Functional metal oxide based heterostructures : design, synthesis and application to electrochemical energy storage

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**NANYANG
TECHNOLOGICAL
UNIVERSITY**

**FUNCTIONAL METAL OXIDE BASED
HETEROSTRUCTURES: DESIGN, SYNTHESIS AND
APPLICATION TO ELECTROCHEMICAL ENERGY
STORAGE**

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SCHOOL OF PHYSICAL AND MATHEMATICAL SCIENCES

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Summary

One sparkling success of current nanoscale science and technology is reflected in the improving capability of engineering individual units and their spatial arrangements of functional materials and devices down to nanometer level. Integrating different nanocrystals with distinct properties into a single subject represents a promising way to achieve this goal. In this thesis, we have designed and prepared various metal oxide based heterostructures for electrochemical energy storage devices.

SnO_2 and Fe_2O_3 , two of the most studied functional semiconductors, have been widely applied in photocatalytic degradation, gas sensing and lithium-ion batteries (LIBs). Recently, many studies have revealed that the physical performances of SnO_2 or Fe_2O_3 can be remarkably improved by forming $\text{Fe}_2\text{O}_3/\text{SnO}_2$ heterostructures. Inspired by this, we have developed two types of novel heterostructures by incorporating SnO_2 and Fe_2O_3 as building blocks, and investigated their corresponding lithium storage performance. The first example is based on grafting 1D SnO_2 nanorods onto both sides of pre-grown 2D Fe_2O_3 nanoflakes, forming a comb-like branched heterostructure. The overall synthetic procedure involves only two steps: direct heating the Fe foil in air for the preparation of Fe_2O_3 nanoflake stems, and the subsequent hydrothermal epitaxial growth of SnO_2 nanorod branches. The other type of novel branched $\alpha\text{-Fe}_2\text{O}_3/\text{SnO}_2$ heterostructure with six-fold-symmetry is prepared by combining a vapor transport deposition and a facile hydrothermal method. While the tree-like branched structures have been reported previously, to our knowledge, it is the first report on the synthesis of high-symmetry branched heterostructures where

the SnO₂ core nanowires are surrounded by ordered α -Fe₂O₃ nanorod branches. When such composite SnO₂/Fe₂O₃ heterostructures are tested as LIB anodes, an enhanced electrochemical performance compared to individual components is obtained, which can be ascribed to the unique 3D structure and the synergistic effects induced by both constituents.

In addition to pure metal oxides, graphene, a hot spot in current research field, is also introduced as a component for constituting new heterostructures. We demonstrate a simple, efficient yet versatile method for the realization of core-shell assembly of graphene around various metal oxide nanostructures, including nanowires and nanoparticles. The process is driven by (i) the ring-opening reaction between the epoxy groups and amine groups in graphene oxide (GO) platelets and amine-modified metal oxide nanostructures, respectively, and (ii) electrostatic interaction between these two components. Nearly every single nanowire or nanoparticle is observed to be wrapped by graphene. As an example of the functional properties of these compound materials, the graphene@ α -Fe₂O₃ core-shell nanoparticles are investigated as the LIB electrode materials, which show high reversible capacity, improved cycling stability and excellent rate capability with respect to pristine α -Fe₂O₃. The superior performance of the composite electrode is presumably attributed to the effectiveness of the graphene shell in preventing the aggregation, buffering the volume change, maintaining the integrity of nanoparticles, as well as improving the conductivity of the electrode.

We have devised an innovative hybridization mode between graphene and metal oxides by integrating the reduced graphene oxide (r-GO) platelets into the Co₃O₄ scrolls. Our strategy is assisted by the lamellar micelles of the surfactant and

subsequent post-annealing. Rather than serving as the supporting substrates for guest materials in most cases, r-GO platelets are incorporated into nearly every single Co_3O_4 scroll and believed to link with Co_3O_4 through the residual oxygen functional groups on their basal planes and the edges. This assembly enables almost every single Co_3O_4 scroll to connect with the r-GO platelets, leading thus to remarkable electrochemical performances in terms of high specific capacitance and good rate capability.

In all, the increase in the degree of structural and compositional complexity on the nanoscale represents one of the major advances in materials science towards more controlled fabrication and function improvement.

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Chapter 1

Introduction

1.1 Heterostructure: A Route toward Multifunctionality

Heterostructure materials have been simplistically defined as “systems in which materials of different compositions meet at interfaces”.¹ Despite comprising a relatively new area of materials science, they have already attracted immense attention due to their outstanding physical/chemical properties and high tailorability in terms of composition, morphology and structure. Many new concepts have been put forward for controlling the synthesis of such heterostructure materials as metal-metal junctions,² metal-semiconductor junctions,³ inorganic semiconductor junctions,⁴ organic-inorganic materials junctions,⁵ semiconductor-carbon nanotube junctions,⁶ etc. More recently, with the emerging and arising of graphene, many graphene and its derivatives based heterostructures have raised the tide of a research reform.⁷⁻⁹ Future design and development of materials with defined functions are expected to be greatly guided by the fabrication of such heterostructures.

1.1.1 Motivation to Grow Heterostructure

In the science and engineering community, the nanoscience revolution is proceeding in an unprecedented rate. The ability of tailoring the dimensional-morphological regime of nanocrystals symbolizes a landmark achievement in nanoscience, since both size and shape dictate the peculiar chemical-physical properties (such as optical, electrical and catalytic) of materials at the nanoscale.¹⁰⁻¹² Given that it is at times desirable for single nanomaterial to perform multiple

technological tasks simultaneously, multicomponent nanomaterials thus come into play as a new pathway in the manipulation of properties of nanomaterials. Researchers hope to devise multicomponent nanostructures and dig out their inbuilt multifunctionality for use in many novel applications. As a matter of fact, in the realm of nanostructures, achievements have already been made in the construction of many kinds of architectures such as core-shell nanostructures,¹³ branched nanostructures,¹⁴ as well as segmented nanostructures¹⁵ consisting of domains of different materials. In these structures, an increasing degree of complexity, and thereby of functionality, is being attained as multiple materials are grouped together in a programmed manner. For instance, luminescence nanoparticles are widely adopted for bio-detection and bio-sensing,¹⁶ while magnetic nanoparticles are very popular for targeted drug delivery, magnetic bio-separation and detection.¹⁷⁻¹⁸ The combination of fluorescence and magnetism into a single nanoprobe would be naturally more profitable, and can be achieved, in a relatively more convenient way, by the fabrication of hybrid nanostructure through colloidal synthesis. In such a protocol, each nanocrystal could be made of any desired materials deliberately assembled together for tailored applications in principle. Moreover, in this case, the control of the topology of the resulting nanostructure is allowed, enabling each of its components to maintain the same properties as those in the isolated material. In some cases, besides merging the properties of individual components, heterostructures could also generate novel or improved properties relative to those of individual units arising from the processes that occur at the interface between the components, thereby realizing synergistic performance (“more than the sum of its parts”).¹⁹⁻²² As can be concluded from above, for these heterostructure materials, the high tailorability and the multifunctionality are two of their most appealing characteristics. The realization of well-defined

heterostructures is generating great interest because of their unique features and potential applications.

1.1.2 Synthesis of Heterostructure

As of today, numerous techniques exist for fabricating heterostructures of diverse components and shapes. We will outline briefly in what follows some most popular and effective approaches, including solution-phase methods, vapor-phase methods and template-directed synthesis.

1.1.2.1 Solution-Phase Methods

Among various synthetic methodologies, solution-phase methods have been particularly acknowledged due to their capability to produce a variety of heterostructures and the fact that they allow a wide range of control over the size and shape with sub-nanometer level accuracy by elegant modulation of the thermodynamic parameters and growth kinetics in solution.²³⁻²⁵

In one of the most successful solution-phase methods, the so-called hydrothermal/solvothermal technique, the chemical reactions are usually carried out in a sealed vessel, in which the temperature of the solvent can be increased well above their boiling points due to the increase of autogenous pressure originating from heating.²⁶ Depending on the solvent is aqueous or not, this process can be classified into hydrothermal (using water as the solvent) and solvothermal (using non-aqueous solvents) processes. Both can provide an excellent possibility for processing of advanced materials regardless of they are bulk single crystals, fine particles or nanoparticles.²⁶⁻²⁷ So far, there are many reports available on producing heterostructures via hydrothermal/solvothermal method.^{19, 28-30} For example, Yan and co-workers solvothermally assembled SnO₂ nanorod arrays onto the surface of α -

Fe_2O_3 nanotubes in a reverse microemulsion system containing heptane, hexanol, sodium dodecylsulfate (SDS) and $\text{Sn}(\text{OH})_6^{2-}$.³¹ The formation process can be schematically illustrated in Figure 1.1(a). Here, the $\alpha\text{-Fe}_2\text{O}_3$ nanotubes were first synthesized by a hydrothermal method, which involved a “coordination-assisted dissolution” process.³² Induced by the hexagonal geometry of preformed $\alpha\text{-Fe}_2\text{O}_3$ nanotubes, the resulting heterostructures were of six-fold symmetry (Figure 1.1b), in which the secondary SnO_2 nanorods grow along $[101]$ direction (Figure 1.1c). As is well-known, (001) is the highest energy plane for rutile SnO_2 , the varied growth from it had been proved the result of decreasing the interfacial lattice mismatch, and therefore lowered the heteronucleation energy barrier. Meanwhile, the author had elucidated that the length of the SnO_2 nanorods could be easily adjusted by modulating the reaction time, implying the advantages of high controllability of solution-phase method. Later, Wang et al. refined this approach by replacing the poisonous organic solvents with environmentally friendly water and verified the determinative role of the least lattice mismatch in governing the growth behaviour of the secondary phase.²²

Figure 1.1 (a) Schematic formation process of the $\alpha\text{-Fe}_2\text{O}_3/\text{SnO}_2$ composite. (b) SEM image of $\alpha\text{-Fe}_2\text{O}_3/\text{SnO}_2$ hierarchical nanostructure, inset reveals the 6-fold symmetry of the branches clearly. (c) HRTEM image recorded from the interface between $\alpha\text{-Fe}_2\text{O}_3$ nanotube core and SnO_2 nanorod branch, indicating the $[101]$ growth direction of the SnO_2 branch.³¹

In addition to the hydrothermal/solvothermal technique, there are many other established chemical protocols to fabricate heterostructures involving the crystallization of solution-phase precursors.²³⁻²⁵ Often, the assistance of selected solvents, ligands, surfactants or catalysts is required. As an example, Alivisatos and co-workers demonstrated a general approach for coupling colloidal quantum dots and rods into branched or linear junctions by elegant manipulation of solution precursors.³³ In all cases, the cation and anion precursors were prepared by complexing Cd oxide with alkylphosphonic acids and dissolving Se, S or Te in tri(n-alkylphosphine), respectively. The reaction was triggered by injecting the anion precursor into the cation precursor at elevated temperature. Linear junction could be formed by simply altering the precursor anions during preparation. Alternatively, branched junctions were generated preferentially at high supersaturation of these precursors. Consequently, they fabricated CdS/CdSe linear rods, CdS/CdTe, CdSe/CdTe branched rods, CdSe/CdTe segmented tetrapods and CdSe/CdTe branched tetrapods as illustrated in Figure 1.2. The different surface energies of precursors should account for the end-selective growth, forming segmented rather than core-shell structures.

Figure 1.2 Survey of nanocrystal heterostructures. Extended rods (a) were formed first by growing CdS nanorods (b), then adding CdSe extensions to each end. Branched rods (e) result from nucleation of CdTe on either end of CdSe nanorods (f). A CdTe zincblende region at one end creates the branch point. CdSe tetrapods (c, g) comprise a zincblende core and four wurtzite arms. Extending each arm linearly with CdTe yields extended tetrapods (d). Branched tetrapods (h) result from nucleation of CdTe zincblende branch points on the end of each arm. The model sequences illustrate the growth processes. In each case, the first generation is shown in grey and the second in yellow, while red and blue indicate the unique crystal faces of the wurtzite structure.³³

Last but not least, in this section, the effectiveness of solution-phase methods on the preparation of core-shell heterostructures is elaborated. In fact, the core-shell geometry is nearly the most often engineered topological configuration of heterostructures, where the core is covered with a shell composed of one or more layers of other materials. Till now, the syntheses of core-shell nanostructures using colloidal strategies have reached an extraordinary level of synthetic ingenuity. Most widely exploited class of chemical protocols to fabricate core-shell heterostructures

relies on the basic seeded-growth principle. As been summarized by Cozzoli and co-workers,³⁴⁻³⁵ the related preparation techniques for shell growth can be classified as follows based on the mechanisms inducing the shell formation: (1-3) direct heterogeneous deposition onto pre-grown seeds, (4) sequential heterogeneous deposition route, in which an amorphous shell is first formed on the existed seeds and followed by converting to crystalline via cation exchange, (5) replacement redox processes, in which the seed surface is converted into the shell material by sacrificial redox reactions between the outmost layer of the seed and appropriate reagents, (6) silica shell growth through a polymerization process, (7) self-modulated nucleation-growth dynamics, (8) crystal-phase separation driven by heating, (9) solid-state diffusion and coalescence. The existence of so many mechanisms involved in shell growth renders it not surprising to envision the huge number of members in core-shell family. So far, established examples have comprised disparate combinations of metals, oxides and semiconductors (Figure 1.4).^{13, 36-41} In one example, Yang and co-workers used highly faceted cubic Pt seeds to direct the heteroepitaxial overgrowth of lattice-matched Pd and lattice-mismatched Au, yielding conformal core-shell structure and anisotropic growth, respectively.³⁶ The growth process of Pt/Pd core-shell nanostructure involved the first reduction of K_2PdCl_4 by ascorbic acid in the presence of Pt nanocube seeds and subsequent epitaxial growth of Pd on the Pt nanocubes (Figure 1.3a). Further modulation of the growth rates along the $\langle 100 \rangle$ and $\langle 111 \rangle$ directions by adding more NO_2 could give Pt/Pd core-shell cuboctahedra (Figure 1. 3b) and octahedra (Figure 1.3c).

Figure 1.3 Gallery of TEM images presenting examples of diverse core-shell heterostructures prepared by solution-phased methods. (a-c) TEM images of Pt/Pd core-shell cubes, cuboctahedra, and octahedra, respectively. Insets in (a-c) are corresponding STEM images of a single nanocrystal, revealing the core-shell structure more clearly.³⁶ (d) TEM image of Au-CdS core-shell nanostructure with single-crystalline shell.¹³ (e) TEM image of Au-TiO₂ core-shell nanostructures with inner hollow space.³⁷ (f) TEM image of silica-coated Au nanorods.³⁸ (g) TEM image of hollow Co₃S₄ phase through nanoscale Kirkendall effect.³⁹ (h) TEM image of Pt@Fe₂O₃ core-shell heterostructures.⁴⁰ (i) TEM image of Pt@Fe₂O₃ yolk-shell nanoparticles. Inset shows the corresponding high-magnification TEM image.⁴¹

1.1.2.2 Vapor-Phase Methods

Another major type of effective approaches to synthesize heterostructures, especially 1D inorganic heterostructures, is vapor-phase method, including chemical vapor deposition (CVD), chemical beam epitaxy (CBE), metal-organic vapor-phase epitaxy (MOVPE), pulsed-laser deposition (PLD), for example.⁴²⁻⁴³ The growth of

heterostructures during these processes usually follows the vapor-liquid-solid (VLS) growth mechanism. For VLS growth to occur, a metal catalyst is necessarily required, which alloys with gaseous reactant to form a nanosized liquid droplet at elevated temperature. Such an alloy will become supersaturated when the gas feedstock is continuously supplied, giving rise to nucleation and axial growth of a nanowire. The diameter and length of the nanowires can be readily modulated by controlling the size of metal catalyst and growth time, respectively. For the synthesis of heterostructures, it generally requires the introduction of two or more kinds of precursors into the chamber either in sequence or all together at a time as discussed in the following.

Lieber's group, as one of most active teams in this direction, has developed various innovative strategies for the realization of intricate heterostructures using vapor-phase methods.⁴⁴⁻⁴⁷ For example, they had demonstrated a laser-assisted catalytic synthesis of superlattice nanostructures from group III-V and group IV materials.⁴⁴ This approach was based on the metal-catalysed nanowire synthesis via a VLS growth process mentioned above (Figure 1.4a). In the case of the formation of a single junction within the nanowire, two vapor sources should be introduced one by one (Figure 1.4b). While to synthesize nanowire superlattices, successive feed-in of different vapor sources were required (Figure 1.4c). The GaAs/GaP superlattices were formed by modulating the laser ablation of GaAs and GaP targets during the growth of nanowires repeatedly. The diameter and length of nanowires were approximately 20 nm and 3 μm , respectively. Although the GaAs and GaP segments are difficult to be distinguished in the TEM image, the elemental mapping results of the nanowire show clear boundary (Figure 1.4d). Similar methodologies were also adopted by other groups.⁴⁸⁻⁴⁹

Figure 1.4 (a-c) Synthesis of nanowire superlattices. (a) A nanocluster catalyst (shown gold) nucleates and directs 1D semiconductor nanowire (blue) growth with the catalyst remaining at the terminus of the nanowire. (b) Upon completion of the 1st growth step, a different material (red) can be grown from the end of the nanowire. (c) Repetition of step a and b leads to a compositional superlattice within a single nanowire. (d) High-resolution TEM image and corresponding elemental mapping of the Ga, P, and As of a GaAs/GaP junction. Scale bar is 20 nm.⁴⁴

In fact, Samuelson's group has contributed many pioneering works to this area as well.^{14, 49-50} Typically, they developed a sequential-seeding method for stepwise growth of tree-like branched heterostructures in a highly controlled way (Figure 1.5).¹⁴ This bottom-up method started with growth of the GaP nanowire backbone via a VLS process, and followed by sequential seeding of branch structures. Although each level of branching required the deposition of seed nanoparticles, this multi-step procedure offered precise control of the length, diameter, as well as chemical composition of each level of branching. Active research has currently focused on the preparation of such branched heterostructures, which can provide large surface area.⁵¹

Figure 1.5 (a) SEM image of ordered array of GaP nanotrees. (b) TEM image of a GaP trunk having five branches, with three visible growth directions. (c) STEM high-angle annular dark field image of a GaP-GaAsP heterostructure, inset is the EDX line scan of one branch.¹⁴

Similar to the way we present in the last section, at the end of this part, the capability of vapor-phase method in preparing core-shell heterostructures is demonstrated.^{45, 52} The pioneering work on synthesizing epitaxial core-shell and core-multishell nanowire heterostructures using CVD method represents a good case in point.⁴⁷ The key of this approach was to exquisitely control the radial versus axial growth, making the shell reactants favor homogenous deposition on the pre-grown core nanowire surface (Figure 1.6a). Take homoepitaxial Si-Si core-shell nanowires for example, they first grew intrinsic Si (i-Si) nanowire cores through a conventional VLS process. Afterwards, diborane acting as both a p-type dopant and an additive to decrease the decomposition temperature of silane was added to trigger the radial p-type Si (p-Si) shell growth. The yielding i-Si/p-Si product exhibited a uniform core-shell structure with the core in the diameter of 19 nm (Figure 1.6b). The shell thickness can be tuned by varying the growth time. Following this idea, heteroepitaxial i-Ge/p-Si core-shell and Si-Ge core-multishell structures can be achieved by altering the synthetic conditions of the shell (Figure 1.6c-d).

Figure 1.6 (a) Synthesis of core-shell nanowires by CVD method. (1) Gaseous reactants (red) decompose on the gold catalyst leading to nucleation and directed nanowire growth via a VLS process. (2) Synthetic conditions are altered to induce homogeneous decomposition of the shell reactant on the nanowire surface (blue). (3) Multiple shells are grown by repeated modulation of reactants. (b) TEM image of a Si-Si homoepitaxial core-shell nanowire. Scale bar is 50 nm. (c) TEM image and corresponding elemental mapping images of Ge-Si core-shell nanowires. Scale bar is 50 nm. (d) Cross-sectional elemental mapping of a double-shell structure with a *i*-Si core (diameter, 20 nm), *i*-Ge inner shell (thickness, 30 nm), and *p*-Si outer shell (4 nm); Si is blue circles and Ge is red circles.⁴⁷

1.1.2.3 Template-directed Synthesis

At the increasing request of low-cost, high yield and ease of processing, template synthesis is becoming an appealing method that can achieve elegant synthetic control of heterostructures particularly consisting of 1D nanobuilding blocks^{1, 43, 53} Depending on the physical state of the template, this technique can be divided into two types: hard template and soft template methods. Typically, hard template is a thin film made

from anodic aluminum oxide (AAO), ion-track-etched membranes (obtained from either polycarbonate or polyester thin films), glass, zeolites, mica, block copolymer films, and so on, among which the first two are the most widely used materials.⁵³ High-yield production of monodisperse nanomaterials guaranteed by the uniform and dense structure of pores in these hard templates together with the exquisite control over the placement and dimensions of different components makes up the two major advantages of this hard template-directed synthesis. One can now apply several techniques, like electrochemical deposition,⁵⁴⁻⁵⁵ sol-gel deposition,⁵⁶ layer-by-layer deposition⁵⁷ and pressure injection,⁵⁸ to fill the pores of these hard templates with various materials. The most common heterostructures resulted from such processes are in the form of segmented and/or core-shell structures. Among diverse deposition techniques, electrochemical deposition is extremely suitable for the synthesis of 1D nanostructure since it can proceed with no need of expensive equipments, high temperature or high-vacuum pressures. The synthesis of multisegmented rods can be simply accomplished by changing the plating solution and varying the potential of deposition accordingly. In addition, the manipulation of the shape of the electrical pulse leading to the deposition can regulate the interface between different segments.⁵³ General steps involved in this process are sketched in Figure 1.7. In the first step, one face of the template is evaporated with a thin metal film, which acts as a working electrode accounting for electrodepositing materials in the pores subsequently. Followed by this step, one can deposit the materials of interest into the pores successively. Final step is to chemically dissolve the thin film electrode, sacrificial metal layer and template to release the targeted nanowires encoded with stripes of different materials. To date, disparate metals, semiconductors and polymers

have been implemented into the realization of 1D segmented heterostructures through the combination of hard template and electrochemical deposition (Figure 1.8).⁵⁹⁻⁶⁷

Figure 1.7 General scheme for the synthesis of 1D segmented heterostructures by electrochemical deposition of materials into nanoporous templates.

Figure 1.8 Gallery of SEM, TEM, and Reflectance optical microscopy images showing examples of 1D segmented heterostructures synthesized by combining electro-deposition and hard templates. (a) SEM image of self-assembled Au-Ppy segmented nanorods. Inset is a schematic diagram of a single Au-Ppy nanorod.⁵⁹ (b)

SEM image of Au-MnO₂/CNT hybrid coaxial nanotubes. Insets are high-magnification SEM images showing Au segmented MnO₂/CNT, and MnO₂ shell and CNT core.⁶⁰ (c) Reflectance optical microscopy image of a nanorod of composition Au- Ag-Ni-Pd-Pt.⁶¹ (d) SEM image of Au/CdSe/Au nanowires.⁶² (e) SEM image of a bundle of Au-Ni rods.⁶³ (f) TEM image of a Cu/Co segmented nanowire.⁶⁴ (g) TEM image of a CoPt/Pt segmented nanowire.⁶⁵ (h) Schematic of a metallic rod composed of 5 segments and corresponding SEM images of such a rod before and after the treatment with 8 nm γ -Fe₂O₃.⁶⁶ (i) SEM images of multisegmented metal nanotubes with a stacking configuration of Au-Ni-Au-Ni-Au along the nanotube axis before and after dissolving the AAO template.⁶⁷

In addition to the electrochemical deposition, other electroless deposition techniques are also able to cooperate with hard templates to produce 1D heterostructures. For example, Kovtyukhova and co-workers grew silica nanotubes in AAO membranes using the “surface sol-gel (SSG)” technique.⁵⁶ Their synthetic procedure consisted only of two steps (Figure 1.9a): the absorption of SiCl₄ molecules on the hydrated surface of AAO template and the hydrolyzation of SiCl₄ resulting in the formation of SiO₂. To obtain free-standing SiO₂ nanotubes, the membrane filled with SiO₂ was subjected to 50% H₂SO₄ to remove the AAO template. The resulting SiO₂ nanotubes were flexible, with smooth and uniform walls (Figure 1.9b-c). The outer diameter was determined by the pore diameter of the AAO template, while the inner diameter could be adjusted by changing the deposition cycles and/or the concentration of SiCl₄.

Figure 1.9 (a) Scheme showing the SSG synthesis of SiO_2 nanotubes. (b-c) TEM images of the as-obtained SiO_2 nanotubes.⁵⁶

Compared with the huge progress achieved in the use of hard template directing the growth of heterostructures, soft template is rarely reported in the generation of multicomponent materials. Normally, soft templates refer to surfactants. Depending on the polarity of the solvent and its own concentration, such surfactants can self-assemble into different micellar structures in the solution and further serve as a template directing the growth of nanostructures. For instance, a novel striped cylindrical assemblies encoded with triblock microrods of 1,3-diphenyl-2-pyroline (DP, a blue-emissive molecule) doped with an orange dye of 4-(dicyanomethylene)-2-methyl-6-(*p*-dimethyl-aminostyryl)-4*H*-pyran (DCM) selectively at both ends was synthesized via a supermolecular synthesis induced by cetyltrimethylammonium bromide (CTAB) micelles.⁶⁸ Figure 1.10(a) depicts the formation mechanism of such a triblock heterostructure. First, some DP and DCM molecules both dissolved into the hydrophobic core of spherical CTAB micelles driven by so-called solubilization process and low concentration of DCM, respectively. In the first stage, those dissolved DP molecules evolved into rod-like micelles, templating the 1D growth of primary DP molecules. Then, the DP and DCM molecules co-deposited onto both ends of preformed 1D rods due to the micelle melting process arising from the micellar sphere-to-rod transition, producing the triblock microrods. SEM (Figure 1.10b) and TEM (Figure 1.10c) images reveal that each microrod yield from above

process has smooth surface and uniform diameter ($\sim 1\ \mu\text{m}$) along its entire length (20–25 μm). The DP and DCM segments were more clearly to be observed located in the middle stripe and at both ends of the triblock heterostructures from the fluorescence microscopy images (Figure 1.10d-e).

Figure 1.10 (a) Molecular Structures of DP and DCM and cartoon for the formation mechanism of triblock microrods. (b) SEM and (c) TEM images of triblock microrods. (d and e) Fluorescence microscopy images of the same microrods excited with unfocused UV (330–380 nm) and blue light (460–490 nm), respectively.⁶⁸

Besides the above methods that are widely and commonly used, there are still many other approaches, like various lithography techniques,^{69–70} growth in supercritical fluids,⁷¹ self-assembly,⁷² solid-solid reactions,⁷³ as well as electrospinning,⁷⁴ towards the preparation of varied heterostructures. In addition, most of these methods can be combined with other methods, yielding numerous pathways to generate complex nanostructures composed of different materials. One can get in-depth understanding and knowledge of the synthetic methodologies existing for constructing heterostructures from some relevant review articles.^{34, 43, 53}

1.2 Electrochemical Energy Storage Devices

In response to the challenge of global warming and rapid depletion of fossil fuels, there is currently a worldwide pursuit for sustainable and renewable resources. Underlying these initiatives are strategies towards developing more sustainable transportation and the ability to increase renewable energy consumption from sun and wind. However, significant electrical storage capabilities are additionally required due to the intermittency of such production and consumption requirements. As a result, more and more energy storage technologies are being developed for the efficient use of energy.⁷⁵ At the forefront of diverse energy storage systems are electrochemical energy storage devices owing to their high efficiency, versatility and flexibility. Electrochemical energy storage/release is realized by electron and ion charge/discharge. Two typical electrochemical storage devices are lithium-ion batteries (LIBs) and Supercapacitors. A general introduction to these two devices will be given in the following sub-sections including their basic configurations, working principles and especially electrode materials which lie at the heart of their performances.

1.2.1 LIBs

1.2.1.1 Introduction to LIBs

Lithium ion technology has emerged as the premier battery chemistry due to the increased energy density over other rechargeable technologies.⁷⁶ A LIB consists mainly of a cathode (positive), an anode (negative), an electrolyte and a separator. Cathode materials can be generally classified into two major categories: (1) Lithiated metal oxides with a layered structure (such as LiCoO_2 , LiMn_2O_4 , LiNiO_2 and $\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$), in which transition metal cations occupy alternate layers between the close-packed anion sheets, and Li^+ can intercalate into the essentially empty remaining

layers, (2) Tunnel-structured materials, which have more open structure. This type is exemplified by vanadium oxides, the tunnel compounds of manganese oxide and transition metal phosphate (e.g. olivine LiFePO_4).⁷⁷ While for anode materials, three classifications are well accepted: (1) insertion-type materials (such as carbon materials, TiO_2 , $\text{Li}_4\text{Ti}_5\text{O}_{12}$), (2) conversion-type materials (such as cobalt oxides, iron oxides, nickel oxides), (3) alloying-type materials (such as Sn, Si, Ge). Prior to being deposited onto metal foil current collectors, such active materials should be mixed with a binder (e.g. polyvinylidene fluoride – PVDF) and conductive additives (e.g. carbon black, graphite, etc.). Figure 1.14(a) illustrates an active material stack consisting of a cathode coated on Al substrate and the anode deposited onto Cu foil; each opposite a commercial separator.⁷⁸ The role of the separator, most often with a microporous polypropylene/polyethylene laminate, is to prevent electrodes from direct contact and to provide abundant channels for transportation of lithium ions during charging/discharging. The electrolytes should be good ionic conductors and electronic insulators. Most of the electrolytes solutions are prepared by dissolving inorganic lithium salts (e.g., LiPF_6) in a mixture of two or more organic solvents (*i.e.* ethylene carbonate (EC), dimethyl carbonate (DMC), etc). A LIB operates based on a rocking-chair concept as Li^+ “rock” back and forth between the cathodes and anodes when the battery is cycled. Specifically, Li^+ are extracted from the cathode intercalation host and intercalated into the anode on charging. Conversely, Li^+ are intercalated into the cathode passing across the electrolyte on discharging (Figure 1.14b). It can be seen that during charge/discharge, Li^+ flow between the two electrodes across the electrolyte while, at the same time, electrons pass around the external circuit, enabling the conversion of chemical energy into electrical energy and storing the electrochemical energy within the battery. The chemical reactions involved

in a typical LIB cell (LiCoO_2 as the cathode, graphite as the anode) can be described as follows:

It is noted that the intercalation process is aided by a necessary formation of solid-electrolyte interface (SEI) on the surface of each electrode (Figure 1.14b). This thin-layer SEI plays a critical role in preventing the electrode surface from further solvent reduction and allowing only Li^+ to diffuse. To form a stable SEI depends intimately on the choice of electrolyte solvent.

Figure 1.14 (a) Photograph of a conventional LIB active layer stack including cathode composite on Al, separator, and anode composite on Cu. (b) Schematic illustrating the mechanism of operation for a LIB including the movement of Li^+ ions between electrodes (solid lines) and the electron transport through the external circuit (dashed lines) during charge (blue) and discharge (red) states.⁷⁸

1.2.1.2 Electrode Materials for LIBs

Cathode materials

Cathode materials for LIBs have been under intense scrutiny since the advent of the Li-ion cell in 1991.⁷⁷ To meet ever-growing requirements for LIBs, the

development of suitable cathode materials is crucial. Typically, cathode materials are oxides of transition metals, which can undergo oxidation to higher valences when lithium is removed and accept/release Li^+ repeatedly (for recharging) and quickly (for high current). With decades of study, the focus of research on cathode materials has been placed on layered LiMO_2 ($\text{M} = \text{Co}, \text{Mn}, \text{Ni}$, and their combinations or substitutions), spinel LiMn_2O_4 , olivine LiFePO_4 and their derivatives.

LiCoO_2 is the first and most successfully commercialized cathode material.⁷⁷ Its theoretical capacity can reach as high as 274 mA h g^{-1} on the assumption of complete Li extraction, however, its practical reversible capacity is only about half of this value ($\sim 150 \text{ mA h g}^{-1}$) because LiCoO_2 cathode materials are normally cycled between the fully lithiated discharge state LiCoO_2 ($\sim 3.0 \text{ V vs Li/Li}^+$) and a nearly half-delithiated charge state Li_xCoO_2 ($x = 0.5\text{-}0.6$, 4.2 V vs Li/Li^+). Within this limited composition range ($0 < x < 0.5$), the Li/LiCoO_2 cell can be cycled with excellent stability. Whereas, its capacity fades quickly once more Li is extracted from the lattice due to the severe degradation of structural stability of lithium-poor phases and the electrolyte decomposition at high voltage upon overcharging.⁷⁹ Besides, the dissolution of the Co^{3+} in the electrolyte can also impact the performance degradation of LiCoO_2 .⁸⁰ Two strategies that can improve the stability of LiCoO_2 are to dope it with trivalent ions (e.g., Al or Cr) and coat it with inert metal oxides or phosphates (e.g., ZrO_2 , Al_2O_3 , AlPO_4 , or FePO_4), which can suppress the Co dissolution and/or mitigate the volume strain.⁸¹⁻⁸⁴ However, the search for alternative cathode materials is still ongoing because Co is less available and highly toxic. LiMnO_2 , LiNiO_2 , LiFeO_2 and their solid-solutions have emerged as appealing candidates subsequently as they utilize the more abundant, cheaper and more environmentally friendly elements like Mn, Ni and Fe to completely or partially substitute Co.

The spinel LiMn_2O_4 is another promising cathode material, in which Mn and Li occupy the octahedral and tetrahedral sites, respectively.⁸⁵ Owing to its good safety and intrinsic rate capability originating from the chemically stable $\text{Mn}^{3+}/\text{Mn}^{4+}$ couple and a 3D network of channels for Li^+ transportation, LiMn_2O_4 and its doped variants have attracted great attention and are being implemented in electric vehicle application.⁸⁶ However, the loss of oxygen during charging,⁸⁷ the dissolution of Mn in the electrolyte,⁸⁸ as well as the changes in particle morphology or crystallinity⁸⁹ result in the poor capacity retention of LiMn_2O_4 cathode materials. One can effectively alleviate this deleterious capacity fading by doping Li on the octahedral sublattice of LiMn_2O_4 forming a lithium-rich spinel compound with high-average-oxidation state, which can diminish Mn dissolution.⁹⁰ Besides, downsizing the LiMn_2O_4 material to nanoscale is another approach to increase its cycling stability.⁹¹⁻⁹² In a nanodomain spinel, the change of lattice parameters upon lithium uptake and removal can be well cushioned due to the decrease in the domain wall boundaries, which can promote the solubility and solid solution properties and thereby influence the kinetics of lithiation processes.

Polyanion-based compounds, $\text{Li}_x\text{M}_y(\text{XO}_4)_z$ (M = metal, X = P, S, Si, Mo, W, etc.), represent another promising class of cathode materials. In particular, much emphasis have been placed on orthorhombic LiFePO_4 with an ordered olivine structure due to the abundance of the FePO_4 , its relatively high reversible capacity ($\sim 170 \text{ mA h g}^{-1}$), favorable reversibility of lithium storage, as well as high safety.⁹³ However, its further development is hindered by its inherently extremely low electronic conductivity ($\sim 10^{-9} \text{ S cm}^{-1}$) and very low lithium diffusivity (10^{-10} - $10^{-16} \text{ cm}^2 \text{ s}^{-1}$).⁹⁴⁻⁹⁵ As a result, various approaches have been adopted to overcome these drawbacks, including doping or coating LiFePO_4 with an electronically or ionically conductive

component or preparing nanosized LiFePO_4 . Along this line, LiFePO_4 nanocomposites have been the focus of research interest.⁹⁶⁻⁹⁷

Anode materials

As far as high energy density is concerned, Li metal is an exceptional anode material due to its extremely light weight. However, the knotty problem of Li dendrite formation which may cause an internal short circuit and thereby safety problems makes the use of Li metal risky. Consequently, diverse anode candidates such as carbonaceous materials, alloys and transition metal oxides, have sprung up in the quest for new alternative anode materials.

Carbonaceous materials currently dominate commercial LIBs and will continue to be well-liked owing to their high abundance, low cost, favorable stability and excellent kinetics.⁹⁸ On charging, Li is intercalated into carbon, resulting in the Li-intercalated carbons with a low potential close to that of a metallic Li anode but avoiding the problem of Li dendrite formation. Generally, there are three types of carbonaceous materials: graphite and graphitized materials, ungraphitized soft carbon and hard carbon.⁷⁵ Among them, graphite is especially interesting due to its high electronic (in-plane) conductivity resulting from the delocalized π -bonds, stable specific capacity, small irreversible capacity, as well as good stability. Also, the Li-intercalation in graphite is the best investigated Li-uptake process by far, which is revealed to proceed via two stages including first fully intercalating into very distant graphene layers and thereafter occupying adjacent graphene layers.⁹⁸ The specific capacity of graphite is however limited to 372 mA h g^{-1} (nominal composition LiC_6), which stimulates the search for other types of carbonaceous anode materials with high capacity. Soft carbon materials could deliver a very high reversible Li-storage capacity but suffer from a serious voltage hysteresis upon Li-extraction.⁹⁹ Hard

carbon also could display a high capacity and good power capability. The main drawbacks of hard carbon materials are nevertheless their low initial columbic efficiency, poor electrical conductivity and low tap density.¹⁰⁰ Under this circumstance, nanostructured carbonaceous anode materials such as 1D carbon nanotube (CNT), carbon nanofiber, 2D graphene and porous carbon-based anodes have been extensively built up to produce more active spaces or sites for Li storage.^{98,}
¹⁰¹ For example, the Li-intercalation could occur between pseudo-graphitic layers and/or inside central tubes of CNTs. Apart from this, the strain on the planar bonds of the hexagon derived from the small diameters of CNTs can induce de-localization of electrons and thereby more electronegative structure. This could increase the degree of Li-intercalation.¹⁰¹ Graphene, a novel 2D aromatic single layer of honeycomb carbon lattice, is another new favourite of LIBs. Li can not only be stored on both sides of graphene sheets, but also on the edges, defects, and covalent sites of graphene nanoplatelets. Many researchers therefore expect that graphene and graphene-based composites may outperform its 3D counterpart (graphite) for improved Li storage in LIBs.^{9, 101-102}

Some main-group elements (e.g., Si, Ge, Sn, Al, Bi, Zn and Sb) can store a large quantity of lithium by reacting with lithium to form alloys at a low potential.⁹³ Representatively, Si, Ge and Sn can form lithium alloys with Li compositions up to $\text{Li}_{4.4}\text{M}$, corresponding to lithium storage capacities of 4200 mA h g^{-1} , 1600 mA h g^{-1} and 990 mA h g^{-1} , respectively. Unfortunately, the use of alloy-based materials as anodes candidates has been lingered up far behind carbonaceous materials due mainly to the enormous volume expansion and contraction accompanying lithium alloying-dealloying process.^{97, 103} The mechanical strain generated from this process could cause cracking and eventual pulverization of the electrode materials and a marked loss

of capacity in the course of a few cycles. Besides, the poor electrical conductivity of Si anode is another hurdle prohibiting fast lithiation. In that the toughness and adhesion effect with grain boundaries may increase at the nanoscale, the strain induced by the dramatic volume change can be effectively accommodated by flexible nanostructured alloys. Substantial research efforts have thus been expended on synthesizing nanostructures of these alloys and/or dispersing the active materials in a stiff matrix to form composite structures to limit the side effects of these obstacles on the electrode integrity.^{75, 93, 97, 101}

Various transition metal oxides (M_xO_y , $M = \text{Fe, Co, Ni, Mn, Cu, etc.}$) have aroused wide interest as anode candidates for LIBs in that they possess diverse chemical and physical properties and can offer significantly higher capacities ($\sim 500\text{--}1000 \text{ mA h g}^{-1}$) than those of graphite anodes endowed with their capability of incorporating more than one Li per 3d metal.¹⁰⁴⁻¹⁰⁵ The electrode reaction mechanism of transition metal oxides anodes can be typically specified into three types: (1) Li insertion/extraction reaction (e.g., $\text{Li}_4\text{Ti}_5\text{O}_{12}$, TiO_2), storing/releasing Li through the insertion and extraction of Li into and from the lattice of the transition metal oxide, (2) Li-alloying reaction (e.g., SnO_2 , SnO), for which the Li storage is accomplished by forming Li-alloy, and (3) conversion reaction (e.g., Co_3O_4 , CoO , Fe_2O_3 , Fe_3O_4), involving the formation/decomposition of Li_2O and the reduction/oxidation of metal nanoparticles. These three reaction mechanisms can be described as follows:

Insertion reaction mechanism:

Li-alloy reaction mechanism:

Conversion reaction mechanism:

Apart from the prominent merits of low cost and high capacity, the development of transition metal oxides anode is still hindered by their poor energy efficiency of the electrode associated with their inherent large voltage separation between the charge and discharge profiles and poor electrical conductivity. Similar to the approaches for improving the performances of above two kinds of anode candidates, namely carbonaceous materials and lithium-alloys, fabrication and design of diverse nanostructured metal oxides and metal oxides-based composites (such as metal oxide/carbon core-shell nanostructure) still represent an attractive route to uplift the capacity and cycling stability of transition metal oxide anodes.^{97, 101}

1.2.2 Supercapacitors

1.2.2.1 Introduction to Supercapacitors

A supercapacitor, also known as electrochemical capacitor or ultracapacitor, is an electrochemical energy storage device consisting of two electrodes immersed in an electrolyte with a separator between the electrodes. It has two working principles: electric double-layer (EDL) mode and pseudo-capacitive mode, based on which supercapacitors can be classified into electric double-layer capacitor (EDLC) and pseudocapacitor.¹⁰⁶ EDLC is more like a physical dielectric capacitor, storing the electric charge electrostatically by reversible adsorption of ions of the electrolyte onto active materials that are electrochemically stable and have high specific surface area (SSA). As there is no charge transfer across the interface, this is a true capacitance effect. However, the insulating barrier in a dielectric capacitor is herein replaced by electrolytes in an EDLC. Different from conventional physical capacitors, it possesses

a much larger capacity. A space charge layer in an electrode, a compact Helmholtz layer together with a diffusive layer in an electrolyte constitute the compartment of an EDL (with a thickness of 1 nm) (Figure 1.15a).⁷⁵ Given that the EDLC stores the electric energy in aggregated charges at the electrode surface, electrode materials having a large pore volume and high surface area are essentially more favorable. The most commonly used electrode materials for EDLC are carbon-based materials with high surface area such as highly porous carbon. A second group of supercapacitor is called pseudocapacitor, which stores charges by fast and reversible surface or near-surface redox reactions between electrode materials and electrolyte ions (Figure 1.15b). Typical pseudo-capacitive active materials are transition metal oxides and electrically conducting polymers. The specific pseudo-capacitance is larger than that of carbon materials employing double-layer charge storage, justifying the interest in these systems. However, pseudocapacitors behave more like batteries using redox reactions to store charges, resulting in the phase changes within the electrode and thereby often suffering from a lack of stability during cycling.¹⁰⁷ For both EDLC and pseudocapacitors, there are generally three categories of electrolyte solutions: aqueous electrolyte, organic electrolyte and ionic liquids (IL). Aqueous electrolyte can provide higher ionic concentration and lower resistance compared with organic electrolyte. However, their small voltage window (~ 1.2 V) is much lower than those of organic electrolyte, which can reach as high as 3.5 V. As a promising candidate, ILs have many desirable properties for supercapacitor electrolytes, such as good thermal and chemical stability, low vapor pressure and flammability, wide voltage window (~ 2 -6 V, typically 4.5 V), high conductivity. Besides, ILs can provide a well determined ion size as they do not have a solvation shell.¹⁰⁷

Supercapacitors can be fully charged or discharged in seconds, providing a much faster power delivery/uptake than primary/secondary batteries. As a result, their energy density ($\sim 5 \text{ Wh kg}^{-1}$) is lower than that of batteries, but a much high power density ($\sim 10 \text{ kW kg}^{-1}$) can be attained in a short time. They are currently filling the gap between batteries and conventional solid state and electrolytic capacitors. The primary advantages of supercapacitors can be enumerated as: environmental benignity, high power density, excellent reversibility, high safety, wide operation temperature range, as well as near-infinite long cycling life.⁷⁵ The performance of supercapacitors depends intimately on the electrochemical activity and kinetic feature of the electrodes. One effective pathway to increase the power density of supercapacitors is to kinetically improve the ion and electron transport in electrodes and at the electrode/electrolyte interface. In this context, a good performing electrode requires a proper pore structure, high surface area and good electrical conductivity. The energy density of supercapacitors can also be improved by optimizing the structure of electrode materials and rational design of energy storage devices in the light of energy storage mechanisms.^{97, 106}

Figure 1.15 The working principle of supercapacitors. a) Electrical double layer, b) redox reaction on surface.⁷⁵

1.2.2.2 Electrode Materials for Supercapacitors

Electrode materials for supercapacitors mainly include carbon, metal oxides and conducting polymer. As aforementioned, carbon materials are the most widely used electrode materials for EDLCs. This is because the low electrical resistivity, large surface area, electrochemical stability, open porosity and low cost of carbon materials can meet almost all the prerequisites for achieving high capacitance of EDLCs.¹⁰⁸ So far, diverse carbons, activated carbons (ACs), carbon nanofibers (CNFs), CNTs, graphene, carbon aerogels, ordered mesoporous carbons (OMCs) for example, have been adopted for EDLC electrodes.^{75, 109} In view of the high SSA and moderate cost, ACs are the most widely investigated materials in EDLCs at present. ACs have an intricate porous structure consisting of micropores (<2 nm), mesopores (2-50 nm), and macropores (>50 nm). The double-layer capacitance of AC is about 100-120 F g⁻¹ in organic electrolytes, while in aqueous electrolyte this value can exceed 150-300 F g⁻¹. The cell voltage is however lower in the latter case as the electrolyte voltage window is limited by water decomposition.¹⁰⁶ Since the charge stored in carbon materials is proportional to their surface area, capacitance improvement can obviously benefit from moving forward from conventional to nanostructured carbons. For example, carbon aerogel, a monolithic 3D mesoporous network of carbon nanoparticles, is able to transport ions and electrons in a high speed and can be potentially used as a binder-less electrode. The capacitance and cyclability can be both markedly improved by replacing standard carbon fiber with carbon aerogel electrodes. For the application of nanotechnology in carbon-based EDLC electrodes, attention should be paid on a compromise between SSA (to ensure high capacitance) and pore-size distribution (to permit easy access for the electrolyte).⁹⁷

Different from carbon materials, metal oxides and conducting polymers are widely utilized for electrode materials of pseudocapacitors, which can generate

pseudocapacitance from chemisorptions process or redox reactions at the electrode/electrolyte interface.¹¹⁰ There are two general categories of metal oxides: noble metal oxides and cheap metal oxides. One representative example for the former is RuO₂, while NiO and MnO₂ are eminent for the latter. The most striking advantage of metal oxides versus carbon materials lies mainly in their much larger capacitance arising from the multielectron transfer during fast Faradaic reactions. Among the numerous metal oxides studied to date, RuO₂ stands out as one of the best active electrode materials for pseudocapacitors due to its conductive nature and three distinct oxidation states accessible within 1.2 V.¹⁰⁶ During the past three decades, a great interest has been placed on the pseudo-capacitive behavior of RuO₂ in acidic solutions, involving a fast, reversible electron transfer and the electro-adsorption of protons on the surface of RuO₂ particles. This process can be described by the following equation:^{108, 111}

where $0 \leq x \leq 2$, Ru oxidation states change from (II) up to (IV). High specific capacitance of 720 F g⁻¹ and very long cycle life have been reached for RuO₂-based pseudocapacitors, but unfortunately, this is undermined by the sheer high cost and rearsness of Ru. Hence, the studies are focused on searching for inexpensive metal oxides but with good capacitive characteristics such as Mn, Co, Mo, Ti, Ir, Fe- based oxides as replacements to RuO₂.¹¹² In particular, MnO₂ is one of the most prominent, which stores charges by surface adsorption of electrolyte cations C⁺ and H⁺ incorporation according to the below reaction.^{60, 106}

However, most cheap metal oxides including MnO_2 suffer from poor electrical conductivity and thus poor cycling stability, which prohibits wide implementation of them in pseudocapacitors.¹¹²

Conducting polymers are another kind of pseudo-capacitive materials capable of delivering Faradaic charge. Till now, many kinds of conducting polymers such as polyaniline, polypyrrole, polythiophene and their derivatives have been tested in pseudocapacitor applications.¹¹³ They have exhibited high gravimetric and volumetric pseudo-capacitance in diverse non-aqueous electrolytes at a fairly wide operating voltage of ~ 3 V. Similar to metal oxide electrodes, however, conducting polymers also suffer from relatively low electrical conductivity and thus a limited stability during cycling in comparison with carbon materials. Besides, the high cost is another consideration when it comes to commercial application.

1.3 Recent Advances in the Application of Heterostructures to Electrochemical Energy Storage Devices

Separate introductions of the properties and functions of heterostructures and two main types of electrochemical energy storage devices have been given in previous sections. The major goal of this section is to highlight some new progresses in using heterostructures as electrode materials to boost the energy storage performances of LIBs and supercapacitors. It is divided into two parts, carbon-based and non-carbon-based heterostructures, for the sake of better illustration.

1.3.1: Carbon-based Heterostructures for LIBs and Supercapacitors

On account of the aforementioned distinct merits, carbon materials have been initially and widely pursued as electrode materials in both LIBs and supercapacitors.

On the other hand, their relatively low capacities have triggered significant research efforts on combining them with other high-capacity active materials. The integration of good electrical conductivity and high surface area of carbon materials and high capacity of other components render such a kind of heterostructures very promising electrode materials for electrochemical energy storage.

It is well-known that Si is a particularly appealing anode candidate for LIBs owing to its extremely high theoretical specific capacity of 4200 mA h g^{-1} . However, the drastic volume change of Si upon cycling leads to rapid loss of capacity due to structural and electronic degradation.¹¹⁴ Yushin and co-workers recently reported a large-scale hierarchical bottom-up assembly route towards the formation of porous Si-C composite (experimental details see Figure 1.16a), in which Si nanoparticles were first deposited on the surface of carbon-black nanochains and subsequently self-assembled into large porous spherical granules (Figure 1.16b).¹¹⁵ Such a porous Si-C composite (estimated with ~50wt% Si) demonstrated a reversible capacity (1950 mA h g^{-1} at C/20) over five times higher than that of the theoretical capacity of graphite (Figure 1.16c). If only Si nanoparticles alone were considered, the specific capacity reached as high as 3670 mA h g^{-1} at C/20, approaching the theoretical capacity of Si. The carbon in the composite only contributed approximately 230 mA h g^{-1} . Also, this self-assembled electrode could overcome the sluggish kinetic problem of Si anodes by virtue of its porous structure and connected conducting carbon network, providing high rate capability. At the fast discharge rates of 1C and 8C, the Si-C composite electrode still delivered high specific capacity of 1590 mA h g^{-1} and 870 mA h g^{-1} , respectively, which is 82 and 45% of that at C/20 (Figure 1.16d). Such high capacity retention at 8C rate even surpassed that of graphite with high Li diffusion coefficients (13%) (Figure 1.16d). The observed high capacity, excellent stability and high rate

capability of the Si-C composite electrode were attributed to this uniquely designed porous architecture with irregular channels, allowing for high accessibility of active Si, rigid and robust framework, rapid access of Li^+ into the particle bulk.

Figure 1.16 (a) Schematic of Si-C nanocomposite granule formation through hierarchical bottom-up assembly. (b) SEM image of Si-C nanocomposite granule. (c) Reversible Li deintercalation capacity and Coulombic efficiency of the Si-C granule electrode versus cycle number in comparison with the theoretical capacity of graphite. (d) Galvanostatic charge-discharge profiles of the Si-C granule electrode at rates of C/20, 1C and 8C in comparison with that of commercial graphite-based electrodes.¹¹⁵

In a recent effort, Hou et al. designed a novel ternary $\text{MnO}_2/\text{CNT}/\text{CP}$ (conducting polymer) composite for high-performance electrochemical electrodes (Figure 1.17a, b).¹¹⁶ Compared with pure MnO_2 film and binary MnO_2/CP composite film, the ternary composite film displayed a nearly rectangular cyclic voltammograms (CV) shape and much improved current values (Figure 1.17c). It also revealed more ideal capacitive behavior with very sharp response and small internal resistance (IR) drop and higher specific capacitance (SC) ($\text{MnO}_2/\text{CNT}/\text{CP}$: 200 F g^{-1} , MnO_2 : 129 F g^{-1} , MnO_2/CP : 132 F g^{-1}) (Figure 1.17d). Besides, the rate capability of the ternary composite electrode was superior to pure MnO_2 and binary MnO_2/CP composite

electrodes as well. In contrast to the significant decrease of specific capacitance for pure MnO_2 film and binary MnO_2/CP composite film, $\text{MnO}_2/\text{CNT}/\text{CP}$ composite preserved 85% of its SC (from 200 to 168 F g^{-1}) as the current density increased from 5 to 25 mA cm^{-2} (Figure 1.17e). Last, the as-designed ternary electrode was also able to exhibit outstanding cycling stability with only less than 1% decay in SC after 1000 cycles (Figure 1.17f). All of these superior performances can be ascribed to the synergistic effects from the combination of each component. Specifically, CNT frameworks provided not only high surface for the deposition of MnO_2 but also improved electrical conductivity and mechanical stability of the composite. The properly selected CP (PEDOT-PSS) acted as both a dispersant to stabilize the composite suspension and a binder material, avoiding the use of conventional insulating binder. The highly porous nanospheres offer high surface area for large SC. The electrochemical utilization of MnO_2 was greatly improved by the introduction of CNT and CP as “inner” and “outer” current collector, tackling the key weakness, poor conductivity of MnO_2 , and concurrently allowing high mass loading and high concentration of MnO_2 of electrode film.

Figure 1.17 (a) Sketch and (b) TEM image of $\text{MnO}_2/\text{CNT}/\text{CP}$ ternary composite. (c) Cyclic voltammograms (50 mV s^{-1} scanned from 0–1 V in 1 M Na_2SO_4), (d)

Galvanostatic charge/discharge curve (at current density of 5 mA cm⁻²), (e) SC at different current densities of MnO₂ film (black), MnO₂/CP composite (red), and MnO₂/CNT/CP ternary composite (blue). (f) Charge-discharge cycle test of MnO₂/CNT/CP ternary composite.¹¹⁶

When it comes to carbon materials, graphene is almost the hottest topic at present. Owing to its unique single atomic layer crystal structure, graphene exhibits the highest possible surface area of all graphitic materials ($\sim 2600 \text{ m}^2 \text{ g}^{-1}$). This together with chemical tolerance, light weight, excellent flexibility, good electrical conductivity and wide electrochemical window makes it pretty interesting from electrochemical energy storage point of view.¹¹⁷ As a result, a gold rush of anchoring various electrochemically active materials, particularly metal and metal oxides, on graphene sheets has been triggered in electrochemical energy storage area (Figure 1.18).¹¹⁸⁻¹²⁵ Almost all of these composites have demonstrated improved electrochemical performances with respect to pristine metal, metal oxides or conducting polymers in terms of high capacity, good rate capability or enhanced stability. Taking a pioneering effort as an example, Honma and co-workers fabricated a SnO₂/graphene nanoporous electrode with delaminated flexible structure, in which the graphene nanosheets (GNS) were homogeneously distributed among the loosely packed SnO₂ nanoparticles (Figure 1.19A, B).¹²⁶ The yielding SnO₂/graphene displayed a reversible capacity of 810 mA h g⁻¹ and much enhanced cyclic performance ($\sim 70\%$ capacity retention after 30 cycles) compared with that of the bare SnO₂ nanoparticles ($\sim 11\%$ capacity retention after 15 cycles) (Figure 1.19C). The important functions of graphene in boosting the electrochemical performances of this composite can be summarized as follows (Figure 1.19D): (1) limiting the volume expansion upon lithium insertion by confining the SnO₂ nanoparticles within the surrounding GNS, (2) buffering the

volume change during charge/discharge through the pores developed between SnO_2 and GNS, (3) providing electronic conductive channels to improve the electrochemical performances, (4) storing lithium as electrochemically active material. In fact, these also represent the general roles of graphene in graphene-based composites for LIBs application.

Figure 1.18 (a) TEM image of Co_3O_4 /graphene composite.¹¹⁸ (b) Dark-field TEM image of graphene oxide- MnO_2 nanocomposites.¹¹⁹ (c) SEM image of a graphene-coated microfiber with conformal decoration of MnO_2 nanostructures. Inset is high-magnification SEM image showing a clear interface between MnO_2 nanoflowers and underneath graphene nanosheets.¹²⁰ (d) SEM image of graphene sheets/ $\text{Ni}(\text{OH})_2$ composite.¹²¹ (e) High-magnification TEM image of SnO_2 -graphene nanocomposites, showing the layered structure of SnO_2 composed of nanocrystalline SnO_2 interspaced by graphene stacks.¹²² (f) SEM image of graphene/polyaniline sheets.¹²³ (g) TEM image of graphene encapsulated silica nanospheres.¹²⁴ (h) TEM image of graphene/ Sn nanocomposite.¹²⁵

Figure 1.19 (A) SEM and (B) cross-sectional TEM images of $\text{SnO}_2/\text{graphene}$. (C) Cyclic performances for (a) bare SnO_2 nanoparticles, (b) graphite, (c) GNS, and (d) $\text{SnO}_2/\text{graphene}$. (D) Schematic illustration for the synthesis and the structure of $\text{SnO}_2/\text{graphene}$.¹²⁶

1.3.2: Non-Carbon-based Heterostructures in LIBs and supercapacitors

Apart from the above combination with carbon materials, non-carbon active materials can also be grouped with each other, showing enhanced performance by the incorporation of respective advantages of individual components.

As can be seen from previous example, tremendous volume changes associated with cycling and the low electron conductivity and ion diffusivity of Si can be well overcome by dispersing Si nanoparticles in carbon matrix. In fact, hybridizing Si with non-carbon materials but also with high conductivity represents another potential alternative to solve the problems related to the huge volumetric expansion of Si, especially when the heterostructures are with rationally designed configurations.¹²⁷ In this context, Paik and co-workers developed a Si/Ge double-layered nanotube (DLNT) heterostructure array (Figure 1.20a).¹²⁸ Considering their mechanical and electrochemical properties, Si and Ge were selected as inner and outer layers, respectively. This architecture can minimize the mechanical stress imposed to the inner Si layer during lithiation and the electrochemical resistance because the Ge shell has smaller volume change and higher electrical conductivity and ion diffusivity.

Despite showing relatively low specific capacity due to the incorporation of low-capacity Ge, the Si/Ge DLNT exhibited lower impedance, higher areal capacity, better capacity retention, more excellent rate capability than pure Si NT (Figure 1.20 b-d). This verified the advanced structural stability and electrochemical conductivity of Si/Ge DLNT stemming from the unique structural and compositional design. Similar strategy can also be extended to metal oxide-based anodes. For example, a novel $\text{SnO}_2\text{-In}_2\text{O}_3$ heterostructured nanowire also demonstrated marked improvements in reversible capacity and cycling performance towards bare SnO_2 nanowire due to enhanced electrical conductivity originating from the formation of Sn-doped In_2O_3 during the nucleation and growth of the In_2O_3 shell nanostructures.¹²⁹

Figure 1.20 (a) SEM image of vertically aligned Si/Ge DLNT arrays. Inset is the TEM image of Si/Ge DLNT. (b) Impedance plots for the Si NT and Si/Ge DLNT. (c) Cycle performance and (d) Rate capabilities of Si NT and Si/Ge DLNT electrodes at various C rates.¹²⁸

Another similar approach holding considerable promise is to hybridize oxide with metal to deal with the poor conductivity of oxide materials. For example, Chen and co-workers recently developed a nanoporous gold/ MnO_2 composite film

involving chemical de-alloying to produce nanoporous gold and electroless plating nanocrystalline MnO_2 into the nanopores (Figure 1.21a, b).¹³⁰ The load mass of MnO_2 can be controlled by adjusting the plating time. When applied as electrode materials for supercapacitor, this gold/ MnO_2 composite film (plating time, 20 min) showed a high SC of the constituent MnO_2 ($\sim 1145 \text{ F g}^{-1}$) that is close to the theoretical value. The area surrounded by the CV curves and the discharge time in the voltage-time profiles significantly increased as the MnO_2 plating time increased to 20 min, implying higher MnO_2 loading in the open porous structure led to a larger SC (Figure 1.21c, d). It can be seen from Figure 1.21(e) that the SC of the gold/ MnO_2 composite film appeared to be much larger than that of the bare nanoporous gold at various current densities, and a longer plating time for the MnO_2 yielded higher SC. The high SC and charge/discharge rates of such hybrid structures were mainly attributed to the good electrical/ionic conductivity of the nanoporous gold to facilitate electron transport through MnO_2 and fast ion diffusion between the MnO_2 and the electrolytes. It needs to be mentioned that this kind of material may suffer from the high-cost problem.

Figure 1.21 (a) Schematic showing the fabrication process for nanoporous gold/ MnO_2 hybrid materials by directly growing MnO_2 (orange) onto nanoporous

gold. (b) Bright-field TEM image of the nanoporous gold/MnO₂ hybrid with a MnO₂ plating time of 20 min. (c) CV curves at a scan rate of 50 mV s⁻¹. (d) Charge-discharge curves at a current density of 0.5 A g⁻¹, and (e) SC versus discharge current density, for bare nanoporous gold electrodes and for nanoporous gold/MnO₂ electrodes for three different plating times.¹³⁰

As can be seen from above results, the realization of heterostructures offers a promising avenue for improving the performances of both LIBs and supercapacitors, as this strategy will bring several advantages.¹³¹ First, heterostructures integrate several kinds of functional materials that can synergistically enhance the properties of each component, e.g., electrical/ionic conductivity, mechanical stability and electrochemical activity.¹³²⁻¹³⁴ Second, the hybrid design, especially with a core-shell structure, can largely decrease the surface energy of active materials, which protects the electrodes against the side reactions with electrolytes and thus reduces the electrochemical irreversibility.¹³⁵⁻¹³⁶ Third, with the assistance of ordered electrode architectures, one can develop metal oxide-based binder-free film/array electrodes, providing a good platform for high and fast energy storage.¹³⁷⁻¹³⁸ Table 1.1 illustrates some relevant values of the electrochemical performances of these hybrid electrodes.

Table 1.1 General electrochemical performances of different kinds of heterostructures.

LIBs				Supercapacitors			
Materials	Current density	Capacity	Ref.	Materials	Current density	Capacity	Ref.
SnO ₂ -Fe ₂ O ₃	0.1-0.6 (mA cm ⁻²)	1.289-0.507 (mA h cm ⁻²)	¹³⁹	MnO ₂ -Co ₃ O ₄	2.67-29.8 (A g ⁻¹)	480-267 (F g ⁻¹)	¹⁴⁰
Cu-Si-Al ₂ O ₃	0.3-14 (A g ⁻¹)	1820-790 (mA h g ⁻¹)	¹⁴¹	Graphene-MnO ₂	0.2 (A g ⁻¹)	74.8-124 (F g ⁻¹)	¹⁴²
V ₂ O ₅ -SnO ₂	0.2-20 (A g ⁻¹)	138-93 (mA h g ⁻¹)	¹⁴³	Fe ₃ O ₄ -SnO ₂	0.2-1.66 (mA cm ⁻²)	7.01-2.26 (mF cm ⁻²)	¹⁴⁴

TiO ₂ -Fe ₂ O ₃	120-690 (mA g ⁻¹)	500-150 (mA h g ⁻¹)	¹⁴⁵	Graphene-Co ₃ O ₄	10-30 (A g ⁻¹)	1100-456 (F g ⁻¹)	¹⁴⁶
Ni-MnO ₂	0.218-220.3 (A g ⁻¹)	196-73 (mA h g ⁻¹)	¹³⁷	Graphene-Mn ₃ O ₄	0.5-20 (A g ⁻¹)	121-83 (F g ⁻¹)	¹⁴⁷
CoO-NiSi _x	0.36-4.58 (mA g ⁻¹)	1533-400 (mA h g ⁻¹)	¹⁴⁸	SWCNT-NiCo ₂ O ₄	0.5-20 (A g ⁻¹)	1642-879 (F g ⁻¹)	¹⁴⁹
Ni-TiO ₂	0.016-0.8 (mA cm ⁻²)	0.161-0.06 (mA h cm ⁻²)	¹⁵⁰	NiO-TiO ₂	5-500 (mV s ⁻¹)	2.6-2.3 (mF cm ⁻²) 100-40 (F g ⁻¹)	¹⁵¹
ITO-TiO ₂	0.168-10.08 (A g ⁻¹)	323-210 (mA h g ⁻¹)	¹⁵²	CNT-RuO ₂	1 (mV s ⁻¹)	592-953 (F g ⁻¹)	¹⁵³

1.4 Motivation, Objectives, and Scope of This Thesis

While the field of electrochemical energy storage is advancing faster than it perhaps has ever done in the past, there are also challenges in keeping pace with the ever-updating requirements of modern electronics and the increasing demand for clean sustainable energy. As addressed before, whatever the considered electrochemical energy storage device (LIBs, supercapacitors or fuel cells), measures of its performance (e.g., capacity, cell potential or cycle life) are closely related to the intrinsic property of electrode materials. Through proper materials engineering one can expect significant improvements in the performances of these devices. Given that heterostructures can integrate the properties of each component and possibly generate novel properties arising from the interface, design and synthesis of various heterostructures towards effective electrochemical energy storage represents a promising way to increase the energy and power density. To this end, the main objectives of this thesis are well established as follows.

- (1) Material selection and rational combination. We aim to construct nanoscale heterostructures by choosing suitable materials that are of both fundamental and applied significances. As mentioned above, materials lie in the heart of performance in any energy storage device. To achieve this objective, one

needs understand first intrinsic properties of materials including but not limited to the electrical conductivity, theoretical volumetric capacitance, crystal structure, etc. For example, carbon materials and transition metal oxides, as two typical and widely studied types of active materials for LIBs and supercapacitors, have complementary properties to certain degree. Generally speaking, carbon materials possess good electrical conductivity and low density but they have low specific capacity (around 300 mA h g^{-1}), whereas transition metal oxides can provide high specific capacity (in the order of $500\text{-}1000 \text{ mA h g}^{-1}$) but suffer from poor electrical conductivity and structural instability. If these two materials are properly engineered to achieve synergy, greatly enhanced performance can be expected.

- (2) To develop simple yet effective methods to synthesize designed heterostructures at the nanoscale. On one hand, simple yet effective methods often imply the operation processes are low-cost, easy to be scaled-up, and thus more suitable for practical application. On the other hand, as can be concluded from sections **1.2.1.2** and **1.2.2.2**, nanostructured materials are especially beneficial for electrochemical energy storage. Several potential advantages associated with the development of nanoelectrodes for LIBs and supercapacitors can be described from following aspects: (i) larger electrode/electrolyte contact area, resulting in higher specific capacity, (ii) short ion/electron transport lengths, allowing faster charge/discharge rate. In particular, when applied in LIBs, nanoelectrodes can accommodate the strain resulting from Li insertion/extraction to a higher degree than bulk materials, leading to improved cycle life.

(3) To achieve higher controllability over the size, shape and nanostructure of targeted heterostructures. Besides the composition (addressed in objective 1), it has been pointed out in the very beginning of this chapter that the properties of heterostructures are dictated by their size, shape and structure as well, which in turn possibly allows us to modulate the properties of heterostructures in a controllable way to a desired level. For example, 1D shape and branched nanostructure are especially favorable for lithium storage because the former can offer direct electron transport path and well cushion the strain in the axial direction, while the latter can offer large electrode/electrolyte contact area endowed with its large surface area.

Built on above objectives, several kinds of metal oxide based heterostructures have been designed and synthesized for efficient electrochemical energy storage. The main content of this thesis can be divided into two major parts.

(i) ***Metal oxide-metal oxide heterostructure.*** In Chapter 2 and 3, two types of novel branched heterostructures comprised of SnO_2 and Fe_2O_3 will be presented. One is based on grafting 1D SnO_2 nanorods onto both sides of pre-grown 2D Fe_2O_3 nanoflakes, forming a comb-like branched heterostructure. The other is a six-fold symmetrically branched $\alpha\text{-Fe}_2\text{O}_3/\text{SnO}_2$ heterostructure prepared by combining a vapor transport deposition and a facile hydrothermal method. It is the first report on the synthesis of branched $\alpha\text{-Fe}_2\text{O}_3/\text{SnO}_2$ heterostructure consisting of SnO_2 backbones and $\alpha\text{-Fe}_2\text{O}_3$ branches. Growth mechanisms are elaborated based on systematic electron microscopy characterizations and control experiments. Both types of heterostructures are applied as working electrodes for LIBs. Their

performances are analytically evaluated and reasons of enhancements are discussed.

(ii) **Graphene-metal oxide heterostructure.** In Chapter 4, a simple and efficient method will be demonstrated for the realization of core-shell assembly of graphene around various metal oxide nanostructures. Such a versatile method can be applied to both nanowires and nanoparticles, and under optimized condition, nearly every single nanowire or nanoparticle can be wrapped by graphene. The graphene@ α -Fe₂O₃ core-shell nanoparticles are investigated as the LIB electrode with detailed characterization of the reversible capacity, cycling stability and rate capability in a comparison to pristine α -Fe₂O₃. In Chapter 5, a new technique for the self-assembly of graphene with metal oxide is demonstrated by incorporating the r-GO platelets into the Co₃O₄ scrolls. Our strategy is assisted by the lamellar micelles of the surfactant and subsequent post-annealing. This assembly enables almost every single Co₃O₄ scroll to connect with the r-GO platelets, leading thus to remarkable electrochemical performances in terms of high specific capacitance and good rate capability.

The thesis is ended with an overall conclusion and suggestions for future research. Our data show that such metal-oxide/metal-oxide and graphene-metal oxides heterostructures are not only interesting for fundamental nanoscience but also technically important for application as new materials in energy storage devices.

Chapter 2

Controlled Growth of SnO₂@Fe₂O₃ Double-sided Nanocombs as Anodes for Lithium-Ion Batteries

2.1 Introduction

SnO₂ and Fe₂O₃, two of the most studied functional semiconductors, which are widely applied in photocatalytic degradation,¹⁵⁴ gas sensing¹⁵⁵⁻¹⁵⁶ and lithium-ion batteries (LIBs),¹⁵⁷⁻¹⁵⁸ have attracted great attentions. Recently, many studies have revealed that the physical performances of SnO₂ or Fe₂O₃ in these areas can be remarkably improved by forming Fe₂O₃/SnO₂ heterostructures.^{22, 159-161} For example, Kang et.al reported that, by integrating α -Fe₂O₃ with SnO₂, the ease of the recombination between photogenerated holes and electrons in α -Fe₂O₃ caused by its short hole diffusion length (2-4 nm) can be effectively mitigated. This is because the photogenerated electrons in the conduction band of α -Fe₂O₃ tend to transfer to that of SnO₂ driven by the decreased potential energy.¹⁶² In fact, many of these applications depend on, and can be reinforced by, the controlled alignment of individual component. Architecturally assembling primary building blocks into the expected geometric heterostructure is thus highly desired. Nevertheless, creating ordered or aligned patterns in high-density arrays is still a challenge in the field of nanoscale science.

Among various heterostructures, branched nanostructures have attracted great interest.^{14, 163-164} Similar to other sophisticated nanostructures, the formation of branched nanostructure offer direct homo- or hetero-epitaxial combination of materials with very different properties at the nanometer scale, which usually give rise to function integration or novel applications. Distinctively, 3D branched heterostructures are able to offer greatly enhanced surface area and function and thus render them promising candidates for potential applications in photocatalysis, photovoltaics, sensing and energy storage devices.^{22, 51, 165-166} Although there are a large variety of hierarchically branched morphologies, in most cases, the composites are based on implementing 1D nanostructures especially nanowires and nanorods as their building blocks.^{160, 167-172} It remains unexploited to add bypasses to 2D nanostructures.

In this chapter, we report the integrative assembly of 1D SnO₂ nanorods and 2D Fe₂O₃ nanoflakes into a novel comb-like free-standing SnO₂@Fe₂O₃ branched nanostructures, in which the SnO₂ nanorods are epitaxially aligned on both sides of Fe₂O₃ nanoflakes in a high density and parallel fashion. It is worth mentioning that such a kind of comb-like nanostructure indicates the emergence of a new paradigm in branched nanostructures, in contrast to previous “tree-like” morphologies. The overall synthetic procedure is very simple and low cost, involving only two steps: direct heating the Fe foil in air for the preparation of Fe₂O₃ nanoflakes stems,^{157, 173} and subsequent hydrothermal epitaxial growth of SnO₂ nanorods branches. Such synthesis procedure does not contain any catalytic impurities and is capable of scaling up. Motivated by the growing interest in LIBs and the good electrochemical performances of SnO₂ and Fe₂O₃, the yielding SnO₂@Fe₂O₃ nanocombs are further exploited as anodes for LIBs application. This unique free-standing hybrid architecture can 1)

completely obviate the need for any ancillary additives such as carbon black and polymer binder, 2) show enhanced reversible capacity and cycling performance compared to pristine Fe₂O₃, which is due both to the prior integration with SnO₂ that can offer high capacity by electrochemically alloying with Li and the large electrode-electrolyte contact area, 3) alleviate the inferior packing problems associated with nanostructures owing to the improved compactness.

2.2 Experiments

2.2.1 Sample Fabrication

The SnO₂@Fe₂O₃ double-sided nanocombs were prepared by a simple two-step process, which can be easily scaled up. The Fe₂O₃ nanoflakes were firstly synthesized by heating the polished (by sand paper) and cleaned (with distilled water) Fe foil (Aldrich, 0.1 mm thick, 99.9+ %) on a hotplate at 400 °C for 24 h in air. Then, a piece of as-obtained Fe foil covered with Fe₂O₃ nanoflakes was placed in a 50 mL sealed Teflon autoclave filling with 30 mL aqueous solution containing 0.174 g of SnCl₄·2H₂O and 0.534 g of NaOH. After growing at 220 °C for 3 h, the substrate was removed from the solution, rinsed with distilled water, and dried with N₂ gas.

2.2.2 Material and Electrochemical Characterizations

Samples were characterized by powder X-ray diffraction (XRD) (Bruker D-8 Advance), scanning electron microscopy (SEM) (JSM-6700F, 10.0 kV), transmission electron microscopy (TEM) (JEM-2010, 200 kV). Electrochemical measurements were performed using two-electrode CR2016 coin-type cells with lithium foil serving as both counter and reference electrodes at room temperature. The SnO₂@Fe₂O₃ nanocombs on Fe foil were directly used as working electrode. Besides, the Fe₂O₃

nanoflakes on Fe foil were also tested for comparison. The electrolyte used was 1.0 M LiPF₆ in a mixture of ethylene carbonate and diethyl carbonate (1:1 by volume). Cell assembly was carried out in an argon-filled glovebox with both moisture and oxygen contents below 0.1 ppm. Galvanostatic charge/discharge tests were performed using a NEWARE battery tester at a voltage window of 0.005–3 V. Cyclic voltammetry (CV, 0.005–3 V, 0.5 mV s⁻¹) and Impedance measurement (0.1-30000 Hz) were performed on the as-made cells using an electrochemical workstation (CHI 760D).

2.3 Results and Discussion

2.3.1 Structure Analysis and Growth Process

Figure 2.1(a) shows the optical images captured during the process flow for the synthesis of SnO₂@Fe₂O₃ heterostructures. For the growth of Fe₂O₃ nanoflakes, the Fe foil is first polished, cleaned, and followed by annealing at 400 °C. At this stage, two phases of Fe₂O₃ and Fe₃O₄ are detected to coexist in the as-obtained sample (Figure 2.2), which is in accordance with our previous results.¹⁷³ The signals of Fe₃O₄ are from a condensed Fe₃O₄ layer formed on top of the Fe foil, acting as the precursor for the growth of Fe₂O₃ nanoflakes.¹⁷³ It can be clearly seen that the color of the Fe foil turned black after annealing. Despite no further visible change in color after subjecting to eventual hydrothermal growth of SnO₂ branches, the branched nanostructures are indeed formed. SEM images evidence the evolution from Fe₂O₃ nanoflakes to SnO₂@Fe₂O₃ nanocombs (Figure 2.1b, c). Pristine Fe₂O₃ nanoflakes are smooth and the thickness is in the range of ~10 nm, having a non-constant planar width in the range of ca. 60-300 nm (Figure 2.1b). After branching with SnO₂, the hierarchical SnO₂@Fe₂O₃ nanostructures look like dog's tail grasses, possessing fuzzy surfaces (Figure 2.1c, d). From magnified SEM images, SnO₂ branches are observed

to emanate from both sides of Fe_2O_3 nanoflakes and are arranged regularly and parallel to each other on each side, forming an intriguing double-sided comb-like structure (Figure 2.1d, e). Though both surfaces are densely covered by SnO_2 nanorods, the edges of Fe_2O_3 nanoflakes remain exposed. The average length and diameter of secondary SnO_2 nanorods are measured to be ca. 150 nm and 20 nm, respectively.

Figure 2.1 (a) Pictures of the samples captured during the process flow. Typical SEM images of (b) Fe_2O_3 nanoflakes and (c) $\text{SnO}_2@\text{Fe}_2\text{O}_3$ heterostructures. (d, e) High-magnification SEM images of $\text{SnO}_2@\text{Fe}_2\text{O}_3$ heterostructures.

Figure 2.2 (a) XRD pattern and (b) Raman spectrum of the as-obtained Fe_2O_3 nanoflakes.

We further characterize the detailed microstructures and composition of such 3D branched nanostructures by TEM. Due to the large varying planar dimension of these $\text{SnO}_2@\text{Fe}_2\text{O}_3$ nanocombs, it is extremely difficult to analyze the epitaxial relationship from the lateral view of the heterostructures. Consequently, we investigate the Fe_2O_3 stem and the SnO_2 branch individually. Three groups of parallel fringes with the same d -spacing of 0.25 nm can be found in the high-resolution TEM (HRTEM) image of a Fe_2O_3 nanoflake (Figure 2.3a). They can be indexed to $(\bar{1}20)$, $(2\bar{1}0)$ and (110) planes of rhombohedral Fe_2O_3 respectively, according to corresponding Fast-Fourier transformation (FFT) pattern (Figure 2.3b). Besides, it can be observed that the FFT pattern is in high consistence with the selected-area electron diffraction (SAED) pattern (Figure 2.3c), which can be indexed in accord with the $[001]$ zone axis of rhombohedral Fe_2O_3 (Figure 2.3d). Thermodynamically, the nanoflakes tend to lay

their basal plane on the TEM grid with fully coated carbon film. The [001] zone axis is observed with several of the nanoflakes with minimal tilting of the samples. Therefore, it can be unambiguously deduced that the exposed surfaces of Fe₂O₃ nanoflake are ($\pm$ 001) planes, acting as the substrates for the epitaxial growth of secondary branches. Similarly, judging from corresponding SAED pattern (Figure 2.3f), the marked interplanar *d*-spacings of 0.32 nm and 0.33 nm in the HRTEM image of a SnO₂ nanorod correspond to the (001) and ($\bar{1}10$) lattice fringes of tetragonal SnO₂ respectively (Figure 2.3e). The SnO₂ nanorod is determined to grow along [001] direction. The TEM analyses suggest that the SnO₂ nanorods prefer to branch perpendicularly to the Fe₂O₃ nanoflake such that the SnO₂ branches epitaxially grow along the [001] direction, on the ($\pm$ 001) planes of Fe₂O₃ nanoflake, forming a (001)_{SnO₂}/(001)_{Fe₂O₃} interface. Energy-dispersive X-ray spectroscopy (EDX) mapping is adopted to further identify the composition of single SnO₂@Fe₂O₃ nanocomb. Clearly, the Fe, Sn, and O signals appear all over the whole structure, showing exactly the same shape as it is observed under TEM (Figure 2.3g). Special attention should be paid to the fact that the SnO₂ nanorods tightly adhered on the surface of Fe₂O₃ nanoflake even after 0.5 h sonication (Figure 2.4). This is especially desirable for energy storage devices that require tough structural integrity, which can endure repeated Li insertion/extraction.

Figure 2.3 (a) HRTEM image, (b) FFT pattern taken from the rectangular area in (a), and (c) corresponding SAED pattern of a Fe_2O_3 nanoflake. (d) Crystal structure of Fe_2O_3 along $[001]$ zone axis. (e) HRTEM image and (f) corresponding SAED pattern of a SnO_2 nanorod separated from a $\text{SnO}_2@\text{Fe}_2\text{O}_3$ nanocomb via sonication. (g) TEM image and corresponding EDX elemental mappings of Fe, Sn and O for a $\text{SnO}_2@\text{Fe}_2\text{O}_3$ nanocomb, showing the uniform distribution of each element.

Figure 2.4 TEM images of $\text{SnO}_2@\text{Fe}_2\text{O}_3$ nanocombs after being sonicated for 0.5 h, suggesting the strong adherent forces between the SnO_2 branches and Fe_2O_3 cores.

To reveal the evolution process of such a branched nanostructure, time-dependent control experiments were carried out. As shown in Figure 2.5(a), no visible change occurred to pristine after initial 1 h of growth. The surfaces of Fe₂O₃ nanoflakes remained clean and smooth. Whereas, it could be seen that small dot- and needle-shaped nuclei appeared on both sides of Fe₂O₃ nanoflakes 1 h later (Figure 2.5b). The complete formation of double-sided comb-like SnO₂@Fe₂O₃ nanostructures took place when the growth time reached 3 h (Figure 2.5c). Afterwards, only the diameter of SnO₂ nanorod branches varied with increasing reaction time (Figure 2.5d). The synthesis and branching process of the SnO₂@Fe₂O₃ hierarchical nanostructures consists mainly of three steps and is schematically illustrated for better understanding (Figure 2.5e). Specifically, the Fe₂O₃ nanoflakes are first grown on the Fe foil through a possible solid-liquid-solid (SLS) mechanism that we proposed previously, involving the melting of surface layer of Fe foil and forming a liquid medium Fe₃O₄ serving as the precursor for the growth of Fe₂O₃ nanoflakes.³¹ Then, the SnO₂ nanoparticles heteronucleate through dehydration of Sn(OH)₆²⁺, followed by epitaxial grow on the surfaces of Fe₂O₃ nanoflakes, establishing the (001)_{SnO₂}/(001)_{Fe₂O₃} interfaces. Finally, these particles anisotropically grow up into aligned nanorod arrays on both sides of Fe₂O₃ nanoflakes along the [001] direction, giving rise to the formation of branched SnO₂@Fe₂O₃ nanostructures with two-fold symmetry.

Figure 2.5 SEM images of products obtained at various reaction stages: (a) 1 h, (b) 2 h, (c) 3 h, (d) 4 h. The insets are corresponding high-magnification SEM images, the scale bars in the insets are 200 nm. (e) Schematic illustration of the formation process of hierarchically assembled $\text{SnO}_2@\text{Fe}_2\text{O}_3$ nanocombs.

2.3.2 LIB Performance

The use of nanomaterials is highly beneficial for LIBs as the small diffusion lengths and large surface areas of nanostructures can improve the capacities and rate capabilities of solid-state electrodes. In particular, those free-standing nanostructures directly grown onto a plane current collector can well maintain the gains in diffusion length and electronic conductivity associated with the reduced size, because they completely rule out the need of ancillaries and further processing. At the same time, they can also avoid the addition of supplementary interfaces (current collector/active

materials, active material/active material, active material/binder, etc.). Recently, the use of composites represents a very effective strategy to solve the problem of the large capacity degradation, we thus intend to employ our self-supported SnO₂@Fe₂O₃ heterostructures directly as a working electrode, to achieve improved performances.

Galvanostatic discharge/charge and CV measurements were used to characterize the electrochemical performances of bare Fe₂O₃ nanoflakes and SnO₂@Fe₂O₃ nanocombs as anodes of LIBs. The working electrodes can be prepared simply by cutting the Fe-foil supported nanostructures into small platelets without further processing (inset in Figure 2.6a). As expected, the nano-architected SnO₂@Fe₂O₃ electrode manifests superior reversibility and cycling stability towards pristine Fe₂O₃ nanoflakes (Figure 2.6). As shown in Figure 2.6(a), after initial fast capacity fading, the SnO₂@Fe₂O₃ nanocombs are able to deliver a stable areal capacity with an average value of 0.43 mA h cm⁻² up to 150 cycles, which is about 1.7 times of that for bare Fe₂O₃ nanoflakes (0.25 mA h cm⁻²). The Coulombic efficiency of the composite electrode is also slightly improved, which is likely due to the synergistic effect between these two components, i.e. the presence of Fe nanoparticles come from the lithiation process of inner Fe₂O₃ core can promote the reversibility of the reaction between SnO₂ and Li⁺.¹⁶¹ Although the SnO₂@Fe₂O₃ heterostructures suffer from severe capacity fading in the beginning, they can always deliver twice the capacities of those for Fe₂O₃ nanoflakes under different current densities (Figure. 2.6b). Noticeably, both electrodes can exhibit high capacity again when the current density is lowered back to 0.18 mA cm⁻². One possible factor accounting for the improved capacity of SnO₂@Fe₂O₃ heterostructures at varied current densities is their slightly reduced charge transfer resistance (23.6 Ω cm⁻²) compared with bare Fe₂O₃ nanoflakes (29.6 Ω cm⁻²) (inset in Figure 2.6b). More direct evidence showing the enhanced

capacity of composite electrode can be viewed from its long plateau during the charge/discharge process and enlarged area surrounding by the CV curve charge-discharge and CV curves compared to those of Fe_2O_3 electrode, respectively (Figure 2.6c, d). While the introduction of SnO_2 definitely contributes to the improved capacity of composite electrode by offering more active materials that can electrochemically alloy with Li, the unique 3D comb-like morphologies are considered to play a crucial role as well. Branching SnO_2 nanorods on both sides of Fe_2O_3 nanoflakes rather than growing them on planar substrate can induce largely increased surface area and simultaneously give rise to loose arrangement of SnO_2 nanorods, allowing sufficient electrolyte infiltration and subsequent enhancement of electrode-electrolyte contact area. Although the specific capacity of the electrode cannot be determined due to the uncertainty of the mass of active materials, the volumetric energy density of the composite electrode is certainly improved. This is because the introduction of SnO_2 branches does not change the initial volume occupied by bare Fe_2O_3 nanoflakes but fill the free spaces between the Fe_2O_3 nanoflakes, resulting in a more dense structure (Figure 2.6e). In this case, the improved areal capacity will undoubtedly lead to enhanced volumetric energy density. It is important to highlight that the lower volumetric energy density is one of the disadvantages that concomitantly appears when nanomaterials are used as the electrodes for LIBs due to the inferior packing of particles. It is even more difficult to improve the volumetric energy densities for those free-standing nanostructures as other materials are hard to be added without destroying their initial structures. When such a situation arises, preparation of composites at the nanoscale is highly important.

Figure 2.6 (a) Cycling behavior and Coulombic efficiency of $\text{SnO}_2@\text{Fe}_2\text{O}_3$ heterostructures and Fe_2O_3 nanoflakes under a current density of 0.18 mA cm^{-2} for 150 cycles. The inset shows the optical images of the $\text{SnO}_2@\text{Fe}_2\text{O}_3$ (right two) and Fe_2O_3 (left two) platelets as working electrodes. (b) Comparison of the rate capabilities of $\text{SnO}_2@\text{Fe}_2\text{O}_3$ heterostructures and Fe_2O_3 nanoflakes cycled under different current densities. The inset shows their respective Nyquist plots. (c) Voltage profiles for $\text{SnO}_2@\text{Fe}_2\text{O}_3$ and Fe_2O_3 electrodes during the 5th cycle under a current density of 0.18 mA cm^{-2} . The arrow indicates the prolonged plateau for $\text{SnO}_2@\text{Fe}_2\text{O}_3$ during the discharge process. (d) CV curves for $\text{SnO}_2@\text{Fe}_2\text{O}_3$ and Fe_2O_3 electrodes during the 5th cycle at a scan rate of 0.5 mV s^{-1} . The presences of the peaks marked

by the blue dashed circles are due to the redox reactions between SnO₂ and Li⁺. (e) Schematic illustration of the improved occupation of the SnO₂@Fe₂O₃ nanocombs within certain volume, thereby establishing high volumetric energy density.

2.4 Conclusion

In summary, a novel SnO₂@Fe₂O₃ comb-like branched heterostructure by hydrothermal grafting 1D SnO₂ nanorods onto both sides of pre-grown 2D Fe₂O₃ nanoflakes has been demonstrated in this chapter. TEM analyses of individual components suggest that SnO₂ nanorods are grown on the (± 001) planes of Fe₂O₃ nanoflakes along [001] direction, leading to the unique two-fold symmetrical structure. The resulting SnO₂@Fe₂O₃ nanocombs show stabilized cycling performance and improved volumetric energy density compared to pristine Fe₂O₃ nanoflakes, which are presumably due to the integration of SnO₂ branches as well as 3D hierarchical structural features. We believe such a novel comb-like SnO₂@Fe₂O₃ heterostructure is also a promising candidate in photocatalytic, water splitting and photovoltaic applications.

Chapter 3

Epitaxial Growth of Branched $\alpha\text{-Fe}_2\text{O}_3@\text{SnO}_2$ Nanowires with Improved Lithium-Ion Battery Performance

3.1 Introduction

As addressed in the previous chapter, branched nanostructures possess a supplementary advantage of large surface area compared to other hierarchical heterostructures (e.g., core-shell, segmented heterostructures). This is especially desirable for energy conversion and storage devices as sufficient light harvest and electrolyte infiltration can be ensured. In particular, hierarchical branching nanowires are extremely favorable. For example, for photovoltaic (PV) and photoelectrochemical (PEC) applications, conventional planar devices are required to be thick enough to absorb incident light, which in turn restricts the materials quality due to limited minority carrier diffusion lengths. In a nanowire, however, the light absorption can occur along the long axis, while carrier separation takes place by diffusing across the short radial axis. It can thus accommodate lower quality materials. The introduction of branches to arrays of nanowires further benefit the light harvesting by adding more materials to absorb incident light, and improving the light scattering and therefore photocarrier generation.⁵¹ Similarly, for LIBs and supercapacitors, the addition of branches can also improve the energy storage by adding more active materials and increasing the electrode/electrolyte contact area and

thus more active sites. Especially, for the secondary branches, branching on loosely arranged nanowires rather than planar substrates can effectively enhance the electrolyte accessibility by providing more free spaces. Besides, for these energy conversion and storage devices, the dendritic-like branched nanostructures are able to optimize efficient carrier collection from the numerous terminals to a central trunk.

In recent years, various materials like PbS,¹⁷⁴ TiO₂,¹⁷⁵⁻¹⁷⁶ V₂O₅,¹⁷⁷ SnO₂,¹⁷⁸⁻¹⁷⁹ Fe₂O₃,^{22, 31, 180} and techniques including sequential seeding of catalysts and self-assembled growth of nanowires have been demonstrated to form 3D branched,¹⁸¹⁻¹⁸² hyperbranched¹⁸³⁻¹⁸⁵ and multibranched nanowire structures.^{14, 164, 186} Nevertheless, the complexity of the required structures and the difficulty in manipulating the entropic and/or energetic constraints of different building blocks remain formidable challenges awaiting to be resolved. Solution-phase growth generally allows a higher degree of control over the size and shape of the resulting nanostructures compared with vapor-phase strategies.^{22, 167} In addition, the salient features of low cost, low growth temperature, environmental friendliness, easy processability and high yield make solution-based methods very promising.

In this work, we continue to choose SnO₂ and Fe₂O₃ as nanobuilding blocks for the construction of heterostructures for LIBs due to their high theoretical capacities. Despite successful attempts have been made on assembling SnO₂ nanorod branches onto various α -Fe₂O₃ stems including the work we introduced in the last chapter,^{22, 31, 180} to our best knowledge, there is no report on branching α -Fe₂O₃ nanorods on SnO₂ nanowire stems. This reverse structure should be more favourable for energy storage devices as the SnO₂ trunk can more effectively transport the collected electrons compared with α -Fe₂O₃ due to its superior electrical conductivity. Herein, we have prepared six-fold-symmetry branched FeOOH/SnO₂ and α -Fe₂O₃/SnO₂

heterostructures by combining CVD (for SnO₂ stem) and hydrothermal route (for FeOOH branches). Due to the high controllability of hydrothermal method, the lengths of FeOOH nanorods can be simply modulated by adjusting the concentration of the reactant and/or the growth time. It should be noted that, in previous reports, the six-fold-symmetry heterostructures including SnO₂@ α -Fe₂O₃ are generally induced by six identical surfaces provided by the stem for the anchoring of branches.^{22, 31, 167, 182} Nevertheless, in this work, the SnO₂ nanowires are determined to only have tetragonal structure with four exposed side surfaces. The reason why secondary FeOOH nanorods still grow with a six-fold-symmetry is proved to be the result of minimization of lattice mismatch on distinct SnO₂ surfaces. A possible growth mechanism is proposed based on a series of control experiments. Finally, a proof-of-concept of the function of such branched α -Fe₂O₃/SnO₂ composites as LIBs anode is demonstrated, showing superior performance to both SnO₂ and α -Fe₂O₃ individual components in terms of lower initial irreversible loss and higher reversible capacity. The synergistic effect between SnO₂ and α -Fe₂O₃ and the characteristic of branched nanostructure are proposed to be the origins of the performance improvement.

3.2 Experimental

3.2.1 Sample Synthesis and Characterizations

The SnO₂ nanowires were pre-synthesized on stainless steels via standard CVD method according to our previous publication.¹⁶⁷ Then the α -Fe₂O₃/SnO₂ hierarchical structures were prepared by a seed, catalyst, and surfactant-free hydrothermal method, the recipe of which was slightly modified from previous reports on preparation of α -Fe₂O₃ nanorod arrays.¹⁸⁷ In a typical process, a piece of stainless steel substrate covered by SnO₂ nanowires was placed within a 50 mL sealed Teflon autoclave

containing 30 mL solution consisted of FeCl₃·6H₂O (0.15 M) and NaNO₃ (1 M), the pH value was adjusted to ~1.5 by hydrochloric acid (36.5%). The hydrothermal reaction was conducted at 100 °C for 24 h. After that, the substrate was removed from the solution, rinsed with deionized water, and blow-dried with N₂ gas. Further heat treatment in air at 450 °C for 2 h is required to the phase transition from the resulting precursors (β -FeOOH) to pure α -Fe₂O₃. By replacing the stainless steel with Ti foil while other conditions keep unchanged, pure α -Fe₂O₃ nanorod arrays could be obtained.

The morphology and the crystalline structure of the as-fabricated SnO₂/ α -Fe₂O₃ nanoheterostructures were characterized with a JEOL JSM-6700F field emission scanning electron microscope (FE-SEM) and a JEM 2010F high-resolution transmission electron microscope (HR-TEM). X-ray powder diffraction (XRD) patterns were recorded on a Bruker D8 Advance diffractometer using Cu K α radiation.

3.2.2 Electrochemical Measurements

The electrochemical tests were carried out using two-electrode cells with pure lithium metal as the counter and reference electrodes at room temperature. The α -Fe₂O₃/SnO₂ semiconductor branched nanostructures on stainless steel were directly used as working electrode. In order to get relatively reliable data of the sample mass, we used an AX/MX/UMX Balance (METTLER TOLEDO, Maximum =5.1 g; d = 1 μ g). The mass of the sample can be calculated after the subtraction of bare substrate's mass. For each sample, 10 pieces of 2 cm² substrates were measured before and after growth to get the statistical average mass. In comparison, the Li-ion batteries performance of pure SnO₂ nanowires and α -Fe₂O₃ nanorod arrays were also tested. The electrolyte used was 1.0 M LiPF₆ in a mixture of ethylene carbonate and diethyl

carbonate (1:1 by volume). The Swagelok-type cell assembly was carried out in an Ar-filled glovebox (Mbraun, Unilab, Germany) with concentrations of moisture and oxygen below 0.1 ppm. The discharge-charge cycling was performed at room temperature by using a multichannel battery tester (model SCN, USA).

3.3 Results and Discussion

3.3.1 Structure Characterization, Growth Control and Mechanism Investigation

As mentioned in the experimental section, we are able to synthesize three samples, namely pristine SnO₂ nanowires, bare α -Fe₂O₃ nanorod arrays and hierarchical α -Fe₂O₃/SnO₂ nanostructures, in this work. Their crystal structures and phase purities are revealed by corresponding XRD patterns (Figure 3.1). It is found that all the diffraction peaks for these three products match well with those of standard XRD patterns of tetragonal rutile SnO₂ (JCPDF: 41-1445) and rhombohedral α -Fe₂O₃ (JCPDF: 33-0664). Although the positions of some standard XRD peaks of tetragonal FeOOH are very close to those of SnO₂ and α -Fe₂O₃, no additional peaks other than these with similar positions were found in the XRD pattern of α -Fe₂O₃/SnO₂ composites, indicating the complete transition from FeOOH to α -Fe₂O₃.

Figure 3.1 XRD patterns of (a): pristine SnO₂ nanowires; (b) bare α -Fe₂O₃ nanorod arrays; (c) α -Fe₂O₃/SnO₂ branched nanostructures. The vertical lines in (a), (b), (c)

denote the standard XRD patterns corresponding to that of rutile SnO_2 (JCPDF: 41-1445), rhombohedral $\alpha\text{-Fe}_2\text{O}_3$ (JCPDF: 33-0664) and tetragonal FeOOH (JCPDF: 34-1266).

Under SEM observation, the multiple rows of branches are clearly viewed in the as-obtained composites and arranged in a parallel way (Figure 3.2a). However, due to the high density of branches, the stems are only visible at the exposed ends of some branched nanowires (Figure 3.2a). Moreover, it is interesting to find that the majority of these branched nanostructures exhibit a six-fold symmetry, i.e. the nanorod branches grow along six directions on the SnO_2 nanowires with the angle of approximately 60° between adjacent branches (Figure 3.2b). There still exist a few “two-fold-symmetry” structures (indicated by the arrows in Figure 3.2a), which are considered to be part of the underdeveloped six-fold-symmetry structures. The magnified SEM and TEM images also reveal that the branches are assembled in bundles, with an average diameter of about 50 nm and length of 500 nm, of well-aligned porous nanorods (Figure 3.2b-d). TEM elemental mapping is conducted to clearly recognize the spatial distributions of Fe, Sn and O in the backbone and branches (as shown in Figure 3.2e-g). The results indicate that the Sn and Fe signals only appear in the backbone and branch region respectively, while the signal of element O is uniformly distributed over the entire structure, further verifying the phase compositions of the stem (SnO_2) and the branches ($\alpha\text{-Fe}_2\text{O}_3$).

Figure 3.2 (a) Typical SEM image; (b, c) High-magnification SEM and TEM images of a single six-fold-symmetry branched nanowire. (d-g) TEM image of a single branched nanowire and corresponding elemental mapping images.

In view of the high symmetry and uniformity of such branched nanostructure, there must be certain epitaxial relationships between the branch and stem. We thus conducted detailed HRTEM imaging of their interface. Figure 3.3(a) presents a TEM image of one as-obtained six-fold-symmetry branched nanowire. Note that $\alpha\text{-Fe}_2\text{O}_3$ branches were obtained via annealing their corresponding precursors. In other words, the branches directly grown on SnO_2 nanowires are the precursors of $\alpha\text{-Fe}_2\text{O}_3$. Hence, the real epitaxial relationship should be investigated is between SnO_2 nanowire and the precursor of $\alpha\text{-Fe}_2\text{O}_3$. In order to determine the phase composition of these precursors, control experiment of growing them directly on the substrate rather than SnO_2 nanowires was carried out to exclude the interference of SnO_2 . XRD characterization of as-obtained precursors reveals the branches before annealing can be assigned to FeOOH with a tetragonal structure (JCPDF: 34-1266, Figure 3.4a).

Figure 3.3(b) is the corresponding HRTEM image of the circled interfacial area in Figure 3.3(a). The lattice spacings of 0.26 nm for the stem and 0.25 nm for the branch are in good agreement with $(10\bar{1})$ and (330) interplanar spacings of tetragonal SnO_2 and FeOOH , respectively. It can be observed that the (330) planes of FeOOH stack parallel to the $(10\bar{1})$ ones of SnO_2 , implying that the FeOOH nanorods epitaxially grow on the $(10\bar{1})$ surface of the SnO_2 along the normal direction of $(330)_{\text{FeOOH}}$ planes, i.e. $[110]_{\text{FeOOH}}$ direction. Corresponding FFT patterns further confirm the parallel relationship between $(330)_{\text{FeOOH}}$ and $(10\bar{1})_{\text{SnO}_2}$ planes (insets in Figure 3.3b). Besides, this parallel stacking model between $(330)_{\text{FeOOH}}$ and $(10\bar{1})_{\text{SnO}_2}$ planes can be observed in the interface of another branched nanowire as well (Figure 3.4b). For SnO_2 with tetragonal structure ($a = b = 4.738 \text{ \AA}$, $c = 3.187 \text{ \AA}$), the (101) plane and $[101]$ direction are not perpendicular but inclined at an angle of 68° . The growth direction of the SnO_2 nanowires, angled 68° to the (101) plane, is determined to be $[101]$.¹⁸⁸ The side surfaces of such SnO_2 nanowires can be further indexed to $\pm(010)_{\text{SnO}_2}$ and $\pm(10\bar{1})_{\text{SnO}_2}$ planes. Thus, the branches satisfying the above epitaxial relationship, namely $(330)_{\text{FeOOH}} // (10\bar{1})_{\text{SnO}_2}$, will grow along the $[110]_{\text{FeOOH}}$ direction and perpendicular to the stem because, in tetragonal SnO_2 , $\pm(10\bar{1})$ planes are parallel to the $[101]$ direction (e.g., the growth direction of SnO_2 nanowires). This perpendicular orientation of the branches to the stem can be straightforwardly viewed from some TEM images (Figure 3.5).

Figure 3.3 (a) TEM image of FeOOH/SnO₂ branched nanostructure; (b) High-resolution TEM image of the circular area in (a); insets are the fast Fourier transformation (FFT) patterns of the SnO₂ stem and FeOOH branch, respectively; (c, d) Schematics of the interface of the (010)_{SnO₂} plane of SnO₂ stem and the ($\bar{3}30$)_{FeOOH} plane of FeOOH branch, revealing the lower interfacial lattice mismatch of slantwise growth mode compared with that of perpendicular growth.

Figure 3.4 (a) XRD pattern of the as-prepared FeOOH, the vertical lines denote the standard XRD patterns corresponding to that of tetragonal FeOOH (JCPDF: 34-); (b) High-resolution TEM image of the as-prepared FeOOH, the vertical lines denote the standard XRD patterns corresponding to that of tetragonal FeOOH (JCPDF: 34-).

1266). (b) HRTEM image of the branch-stem junction, inset is the FFT image of the SnO_2 stem.

Figure 3.5 Typical TEM images of the FeOOH@SnO_2 branched nanowires, showing that the branches are oriented perpendicular to the stems.

Besides this perpendicular growth mode, careful SEM observations indicate that there still exists a slantwise growth mode of the rest four groups of FeOOH branches, each forming 60° with respect to the stem (Figure 3.6). Derived from the parallel relationship between the $(330)_{\text{FeOOH}}$ plane and $(10\bar{1})_{\text{SnO}_2}$ plane, the equivalent planes of $(330)_{\text{FeOOH}}$ plane, i.e. $\pm(3\bar{3}0)_{\text{FeOOH}}$ planes, are thus parallel to $\pm(010)_{\text{SnO}_2}$ planes. Nonetheless, if the $\pm(3\bar{3}0)_{\text{FeOOH}}$ planes also adopt a perpendicular growth mode on the $\pm(010)_{\text{SnO}_2}$ planes, the lattice mismatch can be as large as 47.7% $[(0.474-0.248)/0.474 \approx 47.7\%]$. Instead, the slantwise growth model can significantly reduce the interfacial lattice mismatch to 4.6% $[(0.496-0.474)/0.474 \approx 4.6\%]$ (Figure 3.3d). This implies that the branches anchored on the $\pm(010)_{\text{SnO}_2}$ planes prefer to grow at an inclined angle (e.g., 60°) to better accommodate a thermodynamically stable epitaxial growth from the substrate. The adopted calculation methodology has also

been reported in other works.^{22, 189} Consequently, the growth mode of the branches on $\pm(010)_{\text{SnO}_2}$ planes of the stem differs from that on the $\pm(10\bar{1})_{\text{SnO}_2}$ planes, leading to the formation of a six-fold symmetry rather than four-fold. On the ground of above analysis, it is suggested that the least interfacial lattice mismatch is the major driving force causing different preferential growth orientations of the FeOOH branches on distinct crystallographic surfaces of the SnO₂ stem. Note that almost all of previously reported branched nanostructures with six-fold symmetry are based on a hexagonal-shaped stem, which provides six equivalent planes to induce the secondary growth of the branches.^{22, 31, 171, 182, 190} Therefore, the novelty of our branched nanostructure is reflected in the fact that the six-fold symmetry of the branches is induced by tetragonal SnO₂ nanowire stem with only four exposed side facets. Meanwhile, the angles between the adjacent branches can be derived to be 60° as well, which is also well supported by the SEM and TEM observations (Figure 3.7).

Figure 3.6 SEM images of the ends of the branched nanoheterostructures, showing the rectangular cross-section of inner SnO₂ nanowires and the orientations of the six branches with respect to the SnO₂ side faces.

Figure 3.7 Typical TEM images (a-b) and SEM images (c-d) of the cross-sections of the branched heteronanostructures for the easy measurement of the angles between adjacent branches, which are $\sim 60^\circ$.

The structure of final product $\alpha\text{-Fe}_2\text{O}_3\text{@SnO}_2$ obtained via post-annealing is also characterized by TEM and HRTEM (Figure 3.8a-c). It can be seen that the interface epitaxial relationship has changed from $(330)_{\text{FeOOH}}//(\bar{1}0\bar{1})_{\text{SnO}_2}$ to $(012)_{\alpha\text{-Fe}_2\text{O}_3}//(101)_{\text{SnO}_2}$ after annealing (Figure 3.8b). The single-crystalline feature of the $\alpha\text{-Fe}_2\text{O}_3$ branch is well observed from its HRTEM image and corresponding FFT image (Figure 3.8c and its inset).

Figure 3.8 (a) Low-magnification TEM image of the $\alpha\text{-Fe}_2\text{O}_3/\text{SnO}_2$ branched nanostructure; (b, c) Corresponding high-resolution TEM images of the circular and

square areas in (a); insets are corresponding fast-Fourier transformation (FFT) patterns of the stem and branch.

The evolution processes of nanorod branches were unveiled by collecting the samples at different reaction stages. Corresponding SEM characterization of these products obtained from various growth times clearly reveal the morphological and structural transformation from SnO₂ nanowires to α -Fe₂O₃@SnO₂ branched nanocomposites (Figure 3.9). Specifically, initial 30 min of growth gave rise to no visible change to bare tetragonal SnO₂ nanowires (Figure 3.9a). However, ~10 nm sized nanoparticles were observed to nucleate on the surfaces of SnO₂ nanowires after another 30 min of reaction. The thorn-like shape of these small nanoparticles indicated their anisotropic growth tendency (Figure 3.9b). As expected, when the reaction time increased to 2 h, the earlier-formed thorn-like nanoparticles elongated, establishing the rudiments of nanorods. Instead of exhibiting symmetric feature, these nanoparticles were still of different orientations (Figure 3.9c). However, when the reaction time reached 4 h, hierarchical nanostructures of perfect six-fold-symmetry were formed with the branches lengths of about 250 nm (Figure 3.9d). The overall morphology exhibited no change after further increasing the reaction time, only the lengths of branches increased (350 nm for 10 h; 500 nm for 24 h) (Figure 3.9e-f).

A simple three-step growth process is proposed on the basis of above analysis (Figure 3.9g). First, through a hydrolysis of FeCl₃ under acidic condition, the formed FeOOH nuclei attach to the SnO₂ nanowire surfaces and are oriented along the preferred direction of crystallization. Second, these particles grow into aligned nanorods with increasing time, resulting in six-fold-symmetry branches surrounding the SnO₂ nanowire stem. The basic theory and conditions for such an anisotropic growth have been well elaborated in a previous report.¹⁸⁷ Finally, post annealing

enables the topological transformation from FeOOH@SnO_2 to $\alpha\text{-Fe}_2\text{O}_3\text{@SnO}_2$ branched nanowires.

Figure 3.9 (a-f) SEM images of the products (after annealing) at various reaction stages by setting the reaction time. The insets are the corresponding magnified SEM images. The scale bars in the figures and insets are $2\ \mu\text{m}$ and $500\ \text{nm}$, respectively. (g) Schematic formation process of hierarchically assembled $\alpha\text{-Fe}_2\text{O}_3\text{/SnO}_2$ nanocomposite.

It should be addressed that, besides altering the reaction time, varying the reactant concentration can also tune the length of nanorod branches. For example, the $500\ \text{nm}$ length was achieved from a FeCl_3 concentration of $0.15\ \text{M}$ (Figure 3.10a), while half of that concentration only produced nanorod branches of $\sim 350\ \text{nm}$ long (Figure 3.10b). When the FeCl_3 concentration reduced to $0.037\ \text{M}$, the lengths of the branches were only $70\ \text{nm}$ (Figure 3.10c). The six-fold symmetry was, however, still preserved. With further decreasing the FeCl_3 concentration to $0.025\ \text{M}$, there were

only some nanoparticles and nanoflakes on the surfaces of SnO₂ nanowires without any symmetric features (Figure 3.10d).

Figure 3.10 SEM images of the products (after annealing) obtained from different concentrations of FeCl₃·6H₂O: (a) 0.15 M; (b) 0.075 M; (c) 0.037 M; (d) 0.025 M. The insets are the corresponding magnified SEM images. The scale bars in the insets are 500 nm.

3.3.2 Function as LIBs Anode

Recently, great research attention has been attracted to search for superior anode materials to improve the energy density and safety of LIBs.^{101-102, 114-115, 129} To this end, we also investigate the potential electrochemical performances of our α -Fe₂O₃@SnO₂ branched nanowires as a binder-free anode material for LIBs. The lithium storage properties of such a composite electrode are evaluated by the galvanostatic discharge/charge measurement at a current density of 1000 mA g⁻¹. Figure 3.11(a) depicts the first-cycle charge-discharge profiles of α -Fe₂O₃@SnO₂ branched nanowires, SnO₂ nanowires and α -Fe₂O₃ nanorods. Obviously, the branched

nanowires deliver a much improved first discharge capacity of 1167 mA h g^{-1} , which is almost twice those of SnO_2 nanowires (612 mA h g^{-1}) and $\alpha\text{-Fe}_2\text{O}_3$ nanorods (598 mA h g^{-1}). Moreover, the composite electrode also exhibits the lowest initial irreversible loss of 30.6% compared to 43.9% for $\alpha\text{-Fe}_2\text{O}_3$ nanorods and 56.4% for SnO_2 nanowires. We hereby attribute this much lower irreversible loss of $\alpha\text{-Fe}_2\text{O}_3@\text{SnO}_2$ branched nanowires to a synergistic effect between SnO_2 and $\alpha\text{-Fe}_2\text{O}_3$.¹⁶¹ Specifically, lithium storage reactions occurring on SnO_2 electrodes can be described by the following processes:¹⁹¹⁻¹⁹³

Different from above alloying process, the electrochemical reaction of $\alpha\text{-Fe}_2\text{O}_3$ with Li follows the conversion-reaction mechanism:

which is fully reversible.¹⁰⁴ Note that the metal nanoparticles formed *in-situ* can promote the reversible formation and decomposition of Li_2O nanomatrix. Thus, the presence of Fe nanoparticles (3.3) at the interface between $\alpha\text{-Fe}_2\text{O}_3$ and SnO_2 may improve the reversibility of reaction (3.1) and further result in a higher reversible capacity. In this context, branching SnO_2 with a conversion-type metal oxide can be considered as an effective strategy to resolve one major drawback of SnO_2 -based anode materials, i.e. large initial irreversible loss. This result is also consistent with what we concluded in the last chapter. Comparative cycling performances of these three samples are displayed in Figure 3.11(b). Due to the large initial irreversible loss, a sharp capacity fading is observed for all the samples in the second cycle. Albeit with relatively faster capacity decay, the composite electrode always delivers higher capacity compared to pristine SnO_2 nanowires and $\alpha\text{-Fe}_2\text{O}_3$ nanorod arrays.

Since the composite electrode exhibits a higher capacity than both single components, the enhancement cannot be simply viewed as a result of the introduction of a higher capacity component. Instead, it stems more likely from the unique architecture of the composite electrode. On one hand, the enhanced capacity of branched nanowires compared to bare SnO₂ nanowires can be easily understood because the addition of a higher-capacity α -Fe₂O₃ branches not only provide new Li⁺ hosts but also increase the reversible capacity of SnO₂ by improving the reversibility of reaction (3.1). On the other hand, the reason why branched heterostructures still deliver a higher specific capacity than pure α -Fe₂O₃ nanorod arrays after the introduction of a lower-capacity component, SnO₂, is a little hard to understand. This is hereby believed to be more related to the unique branched nanostructure. It can be seen that bare α -Fe₂O₃ nanorods exhibit a very dense structure when directly grown on planar substrate (Figure 3.12a). This is unfavourable to the accessibility of the electrolyte (thus Li⁺). However, after branching on the SnO₂ nanowires, the α -Fe₂O₃ nanorods have an increased portion of exposed surfaces and thus can provide more active sites for Li⁺ accesses (Figure 3.11c). It can be easily observed from the SEM images of branched heterostructures that there are a lot of free spaces between the branched nanowires, ensuring a high utilization of electrode materials and thus a high capacity. Furthermore, given the porous nature of α -Fe₂O₃ nanorods (Figure 3.7), the effect of sparse arrangement on inducing high capacity will be stronger. The capacity enhancement arising from the higher α -Fe₂O₃ surface areas could thus outperform the introduction of the lower-capacity component, SnO₂. As a result, a higher capacity can still be obtained for the composite electrode than that of pure α -Fe₂O₃ nanorod arrays. Furthermore, the relatively high electrical conductivity of SnO₂ trunks is likely another important factor in enhancing the electrochemical properties of branched

composite electrode, which can transport the electrons to the underneath current collector more efficiently. The effort to improve the capacity retention is undergoing.

Figure 3.11 Application of the branched nanostructures as LIB anodes. (a) First charge-discharge profiles at a rate of 1000 mA g^{-1} , and (b) Cycling performance of bare $\alpha\text{-Fe}_2\text{O}_3$ nanorod arrays, pristine SnO_2 nanowires, and $\alpha\text{-Fe}_2\text{O}_3/\text{SnO}_2$ branched nanostructure. (c) Schematic comparison of the unidirectional nanowires and branched nanostructures for electron collection. The latter provides more active surface sites for Li^+ access than the former, and thus delivers more electrons to the current collector.

Figure 3.12 SEM images of (a) $\alpha\text{-Fe}_2\text{O}_3$ nanorods arrays grown directly on Ti substrate, and (b) the pristine SnO_2 nanowires.

3.4 Conclusion

We demonstrate a novel $\alpha\text{-Fe}_2\text{O}_3@\text{SnO}_2$ branched nanowires with six-fold-symmetry by hydrothermal growing $\alpha\text{-Fe}_2\text{O}_3$ precursor branches on pre-obtained SnO_2 nanowire. The uniqueness of the structure is that, the SnO_2 nanowire stems with four non-equivalent exposed side surfaces can give rise to six-fold-symmetry growth of FeOOH nanorod branches by accommodating different epitaxial orientations on distinct crystallographic surfaces. The lengths of branches can be effectively tailored by modulating the reactant concentration and reaction time. Such a composite anode material has demonstrated superior electrochemical performances in terms of lower initial irreversible loss and higher reversible capacity to both single components. This can be attributed to a synergistic effect between $\alpha\text{-Fe}_2\text{O}_3$ and SnO_2 as well as the increased specific surface areas provided by branched nanostructures.

Chapter 4

A General Strategy toward Graphene@Metal Oxide Core-Shell Nanostructure for High- Performance Lithium Storage

4.1 Introduction

Metal oxides have long hold considerable promise as active electrode materials for LIBs and supercapacitors in view of their high theoretical capacities. However, the commercial implementation of metal oxides is significantly held back by their unsatisfactory cycling performance stemming from large volume variations during charge/discharge, severe aggregation and poor electrical conductivity.^{93, 101, 104} One of the most effective strategies to tackle these problems is to disperse metal oxides in carbonaceous matrices with high electrical conductivity and fair ductility. Among various carbon materials, graphene, an up-and-coming carbon material comprised of monolayered hexagonal sp^2 hybridized carbons, shows some unique merits in energy storage applications such as ultrathin thickness (shorten the diffusion pathways of ions), large specific surface area (provide more electrochemically active sites), excellent electrical conductivity (ensure efficient electron transport), good mechanical flexibility (pave the way for constructing flexible electrodes), wide electrochemical window (increase the energy density) and strong thermal/chemical stability (allow for use under harsh conditions).¹⁹⁴ It thus has been considered as an ideal reinforcing

matrix for metal oxides. Hitherto, a variety of metal oxides have been coupled with graphene and, as expected, demonstrated superior electrochemical performance to bare metal oxides.^{9, 118, 122, 126} It needs to be pointed out that the graphene employed in these composites generally refers to chemically derived graphene, which is prepared by chemical exfoliation methods involving the first oxidation of well-stacked graphite to graphite oxide (see experimental for details), and following chemical reduction of graphene oxide (GO) to obtain reduced GO (r-GO) or thermal exfoliation of graphite oxide to produce graphene. The functional groups on GO and/or residual functional groups on r-GO endows such graphene derivatives with another attractive advantage as a 2D support for uniformly grafting or dispersing metal oxides with well-defined sizes, shapes and crystallinity. Recent efforts reveal that metal oxides tend to aggregate and grow into large particles in the absence of graphene. On the other hand, such chemically derived graphene suffers from its own problems when solely serves as an electrode for LIBs and supercapacitors, i.e. serious agglomeration and re-stacking after removal of dispersed solutions and drying. This in turn can be alleviated by anchoring metal oxide nanoparticles on graphene sheets (GS) acting as the spacers. In this context, fabrication of graphene/metal oxide composites can utilize the advantages of both graphene and metal oxides to a higher level. The functions and synergistic effects of graphene and metal oxides in graphene/metal oxide composites can be briefly epitomized from these aspects: (1) graphene offers chemical functionality to allow easy processing and uniform dispersion of metal oxide particles, (2) metal oxides can provide high capacity and meanwhile suppress the re-stacking of graphene enabling the full use of all potential advantages of graphene, (3) interconnected graphene in the composites functions as conductive channels to improve the poor electrical properties and charge transfer pathways for bare oxides, (4)

graphene can provide an elastic buffer space to accommodate the volume change and prevent the aggregation of metal oxides, and thereby prohibiting cracking or crumbling of electrode material upon cycling.^{9, 195}

Although tremendous efforts have been devoted to preparing graphene/metal oxides nanocomposites, current research accomplishments are mainly focused on coupling graphene with metal oxide nanoparticles.^{124, 195-199} There are few reports on integrating 1D nanostructure with graphene,²⁰⁰⁻²⁰² in spite of its promising applications especially in energy storage and conversion devices. Furthermore, a versatile method for coupling graphene with metal oxide nanostructures of different dimensions is missing.

In this work, we describe a simple and general strategy to wrap graphene onto different metal oxide nanostructures. The whole procedure involves three steps, i.e. pre-modification of metal oxides with amine groups, coating of a GO layer, and finally reduction of the GO shell to graphene. The simplicity of this strategy can be revealed by the fact that all steps are accomplished by simply immersing the pre-grown metal oxides into corresponding functional solutions at room temperature. Remarkably, the GS can cover nearly the whole surface of individual nanostructure. The graphene-wrapped α -Fe₂O₃ nanoparticles are tested as the LIB anode to evaluate the electrochemical performances of such graphene-based core-shell heterostructures. The results disclose that much improved specific capacity, rate capability and cycling stability can be achieved after the coating of graphene. Enhanced electron transport efficiency and structural integrity of the nanoparticles resulting from the graphene encapsulation are believed to account for these performance improvements.

4.2 Experimental

4.2.1 Sample Synthesis and Characterizations

4.2.1.1 GO Preparation

GO was prepared by a modified Hummers method.²⁰³ Firstly, 2 g of graphite powder and 1.5 g of NaNO₃ were added into 150 mL of 98% H₂SO₄ solution in a flask immersed in an ice bath. With the stirring still in progress, 9 g of KMnO₄ was added slowly, bit by bit, to the mixture to prevent a sudden accumulation of heat that is evolved. After that, the mixture was stirred for 5 days at room temperature. Then, 10 mL of 30% H₂O₂ was added into the solution in order to completely react with the remaining KMnO₄, leading to a bright yellow solution. To purify the GO, the resulting mixture was washed by 3% H₂SO₄ and H₂O until the pH value of the solution was approximately 5~6. GO powder was obtained after freeze drying the suspension.

4.2.1.2 Synthesis of Graphene@Metal Oxide Core-shell Nanostructures

Synthesis of SnO₂, CuO, and CoO nanowires: The SnO₂ nanowires on stainless steels (SS) substrate and oriented CuO nanowires on copper substrate were prepared via a standard CVD method¹⁶⁷ and a simple vapor–solid reaction method,¹⁷³ respectively, according to our previous work. CoO nanowires on Ti foil were also prepared through a two-step method reported previously.²⁰⁴

Synthesis of α -Fe₂O₃ nanoparticles: Different from above approaches, the method for synthesizing α -Fe₂O₃ nanoparticles is firstly reported here. In a typical procedure, 0.417 g of FeSO₄·7H₂O and 0.4 g of sodium citrate were dissolved in 30 mL of distilled water. After complete dissolution, the mixture was sealed into a Teflon-lined autoclave and maintained at 180 °C for 8 h. After it was cooled down to room temperature, the precipitation was collected and washed with distilled water and

ethanol. The α -Fe₂O₃ nanoparticles were obtained by annealing the as-collected precursor at 450 °C for 2 h in air.

Preparation of Graphene@Metal Oxide Nanostructures: Wrapping GS onto the surfaces of metal oxide nanostructures was achieved by immersing the pre-formed metal oxides sequentially into the following three solutions for varied durations at room temperature.

(I) Poly (allylamine hydrochloride) (PAH) solution (1 g/L), 1 h.

(II) GO dispersion (0.2 g/L), 5 h.

(III) Hydrazine (N₂H₄, 98%) 0.5 h.

For nanowire samples, all these steps can be accomplished by simple dipping the pre-grown substrate-supported metal oxide nanowires into corresponding solutions. While for α -Fe₂O₃ nanoparticles, each step needs to be assisted with magnetic stirring to ensure a homogeneous mixture and centrifugation to separate the nanoparticles.

4.2.1.3 Characterization

The powder X-ray diffraction (XRD) analysis was performed using a D8 Advance diffractometer with Cu $K\alpha$ line. Transmission electron microscopy (TEM) images were recorded by a JEOL JEM-2010 transmission electron microscope with accelerating voltage of 200 kV. Field-emission scanning electron microscopy (FESEM) analysis was conducted with a JEOL JSM-6700F electron microscope. Raman spectra and images were obtained by a WITeck CRM200 confocal microscopy Raman system with a piezocrystal controlled scanning stage. The excitation light is a 532 nm laser. The laser spot size is estimated to be 500 nm. Atomic force microscopy (AFM) was carried out using a Digital Nanoscope V in the tapping mode. An etched silicon tip was used as a probe for imaging the samples. Thermogravimetry analyses (TGA, Q500) were carried out in the temperature of 40 to

700 °C at a heating rate of 10 °C/min in air. The surface area of graphene@ α -Fe₂O₃ NPs was measured using Brunauer–Emmett–Teller (BET) (Quantachrome Instruments, Autosorb AS-6B). The Fourier-transformed infrared (FT-IR) spectroscopy was measured using the KBr-pellet method in transmission mode on a NEXUS 670 FT-IR spectrometer.

4.2.2 Electrochemical Measurements

The graphene@ α -Fe₂O₃ and pristine α -Fe₂O₃ nanoparticles were dried at 150 °C for 30 min under Ar atmosphere. Then, 80 wt% active material (graphene@ α -Fe₂O₃ or α -Fe₂O₃), 10 wt% acetylene black (Super-P), and 10 wt% polyvinylidene fluoride (PVDF) binder were mixed into N-methyl-2-pyrrolidinone (NMP). The obtained slurry was coated onto Cu foil disks to form working electrodes, which were then dried in vacuum at 50 °C for 12 h to remove the solvent. Electrochemical measurements were performed using two-electrode CR2032 (3 V) coin-type cells with lithium foil serving as both counter and reference electrodes under ambient temperature. The electrolyte was 1M LiPF₆ in a 50:50 (w/w) mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC). Cell assembly was carried out in an argon-filled glove box with both moisture and oxygen contents below 0.1 ppm. Galvanostatic charge/discharge tests were performed using a NEWARE battery tester at a voltage window of 0.005–3 V. Cyclic voltammetry (CV, 0.005–3 V, 0.5 mV s⁻¹) was performed using an electrochemical workstation (CHI 760D).

4.3 Results and Discussion

4.3.1 Wrapping Graphene on Metal Oxide Nanowires

As mentioned in the experimental section, sequential dipping into PAH solution, GO dispersion and N_2H_4 solution for certain durations can realize the coating of GS on pre-synthesized metal oxide nanowires (Figure 4.1a). In fact, each solution has its own function. Specifically, PAH solution is responsible for decorating the surface of metal oxide nanowires with amine end groups. GO dispersion is to provide the GO platelets, which can spontaneously assemble onto the surface of PAH-modified metal oxide nanowires. This process is likely driven by two interactions: (i) the ring-opening reaction between the amine groups in the functionalized nanowires and the epoxy groups in the GO platelets,²⁰⁵⁻²⁰⁷ (2) electrostatic interaction between the positively charged amine-modified nanowires and negatively charged GO platelets.^{124, 208} Abundant amine groups in the PAH-modified nanowires are able to cross-link the GO platelets via the epoxy groups of two or more platelets, stitching them together (Figure 4.1b).²⁰⁷ Together with the electrostatic interaction, such a chemical cross-linking results eventually in the marvellous core-shell assembly between the nanowires and GO platelets. The resulting GO@metal oxide nanowires are then immersed into the N_2H_4 solution to transform GO into graphene (Figure 4.1c). As shown in the scheme, some GO platelets (and subsequent GS) also stretch across the interspaces between nanowires (indicated by the red dashed arrows).

Figure 4.1 (a) Optical image of the solutions used in our dipping method, the sample held by the tweezer is SnO_2 nanowires on stainless steel substrate. (b) The proposed

ring-opening reaction mechanism between the amine groups in the PAH-functionalized metal oxide nanowires and the epoxy groups in the GO sheets. (c) Schematic illustration of the fabrication process for graphene@metal oxide core-shell nanowires. Red dashed arrows indicate the GO and graphene sheets stretching across the nanowires.

The capability and versatility of this protocol in the realization of graphene@metal oxide core-shell nanowires are verified by three typical metal oxide nanowires, e.g., SnO₂, CuO and CoO nanowires. The purities of these nanowires are revealed by their corresponding XRD patterns (Figure 4.2). We firstly test this concept with the SnO₂ nanowires grown on SS substrate. Interestingly, no visible change is noticed after GS coating under low-magnification SEM observation (Figure 4.3a-b). However, the existence of GO and graphene at corresponding steps can be detected using Raman characterization (Figure 4.3c). From the SEM image of graphene@SnO₂ nanowires, the GS just randomly intersperse between rather than discernibly coat on the SnO₂ nanowires (Figure 4.4a). The strong signals of the D and G bands of graphene were thus initially thought to originate from these randomly distributed GS (inset in Figure 4.4a). However, careful observation enables us to grab a clear view of the core-shell structure (Figure 4.4b). The GS are tightly attached on the surface of SnO₂ nanowires. This can be observed from an interesting SEM image, showing the graphene shell tearing up from one end of a SnO₂ nanowire (Figure 4.4c). The thickness of the graphene shell is approximately determined to be in the range from 1 to 3 nm (Figure 4.4d). The complete wrapping of graphene around the nanowires can be more straightforwardly evidenced by Raman mapping. The D and G signals are detected to appear along the entire nanowire, indicating the full coverage of graphene (Figure 4.4e-f).

Figure 4.2 XRD patterns of the as-obtained oxide nanowires. The Cu_2O phase appearing in the XRD pattern of CuO is believed to exist as a thin film precursor for growing CuO NWs during the oxidation of Cu plate.²⁰⁹

Figure 4.3 Low-magnification SEM images of the SnO_2 nanowires: (a) before, and (b) after graphene coating. (c) Raman spectra of the products at different steps, corresponding to the scheme illustrated in Figure 4.1c.

Figure 4.4 (a) Low-magnification and (b-c) High-magnification SEM images of graphene@ SnO_2 nanowires. Inset in (a) is the Raman spectrum taken from those

graphene@SnO₂ nanowires. (d) TEM image of individual graphene@SnO₂ nanowire. (e-f) Raman mapping images of the D and G bands of graphene for individual graphene@SnO₂ nanowire. Inset in (e) shows the optical image of the selected nanowire.

Different from SnO₂ nanowires, a series of immersions in different solutions lead the tips of CuO nanowires to bind together due primarily to the capillary force (Figure 4.5a-b). The GS can be observed to intertwine between CuO nanowires under high-magnification SEM (Figure 4.5c). Although SEM still cannot distinguish the core-shell structure (Figure 4.5d-e), the continuous graphene shell is easily noticed under TEM observation (Figure 4.5f). The full coverage of the GS is proved by Raman mapping individual graphene@CuO nanowire as well (Figure 4.5g-h). Apart from solid SnO₂ and CuO nanowires, porous CoO nanowires are adopted to further confirm the applicability of our method to porous nanowires. The results resemble those for SnO₂ and CuO nanowires, revealing the core-shell structure and complete GS coating along the individual nanowire (Figure 4.6).

Figure 4.5 Low-magnification SEM images of (a) CuO nanowires and (b) graphene@CuO nanowires. (c-e) High-magnification SEM images of

graphene@CuO nanowires. (f) High-magnification TEM image of individual graphene@CuO nanowire, revealing multi-layer graphene coating. (g-h) Raman mapping images of the D and G bands of graphene for individual graphene@CuO nanowire. Inset in (g) shows the optical image of the selected nanowire.

Figure 4.6 Low-magnification SEM images of porous CoO nanowires: (a) before and (b) after graphene coating. Insets in (a) and (b) are corresponding high-magnification SEM images. All the low- and high-magnification SEM images do not show noticeable changes after graphene coating. (c - d) Raman mapping images of the D and G bands of graphene for individual graphene@CoO nanowire, affirming the existence of graphene shell. Inset in (c) shows the optical image of the selected graphene@CoO nanowire. (e) TEM image of individual graphene@CoO nanowire, displaying a thin graphene layer.

4.3.2 Wrapping Graphene on Metal Oxide Nanoparticles

The extendability of this strategy to metal oxide nanoparticles has also been tested using porous α -Fe₂O₃ nanoparticles resulted from thermal-decomposition. Before annealing, the α -Fe₂O₃ precursor nanoparticles are composed of sub-nanoparticles and quite uniform in size and shape with diameters of about 150 nm

(Figure 4.7a-c). It is noticed that these precursor nanoparticles are stacked in a highly ordered way (Figure 4.8), arising probably from the self-assembly process of sub-nanoparticles. Given that no surfactant and other organic molecules are present in the reaction system, such a self-assembled structure is of high possibility caused by the stabilization function of the citrate ligands. After annealing, the precursors transformed into α -Fe₂O₃ with “rose-like” morphology (Figure 4.7d, e and Figure 4.9). Regardless of the phase and shape transition, the high uniformity can still be preserved for the resulting α -Fe₂O₃ “nano-roses” (Figure 4.7d, e). Nevertheless, the decomposition of citrate ligands leads to the damage of the highly ordered stacking mode. The porous structure of these α -Fe₂O₃ “nano-roses” is revealed by TEM characterization, which is likely generated by the removal of CO₂, CO and H₂O gases and lattice contraction during annealing (Figure 4.7f). As a manifestation of the versatility of our protocol, similar procedures for wrapping graphene on metal oxide nanowires have been demonstrated on these α -Fe₂O₃ nanoparticles but conducted in beakers aided by magnetic stirring. The results indicate GS can also be successfully wrapped around the surface of α -Fe₂O₃ “nano-roses” (Figure 4.7g-i). The ring-opening reaction between the epoxy groups in GO and the amine groups in PAH-modified α -Fe₂O₃ nanoparticles can be evidenced by the vanishing of epoxy C-O stretch (centered at 1220 cm⁻¹) in the FT-IR spectrum of GO@ α -Fe₂O₃, which appeared previously in the FT-IR spectrum of GO (see details in Figure 4.10).²⁰⁶ The crinkled and rough textures can be observed for yielding graphene-encapsulated α -Fe₂O₃ “nano-roses” (G@ α -Fe₂O₃). In addition to wrapping on individual NPs, in some cases GS appear to interconnect neighboring nanoparticles (Figure 4.7g-i). Thermogravimetric analysis (TGA) was carried out to quantify the amount of graphene in the G@ α -Fe₂O₃ composite, determining the weight fraction of graphene

is as low as 2.8% (Figure 4.11a). This value is much lower than those of previously reported graphene/metal oxide composites.^{124, 198, 210} Note that the weight loss at the temperature below 100 °C is attributed to the evaporation of moisture.¹⁹⁸ Moreover, the BET specific surface area and the major pore size of G@ α -Fe₂O₃ are characterized to be $\sim 79.5 \text{ m}^2 \text{ g}^{-1}$ and $\sim 20 \text{ nm}$, respectively (Figure 4.11b).

Figure 4.7 (a) Low-magnification, (b) high-magnification SEM images, and (c) TEM image of the as-obtained α -Fe₂O₃ precursor. (d) Low-magnification, (e) high-magnification SEM images, and (f) TEM image of the α -Fe₂O₃ nanoparticles. (g) Low-magnification, (h) high-magnification SEM images, and (i) TEM image of the as-prepared G@ α -Fe₂O₃ nanoparticles. All the scale bars in the figures and insets are 100 nm.

Figure 4.8 SEM images of the as-obtained α -Fe₂O₃ precursor, revealing a highly ordered stacking fashion.

Figure 4.9 XRD pattern of the as-prepared α -Fe₂O₃ NPs (JCPDS 33-0664).

Figure 4.10 FT-IR spectra of GO and GO@ α -Fe₂O₃. Compared with pure GO, the epoxy C-O stretch at 1220 cm⁻¹ disappears in the FT-IR spectrum of GO@ α -Fe₂O₃. As GO contains reactive epoxy groups, its exposure to amine groups could lead to a ring-opening reaction, creating new C-N and O-H bonds. An appearance of a new peak at 1510 cm⁻¹ corresponding to a stretching of the new C-N bonds and possibly remaining PAH is observed for GO@ α -Fe₂O₃. Meanwhile, the intensity of the vibrations at 1385 cm⁻¹ corresponded to O-H bending from hydroxyl groups increases for GO@ α -Fe₂O₃. All these observations are quite supportive of the ring-opening reaction between the epoxy and amine groups. In addition, the intensity of C=O

stretches significantly decrease for $\text{GO}@ \alpha\text{-Fe}_2\text{O}_3$. This could be interpreted as evidence that carboxylic acid groups interact with amine groups.

Figure 4.11 (a) Thermogravimetric analysis and (b) Nitrogen isotherm adsorption-desorption curve of $\text{G}@ \alpha\text{-Fe}_2\text{O}_3$ composite. The inset in (b) shows their pore size distributions.

4.3.3 Electrochemical Performance of $\text{G}@ \alpha\text{-Fe}_2\text{O}_3$ toward Lithium Storage

Galvanostatic charge-discharge measurements were adopted to measure the electrochemical properties of $\text{G}@ \alpha\text{-Fe}_2\text{O}_3$ on the purpose of exploring the effectiveness of graphene/metal oxide composite in improving the lithium storage performance. For comparison, the voltage-capacity trace of pristine $\alpha\text{-Fe}_2\text{O}_3$ nanoparticles was also recorded. Figure 4.12(a) displays the first discharge/charge voltage profiles of $\alpha\text{-Fe}_2\text{O}_3$ and $\text{G}@ \alpha\text{-Fe}_2\text{O}_3$ electrodes in the voltage window of 0.005-3.0 V at a rate of 200 mA g^{-1} ($\text{C}/5$, 1C is defined as 1007 mA g^{-1}), exhibiting the well-known signature of conversion reactions of iron oxides.^{198, 210-211} It can be seen clearly that there are two slopes (marked as 1 and 2) and one long plateau (marked as 3) appeared during discharge process at the voltage of ca. 1.65 V, 1.05 V and 0.85 V, respectively. In general, the first two slopes correspond to the lithium intercalation and reduction reaction of $\alpha\text{-Fe}_2\text{O}_3$ to metallic Fe, respectively. Recently, some reports attribute the slope at ca. 1.05 V to the formation of an intermediate cubic

phase $\text{Li}_2\text{Fe}_2\text{O}_3$.²¹¹⁻²¹² Above processes can be described by the following three lithiation steps.

Despite showing the same electrochemical reaction pathways, the G@ α - Fe_2O_3 composite and pristine α - Fe_2O_3 exhibit distinct cyclic performances (Figure 4.12b). Apparently, the G@ α - Fe_2O_3 composite delivers a much higher capacity than bare α - Fe_2O_3 throughout the cycling. The first discharge capacity of α - Fe_2O_3 is about 1179 mA h g^{-1} . This value is slightly higher than the theoretical capacity of α - Fe_2O_3 ($\sim 1007 \text{ mA h g}^{-1}$),²¹³ which can be explained by the electrolyte decomposition in the low-potential region and the subsequent formation of an organic layer on the surface of the particles. After 100 cycles, however, the α - Fe_2O_3 electrode can only deliver the capacity of 290 mA h g^{-1} with only $\sim 25\%$ retention. On the contrary, the G@ α - Fe_2O_3 composite shows markedly enhanced cycling stability. The capacity of the G@ α - Fe_2O_3 composite at the 100th cycles can still reach $\sim 781 \text{ mA h g}^{-1}$, which is much higher than that of bare α - Fe_2O_3 nanoparticles. Taking the first discharge capacity of 1338 mA h g^{-1} into account, 58% of the reversible capacity can be maintained over 100 cycles for the G@ α - Fe_2O_3 composite electrode. Interestingly, the capacities of both electrodes exhibit an increasing trend after certain cycles. This phenomenon has also been reported by several groups on metal oxide electrodes, which may result from the gradual release of the Li^+ trapped inside the metal oxide frameworks during the initial cycling.^{198, 214-216}

To gain insight into the superior rate capability, both G@ α - Fe_2O_3 and bare α - Fe_2O_3 electrodes are measured under adjoining cycles of different current densities (Figure 4.12c). Note that, with respect to the reference α - Fe_2O_3 , the specific capacity

of G@ α -Fe₂O₃ is substantially increased at all investigated charge-discharge rates from C/5 to 10 C. For example, the specific capacity of G@ α -Fe₂O₃ at a rate of 5 C is as high as 269 mA h g⁻¹, 34 times higher than that of bare α -Fe₂O₃ (8 mA h g⁻¹). At a rate of 10 C, the G@ α -Fe₂O₃ electrode can still deliver a high capacity of 143 mA h g⁻¹, whilst the bare α -Fe₂O₃ cannot store charges any more. Importantly, after high rate tests, both electrodes can maintain good reversibility revealed by the fact that their specific capacities at C/5 are almost able to recover to the initial values.

The unique structure and composition of the G@ α -Fe₂O₃ composite should be account for its outstanding electrochemical performances, i.e. increased specific capacity, good cycling stability and enhanced high-rate capability. As can be seen from above results, the composite electrode has a large weight fraction of high-capacity α -Fe₂O₃, large specific surface area and ultrathin graphene shells as both buffer matrix and conducting pathways, which are all crucial factors ensuring the superior electrochemical properties. The former two characteristics are propitious to reach high specific capacity of the G@ α -Fe₂O₃ composite. It is well-known that one advantage of transition-metal oxides over carbon materials in lithium storage is their high theoretical specific capacities. Hence, a large content of α -Fe₂O₃ could give rise to a high specific capacity. The large specific surface area, obviously, is highly favourable for LIB to achieve high specific capacity as it can provide more electrochemically active sites for Li⁺ insertion/extraction. On the other hand, the presence of GS is more encouraging to improve the cycling stability and rate capability because it can 1) suppress the aggregation, accommodate the volume change of α -Fe₂O₃ nanoparticles and maintain the electrical contact between α -Fe₂O₃ nanoparticles and current collector as well during the cycling, 2) facilitate electron transfer between wrapped porous α -Fe₂O₃ nanoparticles within the whole electrode.

This can decrease the inner resistance, leading thus to a better rate capability. Note that the Li^+ diffusion is accessed through the defective sites of GS resulted from their chemical preparation process. The expected good conductivity of the composite electrode is evidenced by comparing the Nyquist plots of $\text{G}@ \alpha\text{-Fe}_2\text{O}_3$ and $\alpha\text{-Fe}_2\text{O}_3$ nanoparticles (Figure 4.12d). Apparently, the Ohmic resistance revealed by the diameter of the semicircle for $\text{G}@ \alpha\text{-Fe}_2\text{O}_3$ electrode is much lower than that for bare $\alpha\text{-Fe}_2\text{O}_3$ electrode (~ 90 vs. $\sim 199 \Omega$), suggesting the lower contact and charge-transfer impedances for the composite electrode.¹²⁴ Consequently, the $\text{G}@ \alpha\text{-Fe}_2\text{O}_3$ electrode can offer high speed of Li^+ diffusion and electron transfer at high cycling rates.

Figure 4.12 (a) Voltage-capacity profiles of $\text{G}@ \alpha\text{-Fe}_2\text{O}_3$ composite and pristine $\alpha\text{-Fe}_2\text{O}_3$ nanoparticles for the first cycle at the current density of 200 mA g^{-1} . (b) Cycling performance of $\text{G}@ \alpha\text{-Fe}_2\text{O}_3$ composite and pristine $\alpha\text{-Fe}_2\text{O}_3$ nanoparticles at a current rate of $C/5$ (200 mA g^{-1}). (c) Cyclic stabilities of $\text{G}@ \alpha\text{-Fe}_2\text{O}_3$ composite and pristine $\alpha\text{-Fe}_2\text{O}_3$ NPs at various rates. (d) Nyquist plots of the electrodes of $\text{G}@ \alpha\text{-Fe}_2\text{O}_3$ composite and pristine $\alpha\text{-Fe}_2\text{O}_3$ nanoparticles

4.4 Conclusion

A general strategy based on the ring-opening reaction between epoxy groups and amine groups and electrostatic interaction is developed to achieve the self-assembled wrapping of graphene sheets around various metal oxide nanowires and nanoparticles. Raman mapping reveals the full coverage of an entire nanowire by graphene. The effectiveness of the graphene shell in preventing the aggregation, buffering the volume change, preserving the integrity of nanoparticles, as well serving as the conducting matrix possibly account for superior electrochemical performance of the composite electrode with respect to pristine metal oxide. We expect this protocol will open up a new pathway for the realization of various graphene-based hybrid materials for diverse applications.

Chapter 5

Fabrication of Co₃O₄/Reduced Graphene Oxide Scrolls for High-Performance Supercapacitor Electrodes

5.1 Introduction

Despite the short period of research, graphene/metal oxide composites have verified the greatly improved electrochemical performance as electrodes for LIBs and supercapacitors.²¹⁷ In the meantime, the important role of graphene serving as an ideal 2D support for anchoring metal oxides has been demonstrated. Common wet-chemistry strategies, hydrothermal/solvothermal synthesis, chemical *in-situ* deposition, sol-gel processes for example, are extensively adopted for the preparation of diverse graphene/metal oxide composites.^{9, 118-120, 122, 126, 195} These methodologies generally start from a dispersion of suspended graphene which acts as a 2D integrated network for supporting discrete metal nanoparticles (Figure 5.1). Specifically, with the assistance of electrostatic stabilization and chemical functionalization, GO/r-GO is first dispersed in aqueous or organic solvents. The well GO/r-GO dispersibility is guaranteed by the hydrophilic oxygen-containing functional groups such as hydroxyl, epoxy and carboxyl groups grafted on their surfaces and edges. Subsequent addition of metal ions from the precursors of either inorganic or organic metal salts leads to the anchoring of metal oxides on the surface of graphene with abundant functionalities. This process generally undergoes hydrolysis or *in-situ* redox reactions and following

annealing. As mentioned in last chapter, in some cases, the presence of graphene with rich functional groups is beneficial to form uniform and well-defined metal oxide nanoparticles, avoiding the occurrence of uncontrolled aggregation and growth of large particles following their own growth behavior.

Figure 5.1 A general wet-chemistry strategy to fabricate graphene/metal oxide composites.²¹⁷

Till now, there are hundreds of reports available on graphene/metal oxide composites. Nevertheless, the structural models can be generally classified into six types (Figure 5.2): (a) Anchored model: metal oxide particles are anchored on the surface of graphene, (b) Wrapped model: metal oxide particles are wrapped by graphene, (c) Encapsulated model: metal oxide particles are encapsulated by graphene, (d) Sandwich-like model: graphene serves a template for the formation of a metal oxide/graphene/metal oxide sandwich-like structure, (e) Layered model: a structure consisting of alternating layers of metal oxide particles and graphene, (f) Mixed model: metal oxide particles and graphene are mechanically mixed and graphene forms a conductive network among the metal oxide particles.²¹⁷ In these models, graphene normally exists in the form of discrete large sheets serving as a 2D support

for the growth of metal oxides (see schematics in Figure 5.1). One can clearly view the presence of graphene from either SEM or TEM observation.

Figure 5.2 Schematic structural models of graphene/metal oxide composites: (a) Anchored model. (b) Wrapped model. (c) Encapsulated model. (d) Sandwich-like model. (e) Layered model. (f) Mixed model. Red: metal oxide particles. Blue: graphene sheets.²¹⁷

In this chapter, we also start with the dispersion of GO in organic solvents but result in a new hybridization mode between graphene and metal oxides, in which the r-GO platelets are integrated into the Co_3O_4 scrolls. It should be pointed out that the r-GO platelets here refer to the small pieces of r-GO sheets. Rather than serving as the supporting substrates for guest materials in most cases, r-GO platelets are incorporated into nearly every single Co_3O_4 scroll and believed to connect with Co_3O_4 through the residual oxygen functional groups on their basal planes and the edges. Our strategy is assisted by the lamellar micelles of the surfactant and subsequent post-annealing. To demonstrate the potential of this unique structure in electrochemical energy storage, the yielding Co_3O_4 /r-GO is tested as an electrode for supercapacitors. The results show that a large specific capacitance of 163.8 F g^{-1} can be obtained for the Co_3O_4 /r-GO at a current density of 1 A g^{-1} , which is about 13 times higher than

that of pure Co_3O_4 . This is possibly due to the synergistic effect as well as the distinct combination mode between the r-GO platelets and Co_3O_4 .

5.2 Experimental

5.2.1 Sample Fabrication and Characterization

5.2.1.1 GO Preparation

GO was prepared via the same modified Hummers method mentioned in last chapter.²⁰³

5.2.1.1 Synthesis of Co_3O_4 /r-GO

1 mmol of sodium dodecyl sulphate (SDS) was first dissolved in 28 mL of ethylene glycol (EG) and water mixed solvents with the volume ratio of 13:1. After complete dissolution of SDS under magnetic stirring, 10 mg of as-made GO was added to the above solution, with ultrasonication for 0.5 h. Then, 1 mmol of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was added under vigorous stirring. The addition of 1 mmol of $\text{H}_2\text{C}_2\text{O}_4$ was proceeded upon the complete dissolution of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. The resulting mixture was further stirred at room temperature for 10 h. The solid products were collected by centrifugation and washed several times with ethanol and distilled water. The precipitate was dried at 60 °C overnight. Co_3O_4 /r-GO was obtained by annealing the as-obtained precipitate at 450 °C under argon protection for 2 h.

The pure Co_3O_4 scrolls were made by the same two-step method in the absence of GO while keep other conditions unaltered. Control experiments like without SDS, replacing GO with the same amount of high-temperature hydrogen reduced GO (HRGO) were both carried out according to the conditions above to investigate the growth mechanism. Herein, HRGO was prepared simply by annealing the as-

synthesized GO at 950 °C for 3 h under hydrogen atmosphere. Another control experiment was conducted by physically blending pure Co₃O₄ with commercial carbon black on the purpose of comparing the electrochemical properties with Co₃O₄/r-GO. The weight ratio of Co₃O₄ to carbon black is equal to that Co₃O₄/r-GO, which is calculated to be 90:10 according to the initial dosages of the reactants.

5.2.1.1 Characterization

The powder X-ray diffraction (XRD) analysis was performed using a D8 Advance diffractometer with Cu $K\alpha$ line. Transmission electron microscopy (TEM) images were recorded by a JEOL JEM-1400F transmission electron microscope with accelerating voltage of 100 kV. Field-emission scanning electron microscopy (FESEM) analysis was conducted with a JEOL JSM-6700F electron microscope. Raman spectra and images were obtained by a WITeCK CRM200 confocal microscopy Raman system with a piezocrystal controlled scanning stage. The excitation light is a 532 nm laser. The laser spot size is estimated to be 500 nm. Atomic force microscopy (AFM) was carried out using a Digital Nanoscope V in the tapping mode. An etched silicon tip was used as a probe for imaging the samples.

5.2.2 Electrochemical Measurements

The electrochemical properties of the as-obtained products were investigated under a three-electrode cell configuration at room temperature on a CHI 760D electrochemistry workstation with 6 M KOH aqueous solution as the electrolyte. The working electrode was fabricated by casting Nafion-impregnated ink onto a glassy carbon disk electrode with diameter of 5 mm (without any other carbon additives). Typically, 5 mg of the active electrode material was ultrasonically dispersed into 1 mL of an ethanol solution containing 5 μ L of a Nafion solution (5 wt % in water,

DuPont) for 10 min to form the ink; 0.2 mL of the as-prepared ink was dropped onto the glassy carbon disk electrode and baked at 80 °C for 10 min. Platinum foil and a Ag/AgCl electrode (immersed directly into the electrolyte) were used as the counter and reference electrodes, respectively. Cyclic voltammetry studies were performed within a range of 0 to 0.5 V at scan rates of 5 - 100 mV s⁻¹. The SC is calculated using half the integrated area of the CV curve to obtain the charge (Q), and subsequently dividing the charge by the mass of the active material (m) and the width of the potential window (ΔV):

$$C = Q/m(\Delta V) \quad (5.1)$$

Galvanostatic charge-discharge measurement was performed at different constant current densities. The SC can also be calculated using galvanostatic charge-discharge curves by the following equation:

$$C = I(\Delta t)/m(\Delta V) \quad (5.2)$$

Where m is also the mass of electrode material (g), ΔV is the potential window (V), I is the discharge current (A) applied, and Δt is the discharge time.

5.3 Results and Discussion

5.3.1 Structure Characterization

To prepare the Co₃O₄/r-GO scrolls, the CoC₂O₄/GO precursor was first synthesized at room temperature with the assistance of SDS in a mixed solvent. Afterwards, the as-obtained CoC₂O₄/GO precursor was subjected to post annealing, which led to the phase transition from CoC₂O₄ to Co₃O₄ and simultaneous partial reduction of GO (see experimental section for details).

In this work, small GO platelets in the upper suspension were mainly employed for our experiments. The thickness of these GO platelets is determined to ~ 1 nm, indicating such GO platelets are one-layer carbon sheets (Figure 5.3a).²¹⁸⁻²¹⁹ The purities of both CoC_2O_4 /GO precursor and final product Co_3O_4 /r-GO are revealed by their corresponding XRD patterns (Figure 5.3b). The scroll morphology of the CoC_2O_4 /GO precursor can be clearly observed under SEM (Figure 5.4a). The average length and diameter of these scrolls are about 2 μm and 800 nm, respectively. However, the GO is not visible under SEM observation. We thus further characterize these samples with TEM. Through close inspection, the GO platelet can be viewed at the end of the scroll (indicated by the circle in the inset of Figure 5.4b). It can be seen that these precursor scrolls are in fact composed of sub-nanorods stacked parallelly. Unlike most carbon nanoscrolls rolled up from one side of the mother sheet,²²⁰⁻²²¹ our CoC_2O_4 /GO scrolls are rolled up from both sides. The GO signals can be detected in almost every single CoC_2O_4 /GO scroll by Raman characterization (Figure 5.5a, b). The next inquiry is naturally about the distribution of the GO in this scrolled structure. The results of Raman mapping reveal that the GO is distributed all over the whole CoC_2O_4 scroll (Figure 5.4c-e). More evidence can be viewed in the Raman mapping results of other randomly chosen CoC_2O_4 /GO scrolls (Figure 5.5c, d). It can be seen that the GO platelets can even extend outside the main body of CoC_2O_4 scroll (Figure 5.5d). After the heat treatment, CoC_2O_4 is transformed into Co_3O_4 but maintain the scrolled morphology (Figure 5.4f). Besides, the r-GO that should be resulted from the thermal reduction of pre-existed GO can be detected after annealing (Figure 5.4g), indicating the transformation from CoC_2O_4 /GO to Co_3O_4 /r-GO.

Figure 5.3 (a) AFM image of the as-obtained GO platelets in the upper suspension. Inset is depth profile of the line of interest on the GO platelets, the height difference between two arrows is about 1 nm, indicating a single layer GO sheet. (b) XRD patterns of the as-obtained $\text{CoC}_2\text{O}_4/\text{GO}$ (JCPDS No. 25-0250) and $\text{Co}_3\text{O}_4/\text{r-GO}$ (JCPDS No. 42-1647) scrolls.

Figure 5.4 (a) SEM image of the $\text{CoC}_2\text{O}_4/\text{GO}$ scrolls. (b) TEM image of single $\text{CoC}_2\text{O}_4/\text{GO}$ scroll; inset shows the high-magnification TEM image. (c- e) Raman mapping images of CoC_2O_4 and D, G bands of GO for single $\text{CoC}_2\text{O}_4/\text{GO}$ scroll; (f) SEM image of $\text{Co}_3\text{O}_4/\text{r-GO}$ scrolls. (g) Raman spectra of $\text{Co}_3\text{O}_4/\text{r-GO}$ (red line) and Co_3O_4 (black line) scrolls.

inset in c shows the optical image of the selected CoC_2O_4 /GO scroll. The scale bar of the inset is $1\mu\text{m}$. (f) SEM image of the Co_3O_4 /r-GO scrolls. (g) Optical image of the Co_3O_4 /r-GO scrolls and Raman spectra of pure Co_3O_4 (for reference) and Co_3O_4 /r-GO obtained from single scroll marked by red circle in the optical image. The Raman signals of r-GO are highlighted with a blue dashed rectangular box.

Figure 5.5 (a) Optical image of typical CoC_2O_4 /GO scrolls. (b) Raman spectra of pure CoC_2O_4 (for reference), GO [obtained from spot 1 in (a)], and single CoC_2O_4 /GO scroll [obtained from spot 2 in (a)], respectively. (c-d) Raman mapping images of CoC_2O_4 , and D, G bands of GO for different CoC_2O_4 /GO scrolls. The scale bars of the optical images and Raman images are $1\mu\text{m}$.

5.3.2 Growth Mechanism Investigation

In order to investigate the growth mechanism of such scrolled structure, we have carried out a series of control experiments. Initially, GO was considered to template

the formation of these scrolls. Therefore, the first control experiment was conducted in the absence of GO. However, the product still exhibited the scrolled morphology (Figure 5.6a), ruling out the possibility of GO serving as the template for the formation of scrolled structure. Whereas in another control experiment without SDS, the products consisted only of nanorod clusters (Figure 5.6b). Hence, the surfactant SDS must play a constructive role in determining the final scrolled structure of CoC₂O₄. In previous studies, layered structure has been proven to be the basic prerequisite for the formation of the scrolls.²²²⁻²²⁷ Generally, it can originate from either the target material itself or soft templates (e.g., surfactant, organic molecule). Therefore, the SDS is herein believed to form lamellar micelles in this system ready for the subsequent growth of the scrolls. Figure 5.7 illustrates the suggested growth mechanism of the CoC₂O₄/GO scrolls. Note that lamellar micelles should have periodically layered structure. However, for simplicity, we only show mono-layer structure in Figure 5.7. Herein, we describe three cases in the formation of CoC₂O₄ scrolls. Firstly, in the case of no graphene derivatives (left column in Figure 5.7: SDS), the CoC₂O₄ precursor is first nucleated on the lamellar micelles of the SDS due to the electrostatic interaction between Co²⁺ cations and anion groups on the SDS. Subsequently, anisotropic growth together with the rolling process occurs. Since the reaction takes place at room temperature, this rolling is largely driven by a kinetic rather than a thermodynamic process. One possibility is proposed based on the following two steps:²²²⁻²²³ (1) the lamellar micelles first become loose at the edges under vigorous magnetic stirring, (2) the rolling happens due to the structural stress caused by the gravity differences of the CoC₂O₄ between the edges and the centre as well as the interactions between the hydrophobic ends of the SDS in the same layer. The neighboring layers of SDS micelle are believed to roll up to the same direction

due to the connection of Co²⁺ cations between them. The bending direction is determined by the layer with stronger force. The investigation of the exact mechanism for this rolling process is undergoing. Secondly, in the case where GO is present (middle column in Figure 5.7: GO/SDS), the GO is added after the dissolution of SDS and then sonicated for 30 min. By virtue of the oxygen-containing functional groups, the GO platelets could be attached onto the hydrophilic ends of the SDS. After the SDS is washed away, GO can still be preserved in the scrolls (Figure 5.5). This is largely due to the formation of ionic bonding between the oxygen functional groups on the GO platelets and Co²⁺ cations. In order to further confirm this connection between GO and CoC₂O₄, a control experiment is conducted where GO is present without the SDS. Despite not having scrolled structures formed any more (Figure 5.6b), the Raman signals of GO can still be detected in almost every single CoC₂O₄ cluster after being washed with water and ethanol for several times (Figure 5.8). Therefore, there is certain interaction between the GO platelets and CoC₂O₄, which is of high possibility the ionic bonding mentioned above. Thirdly, for the case with hydrogen reduced GO (HRGO, in order to distinguish from the partially reduced GO obtained in the second-step annealing in Ar, we use HRGO to stand for high-temperature hydrogen reduced GO) (right column in Figure 5.7: HRGO/SDS), the absence of functional groups leads HRGO platelets to only have hydrophobic interaction with the alkylated chains of the SDS but without any interaction with CoC₂O₄. In contrast to the second case, SDS here is bridging HRGO and CoC₂O₄. Hence, the removal of SDS template would cause the disappearance of most HRGO platelets. As manifested, the Raman signals of HRGO are either absent or very weak for the samples after washing in this case, even when Raman characterization is conducted on a large amount of CoC₂O₄ scrolls (Figure 5.9).

Figure 5.6 SEM images of the samples obtained from the control experiments: (a) in the absence of GO, (b) in the absence of surfactant (SDS).

Figure 5.7 Schematic diagram showing the formation of the CoC_2O_4 scrolls in the absence and presence of graphene derivatives. (a)-(e) represent the typical reaction stages of the formation of the lamellar micelles of the surfactant, nucleation of CoC_2O_4 , initial growth of CoC_2O_4 nanorods, rolling process and washing away the surfactant, respectively.

Figure 5.8 (a) Optical image of the sample obtained in the absence of SDS. (b) Raman spectra of pure CoC_2O_4 (for reference), GO [obtained from spot 1 in (a)], and single CoC_2O_4 /GO scroll [obtained from spot 2 in (a)], respectively.

Figure 5.9 SEM (a) and optical (b) images of the product obtained by replacing GO with HRGO. (c) Raman spectra of pure CoC_2O_4 (for reference), HRGO [obtained from spot 1 in (b)], single CoC_2O_4 /HRGO scroll [obtained from spot 2 in (a)], and several CoC_2O_4 /HRGO scrolls [obtained from spot 3 in (a)], respectively.

5.3.3 Electrochemical Behavior

The electrochemical properties of the Co_3O_4 /r-GO scrolls are evaluated in a three-electrode cell by CV and galvanostatic charge-discharge measurements. Although three-electrode configuration would overestimate the SC, it can still be used to study the electrochemical behaviour of single electrode.²²⁸ Figure 5.10(a) presents the representative CV curves of the Co_3O_4 /r-GO scrolls at different scan rates in a 6

M KOH electrolyte. The largest SC of 159.8 F g⁻¹ can be reached at a scan rate of 5 mV s⁻¹, which is quite consistent with the largest value (163.8 F g⁻¹, at 1 A g⁻¹) calculated from the charge-discharge curves (Figure 5.10b). In addition, the SC can still remain at a high level above 140 F g⁻¹ with a good retention of about 87% with current density increase from 1 A g⁻¹ up to 10 A g⁻¹ (Figure 5.10b). For comparison, bare Co₃O₄ scrolls are also tested under the same electrochemical conditions (Figure 5.11a). Of note, the area surrounded by the CV curve becomes significantly large after introduction of r-GO to pristine Co₃O₄ scrolls (Figure 5.10c). The nearly rectangular shape of the CV curve implies the good capacitive behaviour of the composite. The SC of the Co₃O₄/r-GO composite is calculated to be as large as 11 times of that of pristine Co₃O₄ at different scan rates (Table 5.1). As aforementioned, the integration of carbonaceous material and metal oxide is of hope to boost the energy storage performance. Herein, the high SC of the composite is believed to stem from the combination of the EDL capacitance and pseudocapacitance from r-GO platelets and Co₃O₄, respectively. Another noteworthy feature of the Co₃O₄/r-GO composite is its good rate capability. The discharge time of Co₃O₄/r-GO at 10 A g⁻¹ (6.3 s) is even longer than that of bare Co₃O₄ at 1 A g⁻¹ (4.6 s, Figure 5.10d).

To further demonstrate the superiority of this unique combination model, we simply prepared another Co₃O₄/carbon black (CB) composite by mechanical blending for comparison, where the amount of CB is equal to that of r-GO in the Co₃O₄/r-GO scrolls. The SC of the mixed Co₃O₄/CB composite calculated from its CV curve is about 52 F g⁻¹ (Figure 5.12b). This value, albeit two times higher than that of pure Co₃O₄ (12.9 F g⁻¹), is much lower than that of Co₃O₄/r-GO (131.2 F g⁻¹). The possible reason is that mechanical blending cannot ensure the uniform distribution of CB in the Co₃O₄ scrolls. Meanwhile, the rapid current response can be observed for both Co₃O₄/r-GO

and $\text{Co}_3\text{O}_4/\text{CB}$ from their respective CV curves (Figure 5.12c), indicating the better electrical conductivity after the introduction of carbonaceous materials. The superiority of $\text{Co}_3\text{O}_4/\text{r-GO}$ towards the pristine Co_3O_4 and $\text{Co}_3\text{O}_4/\text{CB}$ is also reflected in the longest discharge time under galvanostatic charge-discharge testing (Figure 5.12d). Based on these two comparisons, it can be derived that our unique hybrid architecture can (1) improve the electrical conductivity of the overall electrode to a higher level, (2) make full use of both active material and “conducting matrix” by assigning r-GO platelets to almost every single scroll. The appearance of an extra pair of redox peaks (0.33/0.19 V, which can be attributed to the redox transition of $\text{Co}^{2+}/\text{Co}^{3+}$.²²⁹) in the CV curves of $\text{Co}_3\text{O}_4/\text{r-GO}$ further implies the improved electrochemical activity of the $\text{Co}_3\text{O}_4/\text{r-GO}$ composite (Figure 5.11c and 5.12c). Besides, the cycling stability of $\text{Co}_3\text{O}_4/\text{r-GO}$ and Co_3O_4 is demonstrated as well at a relatively high scan rate of 20 mV s^{-1} . The $\text{Co}_3\text{O}_4/\text{r-GO}$ composite still shows a slightly better retention of 93% than that of Co_3O_4 (91%) after 1000 cycles (Figure 5.13).

Figure 5.11 (a, b) CV and Galvanostatic charge-discharge curves of the $\text{Co}_3\text{O}_4/\text{r-GO}$ composite electrode at different scan rates and current densities in a 6 M KOH

electrolyte, respectively. (c) CV curves of pure Co_3O_4 and $\text{Co}_3\text{O}_4/\text{r-GO}$ at a scan rate of 50 mV s^{-1} . (d) Galvanostatic charge-discharge curves of the Co_3O_4 and $\text{Co}_3\text{O}_4/\text{r-GO}$ at a current density of 1 A g^{-1} .

Table 5.1 The specific capacitances for Co_3O_4 and $\text{Co}_3\text{O}_4/\text{r-GO}$ at different scan rates.

	5 mV s^{-1}	10 mV s^{-1}	20 mV s^{-1}	50 mV s^{-1}	100 mV s^{-1}
$\text{SC}_{\text{Co}_3\text{O}_4} (\text{F. g}^{-1})$	14.9	14.7	14.1	12.9	12.2
$\text{SC}_{\text{Co}_3\text{O}_4/\text{GO}} (\text{F. g}^{-1})$	159.8	156.0	151.5	131.2	130.7

Figure 5.12 (a) CV curves of the Co_3O_4 electrode in a KOH (6 M) electrolyte at different scan rates. (b, c) CV curves of the Co_3O_4 (for comparison), $\text{Co}_3\text{O}_4/\text{carbon black (CB)}$ and $\text{Co}_3\text{O}_4/\text{r-GO}$ electrodes at a scan rate of 50 mV s^{-1} . [c is used for clear observation of the initial and final current responses for each kind of materials.] (d) Galvanostatic charge-discharge curves of the Co_3O_4 (for comparison), $\text{Co}_3\text{O}_4/\text{carbon black (CB)}$, and $\text{Co}_3\text{O}_4/\text{r-GO}$ electrodes at a current density of 1 A g^{-1} .

Figure 5.13 Average specific capacitance versus cycle number of the Co_3O_4 and $\text{Co}_3\text{O}_4/\text{r-GO}$ at a scan rate of 20 mV s^{-1} .

5.4 Conclusion

In summary, with the assistance of surfactant micelles, a unique $\text{Co}_3\text{O}_4/\text{r-GO}$ scrolled structure has been prepared. Interestingly, almost every single Co_3O_4 scroll is detected to connect with the r-GO platelets. This is highly beneficial to improve the electrochemical performances. The results show that the $\text{Co}_3\text{O}_4/\text{r-GO}$ composite exhibits both higher specific capacitance and better rate capability than bare Co_3O_4 . Our encouraging results offer a new concept of integration mode between graphene derivatives and other materials, which is believed to be helpful in developing multifunctional graphene composites for potential applications.

Chapter 6

Conclusions and Future Work

6.1 Conclusions

Encouraged by the high capacity offered by metal oxides, in this thesis, we mainly focus on the design and synthesis of metal oxide-based heterostructures for electrochemical energy storage applications. The main purpose is to develop some feasible strategies to improve the electrochemical performances of metal oxides and concurrently avoid some intrinsic problems associated with metal oxides by utilizing the outstanding functionality-integration feature of heterostructures. Besides, the synergistic effect induced from different components represents another attractive motivation to fabricating heterostructures. The major accomplishments and contributions of this thesis can be summarized into the following three points:

(1) Facile synthesis of two novel branched heterostructures consisting of SnO_2 and Fe_2O_3 for high-performance lithium storage. One is based on the controlled assembly of 1D SnO_2 nanorods onto both sides of 2D Fe_2O_3 nanoflakes. The Fe_2O_3 nanoflakes were simply obtained by direct heating the Fe foil in air. Subsequent grafting of SnO_2 nanorod branches was achieved by subjecting the preformed Fe_2O_3 nanoflakes to a batch of hydrothermal growth. The significance of this work includes two aspects: (i) development of a novel comb-like rather than more common tree-like branched heterostructure, (ii) increased volumetric energy density of the nanomaterials by improving the compactness of the structure when applied as the LIB anode. The other type of branched $\alpha\text{-Fe}_2\text{O}_3/\text{SnO}_2$ structure is the SnO_2 core

nanowires with well-oriented α -Fe₂O₃ nanorod branches, both single-crystalline, in a six-fold symmetry. This heterostructure was prepared by combining a vapor transport deposition (for the SnO₂ nanowire stems) and a facile hydrothermal method (for the α -Fe₂O₃ nanorod branches). One novelty of this work, in addition to its non-conventional branched structure, is the unique epitaxial growth behaviour of the branches, i.e. six α -Fe₂O₃ branches grew on four side surfaces of the tetragonal SnO₂ nanowire. This is in contrast to previously reported six-fold-symmetry branches that were mostly induced by six crystallographically equivalent planes of the stems. Detailed analysis of the crystallographic orientation was presented which was proved to be the result of lattice mismatch minimizations. Such a heterostructure demonstrated higher initial Coulombic efficiency and reversible capacity than both α -Fe₂O₃ and SnO₂ single-component electrodes, which is presumably due to the higher surface area and more free space offered by branched structure and the synergistic effect between α -Fe₂O₃ and SnO₂.

(2) Development of a general strategy toward graphene@metal oxide core-shell structures. In Chapter 4, we described a simple, efficient yet versatile method for the realization of core-shell assembly of graphene around various metal oxide nanostructures, including nanowires and nanoparticles. The driving forces of this process are (i) the ring-opening reaction between the epoxy groups and amine groups in GO platelets and amine-modified metal oxide nanostructures and (ii) electrostatic interaction between these two components. Consequently, nearly every single nanowire or nanoparticle was observed to be wrapped by graphene. The graphene@ α -Fe₂O₃ core-shell nanoparticles were investigated as the LIB electrode. The results revealed that the composite electrode exhibited higher reversible capacity, better cycling stability and more excellent rate capability than bare α -Fe₂O₃ electrode. Such

superior performance could be ascribed to the effectiveness of the graphene shell in preventing the aggregation, buffering the volume change, maintaining the integrity of $\alpha\text{-Fe}_2\text{O}_3$ nanoparticles, as well as improving the conductivity of the overall electrode.

(3) Exploration of a novel structural model between graphene and metal oxide. With the assistance of lamellar micelles of the surfactant, a new hybridization model was explored between graphene and metal oxides. In most graphene/metal oxide composites, graphene normally supports as a 2D support for anchoring metal oxide particles. This novel structural model was characterized by incorporating the r-GO platelets into the Co_3O_4 scrolls. The r-GO was believed to link with Co_3O_4 through the residual oxygen functional groups on their basal planes and the edges. However, it was difficult to observe graphene under common SEM and TEM measurements. Raman mapping results revealed that this assembly enabled almost every single Co_3O_4 scroll to connect with the r-GO platelets. This unique structure led thus to remarkably improved electrochemical performance with respect to pure Co_3O_4 in terms of higher specific capacitance and better rate capability.

On the basis of above results, some basic guidelines for designing heterostructures toward high-performance electrochemical energy storage devices can be abstracted as follows: (i) incorporating active nanomaterials into the free space in the hybrid system or into the inter-space between neighboring arrayed hybrid nanostructures. This is to further increase the specific energy density of electrodes, particularly areal and volumetric energy density, by making full use of voids within the electrode, (ii) improving the overall electrical conductivity of metal oxides by grouping with different conducting materials such as carbon materials, conducting polymers, (iii) designing innovative electrode structure, for example, multidimensional nanostructured current collectors which could offer lower densities

of the electrode and make the electrode lightweight, full of porosity and mechanically stable possible. In addition to the research in advanced materials, it is also highly necessary to study the related fundamental scientific issues such as the electrochemical mechanisms of emerging materials, the interfacial investigation within the hybrid system, etc.

6.2 Future Work

(1) Rational design and control of the phase composition and structure of metal oxide based heterostructures. This is important to ensuring the reproducibility and better understanding of the structure-property relationship. As can be seen from the results present in this thesis, texture and composition are the two crucial factors to the properties of heterostructures. The improved capability of controlling these two factors allows more systematic exploration of the potential use of each component in many other applications. Design and synthesis of a series of free-standing graphene-based composites using the strategy introduced in chapter 4, such as $\text{TiO}_2/\text{graphene}/\text{TiO}_2$, $\text{TiO}_2/\text{graphene}/\text{SnO}_2$, $\text{TiO}_2/\text{graphene}/\text{Si}$, etc., for LIBs application, represents one future work in this direction. In these composite structures, TiO_2 is chosen as the inner support largely due to its negligible volume change during Li insertion/extraction, which can ensure the whole integrity of the electrode. The TiO_2 can be synthesized in the form of nanorod arrays, nanowires or nanobelts. The role of graphene in between is to provide a highly conductive pathway for efficient electron transport. The $\text{TiO}_2/\text{graphene}/\text{TiO}_2$ model, where the outer TiO_2 shell is to be coated by atomic layer deposition (ALD), is adopted to verify the role of graphene in improving the electrical conductivity by comparing with the counterpart in the absence of graphene. When the outer shell is SnO_2 or Si , they are adopted to

contribute high capacity because of their high theoretical values. It needs to be mentioned that the thickness of the outer shell is initially designed to be very thin (for example, 5 nm ALD-coated SnO₂), which can support fast Li⁺ diffusion, full use of the shell materials and also avoid the problems associated with the huge volume expansion of these high-capacity materials upon Li intake. As a result, it is optimistic that these rationally designed electrodes have the potential to offer high capacity, long cycle life and good rate capability. From the synthesis point of view, chemically derived graphene can be easily dissolved in solutions and possibly incorporated into a variety of metal-oxide based materials by *in-situ* growth, covalent grafting or self-assembly.

(2) 3D graphene-based composites for efficient energy storage. The 3D graphene structures inherit the intrinsic salient features of 2D graphene while generating some new merits. Well-controlled 3D graphene on conductive substrate can provide higher specific surface area and porosity, more efficient electron transport pathway to the current collector, better electrical connectivity and the possibility of 3D integration to the functional systems. 3D graphene structures can be assembled in controllable ways from individual sheets of graphene materials (e.g., r-GO²³⁰⁻²³¹). Alternatively, they may be obtained using CVD method on suitable 3D substrates or templates (e.g., Ni foams,²³² Cu nanowires²³³). Strategies will be devised to control the porosity and other architectural features of the 3D graphene structures. Furthermore, approaches will be developed to decorate 3D graphene surface with metal oxide nanoparticles in order to achieve desired functionalities in energy storage applications.

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