial discovering high-performance all-flexible device for next-generation secondary batteries.

Chapter 5 SnS Array for Anode of Na-Ion Battery

5.1 Introduction and motivation

In perusing low cost and safe energy storage technologies, one of the most appealing alternatives is to use Na instead of Li because sodium ion batteries (NIBs) do offer the “only” prospects of the very same performance as lithium ion batteries (LIBs) with a much better long-term sustainability perspective.^{147,206,282} Recently, open framework materials have been proved an effective strategy to construct kinetically favorable Na-ion channels especially for cathodes of NIBs.^{147,209,283} Limitation in the anodes of NIBs is getting heeded in view of the more sluggish mass transport and more serious volume expansion which cannot meet either capacity (energy density) or rate (power density) demands of practical applications. The alloying materials (e.g., Na₁₅Sn₄: 847 mAh g⁻¹, Na₃Ge: 1108 mAh g⁻¹, Na₁₅Pb₄: 484 mAh g⁻¹, Na₃Sb: 660 mAh g⁻¹) appear to present the highest capacity for Na-storage so far but accompany a great challenge in mechanical stability due to drastic expansion/contraction during the Na alloying/dealloying, *e.g.* 420 % for Sn, 390 % for Sb, 365 % for Pb.^{116,129,134} To circumvent this issue, a facile approach for buffering the volume change is to develop nanosized materials integrated with a secondary active or inactive matrix.^{129,134} Tin-based oxides and chalcogenides can store Na⁺ through a combined electrochemical conversion and alloying mechanism giving superior theoretical capacities (SnO₂: 1378 mAh g⁻¹, SnS₂: 1136 mAh g⁻¹, SnS: 1022 mAh g⁻¹) as well as an expected improvement in mechanical stability due to smaller volume change. Compared with metal oxide, sulfides are typically more reversible than oxides due to relatively weaker M–S ionic bonds compared with M–O bonds, resulting in kinetically favorable conversion reaction and higher first cycle efficiency.¹⁰² Moreover, it was pointed out that the sodiation progress of SnS₂ experiences a large volume expansion (324 % to Na₁₅Sn₄), which involves the formation of tetragonal-Sn (beta), and another two-phase reaction forming a huge orthorhombic- Na₁₅Sn₄. Whereas, cubic-Sn (alpha) is obtained after conversion reaction of SnS, and followed

by only one easier phase reaction of orthorhombic- Na_xSn . As a result, SnS undergoes a smaller lattice change of 242 %, leading to good structural stability and excellent cycling stability.¹⁰² With merits of high electrical conductivity ($0.193\text{-}0.0083 \text{ S cm}^{-1}$), higher theoretical capacity, abundance, and low cost, layered 2D-SnS is considered to be the most promising anodes for NIBs. Having been a representative for energy density, a leap in power performance is quiet eager for Sn-based alloying materials.

To date, the charge storage mechanism of Li/Na ion can be divided into two parts: (i) diffusion-controlled process, which can be distinguished as insertion, conversion, and alloying mechanism in battery materials; (ii) capacitive charge storage based on double layer capacitance and faradaic charge-transfer reactions occurring at the surface or near-surface of active materials.²⁸⁴⁻²⁸⁶ It is commonly assumed that high rate capacity cannot be achieved by mechanism (i) particularly for NIBs due to the larger size of Na ions. Following this line of thinking, a maximized mechanism (ii) could boost the rate capability due to fast capacitive reactions.^{285,287} As summarized in Table 5.1, this strategy has shown great promise towards high-rate electrodes in LIBs and NIBs driven by an enhanced intercalation and conversion pseudocapacitive mechanism.^{249,288-290} Whereas, alloying mechanism induced pseudocapacitive performance was ignored possibly due to the huge difficulty in achieving fast kinetics in alloying mechanism dominated high-capacity materials.

Table 5.1 Three typical charge storage mechanisms for diffusion-controlled and pseudocapacitive materials between Li/Na ion and electrode materials.

Mechanism	Intercalation	Conversion	Alloying
Battery (diffusion-controlled) materials	Carbon allotropes, Nb_2O_5 , TiO_2 , $\text{Li}_4\text{Ti}_5\text{O}_{12}$, etc.	Fe_2O_3 , Co_3O_4 , V_2O_5 , MnO_2 , etc.	Si, Sn, Ge, etc.
Pseudocapacitive materials	Nb_2O_5 , LiCoO_2 , MoO_3 , TiS_2 , etc.	$\text{Ni}(\text{OH})_2$, MoS_2 , Fe_2O_3 , etc.	

Here we first propose and prove the existence of alloying pseudocapacitive

contribution to the enhanced electrochemical energy storage. With the help of exhaustive kinetics and quantitative analysis, a maximized pseudocapacitive contribution could be obtained by one-step facile controlled SnS nanoarchitecture design from nano-wall (NW) to nano-flake (NF) and nano-honeycomb (NH) electrodes. The as obtained graphene foam (GF) backboned NH electrode exhibits the highest reversible capacity, rate capability compared to the reported carbon allotropes, metal, metal oxides, and sulfides as Na^+ anodes. Surprisingly, for the first time, the Na-insertable host is observed with both superior capacity, rate, and polarization characteristics than its Li^+ ones. Inspired by the presented materials design strategy, existence of alloying pseudocapacitance, and the possibility of superior overall Na^+ performance than Li^+ , NIBs are further confirmed to be the “only” representative for current LIB, and its practical application is highly required.

5.2 Materials preparation

SnS nanostructures were fabricated by a facile hot bath method. Firstly, three pairs of concentration (Tin(II) chloride dihydrate, thioacetamide): (100, 300 mM) for nano-Wall, (50, 150 mM) for Nano-Flake, (25, 75 mM) for Nano-Honeycomb were dissolved with 50 mL ethanol at 80 °C, respectively. Then three piece of 3D graphene foams (GF, 2×5 cm, ca. 0.8 mg cm⁻², prepared by CVD method according to our previously results²¹², or Ni foam, carbon cloth and ITO glass) were immersed into the three reaction solutions respectively and kept for 45 min. Finally, the samples were collected and rinsed with distilled water and ethanol in turn for three times, and dried at 150 °C in vacuum to obtain 3D GF supported SnS freestanding electrodes (with SnS loading ca. 1.1 mg cm⁻² for Nano-Flake and Nano-Honeycomb electrode, and 1.2 mg cm⁻² for Nano-Wall electrode).

5.3 Results and discussion

Fig. 5.1 Fabrication strategies and structure of GF supported SnS nanostructures. (a-c) Tin(II) chloride dehydrate and thioacetamide concentration varies from 100 and 300 mM for (a), 50 and 150 mM for (b), and 25, 75 mM for (c). Scalebar: 200 nm. (d-f) Schematic illustrations of the SnS laminar structure seen from [004], [010], and [100] zone axis.

5.3.1 Morphology, structure, and growth mechanism

Fig. 5.1a-c illustrate the graphene foam (GF) supported SnS electrodes fabrication procedure by a rapid one-step *in-situ* hot bath route (details are described in the Methods section). Representative scanning electron microscope (SEM) images with three different morphologies could be obtained by the same route with different solutes concentration (denoted as Nano-Wall (NW), Nano-Flake (NF), and Nano-Honeycomb (NH) respectively, as the decrease of the concentration). As can be seen from Fig. 5.1a-c and Fig. 5.S1, in addition to the facile fabrication of freestanding flexible architecture of the spontaneous anchored SnS nanostructures,

another benefit of this approach is that it can give a controllable size distribution of SnS nanostructures. The SnS sheets present average lateral sizes of 400-500, 400-500, and 50-70 nm and thickness of approximately 150, 10, and 5 nm for NW, NF, and NH, respectively (Fig. 5.1 and 3). Uniform and randomly interconnected porous 3D nanosheets are well aligned and distributed on the surface of GF (Ni foam, carbon cloth, ITO glass in Fig. 5.S2), forming a stable continuous extended network.

The growth mechanism is proposed based on the crucial roles of GF and ethanol, which involves (i) the hydrolysis of thioacetamide and (ii) the *in-situ* metathesis reactions, “selfassembly” and “oriented crystallization” processes¹⁴⁷. First, sulfur source thioacetamide and hydrated tin chloride could homogeneously disperse in ethanol, then $\text{CH}_3\text{C(S)NH}_2$ reacts with trace water from $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ as shown in Eq. (1)²⁹¹. Furthermore, H_2S was produced slowly and *in-situ* metathesis reacted with Sn^{2+} to form sulfides. In addition to strong crystal anisotropy of the layered metal chalcogenide, the oriented growth of SnS nanocrystals may be closely related to the GF backbone and trace water in the system. During the hot bath reaction, the Sn^{2+} favorably nucleates onto the surface of GF with the help of ethanol, where bonding between the particles reduces the overall energy. Meanwhile, the trace water molecules, which is surrounded by ethanol molecules with hydrogen bonds²⁹¹, would array in chains and drift close to the GF backbone. It is believed that the chain texture of water molecules is preferential to the oriented growth of SnS nanosheets. An implication can be found by the structure evolution during the reactions in Fig. 5.S3. On the other hand, the numerous bubbles, originating from ethanol at appropriate temperature, create a continuous path from the GF substrate to the surface of bubbles²⁹². In other words, the bubbles act not only as a dynamic template for the oriented growth of the SnS nanocrystals, but also as a gas blocker for the formation of 3D porous nanoarchitectures. Herein, strategy of concentration control was employed to facilitate the assembly of preferred SnS nanostructures. As the decrease of the

precursor concentration, the nucleation rate decreases, thus results in smaller nucleation particle sizes and followed by different bubbles generation and edge-to-surface interactions²⁹³.

Fig. 5.S1 Morphologies evolution as the change of solutes concentration. (a-d) GF-SnS NW electrodes. (e-h) GF-SnS NF electrodes. (i-l) GF-SnS NH electrodes.

Fig. 5.2 Structure characterization of GF supported SnS nanostructures. (a) XRD patterns for the GF supported NW, NF, and NH electrodes. (b-d) High-resolution XPS spectra of Sn 3d, S 2p, and C 1s in the GF-SnS NH electrode.

Fig. 5.S2 Photos and SEM of the self-supported SnS electrodes showing similar morphologies like NH electrode. (a) SnS nanosheets on Ni foam. (b) SnS nanosheets on ITO glass. (c) GF-SnS NH electrode that is bent by small force to demonstrate the flexibility and light weight of the electrode. (d,e) SEM images for SnS nanosheets on carbon cloth, inset: high magnification image of SnS on carbon cloth.

Fig. 5.S3 Time-control experiments to reveal the morphology evolution of GF-SnS NH electrode. (a) SnS nucleates after hot bath reaction for 10 min. (b) for 20 min. (c) for 30 min. (d) for 40 min.

Fig. 5.3 TEM images of GF supported SnS nanostructures. (a,b) HRTEM images for Nano-Wall SnS structure. Inset (a): low magnification TEM image and (b): FFT pattern in the [010] zone axis. (c,d) HRTEM images for Nano-Flake SnS structure. Insets: low magnification TEM images. (e) HRTEM images for Nano-Honeycomb SnS structure. Inset: low magnification TEM image. (f) HRTEM images for cross-section of Nano-Honeycomb SnS structure. Inset: FFT pattern in the [004] zone axis.

The X-ray diffraction (XRD) patterns of the samples with are presented in Fig. 5.2a. The XRD peaks can be indexed to the graphitic carbon (JCPDS 75–1621) and orthorhombic SnS (JCPDS 39–0354). Obviously, the (111) peak of orthorhombic SnS in NH shows a broadening feature compared with that of NF and NW, revealing a finer grains character of the SnS NH crystallites. The average crystallite size calculated from the (111) diffraction peak by the Scherrer equation is about 30 nm for SnS NW electrode, while 15 and 8 nm for NF and NH electrodes, respectively. Meanwhile, from the XRD pattern, it can be seen that no impurities are detected in the samples, which was further confirmed by the EDS analysis (Fig. 5.S4a and S5), which illustrates that only Sn and S were detected, and the atomic ratio of Sn:S was

stoichiometric 1:1, in agreement with the expected value. The formation of pure tin sulfides without oxides and hydrates may be related to the weakly acidic system due to the hydrolysis and metathesis reactions. Raman spectrum of the as-prepared GF-SnS electrode (Fig. 5.S4b) further confirms these results. The surface chemical bonding state of GF-SnS electrode is also detected by X-ray photoelectron spectroscopy (XPS). The binding energies located at 295.3 (Mo 3d_{3/2}) and 286.8 eV (Mo 3d_{5/2}) are characteristic peaks of Sn²⁺ in SnS. No evidence of Sn⁴⁺ is found. The ratio of the integral area for Sn 3d to S 2p is about 1:1.02, which is consistent with the EDS results. More importantly, the existence of C-S bonds in GF-SnS is confirmed by spectra of both S 2p (163.7 eV) and C 1s (285.7 eV). These results suggest that SnS nanoclusters are chemically bonded with the GF matrix not merely pure physical adsorption.

Fig. 5.S4 Structure characterization of GF-SnS NH electrode. (a) EDS spectrum, which gives Sn:S ratio of nearly 1:1. (b) Raman spectrum of GF-SnS NH electrode. Two distinct peaks (190 and 221 cm⁻¹ can be assigned to the A_g mode of SnS. But no obvious bands for B_{1g}, B_{2g}, and B_{2g} modes were detected possibly due to the high orientation of the as-synthesized SnS nanosheets. (c) XPS spectrum of GF-SnS NH electrode.

Fig. 5.S5 TEM mapping of GF-SnS NH electrode. (a) Dark-field image of GF-SnS NH electrode. (b) Mixed EDS mapping of C (green), Sn (white), and S (red) elements. (c-e) EDS mapping of C, Sn, and S.

TEM and HRTEM images in Fig. 5.3 further confirm the crystallographic orientation and unique nanosheet-on-microstructure 3D porous Nano-Wall, Nano-Flake, and Nano-Honeycomb architecture. For SnS NW (Fig. 5.3a,b), the lattice-resolved HRTEM image shows interplanar spacing of 2.9 Å for the (101) planes of SnS. Further, the inset Fast Fourier Transform (FFT) spots also exposure the existence of (101), (002), and (100) facets under [010] zone axis, demonstrating that the layers of SnS are stacked along the [010] direction. It could be clearly reasoned that the preferred growth direction of the SnS nuclei takes place along $\langle 101 \rangle$. The nanosheet feature is shown in the schematic illustration along [010] zone axis (Fig. 5.1e). For SnS NF (Fig. 5.3c,d), the interconnected nanoflakes are regular with a periodic stacking of fringes (ca. 15 layers) enforced by van der Waals interactions along a specific direction. The layer distance is measured ca. 6.2 Å, which is slightly larger than the layer-to-layer spacing in reported work possible due to our specific preparation²⁹⁴. The lateral view of the nanoflake in Fig. 5.3d also illustrates a interplanar spacing of 2.9 Å for the (101) planes of SnS with a crystal grain size ca. 20

nm. The results also confirm the formation of nanosheets by stacking of (010) facets. Similarly, SnS NH also presents intrinsic corrugations and lamellar structure in the nanosheets with interlayer spacing ca. 6.2 Å, but with thinner thickness (ca. 6 layers). Interestingly, numerous tiny nanoclusters (ca. 5 nm) and nanocavities (3–5 nm) are also observed from the cross-section of the wrinkles in Fig. 5.3f. Meanwhile, HRTEM and FFT pattern reveals clear lattices with spacings of 3.4 Å and 2.8 Å for (120) and (040) planes respectively under [004] zone axis. A schematic illustration of the SnS laminar structure seen from [004] zone axis can be seen from Fig. 5.1a.

5.3.2 Na-ion storage performance

Fig. 5.4 Electrochemical performance of the GF-SnS electrodes for Na⁺ storage. (a) CV curves of the first 3 cycles of GF-SnS NH electrode at a scan rate of 0.2 mV s⁻¹. (b) Galvanostatic charge/discharge profiles during the first 10 cycles of NH electrode. (c) Galvanostatic charge/discharge profiles of GF-SnS electrodes after 5 cycles activation. (d) Long-term cycling performances of GF-SnS electrodes and pure GF electrode at a current density of 100 mA g⁻¹. (e) Rate performances of GF-SnS electrodes at various current densities from 30 to 30,000 mA g⁻¹. (f) Fast charging (charge at 30 A g⁻¹ in 1 min, discharge at 30 mA g⁻¹ and 1 A g⁻¹ with ca. 13h and 30 min, respectively) properties of NH electrode.

Our designed battery electrodes allow bicontinuous electron and sodium ion transfer channels through the GF-SnS network without the necessity of extra binders,

conductive additives and heavy metal current collectors, which are essential for exploring intrinsic sodium storage properties^{147,222}. Herein, GF serve as both lightweight 3D porous current collector (electron transfer) and compressible/flexible backbone for structural stabilization. The macroporous nanoarray feature and mesoporous crystalline structure prevents the aggregation and expansion of SnS during charge/discharge cycles. During lithiation, electrolyte can enter the interval between nanoarrays on both outside and inner surface of GF, so that the Na ion and electrons can react with the SnS nanoarrays effectively.

Fig. 5.S6 Electrochemical performance of the GF-SnS electrodes. (a,b) Galvanostatic charge/discharge profiles during the first 5 cycles of NF and NW electrodes at 30 mA g⁻¹. (c) Normalized rate capacities of GF-SnS electrodes at various current densities from 30 to 30,000 mA g⁻¹.

The reaction of SnS with sodium is complicated because it undergoes conversion followed by alloying reaction¹⁰². In these processes, both Sn and S uptakes alloying reactions with sodium (Eq. (3), (4)). Therefore, a careful investigation was carried out to understand its mechanism.

The sodium ion storage behavior of the GF-SnS electrodes were first characterized by galvanostatic discharge–charge measurements (Fig. 5.4b-f). The first discharge presents a steep and monotonous decrease of voltage due to a high electrochemical polarization of the conversion reaction from SnS to Sn metal nanograins and

amorphous Na_2S (Eq. (3)). The origination of large polarization may correspond to the passivated surface, structural rearrangement, particle pulverization during initial discharge. Instead, the following discharge shows a higher potential corresponding the conversion reaction, and the charge/discharge curves after the first three cycles almost overlap, indicating a surface state, stable structure and electrochemical reversibility after the first discharge activation process. The detailed reaction mechanism could be disclosed by the CV curves during the first several cycles (Fig. 5.4a). In the first cathodic scan, two prominent peaks were observed at around 0.6-0.7 V and 0.01-0.1 V, respectively. The peak at 0.6-0.7 V is associated with both the conversion reaction (Eq. (3)) as well as the alloying reaction (Eq. (4)) because it is difficult to distinguish the conversion and alloying peaks especially in the first discharge process^{102,130}. Furthermore, the peak at 0.01-0.1 V is regard as the further reaction between Na and Na_xSn alloy due to the multi-step Na-Sn alloying feature. In the anodic scan, a serial of small peaks below 1.4 V (ca. 0.3, 0.7, 1.2-1.4 V) correspond to the multi-step dealloying reaction of Na_xSn ; whereas the distinct peak at ca. 1.7 V could be attributed to the reversible conversion reaction from Sn to SnS . In the following cathodic scans, the conversion peak shifts positively to ca. 0.9 V implying an improved electrochemical kinetics after activation process in the 1st scan.

Fig. 5.S7 Typical SEM (a) and TEM (b) images of NH electrode after 200 cycles which show preserved structures after cycles.

The first discharge (sodiation) and charge (desodiation) capacities of GF-SnS NH are 1416 and 1147 mAh g^{-1} , respectively. The first cycle irreversible capacity loss (ca.

19 %) could be attributed mainly to SEI formation (Fig. 5.4b). Such a high coulombic efficiency of more than 80 % is much higher than peers' reports. A reversible capacity more than 1100 mAh g⁻¹ could be maintained in the following cycles, which is even higher than the theoretical capacity (1022 mAh g⁻¹) of SnS based on Eq. (3) and (4). It should be noted that pure GF contributed negligibly to the capacity (Fig. 5.4d, ca. 30 mAh g⁻¹ for the 1st discharge process and less than 10 mAh g⁻¹ in the following cycles). To our best knowledge, this is almost the highest reported reversible capacity among kinds of sodium alloys, oxides, sulfides, and carbonaceous anodes. Compared with NH electrode, NF presents a similar behavior due to their much alike structure and microtopography. While NW electrode exhibits a suppressed reversible capacity and higher polarization during sodiation/desodiation. More importantly, the voltage profile in NW electrode shows more obvious plateaus which is a typical feature of diffusion-controlled charge storage of battery materials²⁸⁶. The improvements in the coulombic efficiency and reversible capacity of GF-SnS NH electrode should be closely related with its distinct 3D GF-backboned architectures, few layers 2D layered mesoporous SnS nanocrystals, and its unique electrochemical mechanism which should be discussed below. The cycling performance of GF-SnS electrodes were evaluated at a current density of 100 mA g⁻¹. The GF-SnS electrodes deliver excellent capacity retention from the 3rd cycle onwards, reflecting a gradual steady activation process. After prolonged 200 cycles, the capacities of the GF-SnS electrodes still retain values of about 1010, 920, and 840 mAh g⁻¹ for NH, NF, and NW electrodes, respectively (see preserved structures in Fig. 5.S7).

Fig. 5.S8 Electrochemical AC impedance spectrum. At full-charged state after the first three cycles of GF-SnS electrodes. The resistance is simulated using equivalent circuit of $R_s(Q(R_{ct}Z_w))$.

The rate capability of the anode material is a crucial but challenging indicator for large scale application of batteries, such as regenerative braking and fast recharging of electric vehicles and cellphones. Nevertheless, the weakness of power should become particularly evident in high capacity (energy density) materials²⁸⁴. Fig. 5.4e shows the rate capability of GF-SnS electrodes from 30 mA g^{-1} to 30 A g^{-1} , where NH presents the best among them. Although a 1000-fold increase in current density is implemented, a discharge capacity of more than 400 mAh g^{-1} (in one minute) could still be retained. The discharge capacity can be recovered to ca. 900 mAh g^{-1} as the current returned to 800 mA g^{-1} , indicating the resilience and tolerance of NH electrode without damaging its structural integrity after high-rate cycles. If this kind of material is used to power cellphone system, it is estimated that the battery can be charged in one minute and discharged ca. 13 h at 30 mA g^{-1} , and ca. 30 minutes at 1 A g^{-1} (Fig. 5.4f). To our best knowledge, this is the best rate capability among all reported anode materials for SIBs. As a comparison, NW electrode gives the worst rate capacities among them (ca. 40 mAh g^{-1} at 30 A g^{-1} , 1/10 of SnS NH). In addition to their specific nanostructure engineering and crystallographic designing, the fantastical rate capability of NH electrode and their difference among NF and NW electrodes are further studied from aspects of electrochemical kinetics and quantitatively evaluation of sodium storage processes.

Fig. 5.S9 CV curves of NH electrode for Na⁺ storage. (a) CV curves of NH at various scan rate of 0.2, 0.4, 0.6, 0.8 mV s⁻¹. (b) CV curves of NH at various scan rate of 1, 5, 10, 20 mV s⁻¹.

5.3.3 Kinetics and quantitative analysis

Previous trace of evidences, such as huge discharge capacity (exceeding the theoretical value), ultrafast Na uptakes (30 A g⁻¹ in one minutes), and sloped galvanostatic profiles (with less obvious plateaus than NW electrode), are suggesting the existence of a pseudocapacitance-like contribution in GF-SnS NH electrode. To provide deep insight into the charge storage mechanism in these GF-SnS electrodes, we investigated the kinetics of the SnS electrodes (Fig. 5.5) using analytical approaches that provide quantitative information about differences between diffusion-controlled and capacitive charge storage processes. Resulting from stepwise sodiation mechanisms, CV curves with similar shapes at various scan rates from 0.2 to 0.8 mV s⁻¹ (Fig. 5.S9) display two broad cathodic peaks as increase of scan rate. Because cation intercalation reaction can be ruled out from our GF-SnS electrode, we mainly consider below three charge-storage mechanisms: the faradaic contribution from conversion and alloying reaction, the faradaic contribution from charge transfer with surface/subsurface atoms (i.e., pseudocapacitance effect), and the nonfaradaic contribution from electrical double-layer effect²⁸⁷⁻²⁸⁹.

Fig. 5.S10 Kinetics and quantitative analysis of the electrochemical mechanism of GF-SnS NF electrode. (a) CV curves of the first 3 cycles at a scan rate of 0.2 mV s⁻¹. (b) CV curves at various scan rate of 0.2, 0.4, 0.6, 0.8 mV s⁻¹. (c) Capacitive (red) and diffusion-controlled (blue) contribution to charge storage at 0.8 mV s⁻¹. (d) Normalized contribution ratio of capacitive (red) and diffusion-controlled (blue) capacities at different scan rates.

The degree of capacitive effect can be quantitatively analyzed according to the relationship between measured current (i) and scan rate (ν) from the CV curves:

$$i = a\nu^b \quad (5)$$

where a and b are the adjacent values. The b value is determined from the slope of the $\log i$ versus $\log \nu$ plot. Accordingly, for the diffusion-controlled (faradaic contribution) process, b value approaches 0.5 and i is proportional to the square root of ν ²⁹⁵; For the capacitance-dominated process (including pseudocapacitance and double-layer capacitance), b value closes to 1.0 and i is linear with ν ²⁹⁶. As shown in Fig. 5.5a, when $\nu < 30$ mV s⁻¹, b values are 0.94 and 0.92 for NH and NF electrodes respectively, indicating that charge storage mainly comes from conversion and/or alloying capacitive reactions. Differently, b value of NW electrode (0.77) is much suppressed, meaning less contribution from capacitive Na⁺ storage compared with that of NH and NF electrode, which is also implied by the more plateaued discharge profile of NW

electrode at both conversion reaction region (ca. 1.7-0.8 V) and alloying reaction region (ca. 0.7-0.01 V, showing in Fig. 5.4c). As scan rates increase to 30-100 mV s^{-1} , decreases of b values are detected, indicating diffusion-controlled reactions at high rates. Similar phenomena were observed on Nb_2O_5 Li intercalation²⁹⁷ and $\text{TiO}_2/\text{graphene}$ Na intercalation²⁸⁸ cells, due to the possible reasons of increased ohmic contribution and diffusion constraints upon ultrafast Na^+ uptakes.

Fig. 5.5 Kinetics and quantitative analysis of the electrochemical mechanism of GF-SnS electrodes for Na^+ storage. (a) Relationship between logarithm cathodic peak current and logarithm scan rate from 0.2 to 100 mV s^{-1} . Inset: b -values at both low and high scan rate regions. (b) Normalized capacities Q versus $v^{-1/2}$ in the range of 0.2 to 100 mV s^{-1} . (c) Capacitive (red) and diffusion-controlled (blue) contribution to charge storage of NH at 0.8 mV s^{-1} . (d) Normalized contribution ratio of capacitive (red) and diffusion-controlled (blue) capacities of NH at different scan rates.

To understand the fast kinetics and the rate-limiting step of GF-SnS NH electrode, the relationship between capacity q and scan rate v is also established based on the work of Trasatti²⁹⁸:

$$q_t = q_s + q_d = q_s + cv^{-1/2} \quad (6)$$

where q_t , q_s , q_d are attributed to total capacity, surface capacitive capacity (including pseudocapacitance and double-layer capacitance), and diffusion-controlled capacity; c is a diffusion coefficient related constant. In consequence, a large fraction of q_s should result in a high rate capability. A linear character of q_t against $v^{-1/2}$ represents a diffusion limited progress whereas capacitive-dominated progress is independent of the scan rate. Two distinct regions can be found in Fig. 5.5b (from 0.2 to 100 mV s^{-1}). In the region of 0.2–5 mV s^{-1} , the total capacities present no evident difference as scan rate increases, indicating a non-diffusion-limited step. Nevertheless, the capacities decrease linearly in the region of 20–100 mV s^{-1} , indicating diffusion-controlled rate-limiting process. As a result, diffusion is the rate-limiting step for charging times less than 150 s; the capacitive behavior from both conversion and alloying pseudocapacitances are in the charge of rate control as charging times more than 10 minutes.

Fig. 5.S11 Kinetics and quantitative analysis of the electrochemical mechanism of GF-SnS NW electrode. (a) CV curves of the first 3 cycles at a scan rate of 0.2 mV s^{-1} . (b) CV curves at various scan rate of 0.2, 0.4, 0.6, 0.8 mV s^{-1} . (c) Capacitive (red) and diffusion-controlled (blue) contribution to charge storage at 0.8 mV s^{-1} . (d) Normalized contribution ratio of capacitive (red) and diffusion-controlled (blue) capacities at different scan rates.

To further quantitatively determine the ratios of capacitive contribution, approach developed by Dunn is used here by separating the current response i at a fixed potential V into capacitive effects (k_1v) and diffusion-controlled reactions ($k_2v^{1/2}$)^{285,295}:

$$i(V) = k_1v + k_2v^{1/2} \quad (7)$$

By determining both k_1 and k_2 constants, we can distinguish the fraction of the current from Na^+ diffusion and pseudocapacitance. Fig. 5.5c shows the typical voltage profile for the capacitive current (red region) in comparison to the total current. The capacitive contribution is ca. 84 % for NH electrode, indicating that this is the dominant charge storage process. On the other hand, since the pseudocapacitive reaction should play an increasing role as the particle size decreases and/or the porosity increases, so the charge storage from the pure electrical double-layer (5-20 C g^{-1}) is negligible when compared with pseudocapacitive contribution^{249,285}. According to Eq. (3) and (4), the alloying process takes up more than 65 % of the whole capacity. Then, it is reasonable to deduce that more than 75 % of the capacity from alloying reaction originates from pseudocapacitive contribution, even if 100 % of the conversion capacity comes from pseudocapacitive contribution. To our best knowledge, it is for the first time that the alloying pseudocapacitive contribution is proposed and proved as an energy storage mechanism in favor of high capacity and fast cation uptakes. A significantly improved role of capacitive contribution as the increase of scan rate is also quantified in Fig. 5.5d with a maximum value of ca. 95 % at 5 mV s^{-1} . The quantitative studies of capacitive contributions of NH, NF, and NW electrodes (see Fig. 5.S10,11) are consistent with the capacitive contributions shown in Fig. 5.5a,b, strongly suggesting that NH and NF are easier for ion access and charge transfer (Fig. 5.S8) with fast kinetics maximized by conversion and alloying pseudocapacitance.

The reasons for the superior pseudocapacitive contribution of GF-SnS electrodes are also addressed. Firstly, the chemically bonded GF-SnS hybrid demonstrates enhanced structure stability and excellent electronic/ionic conductivity through the

network, which have been proved a necessary prerequisite for the generation of extrinsic pseudocapacitance in nanosized MoO_2 ²⁸⁶. On the other hand, the macroporous and few layers two dimension architecture of the SnS nanosheets provide for easier ion access and short diffusion path lengths¹⁴⁷. Film thickness was emphasized to be an important factor on the rate properties and corresponding redox capacitive contribution in fabrication extrinsic or intrinsic pseudocapacitive electrodes^{289,296,299}. Compared with SnS NW electrode, the interconnected macroporous thin-sheets feature of SnS NH electrode exposes more edges of the layers and enables an interior Na^+ or electrolyte access into the van der Waals gaps of nanosheets²⁸⁵. Moreover, the mesoporous nanocrystals and iso-oriented nature of SnS NH electrode benefits arising of another capacitive contribution: alloying pseudocapacitance. Volume expansion is supposed to occur upon sodiation especially during alloying reaction, which involves an increased van der Waals gaps in layered structures. Whereas for our mesoporous iso-oriented SnS NH, in-plane expansion is accommodated by both the horizontal mesoporous and vertical spacing from van der Waals gaps, which should markedly reduce the stress associated with Na^+ alloying. A unique combination of the three factors is probably responsible for the extraordinary pseudocapacitive behaviors observed in our materials.

5.3.4 Comparison with Li-ion storage capability

After achieving an outstanding Na^+ storage performance with the help of maximized capacitive contribution, we may wonder generally how about its Li^+ ones. With this question, SnS NH on Ni foam electrodes were used for both Na^+ and Li^+ tests in order to avoid the influence upon Li uptakes in GF backbone. Traditionally, it was believed that Na^+ transport and storage are more sluggish and with more serious volume expansion in the Li^+ insertable hosts because of the larger ion radius of Na^+ ^{260,282,300}. So far, it is known that many properties such as discharge capacity, fast charging capability, and polarization are worse in NIBs than LIBs. Incredibly, the rate capacity profiles in Fig. 5.6a present that the reactivity of Na^+ insertion/extraction in NH electrode is remarkably superior to Li^+ uptakes in the high rate region. The

NF-SnS NH electrode delivers a Na^+ discharge capacity of ca. 410 mAh g^{-1} at 30 A g^{-1} , which is much higher than that of Li^+ electrode (ca. 105 mAh g^{-1}). Details of the galvanostatic charge/discharge processes can be observed in Fig. 5.6b. Compared with Na^+ profiles, the Li^+ electrode shows two reversible distinct plateaus at 1.2-1.4 and 0.01-0.4 V vs. Li/Li^+ corresponding with CV curves in Fig. 5.S13a, suggesting a lower fraction of capacitive contribution. Quantitative analysis the capacitive fraction of Li^+ electrode (75 %, inset in Fig. 5.6b) based on previous strategy further verifies this inference. Similar phenomenon was also observed in $\text{Li}_4\text{Ti}_5\text{O}_{12}$ spinel thin film which shows much higher Na^+ insertion capacitive contribution than that of Li^+ but with much lower discharge capacity.²⁸⁹ The same with sodiation processes, the first plateau during lithiation is attributed to the conversion reaction from $\text{SnS} \rightarrow \text{Sn}$ and the second one is the alloying reaction forming $\text{Li}_{15}\text{Sn}_4$ phase, which is consistent with previous reports^{301,302}. Whereas, the polarization from 30 mA g^{-1} to 7 A g^{-1} during lithiation (ca. 340 mV) is calculated twice than that during sodiation (ca. 170 mV). Moreover, the moderate and continuous operation voltage in Na^+ electrode would be more practical than the Li^+ one with obvious stepwise plateaus, due to the possibilities of avoiding the formation of dendrites upon cycling and higher energy density of full cells²⁸⁸.

Fig. 5.S12 Capacitive (red) and diffusion-controlled (blue) contribution to Na^+ charge storage of NF-NH at 0.8 mV s^{-1} .

Although, a much improved cycling performance was achieved in bulk Sb due to

possible amorphous intermediate species during sodiation, the discharge and rate capacities were still inferior than those of Li^+ electrode¹⁰⁹. The outperformance of Na^+ against Li^+ electrode in both capacity, rate, and polarization was never reported. In addition to the suppressed pseudocapacitive contributions from both conversion and alloying reactions during lithiation, other possibilities which could cause less electrochemical activity of Li electrode were also proposed. The strongly solvating groups (carbonyl groups) in polymer electrolyte should arrange in an appropriate manner as a preferred solvation shell of the cations^{303,304}. The de-solvation energy used to evaluate desorption of the last solvent molecule from cations was shown closely related to the cations transfer at the electrolyte/electrode interface by Z. Ogumi, et. al..³⁰⁵ It has been proved that sodium ion presents weaker solvation shell with smaller de-solvation energy and lower activation barrier for sodiation compared to lithium ion^{303,306}. As a result, faster sodiation/desodiation kinetics and more universal pseudocapacitive effect are possible for SIBs as compared to LIBs with the help of fast cation transfer²⁰⁴.

Fig. 5.6 Comparisons between Na-ion and Li-ion storage performance of NF-SnS NH electrodes. (a) Rate performance comparison at various current densities from 30 to 30,000 mA g⁻¹. (b) Galvanostatic profiles of Na, Li electrodes at rate of 30 mA g⁻¹ and 7 A g⁻¹ after activation. Inset: Capacitive (red) and diffusion-controlled (blue) contribution to charge storage at 0.8 mV s⁻¹ during Li uptakes. All of the batteries were tested in the same voltage range of 0.01 to 3 V versus Na/Na⁺ and Li/Li⁺ for NIB and LIB respectively.

Fig. 5.S13 CV curves of NF-SnS NH electrode for Li-ion battery. (a) CV curves of the first 3 cycles at a scan rate of 0.2 mV s⁻¹. (b) CV curves at various scan rate of 0.2, 0.4, 0.6, 0.8 mV s⁻¹.

Fig. 5.6 Schematic illustration showing the mechanism of high-rate charge storage of tailored SnS architecture. During transfer of ions and electrons, the solvated Na⁺/electron can easily enter the open spaces between neighboring ultrathin nanosheets on both outside and inner surface of GF. After de-solvation of Na⁺ on the surface of layered SnS architecture, rapid sodiation takes place by the surface-dominated extrinsic pseudocapacitance.

5.4 Conclusions

The results presented here demonstrates a sodium ion battery with both high capacity (energy density) and high rate capability (power density) by a rapid one-step in-situ hot bath route for the chemically bonded GF-SnS nanosheets. The resultant architecture can provide the highest ever reported reversible capacity of 1100 mAh g⁻¹ at 30 mA g⁻¹ and rate capability of 400 mAh g⁻¹ even if a 1000-fold increase in current density is applied (30 A g⁻¹ in one minutes). Quantitative kinetics analysis

between diffusion-controlled and capacitive charge storage processes were investigated to disclose the mechanism inside. With the help of tailored design of nano-honeycomb, nano-flake, and nano-wall electrodes, a maximized conversion and alloying pseudocapacitance is achieved benefiting from the excellent electronic/ionic conductivity, macroporous and few layers two-dimension architecture, and the mesoporous nanocrystals and iso-oriented nature of SnS electrode. Surprisingly, the as designed SnS Na⁺ electrode also exhibits superior performances in both capacity, rate, and polarization than Li⁺ ones due to higher pseudocapacitive effect and faster Na⁺ transfer at the electrolyte/electrode interface. The experimentally validated breakthrough for good overall Na⁺ performance than Li⁺ could further inspire the fast development of NIBs. Moreover, the as proposed and proved conversion and alloying pseudocapacitive contribution that offer increased power density with maintained high-energy-density should be a brand-new strategy and concept for next generation batteries.

Chapter 6 Future Work

6.1 Future work I: Improvement in nanoarray anode

6.1.1 Limitations and proposals

Even though kinds of merits have been demonstrated by our previous designed 3D graphene foam supported metal chalcogenides composite, there are also limitations. Most of the array electrodes in literatures were grown with limited mass loading ($\sim 1 \text{ mg cm}^{-2}$) on the heavy inactivating metal Cu foil ($\sim 10 \text{ mg cm}^{-2}$). Although, our previous SnS@GF electrode take the advantage of light-weight substrate ($0.5\text{-}0.8 \text{ mg cm}^{-2}$), the active materials mass loading and corresponding areal capacity were still limited.

Herein, we try to conduct a facile hot bath in-processing intervention method for the synthesis of vertically aligned 2D self-branched (big nanoflake core and small nanoflake branches) SnS₂ nanoarrays. The special architecture possesses significantly increased mass loading ($\sim 4 \text{ mg cm}^{-2}$). In-situ Raman technologies were performed to investigate the structural evolution and reversibility, and fast rate response of self-branched SnS₂ nanoarrays electrode.

6.1.2 Preliminary study and work plan

As illustrated in Figure 6.1, self-branched SnS₂ nanoarrays (B-SnS₂) are grown on graphene foam (GF) using a facile hot bath method at 80 °C. SEM images show that the size of SnS₂ nanoarrays is tunable from big-flakes to small-sheets by controlling the concentration of the solution during the reaction. The SnS₂ nanoarrays in Figure 6.1c, which were generated before diluting the reaction solution with fresh ethanol, are vertical big flakes of 200-500 nm in size. After adding fresh ethanol, small sheets (ca. 50 nm) begin depositing onto the lateral surface of big-flakes and form a self-branched nanoarchitecture finally at 40 min later (Figure 6.1 b and e).

Fig. 6.1 Fabrication and FESEM images of B-SnS₂ with different reaction time. a) Schematics of fabricated B-SnS₂ electrode. b) FESEM images of B-SnS₂ obtained 40 min later after adding fresh ethanol. Left inset: Digital photo of GF supported B-SnS₂ electrode that is bent by a small force to show its flexibility and light weight. Middle and right insets: Low and high magnification FESEM images of B-SnS₂ structure. c–e) FESEM images of SnS₂ nanoarrays obtained by hot bath method before adding fresh ethanol, 15, 30 min later after adding fresh ethanol, respectively. Scale bar: 200 nm.

Fig. 6.2 Mechanism analysis of electrochemical process. In-situ Raman spectra of electrodes at different charge/discharge potential at 5 A g⁻¹.

Due to the amorphous feature of the back-converted SnS₂, it is hard to detect the products in the cycled samples by XRD measurement. Nevertheless, as can be seen SnS₂ shows characteristic Raman peaks at ~230 (E_u, weak) and ~316 cm⁻¹ A_{1g}, strong).³⁰⁷ Therefore, in-situ Raman technology was employed with an in-situ Raman reaction cell to confirm the high reversibility of our B-SnS₂ electrode. The spectra in the range between 200 and 1000 cm⁻¹ show only peaks characteristic of SnS₂ besides those of electrolyte ions EC, DEC and PF₆⁻. The yellow-shaded peaks are associate with O=C ring bending mode of EC (~715 cm⁻¹), symmetric ring breathing mode of EC (~892 cm⁻¹) and CH₃-O stretching of DEC (~900 cm⁻¹), respectively. While the blue-shaded peaks refer to the totally symmetric vibration of PF₆⁻ anion at ~742 cm⁻¹.^{308,309} They remain little changed during the entire charge-discharge process and hence will not be discussed. On the other hand, the characteristic A_{1g} peak at 316 cm⁻¹ of B-SnS₂ electrode (Fig. 6.2) is found to decay in intensity and fully limited during the sodiation process, suggesting the consumption of SnS₂. After desodiation, the reappeared broad peak at ~316 cm⁻¹ indicates the good reversibility of SnS₂ nanostructures during high-rate charge/discharge (at 5 A g⁻¹). Surprisingly, as a comparison, no peak vanishing is observed for the SnS₂ electrode without branches (Fig. 6.2), indicating a limited sodiation due to the sluggish kinetics of the SnS₂ electrode. The findings coincide with the higher pseudocapacitive contribution and

specific capacity of B-SnS₂ electrode especially at high rate.

This preliminary result can prove the feasibility of our proposal in certain extent. And this work needs to be continued with surface coating, such as carbon, PANI, and PEDOT in order to improve the cycling stability and further application in full Na-ion device in the future.

6.2 Future work II: All-flexible 3D array sodium ion device

It is quite urgent to fabricate one kind of flexible full device with high performance 3D array cathode and anode after successful trials in both vanadium oxide based cathode and anode.

We found in previous NVOPF array design that the VO₂ NS electrode which is derived from VO₂ precursor exhibits a high reversible capacity of ~440 mAh g⁻¹ (at 200 mA g⁻¹) as anode of SIB (Fig. 6.3a). A superior high-rate capability is also achieved from 454 mAh g⁻¹ at 0.1 A g⁻¹ to 300 mAh g⁻¹ at 1.5 A g⁻¹ and 155 mAh g⁻¹ at 6 A g⁻¹. To understand this high-rate performance, the redox extrinsic pseudocapacitive contribution in the electrode is investigated by kinetics analysis of diffusion-controlled and capacitive charge storage processes^{266,296}. The degree of capacitive contribution can be qualitatively analyzed by the relationship between current i and scan rate ν from the CV curves ($i = a\nu^b$, a and b are constant). The b value is supposed to be between 0.5 (diffusion-controlled process) and 1.0 (surface capacitive-dominated process))²⁸⁵. Herein, the calculated b values stabilize ~0.92 in the most of potential region with a gradual decay at low potential region (inset Fig. 6.3b), suggesting a favorite capacitive behavior of VO₂ NS electrode. The ratio of Na-ion capacitive contribution from the total capacity can be further quantified by separating the current response from diffusion-controlled and capacitive processes^{4, 285}. Around 76% of the total capacity is found to be capacitive even through at a relatively slow rate of 0.8 mV s⁻¹ (Fig. 6.3b). The specific capacitance is found much larger than the typical double-layer capacitance from the conductive surface³¹⁰, suggesting that the capacitive current is dominated by the pseudocapacitive effect. The

pseudocapacitive contribution is located almost entire regions of the CV except for the convex peak region, which is corresponding with the b values. It is pointed out that the mesoporous and thin-sheet features are most likely the source of the fast kinetics and high fraction of capacitive current observed in this system. It is suggested that the GF-VO₂ NS electrode is extremely suitable for high-rate anode application.

Fig. 6.3 Electrochemical Na ion storage performance of the VO₂ NS anode. (a) Galvanostatic charge/discharge profiles of VO₂ NS electrode between 0.1 and 2.5 V. (b) Capacitive (black) and diffusion-controlled (green) contribution to charge storage of VO₂ NS electrode at 0.8 mV s⁻¹. Inset grey line is the anodic b -values for the qualitative analysis of the CV curves.

Fig. 6.4 3D flexible NVOPF array//VO₂ NS sodium ion hybrid device. Galvanostatic charge/discharge profiles from 1C to 20C between 1 and 4 V (1C is defined as 130 mA g⁻¹).

Prompted by the above results, it is anticipated to construct a full Na-ion device based on 3D NVOF oriented nanoarray intercalation cathode and VO₂ nanosheet capacitive anode with the objective of determining how these materials perform as high-rate device. As illustrated in preliminary result in Fig. 6.4, a hybrid sodium ion storage device is assembled which is composed of two pieces of 3D graphene foam supported flexible electrodes. The hybrid device is investigated under galvanostatic conditions at room temperature in the voltage window of 1.0–4.0 V. The discharge profiles in Fig. 6.4 demonstrate two inclined stages as the synthetic effect from the intercalation cathode and capacitive anode. The hybrid device can be effectively charged/discharged at rates from 1C to 20C. It delivers a reversible capacity of 113 mAh g⁻¹ at 1C based on the mass of the cathode, which is calculated ~90 mAh g⁻¹ based on the mass of both anode and cathode materials. Impressively, the reversible capacity at 20C is preserved at ~40 mAh g⁻¹. The performance of the full device still needs to be improved in the future.

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