Three-dimensional graphene and derivative hybrids for electrochemical energy storage

Yao, Xin

2016

Yao, X. (2016). Three-dimensional graphene and derivative hybrids for electrochemical energy storage. Doctoral thesis, Nanyang Technological University, Singapore.

<https://hdl.handle.net/10356/69426>

<https://doi.org/10.32657/10356/69426>

NANYANG
TECHNOLOGICAL
UNIVERSITY

**THREE-DIMENSIONAL GRAPHENE AND
DERIVATIVE HYBRIDS FOR
ELECTROCHEMICAL ENERGY STORAGE**

YAO XIN

**SCHOOL OF PHYSICAL AND MATHEMATICAL SCIENCES
NANYANG TECHNOLOGICAL UNIVERSITY, SINGAPORE**

2016

**THREE-DIMENSIONAL GRAPHENE AND
DERIVATIVE HYBRIDS FOR
ELECTROCHEMICAL ENERGY STORAGE**

YAO XIN

School of Physical and Mathematical Sciences

A thesis submitted to the Nanyang Technological University in
partial fulfillment of the requirement for the degree of

Doctor of Philosophy

2016

ACKNOWLEDGEMENT

First and foremost, I would like to express my sincerest gratitude to my supervisor, Assoc. Prof. Zhao Yanli for his constant support and seasoned guidance throughout the four years of my Ph.D. course. Only with his instruction, inspiration, and encouragement, I'm able to overcome the difficulty and frustration in study and life, and become a capable independent researcher. His knowledge and wisdom always inspire me. It's indeed my great honor and pleasure to receive my Ph.D. education under his supervision.

My gratitude also extends to the colleagues and friends in both Division of Chemistry and Biological Chemistry (CBC) and School of Materials Science and Engineering (MSE), for all sorts of academic supports they gave me, and all the joyful experiences we shared in daily life. The success of my research projects also owes many thanks to Assoc. Prof. Yan Qingyu. Without our productive collaboration and the full assistance from his student, Mr. Guo Guilue, I'm not able to complete the electrochemical studies of my research projects.

I also would like to thank Division of CBC, School of Physical and Mathematical Sciences (SPMS), Nanyang Technological University (NTU) for providing the world-class hardware and software for students to carry out their own research work during their Ph.D. study.

At last, I would like to convey my deepest gratitude to my beloved parents and

girlfriend. It is their love, patience, and blessing that soften the toughness in my Ph.D. course, keeping me on the right track during the pursuit of my dreamed life and career.

TABLE OF CONTENTS

ACKNOWLEDGEMENT	I
TABLE OF CONTENTS	III
ABSTRACT.....	VIII
LIST OF FIGURES	IX
LIST OF SCHEMES.....	XIII
LIST OF TABLES	XIV
Introduction to the fundamentals of electrochemical and materials characterization techniques	XV
Chapter 1. Three-Dimensional Porous Graphene Networks and Derivative Hybrids for Next-Generation Lithium-Ion Battery and Supercapacitor.....	1
1.1 Introduction.....	2
1.2. Structures and fabrication of 3DPGNs	5
1.2.1. Graphene aerogel	6
1.2.1.1. Hydrothermal/solvothermal reduction.	6
1.2.1.2. <i>In-situ</i> chemical reduction.	8
1.2.1.3. Ice-segregation-induced self-assembly (ISISA).	9
1.2.2. Graphene foam.....	11
1.2.2.1. CVD method with NF template.	12
1.2.2.2. Other hard or soft templates.....	14

1.3. Hybrids derived from 3DPGNs	15
1.3.1. GA-based composites	16
1.3.1.1. Inorganic phases/GA.....	16
1.3.1.2. Organic phases/GA.	20
1.3.1.3. Doping strategy.	22
1.3.2. GF-based composites	24
1.3.2.1. Inorganic phases/GF.....	24
1.3.2.2. Organic phases/GF.	27
1.4. Application in next-generation LIB and supercapacitor	27
1.4.1. Lithium-ion battery	27
1.4.1.1. Anode.	28
1.4.1.2. Cathode.	36
1.4.1.3. Advantages of 3DPGN in LIB.	40
1.4.1.4. Flexible binder-free electrodes.	42
1.4.2. Supercapacitor	44
1.4.2.1. EDLC.	45
1.4.2.2. PCM.	47
1.4.2.3. Advantages of 3DPGN in supercapacitor.	50
1.4.2.4. all-solid-state supercapacitor (ASSS).	51
1.5. Conclusion	54

Chapter 2. *In-Situ* Integration of Anisotropic SnO₂ Heterostructures inside Three-

Dimensional Graphene Aerogel for Enhanced Lithium Storage	74
2.1 Introduction.....	75
2.2 Results and discussion	80
2.2.1 Chemical composition and crystal properties	80
2.2.2. Morphological features and porous texture	82
2.2.3. Formation mechanism.....	87
2.2.4. Electrochemical performance as LIB anode.	90
2.2.5. Comprehension on the relationship between structural properties and electrochemical performance	97
2.3 Conclusions.....	99
2.4 Experimental.....	100
2.4.1 Materials synthesis.....	101
2.4.2. Materials characterizations.	103
2.4.3 Electrochemical measurements.....	103
2.5. References.....	104
Chapter 3. Synergistic Effect of Mesoporous Co ₃ O ₄ Nanowires Confined by N-Doped Graphene Aerogel for Enhanced Lithium Storage.....	111
3.1. Introduction.....	112
3.2. Results and discussion	115
3.2.1. Formation mechanism.....	115
3.2.2. Morphological studies.....	117

3.2.3. Chemical composition and crystal properties	124
3.2.4. Proof of nitrogen doping	127
3.2.5. Study on porous structure	130
3.2.6. Electrochemical properties as LIB anode	132
3.2.7. Comprehension on the relationship between structural properties and electrochemical performance	139
3.3 Conclusion	141
3.4. Experimental	142
3.4.1. Materials synthesis	142
3.4.2. Materials characterizations	144
3.4.3. Electrochemical measurements	144
3.5. References	145
Chapter 4. Scalable Synthesis of Three-Dimensional Cellular Monolith Collaboratively Woven from V ₂ O ₅ Nanowires and Carbon Nanotubes for Lithium-Ion Battery Cathode	152
4.1. Introduction	153
4.2. Result and discussion	155
4.2.1. Structural layout and fabrication procedures	155
4.2.2. Morphological studies	159
4.2.3. Chemical composition and crystal properties	162
4.2.4. Electrochemical performance as LIB cathode	164

4.3. Conclusion	170
4.4. Experimental	171
4.4.1. Materials synthesis.....	171
4.4.2. Materials characterization.....	172
4.4.3. Electrochemical measurements.....	172
4.5. References.....	173
Chapter 5. Summary and Outlook	177
5.1. Summary of research work.	177
5.2. Outlook for 3DPGN-based hybrids and its derivative structures in electrochemical energy storage	180
PUBLICATIONS	183
CONFERENCES	184

ABSTRACT

The research work focuses on the design, fabrication, and characterization of novel three-dimensional carbon-based hybrid materials in order to utilize them in next-generation power tools. Through novel functionalization and structuration, several three-dimensional lattices based on graphene or carbon nanotubes are designed and fabricated. A variety of techniques of both materials and chemical science are used to fully characterize the functional hybrids, and evaluate their application potential as anode or cathode for lithium-ion battery.

LIST OF FIGURES

Figure 1. 1. a, b) Digital photos of graphene hydrogel/GA synthesized from hydrothermal approach. c) SEM of the hydrothermal GA. Reproduced with permission from ref. [19]. Copyright 2010 American Chemical Society. d-f) SEM images of graphene elastomer, scale bar 10 μm . g) Scheme of the freeze casting approach, and formation mechanism of graphene elastomer. Reproduced with permission from ref. [33]. Copyright 2012 Macmillan Publishers Limited.

Figure 1. 2. a) Schematics showing the routes to prepare GF from NF templates and CVD growth of graphene. b) SEM image and inset photo of GF. c) TEM image showing the graphene layers of GF. Reproduced with permission from ref. [6]. Copyright 2011 Macmillan Publishers Limited. d) Schematics showing the formation mechanism of the nanoporous GF. e, f) SEM and TEM characterization on the nanoporous GF. Reproduced with permission from ref. [47]. Copyright 2012 WILEY-VCH.

Figure 1. 3. a, b) Morphology of Pt/3D RGO. c, d) SEM images of 3D RGO supported NiO/Ni. e) Scheme of the DSARA method. Reproduced with permission from ref. [77]. Copyright 2014 Royal Society of Chemistry. f) Synthetic routes for the GA functionalized with organic crosslinkers. Reproduced with permission from ref. [116]. Copyright 2010 American Chemical Society

Figure 1. 4. a-d) Morphological characterization on GF (a), VO_2 nanoarrays on GF (b), and GF supported $\text{VO}_2@\text{GQD}$ nanoarrays (c, d). Reproduced with permission from ref. [159]. Copyright 2012 American Chemical Society. e-h) Morphology of Ni_3S_2 nanorod@ $\text{Ni}(\text{OH})_2$ nanosheet core-shell nanostructures on GF. Reproduced with permission from ref. [114]. Copyright 2013 Royal Society of Chemistry.

Figure 1. 5. a) SEM image and digital photo (inset) of the 3D G network. b) SEM images of the 3D G-Si network. c) Capacity-voltage profiles at 200 mA g^{-1} , from 2 to 0.005 V versus Li/Li^+ . d) Rate capability e) Cycling performance accompanied with columbic efficiency, at 200 mA g^{-1} . Reproduced with permission from ref. [91]. Copyright 2015 WILEY-VCH.

Figure 1. 6. a-c) Morphology of the LFP@N-GA hybrid. d) Capacity-voltage profiles of LFP@N-GA electrode and commercial LFP/C at various rates. e) Rate capabilities. f) Cycling performance at 10C, accompanied with columbic efficiency. g) Ragone plot of LFP@N-GA compared with some existing electrochemical energy storage/conversion devices. Reproduced with permission from ref. [190]. Copyright 2015 Royal Society of Chemistry.

Figure 1. 7. a) Model of the flexible LIB based on GF. b, c) Digital photos showing the bending state of flexible LIB. d) Galvanostatic charge/discharge profiles of the LIB full cell functioned under different rates. e) Specific capacity of the full battery run at 10 C. f) Capacity-voltage curves of flat and bent batteries. Red line stands for the as-prepared flat LIB, and blue for the bent one after bending to a radius of 5 mm for 20 times. g)

The cycling performance during bent and flat states. Reproduced with permission from ref. [152]. Copyright 2012 National Academy of Sciences.

Figure 1. 8. a, b) SEM images of the GF/CNT film. c) SEM image of the GF/CNT/MnO₂ film. d) Galvanostatic charge/discharge profiles of the ASC at varied current densities. e) Cycling performance of the ASC, under area current density 1.5 mA cm⁻², over 10000 cycles. f, g) Optical photos showing the ASC powering red LED (f) and small motor (g). Reproduced with permission from ref. [200]. Copyright 2014 Royal Society of Chemistry.

Figure 1. 9. a) Schematic illustration showing the procedures for synthesis of BN-GA, and subsequent fabrication of ASSS. Reproduced with permission from ref. [132]. Copyright 2012 WILEY-VCH. b) Galvanostatic charge/discharge curves of the asymmetric ASSS made from MnO₂/GF and CNT/CF at various current densities. c) Cycling performance of the asymmetric ASSS at current density 5 A g⁻¹ for 10000 cycles. Inset optical images of the functioning asymmetric ASSS. d) Specific capacitance retention of the flexible ASSS upon bending to different angles (left) or different times at constant angle of 180° (right). Reproduced with permission from ref. [222]. Copyright 2014 WILEY-VCH.

Figure 2.1. a) Powder XRD patterns of SnO₂ NCs@GA: (I) hydrothermally synthesized, and (II) after calcination. b) XPS spectrum of SnO₂ NCs@GA. c) TGA curves of SnO₂ NCs@GA.

Figure 2.2. a) FESEM images of GA. b-f) FEM images of SnO₂ NCs@GA. Inset photos in (a, b) show the shape and size of monolithic GA and hybrid.

Figure 2.3. N₂ adsorption/desorption isotherms for GA (a) and SnO₂ NCs@GA (b).

Figure 2.4. a) TEM image of SnO₂ nanorod wrapped by graphene. b, c) High-magnification TEM images of SnO₂ nanorods.

Figure 2.5. FESEM images of the products collected at various reaction stages: a) 0.5 h; b) 1 h; c) 4 h; d) 12 h.

Figure 2.6. Powder XRD spectra of the samples collected at 10 min, 30 min, 1 h, 4 h, 8 h, 12 h, and 24 h of the hydrothermal reaction.

Figure 2.7. a) Galvanostatic discharge/charge profiles of SnO₂ NCs@GA at a current density of 100 mA g⁻¹ for the 1st, 2nd and 50th cycles. b) Columbic efficiency of SnO₂ NCs@GA at 100 mA g⁻¹.

Figure 2.8. Detailed characterization of the two control samples. a, b) SEM images of SnO₂ NPs@GA (a) and SnO₂ NCs@GSs (b). c, d) TGA curves of SnO₂ NPs@GA (c) and SnO₂ NCs@GSs (d).

Figure 2.9. a) Cycling performance of SnO₂ NCs@GA, SnO₂ NPs@GA and SnO₂ NCs@GSs at a current density of 100 mA g⁻¹. b) Rate performance of SnO₂ NCs@GA, SnO₂ NPs@GA, and SnO₂ NCs@GS at different current densities.

Figure 2.10. Nyquist plots of SnO₂ NCs@GA, SnO₂ NPs@GA, and SnO₂ NCs@GS based anodes. Inset shows Randles equivalent circuit. Re is the electrolyte resistance; CPE stands for constant phase element; Rct is the charge-transfer resistance; Zw is the Warburg element.

Figure 3.1. a-c) SEM images of NGA-Co(CO₃)_{0.5}(OH)·0.11H₂O NWs showing the seaming behavior. Arrows in (a-c) denote the areas where the seaming mode could be visualized. d) Cartoon illustration of the seaming mode.

Figure 3.2. a-c) SEM images of NGA-Co(CO₃)_{0.5}(OH)·0.11H₂O NWs showing the bridging behavior. Rectangles in (a) denote the spots where bridging could be found. Dotted lines in (b, c) indicate the gaps between graphene sheets. d) Cartoon illustration of the bridging mode.

Figure 3.3. a-c) SEM images of NGA-Co(CO₃)_{0.5}(OH)·0.11H₂O NWs showing the hooping behavior. Rectangles in (a-c) denote the spots where hoping could be found. d) Cartoon illustration of the hooping mode.

Figure 3.4. a-c) SEM images of NGA-Co(CO₃)_{0.5}(OH)·0.11H₂O NWs showing the bundling behavior. Arrows in (a) indicate the spots where bundling modes could be observed.

Figure 3.5. a) High-magnification SEM image of NGA-Co(CO₃)_{0.5}(OH)·0.11H₂O NWs before calcination. The inset cartoon demonstrates the modeling of the sandwich structure. b) High-magnification SEM image of NGA-Co₃O₄ NWs. SEM image of NGA-Co₃O₄ NWs obtained after calcination. The sandwich spots in (a,b) are marked with arrows.

Figure 3.6. a-c) TEM and HRTEM images of NGA-Co(CO₃)_{0.5}(OH)·0.11H₂O NWs. d-f) TEM and HRTEM images of NGA-Co₃O₄ NWs.

Figure 3.7. Powder XRD patterns of Co(CO₃)_{0.5}(OH)·0.11H₂O NWs (a, pattern I), NGA-Co(CO₃)_{0.5}(OH)·0.11H₂O NWs (a, pattern II), and NGA-Co₃O₄ NWs (b).

Figure 3.8. a) TGA analysis of NGA-Co₃O₄ NWs. b) TGA analysis of Co(CO₃)_{0.5}(OH)·0.11H₂O NWs.

Figure 3.9. High-resolution XPS spectra of carbon and nitrogen elements from undoped GA (a,b), NGA (b,c), and NGA-Co₃O₄ NWs (e,f). g) Full-range XPS spectrum of NGA-Co₃O₄ NWs. h) High-resolution XPS spectrum of Co in NGA-Co₃O₄ NWs.

Figure 3.10. Raman spectra of GA and NGA.

Figure 3.11. Nitrogen adsorption/desorption isotherms and DFT pore size distribution plots of NGA (a, b), mesoporous Co₃O₄ NWs (c, d), and NGA-Co₃O₄ NWs (e, f).

Figure 3.12. Galvanostatic discharge/charge curves of NGA-Co₃O₄ NWs (a), Co₃O₄ NWs (b), and NGA (c) at fixed current density of 100 mA g⁻¹ for the 1st, 2nd, 10th, 55th and 100th cycles. d) Cyclic voltammetry (CV) plot of NGA-Co₃O₄ NWs based half-cells.

Figure 3.13. a) Cycling performance of Co₃O₄ NWs, NGA and NGA-Co₃O₄ NWs during 100 cycles at a current density of 100 mA g⁻¹, accompanied by the coulombic efficiency plots of NGA-Co₃O₄ NW based electrode. b) Rate capabilities of Co₃O₄ NWs, NGA and NGA-Co₃O₄ NWs at various current densities. c) High rate cycling performance of NGA-Co₃O₄ NWs electrode at current density of 1000 mA g⁻¹ for 230 cycles. d) Nyquist plots of half-cells manufactured from Co₃O₄ NWs, NGA and NGA-Co₃O₄ NWs. Inset shows the Randles equivalent circuit for NGA-Co₃O₄ NW based electrode/electrolyte interface.

Figure 4.1. Optimal images of the aerogels before (a) and after calcination (b).

Figure 4.2. TGA analysis for the oxidized CNTs.

Figure 4.3. a-e) SEM images of the $V_2O_5 \cdot xH_2O/CNTs$ aerogel obtained from direct cryodessication. f) SEM image for the $V_2O_5/CNTs$ aerogel after calcination. Yellow arrows mark the positions of CNTs.

Figure 4.4. TEM images of the freeze-dried aerogel.

Figure 4.5. Element mapping of carbon, oxygen and vanadium in the freeze-dried aerogel by using EDX technique.

Figure 4.6. a) XRD pattern of VCN. b) XPS spectrum of VCN. c) High-resolution XPS spectrum for vanadium.

Figure 4.7. a, b) CV profiles of VCN (a) and VN (b). c) Galvanostatic discharge/charge curves of VCN electrode at different current densities.

Figure 4.8. Comparison of rate capabilities among VN and VCN samples with different CNTs contents.

Figure 4.9. a) Cycling performance of the 9.2%-VCN electrode at 100 mA g^{-1} . b) Cyclability of the 9.2%-VCN electrode at a high current density of 1000 mA g^{-1} .

Figure 4.10. EIS plots of VCN and VN-based half-cells. Insets show the enlarged picture and Randles equivalent circuit of the electrode/electrolyte interface.

LIST OF SCHEMES

Scheme 2.1. Synthetic process of SnO₂ NCs@GA through hydrothermal route along with vacuum-assisted impregnation as preconditioning.

Scheme 2.2. Schematic comparison of SnO₂ NCs@GSs, SnO₂ NPs@GA and SnO₂ NCs@GA in terms of lithium access and electron transport. Compared with sphere-shaped nanoparticles, the NCs consisting of 1D nanorods provide additional active sites for lithium access, attributing to their increased electrode-electrolyte contact area. SnO₂ NCs grown on GSs (SnO₂ NCs@GSs) suffer from severe self-stacking, which results in shrinking of surface area. The graphene wrapping in SnO₂ NCs@GA can also accelerate the electron transport by providing more shortcuts to the graphene highway.

Scheme 3.1. Schematic illustration for the synthetic procedures of NGA-Co₃O₄ NWs.

Scheme 4.1 The scale-up synthesis of a large monolith. 16 g commercial V₂O₅ powders were used as the precursor. The volume of as-prepared aerogel is around 2 L. The diameter of the glass dish in the third picture is 19 cm.

LIST OF TABLES

Table 1.1. Summary of anode performance for 3DPGN-based composites in LIB.

Table 1.2. Summary of cathode performance for 3DPGN-based composites in LIB.

Table 1.3. Summary of capacitive performance for 3DPGN-based composites in supercapacitors.

Table 2.1. Comparison of lithium storage performance with other reported anode materials based on SnO₂/graphene.

Table 3.1. Combustible elemental analysis of undoped GA, NGA, NGA-Co(CO₃)_{0.5}(OH)·0.11H₂O NWs and NGA-Co₃O₄ NWs.

Table 3.2. Comparison of lithium storage performance from state-of-the-art anode materials based on graphene and Co₃O₄.

Introduction to the fundamentals of electrochemical and materials characterization techniques

X-ray diffraction is a powerful technique for the study of the atomic and molecular structure of a crystal. Crystalline atoms will cause the patterned diffraction of incident X-rays, according to the Bragg's law. By measuring the angles and intensities of these diffracted X-rays, crystallographers are able to obtain the d-spacings of a mineral, and further identify the mineral for the d-spacings of each mineral is unique.

The nitrogen adsorption/desorption isotherm is a method to probe the surface area and porosity of a solid material, by measuring the amount of nitrogen molecules physically absorbed on solid surface. **Brunauer-Emmett-Teller (BET) theory** is derived from the Langmuir theory. It calculates the surface area of a solid material based on the model of multilayered gas molecule adsorption. **Barrett-Joyner-Halenda (BJH) analysis** is a method used to determine the pore size distribution, and typically involved in nitrogen adsorption/desorption isotherm for mesoporous materials measured at 77 K. This method applied modified Kelvin equation to correlate the size of pores with the amount of adsorbate disassociated from the pores, which is reflected by the reduction of P/P_0 . **Density functional theory (DFT)** refers to a computational quantum mechanical modelling method, which is frequently used in physics, chemistry and materials science. In related to pore size distribution, a function of pressure and pore width were correlated by using nonlocal mean field theory for individual slit pores to predict the adsorption isotherm. Then the pore size distribution can be calculated by fitting this correlation to the experimental adsorption isotherm data.

In electrochemistry, **cyclic voltammetry (CV)** is performed by ramping the potential of a working electrode linearly versus time, and recording the resultant current. In this way, the current can be measured under conditions where voltage is in excess of that predicted by the Nernst equation. The involved reduction and oxidation processes are reflected by current peaks shown on CV graph.

A **galvanostatic charge/discharge** for lithium ion battery is a measurement which controls the current through an electrolytic cell constant, and record the changes of voltage as a function of time.

Electrochemical impedance spectroscopy (EIS) is applied to the characterization of electrode processes and complex interfaces. It investigates the variation of the impedance for an electrochemical system when a small amplitude alternating current perturbation of different frequency was applied. In practice, a function of frequency is used to represent the time-domain of the input and output signals. Analysis on the system response could provide relevant information about the interface, structure and reactions taking place. Different data plots such as the Nyquist, Bode phase and Bode modulus plots are often used in impedance spectroscopy.

An **electron microscope** is a microscope that uses electron beams instead of visible

light as a source of illumination, in order to increase the resolution for the microscope.

X-ray photoelectron spectroscopy (XPS) is a quantitative spectroscopic technology which measures the elemental composition of a material as well as electronic state of the elements exist within it. By irradiating a sample with a beam of X-rays, electrons will escape from the surface of sample. Analyzing the kinetic energy and number of escaped electrons will provide the elemental information about the sample.

Thermogravimetric analysis (TGA) is a thermal analysis where the temperature is linearly increased and the weight of sample is measured as a function of increasing temperature or heating time.

Chapter 1. Three-Dimensional Porous Graphene Networks and Derivative Hybrids for Next-Generation Lithium-Ion Battery and Supercapacitor

ABSTRACT

Recently, three-dimensional porous graphene networks (3DPGNs) including graphene aerogel (GA) generally formulated from self-assembly of graphene oxide (GO) sheets, and graphene foam (GF) first prepared from nickel foam (NF) templated chemical vapor deposition (CVD) approach have aroused tremendous research interest. The intrinsic exceptional assets of both 3DPGNs and functional components render their composite materials the synergic properties that can be useful in a variety of applications, especially related to electronic or electrochemical devices. In this chapter, the latest advancements of the 3DPGN-based hybrids and their promising potential for next-generation power tools will be discussed. Firstly, typical synthetic methods for the preparation of 3DPGNs of different structures as well as their derivative hybrids are introduced, and their pros and cons are also deliberated. Then, state-of-the-art of 3DPGN-based hybrids in applications of electrochemical energy storage are reviewed. Lithium-ion battery (LIB) and supercapacitor with special focus on powering flexible electronics will be highlighted.

1.1 Introduction

Over the past decade, with the rapid development in consumer electronics, healthcare industry, information technology and electric/hybrid vehicles, the demands for various sustainable distributed energy supplies continue to proliferate. Electrochemical energy storage nowadays has become a practical technology of choice for portable and rechargeable power source, intermittent generators and even smart grids which are powered by traditional energy sources.^[1] In efforts to realize economic, efficient, safe, clean and sustainable electricity storage, rechargeable lithium-ion battery (LIB) and supercapacitor have been successfully commercialized for a wide range of real-life applications.^[2, 3] However, despite their great success, the conventional batteries and capacitors can hardly meet the challenging demands of market nowadays. To enhance the energy and power density, cycle life, and charge rate via development of novel electrode materials, based on current schemes of LIB and supercapacitor, is one of the most promising and reliable approaches that lead to the next-generation energy storage. Porous materials with hierarchical structuration have kindled a light in recent development of energy storage and conversion systems, on account of their large surface areas for reaction, interfacial transport and dispersion of active phases, as well as the shortened diffusion paths in porous matrix.^[4] Hierarchical porous materials are

widely utilized as host to support and stabilize other active phases, in order to take full advantage of them. Moreover in the case of porous carbons, they even offer additional electrically conductive element, which is essential for the high performance of electrical devices. Porous electrodes can intrinsically enhance the performance of LIB and supercapacitor, which includes not only energy density, but also the rate capability as a result of the facilitated kinetics of charge diffusion within the bulk electrodes. Take LIB as example, theoretically, the diffusion time of lithium ion to active site is determined by the diffusion length and the diffusion coefficient, of which the relationship could be described as $\tau_{eq} = \frac{l^2}{D}$. To decrease the diffusion time (τ_{eq}), one can either increase the lithium conductivity (D), or shorten the diffusion path (l), of which the latter can be achieved by porous electrodes. Practically, the latter approach is more feasible, and also more effective than the former one for the square relationship.^[5] In respect of supercapacitors which store charges through either interfacial adsorption or surface faradic reactions, porous structures are also beneficial to the electrode performance by providing large electrode/electrolyte contact.

In the efforts to acquire materials for high-performance energy storage, three-dimensional (3D) graphene monolith with interconnected cellular network emerged as a promising candidate among various porous scaffolds.^[6, 7] Graphene (G), the two-dimensional, atomically thin carbon crystal, can materialize stimulating electronic, thermal and mechanical properties.^[8, 9] The ideal single-layered graphene sheet

embodies ultrahigh electron mobility of more than $15000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at room temperature, with ultralow resistivity calculated to be $10^{-6} \Omega \text{ cm}$, even below that of silver. Graphene is also prominent for its large theoretical surface area, $2630 \text{ m}^2 \text{ g}^{-1}$. However, when processed in bulk, graphene sheets would inevitably restack into graphite-like powders or films, during which their accessible surface would irreversibly shrink by 2-3 orders of magnitude. Alternatively, if fabricated into 3D hierarchical frameworks, the balanced space organization would radically relieve the self-restacking of graphene layers, meanwhile, the 3D materials also inherit the intrinsic physical properties of 2D graphene. Through formation of porous channels, the 3D spongy form of graphene has shown much higher surface area than aggregates of 2D sheets. Especially in energy-related applications, porosity became a determinative advantage for 3D porous graphene network (3DPGN) over its 2D counterparts. Typical 3DPGNs reported in literature include graphene aerogel/hydrogel (GA), generally formulated from self-assembly of graphene oxide (GO) sheets, and graphene foam (GF), first prepared from nickel foam (NF) templated chemical vapor deposition (CVD) approach. Despite the diversity in preparation and morphology, GAs and GFs are defined by similar structure layout based on porous network and intriguing physical and mechanical properties.

Development of novel 3DPGN-based hybrid materials currently arouses tremendous research interest. The intrinsic exceptional assets of both 3DPGN and functional

component render their composite the synergic properties that can be useful in a variety of applications, especially related to electronic or electrochemical devices. In this chapter, the latest advancements of the 3DPGN-based hybrids and their promising potential for next-generation power tools will be discussed. Firstly, typical synthetic methods for the preparation of 3DPGNs of different structures as well as their derivative hybrids are introduced, and their pros and cons are also deliberated. Then, state-of-the-art of 3DPGN-based hybrids in applications of electrochemical energy storage is reviewed. Lithium-ion battery and supercapacitor with special focus on powering flexible electronics are lighted. So far, several review articles already presented comprehensive descriptions on diverse 3D graphene (network, papers,^[10] tubes,^[11] spheres,^[12] scrolls,^[13] crumbled graphene^[14] and so on) as well as their derived composites, from preparation, structuration to application.^[7, 15-18] However, very few articles are dedicated to reviewing the specific 3DPGN-based hybrids and therefore it is still necessary to summarize the up-to-date progress in this field, in order to provide a more targeted, balanced and evolutionary perspective. In this original review chapter, those 3D graphene species without network layout or porous geometries will not be included.

1.2. Structures and fabrication of 3DPGNs

1.2.1. Graphene aerogel

1.2.1.1. Hydrothermal/solvothermal reduction. Graphene hydrogels/aerogels are basically developed from self-assembly strategy with GO sheets as the precursor. Xu et al. first reported the preparation of GA monolith (**Figure 1. 1a, b**) from a facile method of hydrothermal-induced self-assembly in 2010.^[7, 19] The reaction started with concentrated GO suspension, in which the GO sheets would be homogeneously dispersed in water, through a force balance between the electrostatic repulsion from the functional groups and the Van der Waals attraction from basal planes of graphene. Then a hydrothermal treatment was applied, during which the removal of major hydrophilic groups and concurrent restoration of the π -conjugation would break the force balance. Driven by the increasing hydrophobicity and π - π stacking interactions, reduced graphene oxide (RGO) sheets will interlock with each other and finally self-assembled into a 3D skeleton, known as the graphene hydrogel or the freeze-dried graphene aerogel. As shown in **Figure 1. 1c**, the microscopy of GA was revealed as a hierarchical macroporous network, assembled from 2D graphene sheets. In 2011 the same group also extended a solvothermal route to the preparation of GA, showing the possibility of introducing specific guest components in organic environments.^[20]

Due to the unique π - π stacking between the partially overlapped graphene, the hydrothermally reduced GA has shown superior mechanical strength (a storage

modulus of 450-490 kPa) and elasticity (elastic modulus of 290 kPa and yield stress of ~24 kPa) comparable to other crosslinked polymer hydrogels.^[21] GA also inherited the remarkable physical and physiochemical properties from its graphene building block. To name a few, it is suggested the Brunauer-Emmett-Teller (BET) surface area and electrical conductivity of GA could achieve 100-700 m² g⁻¹ and 0.5 S m⁻¹, respectively.^[7, 18] To exploit those exclusive properties, GA has been extensively hybridized with other functional components, including metals and alloys, inorganic elements and compounds (metal oxides/sulfides), organic molecules/polymers, carbon nanotubes (CNTs)/fullerene, etc.

Figure 1. 1. a, b) Digital photos of graphene hydrogel/GA synthesized from hydrothermal approach. c) SEM of the hydrothermal GA. Reproduced with permission from ref. [19]. Copyright 2010 American Chemical Society. d-f) SEM images of graphene elastomer, scale bar 10 μm . g) Scheme of the freeze casting approach, and formation mechanism of graphene elastomer. Reproduced with permission from ref. [33]. Copyright 2012 Macmillan Publishers Limited.

1.2.1.2. *In-situ* chemical reduction. After discovering the formation mechanism of GA, another *in-situ* chemical reduction is rationally proposed as the alternative strategy to trigger the self-assembly of graphene sheets. Unlike the hydrothermal methodology which requires high temperature and pressure, the chemical reductions can run in water/oil bath without autoclaves. Moreover, the reduction of GO could be further controlled by using different reducing agents and adjusting their concentration. By applying strong reductants, GO could be reduced more thoroughly, accompanied with increased ratio of restored π -conjugation.^[22] As a result, the aerogel itself would be more consolidated. L-ascorbic acid was a potent reducing agent and antioxidant. Zhang and co-workers use it to reduce GO and form a 3D monolith of graphene.^[23] It is measured that this chemically reduced GA is capable of supporting more than 14000 times of its own weight, and the corresponding Young's modulus in the elastic and yield regions are within 1.2-6.2 MPa and 0.3-2.2 MPa respectively, both higher than the ~ 290 kPa and ~ 24 kPa reported in the case of the hydrothermal GA. More remarkably, it also delivered a super-high conductivity approaching 100 S m^{-1} , 2-3 orders of magnitude higher than the hydrothermally produced GA, which is ascribing from the deeper

reducing state of RGO.^[7, 19] In addition to being used as additives, some reductants could also serve as functionalizing molecules, to crosslink graphene sheets or decorate their surface. In a Chen et al.'s work,^[24] instead of using organic reductants, they employed reductive metallic salt to react with GO, and realized the formation of GA with the decoration of metal oxide nanoparticles inside the 3D network simultaneously. In addition, ethylenediamine ethylenediaminetetraacetic acid, NaHSO₃, Na₂S, Vitamin C, HI, and hydroquinone were proven effective for fabrication of GA through mild chemical reduction.^[25-27]

1.2.1.3. Ice-segregation-induced self-assembly (ISISA). Direct cryodesiccation of highly concentrated dispersion of nanoparticles is a scalable methodology, developed in this decade for production of lightweight cellular monolith of ceramic, polymeric, metallic and carbonaceous materials with highly sophisticated 3D structures, including CNTs and bacteria aerogels. The mechanism is named ice-segregation-induced self-assembly (ISISA),^[28-30] which has also inspired an easier synthetic strategy for cellular graphene assembly. Generally, this synthetic approach starts with a cryogenic solidification of aqueous suspension of graphene (oxide) sheets, during which the phase segregation process will be induced and simultaneously the solid nanosheets will be expelled from the growing crystalline ice. As a result, graphene sheets will be condensed in the boundaries between adjacent ice crystals. Once the fraction of

nanosheets reached the percolation threshold, these entrapped graphene sheets will be self-assembled to afford a continuous framework. Due to the high anisotropy of ice crystallization (differed by 2-3 orders of magnitude for different growing directions),^[31]^{32]} the 2D GO sheets will be directed to align along the moving solidification front, and eventually generate a relatively ordered macroporous architecture. Lately, upon high-vacuum sublimation of ice phase, only the graphene sheets will be left to form a macroporous aerogel, characterized by continuous “walls” enclosing voids originally resided by ice phase.

Contributed by the amphiphilicity of GO sheets, their cryogenic and gelation process involve ice crystals as the hard template usually doesn't require any polymers or surfactants. In addition, due to the light weight of graphene sheets and large pore size originated from ice crystals, the resulted GA are frequently featured with extremely low density. Ling et al. reported a super-elastic aerogel-like graphene elastomer created from freeze casting, a process based on ISISA.^[33] The highly ordered cellular structure of the graphene elastomer was demonstrated by **Figure 1. 1d-f**, and **Figure 1. 1g** depicted the schematics of the freeze casting method, as well as the formation mechanism of this cellular graphene monolith. In this instance, owing to the partial reduction of GO precursor before cryogenic process, the π - π stacking interlock between overlapped graphene was more consolidated compared with normal GO layers, therefore the structural integrity and stability was better secured upon further thawing.

A further reduction was conducted after the thawing step to enhance this π - π stacking, which consequently improved the structural robustness and overall electrical conductivity for the 3D monolith. The graphene elastomer showed an ultrahigh porosity of 99.98% and an ultralight density of $\sim 0.5 \text{ mg cm}^{-3}$, both much lower than 3D graphene formulated from other methods. The cork-like graphene elastomer exhibited strong mechanical properties. It is capable of being compressed to at least 80% strain and recovery rapidly with a speed of $>7,000 \text{ mm min}^{-1}$. Its intern structure can sustain over 50000 times of its own weight without collapse.

In another work, Sun et al. reported a multifunctional, flyweight aerogel composited from chemically exfoliated GO and commercial CNTs, proven to be the lightest materials in this world.^[34] This all-carbon aerogel formed from cryodessication demonstrated a tunable density down to 0.16 mg cm^{-3} , and a super-elasticity invariant to temperature (from $-190 \text{ }^{\circ}\text{C}$ to $900 \text{ }^{\circ}\text{C}$). Adding to the common features shared by GA-like materials, the synergistic combination of 1D CNTs ribs and 2D giant graphene sheets in this all-carbon aerogel, greatly enhanced the temperature-irrelevant elasticity, thermal stability, elasticity-response conductivity and absorption capacity of organic liquid and phase-change materials.

1.2.2. Graphene foam

1.2.2.1. CVD method with NF template. GFs are created primarily from templating strategy. The very first graphene foam is fabricated from the *in-situ* chemical vapor deposition (CVD) of graphene using NF as both substrate and hard template, followed by etching of Ni foam with assistance from poly(methyl methacrylate) (PMMA) protective coating layer in order to strip the hollowed graphene skeleton.^[6] Detailed fabrication procedures were illustrated by the scheme in **Figure 1. 2a**, and morphology of GF was examined with scanning electron microscopy (SEM) and transmission electron microscopy (TEM), as exhibited in **Figure 1. 2b, c**. GF derived from this method has combined the advantageous structure of interconnected 3D network and the superior properties of pristine graphene grown by CVD. Compared with the chemically reduced graphene oxide, of which the graphitic lattice has been irreversibly damaged during harsh exfoliation of graphite (even the reduction process will only restore a part of the defective hexagonal rings), these graphene grown by CVD method is relatively flawless, and much more crystalline, robust and electrically conductive. Different from the strategy to assemble numerous small graphene building blocks into a 3D network, the conception of this GF is to grow a 3D seamless and continuous graphene. Therefore, the thickness of graphene in this GF is limited to averagely 3 layers (according to calculation), thanks to which overlaying of graphene surface and the interlayer resistance were both substantially alleviated. Correspondingly, the BET surface area of the GF reached $850 \text{ m}^2 \text{ g}^{-1}$, and the electrical conductivity could be augmented to and

1000 S m^{-1} , which is 3-4 orders of magnitude higher than the hydrothermal GA. The GF also showed remarkable electromechanical stability as compared with other flexible materials including graphene film.^[35] After bending the GF for 10000 cycles to a radius of 2.5 mm, there is only a small increase of resistance ($\sim 2.7\%$). The resistance of GF would irreversibly increase after stretching, but the changes would be stabilized after 5 cycles of stretch-release. From the 6th cycle onward, the resistance would maintain a constant value while released, and increase by $\sim 30\%$ under 50% stretching.

CVD method is considered as a double-edged sword: it is capable of synthesizing high-quality graphene in a large scale, but on the other hand, it is also costive and limited by expensive equipment. Moreover, despite the remarkable properties of GF, the usage of NF requires etching of the hard template, coating and successive decomposition of protective polymers, which inevitably complicated the synthetic procedures and raised the cost. Therefore, it is still necessary to simplify the processing.

Figure 1. 2. a) Schematics showing the routes to prepare GF from NF templates and

CVD growth of graphene. b) SEM image and inset photo of GF. c) TEM image showing the graphene layers of GF. Reproduced with permission from ref. [6]. Copyright 2011 Macmillan Publishers Limited. d) Schematics showing the formation mechanism of the nanoporous GF. e, f) SEM and TEM characterization on the nanoporous GF. Reproduced with permission from ref. [47]. Copyright 2012 WILEY-VCH.

1.2.2.2. Other hard or soft templates. In the meantime, other hard templates besides NF were explored for preparation of GF. Apart from the bottom-up CVD method, direct attachment of GO sheets onto templates was also a choice for large-scale and feasible production. Templates assembled from numerous build blocks, such as silica spheres,^[36, 37] polystyrene beads,^[38-41] NaCl boxes^[42, 43] could construct 3D GF with highly ordered structure and allow proper control on pore size. Additionally, commercial sponge was also considered a cheap and available template.^[44-46] However, it is noteworthy that the GF prepared from the NF templated CVD is still superior to the many other counterparts abovementioned, in terms of electrical and mechanical properties.

Zhao's group devised the methyl group functionalized silica spheres with uniform diameter of 27.7 nm as the hard template, to build nanoporous graphene foam.^[47] As displayed in **Figure 1. 2d**, GO was used as the precursor, attached onto silica spheres by hydrophobic interactions, then calcination and HF etching processes were conducted in sequence to reduce GO and remove silica templates. The resultant GF showed controllable pore size of 30-120 nm (**Figure 1. 2e, f**) and ultra-high pore volume of $\sim 4.3 \text{ cm}^3 \text{ g}^{-1}$. Ascribing from these ultrasmall nanopores, specific surface area of this GF achieved $851 \text{ m}^2 \text{ g}^{-1}$.

Soft templates like emulsions or surfactant micelles were also explored for fabrication of 3DPGN with tunable pore size.^[38, 48] Huang et al. designed a general emulsion-based soft templating approach to synthesize GF with tailorable porosity.^[48] Various micro-nano emulsions as well as micelles including 3,3',5,5'-Tetramethylbenzidine (TMB), n-hexadecane, dimethyldimethoxysilane, cetyltrimethylammonium bromide, and poly(ethylene oxide)-b-poly(propylene oxide)-b-poly(ethylene oxide) type Pluronic triblock copolymers (F108) were explored to create porous structure after rational modification to acquire desired surface properties. Interfacial forces including π - π interaction, hydrophobic affinity or electrostatic interaction have played important roles in the formation of 3D network. Pore size of the as-formed GF, ranging from tens of nanometers to several micrometers, could also be controlled by using different emulsion templates, or even adding surfactants to adjust the diameters of emulsion templates.

1.3. Hybrids derived from 3DPGNs

In order to exploit the exceptional qualities of 3DPGNs, multifarious functional components have been incorporated with them to realize promoted performance in respective applications. Metals, alloys, inorganic elements/compounds and organic molecules/polymers were extensively introduced into 3DPGN with rational structures,

rendering 3DPGN a wide range of application potential in catalysis,^[49-52] waste absorption,^[26, 48, 53-60] energy conversion^[61-64] and storage,^[49, 65-67] biomedical applications^[68-70] and so forth. 3DPGN-based hybrid materials can be synthesized either from one-step or multi-step approaches. The one-step approaches enable the formation of 3DPGN with simultaneous decoration of guest materials. Alternatively, the construction of host framework and introduction of secondary phases can be realized in separate procedures. Most multi-step synthesis relies on post-modification of 3DPGNs, but there are also rare cases in which the guest phases were first coordinated with 2D graphene and then the composites were assembled into 3D matrix. Hydrothermal/solvothermal treatments,^[65, 71-74] *in-situ* chemical reactions,^[24, 75, 76] electrodeposition,^[77-81] CVD,^[82, 83] co-gelation^[84-86] etc. are frequent approaches for the integration of guest components.

1.3.1. GA-based composites

1.3.1.1. Inorganic phases/GA. Hydrothermal/solvothermal is one of the mainstream methods for formation of highly crystalline and nanotextured inorganic materials, meanwhile it is also a convenient approach to realize the self-assembly of GO sheets. In addition, the oxygen groups on GO could serve as the active sites to anchor guest clusters. Therefore, one-step combined synthetic strategy can be realized through the

hydrothermal/solvothermal approaches. Multi-step hydrothermal/solvothermal synthesis is only considered when the guest phase is complicated or specific structural sophistication is required. Noble metallic nanoparticles, e.g. Ag,^[87] Au,^[52] Pt,^[88-90] Pd,^[91] Rh,^[92] were frequently introduced into GA for electrocatalysis or bio/chemical sensors, with improved mass transfer and optimized accessibility of reactants by the 3D porous architecture. Transitional metal oxides/sulfides and other semiconducting compounds are the major group of candidates that benefit most from the combination with 3DPGNs, due to their scarcity of electrical conductivity. Regarding this aspect, GA supported Fe₂O₃,^[72, 93-96] Fe₃O₄,^[61, 97-100] TiO₂,^[49, 101] SnO₂,^[102, 103], V₂O₅,^[104, 105] Co₃O₄,^[74] CoO,^[106] ZnO^[107], MoS₂,^[108-112] CoS,^[113] LiS,^[114] Si,^[115] were thoroughly examined for LIB, supercapacitor, light harvest, fuel cell, sensor and so forth.

An inspiring study from Qiu and co-workers reported the ultradispersed mesoporous TiO₂ nanocrystals *in-situ* grown on GA surface, via a facile one-step hydrothermal method.^[49] They used glucose in this process to hinder the agglomeration of particles and concurrently shape the growth of TiO₂ nanocrystals, hence generating TiO₂ nanostructures with high exposure of (001) facets (up to 50%) and uniform size distribution. The hydroxyl groups on both ends of glucose would be respectively connected to graphene surface and TiO₂ seeds, serving as linker to direct the growth of TiO₂ *in-situ* onto GA surface. Moreover, during the crystal growth, glucose anchored on graphene surface would continue to act as face-growth inhibitor, creating unique

hollow mesoporous channels in between graphene and TiO₂. Employed as LIB anode, this hybrid delivered a capacity of 99 mA h g⁻¹ at a very high rate of 5000 mA g⁻¹, 4 times higher than TiO₂ nanocrystals.

Figure 1.3. a, b) Morphology of Pt/3D RGO. c, d) SEM images of 3D RGO supported NiO/Ni. e) Scheme of the DSARA method. Reproduced with permission from ref. [77]. Copyright 2014 Royal Society of Chemistry. f) Synthetic routes for the GA functionalized with organic crosslinkers. Reproduced with permission from ref. [116] Copyright 2010 American Chemical Society

There are also many efforts devoted to the general and systematic methodology for fabrication of 3DPGN-based hybrids with desired functionality. Hu and co-workers designed a green and powerful approach, the dual substrate-assisted reduction and assembly (DSARA), to rationally coordinate GA with a series of metals, metal oxides, and even alloys and composites.^[77] As displayed in their work, the DSARA extensively enhanced the merits of implementing graphene in energy storage and conversion

systems including lithium-ion batteries, fuel cells, and photovoltaic devices. To demonstrate the versatility of this approach, Pt, Pd, Ag, Cd, Cu, Pb/PbO, Ni/NiO, Co₃O₄, and Pt-Pd alloy were successfully introduced into 3DPGN (**Figure 1. 3a-d**). This DSARA process sequentially realized three essences: the spontaneous reduction of GO, assembly of RGO to form 3DPGN, and the *in-situ* decoration of desired nanotextured components on RGO sheets. As mentioned in the schematics (**Figure 1. 3e**), during the synthesis, at first active substrates (e.g. Zn, Fe, Cu foils) were immersed in the aqueous dispersion of GO, reducing GO to afford the self-assembly of porous graphene network. Then this modified substrate was placed in the salt solution containing metallic precursors, followed by instant deposition of secondary phases via redox reactions of a galvanic cell. Here graphene act as the cathode to reduce and deposit the metal ions (M^{m+}) from solution, meanwhile the active metal substrate serves as the anode to be oxidized (from Sub^0 to Sub^{n+}) and then dissolved. The electrodeposition of a guest metal is theoretically possible as long as it has a higher redox potential (M^{m+}/M) than the substrate (Sub^{n+}/Sub^0), indicative of the wide range of metals that can be crafted onto 3D RGO via this method. Metals with relatively high activity are readily oxidized to different valence states, which enabled introduction of metal oxides for electrochemical energy storage. The NiO/Ni decorated 3D RGO exhibited record capacity and superior rate capability among the Ni-based nanomaterials. The Pd-Pt alloy crafted 3D RGO exhibited high catalytic activity for oxygen reduction reaction,

also shows adequate tolerance against possible methanol crossover effects, of which both are favored for potential application in direct methanol fuel cells.

1.3.1.2. Organic phases/GA. Organic molecules and polymers could enhance the mechanical, electrical or surface chemical properties of GA, further bestow graphene network with complementary functionalities. From chemical routes, the organic components can be introduced through either covalent bond or non-covalent interactions, and organic moieties usually served as either functional groups on individual graphene surface or crosslinkers in between overlapped graphene sheets to consolidate their adherence.

Crosslinking graphene sheets in 3D graphene by covalent bond could significantly increase the electrical conductivity and mechanical strength of the entire network. As shown in **Figure 1. 3f**, in a study from Worsley and co-workers,^[116] the authors used resorcinol and formaldehyde to react with oxygen groups on graphene and covalently crosslink the neighboring graphene sheets in GA. The bulk electrical conductivity of the product was increased by more than 2 orders of magnitude ($\sim 100 \text{ S m}^{-1}$), as compared to normal GAs assembled from physical bindings alone ($\sim 0.5 \text{ S m}^{-1}$). Li et al. reported the covalently linked graphene-polypyrrole (PPy) organogel, which improved the adsorption capacity of oil molecules and organic solvents for GA.^[117] Other covalent crosslinkers in GA includes chitosan,^[54] poly (vinyl alcohol) (PVA),^[55]

1,8-diaminooctane (OMDA),^[118] glutaraldehyde with resorcinol,^[119] etc.

Apart from being crosslinkers, organic moieties covalently bonded to basal planes of individual graphene sheet were also investigated in the cases of 3DPGNs combined with 2-aminoanthraquinone,^[120] paraphenylene diamine,^[121] and the poly(ethylene oxide)-block-poly(propylene oxide)-block-poly-(ethylene oxide) triblock copolymer.^[122] Zhu et al. reported a GA reduced by ethylenediamine, which served as both reductant and crosslinker at the same time.^[123] Then through salinization, the surface of graphene was further functionalized with bromoalkyl groups, which later would be used to conjugate with the pyridine groups on PH-sensitive block copolymers via quaternization. As a result, the surface of graphene organogel demonstrate a switchable superoleophilicity/superoleophobicity in response to the PH value of medium. It effectively absorbs oil and organic molecules from aqueous solution with their superoleophilicity at PH 7, and releases all the absorbates when condition switched to PH 3.

Non-covalent interactions such as π - π stacking, hydrophobic effects, Van der Waals forces could also be utilized for coordination of organic compounds with GA. In a work reported by Xu et al.,^[66] they utilized a dual-purpose hydroquinone as both reducing agent and functionalizing molecules attached to graphene through π - π stacking. The integration of hydroquinone molecules would secure a satisfactory pseudocapitance. As measured by atomic force microscopy (AFM), the height of functionalized graphene

sheets and normal GO sheets were 1.5 nm and 0.9 nm respectively. Considering the distance of π - π stacking between aromatic moieties (0.35 nm), it is suggested that hydroquinone was conjugated to both sides of graphene surface. The non-covalent binding strategy was also applied in many other studies for integration of hydrophobic organic polymers like epoxy resin^[124], Polyvinylidene fluoride (PVDF),^[125] welan gum,^[58] etc.

1.3.1.3. Doping strategy. Doping of heteroatoms (N, B, S, P etc) has been generally accepted as a useful strategy to upgrade graphene.^[126-128] It is also proven that in graphene networks, doping (usually N) can enhance the charge transfer between neighboring carbon atoms, and thus improve the electrical conductivity as well as electrochemical performance for 3DPGN-based hybrids.^[129-131] As a typical example, in a work reported by Mullen's group, ammonia boron trifluoride (NH_3BF_3) was employed for the co-doping of nitrogen and boron on GA.^[132] For comparison purpose, N doped GA (N-GA) and B doped GA were also fabricated, using dicyandiamide and boric acid as respective precursors of dopants. These flexible monolithic GA were further manufactured into a prototype device named all-solid-state-supercapacitor, with an electrode-separator-electrolyte integrated structure. B, N co-doped GA (BN-GA) exhibited the best performance among all sample electrodes, meanwhile those doped GA with single dopants were also much superior to undoped GA.

Due to the good activity of GO precursor, chemical doping of heteroatoms could be simultaneously achieved during the formation of GA-based composites, as a special bonus. For example, a one-step hydrothermal process was designed by the Mullen's group, where they used GO, iron acetate, and PPy to produce 3D nitrogen-doped GA (N-GA) supported Fe_3O_4 nanoparticles (NP).^[61] As suggested by XPS, PPy (20 mg) afforded 3.5% wt nitrogen heteroatoms for the final product. This hybrid material demonstrated exceptional performance in fuel cell for oxygen reduction reaction, with more positive onset potential, prohibited H_2O_2 yield, higher cathodic current density and electron transfer number as compared with Fe_3O_4 NPs supported by 2D N-doped graphene sheets or N-doped carbon black. It is suggested that those enhancements could be attributed to the macroporosity and high surface area of 3D graphene support. Recently, our group also developed a “killing three birds with one stone” strategy, to realize a sophisticated design that simultaneously integrates three desirable components, e.g. nitrogen dopant, 3D graphene host and 1D nanowires of guest phase into one hybrid material.^[133] The nitrogen content in our N-GA achieved 3.25 % wt as characterized by elemental analysis. Considering the mild reaction conditions compared to pyrolysis or gas-phase deposition,^[134-136] as well as the modicum of nitrogen precursor involved (0.05 M urea), this content of nitrogen heteroatoms is indeed more than sufficient.

1.3.2. GF-based composites

1.3.2.1. Inorganic phases/GF. The superior mechanical and electrical properties of the GF have constantly raised increasing interests, especially in the field of high-performance electrical devices. Fabrication of typical GF involves the CVD growth of graphene, infiltration and subsequent removal of protective polymers and etching of NF template. Due to the multiple steps engaged, further decoration of functional phases is mostly accomplished in separate procedures, but nonetheless allow appropriate control on mass loading and fine crafting on geometries for required sophistication, considering the geometric structures and surface features could substantially influence the physicochemical properties of the nanomaterials themselves.^[137, 138] Up to date, quite a number of inorganic compounds were successfully integrated with GF, with well-defined morphology such as nanoplates, nanoflakes, nanosheets, nanowires, nanospheres, nanorods, hierarchical nanostructures and so on. The guest phases include metals, alloys, semiconductive elements, metal oxides/sulfides/hydroxides, ternary compounds, carbonaceous substances, composites and so on, to list a few, Pt,^[139] Pt-Ru,^[140] Si,^[44, 141, 142] Sn,^[42] Fe₂O₃,^[67] Fe₃O₄,^[143] MnO₂,^[45, 78, 144, 145] ZnO,^[146, 147] NiO,^[81, 148] VO₂,^[149] V₂O₅,^[150] MoS₂,^[151] Li₄Ti₅O₁₂ (LTO)^[152] NiMoO₄,^[153] LiFePO₄ (LFP),^[154, 155] Li₂FeSiO₄,^[156] NiCo₂O₄,^[157] Ni₃S₂@Ni(OH)₂,^[71] CNTs^[158], etc. He et al. fabricated a free-standing ultrathin (<200 μm), lightweight (0.75 mg cm⁻²) and

superconductive (5500 S m^{-1}) GF, composited with MnO_2 hierarchical nanosheets via electrodeposition.^[78] Mass loading of active MnO_2 phase in this case reached 9.8 mg cm^{-2} , and 92.9% weight ratio of the flexible binder free supercapacitor electrode, much higher than hybrids composed from same components constructed on GA hosts. As a result of this high loading, the composite delivered a remarkable area capacitance of 1.42 F cm^{-2} at a scan rate of 2 mV s^{-1} . For a proof-of-concept application, two pieces of this flexible electrodes and one membrane separator could be assembled into a symmetrical supercapacitor of sandwich layout, encapsulated in polyethylene terephthalate membranes. The whole weight is less than 10 mg and thickness is $\sim 0.8 \text{ mm}$, and can be bent to arbitrary angels without failure of device.

Figure 1. 4. a-d) Morphological characterization on GF (a), VO_2 nanoarrays on GF (b), and GF supported $\text{VO}_2@\text{GQD}$ nanoarrays (c, d). Reproduced with permission from ref. [159]. Copyright 2012 American Chemical Society. e-h) Morphology of Ni_3S_2 nanorod@ $\text{Ni}(\text{OH})_2$ nanosheet core-shell nanostructures on GF. Reproduced with permission from ref. [114]. Copyright 2013 Royal Society of Chemistry.

In a Chao and co-workers' work (**Figure 1. 4a-d**), VO_2 nanoarrays were bottom-up

grown on both sides of graphene in the GF network, and subsequently coated with graphene quantum dots (GQD).^[159] As revealed in **Figure 1. 4d**, the coating of GQDs could be directly visualized from high-resolution TEM, and it served as an efficient surface “sensitizer” and protection on VO₂ surfaces, which can further boost the electrochemical properties. As a binder-free electrode, this hierarchical hybrid delivered a Li-storage capacity of >420 mA h g⁻¹ and a Na-storage capacity of 306 mA h g⁻¹ at 100 mA g⁻¹. Corresponding capacity retention achieved 94% for LIB and 88% for Na-ion battery after 1500 cycles at current density of 18 A g⁻¹.

Zhang’s group designed a smart process which employed NF as the precursor for the growth of Ni₃S₂ nanorod@Ni(OH)₂ core-shell nanostructures inside GF, with relevant morphology shown in **Figure 1. 4e-h**.^[71] In this way, NF will be consumed during the reaction so protective polymer coating and etching of template are no longer required, simplifying the overall synthetic procedures. Straightforwardly they used the graphene deposited NF to react with thioacetamide (C₂H₅NS). During the hydrothermal reaction, C₂H₅NS will first release S ions to react with the exposed Ni foam support. Small Ni₃S₂ particles will be nucleated on surface of graphene network, and further matured into nanorods at prolonged reaction times (e.g. 6 h). Further increase of reaction time to 12 h will lead to the partial hydrolysis of Ni₃S₂, and eventually the formation of Ni₃S₂ nanorod@Ni(OH)₂ nanosheet core-shell heterostructure. If the reaction time is longer than 24 h, all the Ni₃S₂ nanorods will be transmuted into Ni(OH)₂ nanosheets.

1.3.2.2. Organic phases/GF. Unlike the inorganic materials, organic polymers/GF hybrids are less reported, partially because of the chemical inertness of pristine graphene grown by CVD. Yet there are several studies documented the introduction of conductive polymers focused on supercapacitor applications, such as PPy,^[160, 161] polyaniline (PANI),^[162] and poly(3,4-ethylenedioxythiophene) (PEDOT).^[163] It should be mentioned that in most cases, these polymers are akin to physically embedded rather than chemically bond to GF.

1.4. Application in next-generation LIB and supercapacitor

1.4.1. Lithium-ion battery

Lithium-ion battery has revolutionized consumable electronics, but now its adoption in electrical and hybrid vehicles are critically confined by its own high cost, lack of safety, low energy density and slow charge rate. Development of electrode candidates with high capacity and rapid charge rate is imperative to unlock the full potential of next-generation LIB, which in turn heavily relies on the rational design and efficient production of novel electrode materials. Since the first exfoliation single-sheet graphene by scotch tape, it has been considered as a very promising conductive support

for lithium-storage materials. 3D graphene has imparted the exceptional electrical and mechanical properties of 2D graphene to the advantageous 3D structural layout. Distinct from other 3D metallic or polymeric scaffolds, 3DPGN materializes several unique properties that are favored principally in electrochemical energy storage and conversion systems. In LIB, a support material of high porosity and electrical conductivity would decisively enhance the gravimetric energy density, rate capability, cycle life for the active phases. In this sense, 3DPGN is the ideal host for the majority of LIB active phases.

1.4.1.1. Anode. In this section, the recent progress of innovative anodic composites based on 3DPGN will be discussed. For clarity sake, herein they are divided into three categories according to the lithium-storage mechanisms of the respective active phases hosted by 3DPGN. LIB performance of these hybrids was tabulated in **Table 1.1**. Some of the representative composites are chosen under each category to illustrate the remarkable improvement brought by 3DPGN.

- 1) Alloy/de-alloy anodes such as Si, SiO, Sn, SnO₂, Ge, etc;
- 2) Conversion anodes such as the majority of transition metal oxides and metal sulfides;
- 3) Intercalation/deintercalation anodes, such as carbonaceous materials, TiO₂, LTO, etc;

Figure 1. 5. a) SEM image and digital photo (inset) of the 3D G network. b) SEM images of the 3D G-Si network. c) Capacity-voltage profiles at 200 mA g⁻¹, from 2 to 0.005 V versus Li/Li⁺. d) Rate capability e) Cycling performance accompanied with coulombic efficiency, at 200 mA g⁻¹. Reproduced with permission from ref. [91]. Copyright 2015 WILEY-VCH.

The next-generation LIBs are expected to power electrical vehicles as well as stationary utilities, so specific capacity is a fundamental criterion to assess an electrode candidate. As one of the most promising groups of anode candidates, alloying mechanism-based materials are prominent for their ultrahigh theoretical capacities, which ranges from 783 mA h g⁻¹ (SnO₂) up to 4211 mA h g⁻¹ (Si). Among them, Si is the most evaluated

one for both highest gravimetric capacity (4200 mA h g^{-1} , $\text{Li}_{22}\text{Si}_5$) and volumetric capacity ($9786 \text{ mA h cm}^{-3}$) over all other anodic candidates. However, although the alloying mechanism allows one portion of Si to react with multiple lithium ions, it nevertheless causes severe volume expansion (even up to 400%) of electrode, resulting in cracking and pulverization, and leading to huge capacity loss and very poor cycle life. Spatial accommodation and confinement are the two general strategies against the volume expansion. From the former approach, 3DPGN stands as an ideal support to buffer the volume changes by the flexible 2D sheets and large void space of pores.^[44, 141, 142, 164-169]

Various carbonaceous materials have long been composited with Si, to harness its ultrahigh capacity more productively. Recently, a 3D graphene scaffold derived from commercial sponge and coated with silicon layer (denominated as 3D G-Si network) was reported for cheap and large-scale fabrication of free-standing flexible electrodes.^[44] Preparation of this 3D graphene avoids usage of costly NF and CVD method, and hence are favored for cost-effective production. Morphology of the as-prepared 3DPGN and 3D G-Si network were respectively shown in **Figure 1. 5a, b**. As indicated by the rate capability measurements shown in **Figure 1. 5c, d**, high rate performance of this materials is very impressive: even in a rapid charge/discharge process (current density of 3200 mA g^{-1} , charge/discharge in 1181 s), it still delivered a capacity of 950 mA h g^{-1} in the voltage range of 0.005-2 V. As indicated in **Figure 1.**

5e of the cycling performance, the 3D G-Si network delivered a remarkable reversible specific capacity of 2450 mA h g^{-1} in the first 30 cycles at current density of 200 mA g^{-1} , and still retained over 2050 mA h g^{-1} after 200 cycles.

In another interesting work, Jing et al. implemented Si into a graphene/CNTs aerogel (carbon aerogel, CA) with face-to-face contact and balanced open void through a CVD approach.^[170] It is advised that the engineered face-to-face contact between Si and the support enabled efficient and rapid electron transportation, and the balanced open-void provided enough space to accommodate Si expansion. Consequently, this nanohybrid demonstrated 96% capacity retention over 270 cycles at 400 mA g^{-1} , and little capacity loss for subsequent 2000 cycles at a high current density of 10 A g^{-1} . As confirmed from morphological characterizations, in this hybrid 3D network, graphene and CNTs were mutually interlaced, with consolidated structural integrity. Therefore, the high reversible capacity (1498 mA h g^{-1} at 200 mA g^{-1}) and excellent rate capability (462 mA h g^{-1} at 10 A g^{-1}) exhibited by Si/CA exceeds not only the undefined Si/graphene-CNTs mixture, but also Si/GA and Si/CNTs aerogel. It is well-grounded in literature that the synergy between graphene and CNTs can further elevate the electrical conductivity, mechanical resilience and stiffness for 3DPGNs.^[34, 171-174]

Among the alloying materials, SnO_2 also attracted a lot of interests for its abundance in earth and environmental benignity. The carbon coated SnO_2 NPs on highly oriented GA support, prepared by Huang et al. through a novel approach of ice-templating co-

assembly of metal oxide/GO composite and PVA followed by thermal treatment. The composite product showed periodic macropores originated from the ISISA, as well as adequate mass loading of active phase (~70%). As LIB anode, the carbon/SnO₂/GA product achieved an excellent reversible capacity of 1665 mA h g⁻¹ (0.2 A g⁻¹, 200 cycles) and rate capability of 300 mA h g⁻¹ at 10 A g⁻¹.^[175] In addition, the preparation protocol could further be extended to implement cathode materials such as FePO₄.

The conversion mechanism is relatively modest compared with alloying, thus associated with less capacity as well as volume expansion. On the other hand, conversion anode materials, including most transition metal oxides and metal sulfides, also possess relatively high reversible capacities (500-1000 mA h g⁻¹), contributed by the multiple electrons participated in conversion reactions. For similar motivations like alloying materials, 3DPGNs are also intensively engaged in conversion-based composites, as provided in **Table 1.1**. For example, Mullen's group reported a 3D GA network crosslinked by Fe₃O₄@graphene sheets core-shell nanoparticles, with decent lithium-storage performance.^[97] Adding to the 3D flexible network which accommodates volume expansion of metal oxide to certain extent, the purposely assembled graphene shell provides additional confinements against Fe₃O₄ expansion. In their synthesis, modified Fe₃O₄ nanospheres and GO sheets were first electrostatically self-assembled to form a core-shell structure, followed by hydrothermal reaction with extra GO suspension to afford the 3D network. The

interlocked network generated a characteristic 3D macro-meso porosity for the hybrid with a high specific surface area of $114.5 \text{ m}^2 \text{ g}^{-1}$. For comparison, surface area of the 2D counterpart ($\text{Fe}_3\text{O}_4/\text{graphene sheets}$) is only $8.1 \text{ m}^2 \text{ g}^{-1}$. The product delivered a stable specific capacity of 1060 mA h g^{-1} over 85 cycles at 100 mA g^{-1} , much superior to the control group of 2D structuration.

The 3D Ni/NiO@RGO hybrid prepared from above-mentioned DSARA method achieved a record capacity of 1493 mA h g^{-1} at 0.5 A g^{-1} for over 100 cycles.^[77] More remarkably, even at a high current density of 10 A g^{-1} , a reversible capacity of $\sim 600 \text{ mA h g}^{-1}$ can still be delivered for 1000 cycles. At 20 A g^{-1} , the capacity remains $\sim 415 \text{ mA h g}^{-1}$ over 2000 cycles. This exceptional cycling and rate performance is the much superior to other reported Ni or NiO-based materials.

Aside from transitional metal oxides, metal sulfides, the other type of conversion materials, have emerged for their abundant existences in nature, high theoretical capacity and high lithium activity. Among them, MoS_2 , SnS_2 with special layered crystal structures are most useful as LIB anode.^[176, 177] **Table 1.1** also recorded some representative composites consisted of layered metal sulfides and 3DPGNs. Gong et al. fabricated a GA backboned MoS_2 hybrid via a one-step hydrothermal route with hydrazine as additional reductant.^[109] The hybrid achieved an extraordinary specific surface area as high as $285 \text{ m}^2 \text{ g}^{-1}$, with 85% weight ratio of active content. High-resolution TEM and element mapping revealed the homogeneous distribution of MoS_2

on graphene surface, and the building block of composite nanosheets had a uniform thickness around 2-3 nm as indicated by cross-sectional AFM. In LIB anode, the MoS₂/GA hybrid achieved an impressive reversible capacity of 1200 mA h g⁻¹ at 0.5 C (1 C = 1200 mA g⁻¹), and retained near 100% for 30 cycles. The rate capability was also exceptional: high reversible capacities of 620 and 270 mA h g⁻¹ were delivered at 12 C (5 min charge) and 140 C (25 s charge), respectively. Most importantly, MoS₂/GA composite showed very high cycling stability at various charge/discharge rates. The electrode demonstrated almost no capacity decay for 3000 cycles at any selected high rates, 12 C, 43 C and 140 C.

Insertion/deinsertion-based materials have been chosen as anodes since the commercialization of rechargeable lithium-ion battery. Lithium ions periodically intercalate/deintercalate in the tunnels of host crystals, which almost generates zero or few strain effect and thus providing good recyclability for battery. The poor specific capacity of these materials, on the other hand can be enhanced by downsizing the particles or using porous hosts to distribute the particles and prevent their future agglomeration. **Table 1.1** documented several typical composites based on 3DPGNs and intercalation phases, with comparison of their lithium storage performances. Yu et al. prepared a novel composite of mesoporous anatase TiO₂ submicrospheres embedded in GA, for enhanced lithium storage. The mesoporous TiO₂ (MTO) spheres comprised from numerous smaller nanocrystals were prepared via low-temperature water-bath

reaction beforehand, followed by hydrothermal co-assembly with GO sheets. The freeze-dried hybrid aerogel showed well-dispersed TiO₂ submicrospheres within the porous network. Adding to the preferable transport kinetics of lithium ions and electrons within the advantageous 3DPGN, the mesoporous structure of TiO₂ further increased the direct contact area between active phase and electrolyte. As a result, a reversible capacity of 197 mA h g⁻¹ was delivered at the end of 100 cycles under 0.5 C current rate, even higher than the theoretical capacity of TiO₂ (170 mA h g⁻¹). In rate capability measurements, a high reversible capacity of 124 mA h g⁻¹ was maintained even at a rapid rate of 20 C, exhibiting improved capabilities than both pure MTO (38 mA h g⁻¹) and MTO supported by 2D graphene sheets (81 mA h g⁻¹). Moreover, when the charge current is set back from 20 C to 0.5 C again, 96% of the initial capacity could still be retained, suggestive of the good cycling stability of the hybrid aerogel.

Table 1.1. Summary of anode performance for 3DPGN-based composites in LIB.

Host	Guest component and structure	Synthesis of 3DPGN	Reversible capacity	Cyclability	Reference
Alloying phases					
GF	Si films	NF templated CVD	1.4 mA h cm ⁻² (0.22 mA cm ⁻²)	60 cycles	[142]
GF	Si coating	Sponge templated adsorption of GO	2025 mA h g ⁻¹ (200 mA g ⁻¹)	200 cycles	[44]
GF	Si/SiO _x core-shell nanowires	NF templated CVD	3603 mA h g ⁻¹ (840 mA g ⁻¹)	100 cycles	[141]
GF	Sn/graphene core-shell NPs	NaCl assembly templated CVD	682 mA h g ⁻¹ (2 A g ⁻¹)	1000 cycles	[42]
GA	Ultrasmall SnO ₂ NPs	Hydrothermal	474 mA h g ⁻¹ (10 A g ⁻¹)	1000 cycles	[165]
N-GA	antimony-doped SnO ₂ NPs	Hydrothermal	887 mA h g ⁻¹ (500 mA g ⁻¹)	110 cycles	[166]
Conversion phases					
GA	Fe ₂ O ₃ nanograins	Solvothermal	733 mA h g ⁻¹ (2000 mA g ⁻¹)	1000 cycles	[72]
GA	Polyhedron-like nanostructured Fe ₂ O ₃	NF templated CVD	864 mA h g ⁻¹ (200 mA g ⁻¹)	50 cycles	[94]
GA	Fe ₂ O ₃ NPs	Solvothermal	1071 mA h g ⁻¹	80 cycles	[95]

			(200 mA g ⁻¹)		
N-GA	Fe ₂ O ₃ nanocubes	Solvothermal	1121 mA h g ⁻¹ (500 mA g ⁻¹)	500 cycles	[96]
GF	porous α -Fe ₂ O ₃ nanorods grown on CNTS	NF templated CVD	>1000 mA h g ⁻¹ (200 mA g ⁻¹)	300 cycles	[67]
GA	Fe ₃ O ₄ /graphene core-shell Nanospheres	Hydrothermal	1059 mA h g ⁻¹ (93 mA g ⁻¹)	150 cycles	[97]
GF	Fe ₃ O ₄ nanospheres	PS sphere templated assembly of GO	859 mA h g ⁻¹ (2 A g ⁻¹)	1000 cycles	[98]
GA	Fe ₃ O ₄ nanoclusters	Solvothermal	577 mA h g ⁻¹ (5.2 A g ⁻¹)	300 cycles	[99]
N-GA	Fe ₃ O ₄ NPs	Hydrothermal	1130 mA h g ⁻¹ (100 mA g ⁻¹)	200 cycles	[100]
GF	Fe ₃ O ₄ NPs	NF templated CVD	785 mA h g ⁻¹ (1 C)	500 cycles	[143]
GA	FeOx coating	Hydrothermal	270 mA h g ⁻¹ (80 C)	1500 cycles	[109]
GA	CoO NPs	Solvothermal	730 mA h g ⁻¹ (1.6 A g ⁻¹)	50 cycles	[73]
PPy-GA	Nanorod-like CoO	Hydrothermal	743 mA h g ⁻¹ (100 mA g ⁻¹)	100 cycles	[106]
GF	Co ₃ O ₄ NPs	PS sphere templated vacuum filtration of GO	1004 mA h g ⁻¹ (50 mA g ⁻¹)	50 cycles	[178]
GA	Mesoporous Co ₃ O ₄ nanosheets	Copper foam templated CVD	523.5 mA h g ⁻¹ (25 mA g ⁻¹)	50 cycles	[179]
GA	Ni/NiO	Electro-reduction	1493 mA h g ⁻¹ (500 mA g ⁻¹)	2000 cycles	[77]
N-GA	ZnCoO ₄ NPs	Solvothermal	1102 mA h g ⁻¹ (100 mA g ⁻¹)	150 cycles	[180]
GA	MoS ₂ flocculent nanostructures	Hydrothermal	997 mA h g ⁻¹ (2 A g ⁻¹)	700 cycles	[181]
GA	MoS ₂ monolayer	Hydrothermal	1200 mA h g ⁻¹ (100 mA g ⁻¹)	200 cycles	[110]
GA	MoS ₂ nanosheets	Hydrothermal	1200 mA h g ⁻¹ (74 mA g ⁻¹)	30 cycles	[182]
N-GA	Carbon coated MoS ₂	Hydrothermal	900 mA h g ⁻¹ (200 mA g ⁻¹)	500 cycles	[112]
CNTs/GA	MoS ₂ quantum dots	Electrostatic spray deposition	886 mA h g ⁻¹ (1000 mA g ⁻¹)	100 cycles	[111]
GF	MoS ₂	NF templated CVD	1127 mA h g ⁻¹ (250 mA g ⁻¹)	100 cycles	[151]
GA	SnS ₂	Hydrothermal	656 mA h g ⁻¹ (50 mA g ⁻¹)	30 cycles	[183]
GA	SnS ₂ nanoplates	Hydrothermal	1060 mA h g ⁻¹ (100 mA g ⁻¹)	200 cycles	[184]
GA	MoSe ₂ nanolayers	Hydrothermal	470 mA h g ⁻¹ (0.5 C)	600 cycles	[185]
Intercalation phases					
GA	Mesoporous anatase TiO ₂ submicrospheres	Hydrothermal	197 mA h g ⁻¹ (1 C)	100 cycles	[101]
GA	TiO ₂ and SnO ₂ NPs	Hydrothermal	750 mA h g ⁻¹ (100 mA g ⁻¹)	100 cycles	[186]
GA	Mesoporous TiO ₂	Hydrothermal	99 mA h g ⁻¹ (5 A g ⁻¹)	50 cycles	[49]
GF	LTO nanosheets	NF templated CVD	160 mA h g ⁻¹ (30 C)	500 cycles	[152]

1.4.1.2. Cathode. During the past 25 years since commercialization, several transitional metal oxide hosts have been developed for LIB cathode, including 2D layered LiMO₂

(M = Mn, Co, Ni), 3D spinel LiMn_2O_4 , olivine LiMPO_4 (M = Mn, Fe, Co, Ni) and their derivatives. At current stage, the cathode capacities are much inferior to anode, terrifically limiting the overall energy density of LIB. The performance of conventional cathodes is greatly hindered by the scarcity of electron conductivity and slow lithium diffusion rate within the bulk electrodes.^[187] To take the olivine LFP as an example, its high electrochemical potential, theoretically capacity, stability and low cost makes it a favorable LIB cathode. However, the insufficient electrical conductivity (10^{-7} S m^{-1})^[188, 189] and the slow lithium diffusivity along [010] direction has greatly confined its further evolution.

Figure 1. 6. a-c) Morphology of the LFP@N-GA hybrid. d) Capacity-voltage profiles of LFP@N-GA electrode and commercial LFP/C at various rates. e) Rate capabilities. f) Cycling performance at 10C, accompanied with columbic efficiency. g) Ragone plot of LFP@N-GA compared with some existing electrochemical energy storage/conversion devices. Reproduced with permission from ref. [190]. Copyright 2015 Royal Society of Chemistry.

In a work reported by Wang et al., they employed 3D nitrogen doped graphene network in the construction of novel LFP composite, which had nanoplate-structured crystals with anisotropic growth along the (010) facets.^[190] As suggested by the SEM characterizations in **Figure 1. 6a, b**, the LFP nanoplates were tightly inlaid in the dents of graphene network, and such close contact between LFP and graphene could guarantee good electron transfer. TEM images (**Figure 1. 6c**) further revealed the well-defined mesopores surrounded by LFP nanoplates, which ensured ample electrolyte accessibility as well as rapid Li diffusion. It can be observed that the LFP nanoplates were encapsulated by flexible graphene sheets to form core-shell structure. As a result of the synergistic combination of LFP nanoplates and N-GA, an excellent rate capability of 78 mA h g⁻¹ was achieved for even 100 C, at which the commercial LFP/carbon electrode is almost un-chargeable (**Figure 1. 6d, e**). As shown in **Figure 1. 6f**, long cycle life for over 1000 cycles at 10 C was maintained for the electrode, with good retention capability (89%). Maximum gravimetric energy density achieved 110-180 W h kg⁻¹ at low specific power of <1 kW kg⁻¹, and ultrahigh power density of 8.6 kW kg⁻¹ can also be realized with specific energy of 49 W h kg⁻¹. In comparison with current

energy-storage devices as shown in the Ragone plot (**Figure 1. 6g**), the LFP@N-GA battery could offer much superior power densities to available nickel metal hydride battery as well as LIB, meanwhile the energy densities also exceeded supercapacitor for several times.

Xin et al. developed an organic solvent-assisted freeze-drying route to fabricate free-standing GA supported $\text{Li}_2\text{MnO}_3 \cdot \text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ on a large scale.^[84] It is noteworthy that solvents can be recycled by the adjunct cold trap, which rendered a green chemical synthesis. The flexible electrode delivered a high capacity of 248.7 mA h g⁻¹ at 0.1 C. At current rate of 4 C, the capacity of hybrid electrode achieved 90.2 mA h g⁻¹, which is 2.5 times higher than that of sole $\text{Li}_2\text{MnO}_3 \cdot \text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$. Without usage of current collector and non-conductive polymer binder, the energy density of the flexible binder-free electrode doubled that of conventional electrode. Other representative cathode composites based on 3DPGNs were listed in **Table 1.2**.

Table 1.2. Summary of cathode performance for 3DPGN-based composites in LIB.

Host	Guest component and structure	Synthesis of 3DPGN	Reversible capacity	Cyclability	Reference
GF	VO ₂ @GQD nanoarrays	NF templated CVD	389 mA h g ⁻¹ (300 mA g ⁻¹)	1500 cycles	[159]
GF	VO ₂ /hydrogen molybdenum bronze core-shell arrays	NF templated CVD	209 mA h g ⁻¹ (30 C)	500 cycles	[149]
GA	AgVO ₃ nanowires	Hydrothermal	116.4 mA h g ⁻¹ (1000 mA g ⁻¹)	50 cycles	[191]
GA	Li ₂ MnO ₃ ·LiNi _{1/3} Co _{1/3} Mn _{1/3} O ₂ NPs	Freeze drying	227 mA h g ⁻¹ (100 mA g ⁻¹)	100 cycles	[84]
GF	LFP coating	NF templated CVD	158 mA h g ⁻¹ (0.2 C)	-	[155]
GA	LFP	Sol-gel method	146 mA h g ⁻¹ (17 mA g ⁻¹)	100 cycles	[86]
GF	LFP	NF templated CVD	98 mA h g ⁻¹ (8.5 A g ⁻¹)	500 cycles	[152]
GA	LFP NPs	Hydrothermal	125.4 mA h g ⁻¹ (10 C)	600 cycles	[192]

GF	Li ₂ FeSiO ₄ NPs	SiO ₂ spheres templated GO assembly	250 mA h g ⁻¹ (166 mA g ⁻¹)	100 cycles	[156]
N-GA	LFP nanoplatelets	Hydrothermal	78 mA h g ⁻¹ (10 C)	1000 cycles	[190]
GA	FePO ₄	Freeze drying	175 mA h g ⁻¹ (50 mA g ⁻¹)	150 cycles	[175]
CNTs-GA	1,5-diaminoanthraquinone (DAA) polymer	Solvothermal	122 mA h g ⁻¹ (10 A g ⁻¹)	20000 cycles	[193]

1.4.1.3. Advantages of 3DPGN in LIB. As a summary, the exploitation of 3DPGN in LIB electrode is multipurpose. (1) The excellent electrical conductivity of graphene, and the interconnected 3D structural layout, make 3DPGN an efficient current collector where the electrons can rapidly transport throughout the entire network. (2) The numerous multidimensional pore channels inside 3DPGN effectively facilitate Li ion diffusion within the bulk electrode. (3) 3DPGN hosts especially GA, still bear some reactive functional groups, which can activate the introduction of secondary phases which impart additional functions. (4) The outstanding elasticity, mechanical strength, flexibility and thermal stability of the graphene building block secures the structural robustness for 3DPGN, preventing collapse, shrinkage or decomposition of the backbone. (5) The good flexibility and large pore volume of 3DPGN can guarantee enough space to accommodate the volume expansion of secondary phases. (6) Last but not the least, 3DPGNs could function as electric double layers, to store energy with a fast capacity response, which in turn benefit the rate performance and cyclability of the hybrid by buffering the impact on active phases at high current.

At the same time, drawbacks of 3D graphene should also be mentioned: (1) increased

occurrence of solid electrolyte interfacial layer, more self-discharge, and inferior cycle life caused by large surface area of hosts; (2) lower volumetric energy density due to light weight of 3DPGN support; (3) complexity in synthesis.

Figure 1. 7. a) Model of the flexible LIB based on GF. b, c) Digital photos showing the bending state of flexible LIB. d) Galvanostatic charge/discharge profiles of the LIB full cell functioned under different rates. e) Specific capacity of the full battery run at 10 C. f) Capacity-voltage curves of flat and bent batteries. Red line stands for the as-prepared flat LIB, and blue for the bent one after bending to a radius of 5 mm for 20 times. g)

The cycling performance during bent and flat states. Reproduced with permission from ref. [152]. Copyright 2012 National Academy of Sciences.

1.4.1.4. Flexible binder-free electrodes. The polymer binders and additives used in battery electrodes are always insulators, which rise the system polarization and hamper device performance. The monolithic nature of 3DPGN support, as well as its smooth manipulability, render itself one of the optimal mediums to construct binder-free electrodes, which will not engage conventional current collectors (e.g. Cu, Al foils) or polymer binders. Hence, the effective mass is maximized with graphene monoliths serving as both binder and current collector at the same time. Moreover, the 3D spatial conductivity within graphene network could further promote the charge transport, allowing the resulted battery to provide more electricity and be charged much faster. Recently, flexible LIBs and supercapacitors are raising tremendous attention for their great promise of powering state-of-the-art flexible electronics such as roll-up displays, soft, portable, wearable devices, conformable health-monitoring electronic skin and implantable biomedical devices. The flexible LIBs should be thin, lightweight, and capable of being bent to arbitrary shapes without structural failure. With regard to this application, binder-free electrodes made from GF^[142, 152] and GA^[111, 194] show unique advantages attributed to their exceptional mechanical properties among the electrochemical active composites.

In an intriguing work on flexible LIB, Li et al. furnished GFs with commercialised

LTO and LFP respectively as anode and cathode, leading to ultrafast charge/discharge rates of the assembled full cell.^[152] Scheme of this flexible full battery was shown by the cartoon model and digital photos in **Figure 1. 7a-c**. The LTO/GF anode (half cell) demonstrated a high rate up to 200 C (18s discharge), meanwhile reached a reversible capacity of 86 mA h g⁻¹ for long cycling. On the other side, the LFP/GF cathode (half cell) delivered a high rate capacity of 98 mA h g⁻¹ at 50 C. With respect to the performance of full cell, as indicated in **Figure 1. 7d, e**, the energy density of this flexible LIB reached ~110 W h kg⁻¹ calculated on total mass of both electrodes. The flexible full battery can be charged/discharged at 10 C rate, and still delivered a capacity of 117 mA h g⁻¹. As revealed in **Figure 1. 7f, g**, the battery can be bended to a radius of 5 mm for 20 times without observable collapse or abnormal performance. The overall performance of the flexible binder and additive free full battery even exceeded most conventional batteries, in terms of high rate and long life, representing the great promise of flexible power tools based on GF.

GA could also be utilized as elastic support for flexible or thin film batteries. To give an example, Zhu and co-workers displayed a design concept that integrates 0 D MoS₂, 1 D CNTs and 2D graphene into one 3D free-standing composite via an electrostatic spray deposition (ESD) technique.^[111] The products were immediately deposited onto current collector without usage of binder additives, and hence can be directly assembled into a flexible battery. Regarding the lithium storage performance, the flexible hybrid

electrode delivered excellent rate capacities as high as 949, 883, 858, 737, 652 mA h g⁻¹ corresponding to current densities of 0.1, 0.5, 1, 5, 10 A g⁻¹. The cycling capacity was retained at 886 mA h g⁻¹ stably for 100 cycles, under current density of 1 A g⁻¹. Furthermore, this simple but powerful ESD technique, could be easily adapted by quite a number of electroactive materials, thus showing great potential to be a general method for fabrication of flexible electrode materials.

1.4.2. Supercapacitor

Supercapacitors, also called electrochemical capacitors or ultracapacitors, have two distinct working mechanisms: electrochemical double layer capacitance that stores electricity through ion adsorption at the solid/electrolyte interfaces, and the pseudocapacitance based on fast reversible redox (faradic) reactions. The concept of supercapacitor was patented in 1957 by Becker, who used high-surface-area carbon as electrode and sulfuric acid as the electrolyte.^[195] The commercialization of supercapacitors was initiated in 1971 when Standard Oil of Ohio (SOHIO) attempted to use aqueous-electrolyte capacitors for power saving units in electronics,^[3] and intensive research efforts have been devoted to it since the 1990s,^[196, 197] in order to afford the rising demand for hybrid vehicles. The high power density, fast charge/discharge rate and long cycle life make supercapacitor a competent power

source for certain applications which LIB couldn't suffice. However, the low energy density and high cost yet have to be solved through the research and development on novel electrode materials. Electrodes of commercial electrochemical double layer capacitors (EDLC) are fabricated from porous carbonaceous materials, i.e. active carbon with high electron conductivity and large surface area, showing excellent rate capability and long cycle life, whereas suffered from insufficient capacitance. Meanwhile, pseudocapacitive materials (PCM) such as electrochemically active metal oxides/hydroxides are featured with higher energy density, but deficient in power density as well as cycling stability. Stabilizing PCM phases within high-surface-area, conductive nanocarbon supports to integrate the merits of both elements, is proven to be a versatile strategy for fabrication of state-of-the-art supercapacitor electrodes. With relevance to 3D graphene, despite its decent capacitance and cyclability when solely used as EDLC electrodes, it is more useful to host the high capacitance PCM phases, where its macro-meso structure and high electric conductivity can be harnessed more effectively.

1.4.2.1. EDLC. 3DPGN has been extensively explored for EDLC applications without decoration of any PCM. ^[23, 132, 198] The charge storage capabilities can be further augmented after doping of heteroatoms, synergistic combination with CNTs, or proper control on structural layout. Both GA and GF can be produced in bulk, and cut into

smaller free-standing pieces for flexible electrodes of supercapacitor.

Xu and co-workers reported the highly efficient capacitive energy storage of a free-standing holey graphene framework (HGF), which was derived from the self-assembly of intentionally perforated graphene sheets.^[198] Creation of nanopores was realized by using excessive H_2O_2 to etch graphene sheets, during the hydrothermal self-assembly process. The HGF showed significantly larger solvated surface area than normal graphene hydrogel (BET surface area of 830 over 260 $\text{m}^2 \text{g}^{-1}$). The electrode was fabricated by slicing and compressing HGF into thin films. The HGF film provided numerous nanoporous channels as shortcuts for ions to transport across different layers, throughout the bulk film. Due to the high packing density of thin film, the volumetric capacitance is not restrained by the porous structure. Respective gravimetric and volumetric energy densities reached 35 W h kg^{-1} and 49 W h L^{-1} for the packed symmetric supercapacitor assembled from HGF electrodes, which are already comparable to lead-acid batteries (25-35 W h kg^{-1} and 50-90 W h L^{-1}).

Wang et al. reported a GF/CNTs-based hybrid film for high fidelity supercapacitors.^[199] Based on the existing method, they derived a modified one-step approach named ambient pressure CVD, using industrial grade metal foam foils as the template, to realize fabrication of the 3D foam comprised from a few layer graphene (~7-10 layers) and multi-walled CNTs. Though densely packed, the hierarchical architecture still generated a large specific surface of 743 $\text{m}^2 \text{g}^{-1}$. Symmetrical EDLC built from this

G/CNT foam possessed a high specific capacitance of 286 F g^{-1} and resultant energy density of $39.72 \text{ W h kg}^{-1}$, under area current density of 1.78 mA cm^{-2} . The capacitance retention achieved 99.34% after 85000 cycles at current density of 21.33 mA cm^{-2} , showing the remarkable cycling stability and long cycle life. The maximum power density reached up to $154.67 \text{ kW kg}^{-1}$, indicating the potential of 3D structures in future energy-storage applications.

1.4.2.2. PCM. 3DPGNs have been more widely investigated as conductive support for construction of high-capacitance electrodes, through integration of PCM phases such as metal oxides, hydroxides, sulfides and conductive polymers. So far, MnO_2 , CoO , NiO , Co_3O_4 , Fe_2O_3 , NiCo_2O_4 , Ni(OH)_2 , Co(OH)_2 , $\text{Co}_x\text{Ni}_{1-x}(\text{OH})_2$, Ni_3S_2 , VO_2 , V_2O_5 , Melamine resin, PPy, PANI, PEDOT etc. in diversified nanostructures have been successfully coupled into 3DPGNs for supercapacitor applications, as tabulated in **Table 1.3**.

In a typical example, GF supported Co_3O_4 nanowires^[65], prepared by Dong and co-workers, have demonstrated ultrahigh capacitive performance. As current density varies among 10, 15, 20 and 30 A g^{-1} , relevant specific capacitance achieved 768, 618, 552, and 456 F g^{-1} . Despite the initial high value, the specific capacitance continued increasing to $\sim 1100 \text{ F g}^{-1}$ (at 10 A g^{-1}) and stay steady afterward for over 30000 cycles, arising from the gradual activation of porous Co_3O_4 nanowires.

Figure 1. 8. a, b) SEM images of the GF/CNT film. c) SEM image of the GF/CNT/MnO₂ film. d) Galvanostatic charge/discharge profiles of the ASC at varied current densities. e) Cycling performance of the ASC, under area current density 1.5 mA cm⁻², over 10000 cycles. f, g) Optical photos showing the ASC powering red LED (f) and small motor (g). Reproduced with permission from ref. [200]. Copyright 2014 Royal Society of Chemistry.

Lou's group devised a robust hybrid foam from graphene and CNTs, loaded by MnO₂ and PPy respectively as positive and negative electrodes of flexible, lightweight asymmetric supercapacitor (ASC).^[200] In this work, CNTs were *in situ* grown on both sides of GF surface (morphology shown in **Figure 1.8a, b**), with pre-deposited catalysts. Then MnO₂ nanosheets and PPy of tunable mass loading were decorated onto the prepared hybrid foams, via hydrothermal and chemical polymerization processes

respectively and the MnO_2 on CNT/GF demonstrated well-defined nanosheets morphology, as observed from **Figure 1. 8c**. Mass loading of MnO_2 could be as high as 8.4 mg cm^{-2} . As suggested by **Figure 1. 8d**, the assembled ASC ($1 \times 4 \text{ cm}^2$) could function with an output voltage of 1.6 V, and could be fully charged within only 30 s. Maximum energy density of 22.8 W h kg^{-1} could be delivered when power density set to 860 W kg^{-1} , and a high power density of 2.7 kW kg^{-1} was obtained at energy density of 6.2 W h kg^{-1} . Remarkable capacitance retention of 90.2%-83.5% for different mass loading of MnO_2 was stably achieved for 10000 cycles (**Figure 1. 8e**), and the electrochemical performance won't degrade by bending to different angles. The authors also demonstrated the potential for real-life applications of this high energy/power-density ASC, which can power three red light-emitting diodes (5 mm diameter, 1.8 V, 20 mA) or drive a 0.45 W motor, as exhibited in **Figure 1. 8f, g**.

In another work, Yu et al. realized a scalable synthesis of 3DPGN from inexpensive graphite paper, which combines the Hummers method^[201] with direct freeze drying.^[51] Adding to the mesoporous structure and resultant high specific surface ($311.8 \text{ m}^2 \text{ g}^{-1}$), this GA constructed from well-exfoliated RGO is also featured with superior electrical conductivity. Subsequently, PANI nanorods were introduced to GA through electrochemical deposition. After processed into supercapacitor electrodes, the hybrid electrode displayed a high capacitance of 931.8 F g^{-1} (calculated from the whole electrode weight) at scan rate of 10 mV s^{-1} , and a capacitance retention of 70.2% for

5000 cycles.

1.4.2.3. Advantages of 3DPGN in supercapacitor. To summarize, 3DPGNs bring about three substantial enhancements to supercapacitor electrode materials. First, 3DPGNs can effectively distribute the PCM species with their high porosity and large surface area, enhancing the accessibility of electrolyte to the active surface. Secondly, the interconnected graphene networks serve as high-speed channels for electron transportation. Thirdly, synergistic effects could be induced by the combination of EDLC and pseudocapacitance-based charge storage.

Table 1.3. Summary of capacitive performance for 3DPGN-based composites in supercapacitors.

Host	Guest component and structure	Synthesis of 3DPGN	Reversible capacitance	Cyclability and capacitance retention	Reference
GF	Flower-like MnO ₂ nanostructures	Sponge templated GO adsorption	450 F g ⁻¹ (1 A g ⁻¹)	10000 cycles, 90%	[45]
GA on NF	MnO ₂ coating	Hydrothermal with NF	234 F g ⁻¹ (1 mV s ⁻¹)	10000 cycles, 98.65%	[202]
GF	MnO ₂ coating	PS spheres templated vacuum filtration of GO	389 F g ⁻¹ (1 A g ⁻¹)	1000 cycles, 95%	[145]
GF	MnO ₂ nanostructure	NF templated CVD	465 F g ⁻¹ (2 mV s ⁻¹)	5000 cycles,	[78]
GA	MnO ₂ NPs	Oil bath reaction	242 F g ⁻¹ (1 A g ⁻¹)	1000 cycles, 89.6%	[75]
GA	MnO ₂ nanospheres/carbon NPs	Freeze drying	150 F g ⁻¹ (20 A g ⁻¹)	1000 cycles, 83%	[85]
GA	MnO ₂ nanoflakes	Hydrothermal	150 F g ⁻¹ (1 A g ⁻¹)	1000 cycles, > 80%	[203]
GA	Co ₃ O ₄ Nanoparticles	Solvothermal	660 F g ⁻¹ (0.5 A g ⁻¹)	2000 cycles, 92.92%	[74]
GA	Co ₃ O ₄ NPs	Hydrothermal	757.5 F g ⁻¹ (0.5 A g ⁻¹)	500 cycles, 94.5%	[204]
GF	CoO nanobundles	NF templated CVD	352.75 F g ⁻¹ (1 A g ⁻¹)	1000 cycles, ~100%	[205]
GA	Fe ₂ O ₃ NPs	Hydrothermal	152.1 F g ⁻¹ (10 A g ⁻¹)	1000 cycles	[206]
GA	VO ₂ nanobelts	Hydrothermal	426 F g ⁻¹	5000 cycles,	[207]

			(1 A g ⁻¹)	92%	
GA	V ₂ O ₅ nanobelts	Hydrothermal	320 F g ⁻¹ (1 A g ⁻¹)	1000 cycles, 70%	[105]
GA	Ni ₃ S ₂ nanoflowers	Hydrothermal	65.4 F g ⁻¹ (4 A g ⁻¹)	5000 cycles, 85.6%	[208]
GF	Ni ₃ S ₂ nanorod@Ni(OH) ₂ nanosheet core-shell nanostructures	NF templated CVD	1037.5 F g ⁻¹ (5.1 A g ⁻¹)	2000 cycles, 99.1%	[71]
GF	Co(OH) ₂	NF templated CVD	~1030 F g ⁻¹ (9.09 A g ⁻¹)	5000 cycles, 94%	[209]
GF	Co(OH) ₂ nanorods	NF templated CVD	1139 F g ⁻¹ (10 A g ⁻¹)	1000 cycles, 74%	[210]
GF	Ni(OH) ₂ nanoflakes	NF templated CVD	1450 F g ⁻¹ (5 A g ⁻¹)	1000 cycles, 78%	[211]
GF	Co _x Ni _{1-x} (OH) ₂ nanorods	NF templated CVD	1037.5 F g ⁻¹ (60 A g ⁻¹)	1000 cycles, 74%	[212]
GF	NiO nanosheets	NF templated CVD	816 F g ⁻¹ (5 mV s ⁻¹)	2000 cycles, 100%	[81]
GA	mesoporous NiCo ₂ O ₄ nanosheets	Freeze drying	778 F g ⁻¹ (1 A g ⁻¹)	10000 cycles, 90%	[213]
GF	NiCo ₂ O ₄ nanosheet	Solvothermal deposition and conversion	1203 (100 A g ⁻¹)	14000 cycles, 94%	[157]
GF	Co ₃ O ₄ /PEDOT-MnO ₂ core/shell NANOWIRES arrays	Porous Ni film templated CVD	353 F g ⁻¹ (5 A g ⁻¹)	20000 cycles, 90%	[214]
GA	Melamine resin	Polymer intercalation and thermal reduction	210 F g ⁻¹ (0.5 A g ⁻¹)	20000 cycles, ~96%	[215]
GA	PANI	Room temperature reaction	334 F g ⁻¹ (2 A g ⁻¹)	5000 cycles	[76]
GF	PANI nanofibers	NF templated CVD	1002 F g ⁻¹ (1 mA cm ⁻²)	5000 cycles 86.5%	[162]
GA	PANI nanofibers	Electro-reduction	716 F g ⁻¹ (0.47 A g ⁻¹)	500 cycles	[216]
GF	PEDOT nanofibers	NF templated CVD	522 F g ⁻¹ (2 mA cm ⁻²)	1000 cycles, 85%	[163]
GA	PVA, Polyvinylpyrrolidone	Hydrothermal	188 F g ⁻¹ (0.5 A g ⁻¹)	10000 cycles, 100%	[217]

1.4.2.4. all-solid-state supercapacitor (ASSS). The smart, lightweight ASSS appears

as a promising candidate to power wearable and miniaturized electronics.^[218-221]

Compared with other nanocarbon materials, 3DPGN shows its own unique advantages in ASSS electrode. At first the free-standing, flexible, monolithic 3D graphene can be easily manufactured into electrode without usage of current collector, polymer binder or additives, and thus avoid the complex solution processing, high-pressure handling, sintering, and sputtering techniques. Moreover, the device performance can be

enhanced since the polymer binders and additives are basically non-conductive. Secondly, the inner porous structure provides ideal channels to hold the solid-state electrolyte made from usually PVA/H₂SO₄ gel. The porous interior also ensures sufficient access to the electrolytes.

Figure 1. 9. a) Schematic illustration showing the procedures for synthesis of BN-GA, and subsequent fabrication of ASSS. Reproduced with permission from ref. [132]. Copyright 2012 WILEY-VCH. b) Galvanostatic charge/discharge curves of the asymmetric ASSS made from MnO₂/GF and CNT/CF at various current densities. c) Cycling performance of the asymmetric ASSS at current density 5 A g⁻¹ for 10000 cycles. Inset optical images of the functioning asymmetric ASSS. d) Specific capacitance retention of the flexible ASSS upon bending to different angles (left) or different times at constant angle of 180° (right). Reproduced with permission from ref. [222]. Copyright 2014 WILEY-VCH.

Mullen's group demonstrated a high-performance ASSS fabricated from nitrogen and boron co-doped 3D GA (BN-GA).^[132] As shown in the schematic illustration (**Figure**

1. 9a), the as-prepared monolithic BN-GA could be easily sliced into smaller pieces and then physically pressed into plates of demanded size. Then two of the plates were subsequently assembled into a sandwich-like ASSS, separated by one polymer spacer. The ASSS fabricated from BN-GA not only abridged the size and thickness of device, but also exhibited decent performance. A specific capacitance of $\sim 62 \text{ F g}^{-1}$ was delivered at scan rate of 5 mV s^{-1} . The high rate capability shows a reversible capacitance of 26.2 F g^{-1} , obtained at 100 mV s^{-1} . Capacitance retention keeps almost 100% for 1000 cycles at 2 A g^{-1} . The energy density achieved $\sim 8.65 \text{ W h kg}^{-1}$ and power density was determined to be $\sim 1650 \text{ W kg}^{-1}$ at less than 3.6 s.

Zhang and co-workers designed a facile and scalable solution casting technique to prepare GF from NF template and GO precursor, and lately decorated these GFs with MnO_2 and CNTs through electrochemical approaches, using them respectively as the positive and negative electrodes to assemble asymmetric ASSS.^[222] As indicated in the electrochemical measurements (**Figure 1. 9b**), the devised asymmetric ASSS is able to function with an output cell voltage of 1.8 V, and deliver high energy/power density (31.8 W h kg^{-1} at 453.6 W kg^{-1} and 9188.1 W kg^{-1} at 18.2 W h kg^{-1}). As shown in **Figure 1. 9c**, the supercapacitor can retain 84.4% of its initial capacitance for over 10000 cycles, at current density of 5 A g^{-1} . Three ASSSs connected in series can power a red LED light. Moreover, unlike conventional supercapacitors packed with liquid electrolytes, the asymmetric ASSS using polymer gel of potassium polyacrylate/KCl as electrolyte

exhibited remarkable stability against mechanical stress. As implied by **Figure 1. 9d**, the influence of bending upon specific capacitance is almost ignorable. Performance of the flexible ASSS shows only minimal fluctuation upon bending to different angles (45°, 90° and 180°). Even after 100 times of bending the asymmetric ASSS to 180°, only 3% capacitance drain is detected, implying the stable charge/discharge behavior regardless of repetitive mechanical stress. To date, a number of hybrids based on 3DPGN have been investigated for ASSS electrodes, such as MnO₂-CNT-graphene-Ni hybrid foam,^[223] NiCo₂S₄ Nanotube@Ni-Mn Layered double hydroxide arrays/graphene sponge,^[224] hierarchical NiCo₂O₄/porous graphene paper,^[225] PPy/GF,^[161] and so on.

1.5. Conclusion

This introduction chapter revolves around the current progress of 3DPGN-based hybrids. Typical structures of 3DPGN were introduced and their respective hybrid materials for advanced LIB and supercapacitor are documented in detail. In the chapters that follow, a series of novel structures modified from conventional 3DPGN-based composites were proposed and fabricated, in order to explore the manipulability of 3D networks as well as to enhance their performance for energy-storage tools. Hybrid materials based on these innovative structures were synthesized as examples and thoroughly analyzed to validate their design concepts. As a result of the rational layout,

these materials did show synergistic properties or enhancements in terms of electrochemical relativities.

1.6. References

- [1] G. Venugopal, A. Hunt, F. Alamgir, *Mater. Matters* **2010**, 5, 42.
- [2] A. Yoshino, K. Sanechika, T. Nakajima (Assahi Chemical Ind.) *Jap 1989293*, **1985**.
- [3] R. A. Rightmire (Standard Oil Co.) *US 3288641*, **1966**.
- [4] Y. Li, Z.-Y. Fu, B.-L. Su, *Adv. Funct. Mater.* **2012**, 22, 4634.
- [5] A. Vu, Y. Qian, A. Stein, *Adv. Energy Mater.* **2012**, 2, 1056.
- [6] Z. Chen, W. Ren, L. Gao, B. Liu, S. Pei, H. M. Cheng, *Nat. Mater.* **2011**, 10, 424.
- [7] Y. Xu, G. Shi, X. Duan, *Acc. Chem. Res.* **2015**, 48, 1666.
- [8] A. K. Geim, K. S. Novoselov, *Nat. Mater.* **2007**, 6, 183.
- [9] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, A. A. Firsov, *Science* **2004**, 306, 666.
- [10] D. A. Dikin, S. Stankovich, E. J. Zimney, R. D. Piner, G. H. Dommett, G. Evmenenko, S. T. Nguyen, R. S. Ruoff, *Nature* **2007**, 448, 457.
- [11] C. Hu, Y. Zhao, H. Cheng, Y. Wang, Z. Dong, C. Jiang, X. Zhai, L. Jiang, L. Qu, *Nano Lett.* **2012**, 12, 5879.

- [12] J. Cao, Y. Wang, P. Xiao, Y. Chen, Y. Zhou, J.-H. Ouyang, D. Jia, *Carbon* **2013**, *56*, 389.
- [13] F. Zeng, Y. Kuang, Y. Wang, Z. Huang, C. Fu, H. Zhou, *Adv. Mater.* **2011**, *23*, 4929.
- [14] J. Luo, H. D. Jang, T. Sun, L. Xiao, Z. He, A. P. Katsoulidis, M. G. Kanatzidis, J. M. Gibson, J. Huang, *ACS Nano* **2011**, *5*, 8943.
- [15] S. Han, D. Wu, S. Li, F. Zhang, X. Feng, *Adv. Mater.* **2014**, *26*, 849.
- [16] X. Cao, Z. Yin, H. Zhang, *Energy Environ. Sci.* **2014**, *7*, 1850.
- [17] X. H. Xia, D. L. Chao, Y. Q. Zhang, Z. X. Shen, H. J. Fan, *Nano Today* **2014**, *9*, 785.
- [18] S. Mao, G. Lu, J. Chen, *Nanoscale* **2015**, *7*, 6924.
- [19] Y. Xu, K. Sheng, C. Li, G. Shi, *ACS Nano* **2010**, *4*, 4324.
- [20] Y. Sun, Q. Wu, G. Shi, *Phys. Chem. Chem. Phys.* **2011**, *13*, 17249.
- [21] P. Calvert, *Adv. Mater.* **2009**, *21*, 743.
- [22] K. Sheng, Y. Xu, C. Li, G. Shi, *New Carbon Mater.* **2011**, *26*, 9.
- [23] X. Zhang, Z. Sui, B. Xu, S. Yue, Y. Luo, W. Zhan, B. Liu, *J. Mater. Chem.* **2011**, *21*, 6494.
- [24] W. Chen, S. Li, C. Chen, L. Yan, *Adv. Mater.* **2011**, *23*, 5679.
- [25] W. Chen, L. Yan, *Nanoscale* **2011**, *3*, 3132.
- [26] Y. Huang, C. Li, Z. Lin, *ACS Appl. Mater. Interfaces* **2014**, *6*, 19766.
- [27] H. Hu, Z. Zhao, W. Wan, Y. Gogotsi, J. Qiu, *Adv. Mater.* **2013**, *25*, 2219.

- [28] M. C. Gutiérrez, M. L. Ferrer, F. d. Monte, *Chem. Mater.* **2008**, *20*, 634.
- [29] M. C. Gutiérrez, M. J. Hortigüela, J. M. Amarilla, R. Jiménez, M. L. Ferrer, F. d. Monte, *J. Phys. Chem. C* **2007**, *111*, 5557.
- [30] X. Yao, H. Yao, Y. Lia, *J. Mater. Chem.* **2009**, *19*, 6516.
- [31] S. Deville, *Adv. Eng. Mater.* **2008**, *10*, 155.
- [32] W. L. Li, K. Lu, J. Y. Walz, *Int. Mater. Rev.* **2013**, *57*, 37.
- [33] L. Qiu, J. Z. Liu, S. L. Chang, Y. Wu, D. Li, *Nat. Commun.* **2012**, *3*, 1241.
- [34] H. Sun, Z. Xu, C. Gao, *Adv. Mater.* **2013**, *25*, 2554.
- [35] K. S. Kim, Y. Zhao, H. Jang, S. Y. Lee, J. M. Kim, K. S. Kim, J. H. Ahn, P. Kim, J. Y. Choi, B. H. Hong, *Nature* **2009**, *457*, 706.
- [36] G. H. Moon, Y. Shin, D. Choi, B. W. Arey, G. J. Exarhos, C. Wang, W. Choi, J. Liu, *Nanoscale* **2013**, *5*, 6291.
- [37] J.-C. Yoon, J.-S. Lee, S.-I. Kim, K.-H. Kim, J.-H. Jang, *Sci. Rep.* **2013**, *3*, 1788.
- [38] S. H. Lee, H. W. Kim, J. O. Hwang, W. J. Lee, J. Kwon, C. W. Bielawski, R. S. Ruoff, S. O. Kim, *Angew. Chem. Int. Ed.* **2010**, *49*, 10084.
- [39] B. G. Choi, M. Yang, W. H. Hong, J. W. Choi, Y. S. Huh, *ACS Nano* **2012**, *6*, 4020.
- [40] H. Wang, D. Zhang, T. Yan, X. Wen, J. Zhang, L. Shi, Q. Zhong, *J. Mater. Chem. A* **2013**, *1*, 11778.
- [41] K. Sohn, Y. Joo Na, H. Chang, K. M. Roh, H. Dong Jang, J. Huang, *Chem. Commun.* **2012**, *48*, 5968.

- [42] J. Qin, C. He, N. Zhao, Z. Wang, C. Shi, E.-Z. Liu, J. Li, *ACS Nano* **2014**, 8, 1728.
- [43] X. Zhang, C. Shi, E. Liu, J. Li, N. Zhao, C. He, *Nanoscale* **2015**, 7, 17079.
- [44] B. Li, S. Yang, S. Li, B. Wang, J. Liu, *Adv. Energy Mater.* **2015**, 5, 1500289.
- [45] J. Ge, H.-B. Yao, W. Hu, X.-F. Yu, Y.-X. Yan, L.-B. Mao, H.-H. Li, S.-S. Li, S.-H. Yu, *Nano Energy* **2013**, 2, 505.
- [46] H. B. Yao, J. Ge, C. F. Wang, X. Wang, W. Hu, Z. J. Zheng, Y. Ni, S. H. Yu, *Adv. Mater.* **2013**, 25, 6692.
- [47] X. Huang, K. Qian, J. Yang, J. Zhang, L. Li, C. Yu, D. Zhao, *Adv. Mater.* **2012**, 24, 4419.
- [48] X. Huang, B. Sun, D. Su, D. Zhao, G. Wang, *J. Mater. Chem. A* **2014**, 2, 7973.
- [49] B. Qiu, M. Xing, J. Zhang, *J. Am. Chem. Soc.* **2014**, 136, 5852.
- [50] Y. Zhao, X. Xie, J. Zhang, H. Liu, H. J. Ahn, K. Sun, G. Wang, *Chem. Eur. J.* **2015**, 21, 15908.
- [51] M. Yu, Y. Huang, C. Li, Y. Zeng, W. Wang, Y. Li, P. Fang, X. Lu, Y. Tong, *Adv. Funct. Mater.* **2015**, 25, 324.
- [52] J. Li, C.-y. Liu, Y. Liu, *J. Mater. Chem.* **2012**, 22, 8426.
- [53] N. H. Le, H. Seema, K. C. Kemp, N. Ahmed, J. N. Tiwari, S. Park, K. S. Kim, *J. Mater. Chem. A* **2013**, 1, 12900.
- [54] Y. Chen, L. Chen, H. Bai, L. Li, *J. Mater. Chem. A* **2013**, 1, 1992.

- [55] Y. Tao, D. Kong, C. Zhang, W. Lv, M. Wang, B. Li, Z.-H. Huang, F. Kang, Q.-H. Yang, *Carbon* **2014**, *69*, 169.
- [56] Y. Shen, Q. Fang, B. Chen, *Environ. Sci. Technol.* **2015**, *49*, 67.
- [57] W. Li, S. Gao, L. Wu, S. Qiu, Y. Guo, X. Geng, M. Chen, S. Liao, C. Zhu, Y. Gong, M. Long, J. Xu, X. Wei, M. Sun, L. Liu, *Sci. Rep.* **2013**, *3*, 2125.
- [58] M. Yu, A. Song, G. Xu, X. Xin, J. Shen, H. Zhang, Z. Song, *RSC Adv.* **2015**, *5*, 75589.
- [59] H. Guo, T. Jiao, Q. Zhang, W. Guo, Q. Peng, X. Yan, *Nanoscale Res. Lett.* **2015**, *10*, 931.
- [60] C. S. Cheng, J. Deng, B. Lei, A. He, X. Zhang, L. Ma, S. Li, C. Zhao, *J. Hazard. Mater.* **2013**, *263*, 467.
- [61] Z.-S. Wu, S. Yang, Y. Sun, K. Parvez, X. Feng, K. Müllen, *J. Am. Chem. Soc.* **2012**, *134*, 9082.
- [62] C. Hu, X. Zhai, Y. Zhao, K. Bian, J. Zhang, L. Qu, H. Zhang, H. Luo, *Nanoscale* **2014**, *6*, 2768.
- [63] Y. Zhang, M. Chu, L. Yang, Y. Tan, W. Deng, M. Ma, X. Su, Q. Xie, *ACS Appl. Mater. Interfaces* **2014**, *6*, 12808.
- [64] C. Hu, H. Cheng, Y. Zhao, Y. Hu, Y. Liu, L. Dai, L. Qu, *Adv. Mater.* **2012**, *24*, 5493.
- [65] X.-C. Dong, H. Xu, X.-W. Wang, Y.-X. Huang, M. B. Chan-Park, H. Zhang, L.-H. Wang, W. Huang, P. Chen, *ACS Nano* **2012**, *6*, 3206.

- [66] Y. Xu, Z. Lin, X. Huang, Y. Wang, Y. Huang, X. Duan, *Adv. Mater.* **2013**, *25*, 5779.
- [67] M. Chen, J. Liu, D. Chao, J. Wang, J. Yin, J. Lin, H. Fan, Z. Shen, *Nano Energy* **2014**, *9*, 364.
- [68] J. K. Wang, G. M. Xiong, M. Zhu, B. Ozyilmaz, A. H. Castro Neto, N. S. Tan, C. Choong, *ACS Appl. Mater. Interfaces* **2015**, *7*, 8275.
- [69] S. R. Shin, B. Aghaei-Ghareh-Bolagh, T. T. Dang, S. N. Topkaya, X. Gao, S. Y. Yang, S. M. Jung, J. H. Oh, M. R. Dokmeci, X. S. Tang, A. Khademhosseini, *Adv. Mater.* **2013**, *25*, 6385.
- [70] A. Paul, A. Hasan, H. A. Kindi, A. K. Gaharwar, V. T. S. Rao, M. Nikkhah, S. R. Shin, D. Krafft, M. R. Dokmeci, D. Shum-Tim, A. Khademhosseini, *ACS Nano* **2014**, *8*, 8050.
- [71] W. Zhou, X. Cao, Z. Zeng, W. Shi, Y. Zhu, Q. Yan, H. Liu, J. Wang, H. Zhang, *Energy Environ. Sci.* **2013**, *6*, 2216.
- [72] R. Wang, C. Xu, M. Du, J. Sun, L. Gao, P. Zhang, H. Yao, C. Lin, *Small* **2014**, *10*, 2260.
- [73] J. Ma, J. Wang, Y.-S. He, X.-Z. Liao, J. Chen, J.-Z. Wang, T. Yuan, Z.-F. Ma, *J. Mater. Chem. A* **2014**, *2*, 9200.
- [74] L. Xie, F. Su, L. Xie, X. Li, Z. Liu, Q. Kong, X. Guo, Y. Zhang, L. Wan, K. Li, C. Lv, C. Chen, *ChemSusChem* **2015**, *8*, 2917.
- [75] S. Wu, W. Chen, L. Yan, *J. Mater. Chem. A* **2014**, *2*, 2765.

- [76] Z. Tai, X. Yan, Q. Xue, *J. Electrochem. Soc.* **2012**, *159*, A1702.
- [77] C. Hu, G. Zheng, F. Zhao, H. Shao, Z. Zhang, N. Chen, L. Jiang, L. Qu, *Energy Environ. Sci.* **2014**, *7*, 3699.
- [78] Y. He, W. Chen, X. Li, Z. Zhang, J. Fu, C. Zhao, E. Xie, *ACS Nano* **2013**, *7*, 174.
- [79] S. Dong, A. Q. Dao, B. Zheng, Z. Tan, C. Fu, H. Liu, F. Xiao, *Electrochim. Acta* **2015**, *152*, 195.
- [80] Y.-T. Kim, S. Gopukumar, K.-B. Kim, B.-W. Cho, *J. Power Sources* **2003**, *117*, 110.
- [81] X. Cao, Y. Shi, W. Shi, G. Lu, X. Huang, Q. Yan, Q. Zhang, H. Zhang, *Small* **2011**, *7*, 3163.
- [82] Shuangqiang Chen, Peite Bao, Xiaodan Huang, Bing Sun, G. Wang, *Nano Res.* **2014**, *7*, 85.
- [83] Y. Zhang, M. Ma, J. Yang, W. Huang, X. Dong, *RSC Adv.* **2014**, *4*, 8466.
- [84] Y. Xin, L. Qi, Y. Zhang, Z. Zuo, H. Zhou, X. Zhang, *Chem. Commun.* **2015**, *51*, 16381.
- [85] Y. Xiong, M. Zhou, H. Chen, L. Feng, Z. Wang, X. Yan, S. Guan, *Appl. Surf. Sci.* **2015**, *357*, 1024.
- [86] J. Yang, J. Wang, D. Wang, X. Li, D. Geng, G. Liang, M. Gauthier, R. Li, X. Sun, *J. Power Sources* **2012**, *208*, 340.
- [87] Z. Fan, B. Liu, J. Wang, S. Zhang, Q. Lin, P. Gong, L. Ma, S. Yang, *Adv. Funct. Mater.* **2014**, *24*, 3933.

- [88] L. Zhao, Z.-B. Wang, J.-L. Li, J.-J. Zhang, X.-L. Sui, L.-M. Zhang, *RSC Adv.* **2015**, *5*, 98160.
- [89] A. Harley-Trochimczyk, J. Chang, Q. Zhou, J. Dong, T. Pham, M. A. Worsley, R. Maboudian, A. Zettl, W. Mickelson, *Sens. Actuators, B* **2015**, *206*, 399.
- [90] L. Zhao, Z.-B. Wang, J.-L. Li, J.-J. Zhang, X.-L. Sui, L.-M. Zhang, *Electrochim. Acta* **2016**, *189*, 175.
- [91] M. Liu, C. Peng, W. Yang, J. Guo, Y. Zheng, P. Chen, T. Huang, J. Xu, *Electrochim. Acta* **2015**, *178*, 838.
- [92] Z. Tang, S. Shen, J. Zhuang, X. Wang, *Angew. Chem. Int. Ed.* **2010**, *49*, 4603.
- [93] L. Xiao, D. Wu, S. Han, Y. Huang, S. Li, M. He, F. Zhang, X. Feng, *ACS Appl. Mater. Interfaces* **2013**, *5*, 3764.
- [94] X. Cao, B. Zheng, X. Rui, W. Shi, Q. Yan, H. Zhang, *Angew. Chem. Int. Ed.* **2014**, *53*, 1404.
- [95] J. Ma, Y.-S. He, W. Zhang, J. Wang, X. Yang, X.-Z. Liao, Z.-F. Ma, *Nano Energy* **2015**, *16*, 235.
- [96] R. Wang, C. Xu, J. Sun, L. Gao, *Sci. Rep.* **2014**, *4*, 7171.
- [97] W. Wei, S. Yang, H. Zhou, I. Lieberwirth, X. Feng, K. Mullen, *Adv. Mater.* **2013**, *25*, 2909.
- [98] X. Lu, R. Wang, Y. Bai, J. Chen, J. Sun, *J. Mater. Chem. A* **2015**, *3*, 12031.
- [99] L. Fan, B. Li, D. W. Rooney, N. Zhang, K. Sun, *Chem. Commun.* **2015**, *51*, 1597.

- [100] Y. Chang, J. Li, B. Wang, H. Luo, H. He, Q. Song, L. Zhi, *J. Mater. Chem. A* **2013**, *1*, 14658.
- [101] S. X. Yu, L. W. Yang, Y. Tian, P. Yang, F. Jiang, S. W. Hu, X. L. Wei, J. X. Zhong, *J. Mater. Chem. A* **2013**, *1*, 12750.
- [102] J. Liang, Y. Liu, L. Guo, L. Li, *RSC Adv.* **2013**, *3*, 11489.
- [103] R. Wang, C. Xu, J. Sun, L. Gao, H. Yao, *ACS Appl. Mater. Interfaces* **2014**, *6*, 3427.
- [104] G. Ye, Y. Gong, K. Keyshar, E. A. M. Husain, G. Brunetto, S. Yang, R. Vajtai, P. M. Ajayan, *Part. Part. Syst. Charact.* **2015**, *32*, 817.
- [105] H. Zhang, A. Xie, C. Wang, H. Wang, Y. Shen, X. Tian, *ChemPhysChem* **2014**, *15*, 366.
- [106] Y. Dong, S. Liu, Z. Wang, Y. Liu, Z. Zhao, J. Qiu, *RSC Adv.* **2015**, *5*, 8929.
- [107] X. Liu, J. Sun, X. Zhang, *Sens. Actuators, B* **2015**, *211*, 220.
- [108] Y. Hou, B. Zhang, Z. Wen, S. Cui, X. Guo, Z. He, J. Chen, *J. Mater. Chem. A* **2014**, *2*, 13795.
- [109] Y. Gong, S. Yang, Z. Liu, L. Ma, R. Vajtai, P. M. Ajayan, *Adv. Mater.* **2013**, *25*, 3979.
- [110] L. Jiang, B. Lin, X. Li, X. Song, H. Xia, L. Li, H. Zeng, *ACS Appl. Mater. Interfaces* **2016**, *8*, 2680.

- [111] C. Zhu, X. Mu, P. A. van Aken, J. Maier, Y. Yu, *Adv. Energy Mater.* **2015**, 5, 1401170.
- [112] D. Xie, W. J. Tang, X. H. Xia, D. H. Wang, D. Zhou, F. Shi, X. L. Wang, C. D. Gu, J. P. Tu, *J. Power Sources* **2015**, 296, 392.
- [113] X. Meng, J. Deng, J. Zhu, H. Bi, E. Kan, X. Wang, *Sci. Rep.* **2016**, 6, 21717.
- [114] G. Zhou, E. Paek, G. S. Hwang, A. Manthiram, *Adv. Energy Mater.* **2016**, 6, 1501355.
- [115] B. Xu, H. Wu, C. X. Lin, B. Wang, Z. Zhang, X. S. Zhao, *RSC Adv.* **2015**, 5, 30624.
- [116] M. A. Worsley, P. J. Pauzauskie, T. Y. Olson, J. Biener, J. H. Satcher Jr, T. F. Baumann, *J. Am. Chem. Soc.* **2010**, 132, 14067.
- [117] H. Li, L. Liu, F. Yang, *J. Mater. Chem. A* **2013**, 1, 3446.
- [118] S. Tong, T. Fan, W. Zeng, D. Zhang, C.-Y. Kao, Y. Liu, Y. Min, A. J. Epstein, *Synth. Met.* **2014**, 196, 27.
- [119] P. M. Sudeep, T. N. Narayanan, A. Ganesan, M. M. Shaijumon, H. Yang, S. Ozden, P. K. Patra, M. Pasquali, R. Vajtai, S. Ganguli, A. K. Roy, M. R. Anantharaman, P. M. Ajayan, *ACS Nano* **2013**, 7, 7034.
- [120] Q. Wu, Y. Sun, H. Bai, G. Shi, *Phys. Chem. Chem. Phys.* **2011**, 13, 11193.
- [121] G. Tang, Z.-G. Jiang, X. Li, H.-B. Zhang, A. Dasari, Z.-Z. Yu, *Carbon* **2014**, 77, 592.

- [122] S.-Z. Zu, B.-H. Han, *J. Phys. Chem. C* **2009**, *113*, 13651.
- [123] H. Zhu, D. Chen, N. Li, Q. Xu, H. Li, J. He, J. Lu, *Adv. Funct. Mater.* **2015**, *25*, 597.
- [124] Z. Wang, X. Shen, M. Akbari Garakani, X. Lin, Y. Wu, X. Liu, X. Sun, J. K. Kim, *ACS Appl. Mater. Interfaces* **2015**, *7*, 5538.
- [125] R. Li, C. Chen, J. Li, L. Xu, G. Xiao, D. Yan, *J. Mater. Chem. A* **2014**, *2*, 3057.
- [126] H. Wang, T. Maiyalagan, X. Wang, *ACS Catal.* **2012**, *2*, 781.
- [127] H. Liu, Y. Liu, D. Zhu, *J. Mater. Chem.* **2011**, *21*, 3335.
- [128] Z.-S. Wu, W. Ren, L. Xu, F. Li, H.-M. Cheng, *ACS Nano* **2011**, *5*, 5463.
- [129] Y. Qiu, X. Zhang, S. Yang, *Phys. Chem. Chem. Phys.* **2011**, *13*, 12554.
- [130] H. M. Jeong, J. W. Lee, W. H. Shin, Y. J. Choi, H. J. Shin, J. K. Kang, J. W. Choi, *Nano Lett.* **2011**, *11*, 2472.
- [131] Y. Xue, J. Liu, H. Chen, R. Wang, D. Li, J. Qu, L. Dai, *Angew. Chem. Int. Ed.* **2012**, *51*, 12124.
- [132] Z. S. Wu, A. Winter, L. Chen, Y. Sun, A. Turchanin, X. Feng, K. Mullen, *Adv. Mater.* **2012**, *24*, 5130.
- [133] X. Yao, G. Guo, Y. Zhao, Y. Zhang, S. Y. Tan, Y. Zeng, R. Zou, Q. Yan, Y. Zhao, *Small* **2016**.
- [134] Y. Ito, C. Christodoulou, M. V. Nardi, N. Koch, H. Sachdev, K. Müllen, *ACS Nano* **2014**, *8*, 3337.

- [135] W. Luo, B. Wang, C. G. Heron, M. J. Allen, J. Morre, C. S. Maier, W. F. Stickle, X. Ji, *Nano Lett.* **2014**, *14*, 2225.
- [136] A. K. Singh, M. W. Iqbal, V. K. Singh, M. Z. Iqbal, J. H. Lee, S.-H. Chun, K. Shin, J. Eom, *J. Mater. Chem.* **2012**, *22*, 15168.
- [137] J. Jiang, Y. Li, J. Liu, X. Huang, C. Yuan, X. W. Lou, *Adv. Mater.* **2012**, *24*, 5166.
- [138] M. H. Huang, S. Mao, H. Feick, H. Yan, Y. Wu, H. Kind, E. Weber, R. Russo, P. Yang, *Science* **2001**, *292*, 1897.
- [139] T. Maiyalagan, X. Dong, P. Chen, X. Wang, *J. Mater. Chem.* **2012**, *22*, 5286.
- [140] C.-C. Kung, P.-Y. Lin, Y. Xue, R. Akolkar, L. Dai, X. Yu, C.-C. Liu, *J. Power Sources* **2014**, *256*, 329.
- [141] C. Peng, H. Chen, Q. Li, W. Cai, Q. Yao, Q. Wu, J. Yang, Y. Yang, *J. Mater. Chem. A* **2014**, *2*, 13859.
- [142] F. Li, H. Yue, Z. Yang, X. Li, Y. Qin, D. He, *Mater. Lett.* **2014**, *128*, 132.
- [143] J. Luo, J. Liu, Z. Zeng, C. F. Ng, L. Ma, H. Zhang, J. Lin, Z. Shen, H. J. Fan, *Nano Lett.* **2013**, *13*, 6136.
- [144] X. Cao, Z. Zeng, W. Shi, P. Yep, Q. Yan, H. Zhang, *Small* **2013**, *9*, 1703.
- [145] B. G. Choi, M. H. Yang, W. H. Hong, J. W. Choi, Y. S. Huh, *ACS Nano* **2012**, *6*, 4020.
- [146] X. Li, Z. Wang, Y. Qiu, Q. Pan, P. Hu, *J. Alloys Compd.* **2015**, *620*, 31.

- [147] H. Y. Yue, S. Huang, J. Chang, C. Heo, F. Yao, S. Adhikari, F. Gunes, L. C. Liu, T. H. Lee, E. S. Oh, B. Li, J. J. Zhang, T. Q. Huy, N. V. Luan, Y. H. Lee, *ACS Nano* **2014**, 8, 1639.
- [148] C. Guan, Y. Wang, Y. Hu, J. Liu, K. H. Ho, W. Zhao, Z. Fan, Z. Shen, H. Zhang, J. Wang, *J. Mater. Chem. A* **2015**, 3, 23283.
- [149] X. Xia, D. Chao, C. F. Ng, J. Lin, Z. Fan, H. Zhang, Z. X. Shen, H. J. Fan, *Mater. Horiz.* **2015**, 2, 237.
- [150] D. Chao, X. Xia, J. Liu, Z. Fan, C. F. Ng, J. Lin, H. Zhang, Z. X. Shen, H. J. Fan, *Adv. Mater.* **2014**, 26, 5794.
- [151] J. Xiang, D. Dong, F. Wen, J. Zhao, X. Zhang, L. Wang, Z. Liu, *J. Alloys Compd.* **2016**, 660, 11.
- [152] N. Li, Z. Chen, W. Ren, F. Li, H.-M. Cheng, *Proc. Natl. Acad. Sci. U. S. A.* **2012**, 109, 17360.
- [153] B. Wang, S. Li, X. Wu, J. Liu, W. Tian, *Phys. Chem. Chem. Phys.* **2015**, 18, 908.
- [154] H. Ji, L. Zhang, M. T. Pettes, H. Li, S. Chen, L. Shi, R. Piner, R. S. Ruoff, *Nano Lett.* **2012**, 12, 2446.
- [155] Y. Tang, F. Huang, H. Bi, Z. Liu, D. Wan, *J. Power Sources* **2012**, 203, 130.
- [156] H. Zhu, X. Wu, L. Zan, Y. Zhang, *ACS Appl. Mater. Interfaces* **2014**, 6, 11724.

- [157] J. Zhou, Y. Huang, X. Cao, B. Ouyang, W. Sun, C. Tan, Y. Zhang, Q. Ma, S. Liang, Q. Yan, H. Zhang, *Nanoscale* **2015**, 7, 7035.
- [158] K. P. Prasad, Y. Chen, P. Chen, *ACS Appl. Mater. Interfaces* **2014**, 6, 3387.
- [159] D. Chao, C. Zhu, X. Xia, J. Liu, X. Zhang, J. Wang, P. Liang, J. Lin, H. Zhang, Z. X. Shen, H. J. Fan, *Nano Lett.* **2015**, 15, 565.
- [160] S. Chabi, C. Peng, Z. Yang, Y. Xia, Y. Zhu, *RSC Adv.* **2015**, 5, 3999.
- [161] Z. Zhang, K. Chi, F. Xiao, S. Wang, *J. Mater. Chem. A* **2015**, 3, 12828.
- [162] S. B. Kulkarni, U. M. Patil, I. Shackery, J. S. Sohn, S. Lee, B. Park, S. Jun, *J. Mater. Chem. A* **2014**, 2, 4989.
- [163] J. S. Sohn, U. M. Patil, S. Kang, S. Kang, S. C. Jun, *RSC Adv.* **2015**, 5, 107864.
- [164] X. Liu, J. Cheng, W. Li, X. Zhong, Z. Yang, L. Gu, Y. Yu, *Nanoscale* **2014**, 6, 7817.
- [165] Y. Li, H. Zhang, P. K. Shen, *Nano Energy* **2015**, 13, 563.
- [166] X. Zhao, J. Zhang, J. Zhang, C. Gong, X. Gu, Z. Ma, J. Zhou, L. Yu, Z. Zhang, *J. Power Sources* **2015**, 294, 223.
- [167] B. Luo, T. Qiu, L. Hao, B. Wang, M. Jin, X. Li, L. Zhi, *J. Mater. Chem. A* **2016**, 4, 362.
- [168] P. Wu, H. Wang, Y. Tang, Y. Zhou, T. Lu, *ACS Appl. Mater. Interfaces* **2014**, 6, 3546.

- [169] X. Xin, X. Zhou, F. Wang, X. Yao, X. Xu, Y. Zhu, Z. Liu, *J. Mater. Chem.* **2012**, 22, 7724.
- [170] S. Jing, H. Jiang, Y. Hu, J. Shen, C. Li, *Adv. Funct. Mater.* **2015**, 25, 5395.
- [171] P. Chen, T. Y. Xiao, Y. H. Qian, S. S. Li, S. H. Yu, *Adv. Mater.* **2013**, 25, 3192.
- [172] S.-H. Bae, K. Karthikeyan, Y.-S. Lee, I.-K. Oh, *Carbon* **2013**, 64, 527.
- [173] X. Dong, Y. Ma, G. Zhu, Y. Huang, J. Wang, M. B. Chan-Park, L. Wang, W. Huang, P. Chen, *J. Mater. Chem.* **2012**, 22, 17044.
- [174] X. Dong, J. Chen, Y. Ma, J. Wang, M. B. Chan-Park, X. Liu, L. Wang, W. Huang, P. Chen, *Chem. Commun.* **2012**, 48, 10660.
- [175] Y. Huang, D. Wu, J. Jiang, Y. Mai, F. Zhang, H. Pan, X. Feng, *Nano Energy* **2015**, 12, 287.
- [176] L. Ji, Z. Lin, M. Alcoutlabi, X. Zhang, *Energy Environ. Sci.* **2011**, 4, 2682.
- [177] S. Goriparti, E. Miele, F. De Angelis, E. Di Fabrizio, R. Proietti Zaccaria, C. Capiglia, *J. Power Sources* **2014**, 257, 421.
- [178] B. G. Choi, S. J. Chang, Y. B. Lee, J. S. Bae, H. J. Kim, Y. S. Huh, *Nanoscale* **2012**, 4, 5924.
- [179] Y. Liu, Z. Cheng, H. Sun, H. Arandiyana, J. Li, M. Ahmad, *J. Power Sources* **2015**, 273, 878.
- [180] F. Jiang, S. Zhao, J. Guo, Q. Su, J. Zhang, G. Du, *Mater. Lett.* **2015**, 161, 297.

- [181] F. Zhang, Y. Tang, H. Liu, H. Ji, C. Jiang, J. Zhang, X. Zhang, C. S. Lee, *ACS Appl. Mater. Interfaces* **2016**, 8, 4691.
- [182] Y. Gong, S. Yang, L. Zhan, L. Ma, R. Vajtai, P. M. Ajayan, *Adv. Funct. Mater.* **2014**, 24, 125.
- [183] X. Jiang, X. Yang, Y. Zhu, J. Shen, K. Fan, C. Li, *J. Power Sources* **2013**, 237, 178.
- [184] H. Tang, X. Qi, W. Han, L. Ren, Y. Liu, X. Wang, J. Zhong, *Appl. Surf. Sci.* **2015**, 355, 7.
- [185] J. Yao, B. Liu, S. Ozden, J. Wu, S. Yang, M.-T. F. Rodrigues, K. Kalaga, P. Dong, P. Xiao, Y. Zhang, R. Vajtai, P. M. Ajayan, *Electrochim. Acta* **2015**, 176, 103.
- [186] S. Han, J. Jiang, Y. Huang, Y. Tang, J. Cao, D. Wu, X. Feng, *Phys. Chem. Chem. Phys.* **2015**, 17, 1580.
- [187] G. Kucinskis, G. Bajars, J. Kleperis, *J. Power Sources* **2013**, 240, 66.
- [188] S. Shi, L. Liu, C. Ouyang, D.-s. Wang, Z. Wang, L. Chen, X. Huang, *Phys. Rev. B* **2003**, 68.
- [189] P. P. Prosini, M. Lisi, D. Zane, M. Pasquali, *Solid State Ionics* **2002**, 148, 45.
- [190] B. Wang, W. Al Abdulla, D. Wang, X. S. Zhao, *Energy Environ. Sci.* **2015**, 8, 869.
- [191] L. Liang, Y. Xu, Y. Lei, H. Liu, *Nanoscale* **2014**, 6, 3536.

- [192] Y. Ma, X. Li, Z. Xie, Z. Xiu, Y. Wu, X. Hao, *J. Mater. Sci.: Mater. Electron.* **2014**, 25, 2716.
- [193] M. Sun, H. Li, J. Wang, G. Wang, *Carbon* **2015**, 94, 864.
- [194] C. Botas, D. Carriazo, G. Singh, T. Rojo, *J. Mater. Chem. A* **2015**, 3, 13402.
- [195] H. I. Becker, (Gen. Electric) *US 2800616*, **1957**.
- [196] R. Kötza, M. Carlenb, *Electrochim. Acta* **2000**, 45, 2483.
- [197] T.C. Murphy, R.B. Wright, R.A. Sutula, in *Electro-chemical Capacitors II, Proceedings*, Vol 96 (Eds: F. M. Delnick, D. Ingersoll, X. Andrieu, K. Naoi), The Electrochemical Society, Pennington, U.S.A., **1997**, Ch 25.
- [198] Y. Xu, Z. Lin, X. Zhong, X. Huang, N. O. Weiss, Y. Huang, X. Duan, *Nat. Commun.* **2014**, 5, 4554.
- [199] W. Wang, S. Guo, M. Penchev, I. Ruiz, K. N. Bozhilov, D. Yan, M. Ozkan, C. S. Ozkan, *Nano Energy* **2013**, 2, 294.
- [200] J. Liu, L. Zhang, H. B. Wu, J. Lin, Z. Shen, X. W. Lou, *Energy Environ. Sci.* **2014**, 7, 3709.
- [201] W. S. Hummers Jr., R. E. Offeman, *J. Am. Chem. Soc.* **1958**, 80, 1339.
- [202] T. Zhai, F. Wang, M. Yu, S. Xie, C. Liang, C. Li, F. Xiao, R. Tang, Q. Wu, X. Lu, Y. Tong, *Nanoscale* **2013**, 5, 6790.
- [203] X. Zhu, P. Zhang, S. Xu, X. Yan, Q. Xue, *ACS Appl. Mater. Interfaces* **2014**, 6, 11665.

- [204] J. Yuan, J. Zhu, H. Bi, X. Meng, S. Liang, L. Zhang, X. Wang, *Phys. Chem. Chem. Phys.* **2013**, *15*, 12940.
- [205] W. Deng, Y. Sun, Q. Su, E. Xie, W. Lan, *Mater. Lett.* **2014**, *137*, 124.
- [206] B. Qiu, M. Xing, J. Zhang, *J. Mater. Chem. A* **2015**, *3*, 12820.
- [207] H. Wang, H. Yi, X. Chen, X. Wang, *J. Mater. Chem. A* **2014**, *2*, 1165.
- [208] H. Lin, F. Liu, X. Wang, Y. Ai, Z. Yao, L. Chu, S. Han, X. Zhuang, *Electrochim. Acta* **2016**, *191*, 705.
- [209] U. M. Patil, M. S. Nam, J. S. Sohn, S. B. Kulkarni, R. Shin, S. Kang, S. Lee, J. H. Kim, S. C. Jun, *J. Mater. Chem. A* **2014**, *2*, 19075.
- [210] U. M. Patil, S. C. Lee, J. S. Sohn, S. B. Kulkarni, K. V. Gurav, J. H. Kim, J. H. Kim, S. Lee, S. C. Jun, *Electrochim. Acta* **2014**, *129*, 334.
- [211] C. Jiang, B. Zhao, J. Cheng, J. Li, H. Zhang, Z. Tang, J. Yang, *Electrochim. Acta* **2015**, *173*, 399.
- [212] U. M. Patil, J. S. Sohn, S. B. Kulkarni, S. C. Lee, H. G. Park, K. V. Gurav, J. H. Kim, S. C. Jun, *ACS Appl. Mater. Interfaces* **2014**, *6*, 2450.
- [213] Y. Wei, S. Chen, D. Su, B. Sun, J. Zhu, G. Wang, *J. Mater. Chem. A* **2014**, *2*, 8103.
- [214] X. Xia, D. Chao, Z. Fan, C. Guan, X. Cao, H. Zhang, H. J. Fan, *Nano Lett.* **2014**, *14*, 1651.

- [215] J. H. Lee, N. Park, B. G. Kim, D. S. Jung, K. Im, J. Hur, J. W. Choi, *ACS Nano* **2013**, 7, 9366.
- [216] K. Chen, L. Chen, Y. Chen, H. Bai, L. Li, *J. Mater. Chem.* **2012**, 22, 20968.
- [217] F. Barzegar, A. Bello, O. O. Fashedemi, J. K. Dangbegnon, D. Y. Momodu, F. Taghizadeh, N. Manyala, *Electrochim. Acta* **2015**, 180, 442.
- [218] Y. Meng, Y. Zhao, C. Hu, H. Cheng, Y. Hu, Z. Zhang, G. Shi, L. Qu, *Adv. Mater.* **2013**, 25, 2326.
- [219] F. Meng, Y. Ding, *Adv. Mater.* **2011**, 23, 4098.
- [220] X. Lu, M. Yu, G. Wang, Y. Tong, Y. Li, *Energy Environ. Sci.* **2014**, 7, 2160.
- [221] C. Meng, C. Liu, L. Chen, C. Hu, S. Fan, *Nano Lett.* **2010**, 10, 4025.
- [222] Z. Zhang, F. Xiao, L. Qian, J. Xiao, S. Wang, Y. Liu, *Adv. Energy Mater.* **2014**, 4, 1400064.
- [223] G. Zhu, Z. He, J. Chen, J. Zhao, X. Feng, Y. Ma, Q. Fan, L. Wang, W. Huang, *Nanoscale* **2014**, 6, 1079.
- [224] H. Wan, J. Liu, Y. Ruan, L. Lv, L. Peng, X. Ji, L. Miao, J. Jiang, *ACS Appl. Mater. Interfaces* **2015**, 7, 15840.
- [225] Z. Gao, W. Yang, J. Wang, N. Song, X. Li, *Nano Energy* **2015**, 13, 306.

Chapter 2. *In-Situ* Integration of Anisotropic SnO₂ Heterostructures inside Three-Dimensional Graphene Aerogel for Enhanced Lithium Storage

NOTE: *This work was published on ACS applied materials & interfaces with the same title.*

ABSTRACT

Three-dimensional (3D) graphene aerogel (GA) has emerged as an outstanding support for metal oxides to enhance the overall energy-storage performance of the resulted hybrid materials. In most cases, metals/metal oxides inside GA are in un-crafted geometries. Introducing structure-controlled metal oxides into GA may further push electrochemical properties of metal oxide-GA hybrids. Using rutile SnO₂ as an instance, this work demonstrated a facile hydrothermal strategy combined with a preconditioning technique named vacuum-assisted impregnation for in-situ construction of controlled anisotropic SnO₂ heterostructures inside GA. The obtained hybrid material was fully characterized in detail, and its formation mechanism was investigated by monitoring the phase-transformation process. Rational integration of the two advanced structures, anisotropic SnO₂ and 3D GA, synergistically led to

enhanced lithium-storage properties (1176 mA h g⁻¹ for 1st cycle and 872 mA h g⁻¹ for 50th cycle at 100 mA g⁻¹) as compared with its two counterparts, namely rough nanoparticles@3D GA and anisotropic SnO₂@2D graphene sheets (618 and 751 mA h g⁻¹ for 50th cycle at 100 mA g⁻¹, respectively). It was also well demonstrated that this hybrid material was capable of delivering high specific capacity at rapid charge/discharge cycles (1044 mA h g⁻¹ at 100 mA g⁻¹, 847 mA h g⁻¹ at 200 mA g⁻¹, 698 mA h g⁻¹ at 500 mA g⁻¹, and 584 mA h g⁻¹ at 1000 mA g⁻¹). The in-situ integration strategy along with vacuum-assisted impregnation technique presented here shows great potential as a versatile tool for accessing a variety of sophisticated smart structures in the form of anisotropic metal oxides within 3D GA toward useful applications.

2.1 Introduction

The manipulability of graphene building blocks enables the creation of sophisticated functional architectures, where the intriguing properties of graphene are effectively harnessed for a wide range of applications.^[1-4] Since the first exfoliation of single-layer graphene,^[5] multifarious smart nanostructures based on it have been realized, including nanoparticles/nanorods/nanowires anchored on the graphene surface,^[6-9] encapsulated nanospheres,^[10, 11] layer-by-layer assembled thin films,^[12, 13] stacked papers,^[14-17]

vertically aligned sheets,^[18] and so forth. Recently, three-dimensional (3D) graphene including graphene aerogel (GA)^[19] and graphene foam^[20] has emerged as an attractive support to fabricate novel functional materials. On account of the interconnected porous framework, high surface area, and mechanical flexibility, these 3D graphene materials present promising applications, especially serving as advanced energy materials. However, the application potential of graphene foam was greatly restricted by the complex and costly synthetic procedure. On the contrary, the synthesis of GA could be achieved via one-step facile route by either hydrothermal treatment or *in-situ* reduction,^[21, 22] which is apparently more cost-effective, scalable and approachable in terms of industrial applications.

With respect to energy applications, metal oxides are competitive candidates but at the same time suffer from poor electric conductivity. Hence, combining metal oxides with graphene of high electron mobility can hopefully retain the advantages of both species. Recently, researchers demonstrated that 3D graphene-metal oxide hybrids could exceed their 2D counterparts both in energy conversion and storage.^[23-25] In the case of lithium-ion battery, 3D GA brings three substantial improvements: (1) interconnected graphene framework facilitates the electron transport across the electrode; (2) numerous multidimensional channels in GA could effectively accelerate the lithium diffusion within the bulk electrode; (3) elastic matrix of GA could accommodate the volume expansion of metal oxides during long-term cycling. Up to date, various metal

oxides/sulfides such as Co_3O_4 ,^[26] SnO_2 ,^[27] Fe_3O_4 ,^[23] and MoS_2 ^[28] have been successfully coupled with GA for high-performance lithium storage. Nevertheless, these metal oxides/sulfides in GA present in un-crafted geometries, and in most cases, they are nanoparticles in the rough. Thus, controlled aqueous growth of well-defined morphologies inside 3D GA still remains a challenge. On the other hand, it is well documented that the geometric shape and surface features could significantly influence the physiochemical properties of metal oxides. Controlled anisotropic morphologies such as nanorods, nanowires, and nanosheets are expected to enhance the electrochemical energy-storage performance of metal oxides over their particle-like counterparts.^[29-31] Therefore, highly ordered nanostructures prepared through *in-situ* growth may unfold the full application potential of GA-based hybrids. Herein, this work present a novel synthetic strategy to construct the purposely designed, coral-like SnO_2 embellished GA heterostructures with enhanced lithium-storage performance. Furthermore, the strategy shows a high promise as a general approach to be applied to other metal oxides such as Fe_2O_3 , TiO_2 , and ZnO .

Scheme 2.1. Synthetic process of SnO_2 NCs@GA through hydrothermal route along with vacuum-assisted impregnation as preconditioning.

A facile strategy was developed, namely a vacuum-assisted impregnation, to fully saturate the porous hydrophobic GA with aqueous precursor solution, followed by an *in-situ* hydrothermal reaction to grow anisotropic SnO_2 crystallites inside 3D architecture of GA prepared beforehand (**Scheme 2.1**). Herein, selective nucleation of SnO_2 nanocorals (NCs) on the surface of reduced graphene oxide (RGO) was achieved through the conjugation of oxygen-containing species. Without vacuum-assisted impregnation as the pretreatment, GA would be floating in aqueous precursor solution, resulting in failure to introduce SnO_2 crystallites into interior pore channels of GA. Alternatively, surfactants or pre-functionalization with hydrophilic groups could be applied to modify the surface properties of GA, which could slightly improve its

saturation in aqueous solution.^[32-34] In this case, by rapidly lowering the systematic pressure below 50 mbar, the air inside pore channels would be pumped out and thus the aqueous solution could enter the inner territories of GA. Ultimately, it was found this technique could improve the effectiveness of impregnation and at the same time secure the purity of precursors. As observed from samples of different reaction times, Na_4SnO_4 was first formed and eventually transmuted into SnO_2 . After the hydrothermal treatment, the product was annealed at 600 °C under nitrogen atmosphere for 3 h to improve the graphitic lattice, as well as the crystallinity and phase purity of SnO_2 NCs. As both GA and SnO_2 were extensively studied as potential energy materials.^[35-37] finally the superior properties of obtained SnO_2 NCs@GA as stable lithium-storage materials was manifested, compared to its counterparts including SnO_2 NCs@GSs and SnO_2 nanoparticles@GA (SnO_2 NPs@GA) in terms of enhanced specific capacity and rate capability. Overall, these results confirmed that the performance improvement of SnO_2 NCs@GA could be achieved through the combination of 3D porous GA and coral-shaped SnO_2 , showing integrated advantages of individual elements, *i.e.*, (1) accelerated electron transport and lithium ion diffusion, as well as accommodated volume expansion of SnO_2 during cycling, and (2) additional contact surface for lithium ions to access.^[23, 38]

2.2 Results and discussion

2.2.1 Chemical composition and crystal properties

Figure 2.1. a) Powder XRD patterns of SnO₂ NCs@GA: (I) hydrothermally synthesized, and (II) after calcination. b) XPS spectrum of SnO₂ NCs@GA. c) TGA curves of SnO₂ NCs@GA.

The preparation of SnO₂ NCs@GA was described in the Experimental section. The phase purity and crystallographic structure of the developed SnO₂ NCs@GA hybrid were investigated by means of power X-ray diffraction (XRD, **Figure 2.1a**). Major diffraction peaks of the hydrothermally synthesized product (pattern I) can be readily indexed to cassiterite SnO₂ (PDF 41-1445), except for four additional minor peaks ($2\theta = 31.6^\circ, 45.3^\circ, 56.5^\circ, 75.3^\circ$) that are assigned to hydroromarchite Sn₆O₄(OH)₄ (PDF 46-1486). Diffraction signal of graphene in the hybrid is weak and indistinguishable as compared with that of SnO₂. After calcination of the hydrothermal product at 600 °C in N₂ flow, the final hybrid was obtained with decreased labile oxygen groups for graphene as well as improved crystallinity for SnO₂. The powder XRD peaks of Sn₆O₄(OH)₄ in pattern II (**Figure 2.1a**) were eliminated, confirming that Sn₆O₄(OH)₄ was totally converted into SnO₂.

In order to verify the chemical composition of the annealed product, X-ray photoelectron spectroscopy (XPS in 0-1200 eV range) was further conducted as a cross-reference. As displayed in **Figure 2.1b**, the presence of carbon, oxygen and tin was traced from the hybrid material. It can be seen from the inset high-resolution spectrum that two peaks at 486.4 eV and 494.9 eV correspond to Sn 3d_{5/2} and Sn 3d_{3/2},

respectively. The peak position and interpeak interval (8.5eV) collectively confirm that SnO₂ is the major form of tin oxide in this material after the calcination treatment.^[39]

Composition percentage of graphene as well as thermal behavior for the hybrid material (after calcination) were probed by thermogravimetric analysis (TGA), which was performed with a ramping rate of 20 °C min⁻¹ in air flow (**Figure 2.1c**). The weight derivative line of SnO₂ NCs@GA suggests that the decomposition of RGO is a two-step process where the first stage denotes the rapid combustion of defective graphene sheets at the vicinity of 500 °C, followed by further disintegration of defect-free graphene around 600 °C. It's noteworthy that the combustion of graphene starts at a relatively high temperature, i.e. 500 °C, which implies the improved crystallinity of graphene after calcination. From the TGA curve, mass fraction of SnO₂ was calculated to be 70.18%, which is comparable to other graphene/metal oxide hybrid materials.

2.2.2. Morphological features and porous texture

The structural and morphological details of the as-prepared SnO₂ NCs@GA were examined by means of field emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM). The bare GA demonstrates a hierarchical interconnected graphene matrix featured with macropores (**Figure 2.2a**). The inset image in **Figure 2.2a** shows the macroscopic shape of the monolithic GA, whose size

was controlled by several factors including reaction temperature, volume/concentration of GO, and shape of Polytetrafluoroethylene (PTFE) containers. As indicated by N₂ adsorption/desorption isotherms (**Figure 2.3a**), a mesoporous structure was generated in addition to the macroporous skeleton during the self-assembly process of forming GA. The N₂ adsorption/desorption plots present the characteristics of both type II and type IV isotherms, corresponding to unlimited monolayer-multilayer adsorption taking place in macroporous adsorbents and capillary condensation in mesopores, respectively.^[40] It also reveals a H3 hysteresis loop with sharp increase of adsorption at the region of relatively high pressure ($P/P_0 = 0.8-0.99$),^[41] indicating the dominance of mesopores arisen from plate-like RGO sheets. Based on Barrett-Joyner-Halenda (BJH) calculation (inset in **Figure 2.3a**), the majority of pore volume is contributed by mesopores with an average diameter of around 4 nm. Such combination of macroporous and mesoporous structures leads to a remarkable specific surface area of 366.9 m² g⁻¹, as probed by the Brunauer-Emmett-Teller (BET) method.

Figure 2.2. a) FESEM images of GA. b-f) FEM images of SnO₂ NCs@GA. Inset photos in (a, b) show the shape and size of monolithic GA and hybrid.

Figure 2.3. N₂ adsorption/desorption isotherms for GA (a) and SnO₂ NCs@GA (b).

For the morphology of SnO₂ NCs@GA (**Figure 2.2b-f**), it is immediately apparent that the porous graphene skeleton became solid after hydrothermal crystallization, and uniformly embellished with highly dispersed SnO₂ NCs. From the magnified images (**Figure 2.2d-f**), it can be observed that these SnO₂ NCs are trapped and segregated inside formicary-like graphene matrix. Moreover, part of the SnO₂ NCs was wrapped by the assembled flexible RGO sheets (**Figure 2.2f**). It is commonly accepted that the graphene wrapping can accommodate the volume expansion of SnO₂ during charge/discharge process,^[42, 43] and curtail the distance of electron transportation from semiconductive SnO₂ to the graphene electron highway.^[44] After embedding with SnO₂ NCs, specific surface area of the hybrid sharply decreased to 60 m² g⁻¹ (**Figure 2.3b**), attributed to the high density of SnO₂. The good consistence in pore size distribution (insets in **Figure 2.3a, b**) indicates that the graphene network remains unimpaired during the SnO₂ growth. It is noteworthy that the featured incorporation of mesopores

and macropores within the hybrid system could enable easier and faster lithium diffusion between electrolyte and active materials, hence augmenting the lithium-storage performance. In addition, it should be mentioned that the N_2 adsorption/desorption isotherms were carried out with grinded fine power samples of GA and SnO_2 NCs@GA, and the obtained results implied that their microscopic architectures were not squished by the grinding procedure.

Figure 2.4. a) TEM image of SnO_2 nanorod wrapped by graphene. b, c) High-magnification TEM images of SnO_2 nanorods.

The low-magnification TEM image (**Figure 2.4a**) exhibits individual SnO_2 nanorods in the coral assembly, which are partially wrapped by few-layered graphene sheets. The diameter of the nanorods was determined to be c.a. 100 nm. The high-magnification TEM images (**Figure 2.4b, c**) denote two sets of dominant crystal lattice in the nanorods with respective interfringe spacing of 0.33 nm and 0.26 nm, corresponding to the (110) and (101) facets from tetragonal rutile SnO_2 . It was confirmed that the anisotropic

growth along c-axis is thermodynamically preferred, since the surface energy of (001) plane is the highest one.^[45]

2.2.3. Formation mechanism

Figure 2.5. FESEM images of the products collected at various reaction stages: a) 0.5 h; b) 1 h; c) 4 h; d) 12 h.

To further investigate the growth mechanism and formation process of such nanostructure inside GA, several control experiments were conducted. Generally, no formation of SnO₂ NCs was found when GA was absent, and the solution remained transparent throughout hydrothermal treatment. The observation is probably due to that the oxygen groups on RGO could reduce the surface-energy barrier as compared to

homogeneous nucleation, hence enabling a heterogeneous nucleation. As displayed in **Figure 2.5a-d**, samples collected from various reaction stages were inspected by FESEM in order to give a detailed demonstration of the structural and morphological evolution during the whole crystal growth process. Within the initial 30 min (**Figure 2.5a**), irregular spherical Na_4SnO_4 phase was formed as the first stage, due to its fast kinetics of crystallization.^[46] After reacting for 1 h (**Figure 2.5b**), a phase transformation from intermediate Na_4SnO_4 to thermodynamically more stable SnO_2 started, as indicated by the formation of primary nanorods. At this preliminary stage, the SnO_2 crystals already illustrated a coral-like contour, which would direct their further growth. When the reaction time was prolonged to 4 h (**Figure 2.5c**), the ripening of SnO_2 nanorods continued, while Na_4SnO_4 still existed. After 12 h of reaction (**Figure 2.5d**), no spheres were observed, indicating that almost 100% of Na_4SnO_4 was converted into SnO_2 NCs along with a modicum of $\text{Sn}_6\text{O}_4(\text{OH})_4$.

Figure 2.6. Powder XRD spectra of the samples collected at 10 min, 30 min, 1 h, 4 h, 8 h, 12 h, and 24 h of the hydrothermal reaction.

The phase transformation process was verified by powder XRD spectra collected at various stages of reaction, as displayed in **Figure 2.6**. At 10 min from the beginning of the reaction, Na_4SnO_4 as an intermediate phase was dominant in solution. Meanwhile, the existence of SnO_2 can also be detected from its (110) peak, indicating the transformation from intermediate phase to final product began at a very early stage. The broad peak domain of (110) facet indicates the disordered manner of SnO_2 crystals at this time point. From the powder XRD spectra gained from 30 min, 1h, 4h and 8h of

the reaction, it is clear that the evolution of SnO_2 was based on the consumption of Na_4SnO_4 . The main reaction is nearly complete at ~ 12 h.

2.2.4. Electrochemical performance as LIB anode.

SnO_2 has been extensively studied as host structure for reversible lithium insertion/desertion.^[47, 48] There are two principle electrochemical processes involved:

According to these processes, the theoretical capacity of SnO_2 was calculated to be 790 mA h g^{-1} .

Figure 2.7. a) Galvanostatic discharge/charge profiles of SnO_2 NCs@GA at a current density of 100 mA g^{-1} for the 1st, 2nd and 50th cycles. b) Columbic efficiency of SnO_2 NCs@GA at 100 mA g^{-1} .

To evaluate the lithium-storage properties of SnO_2 NCs@GA, galvanostatic cyclic measurements were performed at the current density of 100 mA g^{-1} , and the

discharge/charge voltage profiles of the 1st, 2nd and 50th cycles are exhibited in **Figure 2.7a**. Impressively, for the first cycle, SnO₂ NCs@GA electrode shows a considerable discharge capacity of 2569 mA h g⁻¹, while the reversible charge capacity is 1176 mA h g⁻¹. This irreversibility is probably contributed by the reduction of SnO₂, reaction of oxygen functionality with lithium ions, and formation of solid-electrolyte interphase (SEI) during the initial cycle.^[49] The second cycle shows reversible discharge and charge capacities of 1236 and 1112 mA h g⁻¹, respectively. Despite the initial loss, the high capacity of SnO₂ NCs@GA electrode was largely retained. After 50 cycles, its charge capacity still remains at 861 mA h g⁻¹ (73.21% of its initial cycle), which is even beyond the theoretical capacity (790 mA h g⁻¹) of SnO₂. In accordance with the results from other SnO₂/carbon hybrids reported in literature,^[50, 51] the excessive specific capacity could be originated from the enhanced electrochemical activity of graphene supported/wrapped SnO₂. It should be noted that over 97% columbic efficiency of SnO₂@GA electrode was attained beyond 60 cycles, as revealed in **Figure 2.7b**.

Figure 2.8. Detailed characterization of the two control samples. a, b) SEM images of SnO₂ NPs@GA (a) and SnO₂ NCs@GSs (b). c, d) TGA curves of SnO₂ NPs@GA (c) and SnO₂ NCs@GSs (d).

To further demonstrate the superior performance of the anisotropic metal oxide/3D graphene hybrid, SnO₂ NCs@GA was then compared with two control samples, namely SnO₂ NPs@GA and SnO₂ NCs@GSs. As shown in **Figure 2.8a**, in the control samples, SnO₂ nanoparticles inside GA exhibit an un-defined rough shape. The average diameter of the nanoparticles are below 1 μm, at a comparable scale with SnO₂ NCs. **Figure 2.8b** reveals the stacking of GSs and SnO₂ crystals, which decreases the surface area of hybrid materials. This is the main drawback of using GSs as a substrate material. Before the electrochemical measurements, TGA characterization was conducted to ensure that

the weight ratios of SnO_2 in these three materials are at a same level. As demonstrated in **Figure 2.8c, d**, the weight percentages of SnO_2 for SnO_2 NPs@GA and SnO_2 NCs@GA are calculated to be 66.63% and 62.19%, respectively. It is assumed that these three materials are comparable in term of SnO_2 content.

Figure 2.9. a) Cycling performance of SnO_2 NCs@GA, SnO_2 NPs@GA and SnO_2 NCs@GSs at a current density of 100 mA g^{-1} . b) Rate performance of SnO_2 NCs@GA, SnO_2 NPs@GA, and SnO_2 NCs@GS at different current densities.

The details of the comparison between their electrochemical performances were elaborated in **Figure 2.9**. As shown in **Figure 2.9a**, SnO₂ NCs@GA based anode shows better overall performance over the other two groups, which could be explained by its higher surface area and additional active sites. As for their long-term performance, the reversible discharge capacity of SnO₂ NCs@GA electrode maintains at 872 mA h g⁻¹ even beyond 50 cycles, which is much higher than 618 mA h g⁻¹ from SnO₂ NPs@GA and 751 from SnO₂ NCs@GSs. In addition, these three electrodes demonstrate very stable cyclic curves, indicating that graphene is an excellent candidate for metal oxide coupling.

The rate performance of SnO₂ NCs@GA was evaluated at various current densities, namely 100, 200, 500 and 1000 mA g⁻¹ (**Figure 2.9b**). By increasing the current density, it was observed that the specific capacities at all conditions degraded mildly, implying the excellent rate capability of SnO₂ NCs@GA. The corresponding charge capacities gained from each first cycle at 100, 200, 500, 1000 mA g⁻¹ are 1044, 847, 698, 584 mA h g⁻¹, respectively. Even at a current density as high as 1000 mA g⁻¹, a notable specific capacity of 533 mA h g⁻¹ could still be stabilized at the 10th cycle. After 10 cycles, the current density was set back to 100 mA g⁻¹, the charge capacity could be retrieved to 824 mA h g⁻¹, equal to 78.93% of initial reversible capacity. As comparison, the rate capability of SnO₂ NCs@GS and SnO₂ NPs@GA were also examined to provide a

more balanced assessment on the lithium storage performance of the three structures. At each first cycle where current density was 100, 200, 500, 1000 mA g⁻¹ initially and then fell back to 100 mA g⁻¹, the respective charge capacities for SnO₂ NCs@GS were 964, 672, 513, 425, 693 mA h g⁻¹. Meanwhile, specific charge capacities delivered by SnO₂ NPs@GA at the same conditions were 815, 588, 466, 390, 545 mA h g⁻¹ respectively. It was shown that the SnO₂ NCs@GA has the better rate capability than SnO₂ NCs@GS and SnO₂ NPs@GA, and it is in well agreement with their cycling performance. Furthermore, it is notable that at higher current rates, the SnO₂ NCs@GA showed even better relative specific capacity. For example, at the 1st cycle of 200 mA g⁻¹, SnO₂ NCs@GA was capable of delivering a reversible charge capacity which is 26% and 44% higher than SnO₂ NCs@GS and SnO₂ NPs@GA respectively. Later on at 1st cycle of 1000 mA g⁻¹, it was increased to 37% and 49%, for SnO₂ NCs@GS and SnO₂ NPs@GA respectively.

Figure 2.10. Nyquist plots of SnO_2 NCs@GA, SnO_2 NPs@GA, and SnO_2 NCs@GS based anodes. Inset shows Randles equivalent circuit. R_e is the electrolyte resistance; CPE stands for constant phase element; R_{ct} is the charge-transfer resistance; Z_w is the Warburg element.

Alternating current (AC) impedance results shed some light on understanding the mechanisms underlying the improved performance of SnO_2 NCs@GA electrode, which could be specified from two aspects. First, in typical Nyquist plots for anodic materials, the depressed semicircle at high-medium frequency region is associated with the transportation of charges through electrode-electrolyte interface. For the SnO_2 NCs@GA anode shown in **Figure 2.10**, its semicircle is obviously smaller than other samples, indicating lower charge-transfer resistance (R_{ct}) over its two counterparts. Secondly, at low frequency region, the slope of the fitted line is determined by the diffusion behavior of lithium ions inside bulk electrode. It was clearly demonstrated

that the Warburg line for SnO_2 NCs@GA is much steeper than that of SnO_2 NPs@GA, implying more rapid ion diffusion in the case of SnO_2 NCs@GA probably due to increased exposure to electrolyte. Based the electrochemical impedance spectroscopy (EIS), it was confirmed that the combination of 3D graphene and anisotropic SnO_2 could enhance both the electron and lithium ion transport within the electrode.

2.2.5. Comprehension on the relationship between structural properties and electrochemical performance

Scheme 2.2. Schematic comparison of SnO_2 NCs@GSs, SnO_2 NPs@GA and SnO_2 NCs@GA in terms of lithium access and electron transport. Compared with sphere-shaped nanoparticles, the NCs consisting of 1D nanorods provide additional active sites for lithium access, attributing to their increased electrode-electrolyte contact area. SnO_2 NCs grown on GSs (SnO_2 NCs@GSs) suffer from severe self-stacking, which results in shrinking of surface area. The graphene wrapping in SnO_2 NCs@GA can also accelerate the electron transport by providing more shortcuts to the graphene highway.

In accordance with the specialized structure and morphology of SnO_2 NCs@GA, it is reasonable to attribute the enhanced lithium-storage properties to the advances from

both 3D architecture and the patterned growth of metal oxide. On one hand, compared with 2D graphene architecture, a stable 3D structure remarkably improves not only the overall conductivity by providing large surface area with multidimensional channels for electron transport, but also the lithium ion diffusion in electrolyte with the mesoporous structure. On the other hand, compared with nanoparticles with a similar size, SnO₂ NCs assembled from nanorods have larger surface area exposed to electrolyte and therefore additional approaches for lithium ions to access (as explained in **Scheme 2.2**). Moreover, a synergistic interaction observed from morphological characterizations is associated with the unique combination of the two advanced structures by SnO₂ NCs and 3D GA. As already demonstrated in SEM and TEM images, flexible GSs randomly attach onto the surface of SnO₂ NCs, and successively wrap and encapsulate SnO₂. Such wrapping methodology significantly improves the transfer of electrons from semiconducting SnO₂ to conductive graphene. Furthermore, elastic GSs could also accommodate the volume changes during the charge-discharge cycles. As a consequence, by rationally coordinating these two structures, the specific capacity and rate capability of SnO₂/graphene hybrid materials was substantially enhanced, which are comparable to other state-of-the-art anode materials based on the same composition (Tabulated in **Table 2.1**).

Table 2.1. Comparison of lithium-storage performance with other reported anode materials based on SnO₂/graphene.

Materials	Voltage range	Current density (mA g ⁻¹)	Capacity (mA h g ⁻¹)	Cycle numbers	References
SnO ₂ NCs@GA from this work	0.005-3 V	100	872	50	This work
SnO ₂ nanoparticles-graphene foam	0.005-3 V	50	940	150	[52]
SnO ₂ nanoparticles@graphene nanoribbon	0.01-2.5 V	100	825	50	[36]
SnO ₂ @graphene paper	0.01-2.5 V	100	878	200	[53]
Graphene/Fe ₂ O ₃ /SnO ₂ ternary nanocomposites	0.04-3 V	168.2	782	85	[54]
SnO ₂ -graphene nanocomposites	0.01-2 V	100	640	30	[55]
SnO ₂ /graphene composite	0.01-2 V	67	840	30	[56]
SnO ₂ -graphene-carbon nanotube mixture	0-3 V	250	635	80	[57]
SnO ₂ -reduced graphene oxide composites	0.1-3 V	100	776	70	[58]
Layer-by-layer assembled graphene- coated mesoporous SnO ₂ spheres	0.005-3 V	100	502	50	[59]
SnO ₂ nanoparticles confined in a graphene framework	0.01-3 V	100	521	50	[60]

2.3 Conclusions

In conclusion, a novel hydrothermal strategy combined with vacuum-assisted impregnation has been developed to address the *in-situ* construction of metal oxides with crafted geometry inside 3D GA. As an illustration, the coral-shaped SnO₂ have been successfully introduced into 3D GA to afford SnO₂ NCs@GA. Given the limitation that the inevitable SnO₂ pulverization wasn't solved in this work,^[61, 62] the proposed strategy indeed offered accessibility to a variety of sophisticated 3D composites. This unique combination of the two devised structures has led to

synergistic enhancement in the energy-storage applications. Compared with 2D graphene structure and 3D structure coupled with rough nanoparticles, SnO₂ NCs@GA has shown increased reversible capacity and durability. As demonstrated by the rate capability results, SnO₂ NCs@GA has also exhibited impressive performance for rapid charge/discharge. Thus, this strategy allows the introduction of shape-controlled nanocrystals with high exposure of desired facets into GA, potentially enabling other significant applications in catalysis or lithium-air batteries.

2.4 Experimental

It is well-grounded that hierarchical design of highly aligned morphologies could be realized on one-dimensional (such as carbon nanotubes/nanofibers, metal oxide nanowires/nanorods/nanotubes)^[63-65] and two-dimensional substrates (from macroscopic solid thin films such as FTO glass, Al₂O₃ plate, silicon wafer to microscopic sheets like graphene),^[45, 66, 67] but controlled aqueous construction of oriented nanostructures inside a 3D monolithic macroporous support still remains fresh and innovative. Although certain studies have focused on assembling smart nanostructures on 3D graphene foam to show solid performance in sensing and electrode applications,^[68, 69] the thin film nature of graphene foam makes it similar with other 2D substrates. Thus,

specialized treatment and processing techniques are desired to fit the own nature of monolithic porous system.

2.4.1 Materials synthesis

Synthesis of graphene oxide (GO). GO was prepared via chemical exfoliation of graphite powder, according to the modified Hummer's method.^[70] Briefly, graphite powder (0.5 g) was mixed with concentrated H₂SO₄ (15 mL) inside ice bath with mild stirring. Then, KMnO₄ (1.5 g) was gradually added into the mixture. The ice bath was then removed and the concentrated suspension was heated to 50 °C. The suspension was kept at this temperature for 3 h. Subsequently, deionized (DI) water (35 mL, MilliQ, 18.2 MΩ) was added into the suspension, followed by stirring for another 15 min. The reaction was terminated by adding DI water (150 mL), followed by slow addition of H₂O₂ (10 mL, 25%). It could be observed that the color of the suspension changed from brown to bright yellow. Then, the suspension was thoroughly washed through centrifuge, with DI water and HCl solution (10%). The precipitate was collected, re-dispersed in DI water and further purified in a dialysis tube (MW 3500) for one week. Reduced graphene oxide sheets was obtained by chemical reduction using hydrazine hydrate as the agent.^[71]

Synthesis of graphene aerogel (GA). The GA was synthesized via a well-established

hydrothermal method.^[21] A well-suspended GO dispersion (45 mL, 1.5mg/mL) was added into Teflon-lined stainless steel autoclave (100 mL). Then, the autoclave was heated in an electronic oven at 180 °C for 12 h. The autoclave was left to cool down naturally after the reaction. Finally, the hydrogel was freeze-dried for 1 day to obtain GA.

Synthesis of SnO₂ NCs@GA, SnO₂ NPs@GA and SnO₂ NCs@GSs. In a typical synthesis of SnO₂ NCs@GA, SnCl₄·5H₂O (0.1 M, 98%, Sigma-Aldrich USA) and NaOH (1.2 M) were dissolved in DI water to form aqueous solution (15 mL). Then, the as-prepared GA was immersed into this precursor solution with assistance of a vacuum line. After GA was fully saturated by the reaction solution, the solution were transferred into a Teflon lined autoclave (25 mL) and heated at 220 °C for 24 h. After hydrothermal treatment, the sample was thoroughly washed with DI water. Then, the outer layer of the hybrid was peeled off, since a large amount of SnO₂ sediments aggregated on its surface. The product was then freeze-dried for 2 days to obtain SnO₂ NCs@GA. SnO₂ NPs@GA was synthesized by a similar approach, but the reaction temperature as well as concentration of NaOH in the hydrothermal reaction were lowered. For the synthesis of SnO₂ NCs@GSs, reduced graphene oxide sheets (7.5 mg), SnCl₄ 5H₂O (0.1 M) and NaOH (1.2 M) were first dissolved in DI water (15mL). Then, the mixed dispersion was treated with ultrasonication (300 W) for 2 h, followed by hydrothermal treatment at 220 °C for 24 h. All of the three materials were annealed at 600 °C in a N₂ flow for

3 h before electrochemical measurements.

2.4.2. Materials characterizations.

The morphology of materials was characterized with field-emission scanning electron microscopy (FESEM, JSM-7600F, JOEL), transmission electron microscopy (TEM, JEM 1400, JOEL), and high resolution transmission electron microscopy (HRTEM, JEM 2010, JOEL). The crystallographic details were investigated by powder X-ray diffraction (XRD, Bruker D8 Advance diffractometer, Bruker) with Cu K α irradiation. The elemental composition was examined by X-ray photoelectron spectroscopy (XPS, Phoibos 100 spectrometer, SPECS) with a monochromatic Mg X-ray radiation source. Mass ratio of graphene was determined by thermogravimetric analysis (TGA, TGA Q500, TA) with ramping rate of 20 °C per min. The specific surface area and pore size distribution were determined by N₂ adsorption/desorption isotherm with Quantachrome autosorb IQ.

2.4.3 Electrochemical measurements.

The electrochemical measurements were performed in CR 2016 coin-type cells. At first, GA, SnO₂ NCs@GA, SnO₂ NPs@GA, and SnO₂ NCs@GSs were finely grinded into

powders. The working electrode was prepared by mixing respective active materials with carbon black and polyvinylidene fluoride (PVDF), and then dissolving them in N-methyl-2-pyrrolidone (NMP) to obtain a slurry with weight ratio of 80:10:10. The slurry was coated onto a copper foil after stirring overnight. The coating weight is at 1 mg scale. Pure Li foil serves as both reference and counter electrodes. The electrolyte was prepared by dissolving LiPF_6 (1 M) in solution of ethylene carbonate (EC)/diethyl carbonate (DEC) (1:1, w/w). The coin cells were assembled in glove box filled with argon gas. Moisture and oxygen levels inside the box were below 1 ppm. The galvanostatic charge/discharge measurements were performed at different current densities in the voltage range of 0.01-3.00 V using Neware multichannel battery test system. Electrochemical impedance spectroscopy (EIS) was conducted on a Metrohm autolab electrochemical workstation with a sine wave of 10 mv in the frequency range from 100 kHz to 0.01 Hz. The samples had run 50 cycles of charge-discharge before taking to EIS measurement.

2.5. References

- [1] A. K. Geim, K. S. Novoselov, *Nat. Mater.* **2007**, 6, 183.
- [2] H. Y. Mao, S. Laurent, W. Chen, O. Akhavan, M. Imani, A. A. Ashkarran, M. Mahmoudi, *Chem. Rev.* **2013**, 113, 3407.

- [3] D. Chen, H. Feng, J. Li, *Chem. Rev.* **2012**, *112*, 6027.
- [4] D. K. James, J. M. Tour, *Acc. Chem. Res.* **2013**, *46*, 2307.
- [5] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, A. A. Firsov, *Science* **2004**, *306*, 666.
- [6] Y. Liang, Y. Li, H. Wang, J. Zhou, J. Wang, T. Regier, H. Dai, *Nat. Mater.* **2011**, *10*, 780.
- [7] H. Wang, L. Cui, Y. Yang, H. S. Casalongue, J. T. Robinson, Y. Liang, Y. Cui, H. Dai, *J. Am. Chem. Soc.* **2010**, *132*, 13978.
- [8] M. S. Lee, K. Lee, S. Y. Kim, H. Lee, J. Park, K. H. Choi, H. K. Kim, D. G. Kim, D. Y. Lee, S. Nam, J. U. Park, *Nano Lett.* **2013**, *13*, 2814.
- [9] L. He, R. Ma, N. Du, J. Ren, T. Wong, Y. Li, S. T. Lee, *J. Mater. Chem.* **2012**, *22*, 19061.
- [10] S. Yang, X. Feng, S. Ivanovici, K. Mullen, *Angew. Chem. Int. Ed.* **2010**, *49*, 8408.
- [11] S. Sreejith, X. Ma, Y. Zhao, *J. Am. Chem. Soc.* **2012**, *134*, 17346.
- [12] Y. H. Yang, L. Bolling, M. A. Priolo, J. C. Grunlan, *Adv. Mater.* **2013**, *25*, 503.
- [13] X. Li, G. Zhang, X. Bai, X. Sun, X. Wang, E. Wang, H. Dai, *Nat. Nanotechnol.* **2008**, *3*, 538.
- [14] D. A. Dikin, S. Stankovich, E. J. Zimney, R. D. Piner, G. H. Dommett, G. Evmenenko, S. T. Nguyen, R. S. Ruoff, *Nature* **2007**, *448*, 457.

- [15] S. Li, Y. Luo, W. Lv, W. Yu, S. Wu, P. Hou, Q. Yang, Q. Meng, C. Liu, H.-M. Cheng, *Adv. Energy Mater.* **2011**, *1*, 486.
- [16] J. Liang, Y. Huang, J. Oh, M. Kozlov, D. Sui, S. Fang, R. H. Baughman, Y. Ma, Y. Chen, *Adv. Funct. Mater.* **2011**, *21*, 3778.
- [17] H. Gwon, H.-S. Kim, K. U. Lee, D.-H. Seo, Y. C. Park, Y.-S. Lee, B. T. Ahn, K. Kang, *Energy Environ. Sci.* **2011**, *4*, 1277.
- [18] D. H. Seo, S. Kumar, A. E. Rider, Z. Han, K. Ostrikov, *Opt. Mater. Express* **2012**, *2*, 700.
- [19] M. A. Worsley, P. J. Pauzauskie, T. Y. Olson, J. Biener, J. H. Satcher Jr, T. F. Baumann, *J. Am. Chem. Soc.* **2010**, *132*, 14067.
- [20] Z. Chen, W. Ren, L. Gao, B. Liu, S. Pei, H. M. Cheng, *Nat. Mater.* **2011**, *10*, 424.
- [21] Y. Xu, K. Sheng, C. Li, G. Shi, *ACS Nano* **2010**, *4*, 4324.
- [22] W. Chen, S. Li, C. Chen, L. Yan, *Adv. Mater.* **2011**, *23*, 5679.
- [23] W. Wei, S. Yang, H. Zhou, I. Lieberwirth, X. Feng, K. Mullen, *Adv. Mater.* **2013**, *25*, 2909.
- [24] Z. S. Wu, A. Winter, L. Chen, Y. Sun, A. Turchanin, X. Feng, K. Mullen, *Adv. Mater.* **2012**, *24*, 5130.
- [25] Z.-S. Wu, S. Yang, Y. Sun, K. Parvez, X. Feng, K. Müllen, *J. Am. Chem. Soc.* **2012**, *134*, 9082.

- [26] J. Yuan, J. Zhu, H. Bi, X. Meng, S. Liang, L. Zhang, X. Wang, *Phys. Chem. Chem. Phys.* **2013**, *15*, 12940.
- [27] Y. Huang, D. Wu, S. Han, S. Li, L. Xiao, F. Zhang, X. Feng, *ChemSusChem* **2013**, *6*, 1510.
- [28] Y. Gong, S. Yang, Z. Liu, L. Ma, R. Vajtai, P. M. Ajayan, *Adv. Mater.* **2013**, *25*, 3979.
- [29] C. K. Chan, H. Peng, G. Liu, K. McIlwrath, X. F. Zhang, R. A. Huggins, Y. Cui, *Nat. Nanotechnol.* **2008**, *3*, 31.
- [30] G. Zhang, X. W. Lou, *Adv. Mater.* **2013**, *25*, 976.
- [31] R. Ma, T. Sasaki, *Adv. Mater.* **2010**, *22*, 5082.
- [32] D. Wang, C. Wang, D. Choi, J. Li, L. V. Saraf, Z. Yang, J. Zhang, Z. Nie, R. Kou, I. A. Aksay, J. Liu, D. Hu, *ACS Nano* **2009**, *3*, 907.
- [33] M. Lotya, P. J. King, U. Khan, S. De, J. N. Coleman, *ACS Nano* **2010**, *4*, 3155.
- [34] V. Georgakilas, M. Otyepka, A. B. Bourlinos, V. Chandra, N. Kim, K. C. Kemp, P. Hobza, R. Zboril, K. S. Kim, *Chem. Rev.* **2012**, *112*, 6156.
- [35] J. S. Chen, X. W. Lou, *Small* **2013**, *9*, 1877.
- [36] J. Lin, Z. Peng, C. Xiang, G. Ruan, Z. Yan, D. Natelson, J. M. Tour, *ACS Nano* **2013**, *7*, 6001.
- [37] G. Kucinskis, G. Bajars, J. Kleperis, *J. Power Sources* **2013**, *240*, 66.

- [38]D. K. Kim, P. Muralidharan, H.-W. Lee, R. Ruffo, Y. Yang, C. K. Chan, H. Peng, R. A. Huggins, Y. Cui, *Nano Lett.* **2008**, 8, 3948.
- [39]C. D. Wagner, G. E. Mullenberg, *Handbook of X-Ray Photoelectron Spectroscopy: A Reference Book of Standard Data for Use in X-Ray Photoelectron Spectroscopy*, Perkin-Elmer Corp., Waltham, MA, USA 1979.
- [40]K. S. W. Sing, D. H. Everett, R. A. W. Haul, L. Moscou, R. A. Pierotti, J. Rouquerol, T. Siemieniewska, *Pure Appl. Chem.* **1985**, 57, 603.
- [41]M. Kruk, M. Jaroniec, *Chem. Mater.* **2001**, 13, 3169.
- [42]H. Sun, X. Sun, T. Hu, M. Yu, F. Lu, J. Lian, *J. Phys. Chem. C* **2014**, 118, 2263.
- [43]W. Zhou, J. Zhu, C. Cheng, J. Liu, H. Yang, C. Cong, C. Guan, X. Jia, H. J. Fan, Q. Yan, C. M. Li, T. Yu, *Energy Environ. Sci.* **2011**, 4, 4954.
- [44]J. Zhang, F. X. Xiao, G. Xiao, B. Liu, *Nanoscale* **2014**, 6, 11293.
- [45]L. Vayssieres, M. Graetzel, *Angew. Chem. Int. Ed.* **2004**, 43, 3666.
- [46]L. Qin, J. Xu, X. Dong, Q. Pan, Z. Cheng, Q. Xiang, F. Li, *Nanotechnology* **2008**, 19, 185705.
- [47]J. Wang, W. Li, F. Wang, Y. Xia, A. M. Asiri, D. Zhao, *Nanoscale* **2014**, 6, 3217.
- [48]J. Liang, X. Y. Yu, H. Zhou, H. B. Wu, S. Ding, X. W. Lou, *Angew. Chem. Int. Ed.* **2014**, 53, 12803.
- [49]P. Poizot, S. Laruelle, S. Grugeon, L. Dupont, J. M. Tarascon, *Nature* **2000**, 407, 496.

- [50] Z. Chen, M. Zhou, Y. Cao, X. Ai, H. Yang, J. Liu, *Adv. Energy Mater.* **2012**, 2, 95.
- [51] J. Li, C. Wu, L. Guan, *J. Phys. Chem. C* **2009**, 113, 18431.
- [52] C. Botas, D. Carriazo, G. Singh, T. Rojo, *J. Mater. Chem. A* **2015**, 3, 13402.
- [53] S. J. Prabakar, Y. H. Hwang, E. G. Bae, S. Shim, D. Kim, M. S. Lah, K. S. Sohn, M. Pyo, *Adv. Mater.* **2013**, 25, 3307.
- [54] G. Xia, N. Li, D. Li, R. Liu, C. Wang, Q. Li, X. Lu, J. S. Spendelow, J. Zhang, G. Wu, *ACS Appl. Mater. Interfaces* **2013**, 5, 8607.
- [55] M. Ara, K. Wadumesthrige, T. Meng, S. O. Salley, K. Y. S. Ng, *RSC Adv.* **2014**, 4, 20540.
- [56] X. Wang, X. Zhou, K. Yao, J. Zhang, Z. Liu, *Carbon* **2011**, 49, 133.
- [57] B. Zhang, Q. B. Zheng, Z. D. Huang, S. W. Oh, J. K. Kim, *Carbon* **2011**, 49, 4524.
- [58] W. Li, D. Yoon, J. Hwang, W. Chang, J. Kim, *J. Power Sources* **2015**, 293, 1024.
- [59] M. Shahid, N. Yesibolati, M. C. Reuter, F. M. Ross, H. N. Alshareef, *J. Power Sources* **2014**, 263, 239.
- [60] Y.-H. Hwang, E. G. Bae, K.-S. Sohn, S. Shim, X. Song, M. S. Lah, M. Pyo, *J. Power Sources* **2013**, 240, 683.
- [61] H. Wu, Y. Cui, *Nano Today* **2012**, 7, 414.
- [62] J. Wang, F. Fan, Y. Liu, K. L. Jungjohann, S. W. Lee, S. X. Mao, X. Liu, T. Zhu, *J. Electrochem. Soc.* **2014**, 161, F3019.

- [63] T. Zhu, H. B. Wu, Y. Wang, R. Xu, X. W. D. Lou, *Adv. Energy Mater.* **2012**, *2*, 1497.
- [64] Y. Luo, J. Luo, J. Jiang, W. Zhou, H. Yang, X. Qi, H. Zhang, H. J. Fan, D. Y. W. Yu, C. M. Li, T. Yu, *Energy Environ. Sci.* **2012**, *5*, 6559.
- [65] D.-F. Zhang, L.-D. Sun, C.-J. Jia, Z.-G. Yan, L.-P. You, C.-H. Yan, *J. Am. Chem. Soc.* **2005**, *127*, 13492.
- [66] L. Vayssieres, N. Beermann, S.-E. Lindquist, A. Hagfeldt, *Chem. Mater.* **2001**, *13*, 233.
- [67] J. Xiao, D. Mei, X. Li, W. Xu, D. Wang, G. L. Graff, W. D. Bennett, Z. Nie, L. V. Saraf, I. A. Aksay, J. Liu, J. G. Zhang, *Nano Lett.* **2011**, *11*, 5071.
- [68] X.-C. Dong, H. Xu, X.-W. Wang, Y.-X. Huang, M. B. Chan-Park, H. Zhang, L.-H. Wang, W. Huang, P. Chen, *ACS Nano* **2012**, *6*, 3206.
- [69] W. Zhou, X. Cao, Z. Zeng, W. Shi, Y. Zhu, Q. Yan, H. Liu, J. Wang, H. Zhang, *Energy Environ. Sci.* **2013**, *6*, 2216.
- [70] W. S. Hummers Jr., R. E. Offeman, *J. Am. Chem. Soc.* **1958**, *80*, 1339.
- [71] S. Park, J. An, J. R. Potts, A. Velamakanni, S. Murali, R. S. Ruoff, *Carbon* **2011**, *49*, 3019.

Chapter 3. Synergistic Effect of Mesoporous Co_3O_4 Nanowires Confined by N-Doped Graphene Aerogel for Enhanced Lithium Storage

NOTE: *This work was published on Small with the same title.*

ABSTRACT

A one-step multipurpose strategy was developed to realize a sophisticated design that simultaneously integrates three desirable components of nitrogen dopant, 3D graphene and 1D mesoporous metal oxide nanowires into one hybrid material. This facile synthetic strategy includes a one-step hydrothermal reaction followed by topotactic calcination. The utilization of urea as the starting reagent enables the precipitation of precursor nanowires and concurrent doping of nitrogen heteroatoms on graphene during hydrothermal reaction, while at the same time the graphene nanosheets are self-assembled to afford a 3D scaffold. Detailed characterizations on the final calcined product were conducted to confirm the phase purity, porosity, nitrogen composition and morphology. The integration of two representative building blocks, flexible graphene nanosheets and Co_3O_4 nanowires, enabled various intertwining behavior such as seaming, bridging, hooping, bundling, and sandwiching, of which the

synergistic effect substantially enhanced electrical and electrochemical properties of the resultant hybrid. For lithium ion battery application of the hybrid, a remarkably high capacity over 1200 mA h g⁻¹ (at 100 mA g⁻¹) was stabilized over 100 cycles with coulombic efficiency higher than 97%. Even during rapid discharge/charge processes (1000 mA g⁻¹), a reversible charge capacity of 812 mA h g⁻¹ was still retained after 230 cycles.

3.1. Introduction

Rapid development and industrialization of consumer electronics and electric vehicles in a worldwide scale have triggered tremendous research interests in various sustainable and distributed energy supplies. Conventional lithium ion batteries (LIB) fabricated with graphite anode and LiCoO₂ cathode,^[1] known as one of the most successful and commercially portable rechargeable energy sources, nevertheless hardly meet the ever-increasing demand from information technology, electric vehicle, aerospace and military industries.^[2] The development of novel electrode materials is imperative in hope to unlock the full potential of next generation LIB.^[3, 4] Ever since the introduction of nanomaterials for LIB application, they have emerged as promising candidates on account of their potentially high capacity density and rapid charging rate.^[5-8]

Recently, three-dimensional (3D) graphene has raised considerable interests in energy applications, either used separately or combined with other materials as conductive substrates.^[9-12] In regard to LIB, ascribing from high specific surface area and reduced inter-sheet contact resistance, 3D graphene was proven to show superior performance as compared with its two-dimensional (2D) counterpart, *i.e.*, graphene sheets, and the significant improvements include enhanced overall conductivity and internal lithium diffusion rate.^[13-15] In order to further increase the application performance of 3D graphene-based materials, a design concept was proposed, as presented in chapter 2.^[16] By rational integration of anisotropic nanostructured metal oxides with 3D graphene, the energy-storage properties of the resulting hybrid have been drastically enhanced, which even exceeded those materials consisting of 3D graphene and rough metal oxide particles.^[16] In this refined system, the interconnected graphene skeleton could effectively accelerate electron transport, meanwhile the porous channels would enhance both electron and lithium ion diffusion within the bulk electrode.^[17, 18] On the other hand, compared with undefined nanoparticles, anisotropic nanostructures of metal oxide were capable of expanding contact surface with facilitated accessibility for lithium ions.^[19] Therefore, combination of 3D graphene host and nanostructured guest phases through a facile procedure is of great potential for the development of novel electrode materials. Herein, this work successfully incorporated the 3D scaffold of graphene aerogel with one dimensional (1D) mesoporous Co_3O_4 nanowires (NWs). In

addition to these two components, synchronous nitrogen doping on graphene lattice was also achieved, which was considered as one of the most feasible approaches to improve 2D graphene sheets for higher electrical conductivity, thermal stability and electrode/electrolyte wettability.^[20, 21] This nitrogen doping strategy can also be applied to 3D graphene with the same functionality.^[22, 23]

The strategy developed from this work is a one-step multipurpose (or killing three birds with one stone) method, where the chemical doping of nitrogen, self-assembly of 3D graphene and evolution of 1D $\text{Co}(\text{CO}_3)_{0.5}(\text{OH}) \cdot 0.11\text{H}_2\text{O}$ precursor were simultaneously realized in a combined one-step hydrothermal reaction. After a sequential thermal decomposition in static air, the $\text{Co}(\text{CO}_3)_{0.5}(\text{OH}) \cdot 0.11\text{H}_2\text{O}$ precursor was topotactically transformed into mesoporous Co_3O_4 NWs. It is even more intriguing that these three components, *i.e.*, nitrogen doping, 3D graphene and 1D mesoporous Co_3O_4 NWs could synergistically augment the lithium-storage performance of the final hybrid product (NGA- Co_3O_4). By using the material as the anode, a maximum discharge capacity of 1327 mA h g^{-1} was achieved at the 55th cycle, and the discharge capacity was still retained at 1229 mA h g^{-1} for over 100 cycles. Even at a high rate such as 1 A g^{-1} , the anode was capable of delivering 838 mA h g^{-1} charge capacity, and retained 812 mA h g^{-1} for 230 cycles. In comparison with sole mesoporous Co_3O_4 NWs, the respective capacities at 100 and 1000 mA g^{-1} were increased for 4 and 9 folds, respectively.

3.2. Results and discussion

3.2.1. Formation mechanism

Scheme 3.1. Schematic illustration for the synthetic procedures of NGA-Co₃O₄ NWs.

Schematic representation for the preparation of nitrogen-doped graphene aerogel (NGA)-Co₃O₄ NWs is shown in **Scheme 3.1**, and the synthetic details were presented in the experimental section. Through mild hydrothermal treatment at 120 °C, well-defined Co(CO₃)_{0.5}(OH)·0.11H₂O NWs were crystalized from solution and simultaneously captured by the self-assembled 3D graphene network. Subsequently, a

thermal annealing was conducted to topotactically transmute the $\text{Co}(\text{CO}_3)_{0.5}(\text{OH}) \cdot 0.11\text{H}_2\text{O}$ NWs into Co_3O_4 NWs. The step-by-step formation reaction of $\text{Co}(\text{CO}_3)_{0.5}(\text{OH}) \cdot 0.11\text{H}_2\text{O}$ NWs was depicted as follow:^[24]

The reaction began with continuous decomposition of urea when heated above 70 °C, from which the released NH_4^+ and CO_3^{2-} would deposit Co^{2+} from the solution in a sustained manner. During this process, urea could also serve as the precursor for productive nitrogen doping under relatively mild hydrothermal condition, *i.e.*, 120 °C. The digital photograph in **Scheme 3.1** revealed the shape and dimension of the hydrothermal product, a monolithic hydrogel comprised of N-graphene and the confined $\text{Co}(\text{CO}_3)_{0.5}(\text{OH}) \cdot 0.11\text{H}_2\text{O}$ NWs. The hydrogel is shaped by the autoclave and its size is determined by several crucial parameters such as the concentration of graphene oxide dispersion, reaction temperature, and volume of the autoclave. After cryodessication and calcination at 300 °C in static air for 3 h, the final product could be obtained, as $\text{Co}(\text{CO}_3)_{0.5}(\text{OH}) \cdot 0.11\text{H}_2\text{O}$ NWs trapped inside the 3D graphene network were readily converted into Co_3O_4 with similar topology, where the smooth surface of precursor became coarse.

3.2.2. Morphological studies

Figure 3.1. a-c) SEM images of NGA- $\text{Co}(\text{CO}_3)_{0.5}(\text{OH}) \cdot 0.11\text{H}_2\text{O}$ NWs showing the seaming behavior. Arrows in (a-c) denote the areas where the seaming mode could be visualized. d) Cartoon illustration of the seaming mode.

Figure 3.2. a-c) SEM images of NGA-Co(CO₃)_{0.5}(OH)·0.11H₂O NWs showing the bridging behavior. Rectangles in (a) denote the spots where bridging could be found. Dotted lines in (b, c) indicate the gaps between graphene sheets. d) Cartoon illustration of the bridging mode.

Figure 3.3. a-c) SEM images of NGA-Co(CO₃)_{0.5}(OH)·0.11H₂O NWs showing the hooping behavior. Rectangles in (a-c) denote the spots where hoping could be found. d) Cartoon illustration of the hooping mode.

Figure 3.4. a-c) SEM images of NGA- $\text{Co}(\text{CO}_3)_{0.5}(\text{OH})\cdot 0.11\text{H}_2\text{O}$ NWs showing the bundling behavior. Arrows in (a) indicate the spots where bundling modes could be observed.

The NGA- $\text{Co}(\text{CO}_3)_{0.5}(\text{OH})\cdot 0.11\text{H}_2\text{O}$ precursor obtained from direct cryodessication of the hydrothermal product was elaborately investigated by morphological characterizations using scanning electron microscopy (SEM) and transmission electronic microscopy (TEM). As exhibited in **Figure 3.1-3.4**, the interlaced N-graphene afforded a 3D formicary-like skeleton consisting of myriad macropores, which are surrounded by bundles of $\text{Co}(\text{CO}_3)_{0.5}(\text{OH})\cdot 0.11\text{H}_2\text{O}$ NWs in a nest-like manner. Randomly distributed on both sides of the graphene sheets, those NWs revealed thickness ranging from 20 to 50 nm, and remarkable length up to tens of micrometers. Interestingly, these very long NWs enabled multiform intertwining

behaviors with their adjacent graphene nanosheets. Based on extensive SEM observations, the interweaving modes could be divided into 5 major categories: seaming, bridging, hooping, bundling and sandwiching. The seaming mode with electronic images and cartoon illustrations in **Figure 3.1** refers to the coverage of NWs across the graphene surface, where one end of two nanosheets was consolidated. In this manner, a number of small, detached nanosheets were compacted into larger plates. For the seaming mode, the stacked graphene sheets could either be parallel or angular. The bridging pattern (**Figure 3.2**) was that the NWs not only seam the overlapped graphene sheets, but also bridge the gaps between separate ones. The bridging pattern offers additional connections for the hierarchical heterostructures, which may enhance their mechanical and electrical properties. The hooping alignment, as exhibited in **Figure 3.3**, is defined as the wrapping of NWs around the nest-like pore walls of graphene assembly, and hence is frequently found in these macropore-dominated areas (**Figure 3.3a**). The fourth bundling mode as displayed in **Figure 3.4** was observed as a bundle of NWs welding up the twisted tubes formed by graphene. At last, part of the $\text{Co}(\text{CO}_3)_{0.5}(\text{OH}) \cdot 0.11\text{H}_2\text{O}$ NWs were encapsulated or wrapped by the flexible graphene sheets, which is referred as sandwiching mode as indicated in **Figure 3.5a**. It is much easier to observe the sandwiching mode after the calcination treatment, when the NWs were transmuted into Co_3O_4 , as shown in **Figure 3.5b**. This sandwich structure is always considered important for the high performance of LIB devices, for that graphene

wrapping would accommodate the volume expansion of metal oxide during prolonged charge/discharge cycles.^[25] Owing to these diverse interactions, the 3D hybrid matrix was consolidated, and the connection between each components was enhanced, improving the mechanical and electrical properties of the aerogel.^[11] It was evident that most of these consolidations would only be possible when the NWs were used, instead of some primitive structures such as nanoparticles, hence leading to elevated electrical performance.

Figure 3.5. a) High-magnification SEM image of NGA- $\text{Co}(\text{CO}_3)_{0.5}(\text{OH}) \cdot 0.11\text{H}_2\text{O}$ NWs before calcination. The inset cartoon demonstrates the modeling of the sandwich structure. b) High-magnification SEM image of NGA- Co_3O_4 NWs. SEM image of NGA- Co_3O_4 NWs obtained after calcination. The sandwich spots in (a,b) are marked with arrows.

Figure 3.6. a-c) TEM and HRTEM images of NGA- $\text{Co}(\text{CO}_3)_{0.5}(\text{OH}) \cdot 0.11\text{H}_2\text{O}$ NWs. d-f) TEM and HRTEM images of NGA- Co_3O_4 NWs.

Structural and morphological changes from the precursor to product after the calcination were fully characterized with microscopic techniques. As indicated in SEM images under high magnifications (**Figure 3.5**), after the calcination, apparently the graphene substrate was still preserved, meanwhile the smooth exterior of 1D NWs became rough and porous due to the evaporation of crystal water and release of CO_2 during the thermal decomposition of $\text{Co}(\text{CO}_3)_{0.5}(\text{OH}) \cdot 0.11\text{H}_2\text{O}$. This morphological transformation was also confirmed by the complementary illustration of TEM images (**Figure 3.6a, d**). It was found that the porous NWs were assembled by numerous uniform, grain-shaped nanoparticles with average diameter around 10 nm. In the high-resolution TEM (HRTEM) images as shown in **Figure 3.6f**, uneven ruptures with

length and width both around several nanometers between the nanoparticles can be visualized. Three most frequently appeared planar patterns were picked up from selected areas of crystalline $\text{Co}(\text{CO}_3)_{0.5}(\text{OH}) \cdot 0.11\text{H}_2\text{O}$ NWs (**Figure 3.6b, c**), with respective interfringe distances of 2.6, 3.3 and 5.0 Å, corresponding to the (221), (220) and (020) facets of the reported orthorhombic $\text{Co}(\text{CO}_3)_{0.5}(\text{OH}) \cdot 0.11\text{H}_2\text{O}$ (JCPDS card No. 048-0083) respectively. Likewise, three dominant facets for Co_3O_4 , namely (311), (220), and (111), were displayed in **Figure 3.6e** and their respective interplanar spaces were 2.4, 2.9 and 4.7 Å.

3.2.3. Chemical composition and crystal properties

Figure 3.7. Powder XRD patterns of $\text{Co}(\text{CO}_3)_{0.5}(\text{OH}) \cdot 0.11\text{H}_2\text{O}$ NWs (a, pattern I), NGA- $\text{Co}(\text{CO}_3)_{0.5}(\text{OH}) \cdot 0.11\text{H}_2\text{O}$ NWs (a, pattern II), and NGA- Co_3O_4 NWs (b).

By employing powder X-ray diffraction (XRD) analysis, the phase transformation process was confirmed that during the calcination, $\text{Co}(\text{CO}_3)_{0.5}(\text{OH}) \cdot 0.11\text{H}_2\text{O}$ was readily converted to Co_3O_4 NWs. As demonstrated in pattern I of **Figure 3.7a** for the

powder XRD of the pure $\text{Co}(\text{CO}_3)_{0.5}(\text{OH}) \cdot 0.11\text{H}_2\text{O}$ NWs synthesized from another similar hydrothermal approach, all peaks can be precisely indexed to the orthorhombic cobalt basic carbonate phase (JCPDS card No. 048-0083; $a = 8.914 \text{ \AA}$, $b = 10.294 \text{ \AA}$, $c = 4.458 \text{ \AA}$). With the presence of NGA, no axial shifts of diffraction peaks were discovered from pattern II of **Figure 3.7a**. It should be mentioned that the broad hump appeared in the vicinity of 25° is attributed to irregular stacking of graphene sheets.^[26] After thermal transmutation, as implied by the powder XRD profile in **Figure 3.7b**, signals of $\text{Co}(\text{CO}_3)_{0.5}(\text{OH}) \cdot 0.11\text{H}_2\text{O}$ were utterly replaced by that of Co_3O_4 . In addition, a pronounced diffraction peak arose from the original hump at 26.6° accompanied with a new peak at 42.7° , corresponding to the (002) and (100) reflections of graphene lattice respectively. The maturation of graphene signals could be attributed to the removal/recrystallization of defective hexagonal lattice during the thermal annealing.

Figure 3.8. a) TGA analysis of NGA- Co_3O_4 NWs. b) TGA analysis of $\text{Co}(\text{CO}_3)_{0.5}(\text{OH}) \cdot 0.11\text{H}_2\text{O}$ NWs.

The weight ratio of graphene content in this calcined NGA-Co₃O₄ NWs was measured by thermogravimetric analysis (TGA), where the samples were heated up to 800 °C under air flow with a ramping rate of 20 °C min⁻¹. As revealed in **Figure 3.8a**, graphene occupies 33.42% of total weight, which is comparable to other GA-based hybrids.^[27, 28]

The weight loss before 100 °C originates from the evaporation of moisture absorbed by the gel. As indicated by the two noticeable distinct trends of mass decline separately around 400 °C and 650 °C, it was hypothesized that, during the decomposition, the graphene component would first undergo a combustion process where deeper oxidized and defective exteriors were exhausted, and subsequently the disintegration of more thermal-stable and flawless inners. As demonstrated in **Figure 3.8b**, the TGA curve of pure Co(CO₃)_{0.5}(OH)·0.11H₂O NWs, significant mass decline was found at about 300 °C, denoting the decomposition of Co(CO₃)_{0.5}(OH)·0.11H₂O and resultant formation of Co₃O₄. The overall weight loss was about 26%, matching well with the theoretical value. Thus, 300 °C was chosen as the calcination temperature for the post-treatment, at which the conversion of Co(CO₃)_{0.5}(OH)·0.11H₂O was secured and combustion of graphene was also avoided.

3.2.4. Proof of nitrogen doping

Figure 3.9. High-resolution XPS spectra of carbon and nitrogen elements from undoped GA (a, b), NGA (c, d), and NGA-Co₃O₄ NWs (e, f). g) Full-range XPS

spectrum of NGA- Co_3O_4 NWs. h) High-resolution XPS spectrum of Co in NGA- Co_3O_4 NWs.

Figure 3.10. Raman spectra of GA and NGA.

The successful nitrogen doping in NGA- Co_3O_4 NWs was verified by X-ray photoelectron spectroscopy (XPS) and elemental analysis (EA). As a control, both the XPS and EA results showed no nitrogen signals in undoped GA (**Figure 3.9b** and **Table 3.1**). Based on high-resolution XPS spectra of carbon (**Figure 3.9a, c**), after urea was added as a starting agent, the fifth subsignal was revealed due to the formation of C-N bond, in addition to the original four bonds derived from undoped GA, namely C=C, C-O/C-O-C, C=O, and O-C=O.^[29] More affirmatively, the existence of nitrogen dopants could be verified from the emerged signal in the high-resolution XPS spectra

of nitrogen (**Figure 3.9d**), which was further resolved to pyridinic, pyrrolic and graphitic nitrogen.^[30] Through the XPS investigation, it was confirmed that nitrogen doping was successfully realized, and the associated chemical bonding modes of nitrogen heteroatoms were also uncovered. Meanwhile, we also employed Raman spectroscopy to characterize the N doping, as a cross verification. As shown in **Figure 3.10**, the downshift of G peak from 1595 to 1584 cm^{-1} suggests the successful nitrogen doping. Then, EA was employed to investigate the nitrogen content in the precursors and products. As shown in **Table 3.1**, the N content in NGA was detected to be 3.25% (by weight). Considering the mild reaction condition as compared to pyrolysis and gas-phase deposition in other cases^[31-33] as well as a modicum of N precursor involved, this content of nitrogen heteroatoms is indeed more than sufficient. Finally, the XPS results for the calcined product, NGA- Co_3O_4 NWs (**Figure 3.9e, f**), showed high consistency with that of NGA. Therefore, it was confirmed that the majority of dopants was preserved during the calcination. Nevertheless, the post-treatment lowered the content of N heteroatoms in graphene, probably because the nitrogen-heterorized lattice was less stable than those undoped parts. From the full-range XPS spectrum of NGA- Co_3O_4 NWs (**Figure 3.9g**), nitrogen, carbon, cobalt, oxygen and hydrogen could be traced. The high-resolution XPS spectrum of Co (**Figure 3.9h**) displayed an inter-peak distance of 15.1 eV, matching well with that of Co_3O_4 .

Table 3.1. Combustible elemental analysis of undoped GA, NGA, NGA- $\text{Co}(\text{CO}_3)_{0.5}(\text{OH}) \cdot 0.11\text{H}_2\text{O}$ NWs and NGA- Co_3O_4 NWs.

Samples	Wt N%	Wt C%	Wt H%
Undoped graphene aerogel (undoped GA)	0	70.262	1.213
Nitrogen doped graphene aerogel (NGA)	3.253	70.832	0.798
NGA- $\text{Co}(\text{CO}_3)_{0.5}(\text{OH}) \cdot 0.11\text{H}_2\text{O}$ NWs	2.195	33.484	1.400
NGA- Co_3O_4 NWs	0.738	29.643	1.047

3.2.5. Study on porous structure

Figure 3.11. Nitrogen adsorption/desorption isotherms and DFT pore size distribution plots of NGA (a, b), mesoporous Co_3O_4 NWs (c, d), and NGA- Co_3O_4 NWs (e, f).

Since both 3D graphene and mesoporous metal oxides are well documented for their high specific surface area ^[34-36], herein by applying nitrogen adsorption/desorption isotherms, the porous structures of GA and Co₃O₄ NWs could be investigated in detail. As elaborated in **Figure 3.11a**, the nitrogen adsorption/desorption plot of NGA combined the characteristics of both type II and type IV isotherms, which are correspondingly originated from unlimited monolayer-multiplayer adsorption taking place at macropores, and the capillary condensation from mesoporous adsorbents ^[37]. The sharp increase of adsorption at high relative pressure region ($P/P_0 = 0.9-1$) implies that the porosity primarily comes from mesopores. Meanwhile, the adsorption/desorption profile of Co₃O₄ NWs displayed a type IV isotherm (**Figure 3.11c**), which double-confirmed the same mesoporosity as observed from electronic images. In **Figure 3.11e**, the isotherm of NGA-Co₃O₄ NWs resembles the intermediate between NGA and Co₃O₄ NWs, showing well-organized features from both species. By applying the Brunauer-Emmett-Teller (BET) model, it was calculated that the respective specific surface areas of NGA, Co₃O₄ NWs and NGA-Co₃O₄ NWs were 197.9, 39.0, and 95.3 m² g⁻¹ respectively. Given the compositional weight ratios of NGA and Co₃O₄ NWs in the hybrid and their proportional surface areas, the theoretical specific surface area of the NGA-Co₃O₄ hybrid was calculated to be 92.1 m² g⁻¹, which was very close to the measured one. As shown in **Figure 3.11b, d and f**, the pore size distribution plots from Density Functional Theory (DFT) calculations confirm the

dominant mesoporosity of these three samples. The pore width for NGA centralizes in the region of 2-15 nm, and the pore diameter of Co_3O_4 NWs scatters in a relatively wider range of 2-20 nm. Similar to the N_2 adsorption/desorption isotherms, pore size distribution profile of NGA- Co_3O_4 NWs was also depicted as the sum of the two components, namely NGA and Co_3O_4 .

3.2.6. Electrochemical properties as LIB anode

Figure 3.12. Galvanostatic discharge/charge curves of NGA- Co_3O_4 NWs (a), Co_3O_4 NWs (b), and NGA (c) at fixed current density of 100 mA g^{-1} for the 1st, 2nd, 10th, 55th and 100th cycles. d) Cyclic voltammetry (CV) plot of NGA- Co_3O_4 NWs based half-cells

Co_3O_4 as a favorable anode material for lithium ion battery has been extensively studied, for its large theoretical capacity of 890 mA h g^{-1} , which is 2 times higher than that of

commercial graphite (372 mA h g^{-1}).^[38, 39] The mechanism of lithium storage for a Co_3O_4 anode is based on an electrochemical conversion reaction, which could be expressed as follows:

The Li-ion battery performance based on NGA- Co_3O_4 NW anode was first evaluated by galvanostatic cyclic measurements in the voltage window of 0.005-3 V, and the discharge/charge voltage-capacity profiles for the 1st, 2nd, 10th, 55th and 100th cycles at 100 mA g^{-1} were reported in **Figure 3.12a**. In the first cycle, two discharge plateaus could be recognized around 1.0 V and 1.2 V, similar to that of Co_3O_4 NWs shown in **Figure 3.12b**, indicating the transition from Co_3O_4 to the intermediate $\text{Li}_x\text{Co}_3\text{O}_4$ phase and later to metallic cobalt.^[40] These two discharge plateaus at relatively high voltage region are rare to observe but specifically related to nanosized, high-surface-area Co_3O_4 architectures and/or very low current density.^[40-42] The voltage-capacity curves for the second discharge were discriminative from the first ones, suggesting the distinct electrochemical processes during these two cycles. However, charge curves of first 2 cycles are analogous, indicating the similarity of the electrochemical mechanisms involved. An initial discharge capacity of 1679 mA h g^{-1} and a charge capacity of 996 mA h g^{-1} were recorded for the 1st cycle. For the 2nd cycle, discharge/charge capacities were shifted to $1065/999 \text{ mA h g}^{-1}$, accompanied with a coulombic efficiency developed to 94%. As well grounded in literature, the large irreversible capacity loss

could be attributed to the formation of passivating solid-electrolyte-interphase (SEI), which was even aggravated by the large surface of the hybrid.^[43-45] CV measurement for NGA-Co₃O₄ NWs electrode was also carried out in the voltage range of 0-3 V, with a scan rate of 0.5 mV/s. As shown in **Figure 3.12d**, in the first cycle, the major cathodic peak at 0.57 V, and the small current hump in the vicinity of 1.2 V, could be attributed to the multi-step conversion process of Co₃O₄ with lithium.^[40, 46] Correspondingly, the obvious anodic peak at 2.15 V denotes the delithiation from Co₃O₄.^[39] From the second cycle onward, the cathodic peaks have been shifted to 1.18 V and 0.93 V, with significantly dropped current intensity, suggesting the presence of irreversible reaction during the first cycle, i.e. the formation of SEI. The CV profile of the third cycle resembles that of the second one, implying the good stability of electrode.

In the meantime, the lithium storage properties of NGA and Co₃O₄ NWs were also measured separately in order to provide a more balanced, comprehensive assessment on the present design. As shown in **Figure 3.12a-c** and **3.12a**, the overall performance of two control samples was much inferior to that of NGA-Co₃O₄ NWs. The initial charge capacities for NGA and Co₃O₄ NWs were 663 and 699 mA h g⁻¹, both much lower than that of NGA-Co₃O₄ NWs (996 mA h g⁻¹) tested under the same conditions. From the third cycle onward, a rising trend of the specific capacity was immediately observed for the NGA-Co₃O₄ NW electrode, which reached a climax at the 55th cycle with a discharge capacity of 1327 mA h g⁻¹ and a charge capacity of 1294 mA h g⁻¹.

Then, the cycling performance began to slowly drop, but still maintained above 1200 mA h g⁻¹, in the meantime, a steady coulombic efficiency higher than 97% was retained till the end of testing. The capacity rise is probably originated from gradually induced activation of Co₃O₄ grain boundaries, as well as the generation of additional diffusion paths through the mesoporous channels deep inside NGA during prolonged cyclic procedures.^[47] At the end of 100 cycles, a reversible discharge capacity was still retained at 1229 mA h g⁻¹, which was 164 mA h g⁻¹ higher than the 2nd cycle and 3 and 4 folds higher than the capacity of NGA (419 mA h g⁻¹) and Co₃O₄ NW electrode (314 mA h g⁻¹) at the same cycle. Throughout the entire cyclic process, the capacity of NGA-Co₃O₄ NWs was completely higher than the theoretical capacity of Co₃O₄. The durable and compelling excessive capacity could be a result of the enhanced electrochemical activities attributing to the high surface area of 3D graphene and large grain boundaries of mesoporous Co₃O₄ NWs.^[48, 49]

Figure 3.13. a) Cycling performance of Co₃O₄ NWs, NGA and NGA-Co₃O₄ NWs during 100 cycles at a current density of 100 mA g⁻¹, accompanied by the coulombic efficiency plots of NGA-Co₃O₄ NW based electrode. b) Rate capabilities of Co₃O₄ NWs, NGA and NGA-Co₃O₄ NWs at various current densities. c) High rate cycling performance of NGA-Co₃O₄ NWs electrode at current density of 1000 mA g⁻¹ for 230 cycles. d) Nyquist plots of half-cells manufactured from Co₃O₄ NWs, NGA and NGA-Co₃O₄ NWs. Inset shows the Randles equivalent circuit for NGA-Co₃O₄ NW based electrode/electrolyte interface.

The rate capability measurement was then conducted to better demonstrate the superior performance of the devised material (**Figure 3.13b**). Ten discharge/charge cycles were performed for each current density setup, where it was set at 100, 200, 500, and 1000 mA g⁻¹ initially and then fell back to 100 mA g⁻¹. Regardless of rapid charge/discharge rates, impressive rate capability was delivered for NGA-Co₃O₄ NWs in terms of enduring ultra-high specific capacity, superb capacity retention and high cyclic stability.

At each first cycle, the corresponding specific charge capacities were 895, 1044, 1010, 884, and 1090 mA h g⁻¹ respectively. The relevant charge capacities for the first cycle of each current density were 1085, 1097, 1008, 838, and 1252 mA h g⁻¹. For comparison, relevant stabilized charge capacities at the end of each rate were 351, 256, 154, 91, and 278 mA h g⁻¹ for Co₃O₄ NWs, as well as 508, 424, 328, 264, and 493 mA h g⁻¹ for NGA. It is noteworthy that the advantage of NGA-Co₃O₄ NWs is much more pronounced at relatively higher current densities. For instance, at the 10th cycle under 100 mA g⁻¹, NGA-Co₃O₄ NWs were capable of delivering a reversible charge capacity 309% higher than Co₃O₄ NWs and 214% higher than NGA. It then increased to 921% and 317% when cycled at 1000 mA g⁻¹. Even after 230 cycles at this high current density of 1000 mA g⁻¹, a reversible charge capacity of 812 mA h g⁻¹ could still be delivered, and the columbic efficiency kept higher than 98% since the 12th cycle, as shown in **Figure 3.13c**.

Even after 230 cycles at this current density, NGA-Co₃O₄ NWs still retained a The enhancement brought by NGA in NGA-Co₃O₄ NWs could be explained as an overall improvement of lithium diffusion and electron transport throughout the bulk electrode, which in turn result in increased electrochemical activity of Co₃O₄ NWs at high rates.^[50] Even when tabulated with other state-of-the-art anodic materials based on graphene and Co₃O₄ (**Table 3.2**), it was evident that the present hybrid exhibited much better LIB performance in terms of both cyclic stability and rate capability.

Table 3.2. Comparison of lithium storage performance from state-of-the-art anode materials based on graphene and Co₃O₄.

Materials	Long-term stabilized/highest reversible capacity	High rate specific capacity	Reference
NGA-Co ₃ O ₄ NWs	1327 mA h g ⁻¹ (55 th cycle, 100 mA g ⁻¹)	884 mA h g ⁻¹ (1 A g ⁻¹)	This work
Mesoporous Co ₃ O ₄ and CoO@C	1240 mA h g ⁻¹ (30 th cycle, 100 mA g ⁻¹)	N/A	[41]
Graphene anchored with Co ₃ O ₄ nanoparticles	935 mA h g ⁻¹ (30 th cycle, 100 mA g ⁻¹)	484 mA h g ⁻¹ (0.5 A g ⁻¹)	[38]
Peapod-like Co ₃ O ₄ @carbon nanotube arrays	1050 mA h g ⁻¹ (~ 50 th cycle, 100 mA g ⁻¹)	453 mA h g ⁻¹ (1 A g ⁻¹)	[53]
Co ₃ O ₄ nanocubes assembled on graphene	~ 1000 mA h g ⁻¹ (~ 70 th cycle, 100 mA g ⁻¹)	700 mA h g ⁻¹ (1 A g ⁻¹)	[54]
Graphene-encapsulated mesoporous Co ₃ O ₄ microspheres	820 mA h g ⁻¹ (35 th cycle, 100 mA g ⁻¹)	390 mA h g ⁻¹ (1 A g ⁻¹)	[55]
3D graphene-Co ₃ O ₄ nanocrystals	1100 mA h g ⁻¹ (100 th cycle, 100 mA g ⁻¹)	500 mA h g ⁻¹ (2 A g ⁻¹)	[51]
Co ₃ O ₄ /nitrogen modified graphene	910 mA h g ⁻¹ (100 th cycle, 63 mA g ⁻¹)	802 mA h g ⁻¹ (1 A g ⁻¹)	[56]
Co ₃ O ₄ @graphene	740 mA h g ⁻¹ (60 th cycle, 200 mA g ⁻¹)	640 mA h g ⁻¹ (0.625 A g ⁻¹)	[57]
Co ₃ O ₄ -graphene sheet-on-sheet nanocomposites	1036.9 mA h g ⁻¹ (50 th cycle, 100 mA g ⁻¹)	>372 mA h g ⁻¹ (0.8 A g ⁻¹)	[58]
Hollow SnO ₂ @Co ₃ O ₄ core-shell spheres@3D graphene foams	812.2 mA h g ⁻¹ (50 th cycle, 200 mA g ⁻¹)	380 mA h g ⁻¹ (1 A g ⁻¹)	[59]
Porous Co ₃ O ₄ nanospheres@nitrogen-doped graphene	1200 mA h g ⁻¹ (10 th cycle, 89 mA g ⁻¹)	371 mA h g ⁻¹ (4.45 A g ⁻¹)	[60]
Mesoporous Co ₃ O ₄ derived from MOF	1008 mA h g ⁻¹ (30 th cycle, 200 mA g ⁻¹)	442.1 mA h g ⁻¹ (1 A g ⁻¹)	[61]
Porous nanostructured Co ₃ O ₄	~ 1100 mA h g ⁻¹ (30 th cycle, 100 mA g ⁻¹)	543 mA h g ⁻¹ (1 A g ⁻¹)	[62]
Porous Co ₃ O ₄ nanorods	~ 1200 mA h g ⁻¹ (210 th cycle, 200 mA g ⁻¹)	774 mA h g ⁻¹ (1 A g ⁻¹)	[63]
Co ₃ O ₄ mesoporous nanostructures@graphene membrane	~ 800 mA h g ⁻¹ (N/A, 100 mA g ⁻¹)	320 mA h g ⁻¹ (5 A g ⁻¹)	[64]
Co ₃ O ₄ nanoparticle embedded carbonaceous fibers	730 mA h g ⁻¹ (100 th cycle, 89 mA g ⁻¹)	484 mA h g ⁻¹ (0.89 A g ⁻¹)	[65]
Graphene paper-coated Co ₃ O ₄ fibers	840 mA h g ⁻¹ (40 th cycle, 100 mA g ⁻¹)	295 mA h g ⁻¹ (1 A g ⁻¹)	[66]
Nano-sized Co ₃ O ₄ /mesoporous carbon sphere composites	538 mA h g ⁻¹ (30 th cycle, 70 mA g ⁻¹)	469 mA h g ⁻¹ (3.5 A g ⁻¹)	[49]
Carbon nanofiber-Co ₃ O ₄ composites	881 mA h g ⁻¹	~ 300 mA h g ⁻¹	[67]

	(100 th cycle, 50 mA g ⁻¹)	(0.89 A g ⁻¹)	
Co ₃ O ₄ /graphene composite	840 mA h g ⁻¹ (50 th cycles, 100 mA g ⁻¹)	~395 mA h g ⁻¹ (0.7 A g ⁻¹)	[68]

To shed a light on the mechanisms underlying the extraordinary performance of NGA-Co₃O₄ NWs, alternating current (AC) impedance spectroscopy was carried out to inspect the half-cells made from NGA, Co₃O₄ and the NGA-Co₃O₄ hybrid. The Nyquist plots for these three samples showed depressed semicircles at high-medium frequency region owing to the charge-transfer resistance (R_{ct}), and a linear part at low frequency region denoting the Warburg resistance. It was observed from **Figure 3.13d** that the diameter of the semicircle for NGA-Co₃O₄ based electrode was much smaller than that of Co₃O₄ and NGA, indicative of reduced R_{ct} according to the modeling of Randles equivalent circuit. Using electrochemical impedance spectroscopy (EIS), it was confirmed that the lithium reaction kinetics in NGA-Co₃O₄ NW electrode was much faster than that of Co₃O₄, ascribing to numerous multidimensional channels offered by 3D NGA to facilitate the diffusion of lithium ions and electrons.^[51]

3.2.7. Comprehension on the relationship between structural properties and electrochemical performance

Based on the comprehension of all the purpose-driven characterizations on the hybrid material, it was convincible to validate the design concept that the unique combination

of three advanced components, namely nitrogen doping, 3D architecture of graphene and 1D mesoporous nanostructure of Co_3O_4 , could synergistically enhance the electrical and electrochemical properties for the final hybrid, leading to ultra-high specific capacities and impressive retainability when applied in battery electrodes. The advantages of this design could also be interpreted from its three essential elements. First, as well-documented in literature,^[20, 21, 52] the nitrogen dopants significantly enhance the electrical conductivity and electrochemical properties of graphene sheets, the building block of 3D graphene. Secondly, as compared with 2D graphene structures, an interconnected 3D architecture enables easier and faster diffusion of both electrons and lithium ions by creating additional and shortened diffusion paths with innumerable multidimensional channels. The conductive NGA matrix also serves as electron highways inside bulk electrode, leading to improved overall conductivity. Last but not the least, the large grain boundaries arising from the ruptures on the surface of Co_3O_4 NWs could generate extra interfacial entries for lithium ions, enhancing the electrochemical kinetics of the lithiation/delithation processes. More interestingly, instead of simply accumulating advantages from individual components, the integration in this design showed an unexpected synergy originated from various intertwinements of two devised building blocks (3D graphene sheets and Co_3O_4 nanowires), ultimately contributing to multiple capacity increments for the LIB application. Overall, the

present hybrid showed first-class LIB performance even as compared with other state-of-the-art composites based on Co_3O_4 and carbon.

3.3 Conclusion

In summary, this work demonstrated a rational integration of three components, *i.e.*, nitrogen doping, 3D graphene and 1D porous metal oxide, into an advanced hybrid through a facile hydrothermal reaction followed by a topotactic calcination. For energy storage in lithium ion battery, this unique combination of three devised units has brought about phenomenal synergy in enhancing the capacity up to 9 times of the original mesoporous Co_3O_4 NWs. Remarkably high specific capacities of more than 1200 mA h g^{-1} at 100 mA g^{-1} as well as coulombic efficiency of 97% have been stably achieved for the entire 100 cycles. At the same time, it is also capable of delivering high specific capacity of 812 mA h g^{-1} for over 230 cycles, at a rapid discharge/charge rate of 1000 mA g^{-1} . Although the low density of 3D graphene may result in low volumetric capacity for lithium storage, this hybrid electrode does show stably high gravimetric capacity, potentially useful for electrical devices which prefer light-weight electrodes. The hybrid material itself is also promising and intriguing for other potential applications such as supercapacitor, electrocatalysis, and lithium-air batteries. On the other hand, the one-step multipurpose (or killing three birds with one stone) strategy presented here has provided insights and practical approach for the design and synthesis

of complicated hybrids with intentional structures based on 3D graphene. In spite of the extensive study on 3D graphene based composites, at current stage, the guest components inside 3D graphene are mostly present in undefined shapes, for example, rough nanoparticles. A facile method that enables the combination of 3D graphene host and nanostructured guest phases are of great interests, given that the physiochemical properties of nanomaterials could be significantly influenced by their geometric structures and surface features.^[69, 70] As a consequence, the revolutionary one-step strategy is not only a simplification of previous research, but also brings substantial improvement on the performance of the product. Hence, it is valuable to be generalized to similar designs in further studies.

3.4. Experimental

3.4.1. Materials synthesis

Synthesis of NGA: Graphene oxide was prepared by the modified hummer's method.^[71]

The as-obtained product was thoroughly washed by centrifuge with deionized water and 10% HCl solution, and then undergone a dialysis for 1 week. The resultant graphene oxide was diluted with deionized water to afford 2 mg ml⁻¹ homogenous dispersion. NGA was prepared through a hydrothermal method. Briefly, urea (0.05 M) was added into graphene oxide dispersion (15 mL), and then the solution was sonicated

for 30 min. The mixture was transferred into a 25 mL Teflon-lined stainless steel autoclave, and then the autoclave was put into an electronic oven heated at 120 °C for 16 h. After cooling down to room temperature, the monolithic hydrogel was obtained and subsequently freeze-dried for 48 hours. The control sample, undoped graphene aerogel, was fabricated with the same hydrothermal conditions and post-treatment process, but urea was not used in this reaction.

Synthesis of NGA-Co₃O₄ NWs: CoCl₂·6H₂O (0.05 M) and urea (0.05 M) were added into water suspension (15 mL) of freshly synthesized graphene oxide, followed by sonication for 30 min. The precursor solution was then transferred into a 25 mL Teflon-lined stainless steel autoclave, and heated at 120 °C for 16 h. After cleaning and freeze-drying, black-colored NGA-Co(CO₃)_{0.5}(OH)·0.11H₂O NWs were obtained. Final product NGA-Co₃O₄ NWs were acquired after the calcination of the NGA-Co(CO₃)_{0.5}(OH)·0.11H₂O NWs in static air at 300 °C with a slow ramping rate of 0.5 °C min⁻¹ for 3 h.

Synthesis of Co₃O₄ NWs: Mesoporous Co₃O₄ NWs were prepared using above-described method used to synthesize NGA-Co₃O₄ NWs, but graphene was not present in the autoclave as a starting material. In this reaction, CoCl₂·6H₂O (0.05 M) and urea (0.05 M) were directly added into deionized water to afford a pink solution. The rest procedures were exactly the same.

3.4.2. Materials characterizations

Morphological characterization was conducted with FESEM (JSM-7600F, JOEL) and TEM (JEM 1400 and JEM 2010, JOEL). Crystallographic information was acquired with powder XRD (D8 Advance diffractometer, Bruker) by applying Cu K α irradiation. Thermal behavior and graphene content of this hybrid material were analyzed by TGA (TGA Q500, TA) with a ramping rate of 20 °C min⁻¹. The elemental composition of the hybrid was collectively investigated by EA (EuroEA CHNS-O Analyzer, EuroVector) and XPS (Phoibos 100 spectrometer, SPECS) using a monochromatic Mg X-ray radiation exciting source. The N₂ adsorption/desorption isotherm was performed with Quantachrome autosorb IQ at 77K.

3.4.3. Electrochemical measurements

The three samples, namely NGA, Co₃O₄ NWs and NGA-Co₃O₄ NWs, were grinded into fine powders, and then manufactured into CR 2016 coin-type cells inside a glove box filled with argon atmosphere. Powders of these active materials, carbon black (Super P) and polyvinylidene fluoride binder (PVDF) with a weight ratio of 70:20:10 were mixed together and then dissolved in N-methyl-2-pyrrolidone (NMP) to form a relatively thick slurry, which was then constantly stirred for at least 1 week. The

working electrode was prepared by evenly coating the homogenous slurry with a weight roughly about 1 mg onto a copper foil. Pure lithium foil was used as reference as well as counter electrodes. The electrolyte solution used here was 1 M LiPF₆ dissolved in the mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) with weight ratio of 50:50. The galvanostatic discharge/charge testing was conducted with Neware multichannel battery test system at a variety of current densities in the voltage window of 0.005-3.00 V. CV tests were carried out with Metrohm autolab electrochemical workstation, in the voltage range of 0-3 V and a scan rate of 0.5 mV/s. EIS measurement for coin cells was performed with Metrohm autolab electrochemical workstation by applying a sine wave of 10 mV in the frequency range of 10⁵-0.01 Hz.

3.5. References

- [1] A. Yoshino, K. Sanechika, T. Nakajima, (A. C. Ind.) *Jap* 1989293, **1985**.
- [2] J. B. Goodenough, K. S. Park, *J. Am. Chem. Soc.* **2013**, 135, 1167.
- [3] N. Nitta, F. Wu, J. T. Lee, G. Yushin, *Mater. Today* **2015**, 18, 252.
- [4] V. Etacheri, R. Marom, R. Elazari, G. Salitra, D. Aurbach, *Energy Environ. Sci.* **2011**, 4, 3243.
- [5] P. Poizot, S. Laruelle, S. Grugeon, L. Dupont, J. M. Tarascon, *Nature* **2000**, 407, 496.

- [6] C. Jiang, E. Hosono, H. Zhou, *Nano Today* **2006**, *1*, 28.
- [7] X. Su, Q. Wu, J. Li, X. Xiao, A. Lott, W. Lu, B. W. Sheldon, J. Wu, *Adv. Energy Mater.* **2014**, *4*, 1300882.
- [8] P. G. Bruce, B. Scrosati, J. M. Tarascon, *Angew. Chem. Int. Ed.* **2008**, *47*, 2930.
- [9] B. Wang, W. Al Abdulla, D. Wang, X. S. Zhao, *Energy Environ. Sci.* **2015**, *8*, 869.
- [10] B. Li, S. Yang, S. Li, B. Wang, J. Liu, *Adv. Energy Mater.* **2015**, *5*, 1500289.
- [11] H. Sun, Z. Xu, C. Gao, *Adv. Mater.* **2013**, *25*, 2554.
- [12] C. Zhu, T. Y. Han, E. B. Duoss, A. M. Golobic, J. D. Kuntz, C. M. Spadaccini, M. A. Worsley, *Nat. Commun.* **2015**, *6*, 6962.
- [13] B. Qiu, M. Xing, J. Zhang, *J. Am. Chem. Soc.* **2014**, *136*, 5852.
- [14] W. Wei, S. Yang, H. Zhou, I. Lieberwirth, X. Feng, K. Mullen, *Adv. Mater.* **2013**, *25*, 2909.
- [15] Z. Chen, W. Ren, L. Gao, B. Liu, S. Pei, H. M. Cheng, *Nat. Mater.* **2011**, *10*, 424.
- [16] X. Yao, G. Guo, X. Ma, Y. Zhao, C. Y. Ang, Z. Luo, K. T. Nguyen, P.-Z. Li, Q. Yan, Y. Zhao, *ACS Appl. Mater. Interfaces* **2015**, *7*, 26085.
- [17] L. Xiao, D. Wu, S. Han, Y. Huang, S. Li, M. He, F. Zhang, X. Feng, *ACS Appl. Mater. Interfaces* **2013**, *5*, 3764.
- [18] S. Han, J. Jiang, Y. Huang, Y. Tang, J. Cao, D. Wu, X. Feng, *Phys. Chem. Chem. Phys.* **2015**, *17*, 1580.

- [19] G. Armstrong, A. R. Armstrong, P. G. Bruce, P. Reale, B. Scrosati, *Adv. Mater.* **2006**, *18*, 2597.
- [20] H. Wang, T. Maiyalagan, X. Wang, *ACS Catal.* **2012**, *2*, 781.
- [21] D. Hulicova-Jurcakova, M. Seredych, G. Q. Lu, T. J. Bandosz, *Adv. Funct. Mater.* **2009**, *19*, 438.
- [22] X. Liu, Y. Wu, Z. Yang, F. Pan, X. Zhong, J. Wang, L. Gu, Y. Yu, *J. Power Sources* **2015**, *293*, 799.
- [23] P. Chen, T. Y. Xiao, Y. H. Qian, S. S. Li, S. H. Yu, *Adv. Mater.* **2013**, *25*, 3192.
- [24] B. Li, Y. Xie, C. Wu, Z. Li, J. Zhang, *Mater. Chem. Phys.* **2006**, *99*, 479.
- [25] W. Yue, S. Jiang, W. Huang, Z. Gao, J. Li, Y. Ren, X. Zhao, X. Yang, *J. Mater. Chem. A* **2013**, *1*, 6928.
- [26] X. Zhang, Z. Sui, B. Xu, S. Yue, Y. Luo, W. Zhan, B. Liu, *J. Mater. Chem.* **2011**, *21*, 6494.
- [27] Z.-S. Wu, G. Zhou, L.-C. Yin, W. Ren, F. Li, H.-M. Cheng, *Nano Energy* **2012**, *1*, 107.
- [28] R. Wang, C. Xu, J. Sun, L. Gao, H. Yao, *ACS Appl. Mater. Interfaces* **2014**, *6*, 3427.
- [29] H.-L. Guo, P. Su, X. Kang, S.-K. Ning, *J. Mater. Chem. A* **2013**, *1*, 2248.
- [30] C. Shan, W. Zhao, X. L. Lu, D. J. O'Brien, Y. Li, Z. Cao, A. L. Elias, R. Cruz-Silva, M. Terrones, B. Wei, J. Suhr, *Nano Lett.* **2013**, *13*, 5514.

- [31] Y. Ito, C. Christodoulou, M. V. Nardi, N. Koch, H. Sachdev, K. Müllen, *ACS Nano* **2014**, 8, 3337.
- [32] W. Luo, B. Wang, C. G. Heron, M. J. Allen, J. Morre, C. S. Maier, W. F. Stickle, X. Ji, *Nano Lett.* **2014**, 14, 2225.
- [33] A. K. Singh, M. W. Iqbal, V. K. Singh, M. Z. Iqbal, J. H. Lee, S.-H. Chun, K. Shin, J. Eom, *J. Mater. Chem.* **2012**, 22, 15168.
- [34] Y. Qian, I. M. Ismail, A. Stein, *Carbon* **2014**, 68, 221.
- [35] J. Choi, A. Ide, Y. B. Truong, I. L. Kyratzis, R. A. Caruso, *J. Mater. Chem. A* **2013**, 1, 5847.
- [36] H. Bai, X. Li, C. Hu, X. Zhang, J. Li, Y. Yan, G. Xi, *Sci. Rep.* **2013**, 3, 2204.
- [37] K. S. W. Sing, D. H. Everett, R. A. W. Haul, L. Moscou, R. A. Pierotti, J. Rouquerol, T. Siemieniowska, *Pure Appl. Chem.* **1985**, 57, 603.
- [38] Z.-S. Wu, W. Ren, L. Wen, L. Gao, J. Zhao, Z. Chen, G. Zhou, F. Li, H.-M. Cheng, *ACS Nano* **2010**, 4, 3187.
- [39] W. Y. Li, L. N. Xu, J. Chen, *Adv. Mater.* **2005**, 15, 851.
- [40] D. Larcher, G. Sudant, J. B. Leriche, Y. Chabre, J. M. Tarascon, *J. Electrochem. Soc.* **2002**, 149, A234.
- [41] S. Xiong, J. S. Chen, X. W. Lou, H. C. Zeng, *Adv. Funct. Mater.* **2012**, 22, 861.
- [42] L. Tian, H. Zou, J. Fu, X. Yang, Y. Wang, H. Guo, X. Fu, C. Liang, M. Wu, P. K. Shen, Q. Gao, *Adv. Funct. Mater.* **2010**, 20, 617.

- [43] Y. Ein-Eli, *Electrochem. Solid-State Lett.* **1999**, 2, 212.
- [44] S. S. Zhang, K. Xu, T. R. Jow, *Electrochim. Acta* **2006**, 51, 1636.
- [45] P. Verma, P. Maire, P. Novák, *Electrochim. Acta* **2010**, 55, 6332.
- [46] N. Jayaprakash, W. D. Jones, S. S. Moganty, L. A. Archer, *J. Power Sources* **2012**, 200, 53.
- [47] H. Sun, G. Xin, T. Hu, M. Yu, D. Shao, X. Sun, J. Lian, *Nat. Commun.* **2014**, 5, 4526.
- [48] D. Pan, S. Wang, B. Zhao, M. Wu, H. Zhang, Y. Wang, Z. Jiao, *Chem. Mater.* **2009**, 21, 3136.
- [49] H. Liu, S. Bo, W. Cui, F. Li, C. Wang, Y. Xia, *Electrochim. Acta* **2008**, 53, 6497.
- [50] C. Wu, J. Maier, Y. Yu, *Adv. Funct. Mater.* **2015**, 25, 3488.
- [51] L. Ren, K. N. Hui, K. S. Hui, Y. Liu, X. Qi, J. Zhong, Y. Du, J. Yang, *Sci. Rep.* **2015**, 5, 14229.
- [52] Zhong-Shuai Wu, Wencai Ren, Li Xu, Feng Li, H.-M. Cheng, *ACS Nano* **2011**, 5, 5463.
- [53] D. Gu, W. Li, F. Wang, H. Bongard, B. Spliethoff, W. Schmidt, C. Weidenthaler, Y. Xia, D. Zhao, F. Schuth, *Angew. Chem. Int. Ed.* **2015**, 54, 7060.
- [54] J. Xu, J. Wu, L. Luo, X. Chen, H. Qin, V. Dravid, S. Mi, C. Jia, *J. Power Sources* **2015**, 274, 816.

- [55] X. Yang, K. Fan, Y. Zhu, J. Shen, X. Jiang, P. Zhao, C. Li, *J. Mater. Chem.* **2012**, 22, 17278.
- [56] L. Lai, J. Zhu, Z. Li, D. Y. W. Yu, S. Jiang, X. Cai, Q. Yan, Y. M. Lam, Z. Shen, J. Lin, *Nano Energy* **2014**, 3, 134.
- [57] B. Li, H. Cao, J. Shao, G. Li, M. Qu, G. Yin, *Inorg. Chem.* **2011**, 50, 1628.
- [58] Q. Su, W. Yuan, L. Yao, Y. Wu, J. Zhang, G. Du, *Mater. Res. Bull.* **2015**, 72, 43.
- [59] B. Zhao, S.-Y. Huang, T. Wang, K. Zhang, M. M. F. Yuen, J.-B. Xu, X.-Z. Fu, R. Sun, C.-P. Wong, *J. Power Sources* **2015**, 298, 83.
- [60] M. Zhang, R. Li, X. Chang, C. Xue, X. Gou, *J. Power Sources* **2015**, 290, 25.
- [61] C. Li, T. Chen, W. Xu, X. Lou, L. Pan, Q. Chen, B. Hu, *J. Mater. Chem. A* **2015**, 3, 5585.
- [62] D. Ge, H. Geng, J. Wang, J. Zheng, Y. Pan, X. Cao, H. Gu, *Nanoscale* **2014**, 6, 9689.
- [63] J. Guo, L. Chen, X. Zhang, H. Chen, *J. Solid State Chem.* **2014**, 213, 193.
- [64] L. Li, G. Zhou, X.-Y. Shan, S. Pei, F. Li, H.-M. Cheng, *J. Power Sources* **2014**, 255, 52.
- [65] J. Sun, D. Li, Y. Xia, X. Zhu, L. Zong, Q. Ji, Y. A. Jia, D. Yang, *Chem. Commun.* **2015**, 51, 16267.
- [66] X. Yang, K. Fan, Y. Zhu, J. Shen, X. Jiang, P. Zhao, S. Luan, C. Li, *ACS Appl. Mater. Interfaces* **2013**, 5, 997.

- [67] W. Yao, J. Yang, J. Wang, L. Tao, *Electrochim. Acta* **2008**, 53, 7326.
- [68] X. Chi, L. Chang, D. Xie, J. Zhang, G. Du, *Mater. Lett.* **2013**, 106, 178.
- [69] J. Jiang, Y. Li, J. Liu, X. Huang, C. Yuan, X. W. Lou, *Adv. Mater.* **2012**, 24, 5166.
- [70] C. K. Chan, H. Peng, G. Liu, K. McIlwrath, X. F. Zhang, R. A. Huggins, Y. Cui, *Nat. Nanotechnol.* **2008**, 3, 31.
- [71] W. S. Hummers Jr., R. E. Offeman, *J. Am. Chem. Soc.* **1958**, 80, 1339.

Chapter 4. Scalable Synthesis of Three-Dimensional Cellular Monolith Collaboratively Woven from V_2O_5 Nanowires and Carbon Nanotubes for Lithium-Ion Battery Cathode

ABSTRACT

Three-dimensional (3D) cellular monoliths of electrochemically active phases are potentially promising in lithium-ion battery (LIB) industry if their large-scale production could be achieved with practicable and cost-effective methods. Herein a green and scalable route is proposed, to weave a 3D honeycomb-like macroporous network from homogeneously mixed one-dimensional (1D) V_2O_5 nanowires (NWs) and carbon nanotubes (CNTs). This novel design aims to overcome the limitations existing in conventional designs of 3D carbon-supported hybrids, e.g. restricted content ratio of active phase as well as ineffectual utilization of the large surface resulted from the 3D network. The intertwinement between V_2O_5 NWs and CNTs not only integrates nanopores into the macroporous system, but also further elevated the collection and transfer of charges through the conductive network. As a result, the unique asset of V_2O_5 NW and CNT render their composite monolith the synergic properties that substantially enhanced the electrochemical kinetics for lithiation/delithiation when used as LIB cathode. The cathode maintained a high cycling capacity of 152 mA h g^{-1}

for 65 cycles, at 100 mA g⁻¹. The high rate performance achieved 145 mA h g⁻¹ at 1000 mA g⁻¹, which is 3 times higher than that of pure V₂O₅ NWs network, and retained 114 mA h g⁻¹ for 200 cycles.

4.1. Introduction

Smart and ordered alignment of nanoscale building blocks allows construction of three-dimensional (3D) bulky assembly for required sophistication, and further imparts novel physical and mechanical properties for the resultant assembly. Their structural layout as an interconnected network not only brings about hierarchy, but also multifunctionality. Enhanced specific surface, spatial conductivity, and mechanical strength can be achieved by the 3D porous lattice.^[1, 2] One typical example is 3D graphene network.^[3, 4] Through intentional formation of porous scaffold, the restacking of graphene layers in bulky materials are greatly alleviated, which significantly enhanced the accessible surface area.^[5, 6] Moreover, the flexible and robust monolith of highly conductive graphene framework, enriched with multidimensional pores, serves as ideal host for a variety of functional components.^[7, 8] Those intriguing properties originated from 3D network can be exploited by a wide range of metallic, ceramic, polymeric and carbonaceous materials, which can be useful in various applications such as exhaust purification, catalysis support, energy conversion/storage, smart filters, controlled release systems and biotechnologies.^[9]

At current stage of research, the performance of lithium-ion battery (LIB) cathode is lagging far behind the anode, and plays a critical limiting factor for the evolution of LIB itself. Compared with state-of-the-art anodes whose gravimetric capacities can reach 3000 mA h g^{-1} in laboratory,^[10, 11] the current cathode candidates are much inferior, usually with less than 200 mA h g^{-1} from the most studied materials.^[12, 13] Exploitation of porous electrodes is a common and powerful strategy that intrinsically expand the electrode/electrolyte contact and shorten the diffusion length for lithium ions to access active sites, and thus dramatically elevate the energy density and rate capability of resultant battery.^[14, 15] On account of the porous construction and high specific surface, 3D cellular monoliths of electrochemically active phases are potentially promising in LIB industry if their large-scale production could be achieved with practicable and cost-effective methods.

Graphene aerogels (GA), the impressive 3D graphene network materials prepared from self-assembly strategy, have emerged as a promising host for lithium-active phases.^[5, 16, 17] However, the loading of active components within GA-based composites is limited to 50%-80% in terms of mass ratio, in most cases. In other words, the graphene component which comprises up to 50% weight of the whole composite doesn't contribute capacity for cathode. Besides, the utilization of the extraordinary surface area provided by GA host is only to better distribute the nanoparticles of functional phases. However, the active sites that are directly engaged in lithiation processes are

still restricted to the surface of nanoparticles. In this sense, the large surface is not effectually exploited. In order to provide better design concept that can overcome the above-mentioned issues, herein the reverse structure of GA was mimicked, to create a honeycomb-like network constructed from active phases, with minimum amount of conductive carbon decoration. In such a way, the functional component becomes the basic building block as well as the major composition of 3D network. This design is expected to overcome the restricted content of active phases in conventional 3D carbon-supported hybrids, and maximize the utilization of the large surface resulted from 3D network. It is hypothesized that this design can eventually lead to higher energy density for the battery cathode.

4.2. Result and discussion

4.2.1. Structural layout and fabrication procedures

In this work, a 3D network collaboratively woven from V_2O_5 nanowires (NWs) and carbon nanotubes (CNTs) is successfully fabricated (named as V_2O_5 /CNTs network, VCN) from a controllable and scalable cryogenic route. A macroporous monolith of the highly ordered network is produced as a result of the specific formation mechanism named ice-segregation-induced self-assembly.^[9] The one-dimensional (1D) geometry of both V_2O_5 and carbon are preferred in electrical and electrochemical devices for the

efficient transportation of charge carriers along a single direction.^[18] In addition, it is noteworthy that the intriguing asset of 1D V₂O₅ NWs and 1D CNTs has enabled a unique intertwinement behavior throughout the whole scaffold, which substantially facilitated the transfer and collection of charges around active sites. Remarkably, this mutual intertwinement between the two 1D building blocks further integrates nanopores into this macroporous system, which not only significantly expand the electrode/electrolyte contact, but also provide effective shortcuts for lithium diffusion. As a result of these preferable features, the lightweight monolith delivered impressive cathode performance when used in LIB, in terms of high energy density and excellent rate capability.

Figure 4.1. Optimal images of the aerogels before (a) and after calcination (b).

As a revolution to the previous hydrothermal method for preparation of metal oxide NWs/CNT composite,^[19, 20] this fabrication totally avoids the self-agglomeration of CNTs under hydrothermal conditions, which secured the homogeneous mixture

between NWs and nanotubes. Detailed synthetic processes are elucidated in the Experimental section. In a typical synthesis, CNTs were first pre-oxidized by HNO_3 reflux, in order to increase its water dispersity without usage of any surfactants. Then a solution processing is chosen to realize the homogenous mixture of V_2O_5 precursors and CNTs. The porous architectures are shaped during the rapid cryogenic solidification of the aqueous suspension. At first a phase segregation will be induced and simultaneously expel the precipitated $\text{V}_2\text{O}_5 \cdot x\text{H}_2\text{O}$ NWs and CNTs from the growing ice phase^[2], and consequently, they will be trapped in the boundaries between neighboring ice crystals. Lately, upon high-vacuum sublimation of ice phase, only the continuous network will be left to afford the monolithic aerogel, characterized by connected “walls” enclosing voids originally resided by ice crystals. The primary component of the aerogel obtained at direct cryodessication is the hydrated V_2O_5 ,^[21-23] with monolithic nature, cake-like appearance, and controllable contents of CNTs as exhibited in **Figure 4.1a**. A further calcination process at 300 °C is applied, in order to transmute the hydrated precursor into highly crystalline and dehydrated V_2O_5 for fabrication into electrodes. According to TGA analysis (**Figure 4.2**), decomposition temperature of the oxidized CNTs is beyond 600 °C, so the calcination process won’t combust the carbon content. As revealed by the optical image (**Figure 4.1b**), the physical appearance remains almost unchanged after calcination.

Figure 4.2. TGA analysis for the oxidized CNTs.

In addition, the developed method is highly controllable, with respect to both density as well as CNT content of the final product. An ultralow density of $6.5 \times 10^{-3} \text{ g cm}^{-3}$ could be achieved (CNTs weight ratio = 20%) by using low concentrated solution mixture, which is in the same order of magnitude as air density ($1.225 \times 10^{-3} \text{ g cm}^{-3}$). More importantly, the facile method which involves only solution processing and cryodessication can easily scale up. Only water will be drained out as the by-product from the overall procedures, which renders this method a green synthesis. To give an example, we have shown the one-pot fabrication of a large monolith with $\sim 2 \text{ L}$ volume (Scheme 4.1).

Scheme 4.1 The scale-up synthesis of a large monolith. 16 g commercial V_2O_5 powders were used as the precursor. The volume of as-prepared aerogel is around 2 L. The diameter of the glass dish in the third picture is 19 cm.

4.2.2. Morphological studies

Figure 4.3. a-e) SEM images of the $\text{V}_2\text{O}_5 \cdot x\text{H}_2\text{O}/\text{CNTs}$ aerogel obtained from direct cryodessication. f) SEM image for the $\text{V}_2\text{O}_5/\text{CNTs}$ aerogel after calcination. Yellow arrows mark the positions of CNTs.

Morphological features of the aerogels were characterized by scanning electron microscopy (SEM) both before and after calcination, and it could be seen that the calcination process didn't change the morphology much. At low magnification, the

SEM images (**Figure 4.3a-c**) displayed a honeycomb-like lattice with hierarchical open pores and continuous pore walls. Average diameter of visible pores is less than 10 mm. At a closer observation (**Figure 4.3d**), the bent wall resembles two-dimensional (2D) meshy sheet, which is woven from 1D building blocks. In this monolith, the 3D scaffold was assembled from 2D meshy sheets, which in turn is fabricated from mutually intertwined 1D V_2O_5 NWs and CNTs. Interestingly, due to the loosely pack manner, numerous nanotextured holes were generated on the nanosheets (**Figure 4.3e**), which further enlarged the specific surface area, and also promoted the accessibility for electrolytes to reach active surface.

Figure 4.4. TEM images of the freeze-dried aerogel.

The mono-dispersion of CNTs was also thoroughly examined in this 3D network. As a typical example revealed in **Figure 4.3f**, CNTs homogeneously distribute on the 2D nanosheets, without any observed aggregation. As the sample is checked exhaustively, it is confirmed that the CNT chunks frequently appeared in hydrothermal products were eliminated by the cryogenic approach. The transmission electron microscopy (TEM)

images further provided more concrete evidence for the homogeneous mixture of NWs and nanotubes. As shown in **Figure 4.4**, the NWs present as light colored and relatively straight lines, while the curved CNTs entangled around them, in different manners like knots, helixes, lassos and so on. It is due to the similar size of the two 1D building blocks as well as their homogenous blend that enabled this unique intertwinement. The energy-dispersive X-ray spectroscopy (EDX) investigation further provide an elemental mapping for the product, as exhibited in **Figure 4.5**. Although the mapping result of V doesn't show the exact wire shapes due to the limitation of instrument, but one can induce the wire-like contour from the discrete dots, which matched the macroscopic outline of sample present in **Figure 4.5a**.

Figure 4.5. Element mapping of carbon, oxygen and vanadium in the freeze-dried aerogel by using EDX technique.

4.2.3. Chemical composition and crystal properties

Figure 4.6. a) XRD pattern of VCN. b) XPS spectrum of VCN. c) High-resolution XPS spectrum for vanadium.

Phase purity and crystal information of the calcined VCN was examined by X-ray diffraction (XRD). As indicated by **Figure 4.6a**, the XRD pattern displayed a series of well-defined diffraction peaks that can be readily indexed to the orthogonal V_2O_5 phase (JCPDS 41–1426), indicative of the good crystallinity. Diffraction signals of CNTs here were covered by the stronger ones from V_2O_5 , and hence their peaks were hidden in the pattern. In order to confirm the chemical composition of the annealed product, X-ray photoelectron spectroscopy (XPS in 0–1000 eV range) was further employed as a cross-reference. As shown in **Figure 4.6b**, the existence of vanadium, carbon and oxygen are certified for the VCN aerogel. From the high-resolution spectrum in the region of 510–535 eV, as demonstrated in **Figure 4.6c**, the three peaks at 517.5, 525.0 and 530.2 were respectively corresponding to the binding energy of V 2p_{3/2}, V 2p_{1/2}, and O 1s electrons. The 7.5 eV difference between V 2p_{3/2} and V 2p_{1/2} electrons could be indexed to +5 electronic state of vanadium.^[24] Therefore, as implied by the XPS result, the purity of vanadium species is confirmed that V_2O_5 is the only composition of vanadium oxides.

4.2.4. Electrochemical performance as LIB cathode

Figure 4.7. a, b) CV profiles of VCN (a) and VN (b). c) Galvanostatic discharge/charge curves of VCN electrode at different current densities.

Despite the environmental harshness, V_2O_5 is still considered as a potential candidate for high-performance LIB cathode, owing to its layered crystal structure along the c-axis which can simplify the reaction kinetics.^[25-28] The theoretical capacity of V_2O_5 achieved 294 mA h g^{-1} with two Li ions intercalated (in the voltage range of 2.0-4.0 V), which is much higher than $LiFePO_4$ (170 mA h g^{-1}). Therefore, the VCN monolith was also employed as a LIB cathode, to demonstrate its excellent electrochemical properties in terms of energy storage. Detailed electrochemical characterizations were carried out based on the as-assembled half cells, with Li foils serving as the counter and reference electrodes. In order to provide a balanced and comparative perspective, the battery electrodes made from pure V_2O_5 networks (VN) were also tested as the control group. **Figure 4.7a** demonstrate the typical cyclic voltammetry (CV) plots at a scan rate of 0.5 mV s^{-1} and a voltage range of 2.0-4.0 V. Three apparent reduction peaks could be identified at 3.30 V, 3.08 V, and 2.08 V, which are respectively attributed to the multi-step lithiation and consequent formation of first $\epsilon\text{-Li}_{0.5}V_2O_5$, and then $\delta\text{-Li}V_2O_5$, $\gamma\text{-Li}_2V_2O_5$ in sequence. A further reduction below 2 V will lead to the formation of irreversible $\omega\text{-Li}_xV_2O_5$ ($x>2$) phase, which will diminish the electrode.^[25] In this consideration, the voltage range was set within 2.0 to 4.0 V. On the other side, the anodic current peaks (2.61 V, 3.33 V, 3.55 V) arose from lithium extraction reactions. Detailed redox mechanisms could be elaborated as follow ^[29-31]:

Notably, the CV curves of VCN showed sharper current peaks as well as higher overlapping between different cycles, in comparison to that of VN (as shown in **Figure 4.7b**), which is indicative of enhanced electrochemical reactivity as well as cycling stability.^[32] The enhancement could be attributed to the integration of CNTs, which enabled faster transfer and collection of charges, as well as alleviated polarization.^[27]

Figure 4.8. Comparison of rate capabilities among VN and VCN samples with different CNTs contents.

Galvanostatic discharge/charge measurements were carried out at various current densities. As indicated by **Figure 4.7c**, three discharge plateaus could be recognized at the vicinity of 3.38 V, 3.19 V and 2.30 V respectively, which coincide with the peak positions of CV data. In order to verify the hypothesized improvement contributed by

the CNTs, here the rate capabilities of VN with 3 VCN samples of different CNT contents (4.8%, 9.2%, 16.7%) were compared, as shown in **Figure 4.8**. It is found that 9.2% is the optimized ratio of CNTs content (this sample is named as 9.2%-VCN), in terms of much superior lithium-storage property to other control samples. The reversible discharge capacities achieved 241, 202, 170, 145 mA h g⁻¹ respectively corresponding to current densities of 100, 200, 500, 1000 mA g⁻¹. In comparison, under the same current densities, the relevant specific capacities delivered by VN were only 189, 127, 92, 48 mA h g⁻¹, respectively. It is implied that the high rate performance of V₂O₅ NWs benefits more from the integration with CNTs. As the charge/discharge rates increased from 100 to 1000 mA g⁻¹, a superb capacity retention of 60% is maintained for VCN, which is remarkably higher than 25% of VN. At a high current density of 1000 mA g⁻¹ (charge/discharge will be accomplished within 9 min), the specific capacity delivered by VCN is three times higher than VN.

Figure 4.9. a) Cycling performance of the 9.2%-VCN electrode at 100 mA g⁻¹. b) Cyclability of the 9.2%-VCN electrode at a high current density of 1000 mA g⁻¹.

The cycling performance of the 9.2%-VCN sample is evaluated at both low and high

current densities. As demonstrated in **Figure 4.9a**, for the first cycle at 100 mA g^{-1} , this electrode delivered a specific capacity of 274 mA h g^{-1} , and a remarkable columbic efficiency of 88%, of which the later indicates significantly buffered initial irreversibility.^[33] The columbic efficiency then stabilized over 97% from the 2nd cycle onward, and kept close to 100% for most of the cycles. A specific capacity of 152 mA h g^{-1} was maintained after 65 cycles of charge-discharge. **Figure 4.9b** revealed a depressed deterioration of capacity curve during the long-time rapid charge/discharge processes, namely at 1000 mA g^{-1} . After 200 cycles, a high specific capacity of 114 mA h g^{-1} was still delivered, manifesting the endured cyclic stability of VCN electrode.

In addition to CV characterization, electrochemical impedance spectroscopy (EIS) are also essential in order to shed a light on the electrochemical mechanisms underlying the compelling lithium-storage properties of VCN electrode. The comparative tests were carried out with 9.2%-VCN and VN samples. As revealed in **Figure 4.10**, both plots could be simulated to a depressed semicircle at high-medium frequency region plus an inclined line at low frequency region, which are associated with the charge-transfer resistance (R_{ct}) and Warburg element, respectively. It is apparent that the semicircle for VCN is much smaller than that of VN, indicative of the essentially reduced R_{ct} after coordination with CNTs. By modulating the Randles equivalent circuit (**Figure 4.10** inset), each part of the resistance elements in the EIS curves can be calculated. The modeling result shows similar electrolyte resistance (R_e) for VCN

(6.0 Ω) and VN (6.7 Ω). Meanwhile, R_{ct} of VCN was calculated to be 90.2 Ω , which is 2 orders of magnitude lower than 1937 Ω of VN. Therefore, from the EIS result, it is confirmed that the electrochemical kinetics were radically enhanced after incorporation of CNTs, which can be attributed to the substantially accelerated charge transportation in the intertwined V_2O_5 -CNTs network.

Figure 4.10. EIS plots of VCN and VN-based half-cells. Insets show the enlarged plot and Randles equivalent circuit of the electrode/electrolyte interface.

On comprehension of the characteristics inherent in the favorable composition and structuration of this hybrid material, the above-depicted impressive LIB performance can be interpreted from the following aspects. At first, both V_2O_5 and carbon used in this material are crafted into 1D geometries, which are associated with beneficial physiochemical properties.^[34] Secondly, the structural layout as a 3D interconnected framework is preferred for rapid transportation of electrons. Thirdly, the uniform

distribution of CNTs and their homogenous entanglement with V_2O_5 NWs throughout the entire network further generates “highways” to gather and deliver charge carriers in nearby regions. Last but not least, the smart combination of multidimensional nanopores and macropores in the same hierarchical framework, efficiently enhanced the accessibility of electrolyte, and enabled easier and faster diffusion of lithium ions across the bulky electrode. As a comprehensive result of all these characteristic advantages, the 3D hybrid is capable of providing decent specific capacity as well as rate capability.

4.3. Conclusion

As a summary, a rational design concept to mimic the reverse structure of GA-based composite and to construct a 3D network from 1D V_2O_5 NWs and CNTs was realized from a green and scalable synthesis, which generated a lightweight monolith, enriched with hierarchical macropores and nanopores. Via this method, mass loading of V_2O_5 in the composite is optimized and their active surface is also maximized. In a proof-of-concept application, the VCN product demonstrated superb and durable lithium-storage properties as a cathode. It is validated that the unique asset of V_2O_5 NWs and CNTs render their composite monolith the synergic properties that greatly enhanced the electrochemical kinetics during lithiation/delithiation processes. This remarkable electrochemical reactivity could be useful for a variety of applications such as

supercapacitor,^[35, 36] catalysis,^[37] sensor,^[38, 39] and so forth. Furthermore, as a green and scalable synthetic approach, the proposed method could potentially realize the general fabrication of 3D cellular monoliths comprised from inorganic NWs and CNTs, and therefore it deserves further exploration.

4.4. Experimental

4.4.1. Materials synthesis

CNTs used in this study were first oxidized with nitric acid, according to reported methods.^[40] Water dispersity of oxidized CNTs would be significantly improved without usage of any surfactants. After acid reflux, the CNTs were thoroughly washed, cleaned and dispersed to afford 2.6 mg ml⁻¹ aqueous suspension. In a typical synthesis to acquire VCN, commercial V₂O₅ powders (0.364 g) were first added to 30 ml deionized water under vigorous stirring. Then 5 ml 30% H₂O₂ solution was added into the yellow suspension, which was instantly turned into wine solution. After 12 h of mild stirring, thick orange gel could be obtained. Then oxidized CNTs suspension with varied volume (0.5, 1, 2, 4, 5 ml) was added into 5 ml orange gel, and continuously stirred for 30 min. Subsequently, the mixtures were transferred into molds, frozen by liquid nitrogen, followed by cryodessication for 3 days. The dried V₂O₅·xH₂O/CNTs

aerogels were further dehydrated by calcination above 300 °C, for 3 h. The CNTs contents in each samples are calculated to be 2.4%, 4.8%, 9.2%, 16.7%, 20%. VNs were synthesized from the similar route, without adding CNTs.

4.4.2. Materials characterization

SEM, TEM and EDX were conducted respectively with JSM-7600F (JOEL), JEM 1400 (JOEL), and JEM 2100 (JOEL). XRD was performed with D8 Advance diffractometer (Bruker) by applying Cu K α irradiation. XPS was carried out with Phoibos 100 spectrometer (SPECS) by using a monochromatic Mg X-ray radiation exciting source.

4.4.3. Electrochemical measurements

Samples of VCN with different contents of CNTs, as well as VN were first ground into fine powders, and then mixed with carbon black (Super P) and polyvinylidene fluoride (PVDF) binder in N-methyl-2-pyrrolidone (NMP) solvent, according to the weight ratio of 7:2:1. The resulted slurries were stirred at 200 rpm for 1 week. After that, the slurries were coated onto Al foils (mass loading at 1 mg scale) and subsequently assembled into CR 2016 coin-type half-cells as the work electrode. Pure lithium foil serves as both reference and counter electrodes. The electrolyte solution used was 1 M LiPF₆ dissolved

in the mixed solvent of ethylene carbonate (EC) and dimethyl carbonate (DMC) at 1:1 weight ratio. Galvanostatic charge/discharge measurement was performed with Neware multichannel battery test system in the voltage window of 2.0-4.0 V. CV and EIS tests were carried out on Metrohm autolab electrochemical workstation, by using a sine wave of 5 mV in the frequency region of 10^5 -0.01 Hz.

4.5. References

- [1] M. Scheffler, P. Colombo, *Cellular Ceramics: Structure, Manufacturing, Properties and Applications*, John Wiley & Sons., Weinheim, Germany **2005**.
- [2] L. Qiu, J. Z. Liu, S. L. Chang, Y. Wu, D. Li, *Nat. Commun.* **2012**, 3, 1241.
- [3] Z. Chen, W. Ren, L. Gao, B. Liu, S. Pei, H. M. Cheng, *Nat. Mater.* **2011**, 10, 424.
- [4] Y. Xu, K. Sheng, C. Li, G. Shi, *ACS Nano* **2010**, 4, 4324.
- [5] X. Cao, Z. Yin, H. Zhang, *Energy Environ. Sci.* **2014**, 7, 1850.
- [6] Y. Xu, G. Shi, X. Duan, *Acc. Chem. Res.* **2015**, 48, 1666.
- [7] X. H. Xia, D. L. Chao, Y. Q. Zhang, Z. X. Shen, H. J. Fan, *Nano Today* **2014**, 9, 785.
- [8] S. Mao, G. Lu, J. Chen, *Nanoscale* **2015**, 7, 6924.
- [9] M. C. Gutiérrez, M. L. Ferrer, F. d. Monte, *Chem. Mater.* **2008**, 20, 634.
- [10] C. K. Chan, H. Peng, G. Liu, K. McIlwrath, X. F. Zhang, R. A. Huggins, Y. Cui, *Nat. Nanotechnol.* **2008**, 3, 31.

- [11] B. Liang, Y. Liu, Y. Xu, *J. Power Sources* **2014**, 267, 469.
- [12] B. Xu, D. Qian, Z. Wang, Y. S. Meng, *Mater. Sci. Eng., R* **2012**, 73, 51.
- [13] S. B. Chikkannanavar, D. M. Bernardi, L. Liu, *J. Power Sources* **2014**, 248, 91.
- [14] A. Vu, Y. Qian, A. Stein, *Adv. Energy Mater.* **2012**, 2, 1056.
- [15] Y. Li, Z.-Y. Fu, B.-L. Su, *Adv. Funct. Mater.* **2012**, 22, 4634.
- [16] W. Wei, S. Yang, H. Zhou, I. Lieberwirth, X. Feng, K. Mullen, *Adv. Mater.* **2013**, 25, 2909.
- [17] B. Li, S. Yang, S. Li, B. Wang, J. Liu, *Adv. Energy Mater.* **2015**, 5, 1500289.
- [18] W. Zhou, C. Cheng, J. Liu, Y. Y. Tay, J. Jiang, X. Jia, J. Zhang, H. Gong, H. H. Hng, T. Yu, H. J. Fan, *Adv. Funct. Mater.* **2011**, 21, 2439.
- [19] Z. Chen, V. Augustyn, J. Wen, Y. Zhang, M. Shen, B. Dunn, Y. Lu, *Adv. Mater.* **2011**, 23, 791.
- [20] Z. Chen, Y. Qin, D. Weng, Q. Xiao, Y. Peng, X. Wang, H. Li, F. Wei, Y. Lu, *Adv. Funct. Mater.* **2009**, 19, 3420.
- [21] Y. Wang, G. Cao, *Chem. Mater.* **2006**, 18, 2787.
- [22] K. Lee, Y. Wang, G. Cao, *J. Phys. Chem. B* **2005**, 109, 16700.
- [23] W. Avansi Jr, C. Ribeiro, E. R. Leite, V. R. Mastelaro, *Cryst. Growth Des.* **2009**, 9, 3626.
- [24] C. D. Wagner, G. E. Mullenberg, *Handbook of X-Ray Photoelectron Spectroscopy: A Reference Book of Standard Data for Use in X-Ray Photoelectron Spectroscopy*,

Perkin-Elmer Corp., Waltham, MA, USA **1979**.

[25] D. Kong, X. Li, Y. Zhang, X. Hai, B. Wang, X. Qiu, Q. Song, Q.-H. Yang, L. Zhi, *Energy Environ. Sci.* **2016**, *9*, 906.

[26] C. K. Chan, H. Peng, R. D. Twisten, K. Jarausch, X. F. Zhang, Y. Cui, *Nano Lett.* **2007**, *7*, 490.

[27] D. Chao, X. Xia, J. Liu, Z. Fan, C. F. Ng, J. Lin, H. Zhang, Z. X. Shen, H. J. Fan, *Adv. Mater.* **2014**, *26*, 5794.

[28] Y. Wang, H. J. Zhang, W. X. Lim, J. Y. Lin, C. C. Wong, *J. Mater. Chem.* **2011**, *21*, 2362.

[29] A. Pan, J. Zhang, Z. Nie, G. Cao, B. W. Arey, G. Li, S. Liang, J. Liu, *J. Mater. Chem.* **2010**, *20*, 9193.

[30] R. J. Cava, A. Santoro, D. W. Murphy, S. M. Zahurak, R. M. Fleming, P. Marsh, R. S. Roth, *J. Solid State Chem.* **1986**, *65*, 63.

[31] Y. L. Cheah, V. Aravindan, S. Madhavi, *J. Electrochem. Soc.* **2013**, *160*, A1016.

[32] B. Wang, W. Al Abdulla, D. Wang, X. S. Zhao, *Energy Environ. Sci.* **2015**, *8*, 869.

[33] K. Xu, *Chem. Rev.* **2014**, *114*, 11503.

[34] Y. Xia, P. Yang, Y. Sun, Y. Wu, B. Mayers, B. Gates, Y. Yin, F. Kim, H. Yan, *Adv. Mater.* **2003**, *15*, 353.

[35] C. X. Guo, G. Yilmaz, S. Chen, S. Chen, X. Lu, *Nano Energy* **2015**, *12*, 76.

[36] J. Zhu, L. Cao, Y. Wu, Y. Gong, Z. Liu, H. E. Hoster, Y. Zhang, S. Zhang, S. Yang,

Q. Yan, P. M. Ajayan, R. Vajtai, *Nano Lett.* **2013**, *13*, 5408.

[37] C. Karunakaran, S. Senthilvelan, *J. Colloid Interface Sci.* **2005**, *289*, 466.

[38] A. R. Raju, C. N. R. Rao, *J. Chem. Soc.* **1991**, *20*, 1260.

[39] J. Liu, X. Wang, Q. Peng, Y. Li, *Adv. Mater.* **2005**, *17*, 764.

[40] V. Datsyuk, M. Kalyva, K. Papagelis, J. Parthenios, D. Tasis, A. Siokou, I. Kallitsis, C. Galiotis, *Carbon* **2008**, *46*, 833.

Chapter 5. Summary and Outlook

5.1. Summary of research work.

On account of the exceptional properties originated from the optimized spatial organization together with desirable structural sophistication, 3D networks have been extended to a wide range of materials, showing enhanced performance for various utilizations in comparison to random disordered structures, especially related to electrical or electrochemical applications. The scope of our research focused more on the innovation of structures, rather than simple synthesis of materials. As demonstration of concept, we have materialized our designs and fully analyzed them in order to reveal the unique advantages associated with the characteristic structures. It is necessary to mention that the flow of our design in these three projects is evolutionary.

As an archetype of 3D materials, diverse 3DPGNs and their derivative composites have been systematically studied in recent years. Through the rational integration of functional phases within 3DPGNs, the resultant hybrids can lead to synergistically promoted performance up to several times. Starting from the knowledge that an effective method is demanded to control the geometry and structure of the guest phases inside 3D GA, we introduced a multi-step hydrothermal-based strategy combined with a pre-conditioning technique named vacuum-assisted impregnation, which realized the

fabrication of GA and the decoration of controlled nanostructures separately. SnO_2 in the final product shows anisotropic coral-like morphology, which resembles the cluster of nanorods *in-situ* grown on the 3D network of graphene. Rational integration of the two advanced structures, anisotropic SnO_2 and 3D GA, collectively led to a synergistically enhanced lithium-storage properties, which further pushed the anode performance for GA-supported hybrids.

Despite the success of the first design concept, we nevertheless realized its limitation as the formation of GA and *in-situ* growth of nanostructured metal oxides are achieved in separate procedures, and a pre-conditioning step is indispensable to fully saturate the dried GA in the precursor solution. In order to realize the construction of smart structures from a facile synthetic route, we proposed another “killing three birds with one stone” strategy. In the second project, a one-step multipurpose method was developed to realize a sophisticated design that simultaneously integrates three desirable components of nitrogen dopant, 3D graphene and 1D mesoporous metal oxide nanowires into one hybrid material. The realization of the one-step hydrothermal method heavily relies on the utilization of urea as a starting reagent, which enables precipitation of precursor nanowires and concurrent doping of nitrogen heteroatoms on graphene during the hydrothermal reaction, while at the same time the graphene nanosheets are self-assembled to afford a 3D scaffold. The integration of two representative building blocks, namely flexible graphene nanosheets and Co_3O_4

nanowires, enabled various intertwining behavior such as seaming, bridging, hooping, bundling, and sandwiching, of which the synergistic effect substantially enhanced electrical and electrochemical properties of the resultant hybrid.

Along with the deeper study on GA as the host structure, we noted the innate deficiency associated with GA-supported composites, e.g. restricted content ratio of active phase as well as ineffectual utilization of the large surface resulted from the 3D network. Therefore, in the third project, we mimic the reverse structure of GA, in order to overcome these problems. Briefly, a green synthetic route is proposed to weave a GA-like 3D macroporous network from homogeneously mixed 1D V_2O_5 NWs and CNTs. The rational combination of V_2O_5 NWs and CNTs enabled an interesting intertwinement between the two 1D building blocks, which not only integrates nanopores into the macroporous system, but also further elevated the collection and transfer of charges through the conductive network. As a result, the unique asset of V_2O_5 NW and CNT render their composite monolith the synergic properties that radically enhanced the electrochemical kinetics for lithiation/delithiation when used as LIB cathode. In addition to the scalability of our proposed method, it could potentially realize the general fabrication of 3D cellular monoliths comprised from inorganic NWs and CNTs, and therefore it deserves further exploration.

In summary, three newly developed 3D nano-hybrids based on metal oxides and carbon are highlighted in this thesis, to showcase the design and fabrication of 3D networks as

high-performance electrode materials. After the rise of 1D and 2D nanomaterials, recently 3D nanomaterials are arousing tremendous academic interests. The progress on 3D materials represents one of the frontiers in nanotechnology. We hope that our study present in this thesis could potentially inspire other colleagues dedicated to this field.

5.2. Outlook for 3DPGN-based hybrids and its derivative structures in electrochemical energy storage

Regardless of the extensive study on 3DPGN, yet there are still some concerns need to address. First, in related to 3DPGNs themselves, the porosity can only be roughly controlled. More specifically, the pore size distribution always spreads from several nanometers to tens of micrometers (usually in GA), and precise arrangement of pore channels is unsatisfactory as well. Strict control on the porous structure will not only enhance the performance of existing utilization, but also potentially extend 3DPGN for extra applications, since most of the intriguing properties are originated from the porous structure. Secondly, the thickness of stacking graphene layers within the scaffolds can barely be controlled, especially for GAs that are interlocked from numerous RGO sheets. Thirdly, in regard to electrochemical applications, synergistic effects were always discovered from the integration with 3DPGN. However, the detailed

mechanisms underlying those synergies in most cases remain unrevealed. In order to shed a light, the contact between active components and 3DPGN needs to be studied in detail.

In recent researches, 3DPGNs have shown growing significance in related to flexible electronics. 3DPGNs are obviously more suitable for flexible power tools, than conventional models of LIBs or SCs. Due to the monolithic nature and coherent structure, their fabrication into flexible electrodes require no current collectors or polymer binders. Moreover, without usage of non-conductive polymer binders and non-capacitive current collectors, the energy density of flexible LIBs/SCs is comparable or even superior to the conventional ones. From practical consideration, the high cost of graphene at current stage limits the massive production and large-scale industrial applications extended from this material, but the flexible electronics and wearable or implantable devices are always smart, miniaturized, requiring much less amount of raw graphene than normal power tools. So far, a lot of works have demonstrated the fabrication of flexible LIBs and SCs based on the free-standing elastic 3DPGN-hybrids. With the rise of wearable devices and roll up displays, there would be an increasing demand for 3D graphene with tunable resilience and mechanical strength, to meet the diversified requirements of different devices.

Lithium-air battery, sodium-ion battery, lithium-sulfur battery and other alternative chemistry batteries have emerged in combination with 3DPGN as novel techniques for

clean energy generation/storage. Novel 3DPGN hybrids specifically designed for those applications are highly anticipated.

The growing interest for 3D hierarchical nanomaterials is not limited to 3DPGN and its hybrids. In the current stage, self-assembly is still the most accepted strategy for construction of 3D structures, and 3D printing could be potentially promising in this area. 3D cellular monoliths in general should be studied as a system, because their intriguing properties are determined by not only composition but also microscopic structures. Like the study on 1D and 2D nanomaterials, versatile methodologies should be developed for the systematic research on 3D nanomaterials.

PUBLICATIONS

1. Xin Yao, Guilue Guo, Yang Zhao, Yu Zhang, Si Yu Tan, Yongfei Zeng, Ruqiang Zou, Qingyu Yan, Yanli Zhao, Synergistic effect of mesoporous Co_3O_4 nanowires confined by N-doped graphene aerogel for enhanced lithium storage. *Small* **2016**, accepted.
2. Xin Yao, Guilue Guo, Xing Ma, Yang Zhao, Chung Yen Ang, Zhong Luo, Kim Truc Nguyen, Pei-Zhou Li, Qingyu Yan, Yanli Zhao, *In-situ* integration of anisotropic SnO_2 heterostructures inside three-dimensional graphene aerogel for enhanced lithium storage. *ACS Appl. Mater. Interfaces* **2015**, 7, 26085-26093.
3. Guilue Guo, Xin Yao, Huixiang Ang, Huiteng Tan, Yu Zhang, Yuanyuan Guo, Eileen Fong, Qingyu Yan, Using elastin protein to develop highly efficient lithium- O_2 battery cathodes. *Nanotechnology* **2016**, 27, 045401.
4. Yongfei Zeng, Ruyi Zou, Zhong Luo, Huacheng Zhang, Xin Yao, Xing Ma, Ruqiang Zou, Yanli Zhao, Covalent organic frameworks formed with two types of covalent bonds based on orthogonal reactions. *J. Am. Chem. Soc.* **2015**, 137, 1020-1023.
5. Peng Wang, Li Hao, Qiang Gao, Pei-Zhou Li, Xin Yao, Linyi Bai, Kim Truc Nguyen, Ru-Qiang Zou, Yanli Zhao, Fabrication of novel hybrid nanoflowers from boron nitride nanosheets and metal-organic frameworks: A solid acid catalyst with enhanced catalytic performance. *J. Mater. Chem. A* **2014**, 2, 18731-18735.
6. Ajay Dhankhar, Rohit K. Rai, Deepika Tyagi, Xin Yao, and Sanjay K. Singh, Synergistic catalysis with MIL-101 stabilized highly active bimetallic NiPd and CuPd alloy nanoparticle catalysts for C-C coupling reactions. *ChemistrySelect* **2016**, accepted

CONFERENCES

1. Poster presentation, 15th Asian Chemical Congress (15 ACC), Singapore, Aug 19-23, 2013.
2. Poster presentation, The 11th Annual IEEE International Conference on Nano/Micro Engineered and Molecular Systems (IEEE-NEMS 2016), Sendai-Matsushima, Japan, Apr 17-20, 2016.