Functionalized graphene-based materials for li-ion batteries : from anode to cathode

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NANYANG
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**FUNCTIONALIZED GRAPHENE-BASED MATERIALS
FOR LI-ION BATTERIES: FROM ANODE TO CATHODE**

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FUNCTIONALIZED GRAPHENE-BASED MATERIALS FOR LI-ION BATTERIES: FROM ANODE TO CATHODE

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Abstract

Owing to the 2D geometrical structure and extraordinary physicochemical properties, graphene and its derivatives have gained intense attentions in application as the promising alternatives of current graphite anode for rechargeable Li-ion batteries (LIBs). However, the Li storage performance of graphene-based materials is extremely sensitive to their morphology and microstructure. In this PhD project, using chemical approaches, we focus on these two aspects for rational design and fabrication of functionalized graphene-based materials, including both anodes and cathodes, with boosted performance for Li storage. In the meantime, we also aim to contribute to the understanding and exploration of graphene-based materials for next generation LIBs.

Firstly, heteroatom doped graphene anodes include N- and S-codoped graphene (NS-G) and N-doped porous graphene (NPG) are fabricated via organic chemistry enabled *in situ* doping strategies. For the preparation of NS-G, 2-aminothiophenol, functions as both N and S sources, was firstly covalently bonded to graphene oxide (GO) through a polyphosphoric acid catalyzed cyclization reaction. The resultant product was subsequently annealed in Ar atmosphere to achieve NS-G with a doping content of 1.76 at% for N and 0.86 at% for S. While in the case of NPG, a hydrogen-bonded supramolecular polymer consisting of N-enriched molecules, namely, melamine and cyanuric acid, was applied to modify GO. This polymer could be completely decomposed and release a myriad of N-containing gases during the later thermal treatment, which results in N doping and the generation of porous structures in graphene simultaneously. With the merits of unique structure and valuable dopants (N,S-codoping or high N doping level), both NS-G and NPG display excellent anodic

performance for LIBs, that is, stable cycling, high reversible Li storage capacity and good rate charge-discharge capability.

Secondly, ultra-small SnO₂ nanoparticles (~5 nm) decorated graphene was produced via a facile one-step redox reaction between Sn²⁺ and GO in aqueous solution. The nanoparticles are found to be uniformly deposited on graphene with a homogeneous size distribution in the presence of a cationic surfactant — hexadecyltrimethylammonium bromide (HTMAB), whereas inhomogeneously and randomly deposited in the case of without HTMAB. In sharp contrast to the previous method for constructing SnO₂/graphene hybrid, our newly developed one is more appealing and effective because of its simplicity and does not require any further thermal treatment to obtain SnO₂ with high crystallinity. Impressively, as an anode for LIB, the hybrid shows remarkable performance with good capacity retention (~88%) in 120 consecutive cycles.

Thirdly, chemical modulation of the oxygen-based groups on GO are realized via chemoselective removal of the specific functional groups. For example, carbonyl/hydroxyl functionalized GO (C/HGO) was prepared by reacting GO with *n*-Butyllithium, and decarboxylated GO (DCGO) was obtained through silver(I)-catalyzed decarboxylation of GO. The resultant C/HGO and DCGO both exhibit better Li storage performance than GO when evaluated as the cathodes for LIBs in the voltage between 1.5 and 4.5 V (vs. Li/Li⁺). Specifically, C/HGO shows the best cathodic performance with a stable capacity of ~170 mAh g⁻¹ (current rate: 100 mA g⁻¹), which documents the engineering of oxygen functional groups can significantly decrease the irreversible reaction between Li ions and the oxygen-based groups.

Lastly, a general and versatile method involving ultrasonication and hydrothermal treatment was developed for scalable preparation of various vat dye/graphene

composites. The vat dyes, i.e., Vat Green 8 (VB 8), Vat Brown BR (VB BR) and Vat Olive T (VO T), are typical carbonyl compounds with abundant electroactive carbonyl groups bonded to condensed aromatic rings, however, their densely stacked structure stemming from strong intermolecular interactions, associated with low electrical conductivity result in sluggish kinetics for electrochemical reactions. After sonication-induced disassembly and then hydrothermal-promoted reassembly processes, a series of compatible hybrids with vat dye molecules absorbed on graphene sheets were produced, leading to considerably increased conductivity and accessibility for electrolyte as compared to the pristine vat dyes. Due to the novel structure, the hybrids, namely, VB 8/graphene, VB BR/graphene and VO T/graphene, all show exceptional cathodic performance for Li storage with long cyclic durability and high specific capacity.

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List of Abbreviations

LIB: Li-ion battery

CV: cyclic voltammogram

EIS: electrochemical impedance spectroscopy

SEI: solid electrolyte interphase

CVD: chemical vapor deposition

FTIR: Fourier transform infrared spectroscopy

FESEM: field-emission scanning electron microscopy

TEM: transmission electron microscopy

HRTEM: high-resolution transmission electron microscopy

STEM: scanning transmission electron microscopy

XPS: X-ray photoelectron spectroscopy

XRD: X-ray diffraction

BET: Brunauer-Emmett-Teller

TGA: thermogravimetric analysis

GO: graphene oxide

rGO: reduced graphene oxide

EC: ethylene carbonate

DMC: dimethyl carbonate

EMC: ethyl methyl carbonate

PVDF: polyvinylidene fluoride

NMP: N-methyl-2-pyrrolidinone

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Chapter 1. Introduction

1.1 Research background

With the overconsumption of fossil fuels and the associated more and more complex Earth's climate system, it is important and critical to develop clean energy for a sustainable world.^[1] A series of renewable energy technologies, for instance, solar cells, wind generators and piezoelectric systems, have thus been developed to harvest different types of renewable energy (e.g., solar, wind, and hydro), and electricity is the most direct and predominant form of such energy been used.^[2] Considering the intermittent and localized features of such energy, they must be efficiently stored prior to be transported and used for specific applications. Among various energy storage technologies, rechargeable LIB, one kind of electrochemical storage systems, is the most desirable candidate featured by its extraordinary energy storage capability and environmental friendliness.^[3] The energy storage in a LIB is on the basis of reversible shuttle of ions between the cathode (typically, lithium transition metal oxides/phosphates) and anode (commonly, graphite) materials inside the battery, with respect to the shift of electrons outside the battery during the charge/discharge process.^[4, 5] Since the birth in 1990s, LIBs — because of the superior specific energy (gravimetric energy density) and energy density (volumetric energy density) than their counterparts (i.e., nickel-metal hydride, nickel-cadmium and lead-acid batteries), are currently becoming the dominant power source for portable electronics.^[6] Unfortunately, the energy storage performance of LIBs cannot keep pace with the ever-growing demand for energy, in particular the rate of progress in emergent electric vehicles and smart grids.^[7]

Current LIB technology inherently delivers low gravimetric and volumetric energy densities of 210 Wh kg^{-1} and 650 Wh L^{-1} , respectively, compared to 4200 Wh kg^{-1} and 3000 Wh L^{-1} for traditional gasoline fuel.^[8] Further breakthroughs in the energy storage capability of a LIB requires the boost of specific capacity of the electrode materials, including both the anode and cathode materials.

Figure 1.1 Schematic illustration of the relationship between graphene and the other graphitic materials with different dimensionalities.^[9]

As the basic unit of carbon-based materials with various dimensionalities ranging from 0D buckyballs, 1D carbon nanotubes to 3D graphite, graphene is a 2D structure with sp^2 hybrid carbon in a hexagonal lattice (Figure 1.1).^[9] Since the first isolation from graphite crystal in 2004,^[10] graphene rapidly becomes the hottest material and has attracted worldwide extensive research interests because of its fascinating physiochemical properties, including large surface area ($2630 \text{ m}^2 \text{ g}^{-1}$), high Young's modulus ($\sim 1.0 \text{ TPa}$) and good electrical conductivity, etc.^[11] Although the initial mechanical exfoliation method has low yield, chemical oxidation-exfoliation-reduction technique enables a gram-scale production of rGO, which can be regarded as one kind of graphene with a certain amount of defects stemming from the lattice atom missing and covalently bonded O-containing

functional groups.^[12, 13] This imperfect rGO have excited the researchers, especially material scientists to explore its application in electrochemical energy storage during the past few years, because these defects are believed to show enhanced electrochemical reactivity comparing with the defect free pristine graphene.^[14-16]

For the application as the anode of a LIB, graphene is a desirable material with an ideal specific capacity of up to 744 mAh g⁻¹, twice that of the other carbonaceous materials.^[17] It is worth noting that such an intriguing value is based on the absorption of Li on both side of an isolated graphene layer to form a LiC₃ compound, instead of LiC₆ following the traditional intercalation process.^[16] However, the chemical oxidation-exfoliation-reduction approach synthesized rGO suffers from the inevitable problem of restacking of the graphene sheets, which is not only disadvantage for electrolyte penetration and Li ions diffusion in the electrode, but also decreases the electrochemically active sites for Li storage.^[18, 19] Consequently, the restacked rGO with substantially weakened merits of graphene exhibits poor Li storage performances, in terms of low specific capacity, dissatisfactory rate performance and fast capacity fading.

On the other hand, the chemical method produced GO, i.e., graphene functionalized with O-containing groups, can also be applied as the cathode for LIB application.^[20-23] Nonetheless, the mechanism for Li storage is neither Li intercalation nor Li absorption, but relies on the reversible redox reaction between Li ions and the oxygen functional groups at high potential (>2 V; vs. Li/Li⁺), e.g., carbonyl, carboxyl, hydroxyl or epoxy groups.^[24, 25] Therefore, the electrochemical performance GO-based cathode is highly dependent upon the content of oxygen functional groups; meaning, higher oxygen content can deliver larger specific capacity. Notably, when the oxygen content in GO exceeds a certain level, a

dramatic decrease of the electrical conductivity will occur; and meanwhile the electrode will show a larger irreversible capacity. Accordingly, the content of oxygen functional groups in GO must be optimized before they can be used as the cathode for LIBs.

1.2 Motivation

The introduction of heteroatom doping, for instance, B, N, P and S, is one of the effective strategies that could solve the above-mentioned problems of graphene-based anodes to some extent. Compared with rGO, the heteroatom incorporated ones display superior electrochemical performance by virtue of their more active sites for Li accommodation that originates from doping created topological defects on graphene layers, and also the considerably decreased charge transfer resistance.^[26] Aside from heteroatom doping, the creation of porous structure is more direct in preventing graphene from aggregation, hence leading to a high and effective accessibility for electrolyte, and saving the electrochemically active sites for Li ions accommodation as well.^[27] In addition, the decoration of electrochemically active metal oxide nanostructures can modulate the surface features of graphene sheets and thus retard their restacking, while graphene will in turn render good conductivity and buffer the volume variations of the metal oxide.^[28] As a result, the resulting composites show significantly boosted Li storage performance with respect to the bare metal oxide and graphene.

Regarding the cathodic application, the construction of redox-reversible oxygen functional groups grafted graphene while achieving good conductivity could be an effective route towards high performance GO-based cathodes.^[29] To this end, powerful methods that capable of precisely controlling oxygen functional

groups have to be developed, so that to modulate the cathodic performance through tuning the functional groups. Alternatively, the hybrids composed of redox-responsive molecule and highly conducting graphene could be another good choose to achieve high-performance cathodes, which will enrich the family of graphene-based cathodes for practical application.^[30]

1.3 Objectives and outlines

Following the afore-proposed principles for designing functionalized graphene-based materials for LIBs, the objectives of this PhD thesis is mainly focused on the following two parts: 1) fabrication of functionalized graphene-based anodes for LIBs; 2) rational design and fabrication of functionalized graphene-based cathodes for LIBs. Specifically, in the first part, functionalized graphene, including N- and S-codoped graphene, N-doped porous graphene and SnO₂ nanoparticles decorated graphene, will be prepared using general methods. The structure and morphology of these samples will be systemically characterized by XPS, XRD, Raman spectroscopy, BET, FESEM and TEM; and the corresponding anodic performance for LIB application will be explored by CR 2032 coin-type cells. In the second part, carbonylated/hydroxylated GO will be fabricated by chemical modulation of the oxygen functional groups on graphene sheets. Besides, vat dye/graphene hybrids will also be prepared by a facile and scalable technique involving sonication together with hydrothermal processes. The resulting materials will be identified by FTIR, XPS, Raman, XRD, FESEM, TEM and elemental analysis, whereas their potential application as the cathodes for LIBs will be also explored.

On the basis of these aspects, the frame of this PhD thesis can be summarized as below: Chapter 1 is the introduction related to the PhD project, which provides a

brief background on the research project, and also shows the motivation, objectives and outlines of the project. Chapter 2 is the literature review that summarizes the current progress in fabricating functionalized graphene-based materials for LIBs, including both the anode and cathode materials. Chapter 3 depicts the experimental methodology about synthesis of the GO precursor, and the corresponding material and electrochemical characterizations involved in the project. Chapter 4-8 present the details of our achievements in preparation and characterization of functionalized graphene-based anodes (Chapter 4-6) and cathodes (Chapter 7 and 8) for LIBs. Chapter 9 gives a summary of the outcomes and findings of this PhD thesis, together with some interesting perspectives that could be considered for future studies.

Chapter 2. Literature Review

2.1 Overview of Li-ion batteries

LIB, also known as rocking-chair battery, comprising an anode (negative electrode; normally graphite-based materials) with lower redox potential and a cathode (positive electrode; commonly inorganic insertion-type compounds, e.g., lithium transition metal oxides/phosphates) with higher redox potential, as well as an electrolyte (organic liquid) that not only functions as a separator to avoid short circuit of these two electrodes but also acts as a medium for transferring Li ions.^[31] As a typical kind of electrochemical energy storage technology, LIB stores energy based on the charge carriers (i.e., Li ions) shuttling back and forth between the two working electrodes associated with the electrons transport along the external circuit. Specifically, during the charge process, Li ions move from the cathode to the anode inside the cell whilst the electrons transport from the cathode to the anode through the external circuit, and vice versa in the subsequent discharge process (Figure 2.1).^[32] Therefore, the overall performance of a LIB is highly dependent on the physicochemical properties of the electrode materials, including both anode and cathode materials.

Figure 2.1 Schematic illustration of a LIB composition and its working principle.^[32]

Nevertheless, the current state-of-the-art commercialized anode, regardless of graphite or amorphous carbon, is approaching their inherent limit capabilities (372 mAh g^{-1} , theoretically), and moreover, their unsatisfactory rate performance is also unable to meet the requirements of the more and more sophisticated electronic devices.^[33, 34] While for the cathode materials, they generally deliver far smaller capacity ($<200 \text{ mAh g}^{-1}$) compared with the anode, since they only involve one electron reaction.^[35] In addition, the Li storage properties of cathode materials are closely related to their phase-purity and crystallinity, whereas their preparation is not environment-friendly because of the high-temperature reactions accompanied by generating greenhouse, CO_2 . Therefore, the development of new electrode materials with boosted Li storage properties are becoming a necessity.

2.2 Functionalized graphene-based anodes for LIBs

Graphene with a theoretical capacity of 744 mAh g^{-1} has been regarded as a promising alternative to graphite-based anodes for the development of next-generation LIBs with higher energy density and power density, because of its fascinating properties (See Chapter 1) together with its easy large-scale production from the natural abundance graphite precursor.^[13, 16] It is worth mentioning that both the structure and morphology of graphene play a crucial role in affecting its eventual Li storage performance. Despite the feasibility of gram-scale synthesis of rGO in many labs, to date, its corresponding electrochemical performance based on experiments is still not good enough due to the issue of graphene sheets has a strong tendency of restacking during reduction. To this end, further modification, regardless of structure or morphology, or both of them, is required so as to obtain superior performance.

2.2.1 Heteroatoms doped graphene

Doping with heteroatoms that have different electronegativity with regards to carbon (2.55, Figure 2.2), such as S (2.58), N (3.04), B (2.04) and P (2.19), is one kind of effective route to tune the spin density of carbon atoms, thus capable of modulating the charge distribution in graphene and hence evokes structural distortion for suppressing the restacking.^[26] More importantly, the incorporation of dopants into the carbon matrices will also result in new topological defects on graphene, which are far more reactive than the intrinsic carbon atoms. Since these “activated regions” can directly contribute to, or at least indirectly promote the electrochemical reactions, the heteroatom doped graphene are demonstrated to show significantly improved performance.^[36] Notably, this type of functionalized graphene-based materials greatly broadens the application of graphene in electrochemical fields, such as electrocatalysts, sensors and supercapacitors.

Figure 2.2 Basic information of carbon in comparison to the heteroatoms.

So far, N is the most commonly used atom for constructing doped graphene-based materials because of its manifold precursors with low cost and also as a result of its doping is relatively easier than the other atoms.^[37, 38] The sources of N doping range from solid-stated substances (e.g., melamine and urea) to liquid-stated substances (e.g., pyridine and hydrazine) and even to gas-stated substances (e.g., NH_3 and N_2), and in

fact, most of the N-containing small molecules could be a potential precursor under the right condition.^[39] Currently, direct synthesis (includes CVD, arc-discharge and solvothermal techniques) and post treatment (for example, hydrazine, plasma and thermal handlings) are two mainly adopted approaches for preparing N-doped graphene. Despite the former one holds the potential to obtain uniform N doping within the entire bulk material in comparison with the later one, its yield is comparatively lower. Generally, the doped N atoms have three typical bonding configurations, namely, graphite-like N (graphitic N, where the sp^2 -hybridized N atom substitute one C atoms in a hexa-ring), pyrrole-like N (pyrrolic N, where the sp^3 -hybridized N atom is bonded in a penta-ring), and pyridine-like N (pyridinic N, where the sp^2 -hybridized N atom is bonded to two C atoms).^[39] On the basis of theoretical calculations, pyridine-like N is most favorable for Li storage, followed by pyrrole-like N, while graphite-like N has the weakest effect among these three types.^[40] Besides, it is normally believed that the overall Li storage performance of doped graphene will be improved upon increasing the doping level. Note that there is a trade-off between the doping content and electrical conductivity of graphene, e.g., high doping dose may result in a dramatic decrease of the electrical conductivity.^[41] The pioneering work of applying N-doped graphene (9 at%) as the anode for LIBs was reported by Pulickel M. Ajayan's group in 2010 (Figure 2.3a-c), who explored the Li storage properties of a CVD grown N-doped graphene on Cu foil.^[42] Due to the N doping induced numerous defects, the anode shows nearly doubled specific capacity than bare graphene. However, the high cost, low throughput and low mass loading make it infeasible for practical applications. Later, Wang et al. fabricated a N-doped graphene (2 at%) through heat treatment of GO in ammonia atmosphere, and the anode prepared via paste-based technique shows a Li storage capacity of 900 mAh g^{-1} (current density: 42 mA g^{-1}) with good rate performance (250

mAh g^{-1} at 2.1 A g^{-1}) (Figure 2.3d-f).^[43] Almost at the same time, Hui-Ming Cheng's group prepared a N-doped graphene with $\sim 3 \text{ at\%}$ doping level via annealing the chemically exfoliated graphene at 600°C in NH_3 -containing condition (Figure 2.3g-i).^[44] Accordingly, a higher specific capacity of 1043 mAh g^{-1} at 50 mA g^{-1} was achieved, and more strikingly, the electrode is capable of sustaining ultrafast charge-discharge test with a capacity of up to $\sim 200 \text{ mAh g}^{-1}$ even under 25 A g^{-1} , which are superior to the non-doped analogue. After that, various approaches aiming to simplify the fabrication process and further increase the doping level have been emerged, which eventually forward the electrochemical performance to a more and more higher level.^[45-47]

Figure 2.3 (a-c) CVD-grown N-doped graphene:^[42] photographs on Si/SiO₂ substrate (a), HRTEM image of a three-layer specimen (b), and the cycling behavior in

comparison with the pristine graphene anode at $5 \mu\text{A cm}^{-2}$ (c). Inset of (c) shows the schematic of N-doped graphene. (d-f) N-doped graphene prepared from annealing GO in ammonia atmosphere:^[43] FESEM (d) and TEM (e) images, and its corresponding rate behavior compared with the graphene anode (f). (g-i) N-doped graphene prepared from annealing chemically exfoliated graphene in ammonia atmosphere:^[44] TEM image (g), high-resolution N 1s XPS spectrum (h), and its corresponding rate behavior at different current rates (i). Inset of (h) is the schematic of N-doped graphene.

Boron is another element used for modifying the properties of graphene towards LIB application. Different from the other heteroatoms, B is an electron-deficient atom that possesses lower electronegativity with respect to carbon. In this regard, B doping can cause σ electrons locate on carbon atoms, and decrease the electron density of the delocalized π electrons on carbon atoms, as well as reduce the total electron density.^[48] As a consequence of B doping, electron deficient areas are produced in graphene and simultaneously the Fermi level of graphene will shift to the valence band, leading to higher absorption ability for Li ions.^[49] Despite the extensive works on B-doped carbons,^[50-52] the efforts paid to B-doped graphene are reasonably rare, particularly the application of B-doped graphene in LIBs. Alternatively, intensive theoretical calculations have been devoted to studying the Li storage behaviors in B-doped graphene.^[49, 53] It is until 2011 that Hui-Ming Cheng's group first experimentally investigated the anodic performance of B-doped graphene for LIBs (Figure 2.4a-c).^[44] They fabricated a B-doped graphene with a doping level of ~ 0.9 at% by exposing chemically exfoliated graphene to the gas mixture of BCl_3 and Ar (1:4 in volume) at 800°C . Indeed, the resultant B-doped graphene anode exhibit a remarkably improved electrochemical performance than the non-doped electrode, in terms of a larger initial reversible capacity of 1549 mAh g^{-1} at the current rate of 50 mA g^{-1} , with 79.2%

retention after 30 cycles and superb rate capability (235 mAh g^{-1} at 25 A g^{-1}), proving the effectiveness of B doping in upgrading the Li storage performance of graphene. Hereafter, a higher B doping level (5.93 at%) anode was prepared through heating treatment of GO and H_3BO_3 mixture (Figure 2.4d-f).^[54] Although the specific capacity of the B-doped graphene anode doesn't show any increase as compared to the electrode without doping, prolonged cyclic life has been achieved in this electrode. To better understand the role of B doping in tuning the properties of graphene, B-doped nanographene was reported through a molecular level design principle;^[55] however, the structure and electrochemical performance need to be further improved in the future (Figure 2.4g,h).

Figure 2.4 (a-c) B-doped graphene prepared from annealing chemically exfoliated graphene in $\text{BCl}_3\text{-Ar}$ gas mixture:^[44] schematic diagrams of graphene and B-doped graphene (a), cycling (b, 50 mA g^{-1}) and rate (c) behaviors of B-doped graphene anode. (d-f) B-doped graphene prepared through heating treatment of GO and H_3BO_3

mixture:^[54] *schematic diagram (d), and charge-discharge profiles of graphene (e) and B-doped graphene (f) at 100 mA g⁻¹. (g,h) Molecularly designed B-doped nanographene:*^[55] *synthesis (g) and cyclic performance at 0.5 mA cm⁻² (h).*

When it comes to S doping, the research in this area is much more rare than B doping, even for doping in carbons.^[56] For that reason, S doping in carbon-based materials has been regarded as an emerging field. In contrast to the booming carbon-sulfur composites for Li-S batteries, the establishment of S doping in carbons has not been realized until 2011.^[57] Nowadays, with the continuous discovery and report on the potential applications of S-doped carbons in supercapacitors and fuel cells, Yu-Guo Guo's group reported a S-doped porous carbons/graphene hybrid for LIBs in 2012.^[58] In spite of the unusual Li storage performance in this hybrid, it still lacks of representation of S-doped graphene for LIB application since it belongs to a member of graphene-based composites. A typical example of studying the Li storage behaviors of S-doped graphene was reported by Quan and coworkers, who successfully developed a simple solvothermal method for directly converting dimethyl sulfoxide (a common organic solvent) to high-level (22.83 wt%) S-doped bulk graphene (Figure 2.5a-c).^[59] The anodic performance of this doped graphene shows higher initial coulombic efficiency and cycling stability with respect to the non-doped graphene electrode, which documents the introduction of S doping is able to suppress the side electrochemical reactions, for instance, electrolyte decomposition. Meanwhile, it was probably inspired by the technique of constructing carbon-sulfur composites for Li-S batteries, Yun and coworkers reported a S-doped graphene via annealing the mixture of GO and sulfur (1:1 in weight) at 600 °C for 2 h (Figure 2.5d-f).^[60] Astonishingly, a constant S doping level of 4.3 at% was obtained even if the treatment temperature increases from 600 °C to 800 and 1000 °C. Their findings reveal that S-doped graphene anode is capable of

providing exceedingly larger specific capacity and better rate performance, which are closely related to the its increased electrical conductivity and the S doping induced more electrochemically active sites for Li storage.

Figure 2.5 (a-c) Solvothermal method synthesized S-doped graphene:^[59] schematic diagram (a), TEM image (b) and cyclic performance in comparison with the other electrodes at 200 mA g⁻¹ (c). (d-f) S-doped graphene prepared from annealing the mixture of GO and sulfur:^[60] Raman spectra (d) and I_D/I_G ratio maps (e), and rate behaviors of (f) graphene and S-doped graphene.

In comparison to S, until now, the examples of P doping are relatively rare. Interestingly, theoretical calculations have predicted that the incorporation of P doping into the carbon lattice is energetically more favorable than that of S.^[61, 62] In addition, P doping generally shows a more pronounced effect in tuning the electron donor/acceptor properties of carbon-based materials.^[63] While coming to graphene, P doping also offers an additional approach for influencing its band structure. Up to date, P-doped graphene with fascinating properties for electrocatalytic, hydrogen storage and sensing applications have been widely explored,^[64-66] however, there is few report on its application in LIBs. It was Zhang et al. who firstly probed the anodic performance

of P-doped graphene in this field (Figure 2.6).^[67] They fabricated a P-doped graphene anode with a doping content of 1.81 at% by heat treatment of GO and triphenylphosphine, and the resultant electrode displays a quite stable Li storage capacity (460 mAh g⁻¹ at current rate of 100 mA g⁻¹) and higher rate capability than the bare graphene anode. Definitely, more efforts are urgently required to further increase the P doping level and optimize its binding configurations so as to make P-doped graphene closer to practical LIB applications.

Figure 2.6 P-doped graphene:^[67] (a) TEM image, (b) XPS survey spectrum, (c) high-resolution P 2p XPS spectrum, (d) charge-discharge profiles at 100 mA g⁻¹, (e) cycling (100 mA g⁻¹) and (f) rate performances compared with bare graphene. Inset of (a) is the corresponding selected area electron diffraction (SAED) pattern.

2.2.2 Morphologically engineered graphene

Since the Li storage behaviors of graphene is closely related to its microstructures, e.g., crystallinity, lateral sizes, layer numbers and edge-type/defective sites, the engineering of morphology offers a flexible route to regulate its final electrochemical performance. Actually, this concept so far has been revealed to be very effective in improving the

specific capacity and rate capability of graphene anode, which are normally attributed to the following advantages in the morphologically engineered graphene: 1) high BET surface area for penetration of/contact with the electrolyte; 2) less aggregation with maximum maintained active sites for Li absorption; 3) additionally induced edge-type and defective sites for further Li storage; and 4) shortened solid-state diffusion length for Li ions.^[28, 68-70] On the basis of these appealing features, a series of morphologically engineered graphene-based anodes, for example, porous graphene, graphene spheres, graphene nanoribbons, defective graphene and holey graphene, have thus been constructed.

A representative work of fabricating porous graphene-based anode for LIBs was reported by Klaus Mullen's group in 2010 (Figure 2.7a-c).^[27] Following the silica-based hard template method, they obtained a sandwich-like graphene/mesoporous carbon structure, which delivers a Li storage capacity of 770 mAh g⁻¹ at 74.4 mA g⁻¹ and a rate capacity of 370 mAh g⁻¹ was sustained at 1860 mA g⁻¹. In addition, this group also takes the lead in utilizing nanographene, namely, hexa-peri-hexabenzocoronene, as building blocks, and mesoporous silica spheres as the template to fabricate nanographene constructed hollow carbon spheres (Figure 2.7d-f).^[71] As an anode for LIBs, the electrode illustrates a large reversible capacity of 600 mAh g⁻¹ at a current rate of 74.4 mA g⁻¹ and a high rate capacity of ~200 mAh g⁻¹ at 3720 mA g⁻¹. Another example of morphologically engineered graphene for LIBs is graphene nanoribbons because of their reactive edges with respect to the inter-planes. In this case, the pioneering work was carried out by Bhardwaj and coworkers, who prepared graphene nanoribbons anodes through a solution-based oxidative technique for longitudinal unzipping of multiwalled carbon nanotubes (Figure 2.7g-i).^[72] Based on their findings, the oxidized graphene nanoribbons are able to show an initial discharge capacity of

$\sim 1400 \text{ mAh g}^{-1}$, which is larger than its graphite counterpart. Unfortunately, the corresponding coulombic efficiency is as low as $\sim 53\%$ and the electrode also presents inferior cycling stability with an average capacity decay of 3.0% within the 14 consecutive cycles.

Figure 2.7 (a-c) Sandwich-like graphene/mesoporous carbon:^[27] synthesis process for the template (a), and FESEM images of the product (b,c). (d-f) Nanographene constructed hollow carbon spheres:^[71] synthesis procedure (d), and FESEM (e) and TEM (f) images. (g-i) Graphene nanoribbons:^[72] schematic (g), TEM of unzipped nanoribbons (h,i).

Introducing extra electrochemically active sites, i.e., edges and defects, on graphene could be another advisable strategy for tuning its physiochemical properties for Li storage by reason of the so-called edge effects.^[73] Xueliang Sun's group experimentally demonstrated that defective graphene possessing more edges and defects are beneficial for Li storage (Figure 2.8a).^[74] On the other hand, they also found

that rGO with less layer and smaller domain size is capable of rendering better Li storage performance. Correspondingly, the defective graphene can exhibit a large reversible discharge capacity of 1348 mAh g^{-1} (current density: 100 mA g^{-1}) with $\sim 51\%$ retention after 100 cycles. As a special type of defective graphene, holey graphene, also known as graphene mesh, has the potential to enable fast charge/discharge capability due to the presence of abundant in-plane pores in graphene sheets. For example, using $(\text{NH}_4)_3\text{PO}_4$ as the precursor, Ma and coworkers employed a MgO templated CVD methodology for grown N- and P-codoped holey graphene anode (Figure 2.8b,c), which shows a reversible capacity as high as 2250 mAh g^{-1} under 50 mA g^{-1} while $\sim 450 \text{ mAh g}^{-1}$ is still sustained when the current rate goes up to 5 A g^{-1} .^[75] All of the above progress verifies the effectiveness of morphological engineering in boosting the anodic properties of graphene for LIBs.

Figure 2.8 (a) Schematic for morphological evolutions of graphene towards defective graphene with their corresponding FESEM images.^[74] (b,c) Holey graphene.^[75]

schematic diagram (b) and TEM image (c).

2.2.3 Graphene/metal oxide hybrids

Regarding graphene/metal oxide hybrids for LIBs application, intensive works have been devoted to investigating graphene/transition metal oxides with diverse nanostructures.^[76] However, their relevant progress is far beyond the scope of this dissertation since we are focused on graphene/Sn-based oxides composites. There are two reasons why we choose SnO₂ for fabricating functionalized graphene-based anodes. On one hand, the high theoretical capacity of SnO₂ (782 mAh g⁻¹) can effectively upgrade the Li storage performance of graphene. Also, the combination of graphene and SnO₂ brings some significant advantages, which exceeds the intrinsic properties of each component. On the other hand, different from transition metal oxides, the lithiation potential of SnO₂ is close to that of graphene. Therefore, the introduction of electrochemically active SnO₂ will not have negative effects on exploring graphene as the anode for LIBs. Actually, the study on Sn-based oxides for LIBs begins in 1997 by a Japanese group, who synthesized an amorphous Sn(II)-O composite anode with a high Li storage capacity of >600 mAh g⁻¹.^[77] For a long time, such kinds of Sn-based materials suffer from the formidable obstacles of poor conductivity and short cyclic stability. Fortunately, tremendous progress has been achieved when they married with graphene to form electrochemically stable structures, as summarized in Table 2.1. In such hybrids, the decoration of Sn-based oxides is able to weaken the π - π interactions among the graphene sheets and consequently suppress their restacking. More importantly, the Sn-based oxides will contribute a lot to the eventual Li storage capacity without sacrificing the advantages of graphene anode, e.g., low working potential; whereas graphene in turn solves the aforementioned issues of the oxides. As proposed by Prof. Hui-Ming Cheng: “when two is better than one”,^[78] the synergistic effects

between these two components lead to superior electrochemical performances for LIBs.

Table 2.1 Methods for the preparation of graphene/Sn-based oxides composites and their corresponding electrochemical performances.

Material	Method	Electrochemical performance	Ref.
Graphene/SnO ₂	Stirring/ultrasonication	~600 mAh g ⁻¹ for 30 cycles (current rate: 80 mA g ⁻¹)	[79]
Graphene/SnO ₂	Stirring/ultrasonication	~400 mAh g ⁻¹ for 50 cycles (current rate: 10 mA g ⁻¹)	[80]
Graphene/SnO ₂	Electrostatic spray deposition	~510 mAh g ⁻¹ for 100 cycles (current rate: 200 mA g ⁻¹)	[81]
Graphene/SnO ₂	80 °C for 16 h	~870 mAh g ⁻¹ for 200 cycles (current rate: 100 mA g ⁻¹)	[82]
N-doped graphene/SnO ₂	120 °C for 2 h	~1350 mAh g ⁻¹ for 500 cycles (current rate: 500 mA g ⁻¹)	[83]
N-doped graphene/SnO ₂	90 °C for 12 h	~910 mAh g ⁻¹ for 50 cycles (current rate: 50 mA g ⁻¹)	[84]
Graphene/SnO ₂	Hydrothermal	~730 mAh g ⁻¹ for 40 cycles (current rate: 50 mA g ⁻¹)	[85]
Graphene/SnO ₂ -SiC	Ball-milling	~1350 mAh g ⁻¹ for 40 cycles (current rate: 100 mA g ⁻¹)	[86]
Graphene/SnO ₂	Solution-based synthesis	~840 mAh g ⁻¹ for 30 cycles (current rate: 67 mA g ⁻¹)	[87]
Graphene/SnO ₂	Hydrothermal	~590 mAh g ⁻¹ for 50 cycles (current rate: 100 mA g ⁻¹)	[88]
Graphene/SnO ₂	Hydrothermal	~510 mAh g ⁻¹ for 20 cycles (current rate: 50 mA g ⁻¹)	[89]
Graphene/SnO ₂	Hydrothermal	~520 mAh g ⁻¹ for 50 cycles (current rate: 400 mA g ⁻¹)	[90]
Graphene/SnO ₂ /carbon	Hydrothermal	~1420 mAh g ⁻¹ for 150 cycles (current rate: 100 mA g ⁻¹)	[91]
Graphene/SnO ₂ /TiO ₂	50 °C for 15 h	~600 mAh g ⁻¹ for 300 cycles (current rate: 160 mA g ⁻¹)	[92]
Graphene/SnO ₂	180 °C for 10 h	~680 mAh g ⁻¹ for 100 cycles (current rate: 100 mA g ⁻¹)	[93]
Graphene/SnO ₂	Hydrothermal	~1160 mAh g ⁻¹ for 100 cycles (current rate: 100 mA g ⁻¹)	[94]
Graphene/SnO ₂	Stirring/ultrasonication	~775 mAh g ⁻¹ for 50 cycles (current rate: 100 mA g ⁻¹)	[95]
Graphene/SnO	Hydrothermal	~480 mAh g ⁻¹ for 30 cycles (current rate: 44 mA g ⁻¹)	[96]
Graphene/SnO ₂	100 °C for 6 h	~990 mAh g ⁻¹ for 30 cycles (current rate: 100 mA g ⁻¹)	[97]
Graphene/SnO ₂	Hydrothermal	~450 mAh g ⁻¹ for 100 cycles (current rate: 1000 mA g ⁻¹)	[98]
Graphene/SnO ₂	Room temperature for 24 h	~380 mAh g ⁻¹ for 35 cycles (current rate: 200 mA g ⁻¹)	[99]
Graphene/SnO ₂	Hydrothermal	~600 mAh g ⁻¹ for 20 cycles (current rate: 50 mA g ⁻¹)	[100]

Graphene/SnO ₂	Hydrothermal	~440 mAh g ⁻¹ for 55 cycles (current rate: 400 mA g ⁻¹)	[101]
Graphene/SnO ₂	Hydrothermal	~640 mAh g ⁻¹ for 50 cycles (current rate: 120 mA g ⁻¹)	[102]
Graphene/SnO ₂	Hydrothermal	~500 mAh g ⁻¹ for 50 cycles (current rate: 50 mA g ⁻¹)	[103]
Graphene/SnO ₂	190 °C for 5 h	~660 mAh g ⁻¹ for 60 cycles (current rate: 60 mA g ⁻¹)	[104]
Graphene/SnO ₂	Stirring	~700 mAh g ⁻¹ for 90 cycles (current rate: 158 mA g ⁻¹)	[105]
Graphene/SnO ₂	Stirring/ultrasonication	~570 mAh g ⁻¹ for 30 cycles (current rate: 50 mA g ⁻¹)	[106]
Graphene/SnO ₂	Stirring/reduction	~520 mAh g ⁻¹ for 50 cycles (current rate: 200 mA g ⁻¹)	[107]
SnOx/carbon/graphene	Electrospinning/calcination	~500 mAh g ⁻¹ for 180 cycles (current rate: 70 mA g ⁻¹)	[108]
Graphene nanoribbon/SnO ₂	Ultrasonication/calcinations	~820 mAh g ⁻¹ for 50 cycles (current rate: 100 mA g ⁻¹)	[109]
Graphene/SnO ₂	80 °C for 8 h	~630 mAh g ⁻¹ for 50 cycles (current rate: 100 mA g ⁻¹)	[110]
Graphene/SnO ₂	Stirring/ultrasonication	~310 mAh g ⁻¹ for 42 cycles (current rate: 300 mA g ⁻¹)	[111]

Till now, a series of techniques, including physical mixing, ball-milling, hydro/solvothermal and solution-based methods, have been reported for preparing graphene/Sn-based oxides hybrids for Li storage application, see Table 2.1 for details. It is worth mentioning that hydro/solvothermal is the most commonly used strategy for fabricating graphene/Sn-based oxides composites, because of its simplicity and varied Sn-based precursors regardless of Sn⁴⁺ or Sn²⁺ is employed.^[90, 94] For instance, Huang and coworkers obtained a rod-like SnO₂ nanocrystals anchored graphene anode by solvothermal reaction between SnCl₄·5H₂O and GO, which shows improved Li storage capacity and cyclic performance than the bare SnO₂ and graphene electrodes (Figure 2.9a-c).^[89] In another case, Itaru Honma's group physically mixed graphene with the hydrosol of SnO₂ nanoparticles to form a compatible hybrid with homogeneous distribution of graphene in the nanoparticles (Figure 2.9d-f).^[106] The resulting graphene/SnO₂ composite shows a significantly increased reversible capacity of 810 mAh g⁻¹ (at 50 mA g⁻¹) as compared to the anodes of graphene, SnO₂ and the

commercial graphite, with $\sim 70\%$ retention after 30 cycles. While Wang and coworkers developed a solution-based synthesis approach for decorating graphene with 3-5 nm SnO_2 nanoparticles, using Sn^{2+} as the reductant to reduce GO while Sn^{2+} was then converted to SnO_2 (Figure 2.9g-i).^[87] Compared with the above-mentioned work, this composite delivers a slightly larger reversible capacity of 840 mAh g^{-1} at 67 mA g^{-1} with 86% retention after 30 cycles, and $\sim 270 \text{ mAh g}^{-1}$ was sustained when the electrode is cycled at 1 A g^{-1} . Besides, Jun Liu's group adopted a ball-milling technique to synthesize a core-shell nanostructure composed of SiC-supported SnO_2 nanoparticles core and few-layer graphene shell (Figure 2.9j-l).^[86] The core-shell hybrid also exhibits good Li storage behaviors, in terms of a large reversible capacity (810 mAh g^{-1} at 100 mA g^{-1}), good capacity retention (83% after 150 cycles) and high rate performance (425 mAh g^{-1} at 2 A g^{-1}).

Figure 2.9 (a-c) Solvothermal method synthesized graphene/SnO₂:^[89] schematic (a), TEM image (b) and cyclic behavior at 50 mA g⁻¹ (c). (d-f) Physically mixed graphene/SnO₂:^[106] schematic (d), TEM image (e) and cyclic behavior at 50 mA g⁻¹ (f). (g-i) Solution approach synthesized graphene/SnO₂:^[87] schematic (g), HRTEM image (h) and cyclic behavior at 67 mA g⁻¹ (i). (j-l) Ball-milling technique prepared graphene/SnO₂:^[86] schematic (j), TEM image (k) and cyclic behavior at 100 mA g⁻¹ (l). Inset of (b) and (k) is the corresponding SAED pattern of the samples.

2.3 Functionalized graphene-based cathodes for LIBs

As an individual layer of graphite, graphene and its derivatives are generally treated as the desirable anodes for LIBs, though their mechanism for Li storage is different from that of graphite. Interestingly, post-modification by introducing redox-active species, regardless of organic functional groups and molecules, is capable of extending the application of graphene as the cathodes. For the former case, the functional groups, e.g., carbonyl, hydroxyl and organic radical, are grafted onto graphene via covalent bonds.^[112, 113] With such a configuration, graphene not merely serves as the scaffolds for cross-linking of the functional groups but also functions as the conducting network for fast electron transport during electrochemical reactions; where Li storage is based on the reversible reaction between the functional groups and Li ions. While for the latter one, the functional molecules could be attached to graphene through either covalent or non-covalent modifications.^[114, 115] In the case of covalent modification, the situations are somehow like the case of functional groups grafted graphene, except for the use of functional molecules. Differently, in the instance of non-covalent modification, the driving force for the formation of the final hybrids relies on the weak interactions, for example, van der Waals forces and π - π interactions, between the functional molecules

and graphene. Correspondingly, graphene acts as both host for loading these molecules, and framework for electron transport. Principally, covalently functionalized graphene is able to show longer cyclic performance with respect to the non-covalently functionalized ones, since the functional species for Li storage are firmly anchored on graphene; however, their types are less than the non-covalently functionalized graphene and the electrochemical performances based on experiments so far also cannot compete with the non-covalently functionalized graphene.

2.3.1 Redox-active groups grafted graphene

GO, as a typical type of functionalized graphene that enriched with electrochemically active groups, i.e., carbonyl, carboxyl, hydroxyl and epoxy groups, is a good candidate of cathode for LIBs due to the high lithiation potentials of these functional groups.^[24, 25] Actually, the attempts of investigating GO-based clays as the cathodes can be dated back to 1980s,^[20-23] yet the electrochemical performance is still unsatisfactory, which is likely attributed to its poor electrical conductivity and the irreversible cleavage of the functional groups during electrochemical reactions. It was until 2013, Hui-Ming Cheng's group experimentally found that the Li storage behaviors of GO cathode could be tuned by regulating the O-containing functional groups under heat treatment at low temperatures (Figure 2.10a-c).^[116] Based on their results, the content of O-containing functional groups in GO plays a critical role in determining the final Li storage capacity, that is, the deoxygenated GO with lower oxygen concentration shows smaller specific capacity. Specifically, the cathode deoxygenated at 100 °C shows a capacity of ~360 mAh g⁻¹ (current rate: 50 mA g⁻¹) with stable cycling performance, which greatly surpasses the conventional inorganic cathode materials. At the same time, Kisuk Kang' group also noted that GO with different reduction degree illustrates distinct electrochemical performance (Figure 2.10d-f).^[29] They demonstrated that the electrode

with medium content of O-containing functional groups has more rich porous structure and higher electrical conductivity than the electrodes with high and low oxygen contents, thus leading to a gravimetric capacity of $\sim 240 \text{ mAh g}^{-1}$ at current density of 100 mA g^{-1} and long-cyclic performance (2000 cycles without capacity decay at 1 A g^{-1}). The above-mentioned findings were subsequently confirmed by Ha and coworkers, who studied the cathodic performance of rGO film with different oxygen contents, and observed the decrease of capacity upon decreasing the O/C ratio (Figure 2.10g-i).^[117] Despite these pioneering works of probing the Li storage properties of GO-based cathode, it is still lack of effective methodologies for engineering the cathodic performance of GO through precise control of the O-containing functional groups. Note that, the introduction of other active Li storage groups, e.g., organic radical, could also be an advisable route towards the cathodic application graphene.^[118-120]

Figure 2.10 (a-c) Deoxygenated GO cathode:^[116] charge-discharge profiles (a), cycling

behavior at 100 mA g⁻¹ (b) and specific capacity vs. oxygen content, meaning, O 1s concentration and O-containing functional groups from C 1s (c). (d-f) Functionalized GO cathode:^[29] linear relationship between specific capacity and O/C ratio (d), charge-discharge profiles of the cathodes with different oxygen contents (e) and cycling behavior at 1 A g⁻¹ (f). (g-i) rGO film cathode:^[117] photograph and the corresponding SEM image (g), temperature vs. oxygen content (h) and specific capacity vs. oxygen content (i).

2.3.2 Redox-responsive molecule/graphene hybrids

The investigation of organic cathode materials for LIBs starts in 1960s,^[121] however, for a long time, less attention has been paid to this area because of their relatively poor electrochemical performance as compared to inorganic cathodes. Luckily, significant progress has been achieved after incorporating these materials with carbon-based conducting frameworks.^[122] Till now, various electroactive organic cathodes, including carbonyl-based compounds, organic free radical compounds, conducting polymers and organosulfur molecules, have been studied.^[123] Among them, carbonyl-based compounds are particularly special due to their fast kinetics associated with high theoretical capacity.^[124] As a result, carbonyls are the most widely used organic molecules for preparing redox-responsive molecule functionalized graphene; while two approaches, namely, covalent and non-covalent functionalization, are generally exploited. Certainly, covalent functionalization experiences chemical reaction between the functional molecules and graphene. For example, using diazonium reaction and anionic polymerization, Pirnat et al. constructed three kinds of hydroquinone molecules attached graphene nanoribbons, which effectively solve the main issues of bare hydroquinone molecules for Li storage, i.e., dissolution in the electrolyte and low conductivity (Figure 2.11a-c).^[125] Accordingly, the fabricated graphene cathodes

display considerably increased specific capacity and cyclic behavior than the pristine molecules. Compared with covalent functionalization, non-covalent functionalization is more popular and simple by virtue of the abundant electroactive precursors and does not involve complex operate. A notable work in this area was reported by Song and coworker (Figure 2.11d,e), who synthesized two composites, i.e., poly(anthraquinonyl sulfide)/graphene and polyimide/graphene, through one-pot *in situ* polymerization of the corresponding monomer in the presence of graphene.^[126] Benefiting from the introduction of graphene, both of these two hybrids illustrate high electrical conductivity with large surface area, and consequently leading to high-performance organic cathodes with ultrafast charge-discharge capability ($>100 \text{ mAh g}^{-1}$, full charge within a few seconds).

Figure 2.11 (a-c) Hydroquinone molecules covalently grafted graphene nanoribbons cathodes:^[125] schematic diagram (a), mechanism for Li storage (b) and rate capability of the resulting electrodes (c). (d,e) Electroactive polymers non-covalently functionalized graphene cathodes:^[126] synthesis process (d) and redox reactions between the polymers and Li ions (e).

2.4 Summary

Detailed advances in functionalized graphene for LIBs, including both anode and cathode, have been reviewed, which reveal a successful and powerful route to improve the Li storage properties of graphene. Despite the encouraging progress in employing heteroatom-doped graphene as anode, in particular N-doped graphene, the studies related to S, P and B doped ones are relatively rare, and are yet at the initial stage. Further improvements in the anodic performance of graphene could be achieved through the following approaches: 1) adopting cooping, since the introduction of codopants principally have the ability to create more and diverse electroactive sites for Li storage by virtue of their synergistic effect. 2) increasing heteroatom doping level by using novel methodologies, because the Li storage properties of graphene are closely related to doping induced defect sites. Normally, the higher the heteroatom doping content, the better the electrochemical performance. 3) introducing electrochemically active second phases, for example, Sn-based nanoparticles, which have higher theoretical Li storage capacity but comparable discharge potential with graphene. Besides, now that both structural and morphological engineering of graphene are able to tune its electrochemical behaviors, the combination of these two aspects could be more effective with respect to single modification.

When it comes to the cathodic application of functionalized graphene, the electrochemical performance is closely related to its chemical structure or composition. For redox-active groups grafted graphene cathodes, e.g., GO, although literatures have demonstrated that the oxygen content associated with the electroactive carbonyl, carboxyl, hydroxyl and epoxy groups plays a critical role in the eventual Li storage performance, few work has been devoted to precisely controlling these oxygen functional groups. Accordingly, chemical engineering of the type of O-containing

functional groups are urgently required, so as to further boost its electrochemical performance. On the other hand, more rational designs for preparing functionalized graphene cathodes with specific functional groups could also be beneficial for exploring and understanding the Li storage mechanisms in these materials. While for redox-responsive molecule/graphene hybrids, novel organics with well-defined structure are necessary so that to well integrate with graphene. Molecules with larger condensed aromatic ring systems are more competitive than their non-aromatic ring counterparts because of the stronger π - π interactions between the two components. However, facile and generic strategies that capable of enabling large-scale production of the composites are still lacking, which is also an inevitable step for practical application of functionalized graphene for LIBs.

Chapter 3. Experimental Methodology

3.1 Synthesis of GO

GO was synthesized by chemical oxidation of graphite associated with subsequent exfoliation technique, as illustrated in Figure 3.1. In a typical procedure, 1.0 g of graphite was loaded in a 500 mL beaker, and 50 mL of sulfuric acid (98%) was carefully poured into the beaker, which was then transferred into an ice bath. Next, 6.0 g of potassium permanganate was batch-wisely and slowly added into the mixture with constant stirring, and the resulting suspension was kept at room temperature for 1 hour. After that, 80 mL of deionized water (18.2 MΩ) was dropwisely added using a constant-pressure dropping funnel, and the mixture was further stirred at 90 °C for 30 minutes. After adding 200 mL of deionized water followed by 6 mL of hydrogen peroxide solution (30 wt%), a yellow suspension was obtained and the reaction was terminated. The collected precipitates were purified by dialysis for 7 days with repeatedly changing the deionized water, and then freeze-dried for 48 hours. Finally, GO aqueous dispersion with desired concentration was obtained by dispersing the rotten-wood-like sample in deionized water under constant ultrasonication for 1 hour. Prior to using, the obtained GO dispersion was centrifuged at 1000 rpm for 10 minutes to remove the unexfoliated particles.

Figure 3.1 Photographs of the synthesis of GO through chemical oxidation-exfoliation technique.

3.2 Material characterizations

Morphological features of the samples were recorded by FESEM (JEOL JSM-6700F coupled with energy-dispersive X-ray spectroscopy) and TEM (JEOL JEM-2010) observations. The samples were firstly dispersed in ethanol by sonication for 2 minutes, and then dropped onto the corresponding substrates for characterizations, i.e., silicon wafer for SEM and Cu grid for TEM. Structural analysis of samples were performed using XRD (Rigaku D/max-IIIB or Bruker D8 Advanced diffractometer with Cu K α radiation, $\lambda = 1.54184 \text{ \AA}$), XPS (ESCALAB MK II or Perkin-Elmer model PHI 5600 X-ray photoelectron spectrometer with Al K α radiation, X-ray source: 1486.6 eV), TGA (Shimadzu DTG-60H under nitrogen or air condition, heating rate: $10 \text{ }^{\circ}\text{C min}^{-1}$), FTIR (NEXUS 670 spectrometer with the KBr-pellet technique), Raman (WITEC CRM200 Raman system with 457 or 532 nm excitation laser), nitrogen sorption measurements (Micromeritics ASAP 2020 or Micromeritics Tristar II instruments at 77 K), and elemental analysis (FLASH 2000 elemental analyzer).

3.3 Electrochemical characterizations

All cells with CR 2032 coin-type configuration were assembled inside an argon-filled glovebox (MBRAUN UNIlab Plus, $O_2 < 0.1$ ppm, $H_2O < 0.1$ ppm) using pure lithium foil as the counter electrode, Celgard® 2325 as the separator, and 1 M $LiPF_6$ in EC and DMC (1:1 in weight) or EC, EMC and DMC (1:1:1 in volume) as the electrolyte. Standard slurry coating technique was used to fabricate the working electrodes using a blade coater. Typically, the slurry composed of active material, acetylene black (conductive additive) and PVDF (binder) (8:1:1 or 7:2:1 in weight) in NMP was pasted onto the metal foil current collectors, i.e., Cu foil for anode and Al foil for cathode, and dried at 60 or 100 °C in a vacuum oven. Circular working electrodes with 1.2 cm diameter and 200 μm thickness were obtained by a punching machine (Yongxingye company), and the mass loading was determined by a semi-micro analytical balances (A&D company with 0.01 mg readability). Unless otherwise stated, the electrochemical data was all calculated referring to the mass of active material. CV (0.005-3.0 V for anode, and 1.5-4.5 or 1.2-4.2 V for cathode) and EIS (10^5 - 10^{-2} Hz for anode, and 10^5 - 10^{-1} Hz for cathode) tests were recorded on an electrochemical workstation (CHI 760D). Galvanostatic cycling and rate capability measurements were performed on a programmable 8 channel battery tester (Neware instruments) at programmed current rates. All the cells were allowed to stand 12 hours to reach equilibrium before electrochemical characterizations.

Chapter 4. A Versatile Organic Approach to N- and S-codoped Graphene for High-performance LIBs[†]

4.1 Introduction

Since the release of the first commercial prototype from Sony Corporation in 1991, LIBs have rapidly dominated the rechargeable battery market for portable electronics owing to their high energy density and environmentally benign.^[127] Nowadays, with the continuous breakthroughs in these electronic devices, meaning their functionalities become more and more sophisticated, LIBs with improved energy capacity, rate capability and structural stability are still in need of significant progress. However, the commercial graphite anode used in current LIB technology is approaching its maximum ability for Li storage, that is, limited theoretical capacity (372 mAh g⁻¹ with the formation of the first-stage lithium graphite intercalation compound, LiC₆) and poor rate performance (because of its low Li diffusion coefficient), and soon will become the bottleneck for further increasing the energy storage capability of LIBs.

As the individual layer of graphite, graphene has attracted appreciable attention for use as an anode material for LIBs since its first preparation in 2004. Owing to the fascinating physicochemical properties of graphene, the Li storage capacity is believed to be doubled as compared to its graphite counterpart; while its 2D geometrical structure is capable of drastically shortening the Li ion diffusion length, thus leading to superior rate capability. As the electrochemical performance of graphene is sensitive to its

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structure and morphology, post-modification offers a powerful route to engineering its Li storage behaviors.^[26, 72] Similar to other carbonaceous materials, both theoretical calculation and experiment results have demonstrated that the introduction of N, P, S or B doping is able to improve the electrical properties and chemical activities of graphene, which is beneficial for energy storage.^[42, 44, 67, 128] To date, two main synthetic routes, namely, post-treatment and *in situ* doping, have been developed to fabricate heteroatom-doped graphene materials. Post-treatment is based on chemical reactions between graphene precursors (e.g., GO, exfoliated graphene) and the reactive heteroatom sources,^[44, 67, 129, 130] whereas *in situ* doping involves CVD or pyrolysis process to incorporate the heteroatoms into the lattice of carbon networks.^[131, 132] Nevertheless, limited progress has been achieved due to the facts that graphene layers have a strong tendency of aggregation, and the low heteroatom doping level, particularly for the cases of P, S or B doping. Compared with the increasing doping level of single heteroatom, co-doped graphene with two different heteroatoms is another promising option for LIB application by virtue of the new/more created defects sites for Li storage.

In this Chapter, we report a novel approach for the synthesis of N and S co-doped graphene (NS-G) through covalent functionalization of GO by using 2-aminothiophenol (ATP) as both N and S sources followed by a subsequent thermal treatment. Benefiting from the unique structural feature and synergistic effects of N and S codoping, the resultant NS-G is demonstrated to be a superior anode material for LIBs in terms of superhigh reversible capacity and excellent rate capability, as well as long-term cycling performance. We also envisage that our NS-G could be an advisable candidate for other applications such as supercapacitors, metal-free electrocatalyst, photocatalysis and lithium-air batteries.

4.2 Experiments

4.2.1 Synthesis of NS-G

GO solution (2 mg mL^{-1}) was prepared by ultrasonic exfoliation of graphite oxide (800 mg) into deionized water (400 mL) for 50 min, and the solution was centrifuged at 1000 rpm for 10 min to remove the unexfoliated particles. After that, ATP (3 mL) was added into the solution and sonicated for another 5 min. Then, polyphosphoric acid (5 mL) was dropwised under vigorous stirring, and the solution was refluxed at 80°C in the darkness for 24 h. The product was collected by filtration and washing (ethanol and then water, 4 times each), then redispersed into deionized water (400 mL) by sonication for 5 min. Afterwards, hydrazine monohydrate (3 mL) was added and refluxed at 80°C for 24 h. The as-obtained product was filtrated and washed with deionized water for several times, then dried in vacuum at 120°C for 12 h. Finally, the product was placed in the center of the quartz tube furnace. Then, the system was heated to 650°C (considering the higher calcination temperature will result in lower heteroatom doping level, while lower calcination temperature will lead to a low degree of graphitization.) with a heating rate of 5°C min^{-1} under a nitrogen flow, kept at 650°C for 30 min and followed by a natural cool down process.

4.2.2 Synthesis of rGO

rGO was synthesized via chemical reduction of exfoliated GO by hydrazine.^[133] Typically, 2 mg mL^{-1} GO solution (100 mL) was prepared by ultrasonic exfoliation of graphite oxide in deionized water. Then, hydrazine hydrate (0.75 mL) was added and the mixture was kept at 80°C for 24 h. The product was collected by filtration, washed with deionized water for several times, and dried under vacuum condition. For comparison, the as-obtained rGO was also calcined under the same thermal annealing

conditions with NS-G.

4.3 Results and discussion

The following three steps are involved for the synthesis of NS-G: (i) the introduction of N and S atoms onto graphene sheets via a polyphosphoric acid-catalyzed cyclization process, (ii) the reduction of functionalized GO by hydrazine to remove the oxygen-functional groups, and (iii) the subsequent calcination at 650 °C to get the final NS-G (Figure 4.1a). XPS measurements were performed to investigate the elemental compositions and chemical status of the elements in NS-G. The XPS survey spectrum of NS-G (Figure 4.1b) shows four characteristic peaks located at ca. 164, 285, 399 and 532 eV, successively corresponding to the S 2p, C 1s, N 1s and O 1s.^[134] The N and S elemental content in NS-G is determined to 1.76 at% and 0.86 at%, respectively. For the rGO (prepared under the same condition except the absence of ATP in step (i)), no N and S signals were recorded (Figure 4.2a), verifying the successful incorporation of N and S atoms into graphene sheets. The high-resolution spectrum of C 1s in rGO and NS-G could be fitted by several peaks; both samples possess the peaks of C-C (284.6 eV), C-O (286.7 eV), C=O (288.0 eV) and O-C=O (289.2 eV) (Figure 4.2b,c).^[135] While for the NS-G sample, the particular peak located at 285.6 eV suggests the presence of C-S and C-N. Moreover, high-resolution N 1s spectrum of NS-G reveals the presence of both pyridine-like N (398.5 eV) and pyrrole-like N (400.6 eV) species (Figure 4.1c),^[136] whereas the S 2p spectrum of NS-G reveals the formation of thiophene-like structures between sulfur atoms and their neighboring carbon atoms due to spin-orbit couplings. As shown in Figure 4.1d, two peaks with an intensity ratio of 2:1 are presented at 163.9 and 165.2 eV, respectively, agreeing well with S 2p_{3/2} and S 2p_{1/2}.^[137] Based on the above characterizations, we have made the corresponding

schematic illustration on the products of NS-G, as displayed in Figure 4.1e.

Figure 4.1 (a) Schematic illustration of the procedures for the synthesis of NS-G. (b) XPS survey spectrum of the NS-G. High-resolution (c) N 1s and (d) S 2p XPS spectra of NS-G. (e) Schematic illustration of the structure of NS-G.

Further structural information of NS-G can be obtained from XRD, FTIR and Raman spectra measurements. In XRD patterns (Figure 4.2d), GO has a diffraction peak at $2\theta = 9.98^\circ$, corresponding to the interlayer spacing of 0.885 nm due to the intercalation of O-containing functional groups in between graphene sheets.^[138] Differently, rGO exhibits a well-defined peak at 26.3° corresponds to an interlayer

spacing of 0.339 nm, and NS-G exhibits a broader peak at 25.6° with a relatively larger interlayer spacing of 0.348 nm. These results are highly in accordance with the HRTEM data shown in Figure 4.3a-d. Notably, the broadened full width at half maximum and the evidently decreased intensity imply the low graphitization degree of NS-G. In the FTIR spectra of rGO and NS-G (Figure 4.2e), the peaks related to the O-containing functional groups almost totally disappeared, suggesting the successful removal of the oxygen groups on graphene sheets. Raman spectra (Figure 4.2f) of all three samples show two remarkable peaks around 1594 and 1348 cm^{-1} . The G band located at 1594 cm^{-1} is attributed to the first-order scattering of the E_{2g} mode of sp^2 carbon atoms while the D band at 1348 cm^{-1} is induced by the defects or disorders. Moreover, the intensity ratio (I_D/I_G) of D and G bands of GO, rGO and NS-G is 0.99, 1.05 and 1.16, respectively. The increase of I_D/I_G is due to the formation of defects in graphene sheets,^[139] further confirming the successful doping of N and S atoms.

Figure 4.2 (a) XPS survey spectrum of the rGO. The C 1s XPS spectrum of (b) rGO and (c) NS-G. (d) XRD patterns, (e) FTIR spectra and (f) Raman spectra of GO, rGO and NS-G.

Figure 4.3 (a,c) TEM and (b,d) HRTEM images of rGO and NS-G, respectively. The inset in (b) and (d) is the corresponding profile of interlayer spacing of the sample. (e,f) FESEM images of rGO at different magnifications.

FESEM and TEM images (Figure 4.4a,b) reveal that ultra-thin crumpled graphene sheets are randomly aggregated and overlapped with each other, forming an interconnected network in the porous NS-G. From the SAED pattern (inset of Figure 4.4b), we conclude that NS-G is disordered, highly consistent with previous XRD and Raman results. In contrast, rGO shows a restacked graphite structure (Figure 4.3e,f) due to the strong π - π stacking and van der Waals interactions between graphene sheets. Moreover, STEM image and the corresponding elemental mapping of NS-G illustrates a homogeneous distribution of N and S atoms in graphene sheets (Figure 4.4c-f). The surface area of NS-G determined by BET measurements using N_2 adsorption-desorption analysis was $153 \text{ m}^2 \text{ g}^{-1}$ (Figure 4.5). The close to type IV N_2 adsorption-desorption isotherm with a clear hysteresis loop illustrates the coexistence of micropores ($<2 \text{ nm}$) and mesopores ($2\text{-}50 \text{ nm}$) in NS-G.^[140] This was confirmed by further pore-size distribution analysis, revealing the NS-G has a multiple pore structure

with the average pore size of 6.4 nm.

Figure 4.4 (a) FESEM image of the NS-G, inset: a magnification FESEM image of the NS-G. (b) TEM image of the NS-G, inset: the corresponding SAED pattern of the NS-G. (c) STEM image of the NS-G with the corresponding (d) carbon, (e) nitrogen and (f) sulfur elemental mapping images.

Figure 4.5 (a) Nitrogen adsorption-desorption isotherms and (b) pore-size distribution curve of NS-G.

Figure 4.6a and Figure 4.7a show the CV curves of NS-G and rGO electrodes, in accordance with the previously reported carbon-based anode materials.^[67] In the first cycle, a pronounced reduction peak between 1.0 and 0.29 V is due to the formation of

SEI on the surface of electrode.^[141] CV curves are overlapped in the following cycles, indicative of a stable SEI layer formation. The capacity below 0.5 V is ascribed to the Li ions absorption onto the graphene layers, whereas the capacity above 0.5 V is attributed to the faradic capacitance on the surface or edge sites of graphene layers.^[142] Figure 4.6b shows charge/discharge profiles of the NS-G and rGO electrodes at a current density of 200 mA g⁻¹ between 0.005 and 3.0 V (vs. Li/Li⁺). An initial discharge capacity for NS-G is 1636 mAh g⁻¹ with a coulombic efficiency of 44.7%, much higher than the value of rGO (817 mAh g⁻¹). The large irreversible capacity in the first cycle could be assigned to the formation of SEI layer, as observed by the CV curves. However, the coulombic efficiency increases dramatically upon cycling, reaching over 86% in the second cycle and over 98% after following cycles. The cyclic performance of NS-G and rGO electrodes was investigated at a current rate of 200 mA g⁻¹, as shown in Figure 4.6c. The NS-G electrode still delivers a reversible capacity of 1090 mAh g⁻¹ after 500 cycles, more than two times higher than that of rGO (420 mAh g⁻¹). Notably, the capacity of the NS-G electrodes decreases in the first 20 cycles but then gradually increases upon cycling. The increase of capacity may be attributed to the improvement of Li ions accessibility into the inner part of porous NS-G upon the cycling process, which leads to an increased accommodation behavior for Li.^[128, 143] Meanwhile, the enhanced conductivity of NS-G electrode, as demonstrated by the EIS (Figure 4.7b), could also take responsibility for such capacity enhancement. Figure 4.6d shows the rate capability of the NS-G electrode at various current densities in comparison with the rGO electrode (Figure 4.7c). The NS-G material can sustain high capacities of 896, 882, 844 and 297 mAh g⁻¹ with coulombic efficiency over 99%, at current densities of 400, 800, 2000 and 5000 mA g⁻¹, respectively, even after 700, 900, 1300 and 1500 cycles. These values are much higher than that of rGO, and also the reported graphene-

based materials.^[67, 144] EIS measurements were also carried out on the rGO and NS-G electrodes in the frequency range of 1×10^5 -0.01 Hz. Nyquist plots and corresponding equivalent circuit are shown in Figure 4.7d. The fitted data reveals that the NS-G electrode has a lower electrolyte resistance ($R_s = 4.5 \Omega$) and charge transfer resistance ($R_{CT} = 35 \Omega$), with respect to the values of rGO electrode ($R_s = 6.1 \Omega$, $R_{CT} = 59 \Omega$).

Figure 4.6 (a) CV curves of the NS-G electrode at a sweep rate of 0.5 mV s^{-1} . (b) Initial galvanostatic charge-discharge voltage vs. capacity profiles of the rGO and NS-G electrodes at the current density of 200 mA g^{-1} . (c) Cycling performance of the rGO and NS-G electrodes at the current density of 200 mA g^{-1} . (d) Rate capability of the NS-G electrode at different rates.

Figure 4.7 (a) CV curves of the rGO electrode at a sweep rate of 0.5 mV s⁻¹. (b) Nyquist plots of the NS-G electrode after 10 and 580 cycles at a current density of 200 mA g⁻¹. (c) Rate capability of the rGO electrode at different rates. (d) Nyquist plots of rGO and NS-G electrodes and the corresponding simulation results, inset: the equivalent circuit used to fit the experiment data.

The superior electrochemical performance of NS-G is benefitted from the unique structural feature and the synergistic effects of N and S codoping in graphene.^[84, 145] From above results, the interconnected graphene network that formed by the random aggregation of crumpled graphene sheets can serve as continuous channels for electron transportation, whereas doping-induced topological defects together with the as-formed micropores and mesopores can act as the reservoirs for Li storage.^[67, 143] Moreover, the ultrathin 2D structure of the NS-G shortens the solid-state diffusion length for Li ions, and simultaneously ensures high Li storage property by utilizing both sides of graphene sheets.^[146] On the other hand, the large surface area provides sufficient contact areas between the electrode and electrolyte, facilitating rapid diffusion of Li ions within the

electrode material, while the increased interlayer spacing guarantees fast kinetics of Li intercalation.^[147] In addition, due to the different size and electronegativity of the codopants (N and S) with the carbon atoms, structural distortion and changes of the charge density are induced in the graphene sheet. These will not only result in the increased conductivity but also cause a large number of topological defects on the graphene sheet, which finally leads to the enhanced electrochemical activity.^[26, 67]

4.4 Summary

In summary, we have developed a novel methodology for the synthesis of NS-G via covalent functionalization of GO followed by a subsequent thermal treatment. The unique structural properties and synergistic effects of N and S codoping make NS-G a superior anode material for LIBs in terms of superhigh reversible capacity, excellent rate capability and long-term cycling performance. Clearly, this method could be easily extended to the other carbon-based materials (e.g., porous carbons, carbon nanofibers, carbon nanotubes, etc.), which may shed light on the synthesis of codoped carbon-based materials for future applications.

Chapter 5. Supramolecular Strategy for *In Situ* Fabrication of N-doped Porous Graphene Anodes for LIBs[†]

5.1 Introduction

Although graphene is an advisable alternative for the current graphite anode, the inevitable issue of restacking or aggregation dramatically decreases its advantages for LIBs. Specifically, the fascinating properties for single-layer graphene, for example, large theoretical specific surface area and fast electron/ion transport, are no longer available in a highly restacked graphene.^[148, 149] Moreover, restacking will also cause the loss of electroactive sites, such as nanopores and edge-type sites, for Li accommodation.^[150] Further structural engineering of graphene, for instance, heteroatom doping can significantly improve its Li storage property, however, the relatively low doping level (<10 at%) usually leads to limited progress on enhancing the electrochemical performance.^[39] Aside from graphene, porous carbon with large surface area and high porosity is another choice owing to its unique transport properties and additional Li storage inside the pores.^[151, 152] According to the falling card model,^[146, 153] the Li storage properties of porous carbon can be further boosted by reducing the thickness of carbon layers to fewer-layer graphene, so as to promote Li ions absorption on both sides of graphene sheets. Therefore, it is hypothesized that a combination of these two types of carbons will give a birth to high-performance materials, that is, single or few-layer graphene constructed porous structure with high

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heteroatom doping level.

In this Chapter, we present a novel strategy towards the above goal and successfully demonstrate a simple yet very effective approach for *in situ* fabrication of nitrogen-doped porous graphene (NPG) by using a supramolecular polymer (melamine cyanurate (MC), chemical structure shown in Figure 5.1a) as both N source and pore-forming agent. The post annealing process decomposes the sacrificial MC component and releases a large amount of N containing gases, which induce N doping and simultaneously generate porous structure. Benefiting from the unique porous architecture and high N doping level, the NPG materials exhibit impressive electrochemical performances when applied as the anode materials for LIBs. Furthermore, this low cost and facile method could be suitable for mass production, which implies the great potential of the NPG materials for advanced energy storage.

5.2 Experiments

5.2.1 Preparation of NPG materials

400 mg GO was dispersed in 100 mL deionized water by ultrasonication for 2 h, and subsequently centrifuged at 1000 rpm for 5 min to remove the unexfoliated particles. Then, 562 mg melamine was dissolved in the GO dispersion under stirring at 80 °C. Afterwards, 38 mL of freshly prepared 15 mg mL⁻¹ cyanuric acid solution was dropwised into the mixture and then stirred at 80 °C for 1 h. The obtained product was collected by hot-filtration, washed with deionized water for several times, and dried in an oven at 90 °C. Finally, the sample was annealed under Ar atmosphere at a flow of 100 cm³ min⁻¹ with a heating rate of 5 °C min⁻¹ to pyrolysis temperature (450, 650 and 850 °C) for 2 h.

5.2.2 Preparation of rGO

rGO was prepared by annealing GO powder at 650 °C under the same experimental parameters.

5.3 Results and discussion

The NPG materials were synthesized by a novel two-step methodology (Figure 5.1b). In the first step, graphene oxide@melamine cyanurate composite (GO@MC) was synthesized by supramolecular polymerization. Firstly, melamine was dissolved into the GO solution, which will be spontaneously absorbed on GO through π - π interaction.^[154, 155] Afterwards, cyanuric acid was added into the mixture. The hydrogen-bond between melamine and cyanuric acid induces a supramolecular polymerization,^[156] causing the formation of GO@MC. In the second step, GO@MC was subjected to annealing treatment at different temperatures (higher than the maximum thermal decomposition of MC (~410 °C)). During this process, the decomposition of sacrificial MC component releases a large amount of nitrogen containing gas (e.g., NH₃, HCN and HNCO) from the interlayer space of graphene sheets,^[157] which consequently produces substantial internal stresses, leading to the expansion of graphene sheets to single or few-layer with porous structures. Simultaneously, the removal of thermally labile oxygen functional groups from graphene sheets induces active sites for *in situ* N doping, which finally results in the formation of NPG materials (labeled as NPG-T, where T is the pyrolysis temperature). It should be mentioned that this strategy is conceptually different and in fact superior to the previously reported ones as evidenced by the remarkably improved performance. In the previous works, polymers or ionic liquid was annealed together with GO, which eventually leads to the formation of graphene-based composites.^[58, 158-160] On clear

contrast, our proposed process could completely decompose the supramolecular MC and yield a pure N doped graphene, which is particularly appealing since it provides an exclusive opportunity for investigating whether graphene is a potential valid alternative anode for next generation LIBs.

Figure 5.1 (a) Supramolecular polymerization of melamine and cyanuric acid results in the formation of MC. (b) Schematic illustration of the synthesis procedure of NPG materials.

To evaluate the proposed strategy and unveil the properties of our products, systematic characterizations are performed. The materials were firstly studied by FESEM and TEM. The morphology of GO is flaky texture, leading to a rippled or wrinkled structure (Figure 5.2a). FESEM image of GO@MC shows that the rod-like MC supramolecular crystals with an average size of $1.45\ \mu\text{m} \times 560\ \text{nm}$ are wrapped by GO sheets (Figure 5.2b). Notably, these supramolecular crystals disappeared in the FESEM images of NPG materials after the corresponding annealing process. As shown in Figure 5.2d-f, NPG-450, NPG-650 and NPG-850 exhibit a crumpled and loose-

packed thin layer morphology. The overlapping and interconnecting of graphene sheets result in the formation of porous structure with the diameters ranging from submicrometer to few micrometers. In contrast, the thermally reduced graphene oxide (G-650) prepared in the absence of MC tends to aggregate, forming a graphite-like structure (Figure 5.2c). Meanwhile, no pores are observed in G-650, demonstrating the importance of MC for effectively preventing the restacking of graphene sheets and promoting the formation of pores. The complete decomposition of MC and successful formation of graphene thin layers constructed porous structure after annealing can also be readily observed by TEM images (Figure 5.3a). These features would facilitate the accessibility of electrolyte and shorten the diffusion length of Li ions, which could be advantageous for Li storage. In addition, the recovery of graphitic carbon structures can guarantee fast electron transportation, as displayed in the HRTEM image of NPG-650 (Figure 5.3b). Moreover, STEM image with the corresponding elemental mapping images (Figure 5.3c-e) reveal that nitrogen is homogeneously distributed in graphene sheets.

Figure 5.2 FESEM images of (a) GO, (b) GO@MC, (c) G-650, (d) NPG-450, (e) NPG-650 and (f) NPG-850.

Figure 5.3 (a) TEM and (b) HRTEM images of NPG-650. (c) STEM image of NPG-650 with the corresponding (d) carbon and (e) nitrogen elemental mapping images.

Nitrogen adsorption-desorption technique was also used to investigate the porous structure of NPG materials. Figure 5.4a reveals that the isotherms of these materials show close to type IV (G-650 and NPG-650) and type II (NPG-450 and NPG-850) patterns according to the IUPAC classification.^[161] The obtained pore structure parameters of these materials are summarized in Table 5.1. Remarkably, the BET surface area of NPG materials ($106\text{--}152\text{ m}^2\text{ g}^{-1}$) is larger than G-650 ($69\text{ m}^2\text{ g}^{-1}$) and the directly annealed GO with melamine ($6\text{ m}^2\text{ g}^{-1}$),^[162] indicating the introduction of MC can effectively prevent the restacking of graphene sheets, which is in good agreement with previous FESEM and TEM results. Compared to the theoretical value of graphene ($2630\text{ m}^2\text{ g}^{-1}$), the relative low surface area of NPG must be due to the existence of few-layer graphene sheets in its unusual structure. Additionally, it is also found that the BET surface area of NPG materials is dependent on the annealing temperature. As shown in

Table 5.1, the BET surface area of NPG materials increases from 106 to 152 m² g⁻¹ with increasing the annealing temperature from 450 to 650 °C but decreases to 136 m² g⁻¹ at 850 °C, probably owing to the higher graphitization degree in NPG-850 as demonstrated by XRD results (see below). Pore size distribution curves (Figure 5.4b) reveal that the NPG materials have a multimodal pore distribution. It should be noted that NPG-650 has the largest BET surface area but the smallest pore volume, which implies the existence of large amounts of micro- and meso-pores in NPG-650 structure. The high surface area, large pore volume and plentiful pores of NPG-650 are supposed to not only facilitate the accessibility of electrolyte, but also provide additional active sites for Li storage.

Figure 5.4 (a) Nitrogen adsorption-desorption isotherms and (b) the corresponding pore size distribution of G-650, NPG-450, NPG-650 and NPG-850. (c) XRD patterns and (d) Raman spectra of GO, G-650, NPG-450, NPG-650 and NPG-850.

Table 5.1 Pore structure parameters of G-650, NPG-450, NPG-650 and NPG-850, and the atomic percentage of N species in the NPG materials.

Sample	BET surface area (m ² g ⁻¹)	Total pore volume (cm ³ g ⁻¹)	Average pore diameter (nm)	Total N content	Pyridine-like N	Pyrrrole-like N	Graphite-like N
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G-650	69	0.24	14.0	0	0	0	0
NPG-450	106	0.25	9.78	18.8	47.3%	21.2%	31.5%
NPG-650	152	0.20	5.2	12.0	42.5%	25.2%	32.3%
NPG-850	136	0.30	8.7	8.9	64.4%	20.5%	15.1%

Further structural information about the NPG materials was obtained from XRD, XPS and Raman spectroscopy. XRD pattern of GO (Figure 5.4c) shows a characteristic diffraction peak located at $2\theta = 11.2^\circ$ with an interlayer spacing of 0.79 nm, which is assigned to the (002) plane of graphite due to the intercalation of oxygen functional groups in between the graphite layers. For G-650 and NPG materials, the removal of oxygen functional groups from graphene sheets makes this peak up-shifted to $\sim 26.2^\circ$, corresponding to an interlayer spacing of 0.34 nm. It is worth noting that G-650 presents a well-defined peak, whereas NPG materials display a broad hump-shaped peak, once again demonstrating the disordered graphene phases in NPG materials. Comparing with NPG-450 and NPG-650, the diffraction peak of NPG-850 is more defined and evidently shifts to a larger angle, which suggests its higher graphitization degree. Moreover, the increased I_D/I_G ratio in the Raman spectra of NPG materials (Figure 5.4d) also illustrates their disordered feature that caused by the porous structure and N doping induced structural distortion in the graphene sheets.^[44, 163] To analyze the elemental composition and their chemical status in the samples, XPS measurements were carried out. The survey scan of GO (Figure 5.5a) shows the presence of C and O atoms located at ca. 285 and 532 eV, with an atomic percentage of 40.9% and 50.1%, respectively.^[136] However, the O content in G-650 and NPG materials is dramatically decreased, which suggests the reduction of GO after the annealing treatment. In addition, the N 1s peak located at ca. 399 eV is observed in NPG materials, clearly implying the successful doping of graphene with N atom.^[162] The N content in NPG-450, NPG-650 and NPG-850 is calculated to be 18.8 at%, 12.0 at% and 8.9 at%, respectively. Figure 5.5b-d

presents the high-resolution N 1s spectra of NPG materials. The deconvoluted peaks located at ca. 398.4, 399.8 and 401.3 eV could be successively ascribed to the pyridine-like N, pyrrole-like N and graphite-like N.^[162, 163] It is found that pyridine-like N is the primary N bonding state in NPG materials as shown in Table 5.1. Theoretical calculations demonstrate that the pyridine-like N is mostly favorable for Li storage due to its stronger binding energy with Li, along with lower Li diffusion and desorption barrier.^[43, 164]

Figure 5.5 (a) XPS survey spectra of GO, G-650, NPG-450, NPG-650 and NPG-850. High-resolution N 1s XPS spectra of (b) NPG-450, (c) NPG-650 and (d) NPG-850.

Figure 5.6 (a) CV curves of the NPG-650 electrode at a scanning rate of 0.5 mV s⁻¹ in the voltage range of 0.005–3 V (vs. Li/Li⁺). (b) Galvanostatic charge-discharge curves of the NPG-650 electrode at a current density of 74.4 mA g⁻¹. (c) Cycling performance of the G-650, NPG-450, NPG-650 and NPG-850 electrodes at a current density of 74.4 mA g⁻¹. (d) Rate performance of the G-650, NPG-450, NPG-650 and NPG-850 electrodes at different current densities (from 74.4 to 3720 mA g⁻¹).

To evaluate the potential of NPG materials as anode for LIBs, we fabricated a series of coin-type cells. As shown in Figure 5.6a and Figure 5.7a–c, all samples show similar CV curves that belong to typical carbon-based anodes.^[67, 143] During the first cycle, a reduction peak in the potential range of 0.3–0.9 V is clearly detected, which is ascribed to the formation of a SEI layer on the electrode surface caused by electrolyte decomposition. In the subsequent cycles, the disappearance of this SEI formation peak together with the almost overlapped CV curves imply the formation of a stable SEI layer after the first cycle. Two weak peaks are also observed during the first CV curve

of NPG-850 in the potential range of 1.5–2.5 V (Figure 5.7c), which should be related to the trap of Li in the irreversible sites caused by high temperature induced collapse of the pores.^[165, 166] Figure 5.6b and Figure 5.7d–f depict the galvanostatic charge-discharge curves of the materials at 74.4 mA g⁻¹. It can be seen that the first discharge curves show a sloping plateau at ~0.7 V, indicative of the formation of SEI layer, which matches well with the CV results. The first discharge capacity of G-650, NPG-450, NPG-650 and NPG-850 is 1025, 1381, 1440 and 1167 mAh g⁻¹, corresponding to a coulombic efficiency of 52.2%, 37.7%, 55.3% and 51.8%, respectively. The large irreversible capacity loss is attributed to SEI formation that is commonly observed in carbon-based anodes. However, the coulombic efficiency of these materials increases dramatically in the following cycles, as shown in Figure 5.8.

Figure 5.7 CV curves of the (a) G-650, (b) NPG-450 and (c) NPG-850 electrodes at a scanning rate of 0.5 mV s⁻¹ in the voltage range of 0.005–3 V (vs. Li/Li⁺). Galvanostatic charge-discharge curves of the (d) G-650, (e) NPG-450 and (f) NPG-850 electrodes at a current density of 74.4 mA g⁻¹.

The cycling performance of these materials is investigated under the same current density of 74.4 mA g⁻¹ (Figure 5.6c). Evidently, NPG-650 electrode exhibits

substantially higher capacity than the other three electrodes throughout the whole cycles. The reversible capacity of NPG-650 electrode is 900 mAh g^{-1} after 150 cycles, over two times larger than the theoretical value of graphite (372 mAh g^{-1}), and far larger than the value of G-650 (516 mAh g^{-1}), NPG-450 (313 mAh g^{-1}) and NPG-850 (563 mAh g^{-1}). The gradually increase of capacity upon cycling can be assigned to the electrochemical activation process, which results in an improved accessibility of Li ions into the inner area of the electrode, thus more activated sites for Li storage.^[128, 143] More significantly, the NPG-650 electrode also shows superior rate capability. As illustrated in Figure 5.6d and the insets in Figure 5.8, NPG-650 electrode always delivers higher capacity than the other electrodes with current density increasing from 74.4 to 3720 mA g^{-1} . The reversible capacities of NPG-650 electrode are 723, 631, 566, 501, 418 and 356 mAh g^{-1} , at 74.4, 186, 372, 744, 1860 and 3720 mA g^{-1} , respectively. These values are competitive with the other recently reported graphene-based anode materials, such as P-doped graphene,^[67] edge-selectively halogenated graphene^[167] and mesoporous graphene.^[144] Moreover, even after deep cycling at 3720 mA g^{-1} , the capacity of NPG-650 electrode can be recovered to its initial value when the current density is restored to 74.4 mA g^{-1} , indicating its excellent reversibility.

Considering different heating rate may result in different pore structures in the NPG materials, we further investigated the influence of heating rate on the final electrochemical performance. Figure 5.9a,b show the FESEM images of NPG-650' (prepared at a heating rate of $20 \text{ }^{\circ}\text{C min}^{-1}$). It is interesting to note that NPG-650' also has a porous structure that consisted of crumpled and loose-packed graphene thin layers, showing no much difference from that of NPG-650. Meanwhile, the electrochemical performance of NPG-650' (Figure 5.9c) is also comparable to NPG-650, implying the Li storage property of NPG materials is independent on the heating rate. EIS was

employed to investigate the kinetic behavior of the electrochemical reaction (Figure 5.9d). The data fitted from the semicircle at high frequency region by using the equivalent circuit (Inset of Figure 5.9d) reveals that the charge transfer resistance (R_{CT}) of G-650, NPG-450, NPG-650 and NPG-850 is 78, 116, 42 and 52 Ω , respectively, which suggests NPG materials with N doping and porous structure possess higher electrolyte accessibility and better charge transport capability than G-650. The relative high R_{CT} of NPG-450 is due to its low reduction degree, as demonstrated by previous XPS and XRD results. At low frequency range region, the straight lines with larger phase angles, evidencing lower Li-ion diffusion resistance in NPG materials compared with G-650.

Figure 5.8 Coulombic efficiency of the (a) G-650, (b) NPG-450, (c) NPG-650 and (d) NPG-850 electrodes at a current density of 74.4 mA g⁻¹. Insets are the corresponding galvanostatic charge-discharge curves of the electrodes at different current densities.

Figure 5.9 (a,b) FESEM images of NPG-650' at different magnifications. (c) Cycling performance of NPG-650' electrode at a current density of 74.4 mA g⁻¹. (d) Nyquist plots of the G-650, NPG-450, NPG-650 and NPG-850 electrodes. Inset is the equivalent circuit model.

The outstanding electrochemical performance of NPG materials mainly originates from their unique porous architecture and high N doping level. On one hand, the high surface area and porous structure are favorable for electrolyte accessibility and fast Li diffusion throughout the electrode material.^[44, 143] With this design, the as-formed mesopores can also act as “cavities” for further Li storage, which additionally contributes to the remarkable electrochemical properties.^[144, 168] In particular, the graphene thin layers with corrugated and interconnected structure can greatly increase Li ions adsorption, shorten Li ion diffusion length and facilitate electron transportation. On the other hand, N doping further enhances the conductivity of graphene sheets, whereas the doping induced topological defects are beneficial for Li accommodation.^{[42,}

^{67]} All of these merits lead to the final outstanding electrochemical performance. It is also noted that the electrochemical performance of NPG materials highly depends on the annealing temperature. 650 °C is the ideal temperature that can ensure the as-obtained NPG material has high N content and good conductivity, as well as appropriate porous structure, thus superior Li storage capacity, i.e., capacity of NPG-650 > NPG-850 > NPG-450. Further increasing the annealing temperature will induce lower N doping content and porosity (NPG-850), while decreasing the annealing temperature will result in poor reduction degree (NPG-450), both of which are disadvantageous for Li storage performance.

5.4 Summary

In summary, we have demonstrated a novel chemical approach to prepare NPG by using a supramolecular polymer as the N source and pore-forming agent. The successful realization of graphene thin layers constructed porous structure with high N doping level mainly arises from the introduction of sacrificial MC template, which can effectively suppress graphene restacking, promote pore formation, and simultaneously induce N doping by releasing a large amount of N containing gases during the annealing process. With this design, NPG exhibits exceptional electrochemical performance in terms of high reversible capacity (900 mAh g⁻¹ after 150 cycles) with good cycling and rate performances, highlighting it might be a promising candidate for high performance LIBs. We also demonstrate that the annealing temperature is a key step for the final electrochemical performance of NPG materials since it has significant impact on the N doping level and porous structure. More importantly, this simple strategy might be helpful for the rational design of functionalized graphene-based materials for advanced energy storage.

Chapter 6. Graphene Encapsulated SnO₂ Nanoparticles as Advanced Anodes for LIBs[†]

6.1 Introduction

To address the restacking issue of graphene, surface modification, for example, introducing spacers to decorate graphene basal plane, is a versatile technique. Functional materials with the ability of modifying SEI formation, suppressing restacking, or promoting electron/ion transport, are the best choices because of their potential in further upgrading the Li storage performance of graphene. Owing to the enthralling features, such as high Li storage capacity (782 mAh g⁻¹), low discharge potential, non-toxicity and low cost,^[169] SnO₂ has been regarded as one of the most profitable decorative materials to modify graphene. Actually, with these merits, SnO₂ itself is also a good candidate to replace the traditional graphite anode for next-generation LIBs. Nonetheless, the practical application of SnO₂ anode suffers from a severe pulverization-induced capacity fading, arising from its large volume changes (~300%) and agglomeration during the repeated Li insertion/extraction process.^[170] Interestingly, the introduction of graphene can not only buffer the associated volume changes of SnO₂ but also prevent their agglomeration, as well as increase the conductivity.^[171, 172] Therefore, high-performance anodes are expected by constructing SnO₂ decorated graphene nanostructures.

As summarized in Chapter 2, so far, various types of techniques, including hydrothermal process,^[93, 173] physical mixing method,^[106] solution-based synthesis approach^[87, 95] and ball-milling technique,^[86] have been developed to fabricate

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SnO₂/graphene composites. However, the electrochemical performance of SnO₂/graphene composites is still not satisfying due to the facts involving: (i) the SnO₂ nanoparticles are only simply decorated on the surface of graphene in most cases rather than confined in graphene layers, making them easily peeled off from the graphene sheets during long-term cycling.^[174, 175] (ii) The inhomogeneous size distribution of SnO₂ nanoparticles makes it difficult for the graphene sheets to effectively prevent their agglomeration within electrode because of the high surface energy.^[176] Until now, SnO₂/graphene composites with uniform structure and thus superior electrochemical performance, especially high rate capability have rarely been achieved.^[83]

In this Chapter, we develop a facile one-pot approach for the synthesis of SnO₂/graphene composite via a surfactant-assisted redox process. The SnO₂ nanoparticles are formed via Sn²⁺-induced reduction of GO, and simultaneously encapsulated into graphene layers due to the random aggregation of graphene sheets. Furthermore, the presence of surfactant is indispensable for guaranteeing the uniformity of SnO₂ nanoparticles with a tiny size of ~5 nm and homogeneous distribution on graphene sheets. As expected, the resultant SnO₂/graphene composite exhibits superior Li storage properties with large reversible capacity, good cyclic lifespan and excellent rate capability, highlighting its great potential applications in future LIBs.

6.2 Experiments

6.2.1 Preparation of surfactant-assisted encapsulation of SnO₂ nanoparticles in graphene layers (SAE SnO₂/G)

1 g hexadecyltrimethylammonium bromide (HTMAB) was dispersed in 150 mL GO aqueous solution (~0.5 mg mL⁻¹) under stirring at 40 °C. Subsequently, 14 mL ethanol solution of SnCl₂ (500, 250 and 125 mg) was dropwised into the solution, and then

further stirred at 40 °C for 2 h. Finally, the obtained products were collected by centrifugation and repeatedly washing with deionized water for several times, and dried in an oven at 100 °C for 12 h. The resultant powders were denoted as SAE SnO₂/G-6.7, SAE SnO₂/G-3.3 and SAE SnO₂/G-1.7, respectively, according to the mass ratio of SnCl₂ and GO.

6.2.2 Preparation of SnO₂ nanoparticles decorated graphene (SnO₂/G)

For comparison, SnO₂/G was prepared under the same condition as SAE SnO₂/G-3.3, except the absence of HTMAB, and denoted as SnO₂/G-3.3.

6.3 Results and discussion

The fabrication of SnO₂/G and SAE SnO₂/G composites is schematically illustrated in Figure 6.1. Briefly, the composites were prepared via redox reaction between GO and Sn²⁺, which results in the reduction of GO into graphene associated with the oxidation of Sn²⁺ to SnO₂. Normally, this process is conducted by mixing GO dispersion with Sn²⁺,^[177] during which Sn²⁺ is captured by the O-containing functional groups on GO, and then the redox reaction occurs. However, the randomly distributed O-containing functional groups leads to the generation of multiple nucleation sites and thus inhomogeneous distribution of SnO₂ nanoparticles, yielding unsatisfied electrochemical performance of SnO₂/G.^[99] The improved method we proposed here is to introduce a cationic surfactant HTMAB. In this process, the positively charged hexadecyltrimethylammonium ions of HTMAB would be firstly absorbed on the basal plane of GO, forming lamellar micelles with a sandwich-like structure. The close-packed micelles not only serve as homogeneous nucleation sites for SnO₂ nanoparticles formation, but also prevent their further growth or agglomeration, resulting in a uniform distribution of SnO₂ nanoparticles loaded on graphene sheets. In addition, the random

aggregation of graphene sheets ensures the formation of SAE SnO₂/G and hence excellent Li-storage properties. Besides, this method is more efficient and effective than the conventional solution-based synthesis method,^[87, 95] as high-temperature annealing treatment for phase-purity/crystallinity is not required.

Figure 6.1 Schematic illustration of the fabrication of SnO₂/G and SAE SnO₂/G composites.

The morphologies of the as-prepared SnO₂/G and SAE SnO₂/G samples were investigated by FESEM and TEM. Figure 6.2a,e,f reveal that the SnO₂/G-3.3 composite presents a large number of SnO₂ nanoparticles on graphene layers with sizes varying from several nanometers to dozens of nanometers. As discussed above, the wide particle-size distribution range is mainly due to the multiple nucleation sites for SnO₂ nanoparticles formation. After the introduction of surfactant, the aggregation of SnO₂ nanoparticles does not appear in the SAE SnO₂/G-1.7 and SAE SnO₂/G-3.3 composites (Figure 6.2b,c), thus only randomly aggregated graphene sheets are observed. However, a large excess of Sn²⁺ precursor in the composite (SAE SnO₂/G-6.7) will induce further growth or agglomeration of SnO₂ nanoparticles (Figure 6.2d). TEM and HRTEM images (Figure 6.2g,h) disclose the homogenous distribution of SnO₂ nanoparticles on the graphene layers with a uniform size of ~5 nm in the SAE SnO₂/G-3.3 composite,

demonstrating the importance of the introduced surfactant for the formation of SnO₂ nanoparticles.

Figure 6.2 FESEM images of (a) SnO₂/G-3.3, (b) SAE SnO₂/G-1.7, (c) SAE SnO₂/G-3.3 and (d) SAE SnO₂/G-6.7 composites. (e,f) TEM images of SnO₂/G-3.3 composite. (g) TEM and (h) HRTEM images of SAE SnO₂/G-3.3 composite.

The SnO₂/G and SAE SnO₂/G composites were further analyzed by XPS, XRD and Raman spectroscopy to investigate their structural characteristics. From the XPS survey spectra (Figure 6.3a), C, O and Sn are clearly detected in the composites. Meanwhile, the Sn 3d spectra of the composites (Figure 6.3b) show two symmetric peaks at about 487.6 and 496.0 eV, corresponding to the Sn 3d_{5/2} and Sn 3d_{3/2} peaks, respectively.^[178] The energy splitting between the two peaks is 8.4 eV, indicating the formation of SnO₂ nanoparticles.^[179] Figure 6.3c shows the XRD patterns of samples. GO exhibits a characteristic diffraction peak at $2\theta = 11^\circ$ due to the intercalation of O-containing functional groups between graphene sheets. The diffraction peaks of the composites at $2\theta = 26.3^\circ$, 33.4° , 51.9° and 65.5° can be successively assigned to the (110), (101), (211) and (301) planes of SnO₂ phase (JCPDS No. 41-1445),^[180] further confirming the formation of SnO₂ nanoparticles. The significant structural changes of GO after the redox process were detected by Raman spectroscopy. As shown in Figure 6.3e, the Raman spectrum of GO contains both D band at 1356 cm^{-1} (k-point phonons

of A_{1g} symmetry) and G band at 1584 cm⁻¹ (E_{2g} phonon of sp² atoms), with a I_D/I_G ratio of 0.84.^[128] Notably, the frequencies of the D and G bands in the composites do not show any relative shifts in comparison with that observed in GO. However, an increased I_D/I_G ratio is observed in the composites, which is attributed to the formation of numerous small sp² domains in graphene sheets after Sn²⁺ induced reduction.^[161, 181]

Figure 6.3 (a) XPS survey spectra of SnO₂/G and SAE SnO₂/G composites. (b) XPS Sn 3d spectra of SnO₂/G and SAE SnO₂/G composites. (c) XRD patterns, (d) TGA curves and (e) Raman spectra of GO, SnO₂/G and SAE SnO₂/G composites.

To determine the content of graphene in the composites, TGA was carried out in air. As shown in TGA curves (Figure 6.3d), the initial mass loss of the samples below 100 °C is due to the loss of adsorbed water. A rapid mass loss can be observed with the increase of the temperature from 100 to 700 °C, which is assigned to the combustion of graphene in air (yielding CO₂).^[182] The content of graphene in these composites is calculated to be 28 wt%, 51 wt%, 24 wt% and 18 wt% for SnO₂/G-3.3, SAE SnO₂/G-1.7, SAE SnO₂/G-3.3 and SAE SnO₂/G-6.7, respectively.

Figure 6.4 shows the first three CV curves for the SnO₂/G and SAE SnO₂/G electrodes at a scan rate of 0.5 mV s⁻¹. The cathodic peak at ~0.9 V in the first cycle is

due to the formation of SEI and reduction of SnO₂ to Sn.^[173] This peak disappeared in the following cycles, and a new reversible peak at ~1 V is observed, indicating the conversion reaction of SnO₂.^[83] While the peak at ~0.02 V can be ascribed to the alloying reaction of Sn with Li to form various Li_xSn alloys.^[183] In the anodic sweep, two peaks at ~0.6 and ~1.3 V are observed. The first peak corresponds to the dealloying reaction of Li_xSn alloys, whereas the second peak represents the partially reversible reaction of SnO₂ with Li.^[184, 185] After the first cycle, the CV curves of the composites are almost overlapped, implying the good reversibility of the electrochemical reactions on the electrodes.

Figure 6.4 CV curves of the first three cycles of the (a) SnO₂/G-3.3, (b) SAE SnO₂/G-1.7, (c) SAE SnO₂/G-3.3 and (d) SAE SnO₂/G-6.7 electrodes at a scan rate of 0.5 mV s⁻¹ in the voltage window 0.005–3 V.

Insets of Figure 6.5 show the galvanostatic charge-discharge profiles of the SnO₂/G and SAE SnO₂/G electrodes at a current density of 100 mA g⁻¹. The capacity

values were calculated based on the mass of the composite. Notably, the first discharge capacity for the SnO₂/G-3.3, SAE SnO₂/G-1.7, SAE SnO₂/G-3.3 and SAE SnO₂/G-6.7 electrode is 1779, 1755, 2033 and 1821 mAh g⁻¹, corresponding to the coulombic efficiency of 62%, 47%, 56% and 59%, respectively. The initial irreversible capacity loss is attributed to the SEI formation and irreversible reactions on the electrodes. However, after the first cycle, the electrochemical reactions become more and more reversible upon cycling, leading to the significantly increased coulombic efficiency (Figure 6.5). This is highly consistent with the CV results.

Figure 6.5 Coulombic efficiency of the (a) SnO₂/G-3.3, (b) SAE SnO₂/G-1.7, (c) SAE SnO₂/G-3.3 and (d) SAE SnO₂/G-6.7 electrodes at a current density of 100 mA g⁻¹. The insets are the corresponding galvanostatic charge-discharge profiles of the electrodes.

The cycling performance of SnO₂/G and SAE SnO₂/G electrodes was investigated at a current rate of 100 mA g⁻¹, as shown in Figure 6.6a. It can be seen that the SnO₂/G-

3.3 electrode delivers a high initial reversible capacity of 1110 mAh g⁻¹. However, a rapid capacity fading is observed from the 30th cycles because of the severe pulverization of the electrode caused by the significant volume change during the charge and discharge processes. The charge capacity of SnO₂/G-3.3 electrode is only 582 mAh g⁻¹ after 120 cycles, which is 52.4% retention of the reversible capacity. The poor cycling stability of SnO₂/G-3.3 electrode might be attributed to the inhomogeneous distribution of SnO₂ nanoparticles on graphene sheets, as it is observed by previous FESEM and TEM images. Thus, the graphene matrix cannot effectively buffer the associated volume changes. Definitely, the SAE SnO₂/G electrodes exhibit greatly improved cyclic stability over that of the SnO₂/G-3.3. It is worth noting that the electrochemical performances of SAE SnO₂/G correlate closely to the content of graphene in the composite. The SAE SnO₂/G-3.3 electrode with a graphene loading content of 24 wt% displays the best Li storage performance in terms of high reversible capacity and good cycling stability. After 120 cycles, the SAE SnO₂/G-3.3 electrode can sustain a high reversible capacity of 998 mAh g⁻¹, 87.5% retention of the initial reversible capacity, which suggests its good cycling stability. The gradual increase of capacity from the 10th to 60th cycles could be attributed to the improved access of Li ions into the electrode, leading to an increased accommodation behavior for Li.^[120] Further increasing the graphene content in the composite (SAE SnO₂/G-1.7) will result in low Li storage capacity, while decreasing the graphene content (SAE SnO₂/G-6.7) will lead to poor cycling stability.

Figure 6.6 (a) Cycling performance of the SnO₂/G and SAE SnO₂/G electrodes at a current density of 100 mA g⁻¹. (b) Rate capability of the SnO₂/G and SAE SnO₂/G electrodes at various current densities. Galvanostatic charge-discharge profiles of the (c) SnO₂/G-3.3, (d) SAE SnO₂/G-1.7, (e) SAE SnO₂/G-3.3 and (f) SAE SnO₂/G-6.7 electrodes at various current densities.

The rate capability of the SnO₂/G and SAE SnO₂/G electrodes was evaluated at stepwise current densities (Figure 6.6b). As the current densities increase from 100 to 200, 400, 800, 1600 and 3200 mA g⁻¹, the SAE SnO₂/G-3.3 electrode still exhibits stable

capacities of 1144, 1078, 1073, 1032, 910 and 682 mAh g⁻¹, respectively. Moreover, with the current density returns to 100 mA g⁻¹, the capacity of the electrode is able to recover to its initial value, indicating its excellent rate capability. As far as we know, such superior Li storage performance is rarely reported in the SnO₂/G composites.^[82-84, 86, 87, 90, 91, 107-109] Remarkably, the SAE SnO₂/G-3.3 electrode always delivers higher capacities than the other electrodes at various current densities (also shown in Figure 6.6c-f). EIS measurements (Figure 6.7) illustrate that the charge transfer resistance of SAE SnO₂/G-3.3 electrode is 37 Ω, which is much smaller than the SnO₂/G-3.3 (79 Ω), SAE SnO₂/G-1.7 (54 Ω) and SAE SnO₂/G-6.7 (111 Ω) electrodes.

Figure 6.7 Nyquist plots of the SnO₂/G and SAE SnO₂/G electrodes.

The excellent electrochemical performances of the SAE SnO₂/G-3.3 composite can be attributed to its unique structural features. First of all, the intrinsic activity of the SnO₂ nanoparticles component in the composite endows high Li storage capacity by providing large interfacial areas for fast Li insertion/extraction within the electrode, and shortening the solid-state diffusion length of Li ions. In addition, the uniform distribution of SnO₂ nanoparticles on graphene sheets can effectively prevent the agglomeration Sn particles formed during Li insertion. Secondly, the graphene

component in the composite can act as not only continuous channels for electron transport but also Li storage material, which additionally contributes to its exceptional performance. More importantly, the random aggregation of graphene sheets results in the encapsulation of SnO₂ nanoparticles in graphene layers, producing a mechanically robust structure. Therefore, the graphene sheets can function as a 3D scaffold for preventing the SnO₂ nanoparticles being peeled off and buffering the associated volume changes.

6.4 Summary

In summary, we have developed a facile and effective approach to synthesis SnO₂/G composite through a surfactant-assisted redox method. This composite is composed of uniform SnO₂ nanoparticles with a size of ~5 nm, which are homogeneously encapsulated in the graphene layers. Benefiting from the unique structural features, the composite exhibits high reversible capacity (1141 mAh g⁻¹ at a current density of 100 mA g⁻¹) and long-term cycling stability (120 cycles with 87.5% retention), as well as excellent rate capability when applied as an anode material for LIBs. Considering the simple, low cost and high throughput fabrication process of this approach, we believe the composite may be a promising alternative anode material for next generation high-performance LIBs. Moreover, our strategy could also be helpful in fabricating other graphene-based composites for diverse applications.

Chapter 7. Engineering the Cathodic Performance of Graphene for LIBs[†]

7.1 Introduction

In response to the limited practical capacity (150-200 mAh g⁻¹) of the conventional inorganic cathodes, and their use and preparation induced environmental problems, organic cathode materials with higher energy density/power density have been rapidly developed recently. Compared to their inorganic counterparts, organic cathodes have some special advantages as follows: (i) Structural diversity, which endows great opportunities for tuning the physicochemical properties/structures of the electrode materials. In sharp contrast, very few kinds of inorganics are suitable for the application as cathode materials; and most importantly, the development of inorganic cathodes with breakthroughs on energy/power densities becomes more and more challenging in the future.^[124, 186] (ii) Energy-saving and nature-friendly, because high-temperature annealing treatments on inorganic cathodes for achieving phase-purity/crystallinity are not required in the case of using organics as the cathodes. In addition, organic cathodes could be synthesized from the abundant/ renewable biomass resources, which involve low CO₂ production and far less energy consumption.^[187, 188]

The only fly in the ointment is that the electrochemical performance of organic cathodes cannot compete with the inorganic ones because of their poor electrical conductivity and severe solubility in the electrolyte.^[123, 124] Commonly, the cycling stability of polymeric molecules is much better than that of small molecules since the robust backbone of polymer can effectively prevent the unwanted dissolution of the

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electrode materials. GO can also be considered as a two-dimensional polymer that is functionalized with various O-containing groups, i.e., carbonyl/carboxyl groups at the edge and hydroxyl/epoxy groups on the basal plane.^[128, 189] Since these functional groups are electrochemically active that capable of reversibly reacting with Li ions,^[29, 116] it would be appealing to chemically tune them so that to achieve high-performance cathodes comprising of stable and highly conducting graphene framework for electron transport while abundant electroactive functional groups for Li storage.

We herein report chemical engineering strategies for the fabrication of carbonylated/hydroxylated graphene oxide (C/HGO) and decarboxylated graphene oxide (DCGO) via selective removal of the oxygen functional groups on GO. The resultant C/HGO and DCGO are proved to be superior cathode materials, showing a high potential (vs. Li/Li⁺) for LIBs and significantly enhanced Li storage properties when compared with the pristine GO. There is a special highlight that C/HGO exhibits much better electrochemical performances than conventional LiCoO₂ and LiFePO₄ cathodes, with upper capacity, good rate capability and excellent cycling behavior, which is mainly due to the graphene framework for fast electron transport and the abundant carbonyl/hydroxyl functional groups for Li storage. We believe that these functionalized graphene-based materials made by our facile chemically engineered method may open up an opportunity to develop high-performance GO-based cathodes for future LIBs with high energy density.

7.2 Experiments

7.2.1 Synthesis of DCGO

DCGO was prepared via chemoselective decarboxylation of GO.^[190] GO (500 mg) was dispersed in 300 mL DMF by ultrasonication, then K₂CO₃ (460 mg) and AgNO₃ (330

mg) were added under stirring. The mixture was stirred at 80 °C for 16 h. Afterwards, the product was collected by centrifugation, and successively washed with 30% v/v of HNO₃ for 4 times, then deionized water for several times, and finally dried under vacuum condition.

7.2.2 Synthesis of C/HGO

GO (1.0 g) was added into 200 mL of anhydrous THF under stirring, and then 40 mL BuLi was dropwised under N₂ condition. The mixture was stirred at room temperature for 24 h. Subsequently, the suspension was centrifuged and washed with deionized water for several times, and finally dried under vacuum condition.

7.3 Results and discussion

A general description of the methods used to synthesize DCGO and C/HGO is illustrated in Figure 7.1. DCGO is synthesized through chemoselective decarboxylation of GO, while C/HGO was prepared via n-Butyllithium-promoted carbonylation/hydroxylation of GO, which are both described in the Experimental Section for details. A comprehensive structural analysis was carried out to ensure that DCGO and C/HGO were successfully obtained (see below).

Figure 7.1 Schematic illustration of the synthesis of DCGO and C/HGO.

XPS was firstly employed to analyze the surface functional groups on graphene sheets. In Figure 7.2a, the C 1s spectrum of GO was fitted into four components, that is, C-C bonds (sp^2 carbon, 284.5 eV), C-O bonds (hydroxyl/epoxy, 286.6 eV), C=O bonds (carbonyl, 288.1 eV) and O-C=O bonds (carboxyl, 288.9 eV),^[189] and their

corresponding content is calculated to be 42.5%, 47.9%, 7.0% and 2.6%, respectively. After chemoselective decarboxylation, the peak intensity of O-C=O bonds in DCGO reduced by ~100%, however, the intensity of C-O bonds is comparable to that of pristine GO (Figure 7.2b). The slightly increased intensity of C-C bonds (50.6%) could be attributed to the partial reduction of GO during the removal of carboxyl groups. Similarly, in the case of C/HGO, the peak intensities of C-O bonds (21.9%) and O-C=O bonds (0%) are decreased, whereas the intensities of C=O (9.4%) and C-C bonds (68.7%) are increased after the reaction (Figure 7.2c). The C 1s/O 1s atomic ratio of GO, DCGO and C/HGO is determined to be 2.0, 2.6 and 3.2, respectively, suggesting that the n-Butyllithium-promoted carbonylation/hydroxylation is more effective in removal of the O-containing groups on GO as compared with the chemoselective decarboxylation.

To gain more insight into the chemical composition of the as-obtained DCGO and C/HGO, FTIR, TGA, XRD and Raman spectroscopy were used to further probe their structural properties. Figure 7.2d shows the typical FTIR spectrum of GO, the adsorption bands at ~1730, ~1620 and ~1229 cm^{-1} , corresponding to the C=O, C=C and C-O stretching vibrations, respectively.^[191] While DCGO exhibits similar FTIR spectrum to that of GO, except for the decreased intensity of C=O bonds due to the chemoselective decarboxylation. Compared with GO and DCGO, C/HGO displays a different spectrum feature with clearly changed frequency and/or intensity of the oxygen functional groups. Specifically, the weak adsorption band at ~1716 cm^{-1} suggests the presence of new carbonyl species, which can be assigned to the stretching vibration of conjugated ketones.^[192] In addition, the C-O adsorption band illustrates an upshift with relative low intensity. The new adsorption bands at ~1596, ~1493 and ~1436 cm^{-1} are ascribed to the skeletal vibrational modes of the benzene ring from

graphene, while the peak at $\sim 860\text{ cm}^{-1}$ is due to the C-H bending vibration.^[193] These results are consistent with the XPS measurements, which distinctly document the successful fabrication of DCGO and C/HGO after the reactions.

Figure 7.2 The C 1s XPS spectra of (a) GO, (b) DCGO and (c) C/HGO. (d) FTIR spectra, (e) TGA curves and (f) XRD patterns of GO, DCGO and C/HGO.

Figure 7.3 Raman spectra of GO, DCGO and C/HGO.

Figure 7.2e shows the TGA curves of GO, DCGO and C/HGO. It can be observed that the thermal stability of DCGO and C/HGO was enhanced after the chemical manipulation of GO through the chemoselective decarboxylation and the n-

Butyllithium-promoted carbonylation/hydroxylation. All these materials have an initial mass loss even below 100 °C, attributable to the evaporation of water molecule trapped in the π -stacked graphene sheets.^[154] The rate of mass loss increased in the heating period of 100-200 °C is due to the decomposition of the labile O-containing functional groups, yielding CO, CO₂ and steam.^[189] However, compared to GO, the mass loss with temperature in the range of 100-200 °C for DCGO and C/HGO is significantly lower, and smaller mass loss are observed throughout the whole test, which suggest the partial removal of oxygen functional groups after the reactions. XRD patterns were used to further study the structural properties of these materials as shown in Figure 7.2f. The interlayer distance of DCGO and C/HGO is calculated to be 7.49 and 8.18 Å, respectively, much lower than that of GO precursor (8.85 Å). The decreased interlayer distance could be attributed to the partial removal of the oxygen functional groups on GO, which results in a weakened electrostatic repulsion between the graphene sheets, as confirmed by previous TGA and XPS analysis. Raman spectra of all these materials show two typical peaks, that is, defects or disorders induced D band at $\sim 1350\text{ cm}^{-1}$ and the tangential G band at $\sim 1600\text{ cm}^{-1}$ (Figure 7.3). Notably, the frequency of the D and G band in DCGO and C/HGO are very similar to that observed in GO. However, the I_D/I_G ratio of DCGO and C/HGO is slightly larger than that of GO, which could be assigned to the decrease in size of sp^2 domains and a partially ordered crystal structure after the chemical reactions.^[194]

As observed by previous studies, the FESEM image of GO shows a typical crumpled morphology (Figure 7.4a).^[195] In contrast, DCGO and C/HGO exhibit a thin and graphite-like structure due to the weakened electrostatic repulsion between the graphene sheets after partial removal of the oxygen functional groups (Figure 7.4b,c). Meanwhile, pore structures with several micrometers are also observed in the FESEM

images of DCGO and C/HGO, which are originated from the interconnected graphite-like structure. Such a feature is favorable for better access of the electrolyte, thus facilitating the rapid diffusion of Li ions from electrolyte to the electrode materials. Moreover, the electrolyte can also penetrate into the electrode materials due to the large interlayer distance of these materials (comparing to graphite) that caused by the intercalation of O-containing functional groups on the graphene sheets, as demonstrated by XRD patterns (Figure 7.2f). These characteristics can ensure fast Faradaic reaction of the electroactive functional groups with Li ions, especially at high charge/discharge rates. In addition, some small dots are observed in the FESEM image of DCGO, which may correspond to the silver-based nanoparticles during the chemoselective decarboxylation process. However, it has no deep influence on the final electrochemical performance of DCGO since Li insertion into silver is below 0.1 V (vs. Li/Li⁺).^[196] TEM was used to further investigate the morphology of C/HGO. As shown in Figure 7.4d, C/HGO exhibits a stacked layer structure (inset of Figure 7.4d) as appearing in the FESEM image. HRTEM image clearly indicates the recovery of graphitic carbon structures in C/HGO, which can act as the channels for electron transport, while the remaining C=O and -OH functional groups can serve as the Faradaic reactions centers for efficient Li storage.

Figure 7.5a and Figure 7.6a,b show the CV curves of the three samples. It can be seen that the DCGO and C/HGO electrodes show a reversible lithiation/delithiation process and better resolved CV peaks. Nevertheless, the reversibility of GO is quite poor due to the irreversible cleavage of the oxygen functional groups.^[20] In the initial cycle, a couple of redox peaks is observed at about 1.7/4.2 for DCGO and 1.8/4.2 for C/HGO, resulting from the lithiation/delithiation processes between Li ions and the carbonyl, hydroxyl and epoxy groups on the electrode materials.^[197] Obviously, the

cathodic peak of these two materials shifts to a higher potential at ~ 2.2 V in the following cycles, indicative of an improved reversibility of the electrochemical reactions upon cycling.^[198] Galvanostatic charge/discharge testing of these GO-based electrodes at various current densities with a voltage range from 1.5 to 4.5 V are shown in Figure 7.5b and Figure 7.6c,d. Notably, the discharge capacity of C/HGO is always higher than that of GO and DCGO electrodes under the same current density. For example, the average discharge capacity of C/HGO is 175 mAh g^{-1} at a current density of 100 mA g^{-1} (Figure 7.5c), while GO and DCGO electrodes show an average capacity of 55 and 107 mAh g^{-1} , respectively. Besides, C/HGO also exhibits a much larger capacity throughout the whole cycling testing. It is interesting to note that the capacity of GO and DCGO in the first cycle is comparable to C/HGO, then gradually decreased in the following few cycles, which might be derived from the irreversible cleavage of the oxygen functional groups, as demonstrated in the CV test.^[20, 197] The capacity increasing of DCGO after certain cycles could be attributed to the activating process of the electrode, which has been widely observed in carbon-based materials.^[120, 143] In contrast, C/HGO shows much improved cycling stability over 600 cycles, indicating the manipulation of the oxygen functional groups on GO is indeed an effective strategy to decrease the irreversible reactions of GO cathode while enabling high potential (vs. Li/Li^+) and significantly enhanced Li storage properties. On the other hand, the remarkably enhanced conductivity of C/HGO, demonstrated by XPS analysis and the EIS, can also be responsible for its higher capacity. As shown in Figure 7.7, the C/HGO electrode shows lower bulk resistance R_b (electrolyte resistance, contact resistance...) and lower charge transfer resistance R_{CT} ($\text{GO } (126.4 \text{ } \Omega) < \text{DCGO } (111.3 \text{ } \Omega) < \text{C/HGO } (70.9 \text{ } \Omega)$), as well as lower Warburg impedance Z_w , in comparison with GO and DCGO electrodes.

Figure 7.4 FESEM images of (a) GO, (b) DCGO and (c) C/HGO. (d) HRTEM image of C/HGO. Inset shows the TEM image of C/HGO. (e) Schematic illustration of the Faradaic reactions on the C/HGO electrodes.

Figure 7.5 (a) CV curves of C/HGO electrode at a scan rate of 0.2 mV s^{-1} . (b) Charge-discharge curves of C/HGO electrode at various current densities. (c) Cycling performance of GO, DCGO and C/HGO electrodes at a current density of 100 mA g^{-1} . (d) Cycling performance of C/HGO electrode at various current densities.

(d) Rate capability of C/HGO electrode at different rates.

Figure 7.6 CV curves of (a) GO and (b) DCGO electrodes at a scan rate of 0.2 mV s⁻¹. Charge-discharge curves of (c) GO and (d) DCGO electrodes at various current densities. Rate capability of (e) GO and (f) DCGO electrodes at different rates.

To further exploit the advantages of our method in tuning the cathodic performance of GO, rate performance of the as-obtained GO-based materials is investigated (Figure 7.5d and Figure 7.6e,f). It can be seen that, with respect to the reference GO cathode, the specific capacity of both DCGO and C/HGO is substantially increased at all investigated charge-discharge rates (100–800 mA g⁻¹). In particular, the

C/HGO cathode exhibits much superior rate performance with good capacity retention. The discharge capacity of C/HGO at a rate of 800 mA g^{-1} is as high as 84 mAh g^{-1} , which is almost twice that of GO electrode (45 mAh g^{-1}) and over three times of that of DCGO (24 mAh g^{-1}). Even after extended rate cycling at high rate measurements, the high capacity of C/HGO cathode can still be recovered to almost the initial value, suggesting its good reversibility. Note that, at the high current rates (400 and 800 mA g^{-1}), DCGO exhibits a lower capacity than that of GO, which can be ascribed to its long activating process as observed in the cycling test (Figure 7.5c).

Figure 7.7 Nyquist plots of GO, DCGO and C/HGO electrodes.

The increased capacity, long-term cycling stability and high rate capability of the C/HGO electrode are attributed to its novel structure. As illustrated in Figure 7.4d,e, the graphene framework of C/HGO can serve as channels for fast electron transport, whereas the remaining hydroxyl and carbonyl groups in C/HGO may act as the reservoirs for Li storage.^[198] The pores together with the enlarged interlayer distance can ensure easy contact of the electrode with the electrolyte, and shorten the diffusion length of Li ions, as well as fasten their diffusion from electrolyte to electrode. On the other hand, the much decreased oxygen content in C/HGO endows its high electrical

conductivity, which will provide a fast and efficient pathway for electron transfer between the active materials and the current collector. Comparing with other reported organic carbonyl compounds cathode materials, the excellent electrochemical performance of the C/HGO is attributed to (i) its insolubility in the electrolyte, (ii) good conductivity for electron transport, (iii) abundant hydroxyl and carbonyl groups for Li storage. With these merits, C/HGO could be a potential cathode material for high-performance energy storage applications.

7.4 Availability of all-carbon LIBs

To appraise the viability of all-carbon LIBs, prototype full-cell devices comprising the NPG-650 anodes and the C/HGO cathodes were built. The full cells were designed with a negative (anode) to positive (cathode) capacity ratio of ~ 1.5 . Prior to full-cell assembly, the anodes were discharged at 100 mA g^{-1} with half-cell configuration to fulfill lithiation, while the cathodes were cycled at 100 mA g^{-1} for 10 cycles to achieve stable Li storage capacity. Once these procedures were completed, the cells were disassembled inside the glovebox and then reassembled into full-cells using the lithiated NPG-650 and the cycled C/HGO as anodes and cathodes, respectively. The as-obtained full-cells were allowed to stand 2 hours to reach equilibrium before testing. Electrochemical tests were performed at a current rate of 100 mA g^{-1} in the voltage window between 0.01 and 4 V, and the specific capacities were calculated referring to the mass of C/HGO cathode. As shown in Figure 7. 8a,b, the cell is able to deliver a reversible and stable capacity of $\sim 78 \text{ mAh g}^{-1}$ with a coulombic efficiency of $\sim 99.8\%$ even after 100 cycles. The initial capacity decay in the first 10 cycles is probably attributed to the residual SEI film formation process. Excitingly, one cell, charged at 50 mA g^{-1} , has been successfully used to power 25 parallel-connected yellow light-

emitting diodes (LEDs) for more than 7 min (Fig. 7. 8c,d), highlighting the great availability of all-carbon LIBs for practical applications. We note that although the cycling stability of the cells is now not satisfactory, this can be potentially improved by refining the skill for full-cell fabrication and employing prelithiation technique, which have been marked as important aspects for future studies.

Figure 7.8 Electrochemical testing of all-carbon LIBs with full-cell configuration. Cycling performance (a) and the corresponding charge-discharge curves (b) of the cell at a current density of 100 mA g⁻¹. Photographs of 25 yellow LEDs with IAM pattern, powering by one cell, under light (c) and dark (d) conditions.

7.5 Summary

We have demonstrated that high-performance GO-based cathodes can be successfully fabricated via chemical engineering of GO. The effectiveness of this strategy is to chemoselectively remove the oxygen functional groups on GO, so as to construct highly conducting graphene framework bonded with electroactive functional groups for

reversible and fast Li storage. The novel structure of the obtained GO-based cathodes enables these materials being superior to the conventional inorganic intercalation cathodes, such as lithium transition metal oxides or phosphates. Especially, C/HGO cathode exhibits excellent electrochemical performance in terms of high capacity, good rate capability and cycling stability. Furthermore, prototype full-cell devices based on the NPG-650 anodes (reported in Chapter 5) and the C/HGO cathodes were built to successfully power LED lights, highlighting the great potential of functionalized graphene-based cathodes for future all-carbon LIBs. We believe that this chemical engineering strategy could be broadly applicable for the fabrication of other carbon-based cathodes for next-generation high-performance LIBs.

Chapter 8. Vat dye/Graphene Composites as Advanced Organic Cathodes for LIBs[†]

8.1 Introduction

Current LIB technology relies on the use of inorganic materials as the cathodes, however, the practical capacities of these insertion-type cathodes are normally limited to 200 mAh g⁻¹ associated with one electron reaction, which brings about a bottleneck for further breakthroughs in LIB performance.^[199, 200] In sharp contrast to inorganic cathodes, organic cathodes are capable of providing multi-electron reactions, thus leading to higher theoretical capacity.^[35] Meanwhile, organic cathodes have several distinctive advantages, such as low molecular weight, structural diversity and redox potential adjustment,^[123, 124, 201] and more strikingly, they could be directly extracted from biomass precursors and then recycled through photosynthesis, consequently making the concept of “green and sustainable” LIBs possible.^[187, 188]

In the pursuit of high-performance organic electrodes, organic carbonyl compounds containing single or multiple conjugated electrochemically active carbonyls have been overwhelmingly studied owing to their high capacity and intrinsically fast kinetics.^[202, 203] Each carbonyl can undergo a reversible one electron transfer reaction during charge and discharge processes, that is, one electron reduction to generate monoanion and thereafter one electron oxidation to convert back to carbonyl. Indeed, the exploration of carbonyl cathodes could be traced back to the early 1969,^[121] however, in most cases, these cathodes suffer from fast capacity decay due to their severe solubility in the electrolyte and poor rate capability arising from the low

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electrical conductivity. Aiming to tackle these issues, to date, diverse strategies including optimization of molecular structure,^[204-206] immobilization of carbonyl species on conducting matrix/substrates,^[207, 208] polymerization of small molecule carbonyls^[209-211] and employment of solid-state electrolytes^[212-214] have been proposed. Recently, it has been demonstrated that the construction of carbon-supported organic composites is another effective and intriguing approach for achieving advanced organic cathodes.^[122] As a result, a series of carbonyl/carbon composites with significantly improved electrochemical performances have been prepared by means of solution mixing,^[215] ball milling,^[216] impregnation,^[217] *in situ* polymerization,^[126] self-assembly^[218] and chemical vapor deposition^[219] methods. Despite these achievements, till now, it still remains a great challenge to prepare carbonyl/carbon composites with high and uniform quality on a large scale before their practical applications become possible. Note that the commercially available carbonyl products, for example, vat dyes, are desirable cathodes capable of mass production because they can now be readily obtained from plants or synthesized artificially.^[220] Nevertheless, to the best of our knowledge, vat dyes which are normally used for fabric dyeing have not been reported as the cathode for LIBs.

In this Chapter, for the first time we develop a universal method, that is, a combination of sonication and hydrothermal process, to scalable synthesis of vat dye/graphene composites as novel organic cathodes for high-performance LIBs. As a representative example of vat dyes, Vat Green 8 (molecular structure shown in Figure 8.1) is a green color dye containing a large condensed aromatic ring system with electroactive conjugated carbonyl groups, making it a perfect electrode for LIBs. We propose that the π - π interactions between Vat Green 8 and graphene sheets can afford a stable composite structure, which not only effectively suppresses the dissolution of

active material but also guarantees fast electron transportation during the electrochemical reactions. In this case, the aforementioned two common issues of organic electrodes could be simultaneously and effectively solved in our system. Consequently, the Vat Green 8/graphene (VG 8/G) composite exhibits long-term cyclic stability and excellent high-rate capability. This simple and elegant design has also been readily extended to fabricate Vat Brown BR/graphene (VB BR/G) and Vat Olive T/graphene (VO T/G) composites, both of which show exceptional electrochemical performance, verifying the universality of our method. Importantly, the present strategy provides a scalable route for developing advanced organic cathodes for LIBs, making a significant step forward to their practical applications.

8.2 Experiments

8.2.1 Preparation of VG 8/G composites

A precalculated amount (90, 180 and 360 mg) of Vat Green 8 (Xuzhou Kedah Fine Chemical Co., Ltd) was dispersed in 180 mL GO aqueous solution (2 mg mL^{-1}) under sustained sonication for 30 min. Then the resulting mixture was sealed in a 200 mL Teflon autoclave and heated at 180°C for 24 h. After the autoclave was naturally cooled down to room temperature, the formed hydrogel was taken out gently and rinsed with deionized water for several times to remove any impurities. Finally, the sample was freeze-dried in a freeze drying machine.

8.2.2 Preparation of other vat dye/graphene composites

VB BR/G and VO T/G composites were prepared under the same experimental parameters, except the change of Vat Green 8 to Vat Brown BR or Vat Olive T.

8.3 Results and discussion

Figure 8.1 depicts the scheme for the synthesis of VG 8/G composite. Briefly, Vat Green 8 was firstly dispersed into GO aqueous solution with different weight ratios under continuous sonication, which was then subjected to hydrothermal reaction and freeze-drying sequentially. The formation of VG 8/G hybrid architecture experiences the initial disassembly of Vat Green 8 crystal structure and the following reassembly on the graphene sheets through the π - π interactions between them.^[154] The resultant product was denoted as VG 8/G-X, where X represents the weight ratio of Vat Green 8 to GO.

Figure 8.1 Schematic illustration of the synthesis of VG 8/G composite, which was formed through the disassembly of Vat Green 8 crystal structure and then reassembly on the graphene sheets.

Figure 8.2a,b present the schematic structures of Vat Green 8 and VG 8/G composites for Li storage. Due to strong intermolecular interactions, Vat Green 8 alone tends to self-assemble into a stacking structure, resulting in greatly diminished accessible active sites and long diffusion length for Li ions. In contrast, when integrated with graphene, the aromatic Vat Green 8 molecules can absorb tightly on the surface of graphene sheets through π - π interactions, hence more desirable for Li storage in terms of better Li ions accessibility, shorter Li ions diffusion paths and higher electrical conductivity. FESEM images show that pristine Vat Green 8 is composed of micro-sized bulk particles due to the spontaneous stacking of molecules (Figure 8.2c), whereas the

bare hydrothermally reduced graphene oxide (HrGO, prepared through hydrothermal reduction of GO) exhibits an interconnected three dimensional porous network with randomly distributed pores that are consisted by graphene thin layers (Figure 8.3a). Interestingly, the VG 8/G composites display an appealing 3D graphite-like structure with Vat Green 8 molecules confined in between the graphene layers (Figure 8.2d and Figure 8.3b,c). Note that excess Vat Green 8 would generate bulk particles in the composite, as observed in the FESEM image of VG 8/G-1. The microstructure of the samples was further studied by TEM. The Vat Green 8 molecules show an asphaltum-like morphology with densely stacked structure (Figure 8.2e), while HrGO presents a smooth and transparent thin layer with wrinkled and folded edges (Figure 8.3d). However, after the incorporation of Vat Green 8 on the graphene sheets, VG 8/G-0.5 exhibits thick layers and rough surfaces (Figure 8.2f). Moreover, no evident bulk Vat Green 8 is viewed, indicating Vat Green 8 is well embedded in between the graphene layers. This is further confirmed by HRTEM images. As shown in the inset of Figure 8.2f, VG 8/G-0.5 reveals the presence of amorphous layers representing the absorbed Vat Green 8 molecules, which are not detected in bare HrGO (Inset of Figure 8.3d).

Figure 8.2 Schematic structures of (a) Vat Green 8 and (b) VG 8/G composites for Li storage. FESEM images of (c) Vat Green 8 and (d) VG 8/G-0.5. The insets are higher-magnification FESEM image of the corresponding samples. (e) TEM image of Vat

Green 8. Inset: higher-magnification TEM image. (f) TEM image of VG 8/G-0.5. Inset: HRTEM image of VG 8/G-0.5.

Figure 8.3 FESEM images of (a) HrGO, (b) VG 8/G-0.25 and (c) VG 8/G-1. The insets are higher-magnification FESEM image of the corresponding samples. (d) TEM image of HrGO. Inset: HRTEM image of HrGO.

XPS technique was applied to examine the elemental composition of the samples. Figure 8.4a shows the comparison of XPS survey spectra for GO and VG 8/G composites. The appearance of N 1s signal located at approximately 400 eV in VG 8/G composites yet not observed in GO suggests the existence of Vat Green 8 in the hybrids. The content of nitrogen increases from 1.29 at% in VG 8/G-0.25 to 1.38 at% in VG 8/G-0.5 and 2.14 at% in VG 8/G-1, indicating the increased amount of Vat Green 8 in the composite. Compared with GO, the VG 8/G composites exhibit substantially increased carbon content associated with considerably decreased oxygen content, which implies the efficient reduction of GO after the hydrothermal treatment. This is

further evidenced by high-resolution C 1s XPS spectra shown in Figure 8.4b. The deconvolution of GO displays four peaks correspond to C-C (sp^2 carbon, 284.6 eV), C-O (hydroxyl/epoxy groups, 286.7 eV), C=O (carbonyl groups, 288.1 eV) and O-C=O (carboxyl groups, 289.2 eV). In the spectra of VG 8/G composites, the oxygen functional species show significantly decreased intensity compared to that of GO, demonstrating the removal of O-containing groups with concomitant reconstruction of sp^2 carbon network. Besides, an additional peak located at 285.6 eV is detected, which originates from the C-N bonds of Vat Green 8 molecules. High-resolution N 1s XPS spectra of the VG 8/G composites (Figure 8.4c) exhibit a single predominant peak at about 399.9 eV, assignable to the pyrrole-like N atoms, which agrees well with the N bonding configuration in Vat Green 8. These results document that the chemical structure of Vat Green 8 is well-preserved in the VG 8/G composites. FTIR was also employed to analyze the structural information of the samples. As shown in Figure 8.5a, VG 8/G composites exhibit almost the same spectral features, e.g., peak position and peak intensity, as those of pristine Vat Green 8 molecules. Therefore, it can be concluded that the achievement of VG 8/G hybrid architecture is merely a physical process without any structural variations of Vat Green 8 molecules.

Figure 8.4 (a) XPS survey spectra and (b) high-resolution C 1s XPS spectra of GO, VG 8/G-0.25, VG 8/G-0.5 and VG 8/G-1. (c) High-resolution N 1s XPS spectra of VG 8/G-0.25, VG 8/G-0.5 and VG 8/G-1.

Further structural analyses of the samples are obtained by XRD, Raman spectroscopy and TGA characterizations. Figure 8.5b depicts the XRD patterns of Vat Green 8 before and after hybridization. The bulk Vat Green 8 particles display three characteristic diffraction peaks located at 11.2° , 18.9° and 26.1° , referring to the crystalline Vat Green 8 molecules. Interestingly, these peaks are not detected in the XRD patterns of VG 8/G-0.25 and VG 8/G-0.5, evidencing the disassembly of Vat Green 8 crystal associated with its reassembly on graphene sheets through π - π supramolecular interactions. However, excess Vat Green 8 precursor will induce the formation of bulk particles in the final composite. As a consequence, a diffraction peak at 11.2° which belongs to crystalline Vat Green 8 is observed in the XRD pattern of VG

8/G-1, corroborating previous FESEM results (Figure 8.3c). Besides, all the three VG 8/G composites show a predominant diffraction peak at about 25.5° , which should be ascribed to the (002) plane of HrGO. Compared with the sharp (002) peak of graphite at 26.5° (d spacing = $3.35 \text{ \AA}$), the VG 8/G composites display a relatively broad peak with a slightly larger d spacing of $3.49 \text{ \AA}$, which suggests their poorly ordered stacking due to the presence of Vat Green 8 molecules in between the graphene layers. Raman spectroscopy was used to probe the interaction between Vat Green 8 and graphene. As presented in Figure 8.5c, bare HrGO exhibits two typical peaks at 1340 and 1586 cm^{-1} , corresponding to the breathing mode of A_{1g} symmetry (D band) and E_{2g} vibration mode of sp^2 C atoms (G band), respectively. Meanwhile, VG 8/G composites show quite similar spectral feature as compared to HrGO, except for the G band down-shifted to 1576 cm^{-1} . Such a clear shift of G band to lower frequency highly supports the charge transfer from the aromatic Vat Green 8 molecules to graphene sheets,^[221, 222] indicating the strong π - π interactions between them.

Figure 8.5 (a) FTIR spectra of Vat Green 8 and VG 8/G composites. (b) XRD patterns of Vat Green 8, graphite and VG 8/G composites. (c) Raman spectra of HrGO and VG 8/G composites. (d) TGA curves of Vat Green 8 and VG 8/G composites.

8/G composites. (c) TGA curves of Vat Green 8 and VG 8/G composites under N_2 atmosphere.

Table 8.1 Elemental content of Vat Green 8 and VG 8/G composites obtained from elemental analysis. Each sample was tested twice, and the standard deviation for N content was determined to be < 0.14 wt%.

Sample	N (wt%)	C (wt%)	H (wt%)
Vat Green 8	3.35	62.03	4.01
VG 8/G-0.25	1.03	75.37	1.81
VG 8/G-0.5	1.57	74.69	1.98
VG 8/G-1	2.02	72.49	2.61

TGA curves reveal that both Vat Green 8 and VG 8/G composites have good thermal stability up to over 300 °C (Figure 8.5d). All of the samples illustrate an initial weight loss of about 4.5% at temperature below 150 °C, attributable to the removal of physically adsorbed water. The samples are relatively stable at temperatures ranging from 150 to 300 °C. After that, a continuous and steady weight loss is observed with temperature increases from 300 to 800 °C due to the carbonization of Vat Green 8. To determine the content of Vat Green 8 in the composites, the samples are further characterized by elemental analysis (Table 8.1). The measured N contents in Vat Green 8, VG 8/G-0.25, VG 8/G-0.5 and VG 8/G-1 are 3.35 wt%, 1.03 wt%, 1.57 wt% and 2.02 wt%, respectively. Therefore, the content of Vat Green 8 is calculated to be 31.6 wt% in VG 8/G-0.25, 46.6 wt% in VG 8/G-0.5 and 60.3 wt% in VG 8/G-1.

The electrochemical performances of VG 8/G composites as cathodes for LIBs were evaluated using traditional CR 2032 coin-type cells with pure Li metal foils as the anodes. For comparison, the commercial Vat Green 8 is also tested under the same conditions. All the cells were pre-cycled at 10 mA g⁻¹ for 10 cycles for activation before loaded to the test instrument. Figure 8.6a shows the electrochemical Li storage

mechanism of a single VG 8/G unit, which involves multistep reduction of the conjugated carbonyl groups in Vat Green 8 molecule during discharge process and then reoxidation of the as-formed alkoxide groups in the subsequent charge process.^[122, 123] The presence of graphene can efficiently facilitate charge transfer, leading to increased kinetics of electrochemical reactions. CV curves of different electrodes tested at 0.5 mV s⁻¹ in the voltage range between 1.2 and 4.2 V (vs. Li/Li⁺) are presented in Figure 8.6b. Evidently, all the VG 8/G composites exhibits significantly improved gravimetric current compared to that of Vat Green 8. The low current density should be attributed to its low electrical conductivity and the densely stacked structure, which induce limited accessibility to the electrolyte. After the disassembly and reassembly hybridization processes, these problems have been well addressed in the VG 8/G composites. With increasing the content of Vat Green 8 from ~32 wt% (VG 8/G-0.25) to ~47 wt% (VG 8/G-0.5) in the composite, the current density of VG 8/G composites exhibits an obvious increase trend. However, a dramatic decay of current density is observed when the value reaches ~60 wt% (VG 8/G-1), due to the formation of bulk Vat Green 8 particles in the composite, as demonstrated by previous FESEM images. A pair of redox peaks at around 2.14 and 2.46 V correspond to the reduction of the conjugated carbonyl groups and reoxidation of the alkoxide groups, respectively. This matches well with the scheme shown in Figure 8.6a. The relative broad peaks are probably caused by the multistep reaction processes,^[212, 213] which can also be identified by the charge-discharge voltage profiles without obvious plateaus (Figure 8.6c).

Figure 8.6 (a) Electrochemical Li storage mechanism of a single VG 8/G unit. (b) CV curves of different electrodes tested at 0.5 mV s^{-1} . (c) Charge-discharge voltage profiles of VG 8/G-0.5 electrode under various current rates. (d) Cycling performance of different electrodes measured at 100 mA g^{-1} . (e) Rate performance of different electrodes under various current rates.

Galvanostatic cycling tests of the electrodes are measured at 100 mA g^{-1} for 200 cycles (Figure 8.6d). It is predictable that the Vat Green 8 would exhibit poor Li storage behavior in terms of low capacity and fast capacity fading. The discharge capacity is as

low as 9 mAh g⁻¹ in the first cycle and decreased to 2 mAh g⁻¹ after 200 cycles. On the contrary, the Li storage capacity and cyclic stability of VG 8/G composites have been extremely improved after immobilization of Vat Green 8 on the graphene sheets. The initial discharge capacities for VG 8/G-0.25, VG 8/G-0.5 and VG 8/G-1 are up to ~240, ~272 and ~121 mAh g⁻¹, respectively, which maintain at ~223, ~319 and ~153 mAh g⁻¹ after 200 cycles. These values are definitely superior to previously reported organic cathodes,^[223, 224] functionalized carbon-based cathodes^[116] and even some organic/carbon hybrid cathodes.^[126, 215] The slight increase of capacity upon cycling observed in VG 8/G-0.5 and VG 8/G-1 might be ascribed to the delayed electrolyte infiltration into the electrodes.^[128] With continuous charge-discharge processes, Li ions could gradually go into the inner deep regions of the electrodes, leading to more available active sites for Li storage and hence a progressively raised capacity. To further examine their rate capability, the electrodes are tested under programmed current densities from 50 to 3200 mA g⁻¹ (Figure 8.6e). It can be seen that the capacities of VG 8/G composites are consistently higher than those of Vat Green 8 throughout the whole rate cycles. In particular, the VG 8/G-0.5 electrode still shows the best rate performance with respect to other electrodes (VG 8/G-0.25, VG 8/G-1), which should be related to its moderate loading content of the electrochemically active Vat Green 8 associated with the as-formed peculiar nanostructure (see previous discussions). The capacities of VG 8/G-0.5 electrode obtained at 50, 100, 200, 400, 800, 1600 and 3200 mA g⁻¹ are ~330, ~274, ~216, ~172, ~135, ~107 and ~74 mAh g⁻¹, respectively. More strikingly, the capacity of VG 8/G-0.5 electrode is capable of gradual recovery to ~332 mAh g⁻¹ with the current density switched back to 50 mA g⁻¹ after being tested at varied current densities, indicating its excellent rate capability.

Figure 8.7 (a) Nyquist plots of the Vat Green 8, VG 8/G-0.25, VG 8/G-0.5 and VG 8/G-1 electrodes. The brown, green and pink arrows refer to the R_b , R_{sf} and R_{ct} , respectively. (b) The equivalent circuit model used for fitting the EIS, and (c) the fitting results for different electrodes.

To evaluate the kinetics of electrochemical reactions on the electrode, EIS was carried out in the frequency range of 100 kHz to 0.1 Hz. As shown in Figure 8.7a, the Nyquist plots of all the samples possess the same features with two semicircles in the high-to-medium frequency range and a tail (short inclined line) in the low frequency range, which can be successively assigned to the surface film impedances (R_{sf}) due to the SEI formation, charge transfer resistance (R_{ct}) and Warburg impedance.^[225] The simulated values of EIS by using the equivalent circuit model (Figure 8.7b) are summarized in Figure 8.7c for better comparison. It can be seen that all the electrodes show comparable bulk resistance (R_b) that is related to the electrolyte and contact resistances. Nonetheless, the electrode of VG 8/G composites show substantially lower R_{sf} and R_{ct} compared to Vat Green 8, as reflected by the smaller semicircle at both high and middle frequency ranges in the Nyquist plots, demonstrating the enhanced kinetics of Li ions migration through the SEI film and faster charge transfer reaction. Meanwhile,

the short inclined lines with larger phase angles at low frequency region suggest lower Warburg impedance in VG 8/G composites, which represents the diffusion of Li ions within the electrodes. As discussed in Figure 8.2a, in the crystalline Vat Green 8 electrode, Li ions need to diffuse only along the intermolecular space to the entire electrode due to its stacked structure with limited exposure to the electrolyte. In sharp contrast, the disassembled Vat Green 8 molecules are anchored on graphene layers, thus more readily accessible to Li ions with shorter Li ion diffusion paths (Figure 8.2b). The above results exclusively identify the significantly improved electrochemical properties of VG 8/G composites over Vat Green 8 cathode. Such exceptional performances in terms of high capacity, long cyclic life and outstanding rate capability mainly arise from the synergistic effects between Vat Green 8 molecules and graphene: firstly, the Vat Green 8 with substantial conjugated carbonyl groups primarily contributes to the Li storage capacity, whereas graphene with high electrical conductivity benefits the electron transfer. Secondly, the strong π - π interactions between Vat Green 8 and graphene sheets can effectively suppress the dissolution of Vat Green 8 into the electrolyte, thus guaranteeing high capacity retention. Thirdly, the immobilization of disassembled Vat Green 8 molecules on graphene sheets facilitates easy accessibility of Li ions to the electrode and accordingly ensures more active sites for Li storage with shorter Li ion diffusion paths. Finally, the remaining oxygen functional groups on graphene can also contribute to the high Li storage capacity through surface redox reactions with Li ions.

Figure 8.8 FESEM images of (a) Vat Brown BR, (b) VB BR/G-0.25, (c) VB BR/G-0.5, (d) VB BR/G-1, (e) Vat Olive T, (f) VO T/G-0.25, (g) VO T/G-0.5 and (h) VO T/G-1. The insets are higher-magnification FESEM image of the corresponding samples. The molecular structure of Vat Brown BR and Vat Olive T is shown in (a) and (e), respectively.

Besides VG 8/G, our method has also been successfully applied to fabricate other vat dye/graphene composites, such as VB BR/G and VO T/G. The corresponding FESEM images (Figure 8.8) reveal their morphologies are similar to those of VG 8/G composites. Specifically, the vat dyes are confined in the graphene layers when the weight ratio of vat dye to GO is 0.25 and 0.5; however, bulk particles are observed when the value is increased to 1. Thanks to the smart design and unique architectures, both composites manifest distinguished electrochemical performances when used as the cathodes for LIBs (Figure 8.9 and Figure 8.10). For example, pure Vat Brown BR and Vat Olive T do not have any electrochemical activities for Li storage with extremely low capacities ($<10 \text{ mAh g}^{-1}$); whereas the VB BR/G and VO T/G composites display unexpectedly high Li storage capacities and particularly impressive rate capabilities. Especially, the VB BR/G-0.5 electrode delivers a high capacity of $\sim 270 \text{ mAh g}^{-1}$ at a current density of 100 mA g^{-1} with no capacity fading after 200 continuous charge/discharge cycles, and meanwhile, a capacity of $\sim 41 \text{ mAh g}^{-1}$ is still retained at a

high current density of 3200 mA g^{-1} . In addition, the VO T/G-0.5 electrode also shows a high capacity of $\sim 240 \text{ mAh g}^{-1}$ at 100 mA g^{-1} and good capacity retention at high charge rate ($\sim 48 \text{ mAh g}^{-1}$ at 3200 mA g^{-1}). These fascinating results highlight the applicability of our approach for other aromatic vat dyes towards low-cost and large-scale fabrication of high performance organic-based cathodes.

Figure 8.9 (a) Electrochemical Li storage mechanism of a single VB BR/G unit. (b) CV curves of different electrodes tested at 0.5 mV s^{-1} . (c) Charge-discharge voltage profiles of VB BR/G-0.5 electrode under various current rates. (d) Cycling performance of

different electrodes measured at 100 mA g^{-1} . (e) Rate performance of different electrodes under various current rates.

Figure 8.10 (a) Electrochemical Li storage mechanism of a single VO T/G unit. (b) CV curves of different electrodes tested at 0.5 mV s^{-1} . (c) Charge-discharge voltage profiles of VO T/G-0.5 electrode under various current rates. (d) Cycling performance of different electrodes measured at 100 mA g^{-1} . (e) Rate performance of different electrodes under various current rates.

8.4 Summary

In summary, we have successfully developed a simple, universal and scalable strategy

to prepare the vat dye/graphene composite cathodes for LIBs. The hybridization process involves the disassembly of commercialized vat dye crystals along with their reassembly onto the graphene sheets by π - π supramolecular interactions. With this design, the accessibility of electrochemically active vat dye molecules to Li ions could be significantly enhanced, and meanwhile, their dissolution into the electrolyte could be effectively restrained. Furthermore, the unique structure is also beneficial for efficient electron transfer and shortens the Li ion diffusion length. As a proof-of-concept demonstration, several types of vat dye/graphene composites, namely, VG 8/G, VB BR/G and VO T/G, have been applied as cathodes for LIBs, which all exhibit excellent electrochemical performance with high Li storage capacity, good capacity retention and advanced rate capability. Among them, VG 8/G-0.5 shows the best performance with a capacity of $\sim 272 \text{ mAh g}^{-1}$ without any decay upon 200 consecutive cycles (at a current density of 100 mA g^{-1}) and superior rate performance ($\sim 74 \text{ mAh g}^{-1}$ at 3200 mA g^{-1}). It is believed that this work provides a facile and effective approach for engineering organic cathodes towards high-performance Li storage, and more meaningfully opens up new horizons in developing a versatile and cost-effective platform for large-scalable fabrication of advanced organic-based electrode materials for practical use.

Chapter 9. Conclusions and Outlook

9.1 Conclusions

Graphene holds a great potential in application as the electrode for next-generation LIBs by virtue of its notable physicochemical properties with 2D geometrical structure, high theoretical Li storage capacity (744 mAh g^{-1} , twice that of the current graphite anode), as well as its naturally abundant graphite precursor. Given that the Li storage properties of graphene are closely related to its structure (e.g., interlayer spacing and disorder degree), morphology and surface functional groups, post-functionalization offers a versatile route to tune its electrochemical performance so as to bridge the gap towards practical application. This thesis presents diverse chemical approaches to engineering the microstructure and morphology of graphene, and to build graphene derivatives with better electrochemical performance. A series of functionalized graphene-based materials have been obtained, and their application as the electrode materials, including both anode and cathode, for LIBs have been evaluated. The main findings from these studies are summarized as follows:

In Chapter 4, we adopted an organic functionalization enabled codoping strategy to fabricate N- and S-codoped graphene. The functional groups containing both N and S atoms were firstly covalently bonded to graphene, which can effectively prevent graphene sheets from restacking during reduction. With a subsequent annealing treatment, these functional groups will be decomposed and then N and S atoms are successfully incorporated into the carbon network with a doping level of 1.76 at% and 0.86 at%, respectively. Meanwhile, the decomposition of the functional groups also induces wrinkles and folds in graphene sheets, and their random aggregation generates

a 3D interconnected network for fast electron/ion transport. As a consequence, the unique thin-layer structure of graphene and the synergistic effects of the N and S codopants confer an exceptional Li storage performance, including large reversible specific capacity, long-cyclic behavior and superb rate capability.

Aside from that, in Chapter 5, using a N-containing organic supramolecule, melamine cyanurate (MC), as the template, we successfully fabricated N-doped porous graphene (12 at% based on XPS analysis). The polymer, synthesized via hydrogen bond induced supramolecular polymerization between melamine and cyanuric acid, has multifunctions in promoting the formation of the final product. On one hand, MC acts as the spacer to prevent graphene sheets from aggregation during polymerization. On the other hand, under thermal treatment, MC serves as both N source and pore agent by virtue of complete decomposition and release a myriad of N-containing gases, consequently leading to high N doping level while achieving rich porosity at the same time. With the merits of loosely-packed porous structure and high N doping content, the obtained graphene anode shows a stable capacity of 900 mAh g⁻¹ within 150 cycles. Considering the low-cost and scalable features of this approach, this material holds the potential of large-scale production for a wide range of applications.

Chapter 6 presents a facile one-pot route for the synthesis of SnO₂/graphene hybrid, which is based on the redox reaction between GO and Sn²⁺. We noted that surfactant plays a vital role in determining the uniformity of SnO₂ nanoparticles, including both the sizes and their distribution on graphene sheets. With the help of surfactant, SnO₂ nanoparticles with a supersmall size of ~5 nm are homogeneously encapsulated in the graphene layers; while the sizes and distribution of the particles are random in the case without surfactant. The mechanism of such a phenomenon was proposed, and the influence of weight ratio between Sn²⁺ and GO on the properties, i.e., morphology,

structure and electrochemical performance, of the as-obtained hybrids was studied as well. Based on our findings, the composite with 24 wt% content of graphene shows the best Li storage behaviors, such as large specific capacity ($>1100 \text{ mAh g}^{-1}$ at 100 mA g^{-1}), long-cyclic performance (87.5% retention after 120 cycles) and distinctive rate capability ($>680 \text{ mAh g}^{-1}$ at 3200 mA g^{-1}).

In order to broaden the application of graphene for LIBs, in Chapter 7, we developed two chemical methodologies for the manipulation of oxygen functional groups on GO. In this study, we aim to probe the electrochemical performance of GO as the positive electrode for LIBs. Decarboxylated GO (DCGO) was prepared through chemoselective decarboxylation of GO, while carbonylated/hydroxylated GO (C/HGO) was fabricated by n-Butyllithium-promoted carbonylation/hydroxylation of GO. We demonstrated that the engineering of O-containing functional groups is an effective pathway to upgrade the Li storage properties of GO because of the significantly increased conductivity and decreased irreversible reactions between the oxygen functional groups and Li ions in the resultant products. Specifically, C/HGO with recovered sp^2 network for fast electron transport and rich electroactive carbonyl/hydroxyl groups for Li storage illustrates exceptional electrochemical behavior, in terms of stable cycling performance (600 cycles without notable capacity decay), large average discharge capacity ($\sim 180 \text{ mAh g}^{-1}$ at 100 mA g^{-1}) and good rate capability ($\sim 80 \text{ mAh g}^{-1}$ at 800 mA g^{-1}), suggesting its potential application in advanced LIBs.

With the goal of exploring high-performance organic cathodes that capable of scalable production, in Chapter 8, we developed a universal method, i.e., sonication combined with hydrothermal treatment, for constructing vat dye/graphene hybrids for LIBs. Vat dyes are commercially available products that mainly employed for fabric

dyeing, while these molecules also contain rich electrochemically active carbonyl groups, making them potential application as the cathodes for LIBs. However, both low electrical conductivity and their stacked bulk structure stemming from the strong intermolecular interactions are disadvantages for electrochemical reactions. Our proposed technique involves the disassembly of vat dye associated with its subsequent reassembly on graphene layer to form a compatible hybrid. Thanks to the strong π - π interactions between the vat dye and graphene, the obtained composites display remarkably increased conductivity, and shorten Li ion diffusion length, as well as improved accessibility of the electrolyte. As a consequence, a series of vat dye/graphene hybrids, including Vat Green 8/graphene, Vat Brown BR/graphene and Vat Olive T/graphene, were prepared, and their cathodic performance for LIBs was also investigated. Correspondingly, the composites all present outstanding electrochemical behaviors, for example, stable Li storage capacity, advanced rate capability and long-cyclic lifespan. The electrochemical characteristics of our fabricated functionalized graphene together with the commercial cathodes have been summarized in Table 9.1 for better comparison. Our success in this work provide a cost-effective platform for engineering the electrochemical performance of commercially available products for LIBs, and must be interested to those who works on exploring advanced organic cathodes for practical applications.

Table 9.1 *Electrochemical characteristics of our functionalized graphene cathodes in comparison with the conventional inorganic cathodes.*

Classification	Compound	Capacity (mAh g ⁻¹)	Potential (V vs. Li/Li ⁺)
Inorganics	LiCoO ₂	~270	~4.2
	LiMn ₂ O ₄	~150	~4.1
	LiFePO ₄	~170	~3.4
Organics	C/HGO	~180	~4.2

VG 8/G-0.5	~330	~2.5
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9.2 Outlook

This thesis, together with the other interesting works that summarized in Chapter 2, has demonstrated the significant improvement in upgrading the electrochemical performance of graphene through post-functionalization. These materials greatly enrich the families of graphene, and expand its application from anode to cathode in a LIB. Despite these exciting achievements, the cost of graphene-based materials still cannot compete with the existing materials. Further works on functionalized graphene that capable of mass production with low cost for advanced battery technologies are still required. This will significantly decrease the gap between fundamental research and practical applications. Some interesting topics that could be considered for future studies have been proposed.

1. Since heteroatom doping induced defect sites contribute a lot to the eventual Li storage capacity of graphene, the introduction of codoping or multidoping could be more beneficial for boosting the electrochemical performance. Principally, the synergistic effects between the dopants, even with a low doping level, are able to generate new/more electroactive sites for Li accommodation in comparison with single atom doping, as demonstrated in Chapter 4. Meanwhile, codoping or multidoping is much easier and energetically favourable, as compared to the increase of doping concentration for the cases of single-doping. Aside from heteroatom doping, the introduction of metal atom doping can also induce similar positive effects on improving the electrochemical performance of graphene. However, to date, this research field is still very young, and is only limited to theoretical calculations.^[226-228] It could be very interesting to follow further

- experimental progress in fabricating metal-doped graphene for LIB application.
2. In addition to blindly increase the heteroatom doping level in graphene, the investigation of heteroatom with well-defined chemical status could be more meaningful since the Li storage properties are closely to the configuration of the heteroatoms. Taking N doping as an example, pyridine-like N are much more favourable for Li storage with respect to pyrrole-like N and graphite-like N, because of its lower barrier for Li diffusion/desorption and stronger binding for Li. However, so far, researches related to the construction of N-doped graphene with pure pyridinic N configuration have rarely been reported,^[229, 230] let alone their applications in LIBs.
 3. In view of the electrochemical performance of graphene is determined by both of its microstructure and morphology, the combination of structural and morphological engineering well satisfies the criteria for designing advanced electrodes towards electrochemical applications. As demonstrated in Chapter 5, the porous structure of graphene greatly suppresses the aggregation of graphene sheets, whereas N doping induces additional active sites for Li storage. Therefore, similar strategies toward the preparation of functionalized graphene-based materials with high Li storage properties are expected, in particular, they may potentially enable mass production with low cost.
 4. Compared with their organic cathodes counterparts, functionalized graphene has the advantages of better electrolyte durability and higher conductivity for LIB application. Therefore, it is essential to modulate the electroactive groups on graphene so as to achieve high-performance cathodes with fast electron transport channels, and at the same time with rich Li storage functional groups. For example, developing novel strategies that capable of precisely controlling the oxygen

functional groups on GO could enable the possibility to systematic investigation its cathodic performance and the associated Li storage mechanisms. Correspondingly, methodologies with the ability to finely tune the oxygen functional groups on GO are also beneficial.

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