Bio-inspired synthesis of functional micro/nano-structured materials

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NANYANG
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**BIO-INSPIRED SYNTHESIS OF FUNCTIONAL MICRO/NANO-
STRUCTURED MATERIALS**

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SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

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BIO-INSPIRED SYNTHESIS OF FUNCTIONAL MICRO/NANO- STRUCTURED MATERIALS

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Abstract

Materials in the nano-scale can exhibit unique chemical, physical, and electronic properties compared to the bulk materials. However, for practical application, the organization of nanoparticles into superstructures with micrometer dimensions that are easy for handling is necessary. Recently, inspired by the complex structures in nature, scientists have put much attention on applying bio-systems such as DNA, polypeptides, bacteria, and viruses towards the synthesis of controlled and defined micro/nano-structures of functional materials. With the advent of recombinant engineering, it is possible to genetically engineer these bio-molecules to interact with specific precursors under benign conditions, and to create inorganic nanostructures with precise control over their compositions, phase, shape and size. Here, we demonstrate the use of bacteria and polypeptides in directing the synthesis of micro/nano structured functional materials.

Bacteria have the natural ability to synthesize inorganic materials, and are considerably low cost and reproducible materials for nanomaterial synthesis. In this work, we developed two routes for bacteria-directed synthesis of functional materials. First, we exploited the inherent ability of magnetotactic bacteria to synthesize well-crystallized Fe_3O_4 nanoparticles. Further treatment with glucose allowed us to maintain the 1D structure of the Fe_3O_4 chains. The “candy haw-like” chains exhibited discharge capacities of 947, 857, 757, 615, 518, 388, 282 mA h g^{-1} at 0.2, 0.5, 1, 3, 5, 8 and 10 C for lithium ion batteries. Likewise, we also investigated the feasibility of using genetically engineered bacteria as templates for nanomaterial synthesis. Here, bacteria with the ability to acquire phosphates from their surroundings were subsequently used as templates for the synthesis of lithium metal phosphates nanostructures. The discharge capacities of the as-synthesized LiFePO_4/C nanocomposite electrodes were 145.6, 130.6, 117.8, and 92.3 mA h g^{-1} at discharge rates of 0.1, 0.5, 1 and 5 C respectively for lithium ion batteries.

While bacteria templates provide a promising strategy for the synthesis of nanomaterials, there is little control over their macrostructures. In order to fabricate three-dimensional hierarchical nanostructures, alternative templates are required. Recombinant proteins are ideal templates for nanomaterial synthesis due to their tailorable physical and chemical properties. For instance, elastin-like polypeptides (ELPs) are well-studied for their tunable structural properties, and have

been used widely in tissue engineering to generate 3D biomaterials. ELPs exhibit thermo-responsive behaviors, and can be readily purified via inverse thermal cycling. In this work, we showed that recombinant ELPs containing C-terminal hexahistidine tag (His tag) can be used to prepare metal oxides quantum dots encapsulated in 3D porous carbon microspheres. The as-synthesized $\text{Fe}_3\text{O}_4@\text{C}$ electrode delivered specific charge capacities of 510, 425, 330, 246 and 163 mA h g^{-1} at 0.2, 0.5, 1, 2 and 5 A g^{-1} respectively for sodium ion batteries. Finally, we demonstrated a facile strategy for the preparation of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ and $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ nanostructures supported on hierarchically porous 3D carbon aerogels using recombinant ELPs. The as-synthesized 3D $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ and $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ nanostructures show ultrahigh capacities at ultrafast charging/discharging properties and excellent cycle performance as cathodes for Li/Na secondary batteries.

In summary, we show that bio-inspired synthesis is indeed a promising strategy for functional materials fabrication.

Table of Contents

ACKNOWLEDGEMENTS	I
Abstract.....	III
Table of Contents	V
List of Figures	VIII
List of Tables	XIV
Chapter 1: Introduction.....	1
1.1 Background	1
1.2 Hypothesis.....	1
1.3 Objectives and Novelty	2
1.4 Thesis Organization.....	3
Chapter 2: Literature Review.....	4
2.1 Biological routes for inorganic material synthesis.....	4
2.2 Biomineralization of nanomaterials using bacteria	4
2.3 Magnetotactic bacteria	5
2.4 Biomineralization of nanomaterials using polypeptides	6
2.5 Elastin-like polypeptides (ELPs).....	7
2.6 Lithium / sodium ion batteries	11
2.6.1 General introduction of lithium ion battery	11
2.6.2 General introduction of sodium ion battery.....	12
2.6.3 Factors affecting anode / cathode materials' electrochemical performance to store lithium / sodium.....	13
2.7 Transitional metal oxides	15
2.7.1 Transitional metal oxides as anodes for LIBs	15

2.7.2 Current synthesis of iron oxides and cobalt oxides nanostructures for lithium ion batteries.....	16
2.7.3 Current application of iron oxides and cobalt oxides for SIBs.....	18
2.8 Lithium iron phosphates.....	19
2.8.1 Lithium iron phosphates as cathode in lithium ion batteries	19
2.8.2 Current synthesizing methods of LiFePO_4	20
2.9 Monoclinic trilithium divanadium(III) tris(orthophosphate), $\text{Li}_3\text{V}_2(\text{PO}_4)_3$	22
2.9.1 General introduction of monoclinic $\text{Li}_3\text{V}_2(\text{PO}_4)_3$	22
2.9.2 Current synthesizing methods for monoclinic $\text{Li}_3\text{V}_2(\text{PO}_4)_3$	23
Chapter 3: Magnetotactic bacteria assisted synthesis of Fe_3O_4 nanoparticle chains with N-doped carbon coating for high-rate lithium storage.	26
3.1 Introduction	26
3.2 Materials and Methods	27
3.2.1 Materials	27
3.2.2 Synthesis of 1D $\text{Fe}_3\text{O}_4/\text{C}$ chains	27
3.2.3 Characterization.....	28
3.2.4 Electrochemical measurements	28
3.3 Results and Discussion.....	29
3.4 Conclusion.....	37
Chapter 4: Recycling Bacteria for the Synthesis of LiMPO_4 ($\text{M} = \text{Fe}, \text{Mn}$) Nanostructures for High-Power Lithium Ion Batteries.....	38
4.1 Introduction	38
4.2 Materials and Methods	39
4.2.1 Materials	39
4.2.2 Synthesis of LiMPO_4	39
4.2.3 Electrochemical measurement	40

4.3 Results and Discussion.....	40
4.4 Conclusion.....	47
Chapter 5: Elastin-Like Polypeptides-Derived Porous Carbon-Encapsulated Metal Oxide Quantum Dots for Enhanced Sodium Storage	48
5.1 Introduction	48
5.2 Materials and Method.....	49
5.2.1 Protein expression, purification and metal oxide synthesis.....	49
5.2.2 Electrochemical measurements	51
5.3 Results and Discussion.....	51
5.4 Conclusion.....	62
Chapter 6: Biochemistry-Enabled 3D $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ / $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ Foams for Ultrafast Battery Cathodes	64
6.1 Introduction	64
6.2 Materials and Method.....	65
6.2.1 Products preparation method	65
6.2.2 Electrochemical measurement	65
6.3 Results and Discussion.....	66
6.4 Conclusion.....	79
Chapter 7: Conclusions and Outlook	80
7.1 Conclusions	80
7.2 Outlook.....	81
References	83
List of Publications	104

List of Figures

Figure 2.1 TEM images showing cells of different magnetotactic bacteria (a – d) and magnetosome crystals (e – h). ²⁰ Reprinted with permission from ref. 20. Copyright 2002, Springer.	6
Figure 2.2 Proposed mechanism for magnetosome formation in <i>Magnetospirillum gryphiswaldense</i> . ²⁰ Reprinted with permission from ref. 20. Copyright 2002, Springer.	6
Figure 2.3 Aggregation mechanism of ELPs. ²⁷ Reprinted with permission from ref. 27. Copyright 2014, Springer.	8
Figure 2.4 Scheme of ELPs purification process based on inverse transition cycling. ²⁸ Reprinted with permission from ref. 28. Copyright 2002, Springer.	8
Figure 2.5 General design principle illustrating the formation of ELP particles. ³¹ Reprinted with permission from ref. 31. Copyright 2012, American Chemical Society.	9
Figure 2.6 a) Schematic diagram of micelle formation above T_t at low and high salt concentration; b) Diameter of spherical micelles and length of cylindrical micelles as a function of salt concentration. ³³ Reprinted with permission from ref. 33. Copyright 2013, American Chemical Society.	9
Figure 2.7 TEM images of different morphologies derived from ELPs. ³⁴⁻³⁶ Reprinted with permission from ref. 34. Copyright 2009, American Chemical Society; Reprinted with permission from ref. 35. Copyright 2011, Elsevier; Reprinted with permission from ref. 36. Copyright 2014, AIP Publishing LLC.	10
Figure 2.8 Schematic principle of a typical rechargeable LIBs. ⁴³ Reprinted with permission from ref. 43. Copyright 2011, Royal Society of Chemistry.	12
Figure 2.9 Ideal LiFePO ₄ /carbon core-shell nanoparticle network and electron, lithium ion transfer mechanism. ⁴⁴ Reprinted with permission from ref. 44. Copyright 2010, Royal Society of Chemistry.	14
Figure 2.10 Different heterogeneous nanostructured materials based on structural complexity. ⁴⁴ Reprinted with permission from ref. 44. Copyright 2010, Royal Society of Chemistry.	15

Figure 2.11 SEM image (a), TEM image (b), and cycling performance of Fe ₃ O ₄ /C nanofibers. ⁴⁶ <i>Reprinted with permission from ref. 46. Copyright 2008, Elsevier. ....</i>	17
Figure 2.12 (a) Cycling performance of the Fe ₂ O ₃ /GNS and Fe ₂ O ₃ @GNS samples at a current density of 100 mA g ⁻¹ , and coulombic efficiency of the Fe ₂ O ₃ @GNS sample; (b) Cycling performance for Fe ₂ O ₃ @GNS cycled at current densities of 200, 500, and 1000 mA g ⁻¹ . ⁶⁷ <i>Reprinted with permission from ref. 67. Copyright 2015, Royal Society of Chemistry. ....</i>	18
Figure 2.13 SEM images of the as-prepared Fe ₂ O ₃ (a), Co ₃ O ₄ (b) film and corresponding cycle performance at a current density of 100 mA g ⁻¹ . ⁶⁸ <i>Reprinted with permission from ref. 68. Copyright 2014, Elsevier. ....</i>	19
Figure 2.14 The crystal structure of LiFePO ₄ . The Fe atoms occupy octahedral sites (grey) and the P atoms occupy tetrahedral sites (brown). The Li ions (small circles) occupy the one-dimensional tunnels. ⁷⁴ <i>Reprinted with permission from ref. 74. Copyright 2009, Elsevier. ....</i>	20
Figure 2.15 Preparation process for the LiFePO ₄ /C particle via an in situ polymerization that restricts the size of the particles. ⁷⁶ <i>Reprinted with permission from ref. 76. Copyright 2008, WILEY-VCH Verlag GmbH & Co. KGaA. ....</i>	21
Figure 2.16 The crystal structure of monoclinic Li ₃ V ₂ (PO ₄) ₃ . ⁹¹ <i>Reprinted with permission from ref.91. Copyright 2014, Elsevier. ....</i>	23
Figure 2.17 The morphology of Li ₃ V ₂ (PO ₄) ₃ cathode materials prepared by different methods: a) solid-state reaction, ⁹³ <i>Reprinted with permission from ref.93. Copyright 2006, Elsevier.</i> b) sol-gel chemistry, ⁹⁸ <i>Reprinted with permission from ref.98. Copyright 2010, Elsevier.</i> c) hydrothermal method, ¹⁰¹ <i>Reprinted with permission from ref.101. Copyright 2013, Royal Society of Chemistry.</i> d) spray pyrolysis, ¹⁰² <i>Reprinted with permission from ref.102. Copyright 2011, Elsevier.</i> e) freeze-drying method, ¹⁰³ <i>Reprinted with permission from ref.103. Copyright 2012, Royal Society of Chemistry.</i> f) electrospinning. ¹⁰⁴ <i>Reprinted with permission from ref.104. Copyright 2013, Elsevier. ....</i>	25
Figure 3.1 Schematic illustration of the nucleation and growth of the magnetotactic bacteria and the glucose aided synthesis of Fe ₃ O ₄ /C chain structure.....	28
Figure 3.2 a) SEM images of as-cultivated magnetotactic bacteria; b) and c) corresponding TEM and high magnification TEM image; d) XRD pattern of the bacteria before annealing.....	30

Figure 3.3 The TEM image of the 100 °C treated bacteria without the addition of glucose.	31
Figure 3.4 The FTIR spectrum of as cultivated bacteria.	31
Figure 3.5 (a) FESEM images of annealed magnetotactic bacteria; (b) and (c) corresponding TEM and high resolution TEM images; (d) Fast Fourier Transform (FFT) pattern and magnified image plotted from the rectangular area denoted in (c).	32
Figure 3.6 The Raman spectra for the annealed Fe ₃ O ₄ /C chains. (D refers to diamond band, and G refers to graphite band)	33
Figure 3.7 TGA analysis result for the Fe ₃ O ₄ /C chains.	34
Figure 3.8 (a) The XPS result for the annealed Fe ₃ O ₄ /C chains; (b) N1s spectra for the as-cultivated bacteria; (c) N1s spectra for the Fe ₃ O ₄ /C chains.	34
Figure 3.9 Electrochemical performances of Fe ₃ O ₄ /C chains: a) cyclic voltammograms at a scan rate of 0.5 mV s ⁻¹ ; b) charge/discharge curves at 185.2 mA g ⁻¹ ; c) cyclability of both Fe ₃ O ₄ /C chains and co-precipitated Fe ₃ O ₄ nanoparticles at 185.2 mA g ⁻¹ ; and d) capacity over cycling of the two samples at different rates.	36
Figure 3.10 TEM image of Fe ₃ O ₄ NPs prepared by co-precipitation method.	36
Figure 4.1 Schematic of biological route for conversion of P-rich bacteria into carbon-coated LiMPO ₄ nanocrystals.	40
Figure 4.2 Time course of phosphate concentration during growth of <i>E. coli</i> + pBC29 and wild-type <i>E. coli</i> in T media. Data are means ± SEM from three independent experiments.	41
Figure 4.3 (a) TEM images of recombinant <i>E. coli</i> + pBC29 taken at 5.5 h of a phosphate uptake experiment. White arrows indicate polyP granules. Insets in (a) show enlarged images of polyphosphate granules; (b) EDX mapping of recombinant <i>E. coli</i> + pBC29 sample in (a), showing the presence of elemental P (yellow). (c) TEM image of recombinant <i>E. coli</i> + pBC29 after treatment with Fe ³⁺ solution (pH 2.5). (d) Magnified image of sample in (c) and the corresponding EDX mapping images showing presence of elemental P (e) and elemental Fe (f).	42
Figure 4.4 (a) X-Ray diffraction pattern and (b) TEM image of LiFePO ₄ synthesized in this work. Black dots in (b) are LiFePO ₄ nanocrystals. (c) TEM image of a single LiFePO ₄ nanocrystal and	

(d) measured the lattice spacings (0.242 nm) of the crystals corresponding to (121) plane of triphylite LiFePO_4	43
Figure 4.5 Thermal gravimetric analysis of as synthesized LiFePO_4/C nanoparticles.....	44
Figure 4.6 (a) Charge-discharge voltage profiles of the LiFePO_4/C electrodes at a current rate of 0.1 C for the first three cycles; (b – c) Cycling performance of the LiFePO_4/C electrodes at 0.1 C and 1 C, respectively. The performance of LiFePO_4 electrodes without addition of carbon has also been shown for comparison. (d) Cycling performance of the LiFePO_4/C and LiFePO_4 electrodes at various current rates.	45
Figure 4.7 (a) TEM image of recombinant <i>E. coli</i> + pBC29 after treatment with Mn^{2+} solution (pH 2.5), and the corresponding EDX mapping images showing presence of elemental P (b) and elemental Fe (c).....	46
Figure 4.8 (a) X-ray diffraction pattern and (b) TEM image of LiMnPO_4 synthesized in this work. Black dots in (b) are LiMnPO_4 nanocrystals. (c) TEM images of LiMnPO_4 nanocrystals. Inset in (c) show the lattice spacings of 0.273 nm and 0.198 nm, corresponding to (301) and (230) planes of lithiophilite LiMnPO_4	47
Figure 5.1 Scheme illustrating the synthesis of carbon-encapsulated metal oxides using recombinant elastin-like polypeptides (ELP16-His). The amino acid sequence of ELP16-His is also shown.....	51
Figure 5.2 FESEM images of crosslinked ELP16-His (a) before and (b) after treatment with Fe^{3+}	52
Figure 5.3 XRD pattern of as-synthesized Fe_3O_4	53
Figure 5.4 The high-resolution X-ray photoelectron spectroscopy spectrum of Fe 2p.	53
Figure 5.5 (a - b) FESEM images of as-synthesized $\text{Fe}_3\text{O}_4/\text{C}$ at different magnifications; (c - d) TEM images of as-synthesized $\text{Fe}_3\text{O}_4/\text{C}$, showing nanoparticles of around 5 nm embedded in a carbon matrix.	54
Figure 5.6 (a) Thermal gravity analysis and of as-synthesized $\text{Fe}_3\text{O}_4/\text{C}$; (b) Nitrogen adsorption and desorption isotherms at 77 K for as-synthesized $\text{Fe}_3\text{O}_4/\text{C}$	55

Figure 5.7 XPS analysis of as-synthesized $\text{Fe}_3\text{O}_4/\text{C}$, showing none peak of element N.....	55
Figure 5.8 Rate capabilities of carbonized ELP16-His scaffold as anode in SIBs.	57
Figure 5.9 (a) CV curves of a fresh SIB with $\text{Fe}_3\text{O}_4/\text{C}$ electrode at a scan rate of 0.1 mV s^{-1} within a potential range of 0.001 to 3.0 V (vs. Na/Na^+); (b) The 1 st charge-discharge profiles of the cells with $\text{Fe}_3\text{O}_4/\text{C}$, bare Fe_3O_4 , and Fe_2O_3 electrodes at a current density of 0.1 A g^{-1} ; (c) Rate capabilities of the cells with $\text{Fe}_3\text{O}_4/\text{C}$, bare Fe_3O_4 , and Fe_2O_3 electrodes; (d) Cycling performance of cell with the $\text{Fe}_3\text{O}_4/\text{C}$ electrode at 0.1 A g^{-1} ; (e) Cycling performance of the cell with $\text{Fe}_3\text{O}_4/\text{C}$ electrode at 0.2 and 0.5 A g^{-1}	58
Figure 5. 10 XRD pattern of as-synthesized $\text{Co}_3\text{O}_4/\text{C}$	60
Figure 5.11 (a) FESEM image of as-synthesized $\text{Co}_3\text{O}_4/\text{C}$; (b - c) TEM images of as-synthesized $\text{Co}_3\text{O}_4/\text{C}$, showing nanoparticles of around 5 nm embedded in a carbon matrix.	61
Figure 5.12 (a) Thermal gravity analysis and of as-synthesized $\text{Co}_3\text{O}_4/\text{C}$; (b) Nitrogen adsorption and desorption isotherms at 77 K for as-synthesized $\text{Co}_3\text{O}_4/\text{C}$	61
Figure 5.13 (a) Rate capability of the cell with $\text{Co}_3\text{O}_4/\text{C}$ electrode. Inset shows the 1 st charge-discharge profile of the cell at 0.1 A g^{-1} ; (b) Cycling performance of the cell with $\text{Co}_3\text{O}_4/\text{C}$ electrode at 0.5 A g^{-1}	62
Figure 6.1 XRD patterns of as-synthesized (a) LVP and (b) NVP.....	66
Figure 6.2 (a – c) FESEM images of as-synthesized LVP 3D foams at various magnifications; (d) TEM image showing the presence of LVP nanoparticles embedded within a carbon matrix; (e) measured lattice spacing (0.367 nm) of the crystals corresponding to (211) plane of the LVP..	67
Figure 6.3 TEM images of as-synthesized LVP, showing inter-connected fibrous carbon matrix.	68
Figure 6.4 XPS analysis of as-synthesized LVP, showing none peak of element N.....	68
Figure 6.5 Nitrogen adsorption and desorption isotherms at 77 K for as-synthesized LVP@C/CAs, with inserts showing pore size distributions.	69

Figure 6.6 (a – c) FESEM images of as-synthesized NVP 3D foams at various magnifications; (d) TEM image showing the presence of NVP nanoparticles embedded within a carbon matrix; (e) measured lattice spacing (0.442 nm) of the crystals corresponding to (104) plane of the NVP.	70
Figure 6.7 TEM images of as-synthesized NVP@C/CAs at low magnification, showing interconnected fibrous carbon matrix.....	70
Figure 6.8 Nitrogen adsorption and desorption isotherms at 77 K for as-synthesized NVP@C/CAs, with inserts showing pore size distributions.	71
Figure 6.9 FESEM images of (a) ELP16 and both precursors, (b) ELP16 and LiH_2PO_4 , (c) ELP16 and NH_4VO_3 mixtures, and (d) ELP16 only obtained after freeze drying, with insets showing the corresponding FESEM images at higher magnifications.....	72
Figure 6.10 FTIR spectra of LVP precursors (curve a), ELP16 + LVP precursors (curve b), and ELP16 (curve c). The shifts in P-O stretching, V-O-V stretching, and C-NH ₂ stretching peaks are indicated.....	73
Figure 6.11 Schematic illustrating the mechanisms in the synthesis of MVP 3D foams using recombinant ELP16 proteins.....	74
Figure 6.12 FESEM image of ELP16+ LVP precursor solution placed at room temperature for 1 h, followed by freeze drying. No fibrous structures were observed.	74
Figure 6.13 Initial charge-discharge voltage profiles of (a) LVP and (b) NVP cathodes at 1C. Insets show the corresponding cycling performances for each material.....	75
Figure 6.14 Galvanostatic discharging profiles of (a) LVP and (b) NVP cathodes at current rates of 5 C to 200 C (their discharge capacities versus C rates are summarized in the insets). (c) Cycling stability of LVP and NVP at 100 C. (d) Ragone plots of our 3D MVP cathodes, compared with some advanced active materials of $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ (up triangles), CNT/ FePO_4 nanowires (down triangles), LiFePO_4/C (diamonds), LVP/C thin film (right triangles), $\text{Na}_3\text{Ni}_2\text{SbO}_6$ (hexagons), NVP/graphene (stars).....	77

List of Tables

Table 5.1 A comparison of our $\text{Fe}_3\text{O}_4@\text{C}$ to previously reported iron oxides anodes in sodium ion batteries.	59
Table 5.2 A comparison of our $\text{Co}_3\text{O}_4@\text{C}$ to previously reported Co_3O_4 anodes in sodium ion batteries.	62
Table 6.1 A comparison of our LVP@C/CAs to previously reported LVP cathodes in the voltage range of 3.0-4.3 V vs. Li^+/Li	78
Table 6.2 A comparison of our NVP@C/CAs to previously reported NVP cathodes in the voltage range of 2.5-3.8 V vs. Na^+/Na	78

Chapter 1: Introduction

1.1 Background

Owing to their small size, nanoparticles (NPs) exhibit unique chemical, physical, and electronic properties that bulk materials lack. Hence, nanomaterials have received tremendous attention for their potential applications in energy storage, catalysis, sensors, drug delivery, adsorption, and so on. However, it is necessary to organize nanoparticles into superstructures with micrometer dimensions that are easy to handle. Yet the assembly and organization of NPs into micro-scaled structures remains challenging. Therefore, it is necessary to seek new strategies to synthesize nanostructured functional materials with micro-scale features.

In general, the most applicable and simplest synthetic routes of hierarchical structures are probably templating or via self-assembly of low-dimensional building blocks. Nonetheless, it remains a challenge to develop hierarchically micro/nano architectures with tailored chemistries and controllable morphologies; both factors greatly affect the functional properties of the nanomaterials.

1.2 Hypothesis

Biological templates found in nature, *e.g.* bamboo, crab shells, pollen grains, and flowers, have unique structures, complex surfaces, and uniform geometries. These materials have been explored as templates for synthesis of a wide variety of hybrid inorganic materials due to their mild and environmentally friendly synthesis conditions. In particular, single-component biological systems such as DNA, proteins, bacteria, and virus have been considered as templates for preparing 0D or 1D nanomaterial synthesis. Yet, three-dimensional (3D) inorganic nanostructures with both micro- and nano-scaled morphologies have not been prepared using biological routes.

In this work, I hypothesize that genetically engineered bio-molecules interact with specific precursors under benign conditions to result in 3D inorganic nanostructures with complex stoichiometry, and with both micro- and nano- topographical features. In addition, these nanomaterials demonstrate superior functional properties when evaluated in energy storage applications.

1.3 Objectives and Novelty

The main objectives of this thesis are (1) to investigate the feasibility of several types of biological templates for the preparation of nanostructured inorganic materials, and (2) to evaluate the functional properties of the as-prepared materials in energy storage applications. In this work, we test our hypotheses using bacteria and recombinant proteins as novel templates.

Bacteria are attractive raw materials for nanomaterial synthesis due to their abundance in nature, and ease to culture them in large quantities in the laboratories. In addition, some native bacteria possess unique biomineralization abilities, and can serve as interesting templates for nanomaterial synthesis. In this thesis, magnetotactic bacteria were evaluated for the synthesis of Fe_3O_4 nanoparticles, utilizing their innate biomineralization capabilities. Likewise, bacteria that have been developed for waste removal were also evaluated as a candidate for material synthesis. In both instances, the synthesis routes occur under environmentally friendly conditions, and can offer more precise control over the particle stoichiometric chemistries and morphologies.

Bacteria-assisted syntheses however, are also limited to several morphologies (mostly hollow structures) and determined by the type of bacteria chosen. Polypeptides on the other hand, have almost limitless sequence design, and can be readily programmed to self-assemble into specific structures or shapes. Further, metal-binding sequences can be incorporated within the backbone of genetically engineered polypeptides to interact specifically with metal precursors. Hence, polypeptides are attractive templates for the synthesis of functional materials, and are also evaluated in this work, particularly to prepare nanomaterials with more complex inorganic compositions and architectures (*e.g.*, 3D foams).

In particular, elastin-like polypeptides (ELPs) consist of repetitive VPGXG sequences, where X is any amino acid except proline. ELPs are soluble in water below their inverse transition temperature (T_i) but aggregate at temperatures above T_i . As such, the thermosensitive properties of ELPs confer them as popular building blocks for 3D scaffolds in tissue engineering and drug delivery applications. Yet, ELPs have yet to be explored for synthesis of inorganic materials for energy storage applications.

1.4 Thesis Organization

This thesis reports bacteria and polypeptides directed synthesis of various architectures of different functional materials. In Chapter 1, the background and objectives of this project are described. In Chapter 2, detailed literature reviews on the applications and advantages of biomolecules on the synthesis of inorganic functional materials, magnetotactic bacteria, ELPs, lithium / sodium ion batteries, current synthesis methods and applications of metal oxides, lithium metal phosphates in lithium / sodium ion batteries, are provided. Chapters 3 - 6 describe my attempts to prepare nanomaterials using various bacteria and recombinant polypeptide templates. Finally, a summary of my findings and future work are outlined in Chapter 7.

Chapter 2: Literature Review

2.1 Biological routes for inorganic material synthesis

Inspired by the intricate and sophisticated nanostructures in nature, scientists have placed increasing attention on application of biological scaffolds in nanostructured materials fabrication. The nanostructures obtained from biological routes have advantages over those obtained even with the most advanced synthetic technologies. Up to now, biologically derived materials such as fungi, phages, bacteria, DNA, viruses, peptides, and proteins have been successfully been applied for the formation of various inorganic functional materials including 5 nm sized FePt nanoparticles, Co_3O_4 hollow structures and nanowires, uniformly sized iron oxide nanoparticles around 6 nm, 4 – 5 nm sized BaTiO_3 nanoparticles, FePO_4 nanofibers, 3 – 5 nm sized CdS, CdSe nanoparticles, controlled deposited and organized Pt, Au, Ag nanoparticles, and so on.¹⁻⁸

2.2 Biomineralization of nanomaterials using bacteria

In bio-mineralization process, minerals are produced through intricate in-cell biochemical reactions. Since bio-mineralization happens at mild conditions, it is considered energy efficient and green compared to traditional approaches that require high energy, stringent conditions, and might produce toxic byproducts. Many bacteria are known to be able to undergo bio-mineralization processes. Examples include bio-mineralization of Au nanoparticles in *Cupriavidus metallidurans* CH34,⁹ bio-mineralization of magnetite (crystal of Fe_3O_4 or Fe_3S_4) and tellurium nanocrystals in magnetotactic bacteria,^{10,11} bio-mineralization of selenium by bacterium *Thauera selenatis*,¹² and so on.

Bacteria have also been used as physical templates for synthesizing hierarchical structures of inorganic materials. Bacteria exist as plenty of well-defined morphologies and geometries (*e.g.* coccus, bacillus, square-shaped bacteria, star-shaped bacteria). These interesting morphologies offer natural templates to produce various micro/nano structures. There are also large amount of functional groups in the bacterial cell membrane, providing binding sites for various precursors. Much work has been done regarding the synthesis of hollow structures of inorganic materials based on the template effect of bacteria (*e.g.* silver microspheres with hollow and porous structures,¹³ titanium dioxide micro/nano structures,¹⁴ cadmium sulfide hollow microrods,¹⁵ porous cobalt

oxide nanostructure,⁵ zinc sulfide hollow spherical nanostructure,¹⁶ etc.). Hollow structures generally feature high surface areas, and thus enhanced performance. Indeed, the reported works show that materials synthesized from bacteria templates exhibit excellent and enhanced performances.

2.3 Magnetotactic bacteria

Magnetotactic bacteria are known to biomineralize iron oxide magnetosomes that are highly crystalline and uniformly-sized.¹⁰ Studies have shown that magnetosomes taken from magnetotactic bacteria demonstrate magnetic properties that have applications in high-density data storage, electromagnetic shielding, applications in diagnostic medicine, drug targeting, and magnetic resonance imaging.¹⁷⁻¹⁹

There are various types of magnetotactic bacteria containing magnetosome crystals with distinct morphologies (Figure 2.1). *Magnetospirillum gryphiswaldense* is the mostly readily cultivated magnetotactic bacteria, and thus was widely chosen as a model to study the mechanism of magnetosome formation. Generally, the mechanism was proposed as shown in Figure 2.2.²⁰ Fe₃O₄ NPs are formed in magnetosome vesicles via a spontaneous biomineralization process. Fe (III) passes through the outer membrane under the help of certain functional proteins, and loses one electron to form Fe (II). Further, Fe (II) enters into the magnetosome vesicles, during which two thirds of the Fe (II) is oxidised again and self-assembled Fe₃O₄ nuclei are formed. This whole process is regulated by Mam proteins in the magnetosome membranes. It was also found that both the uptake of iron and the formation of magnetosomes are stimulated by microaerobic conditions.²¹ The iron taken up by the cell is transformed into Fe₃O₄ spontaneously. Under either anaerobic or aerobic conditions, magnetite formation will not occur.

Figure 2.1 TEM images showing cells of different magnetotactic bacteria (a – d) and magnetosome crystals (e – h).²⁰ Reprinted with permission from ref. 20. Copyright 2002, Springer.

Figure 2.2 Proposed mechanism for magnetosome formation in *Magnetospirillum gryphiswaldense*.²⁰ Reprinted with permission from ref. 20. Copyright 2002, Springer.

2.4 Biomineralization of nanomaterials using polypeptides

Polypeptides (or proteins) have been used extensively to biomineralize nanomaterials with intricate architectures. Examples include syntheses of iron oxides / cobalt oxides minerals within the protein cages of ferritins, proteins isolated from sponge *T. aurantia* directed the synthesis of titanium dioxide under gentle reaction conditions, synthesis of Ag₂S nanorods in the presence of bovin serum albumin and so on.²²

Genetically engineered polypeptides have also attracted interests as potential templates for nanomaterial synthesis; their physical and chemical properties structures can be readily tailored by incorporating the desired functional sequences through recombinant protein engineering. Examples include nanowires coated with uniform Au nanocrystals obtained via histidine-rich peptides,²³ metal phosphates nanofibers based on mineralization of self-assembled hydrophobic peptides,²⁴ mono-dispersed silver nano-particles grown inside the cavity of a peptide nano-reactor,²⁵ and so on.

Nonetheless, most of the efforts reported in the literature are focused on preparing 0D or 1D nanostructured materials. Few works have been reported concerning polypeptides-directed synthesis of inorganic materials with 3D hierarchically porous nanoarchitectures. There have also been no attempts to prepare such 3D nanocrystals with complex chemical stoichiometric compositions.

2.5 Elastin-like polypeptides (ELPs)

Elastin is an extracellular matrix protein found in elastic fibers and provides elasticity to lung, skin and arteries.²⁶ Elastin consists of crosslinked tropoelastin, which are alternating hydrophobic domains containing repeats of valine (Val), proline (Pro), glycine (Gly), alanine (Ala). Elastin-like polypeptides (ELPs) that mimic the activities of natural elastin have been successfully prepared. ELPs consist of repetitive Val-Pro-Gly-Xaa-Gly (VPGXG) sequences, where X is any amino acid except proline. ELPs have been shown to exhibit inverse temperature phase transition characteristics.²⁷ They are soluble in water at temperatures below their inverse transition temperature (T_i) in an unordered conformation, and aggregate at temperatures above T_i showing more ordered β -spiral structure due to hydrophobic interactions as shown in Figure 2.3. The T_i value is influenced by the guest amino acid, the concentration of ELPs, the ionic strength of solution, and the length of used polymers.²⁷

Figure 2.3 Aggregation mechanism of ELPs.²⁷ Reprinted with permission from ref. 27. Copyright 2014, Springer.

ELPs can be readily isolated due to their inverse temperature phase transition characteristics. As shown in Figure 2.4, ELPs are subjected to repeated cold and hot spins, known as inverse transition cycling (ITC). During the cold spins, ELPs are collected in the supernatant, and non-soluble impurities are removed. During the hot spin, ELPs are collected in the pellet, and soluble impurities are removed. By repeating the cold and hot spin cycles several times, ELPs can be readily purified.

Figure 2.4 Scheme of ELPs purification process based on inverse transition cycling.²⁸ Reprinted with permission from ref. 28. Copyright 2002, Springer.

Elastin-like polypeptides also possess high elasticity and resilience, making them highly popular in many areas, including tissue engineering, bioremediation, drug delivery, and protein purification.^{27,29,30} ELPs can be self-assembled through a coacervation process to form micron-sized particles when heated to temperatures higher than their T_t values. Take fusion protein

containing both hydrophilic and hydrophobic ELP domains for example. The two sects of ELP domains have different T_t values. When heated to temperatures between the two T_t values, micelles can be obtained,^{31,32} and when the temperature rises beyond both T_t values, micro spherical particles are obtained instead (Figure 2.5).

Figure 2.5 General design principle illustrating the formation of ELP particles.³¹ Reprinted with permission from ref. 31. Copyright 2012, American Chemical Society.

Besides temperature, salt concentration can also affect the self-assembling behavior of ELPs. For instance, Ghooarchian *et al.* found that the spherical micelles of a three-armed star ELP became larger as salt concentration increased, as shown in Figure 2.6.³³ At higher salt concentrations, cylindrical micelles were obtained instead.

Figure 2.6 a) Schematic diagram of micelle formation above T_t at low and high salt concentration; b) Diameter of spherical micelles and length of cylindrical micelles as a function of salt

concentration.³³ *Reprinted with permission from ref. 33. Copyright 2013, American Chemical Society.*

Functional groups can be incorporated within the elastin-like domains to serve as crosslinking sites. For instance, lysine residues found within ELPs can be chemically crosslinked to yield micro/nano porous structured scaffolds (Figure 2.7a) for tissue engineering applications.³⁴ In addition, the porosity could be tuned by varying the amount of NaHCO_3 present during the crosslinking. Dash *et al.* reported the use of negatively-charged polystyrene beads to create ELP hollow spheres.³⁵ They further showed that such ELP hollow spheres allowed a higher DNA loading efficiency compared to unaltered ELP particles (Figure 2.7b). Separately, ELPs can provide binding sites for metal cations, and direct the aggregation of metal precipitation, such as in the case of nanoflowers reported by Ghosh *et al* as shown in Figure 2.7c.³⁶

Figure 2.7 TEM images of different morphologies derived from ELPs.³⁴⁻³⁶ *Reprinted with permission from ref. 34. Copyright 2009, American Chemical Society; Reprinted with permission from ref. 35. Copyright 2011, Elsevier; Reprinted with permission from ref. 36. Copyright 2014, AIP Publishing LLC.*

There are three methods for crosslinking ELPs: chemical crosslinking, physical crosslinking, enzymatic crosslinking.²⁸ Among these three methods, chemical crosslinking is most widely used due to its easy handling. In chemical crosslinking process, ELP molecules are crosslinked using amine-reactive agents, including glutaraldehyde, bis(sulfosuccinimidyl), hexamethylene diisocyanate, and disuccinimidyl suberate.³⁷⁻⁴¹ The positions and number of lysine residues found in the ELP backbone determine the physical properties of the crosslinked ELP hydrogels.⁴²

2.6 Lithium / sodium ion batteries

2.6.1 General introduction of lithium ion battery

Long-life, reliable, low cost, and environmentally friendly batteries are urgently needed to meet the growing electric energy storage demands. Lithium ion batteries (LIBs) meet all the requirements above, and offer energy densities (2-3 folds) and power densities (5-6 folds) more than that of their nickel-cadmium counterparts. In addition, LIBs have many other advantages including low self-discharging, high working voltage, wide temperature range, safety and so on. Hence, it is not surprising that LIBs are gradually replacing nickel-cadmium batteries in many electronic devices.

The schematic operating principle of LIBs is shown in Figure 2.8. Typically, a LIB consists of a cathode (*e.g.*, lithium cobalt oxide), an anode (*e.g.*, graphene), and a separator that prevents contact between the cathode and anode, while allowing lithium (Li^+) ions to pass through. The ensemble is filled with electrolyte for conducting lithium. When the battery is charging, lithium ion intercalated in the cathode moves through the electrolyte to the anode where it receives an electron, and be reduced back to lithium metal. The elemental lithium is then stored in the structure of anode materials. During discharge, the lithium stored in the anode loses an electron and is transformed into Li^+ , which moves through the electrolyte to reach the cathode, intercalates into the crystal structure of cathode and stays there. Here we take LiCoO_2 and graphene as examples to show the chemical mechanisms of LIBs, as seen in equation 2.1 and 2.2. Therefore, the capacities of applied anode / cathode materials for lithium storage are critical to the performance of LIBs.

Figure 2.8 Schematic principle of a typical rechargeable LIBs.⁴³ Reprinted with permission from ref. 43. Copyright 2011, Royal Society of Chemistry.

Reaction of anode:

Reaction of cathode:

2.6.2 General introduction of sodium ion battery

Large-scale storage using battery technology is necessary in order to compete with the growing popularity of other renewable energy technologies such as wind and solar large-scale storage. While LIB technology is relatively matured, the high cost of lithium drives researchers to

look for alternatives. Sodium, which is next to lithium in elemental group I, is a promising alternative to lithium. Sodium, as the fourth most abundant Earth element, is much cheaper (*e.g.*, about \$ 135-165 / ton) compared to lithium-containing precursors (*e.g.*, lithium carbonate about \$ 5000 / ton). Besides, the redox potential of Na^+ / Na is -2.71 V, only 0.3 V higher than that of Li^+ / Li . These factors make sodium ion batteries (SIBs) very attractive in large-scale battery applications such as renewable energy stationary storage, where high energy density is not that critical. The fundamental principles of SIBs are similar to that of LIBs. Sodium ions shuttle between the cathode and anode in a SIB system during charge and discharge. Like LIBs, the electrochemical performance of SIBs also depends on the sodium storage ability of the active anode/cathode materials. Currently, SIBs are not as well investigated as LIBs, hence seeking suitable materials for SIBs would be necessary to advance the development of SIBs.

2.6.3 Factors affecting anode / cathode materials' electrochemical performance to store lithium / sodium

From the working mechanisms of LIBs and SIBs shown in Figure 2.8, we can see that the electrochemical performance of the electrodes is generally affected by the nature properties of the electrode materials, the rates of lithium and electron transportation inside the electrode materials, as well as the accessibility of lithium to the material surface. Therefore, there is tremendous efforts in the literature to improve the electrochemical performances of the electrodes in LIBs and SIBs.

First, much work has been done to increase the electron and ion conductivity of the active materials, including tailoring the particle size and applying carbon coating. By synthesizing the particles with smaller diameters, the diffusive lengths for lithium / sodium ions and electrons within the solid material can be shortened. According to the time constant (t) equation for lithium diffusion: $t=L^2/D$ where L is the diffusion length, D is the diffusion constant, the time for lithium intercalation / de-intercalation decreases significantly as the particle size decreases from micro- to nano scale. Carbon is regarded as a low cost, excellent electron conductor. As the electron conductivity of most cathode materials is limited, nano-sized electrode materials encapsulated by a thin layer of carbon coating are expected to exhibit enhanced electrochemical performance in LIBs and SIBs. Figure 2.9 illustrates the ideal LiFePO_4 /carbon core-shell nanoparticle network

for electron/lithium ion transfer. As shown in the schematic, nanoparticles encapsulated with a layer of carbon can facilitate electron transport through the network.

Figure 2.9 Ideal LiFePO_4 /carbon core-shell nanoparticle network and electron, lithium ion transfer mechanism.⁴⁴ Reprinted with permission from ref. 44. Copyright 2010, Royal Society of Chemistry.

Secondly, much work has been done to obtain nanostructured electrode materials with various morphologies, ranging from 0D nanoparticles to 3D complex porous frameworks, as shown in Figure 2.10. Zero dimensional nanostructured materials feature high surface areas that allows high electrode / electrolyte contact areas, leading to a high Li^+ flux across the interfaces of active materials. Compared to 0D nanostructures, 1D nanostructures can provide a pathway along its micro-scale axis for efficient transport of electrons and lithium ions while its nano-scale dimension maintain the benefits of 0D nanoparticles. However, if the aspect ratios of the 1D nanomaterials increase, it will lead to higher electrical resistance as well as poorer mechanical stabilities. Three-dimensional nanostructures can provide a solution to these problems due to their interconnected open-pore structures. The mesopores provides high contact areas between electrolyte and electrodes while the micropores can act as transport system for lithium ions.

Figure 2.10 Different heterogeneous nanostructured materials based on structural complexity.⁴⁴
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2.7 Transitional metal oxides

2.7.1 Transitional metal oxides as anodes for LIBs

Metallic lithium is the most attractive material for anodes from the aspect of energy density. However, lithium dendrites may form during the reaction to cause internal short circuits. Commercially, graphite is being applied as the anode in LIBs, and its theoretical capacity is 372 mA h g^{-1} . Transitional metal oxides (*e.g.* Fe_2O_3 , Fe_3O_4 , Co_3O_4) are regarded as promising alternatives to graphite anodes because they give much higher capacities for storing lithium (*e.g.* 1007 mA h /g for Fe_2O_3).

The reaction mechanism of the metal oxides, M_xO_y , as anode is shown in Equation (2.3). The M_xO_y are reduced to the metallic state and lithium oxides are formed during the charging process. During discharge, the metal can be oxidized into metal oxides again, and the lithium ion is subsequently released. There are multiple electrons involved in the charging / discharging reactions. As such, metal oxides exhibit high reversible capacities for lithium storage.

However, there are also some drawbacks of transitional oxides as anodes, including low initial Coulombic efficiency, large volume change during charge and discharge, formation of unstable solid electrolyte interfaces (SEI) layers, and poor cycling performance. Consequently, a lot of work has been done to overcome these problems. Iron oxides (Fe_2O_3 and Fe_3O_4) and cobalt oxides (Co_3O_4) are the mostly widely studied ones in this category. Especially, iron oxides are attractive in LIBs for their low cost and non-toxicity.

2.7.2 Current synthesis of iron oxides and cobalt oxides nanostructures for lithium ion batteries

To date, various morphologies of iron oxides ranging from 0D nanoparticles to 3D hierarchically porous architectures have been developed for lithium ion batteries using different approaches. For 1D iron oxide structures, Wu *et al.* synthesized Fe_2O_3 radial nanorods on the vapor-grown carbon nanofiber through electrodeposition.⁴⁵ By electrospinning and subsequent carbonization in Ar atmosphere, Wang *et al.* synthesized Fe_3O_4/C composite nanofibers that exhibit a specific capacity of 1007 mA h g^{-1} at a current density of 200 mA g^{-1} , as shown in Figure 2.11.⁴⁶ Muraliganth *et al.* reported a microwave-hydrothermal approach for synthesizing 1D single-crystalline Fe_3O_4 nanowires that exhibit excellent cyclability and rate performance for lithium ion storage.⁴⁷ In addition to nanorods, nanowires, iron oxides nanotubes are also widely synthesized for lithium ion batteries using approaches such as electrospinning, hard templating, and so on.⁴⁸⁻⁵⁰ For 2D structures of iron oxides, Wu *et al.* reported synthesis of iron oxides nanosheets via direct chemical precipitation of $Fe(NH_4)_2(SO_4)_2$ in the solution, followed by annealing.⁵¹ Reddy *et al.* reported a Cu-substrate-assisted synthesis of iron oxide flakes by using radio frequency magnetron sputtering.⁵²

Figure 2.11 SEM image (a), TEM image (b), and cycling performance of $\text{Fe}_3\text{O}_4/\text{C}$ nanofibers.⁴⁶
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For 3D structures of iron oxides, single-shelled and multi-shelled hollow microspheres have been synthesized *via* hard templating approaches, template free solvothermal methods, template free sonochemical methods, and so on.⁵³⁻⁵⁷ Beside of hollow spheres, hierarchically micro/nano porous structured iron oxides have also been widely fabricated and applied in lithium ion batteries. For example, Hao *et al.* directly precipitate FeSO_4 in H_3COONa solution and further hydrothermally treated the precipitation.⁵⁸ Subsequently, urchin-like micro/nano structured $\text{Fe}_3\text{O}_4/\text{C}$ composite was obtained, exhibiting a reversible capacity of 830 mA h g^{-1} at 0.1 C, 788 mA h g^{-1} at 1 C, and 594 mA h g^{-1} at 2 C (1 C equals to the electrode's capacity divided by 1 hour). Li *et al.* synthesized iron oxides / carbon composite microspheres by a simple solution polymerization followed by pyrolysis in N_2 .⁵⁹ From all the work above, it can be seen that carbon matrix with iron oxides nanoparticles embedded within it can increase the Coulombic efficiency, buffer the large volume change during charge and discharge, and enhance the cycling performance of iron oxides in lithium ion batteries.

Similarly, cobalt oxides nanofibers, nanorods, nanotubes, snow-shaped flakes, microspheres, hollow spheres, flower-like microspheres, star-like micro/nano structures *etc.* have been synthesized for lithium ion batteries *via* electrospinning, common hydrothermal treatment, microwave-assisted hydrothermal treatment, ammonia-assisted hydrothermal treatment, ammonia-assisted reflux condensation, hard templating methods, template-free impregnation-reduction approaches, ammonia-evaporation-induced method, template-free chemical co-precipitation method, and so on.⁶⁰⁻⁶⁶

2.7.3 Current application of iron oxides and cobalt oxides for SIBs

Since iron oxides and cobalt oxides have been extensively studied in lithium ion batteries, they are likely promising for use in SIBs. However, the exploration of transitional metal oxides as anodes in SIBs has only been initiated very recently, and hence, there has been little advancement in this field. Jian *et al.* reported the application of Fe_2O_3 nanocrystals anchored on graphene nanosheets (GNS) in sodium ion battery.⁶⁷ The electrochemical performance of the as-synthesized iron oxides composites as anodes in sodium ion battery is shown in Figure 2.12. Jiang *et al.* fabricated transitional metal oxides films for sodium ion batteries using electrostatic spray deposition technique.⁶⁸ The morphologies and corresponding electrochemical performance of the as-synthesized Fe_2O_3 and Co_3O_4 films are shown in Figure 2.13. Kumar *et al.* and Hariharan *et al.* used hydrothermal methods to synthesize Fe_3O_4 nanoparticles embedded in carbon matrix and applied the as-synthesized materials in sodium ion batteries.^{69,70} In addition, Co_3O_4 / MCNTs composite fabricated via solid-state reaction,⁷¹ bowl-like hollow Co_3O_4 microspheres obtained by thermal treatment of Co-containing gel in air,⁷² Co_3O_4 sheets / 3D graphene networks obtained from hydrothermal treatment⁷³ have been reported for sodium ion batteries. In all, investigations on applying transitional metal oxides as anodes in sodium ion batteries are still very limited. More importantly, the electrochemical performance reported thus far are not satisfactory.

Figure 2.12 (a) Cycling performance of the $\text{Fe}_2\text{O}_3/\text{GNS}$ and $\text{Fe}_2\text{O}_3@\text{GNS}$ samples at a current density of 100 mA g⁻¹, and coulombic efficiency of the $\text{Fe}_2\text{O}_3@\text{GNS}$ sample; (b) Cycling performance for $\text{Fe}_2\text{O}_3@\text{GNS}$ cycled at current densities of 200, 500, and 1000 mA g⁻¹.⁶⁷ Reprinted with permission from ref. 67. Copyright 2015, Royal Society of Chemistry.

Figure 2.13 SEM images of the as-prepared Fe₂O₃ (a), Co₃O₄ (b) film and corresponding cycle performance at a current density of 100 mA g⁻¹.⁶⁸ Reprinted with permission from ref. 68. Copyright 2014, Elsevier.

2.8 Lithium iron phosphates

2.8.1 Lithium iron phosphates as cathode in lithium ion batteries

Lithium iron phosphates (LiFePO₄) have gained considerable attention as an ideal material for battery cathodes due to their stable and high voltage profile (~3.4 V vs. Li/Li⁺), large theoretical capacities (~170 mA h g⁻¹), low material costs and environmental compatibility. LiFePO₄ belongs to the olivine family with an orthorhombic lattice structure in the space group *Pnma*, as can be seen from the crystal structure of LiFePO₄ in Figure 2.14.⁷⁴ The oxygen atoms are strongly bonded to both Fe and P atoms, which makes frameworks of LiFePO₄ much more stable than that of LiCoO₂, and thus better cycling performance compared to the commercially applied LiCoO₂. Upon delithiation, the Li ions are extracted to yield FePO₄ without changing the framework of the olivine structure. After undergoing the reaction of $\text{LiFePO}_4 \leftrightarrow \text{Li}^+ + \text{e}^- + \text{FePO}_4$, the volume change of the crystal was reported to be only 6.6%.

Figure 2.14 The crystal structure of LiFePO_4 . The Fe atoms occupy octahedral sites (grey) and the P atoms occupy tetrahedral sites (brown). The Li ions (small circles) occupy the one-dimensional tunnels.⁷⁴ Reprinted with permission from ref. 74. Copyright 2009, Elsevier.

2.8.2 Current synthesizing methods of LiFePO_4

In a typical solid-state synthesis, a mixture of iron salt, a lithium compound and P source is annealed at a temperature between 400 and 800 °C.⁷⁵ During calcination, a slightly reductive atmosphere is necessary to prevent Fe (II) oxidation. The dimensions of LiFePO_4 particles produced by solid-state reactions are typically in the micron range, limiting their use in energy storage applications. To reduce the particle size, carbon is added to the LiFePO_4 precursor and subjected to thermal treatment. An example showing the preparation of getting LiFePO_4/C composite is shown in Figure 2.15.⁷⁶ In cases where polymers were used as the carbon sources, lower annealing temperatures can be applied. This is due to the reductive atmosphere derived from pyrolysis of the polymer.⁷⁷ However, the proportion of carbon added to the reaction must be controlled given that excess carbon additive can decrease the purity of LiFePO_4/C composites and lead to the production of Fe_2P byproducts.⁷⁸

Figure 2.15 Preparation process for the LiFePO₄/C particle via an in situ polymerization that restricts the size of the particles.⁷⁶ Reprinted with permission from ref. 76. Copyright 2008, WILEY-VCH Verlag GmbH & Co. KGaA.

Solvothermal treatment is another common method to synthesize LiFePO₄. FeSO₄, H₃PO₄, and LiOH mixed in a molar ratio of 1:1:3 could be used as the starting materials and exposed to a hydrothermal process at 120 °C for 5 h.⁷⁹ However, this method creates lithium/iron disorders with 7% iron substitution in the lithium sites.⁸⁰ Annealing of the hydrothermally treated material at 700 °C with carbonaceous materials has been proved to alleviate the disorder.⁸¹ Reports have also shown that hydrothermal synthesis performed above 175 °C can help to reduce iron disorder.^{82,83} In these modified methods, LiFePO₄ in the micro-scaled size with thicknesses of hundreds nanometers in the diffusion direction were obtained.⁸⁴ However, hydrothermal synthesis with the aid of surfactant compounds such as cetyltrimethylammonium bromide (CTAB) produces lithium iron phosphate powder with high surface area and better electrochemical performances. The pyrolysis of CTAB prevents unwanted Fe²⁺ oxidation as well as formed an in situ carbon layer over the particle surface.⁸² Solvothermal treatment in other solvent was also explored. For example, in ethylene glycol, nanoplates of LiFePO₄ were yielded.⁸⁵

The sol-gel method is particularly attractive to the lower processing temperatures compared to traditional ceramic powder methods. Various solvents including water with ascorbic acid, or citric acid, ethylene glycol, ethanol have been used.⁷⁴ The sol-gel method allows homogeneous

mixing of precursors at the molecular level. The as-obtained sols were dried and annealed at 500 – 700 °C in inert atmosphere. In cases where carbon-based solvents were used, a layer of carbon coating could also be formed in situ, which can further increase the overall conductivity of the LiFePO_4 .

Electrospinning method is an efficient way to prepare 1D structures of functional materials. Various polymers and solvent have been applied in the synthesis of LiFePO_4 nanowires and nanotubes through electrospinning process.^{86,87} During the following annealing process, the polymers were transformed into in-situ carbon coating and carbon matrix that increased the conductivity of LiFePO_4 nanoparticles as well as preventing them from growing bigger.

Lithium iron phosphate could also be obtained by heating a solution containing Li^+ , Fe^{2+} , and P^{5+} ions above 105°C at pH values between 6 and 10.⁸⁸ Additives are needed to elevate the water solution boiling point. Precipitation of LiFePO_4 will occur when the temperature of the solution reaches the boiling point of the solvent. The precipitate is further annealed at 500 °C under slightly reducing atmosphere. Separately, LiFePO_4 can also be obtained by lithiation of $\text{FePO}_4 \cdot \text{H}_2\text{O}$ precipitated from FeSO_4 and $\text{NH}_4\text{H}_2\text{PO}_4$ with hydro-peroxide, followed by annealing at 500 °C.^{89,90}

2.9 Monoclinic trilithium divanadium(III) tris(orthophosphate), $\text{Li}_3\text{V}_2(\text{PO}_4)_3$

2.9.1 General introduction of monoclinic $\text{Li}_3\text{V}_2(\text{PO}_4)_3$

Monoclinic $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ has a theoretical capacity of 197 mA h g⁻¹, and an average operating voltage of 3.8 V. Together with its safety, rapid ionic diffusion and abundant resources, make $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ make desirable anodes for LIBs. The crystal structure of monoclinic $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ is shown in Figure 2.16.⁹¹ The stable frame is built from the VO_6 octahedral and PO_4 tetrahedral sharing oxygen vertexes. Lithium ions have three distinct positions. Li (1) resides in the tetrahedral site. Li (2) and Li (3) are located in two pseudotetrahedral sites. The three Li ions in monoclinic $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ are all mobile, providing it better electrochemical properties than the rhombohedral $\text{Li}_3\text{V}_2(\text{PO}_4)_3$. When in charge, monoclinic $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ undergoes the reactions as follows shown in Equations 2.4 – 2.7. Therefore, there are four plateaus located at around 3.6, 3.7, 4.1, and 4.6 V corresponding to the four steps reaction. Li (3) with the highest energy is extracted

firstly upon oxidation. Secondly, Li (1) is extracted due to the repulsion energy of the Li (1)⁺ -- V⁴⁺ pair. Finally, Li (2) is extracted at the voltage of 4.6 V. The volume contraction during charge is 7.8%.

Figure 2.16 The crystal structure of monoclinic $Li_3V_2(PO_4)_3$.⁹¹ Reprinted with permission from ref.91. Copyright 2014, Elsevier.

2.9.2 Current synthesizing methods for monoclinic $Li_3V_2(PO_4)_3$

Solid-state method is the most common method to prepare crystalline inorganic materials. In a typical solid-state synthesis of $Li_3V_2(PO_4)_3$, a mixture of lithium compound (*e.g.*, Li_2CO_3 , $LiOH$, $LiAc$), vanadium source (*e.g.*, V_2O_5 , NH_4VO_3), and P source is annealed at a temperature ranging from 600 to 1000 °C under inert atmosphere or slightly reducing atmosphere. Also, usually carbon sources will be added into the precursors mixture, and annealed together to generate $Li_3V_2(PO_4)_3/C$ composites. Different starting precursors required different annealing temperatures

and time in order to obtain well-crystalized $\text{Li}_3\text{V}_2(\text{PO}_4)_3$. For example, LiF was reported to require lower calcination temperature than Li_2CO_3 did, thus yielding smaller $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ particle size and exhibiting better electrochemical performance.⁹² At some conditions, Li_3PO_4 impurity will be generated.⁹³ Solid-state synthesizing method suffers disadvantages such as big particle size, uncontrollable particle growth, inhomogeneity, and so on. The SEM image of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ obtained from solid-state method is shown in Figure 2.17a.

Sol-gel synthesis route allows precursors to mix homogeneously, requires low annealing temperature and short annealing time, thus is very popular in fabricating $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ nano-scale particles with uniform particle size distribution. Chelating reagents and $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ precursors are mixed, followed by evaporation at high temperature to obtain the gel bulk, which is further annealed to generate $\text{Li}_3\text{V}_2(\text{PO}_4)_3$. Chelating agents such as citric acid, oxalic acid, glycine, polyvinylpyrrolidone have been used to facilitate the formation of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ precursors sol-gel bulk.⁹⁴⁻⁹⁸ The particle size of the as-synthesized $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ is between 200 – 500 nm. The SEM image of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ obtained from sol-gel method is shown in Figure 2.17b.⁹⁸

Hydrothermal method is another approach for $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ fabrication. Chang *et al.* used LiOH, NH_4VO_3 , and $\text{NH}_4\text{H}_2\text{PO}_4$ in a molar ratio of 3:2:3 mixed with glucose as starting material to go under hydrothermal reaction at 160 °C for 2 h, followed by annealing at 700 °C for 6 h in Ar.⁹⁹ The produced $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ flakes showed a discharge capacity of 142 mA h g⁻¹ at 1 C. Liu reported the formation of $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ nanorods from hydrothermal treatment at 180 °C for 24 h without subsequent annealing.¹⁰⁰ $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ synthesized by hydrothermal method shows smaller particle size than those by sol-gel method. The SEM image of $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ obtained from hydrothermal method is shown in Figure 2.17c.¹⁰¹

Spray pyrolysis gives yield to products with high purity, and small particle size with spherical morphology. Ko *et al.* reported the fabrication of $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ by spray pyrolysis to get spherical precursors powders, followed by annealing at 700 °C for 3 h.¹⁰² The SEM of the product of is shown in Figure 2.17d.

Freeze-drying approach is used commonly to prepare fine particles and porous structures. Wang *et al.* poured a colloid sol containing NH_4VO_3 , LiOH, H_3PO_4 , and citric acid into liquid nitrogen, and freeze dry the samples at -40 °C. $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ was obtained after annealing at high

temperature in Ar.¹⁰³ The SEM of as synthesized product is shown in Figure 2.17e. A porous structure was also achieved, which is probably due to the quick removal of solvent during the freeze drying process.

Electrospinning is popular method to produce continuous nanofibers of functional materials. In the case of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$, Chen *et al.* first reported the synthesis by using raw materials of NH_4VO_3 , $\text{NH}_4\text{H}_2\text{PO}_4$, LiAc, PVP, and citric acid.¹⁰⁴ The electrospun product was annealed at 800 °C for 4 h in Ar. The SEM image of as-obtained $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ nanofibers is shown in Figure 2.17f. The specific surface area is as high as $160 \text{ m}^2 \text{ g}^{-1}$, and the discharge capacity reaches 132 mA h g^{-1} at 20 C.

Figure 2.17 The morphology of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ cathode materials prepared by different methods: a) solid-state reaction,⁹³ Reprinted with permission from ref.93. Copyright 2006, Elsevier. b) sol-gel chemistry,⁹⁸ Reprinted with permission from ref.98. Copyright 2010, Elsevier. c) hydrothermal method,¹⁰¹ Reprinted with permission from ref.101. Copyright 2013, Royal Society of Chemistry. d) spray pyrolysis,¹⁰² Reprinted with permission from ref.102. Copyright 2011, Elsevier. e) freeze-drying method,¹⁰³ Reprinted with permission from ref.103. Copyright 2012, Royal Society of Chemistry. f) electrospinning.¹⁰⁴ Reprinted with permission from ref.104. Copyright 2013, Elsevier.

Chapter 3: Magnetotactic bacteria assisted synthesis of Fe₃O₄ nanoparticle chains with N-doped carbon coating for high-rate lithium storage.

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3.1 Introduction

Magnetite Fe₃O₄ is attractive as anode for LIBs because of its high theoretical capacity, cost-effectiveness, and environmental benignity.^{105,106} However, it suffers from drastic particle pulverization which leads to rapid capacity fading, and thus hinders its commercialization.¹⁰⁷ One-dimensional (1D) inorganic nanoparticle chains (NPs) have gained popularity in applications ranging from electronics,¹⁰⁸ sensors,¹⁰⁹ catalysis,¹¹⁰ to energy conversion/storage devices.¹¹¹ Transition metal oxide anodes exhibit a large volumetric expansion upon the lithium insertion, which may lead to the collapse of self-assembled chains as a result of the weak ‘NP-to-NP’ interactions. Reports suggest that LIB electrodes containing 1D nanomaterials have shorter Li⁺ transport distance, experience facile strain relaxation upon electrochemical cycling, and have larger contact areas of active materials with the electrolyte compared to electrodes with dispersed NPs which tend to self-aggregate.¹¹²

Magnetotactic bacteria are well-known for their ability to generate uniform nano-sized 1D Fe₃O₄ chains via a spontaneous bio-mineralization process. Preparation of Fe₃O₄ nanomaterials via magnetotactic bacteria is also considered a sustainable and environmentally friendly strategy.^{113,114} Importantly, the Fe₃O₄ nanoparticles are expected to have larger Li storage capacities at high charging / discharging rates in LIBs due to the presence of heteroatoms, such as N and B, doped into the carbon.¹¹⁵⁻¹¹⁸

It is likely that 1D Fe₃O₄ chains can have improved electrochemical performance and stability as anodes in LIBs. Yet, the chain structures are often easily destroyed during annealing. In this work, we developed an alternative synthesis process that allows the preservation of the Fe₃O₄ chain structures. We further evaluated the electrochemical properties of these 1D Fe₃O₄ chains as anodes in LIBs.

3.2 Materials and Methods

3.2.1 Materials

Magnetospirillum gryphiswaldense strain MSR-1 was purchased from DSMZ (Germany). Yeast extract was purchased from BD Biosciences (San Jose, CA). All the other chemicals (with purity higher than 98%) were purchased from Sigma (St. Louis, MO).

3.2.2 Synthesis of 1D Fe₃O₄/C chains

Growth of *Magnetospirillum gryphiswaldense* was carried out under microaerobic condition in sealed 100 mL vials containing 70 mL *Magnetospirillum gryphiswaldense* medium, which was optimized in our study based on Flask Standard Medium. It contained (per liter solution) 2.38 g HEPES, 3 g sodium pyruvate, 3 g soybean peptone, 0.34 g NaNO₃, 0.15 g MgSO₄·7H₂O, 0.1 g yeast extract, 0.1 g KH₂PO₄, 100 µM ferric citrate, and 1 mL EDTA-chelated trace element solution, which was composed of 3 mg L⁻¹ FeCl₃·6H₂O, 0.3 mg L⁻¹ H₃BO₃, 0.06 mg L⁻¹ CuSO₄·5H₂O, 0.36 mg L⁻¹ KI, 0.24 mg L⁻¹ MnCl₂·4H₂O, 0.12 mg L⁻¹ Na₂MoO₄·2H₂O, 0.24 mg L⁻¹ ZnSO₄·7H₂O, 0.3 mg L⁻¹ CoCl₂·6H₂O, 25.5 mg L⁻¹ EDTANa₂·2H₂O. Vials were sealed with butyl rubber septum, and purged with a gas mixture containing 1% oxygen and 99% nitrogen for 2 min before autoclaving to create a microaerobic condition for the sake of magnetite formation.²⁰ Cultures were inoculated by injection through the rubber cap, and cultivated at 28 °C for 4 days.

The cultivated bacteria was collected and washed with DI water, and stored for further usage. Scheme of the synthesis is shown in Figure 3.1. The harvested bacteria slurry was dispersed in glucose solution. The resulted mixture was allowed to settle down overnight followed by centrifugation to remove the supernatant. The cell pellet was dried, and annealed at 400 °C in argon for 1 h.

Figure 3.1 Schematic illustration of the nucleation and growth of the magnetotactic bacteria and the glucose aided synthesis of $\text{Fe}_3\text{O}_4/\text{C}$ chain structure.

3.2.3 Characterization

Field-emission scanning electron microscopy (FESEM, JEOL, Model JSM-6340F) and transmission electron microscopy (TEM, JEOL, Model JEM-2010) were used to characterize the morphologies and nanostructures of the samples. The TEM samples were prepared by loading a suspension of materials onto copper grids and dried at 37 °C. X-ray diffractometer (XRD) was used to identify the crystal phases of as-synthesized samples. IR spectra were obtained with an infrared spectrometer (Perkin-Elmer). Thermogravimetric analysis (TGA, Q500) was carried out between the temperature range of 25 °C to 500 °C, at a heating rate of 10 K min⁻¹ in air. Theta Probe X-ray photoelectron spectroscopy (XPS, ESCALab 250i-XL & Thetaprobe A1333) was used to verify the valence state of nitrogen.

3.2.4 Electrochemical measurements

Pure lithium foil was used as the counter electrode.¹¹⁹ The working electrode consisted of the active material (e.g., $\text{Fe}_3\text{O}_4/\text{C}$ nanocomposites), a conductive agent (carbon black, Super P-Li) and a polymer binder [poly(vinylidene difluoride), PVDF, Aldrich] in a weight ratio of 7:2:1 in N-methylpyrrolidone (NMP) solvent. The loading mass is about 1 mg cm⁻². The electrolyte consisted

of 1.0 M LiPF₆ in a 50:50 wt:wt solution of ethylene carbonate and diethyl carbonate. The charge/discharge tests were performed with a NEWARE battery tester at a voltage window of 0.01-1.5 V.

3.3 Results and Discussion

As shown in Figure 3.1, Fe₃O₄ NPs were nucleated as magnetosomes via a spontaneous bio-mineralization process.²⁰ Fe (III) passes through the outer membrane with the help of functional proteins, and loses one electron to form Fe (II). Further, Fe (II) enters into the magnetosome vesicles, during which two thirds of the Fe (II) is oxidised again and self-assembled Fe₃O₄ nuclei are formed. This repeated reduction-oxidation behaviour is regulated by the Mam proteins in the magnetosome membranes, which are also found to be critical in the pH control.

The FESEM and TEM images of as cultivated bacteria are shown in Figure 3.2. Chain structures about 1-2 µm long are observed. The NPs within in the chains are around 50 nm. High-magnification TEM image (Figure 3.2c) shows that there is a thin layer of carbon encapsulating the iron oxide NPs, probably from the membranous components of the bacteria. The X-ray diffraction (XRD) spectra of a dried bacteria sample shown in Figure 3.2d indicated that well-crystallized cubic magnetite Fe₃O₄ (JCPDS no. 89-2355) was present. The Al peaks are originated from the sample holder. No impurity peaks are detected.

Figure 3.2 a) SEM images of as-cultivated magnetotactic bacteria; b) and c) corresponding TEM and high magnification TEM image; d) XRD pattern of the bacteria before annealing.

Unfortunately, the as-obtained chain structures derived from bacteria were very sensitive to heat treatment. At 100 °C, the chain structures disappeared and only randomly oriented NPs were obtained (Figure 3.3). This is probably due to the disorganization of membrane molecules caused by the melting of alkyl chains at 100 °C.

Figure 3.3 The TEM image of the 100 °C treated bacteria without the addition of glucose.

The bacteria samples were also subjected to FTIR analysis (Figure 3.4). As can be seen, characteristic absorption peaks corresponding to the $\text{C}=\text{O}$ stretching vibration at 1740 cm^{-1} and carbonate symmetrical stretching at 1402 cm^{-1} are observed, indicating the presence of carboxyl groups. The peaks at 1656 cm^{-1} , 1550 cm^{-1} and 1455 cm^{-1} are attributed to amide bonds. The peaks at 1171 cm^{-1} and 1074 cm^{-1} are associated with P-O and C-S bonds.

Figure 3.4 The FTIR spectrum of as cultivated bacteria.

Given the overall functional groups on the bacteria cell membrane, non-evaporative glucose was added to the bacteria before annealing to see if the chain structures would be preserved. It is likely that the COOH groups in glucose would interact with the bacteria cell membrane via hydrogen bonding.

Indeed, addition of glucose did preserved the chain structures of Fe_3O_4 nanoparticles. FESEM and TEM images of the glucose-wrapped bacteria after annealing at 400 °C for 1 h in Ar were shown in Figure 3.5. From these images, the chain structures of Fe_3O_4 nanoparticles were well preserved during the thermal treatment. We also noted a 10 nm thick layer of amorphous carbon coating in all of the chains observed. Raman spectroscopy further confirmed the amorphous nature of the carbon coating, since the ratio between the “D” (diamond) and “G” (graphite) bands is approximately 1 (Figure 3.6). Additionally, high-resolution TEM image and corresponding Fast Fourier Transform (FFT) pattern (Figure 3.5d) indicate that the Fe_3O_4 NPs are single crystalline. The lattice fringes of 0.25 and 0.16 nm (Figure 3.5e) correspond to the crystal (311) and (511) planes of cubic magnetite Fe_3O_4 (JCPDS no. 89-2355), respectively.

Figure 3.5 (a) FESEM images of annealed magnetotactic bacteria; (b) and (c) corresponding TEM and high resolution TEM images; (d) Fast Fourier Transform (FFT) pattern and magnified image plotted from the rectangular area denoted in (c).

Figure 3.6 The Raman spectra for the annealed $\text{Fe}_3\text{O}_4/\text{C}$ chains. (D refers to diamond band, and G refers to graphite band)

TGA result shown in Figure 3.7 shows that the carbon content was about 18 %, which was mainly derived from the pyrolysis of glucose and cell membrane. Further, XPS was carried out to further investigate the composition of the product. From Figure 3.8, we can see there is elemental N existing in the sample. The as-obtained bacterial sample showed peaks at 399.3 and 401.1 eV, indicating the presence of the pyrocinic-N.¹²⁰ After annealing, the two peaks shifted to 400.4 and 402.9 eV respectively, which were attributed to the substitution of N in the carbon structure, indicating N element has been successfully doped in the coating layer of the $\text{Fe}_3\text{O}_4/\text{C}$ chain structure.¹²¹ The N content was calculated to be about 5 %. Since XPS is a surface chemical analysis technique that is used to detect elemental composition of the top 1-10 nm surface, peak of elemental Fe can't be seen in the spectra as Fe_3O_4 nanocrystals were wrapped by a layer of carbon about 10 nm wide (Figure 3.5).

Figure 3.7 TGA analysis result for the Fe₃O₄/C chains.

Figure 3.8 (a) The XPS result for the annealed Fe₃O₄/C chains; (b) N1s spectra for the as-cultivated bacteria; (c) N1s spectra for the Fe₃O₄/C chains.

Further, the as-synthesized Fe₃O₄/C chains were tested as anodes in LIBs. Figure 3.9a shows the cyclic voltammograms of the Fe₃O₄/C chain electrodes at a scan rate of 0.5 mV s⁻¹ between 0.005 - 3.0 V (vs Li⁺/Li) for the first three cycles. In the first cycle, two peaks in the cathodic processing are observed at about 1.5 and 0.5 V, which can be attributed to the insertion of Li⁺ into Fe₃O₄ and reduction of Fe³⁺ and Fe²⁺ to Fe⁰ and some irreversible reaction with the electrolyte, as indicated in equation (1) and (2). Meanwhile, a main peak is recorded at about 1.75 V in the anodic process, corresponding to the oxidation of Fe⁰ to Fe³⁺/Fe²⁺ during the anodic processing, as indicated in equation (3).^{121,122}

The charge-discharge voltage profiles for the first three cycles were examined (Figure 3.9b) between 0.005 - 3 V at a current density of 185.2 mA g⁻¹ (0.2 C, and 1 C equals to 926 mA g⁻¹). The first discharge capacity was 1400 mA h g⁻¹ and the corresponding charge capacity was 919 mAh g⁻¹. The irreversible capacity loss (481 mA h g⁻¹) can be attributed to the formation of a solid electrolyte interphase film, and the decomposition of electrolyte.¹²³ Besides, the inherent poor electrical/ionic conductivity of the Fe₃O₄/Fe/Li₂O matrix formed during the charge/discharge process may also cause irreversible lithium loss.¹²⁴ During the 2nd cycle, the nanocomposites delivered a discharge capacity of 921 mA h g⁻¹ and a charge capacity of 905 mA h g⁻¹, corresponding to a high Coulombic efficiency of 98.2 %.

Good cycling performance is also one of the prerequisite for practical application of LIBs. Figure 3.9c shows the charge/discharge cycling performance of the as-synthesized Fe₃O₄/C chains at 0.2 C. Notably, the specific capacities of this electrode decrease slightly during the first 10 cycles and then increase afterwards, and a high discharge capacity of 1146 mA h g⁻¹ was delivered during the 100th cycle. The capacity fading during the initial cycles can be attributed to the volume change of the metal oxide crystal structure during the Li⁺ insertion and extraction processes. As the charge/discharge proceeded, organic polymeric/gel-like layer continuously formed due to the electrolyte decomposition at low potential, leading to the additional reversible Li storage capacity.¹²⁵ In contrast, Fe₃O₄ NPs around 25 nm in size (see corresponding TEM image in Figure 3.10) prepared by a co-precipitation method suffer from an abrupt capacity fading (1400 mA h g⁻¹ at the first cycle to 510 mA h g⁻¹ at the 100th cycle).

The cycling performance of Fe₃O₄ electrodes at different charge/discharge rates is also evaluated (Figure 3.9d). With increased C rates, the discharge capacities for both samples decrease gradually, indicating the diffusion-controlled kinetic processes. More specifically, the bacteria derived Fe₃O₄/C NP chains depict discharge capacities of 947, 857, 757, 615, 518, 388, 282 mA h g⁻¹ at 0.2, 0.5, 1, 3, 5, 8 and 10 C during the 9th cycle, respectively. For the Fe₃O₄ reference electrode, it depicts discharge capacities of only 615, 454, 398, 332, 223, 151, and 101 mA h g⁻¹ at 0.2, 0.5, 1, 3, 5, 8 and 10 C during the 9th cycle, respectively.

Figure 3.9 Electrochemical performances of $\text{Fe}_3\text{O}_4/\text{C}$ chains: a) cyclic voltammograms at a scan rate of 0.5 mV s^{-1} ; b) charge/discharge curves at 185.2 mA g^{-1} ; c) cyclability of both $\text{Fe}_3\text{O}_4/\text{C}$ chains and co-precipitated Fe_3O_4 nanoparticles at 185.2 mA g^{-1} ; and d) capacity over cycling of the two samples at different rates.

Figure 3.10 TEM image of Fe_3O_4 NPs prepared by co-precipitation method.

The stable cycling performance and excellent rate capability of $\text{Fe}_3\text{O}_4/\text{C}$ chains can be ascribed to the N-doped carbon coating outside the Fe_3O_4 NPs. First, the carbon coating layer is

highly beneficial to buffer the large volume expansion that occurs during the lithiation process, which in turn circumvent the pulverization issue and enhance the cycling stability. Second, the N-doped carbon could enhance the electrochemical reactivity and electrical conductivity of Fe_3O_4 NPs, contributing to the exceptional rate performance. Last, it is probably that the interconnected carbon layer in the 1D chain structure that provided a continuous pathway for electron transportation and enhances the transportation of electrons among Fe_3O_4 NPs.

3.4 Conclusion

In summary, synthesis of $\text{Fe}_3\text{O}_4/\text{C}$ 1D chains derived from the magnetotactic bacteria has been demonstrated. The uniform Fe_3O_4 NPs are enveloped in a homogeneous N-doped carbon coating layer. Due to the unique chain structure and the uniform N-doped carbon layer, the as-obtained product showed superior cycling stability and excellent rate capability when tested as anodes for LIBs. This work opens up the possibility of exploiting biomolecules for the energy storage application.

Chapter 4: Recycling Bacteria for the Synthesis of LiMPO₄ (M = Fe, Mn) Nanostructures for High-Power Lithium Ion Batteries.

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4.1 Introduction

In the previous chapter, we showed that magnetotactic bacteria can serve as novel templates for nanomaterials with 1D chain structures. We next wondered if other nanomaterials with complex chemistries could be also fabricated using bacteria that could also have promising applications in LIBs. In particular, lithium metal phosphates (LiMPO₄) are heavily investigated as cathodes in LIBs due to their high stabilities and exceptional rate-cycling properties. Compared to other cathode materials such as lithium metal oxides, LiMPO₄ do not suffer from unstable performance or low circuit voltages, like in the case of vanadium oxides.^{126,127} The power densities of LiMPO₄ can also be further increased when fabricated as nanoparticles due to their large surface areas.

Traditionally, chemical routes are used to synthesize LiMPO₄. But recently, bio-molecules have received much attention in facilitating the fabrication of inorganic nanomaterials nano-architectures.^{5,8,24,128,129} For example, Kim and coworkers reported bacteria-directed synthesis of porous Co₃O₄ hollow nanorods that showed comparable electrochemical performance for LIBs to the chemically synthesized Co₃O₄ nanostructures.⁵ Belcher and co-workers engineered viruses to nucleate amorphous FePO₄ at room temperature and the as-obtained FePO₄/single-walled carbon nanotubes composites showed excellent electrochemical performance.⁸ To our knowledge, successful preparation of LiMPO₄ nanomaterials using biological routes has not been reported.

In this work, we attempted to develop a bacteria-assisted route for the preparation of LiMPO₄. Various bacteria including *E. coli*, *Acinetobacter* and *Actinobacter et al.* are known to store phosphorus naturally inside their cell bodies as polyphosphate (polyP) granules.^{130,131} Since there is little variation in the compositions and morphologies of polyP granules in different bacterial cells, *E. coli* was chosen as a model bacterial system given their simple culture conditions. Particularly, an industrially relevant strain of *E. coli* that had been genetically modified to remove

phosphorus efficiently from wastewater was selected.¹³⁰ Here, bacteria accumulated with polyphosphate were exposed to Li and Fe precursors and subjected to annealing. The as-annealed products were characterized and evaluated as cathodes in LIBs.

4.2 Materials and Methods

4.2.1 Materials

The plasmid pBC29 containing the poly-phosphate kinase (ppk) gene and promoter was a generous gift from H. Ohtake (Osaka University, Japan).¹³² T-minimum media (T media) containing phosphate was purchased from Invitrogen (Life Technologies, Carlsbad, CA). All the other chemicals and reagents were purchased from Sigma-Aldrich (Seelze, Germany).

4.2.2 Synthesis of LiMPO_4

E. coli BL21 cells (Stratagene) were transformed with plasmid pBC29 via heat shock to obtain *E. coli* + pBC29. Phosphate concentration was quantified using the ascorbic acid method.¹³³ Transformed *E. coli* cells were grown in T-media as previously reported¹³⁴ and harvested by centrifugation after 5.5 h. Cells were washed with DI water and fixed with 4% paraformaldehyde water solution for 10 min, which were washed again to remove the residual salts. The cells were further treated as outlined in Figure 4.1. Briefly, cells with polyP granules were rinsed in MCl_n solution (equimolar amounts of MCl_n solution was added to the calculated molarity of phosphate taken up by cells from the media after 5.5 h), and stirred at 50 °C for 2 days. Equimolars of lithium acetate was added, mixed homogenously, dried, and annealed at 600 °C for 5 h. Characterization of the as-annealed samples were performed as described in Chapter 3 under section 3.2.3.

Figure 4.1 Schematic of biological route for conversion of P-rich bacteria into carbon-coated LiMPO_4 nanocrystals.

4.2.3 Electrochemical measurement

The coin-type cells were assembled as described in chapter 3 under section 3.2.4. The synthesized LiFePO_4/C composites, multiwalled carbon nanotubes and PVDF were mixed in the ratio of 7:2:1 in NMP solvent. The mass loading of the composite was around 1.0 mg cm^{-2} . Lithium foils were used as anodes. The same electrolyte was used as described in chapter 3. The cells were tested using the same tester in the voltage ranges of 2.5 – 4.3 V. The specific capacity values in this paper were calculated based on pure LiFePO_4 .

4.3 Results and Discussion

The presence of pBC29 plasmid in the *E. coli* strain results in constitutive overexpression of the polyphosphate kinase (PPK). The PPK enzyme catalyzes the formation of polyP from phosphate¹³⁰, in turn resulting in cellular uptake of phosphate from the surrounding media. The genetically modified *E. coli* + pBC29 strain has been previously shown to deplete phosphate when cultured in phosphate-rich media. Here, we confirmed that *E. coli* + pBC29 strain indeed acquired the ability to accumulate phosphate. Figure 4.2 shows phosphate concentration present in the media depleted by 40% in the *E. coli* + pBC29 system while it decreased by only 20% for the wild-type *E. coli* cells.

Figure 4.2 Time course of phosphate concentration during growth of *E. coli* + pBC29 and wild-type *E. coli* in T media. Data are means $\pm$ SEM from three independent experiments.

Figure 4.3a shows the TEM image of the recombinant *E. coli* after 5.5 h from the phosphate uptake experiment. Granules about 200 nm were observed (indicated by white arrows). The morphologies of the granules are consistent with those found in activated sludge of wastewater treatment plants.¹³⁴ TEM images at higher magnifications showed that the polyP granules were highly porous. EDX mapping in Figure 4.3b indicated that the granules consisted mostly of elemental phosphorus.

The phosphorus-rich *E. coli* cells were further treated with FeCl_3 solution at pH 2.5. High-energy phosphoanhydride bonds found between phosphate units in polyP are known to be readily broken down under acidic conditions, releasing phosphates via the reaction of $\text{HO}[\text{PO}_3\text{H}]_n\text{H} + n \text{H}_2\text{O} \leftrightarrow n \text{H}_3\text{PO}_4$.^{135,136} At higher temperatures (*i.e.*, 50 °C), the kinetics of this reaction are further accelerated. Figures 4.3c and 4.3d show the TEM images of cells after treatment with Fe^{3+} solution. Bacteria cell bodies were found to be perforated, and voids previously occupied by the polyP granules were observed. There are also numerous smaller particulates dispersed throughout the cell matrix, likely from the degradation of polyP granules. The small particulates were found to be amorphous in nature, as confirmed by the electron diffraction patterns of the area enclosed by the white square in Figure 4.3d. Energy-dispersive X-ray (EDX) mapping images of P and Fe (Figure 4.3e, 4.3f) further confirmed that the small particles were primarily composed of element P and Fe. It is likely that the small particulates were FePO_4 complexes derived from the released

phosphate from hydrolysis of polyphosphate reacting with in-situ Fe³⁺ ions through the reaction of $\text{H}_3\text{PO}_4 + \text{Fe}^{3+} \leftrightarrow \text{FePO}_4 + 3\text{H}^+$.

Figure 4.3 (a) TEM images of recombinant *E. coli* + pBC29 taken at 5.5 h of a phosphate uptake experiment. White arrows indicate polyP granules. Insets in (a) show enlarged images of polyphosphate granules; (b) EDX mapping of recombinant *E. coli* + pBC29 sample in (a), showing the presence of elemental P (yellow). (c) TEM image of recombinant *E. coli* + pBC29 after treatment with Fe³⁺ solution (pH 2.5). (d) Magnified image of sample in (c) and the corresponding EDX mapping images showing presence of elemental P (e) and elemental Fe (f).

Lithium acetate (LiAc) solution was next added to the mixture, dried and further annealed under Ar at 600 °C for 5 h. Figure 4.4a shows the XRD patterns obtained from the as-annealed samples. Peaks characteristic of well-crystallized triphylite LiFePO₄ (JCPDF no. 15-7065) were obtained. The Al peak was from the sample holder. We also did not detect any other impurity phases, indicating that we had successfully obtained LiFePO₄. Figure 4.4b shows a TEM image of the annealed sample, showing small nanoparticles embedded within a carbon matrix. At higher magnifications, we found that LiFePO₄ nanoparticles were about 20 nm in diameter, polycrystalline in nature (see Figure 4.4c), and encased by an amorphous carbon shell which was

around 3 nm thick. The observed lattice spacing of 2.42 Å corresponded to (121) planes of triphylite LiFePO_4 . The overall carbon content derived from the bacteria was determined by thermal gravimetric analysis (TGA), and was found to be about 20 wt% (see Figure 4.5). During annealing, the bacteria cell bodies were transformed into the carbon, providing a carbon coating as well as a conductive carbon matrix that dispersed the LiFePO_4 nanoparticles, preventing them from aggregating into bigger particles at high temperatures. Both carbon coating and the reduced particle size are likely to contribute to improved electrochemical performances in LIBs.^{137,138}

Figure 4.4 (a) X-Ray diffraction pattern and (b) TEM image of LiFePO_4 synthesized in this work. Black dots in (b) are LiFePO_4 nanocrystals. (c) TEM image of a single LiFePO_4 nanocrystal and (d) measured the lattice spacings (0.242 nm) of the crystals corresponding to (121) plane of triphylite LiFePO_4 .

Figure 4.5 Thermal gravimetric analysis of as synthesized LiFePO_4/C nanoparticles.

The LiFePO_4 synthesized in this work was prepared as cathodes to evaluate their electrochemical properties. The initial galvanostatic charge-discharge voltage profiles of LiFePO_4/C were tested at a rate of 0.1 C (Figure 4.6a, 1 C = 170 mA g^{-1}) using Li half-cell configurations. The cells exhibited the typical voltage plateaus along 3.5 V, corresponding to the Li^+ extraction/insertion processes via the reaction of $\text{LiFePO}_4 - \text{Li}^+ - \text{e}^- \leftrightarrow \text{FePO}_4$. The initial charge capacity was $148.6 \text{ mA h g}^{-1}$ with Coulombic efficiency of 94.8 %. The Coulombic efficiency for the third cycle increased up to 99.5 % with a charge capacity of $144.2 \text{ mA h g}^{-1}$. Moreover, the composites exhibited good cycling stabilities (Figure 4.6b and 4.6c). During the 65th cycle under a rate of 0.1C, it retained reversible discharge capacities of $139.9 \text{ mA h g}^{-1}$, corresponding to 94.1 % of their initial discharge capacities (Figure 4.6b). For comparison, the performance of commercial LiFePO_4 without addition of any carbon has also been evaluated. At a low rate of 0.1 C, the reversible discharge capacity of LiFePO_4 was $132.1 \text{ mA h g}^{-1}$ at the end of the 65th cycle. When the cell was cycled at a relative high rate (1 C), a reversible discharge capacity of 120 mA h g^{-1} could still be achieved for the LiFePO_4/C composites at the 65th cycle, while the discharge capacity retained for LiFePO_4 was only 81.8 mA h g^{-1} (Figure 4.6c). Another remarkable advantage of nanostructured LiFePO_4/C nanocomposites is their excellent rate capability, which is highly desirable for high-power LIB applications such as hybrid electric vehicles (HEVs) and electric vehicles (EVs). The cycling responses of the LiFePO_4/C nanocomposites at different C rates (each sustained for 10 cycles) were evaluated and the results were shown in Figure 4.6d. The discharge capacities of LiFePO_4/C nanocomposite electrodes were 145.6, 130.6, 117.8, and 92.3 mA h g^{-1} at discharge rates of 0.1, 0.5, 1 and 5 C respectively. Stable cycling performances could be obtained

for all rates, even at a high rate of 10 C, a high-performance discharge capacity of 75.4 mA h g^{-1} could still be achieved. Remarkably, after repeated cycling at high C-rates, the discharge capacity could still be quickly recovered back to $145.5 \text{ mA h g}^{-1}$ even when the C-rate was lowered to 0.1 C. In comparison, the discharge capacities of LiFePO_4 without carbon additives were only 139.2, 118.3, 102.5, 79.8 and 60.7 mA h g^{-1} at discharge rates of 0.1, 0.5, 1, 5 and 10 C, respectively. When the C-rate was lowered to 0.1 C, the discharge capacity recovered was only $131.2 \text{ mA h g}^{-1}$. The above results indicate that the LiFePO_4/C nanocomposites generated in this work exhibited excellent stabilities and rate capabilities, compared to commercially available LiFePO_4 , in the absence of carbon additives. The superior performance may be originated from the unique nanostructure and the carbon generated from the cell membrane, which can facilitate the lithium ion and electron transport efficiently.

Figure 4.6 (a) Charge-discharge voltage profiles of the LiFePO_4/C electrodes at a current rate of 0.1 C for the first three cycles; (b – c) Cycling performance of the LiFePO_4/C electrodes at 0.1 C and 1 C, respectively. The performance of LiFePO_4 electrodes without addition of carbon has also

been shown for comparison. (d) Cycling performance of the LiFePO_4/C and LiFePO_4 electrodes at various current rates.

Finally, similar scheme was applied to the preparation of LiMnPO_4 . The TEM image and EDX mapping images of recombinant *E. coli* cells treated with MnCl_2 at pH 2.5 were shown in Figure 4.7. Like in the case of LiFePO_4 , we obtained perforated cell bodies with the absence of polyP granules; likewise, dispersed small particles were observed. After mixing with LiAc and annealing, XRD spectra shown in Figure 4.8a confirms the product to be lithiophilite LiMnPO_4 (JCPDF no. 15-7067). Figure 4.8 b – c show TEM images of the samples. Similarly, nanocrystallites of LiMnPO_4 were obtained embedded inside the carbon matrix; the observed lattice spacing of 2.72 Å and 1.98 Å corresponded to (301) and (230) planes of lithiophilite LiMnPO_4 , respectively. The results demonstrated the generality of our approach to utilize bacteria accumulated with extra P for synthesizing lithium metal phosphate nanostructures.

Figure 4.7 (a) TEM image of recombinant *E. coli* + pBC29 after treatment with Mn^{2+} solution (pH 2.5), and the corresponding EDX mapping images showing presence of elemental P (b) and elemental Fe (c).

Figure 4.8 (a) X-ray diffraction pattern and (b) TEM image of LiMnPO_4 synthesized in this work. Black dots in (b) are LiMnPO_4 nanocrystals. (c) TEM images of LiMnPO_4 nanocrystals. Inset in (c) show the lattice spacings of 0.273 nm and 0.198 nm, corresponding to (301) and (230) planes of lithiophilite LiMnPO_4 .

4.4 Conclusion

In this work, bacteria containing rich in phosphates were used for the preparation of LiMPO_4 nanomaterials. When applied as cathodes for LIBs, the as-obtained LiFePO_4 nanomaterials showed comparable electrochemical performance to those derived from inorganic phosphorus precursors reported in the literature.

Chapter 5: Elastin-Like Polypeptides-Derived Porous Carbon-Encapsulated Metal Oxide Quantum Dots for Enhanced Sodium Storage

5.1 Introduction

In chapters 3 and 4, we demonstrate the feasibility of using bacteria for the synthesis of metal oxides and LiMPO_4 nanomaterials. However, there is little control over the hierarchical architecture of the nanomaterials. There is now a general consensus that nanomaterials presented with a 3D complex porous framework exhibit significantly improved electrochemical properties. Recently, reports on the potential application of transitional metal oxides (iron oxides, cobalt oxides *et al.*) as anodes for sodium ion batteries (SIBs) have emerged.^{67,72,139,140} The theoretical capacities of transitional metal oxides for LIBs are high by means of conversion reaction (*e.g.*, 1007 mA h g^{-1} for Fe_2O_3 , much higher compared to 372 mA h g^{-1} for graphite).¹⁴¹ Theoretically, such metal oxides are also able to store sodium via similar conversion reaction mechanisms to achieve similar theoretical capacities as lithium storage. However, due to the sluggish sodiation/desodiation reaction kinetics induced by the large ionic radius of Na^+ , the reported metal oxides materials exhibit much inferior capacity for sodium storage compared to that for lithium storage.¹⁴² In order to increase the deliverable capacity for sodium storage, engineering robust nano-structured electrode materials is urgently needed. It is expected that the ion transportation pathway would be significantly decreased and more reactive sites would be created, thereby resulting in fast sodiation/desodiation reactions. In addition, hierarchically porous 3D architectures are highly desired for batteries from a practical viewpoint.¹⁴³⁻¹⁴⁵ The presence of micro-pores can act as a transport system while the meso-pores provide high surface areas to facilitate the transportation of Na^+ and electrons. To date, much effort has been put to prepare 3D metal oxides architectures, including post-template oxidation,¹⁴⁶ template-free hydrothermal synthetic route,¹⁴⁷ ethylene glycol-mediated self-assembly process,¹⁴⁸ ionic liquid-assisted synthesis¹⁴⁹ and so on. However, despite this recent progress, assembly of 0D nanoparticles into 3D hierarchically porous superstructures still remains a challenge.

In order to achieve 3D hierarchically porous structures, novel templates are needed for the synthesis of nanomaterials. Polypeptides emerge as an alternative to bacteria due to their controllable physical and chemical properties. For example, polypeptides can be designed to

contain tunable structures and motifs to guide the self-assembly of metallic precursors.¹⁵⁰ Examples include Au nanowires formed from the self-assembly of gold ions with histidine-rich peptides,¹⁵¹ metal phosphates nanofibers mineralized by self-assembled hydrophobic peptides,²⁴ mono-dispersed silver nano-particles grown inside the cavity of a peptide nanoreactor,²⁵ *et al.* More importantly, polypeptides can also be crosslinked or self-assembled to yield 3D structures such as foams and gels. Taken together, polypeptides are promising candidates for use as templates in nanomaterial synthesis.

In this work, we explore the use of a self-assembling recombinant elastin-like polypeptides containing hexahistidine tag [(VPGIG)₂VPGKG(VPGIG)₂]₁₆HHHHHH (named ELP16-His) for the synthesis of 3D hierarchically porous carbon-encapsulated metal oxides. Most reports in the literature utilize polypeptides for the preparation of 0D or 1D nanostructured materials. Relatively few reports exist on polypeptide-directed synthesis of inorganic materials with 3D hierarchically porous nanoarchitectures. ELPs are composed of repetitive VPGXG sequences, where X is any amino acid except proline. ELPs are known to be soluble in water below their inverse transition temperature (T_i) and aggregate at temperatures above T_i .^{152,153} As such, the physical properties of ELPs make them versatile as tunable 3D scaffolds for tissue engineering and drug delivery applications.¹⁵⁴⁻¹⁵⁶ In addition, the hexahistidine (His tag) is known to bind selectively to several metal cations.¹⁵⁷ Here, the ELP domain facilitates the formation of a 3D macro-porous scaffold, where metal cations are recruited within the matrix via specific interactions with the His tag. As such, the biochemistry synthesis approach provides a green strategy to control the nucleation of the metal oxides nanoparticles in the 3D scaffold by manipulating the positions and amounts of His tag through adjusting the synthetic conditions or the ELPs molecular structures. The scaffold is further annealed to yield metal oxides that are uniformly dispersed in a 3D porous carbon matrix. The 3D hierarchically porous carbon-encapsulated metal oxides were further tested as anodes in SIBs.

5.2 Materials and Method

5.2.1 Protein expression, purification and metal oxide synthesis

Plasmid pET22b containing the gene encoding for ELP16-His (named pET-ELP16-His) was constructed by cloning the gene encoding for ELP16 from pET-ELP16 to a commercially

purchased pET22b vector via SalI and XhoI double digestion and T4 ligase ligation. Subsequently, the pET-ELP16-His plasmid was transformed into *E. coli* BL21(DE3)pLysS cells via heat shock. The transformed *E. coli* cells were grown in 50 mL TB (Terrific broth) media containing 50 mg L⁻¹ ampicillin and 34 mg L⁻¹ chloramphenicol overnight. Afterwards, 10 mL of bacterial culture was re-inoculated into 1 L TB media containing the same antibiotics, and grown to an optical density at 600 nm (OD₆₀₀) of 0.7 - 0.8 at 37 °C. To induce protein expression, isopropyl β-D-1-thiogalactopyranoside (ITPG) was added to a final concentration of 1 mM. Bacteria were harvested after 5 h by centrifugation at 8000 rpm at 4 °C for 20 min before re-suspending in TEN buffer (0.1 M Tris, 0.01 M EDTA, 1 M NaCl). The cell mixture was sonicated on ice and subsequently centrifuged at 4 °C to collect the supernatant. ELP16-His were purified via inverse thermal cycling as previously described.¹⁵⁸ Purified protein was dialyzed against water and lyophilized.

The synthesis route of the carbon-encapsulated metal oxide quantum dots is illustrated in Figure 5.1. Purified ELP16-His and Bis (sulfosuccinimidyl) suberate (BS3) were dissolved in cold DI water separately. BS3 solution was added into the ELP16-His solution at 4 °C with molar ratio of BS3 to amino groups be 1.5:1 to ensure complete cross-linking. The final concentration of ELP16-His was 10% wt/vol. The mixed solution was pipetted between two pieces of parafilm-coated glasses and allowed to crosslinked overnight at room temperature. The cross-linked protein was retrieved and freeze-dried. The freeze-dried scaffold was rinsed in concentrated Fe(NO₃)₃ / Co(NO₃)₂ ethanol solution at room temperature for 1 h, washed briefly with water, freeze-dried and annealed in air at 300 °C for 30 min. Products characterization was performed as described in previous two chapters. The adsorption / desorption isothermals of N₂ were measured at 77 K using the surface area and pore size analyzer (Tristar-ASAP-2020, Micromeritics Inc.). The surface area was calculated using the Brunauer-Emmett-Teller (BET) method.

Figure 5.1 Scheme illustrating the synthesis of carbon-encapsulated metal oxides using recombinant elastin-like polypeptides (ELP16-His). The amino acid sequence of ELP16-His is also shown.

5.2.2 Electrochemical measurements

For battery testing, Fe_3O_4 / C or Fe_3O_4 , carbon nanotubes and PVDF were mixed thoroughly at a weight ratio of 70:20:10 in N-Methylpyrrolidone (NMP) solvent. The slurry was pasted on copper foils followed by drying at 70 °C. The mass loading in electrodes was around 1.0 mg cm⁻². The sodium foils were used as counter/reference electrodes, Whatman GF/D microfiber filter paper was used as the separator, and 1 M NaClO₄ dissolved in propylene carbonate (PC) with 5% fluoroethylene carbonate (FEC) was used as electrolyte. The coin-type half cells were tested using the same tester with before in the voltage range of 0.005 - 3.0 V. The cyclic voltammetry (CV) curves and electrochemical impedance spectroscopy (EIS) of half cells were carried out by an electrochemical workstation (Solartron, 1470E).

5.3 Results and Discussion

The recombinant ELP16-His protein (Figure 5.1) contains lysine (K) residues interspersed within the ELP backbone to serve as crosslinking sites. Afterwards, BS3 was added to ELP16-His to crosslink adjacent lysine groups within the ELP16-His molecules via amine-mediated chemistry.¹⁵⁹ Based on similar amino acid content, ELP16-His is expected to have a T_i above room

temperature. Addition of BS3 also depressed the T_i of ELP16-His to be below 25 °C, resulting in aggregation of ELP domains when the mixture was placed at room temperature.¹⁶⁰ Figure 5.2a shows the FESEM images of ELP16-His scaffold after crosslinking. A micro-porous structure with inter-connected micro-spheres was obtained, suggesting that there was self-aggregation of ELPs within a highly cross-linked protein network.^{152,161,162} This self-aggregation process was likely driven by the hydrophobic nature of ELP16-His molecules in water. The cross-linked ELP16-His was then rinsed in metal nitrate ethanol solution, where metal cations such as Fe^{3+} and Co^{2+} fit readily within the pocket of the imidazole nitrogen of His-tag (Figure 5.1).¹⁵⁷ Figure 5.2b shows the FESEM image of cross-linked ELP16-his after loaded with Fe^{3+} , where the 3D porous structure was clearly maintained, confirming the stability of the scaffold. After annealing, from the XRD pattern of the as-annealed sample, Fe_3O_4 was obtained (Figure 5.3), although the particles were not well crystallized.

Figure 5.2 FESEM images of crosslinked ELP16-His (a) before and (b) after treatment with Fe^{3+} .

Figure 5.3 XRD pattern of as-synthesized Fe_3O_4 .

The chemical composition of the iron oxide was further confirmed using high-resolution X-ray photoelectron spectroscopy (XPS) (Figure 5.4). The peaks at 712 eV and 726 eV can be attributed to $\text{Fe } 2p_{3/2}$ and $\text{Fe } 2p_{1/2}$, respectively, which are very close to the values for Fe_3O_4 reported in the literatures. It should be noted that no charge transfer satellite peak of $\text{Fe } 2p_{3/2}$ at around 720 eV was detected, further confirming the formation of Fe_3O_4 containing Fe^{3+} and Fe^{2+} .

Figure 5.4 The high-resolution X-ray photoelectron spectroscopy spectrum of Fe 2p.

Figures 5.5a – b show the FESEM images of the annealed Fe_3O_4 sample, where interconnected micro-spheres with diameters around 6 μm could be observed. The microstructure of

the sample was further examined using TEM (Figures 5.5c - d). Clearly, Fe_3O_4 nanoparticles (around 5 nm) were uniformly embedded within a carbon matrix (named $\text{Fe}_3\text{O}_4@\text{C}$). Compared with metal oxides/carbon composites prepared by other processes, the dispersion of Fe_3O_4 nanoparticles in carbon matrix is highly homogeneous. The homogenous dispersion of nanoparticles could be due to specific interactions between Fe^{3+} and the His tags distributed throughout the crosslinked network. In addition, the nano-scale dimensions of the Fe_3O_4 nanoparticles are critical for enhancing sodiation/desodiation reaction kinetics. The carbon content in the sample was estimated to be 25% (Figure 5.6a), and the surface area of the as-synthesized product was $30 \text{ m}^2 \text{ g}^{-1}$ (Figure 5.6b). The carbon matrix derived from the pyrolysis of ELP16-His also prevented the Fe_3O_4 nanoparticles from growing in size or aggregating. The porous carbon matrix can also buffer volume change caused by the sodiation/desodiation of Fe_3O_4 , which is vital to enhance the electrode's cycling stability. XPS analysis of as-obtained product shown in Figure 5.7 indicates that there isn't any N doping in the coating carbon.

Figure 5.5 (a - b) FESEM images of as-synthesized $\text{Fe}_3\text{O}_4@\text{C}$ at different magnifications; (c - d)

TEM images of as-synthesized $\text{Fe}_3\text{O}_4@\text{C}$, showing nanoparticles of around 5 nm embedded in a carbon matrix.

Figure 5.6 (a) Thermal gravity analysis and of as-synthesized $\text{Fe}_3\text{O}_4/\text{C}$; (b) Nitrogen adsorption and desorption isotherms at 77 K for as-synthesized $\text{Fe}_3\text{O}_4/\text{C}$.

Figure 5.7 XPS analysis of as-synthesized $\text{Fe}_3\text{O}_4@\text{C}$, showing none peak of element N.

The electrochemical performance of the as-synthesized $\text{Fe}_3\text{O}_4@\text{C}$ composite was evaluated. Since the specific capacity of carbonized ELP16-His scaffold is very low and shows only 27 mA h g^{-1} at 0.1 A g^{-1} as shown in Figure 5.8, the capacity contributed by the carbon matrix is negligible for the composite containing metal oxides. Therefore, the specific capacity is calculated based on the mass of metal oxides. Figure 5.9a shows the cyclic voltammetric (CV) curves of the cell with carbon-encapsulated Fe_3O_4 anode cycled at a scan rate of 0.1 mV s^{-1} . During the first cathodic cycle, the peak at 1.0 V corresponded to the insertion of Na^+ into Fe_3O_4 leading to the formation of $\text{Na}_x\text{Fe}_3\text{O}_4$. This process is irreversible, similar to that observed for Li^+ insertion reaction. The peak at 0.6 V could be due to the extended conversion reaction from $\text{Na}_x\text{Fe}_3\text{O}_4$ to metallic Fe and the formation of the solid electrolyte interfaces (SEI) layer.⁷⁰ In the anodic scan, the two broad peaks at 0.74 and 1.34 V corresponded to the two-step re-oxidation of metallic Fe to Fe_3O_4 . The two reduction peaks present in the first cycle merged at around 0.78 V in the following cycles. The peak intensity also dropped significantly, suggesting that irreversible reactions such as the formation of SEI layer occurred. In subsequent cycles, the reduction/oxidation peaks for the conversion reaction were found to stabilize and overlap, demonstrating a highly reversible sodiation/desodiation reaction after the activation during the first cycle. Figure 5.9b shows the typical galvanostatic charge-discharge profiles of the cell with $\text{Fe}_3\text{O}_4@\text{C}$ composite anode at a current density of 0.1 A g^{-1} , and the corresponding profiles of bare Fe_3O_4 and Fe_2O_3 nanoparticles were also plotted for comparison. No obvious discharge plateaus could be seen from the curves. The first discharge capacity of $\text{Fe}_3\text{O}_4@\text{C}$ was 1338 mA h g^{-1} , higher than the theoretical capacity of Fe_3O_4 (924 mA h g^{-1}). The cell delivered a charge capacity of 657 mA h g^{-1} in the first cycle, showing a Columbic efficiency of 49.1% . The irreversible capacity was mainly caused by the irreversible reactions of SEI film formation and/or electrolyte decomposition. In contrast, the first discharge and charge capacity of bare Fe_3O_4 nanoparticles is 1010 and 373 mA h g^{-1} at 0.1 A g^{-1} . Fe_2O_3 nanoparticle, which has a higher theoretical capacity of 1007 mA h g^{-1} , delivered 816 and 398 mA h g^{-1} at 0.1 A g^{-1} for the first discharge and charge capacity. Obviously, the capacity values of bare iron oxides are lower than their theoretical capacities, implying that iron oxides nanoparticles only partially participate in the conversion reaction because of the sluggish reaction kinetics. The rate performance of the cells is shown in Figure 5.9c. The cell with $\text{Fe}_3\text{O}_4@\text{C}$ electrode delivered specific charge capacities of $510, 425, 330, 246$ and 163 mA h g^{-1} at $0.2, 0.5, 1, 2$ and 5 A g^{-1} , respectively. In contrast, the cell with bare Fe_3O_4 electrode showed specific charge

capacities of 154, 138, 120, and 94 mA h g⁻¹ at 0.5, 1, 2, and 5 A g⁻¹, respectively, while bare Fe₂O₃ exhibited similar charge capacities of 124, 106, 91, and 66 mA h g⁻¹, which are much lower than those of Fe₃O₄@C. Besides, our Fe₃O₄@C composite also shows significant capacity superior to other previously reported iron oxide-based materials for sodium storage (Table 5.1), confirming the unique architecture advantage of the 3D Fe₃O₄@C nanocomposite for high-capacity and high-rate sodium storage. Notably, the capacity at a high current density of 2 A g⁻¹ was comparable to or better than most carbonaceous materials reported,¹⁶³⁻¹⁶⁷ suggesting a great potential of this composite as an anode materials for SIBs. The capacity increased to 647 mA h g⁻¹, which was close to the value of the initial cycle when the current density was switched to 0.1 A g⁻¹. The cycling performances of the cell with Fe₃O₄@C electrode at 0.1 A g⁻¹ are shown in Figure 5.9d. As can be observed, the cell shows good performance stability. The Columbic efficiency of the cell increases significantly upon cycling, eventually reaching around 98 %. The cell delivers a specific capacity of 513 mA h g⁻¹ during the 60th cycle at 0.1 A g⁻¹. Even at a relatively high current density of 0.2 and 0.5 A g⁻¹ (Figure 5.9e), the Fe₃O₄@C electrode still exhibits promising cycling stability (309 mA h g⁻¹ during the 100th cycle at 0.5 A g⁻¹) and high Columbic efficiency (around 98%).

Figure 5.8 Rate capabilities of carbonized ELP16-His scaffold as anode in SIBs.

Figure 5.9 (a) CV curves of a fresh SIB with $\text{Fe}_3\text{O}_4@\text{C}$ electrode at a scan rate of 0.1 mV s^{-1} within a potential range of 0.001 to 3.0 V (vs. Na/Na^+); (b) The 1st charge-discharge profiles of the cells with $\text{Fe}_3\text{O}_4@\text{C}$, bare Fe_3O_4 , and Fe_2O_3 electrodes at a current density of 0.1 A g^{-1} ; (c) Rate capabilities of the cells with $\text{Fe}_3\text{O}_4@\text{C}$, bare Fe_3O_4 , and Fe_2O_3 electrodes; (d) Cycling performance of cell with the $\text{Fe}_3\text{O}_4@\text{C}$ electrode at 0.1 A g^{-1} ; (e) Cycling performance of the cell with $\text{Fe}_3\text{O}_4@\text{C}$

electrode at 0.2 and 0.5 A g⁻¹.

Table 5.1 A comparison of our Fe₃O₄@C to previously reported iron oxides anodes in sodium ion batteries.

	200 mA g ⁻¹	500 mA g ⁻¹	1 A g ⁻¹
Our Fe₃O₄@C	510	425	330
Ref.⁷⁰	248 (83 mA g ⁻¹)		<100 (834 mA g ⁻¹)
Ref.⁶⁷	350	260	190
Ref.¹⁶⁸	250 (130 mA g ⁻¹)		
Ref.⁶⁸	474	418	
Ref.⁶⁹	<250 (15 mA g ⁻¹)		

The unit is mAh g⁻¹

The superior performance of the current Fe₃O₄@C composite can be ascribed to the following reasons. First, the much smaller Fe₃O₄ grain size (5 nm) in the composite is highly beneficial to shorten ion diffusion pathway and enhance the sodiation/desodiation reaction kinetics, thus delivering higher sodium storage capacity.^{169,170} Secondly, the porous carbon matrix (with a specific surface area of 30 m² g⁻¹) facilitates the quick infiltration of the electrolyte into the active materials and improves ion diffusion efficiency, which is another key reason for the high-rate performance of the Fe₃O₄@C composite. Thirdly, the electrochemical process for sodium storage would induce a very high volume change if Fe₃O₄ was fully involved in the conversion reaction. The carbon matrix combined with the porous structure of the Fe₃O₄@C nanocomposite helped to buffer volume change during the sodiation/desodiation reaction and effectively mitigate the electrode microstructure fading.¹⁷⁰ Besides, the aggregation of the Fe₃O₄/Fe nanoparticles might be significantly suppressed with the help of the carbon matrix. These two factors are vital to the good cycling stability of the Fe₃O₄@C composite electrode. In all, the synergistic effect of the factors mentioned above ensures the good electrochemical performance of the Fe₃O₄@C composite.

Similarly, $\text{Co}_3\text{O}_4/\text{C}$ nanocomposite was obtained by loading the porous 3D scaffold with Co^{2+} , followed by annealing at 300°C for 30 min in air (see XRD spectra, Figure 5.10). Figure 5.11a shows a typical FESEM image of the annealed porous carbon-encapsulated Co_3O_4 composite ($\text{Co}_3\text{O}_4/\text{C}$). Likewise, the $\text{Co}_3\text{O}_4/\text{C}$ composite showed a similar morphology to $\text{Fe}_3\text{O}_4/\text{C}$ as presented in Figure 5.5, and also consists of meso-porous microspheres within an inter-connected network. Figures 11b - c present the TEM images of the sample. It can be observed that Co_3O_4 quantum dots around 5 nm in size are also distributed homogeneously within the carbon matrix. The carbon content in the $\text{Co}_3\text{O}_4/\text{C}$ composite is about 28% according to the TGA analysis (Figure 5.12a), and the BET specific surface area of the as-synthesized product was determined to be $28\text{ m}^2\text{ g}^{-1}$ (Figure 5.12b). The morphology similarity of the two hybrid metal oxide/carbon composites demonstrate that the ELP16-His is an efficient template for synthesizing carbon-encapsulated well-dispersed metal oxide quantum dots via the biochemistry process.

Figure 5.10 XRD pattern of as-synthesized $\text{Co}_3\text{O}_4/\text{C}$.

Figure 5.11 (a) FESEM image of as-synthesized $\text{Co}_3\text{O}_4@\text{C}$; (b - c) TEM images of as-synthesized $\text{Co}_3\text{O}_4@\text{C}$, showing nanoparticles of around 5 nm embedded in a carbon matrix.

Figure 5.12 (a) Thermal gravity analysis and of as-synthesized $\text{Co}_3\text{O}_4/\text{C}$; (b) Nitrogen adsorption and desorption isotherms at 77 K for as-synthesized $\text{Co}_3\text{O}_4/\text{C}$.

The $\text{Co}_3\text{O}_4@\text{C}$ nanocomposite also exhibits good sodium storage capability due to the efficient nanostructure for fast sodiation/desodiation reaction. Figure 5.13a shows the rate performance of the cell with $\text{Co}_3\text{O}_4@\text{C}$ electrode. The cell delivered specific charge capacities of 583, 416, 310, 251, and 183 mA h g^{-1} at 0.1, 0.2, 0.5, 1, and 2 A g^{-1} , respectively. The specific capacities at high current densities also outperformed other reported Co_3O_4 -based materials for sodium storage (Table 5.2). In addition, the $\text{Co}_3\text{O}_4@\text{C}$ electrode also shows promising cycling performance, as shown in Figure 5.13b. The cell delivered a specific capacity of 228 mA h g^{-1} at 0.5 A g^{-1} during the 150th cycle with a high Coulombic efficiency of 99%. The good electrochemical performance of $\text{Co}_3\text{O}_4@\text{C}$ nanocomposites further confirms that carbon-encapsulated metal oxide quantum dots are efficient anode materials for high-capacity, high-rate and durable sodium storage.

Figure 5.13 (a) Rate capability of the cell with $\text{Co}_3\text{O}_4@\text{C}$ electrode. Inset shows the 1st charge-discharge profile of the cell at 0.1 A g^{-1} ; (b) Cycling performance of the cell with $\text{Co}_3\text{O}_4@\text{C}$ electrode at 0.5 A g^{-1} .

Table 5.2 A comparison of our $\text{Co}_3\text{O}_4@\text{C}$ to previously reported Co_3O_4 anodes in sodium ion batteries.

Our $\text{Co}_3\text{O}_4@\text{C}$	100 mA g^{-1}	200 mA g^{-1}	500 mA g^{-1}
	583	416	310
Ref. ⁷¹	293 (34 mA g^{-1})		
Ref. ¹⁷¹	447 (25 mA g^{-1})		
Ref. ⁷²	290 (58 mA g^{-1})		
Ref. ⁷³	524 (25 mA g^{-1})		82
Ref. ¹⁷²		390 (160 mA g^{-1})	

The unit is mAh g^{-1}

5.4 Conclusion

In this work, two types of porous carbon-encapsulated metal oxide quantum dots (Fe_3O_4 and Co_3O_4) were prepared using biochemistry routes. Using recombinant elastin-like polypeptides (ELP16-His) templates, we showed that metal precursors interact specifically with the protein microstructure to yield Fe_3O_4 and Co_3O_4 quantum dots with 5 nm in diameters. After annealing,

the protein matter degraded into a porous, carbonaceous matrix, encapsulating the Fe_3O_4 and Co_3O_4 nanoparticles. The carbon-encapsulated metal oxides demonstrated excellent sodium storage capability with high specific capacities, good rate capabilities and cycling stabilities. The cell delivered a specific charge capacity of 657 and 583 mA h g^{-1} at 0.1 A g^{-1} for carbon-encapsulated Fe_3O_4 and Co_3O_4 , respectively, while maintaining the charge capacities of 246 and 183 mA h g^{-1} at 2 A g^{-1} . In summary, we demonstrate a versatile biochemistry approach for the synthesis of highly efficient carbon-encapsulated metal oxide quantum dots for sodium-based energy storage and conversion applications.

Chapter 6: Biochemistry-Enabled 3D $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ / $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ Foams for Ultrafast Battery Cathodes

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6.1 Introduction

In the previous chapter, we successfully prepared metal oxide quantum dots within a 3D porous scaffold. The as-prepared materials possess superior rate capabilities and cycling stabilities when tested as anodes in LIBs and SIBs. In this work, we further investigated the possibility of polypeptides in directing the synthesis of 3D micro/nano-structure of functional materials with complex stoichiometric compositions.

Three-dimensional (3D) hierarchical foam nano-architectures have recently attracted significant attention for lithium / sodium energy storage applications by offering sufficient contact area between the electrolyte and electrode, high-rate transportation of ions and electrons, and short solid-state ion diffusion lengths. These properties favor the use of 3D foam nanomaterials in advanced plug-in hybrid vehicles (PHEVs) and electric vehicles (EVs) with rapid charge and discharge requirements.¹⁷³⁻¹⁷⁵ In the field, intensive research effort has been devoted to fabrication of numerous 3D structured battery anodes, such as Cu_6Sn_5 alloy foams,¹⁷⁶ Ni-foam-supported $\text{CoO-Li}_2\text{O}$,¹⁷⁷ Fe_3O_4 /graphene foams¹⁷⁸⁻¹⁸⁰ and MoS_2 /graphene foams.¹⁸¹ Current strategies used for the preparation of such 3D foams include hydrothermal self-assembly, template-assisted preparation, electrostatic spray deposition, chemical vapor deposition (CVD) and atomic layer deposition (ALD). However, it is difficult to use these conventional approaches to produce 3D foam cathodes, particularly cathode materials with complex stoichiometric compositions.

Metal vanadium phosphates (MVP), particularly LVP and NVP NPs are promising cathode materials for lithium ion batteries and sodium ion batteries due to their excellent thermal stabilities, large reversible capacities, high operating potentials and relatively rapid ionic mobilities. Currently, LVP and NVP are manufactured at the micro or sub-micro scales using traditional energy-intensive solid-state ceramic processes.^{91,182-185}

Here, we demonstrate a facile strategy for the preparation of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ (LVP) and $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ (NVP) nanostructures supported on hierarchically porous 3D carbon aerogels using recombinant elastin-like polypeptides. The as-synthesized 3D MVP nanostructures show ultrahigh capacity at ultrafast charging/discharging properties and excellent cycle performance as cathodes for Li/Na secondary battery.

6.2 Materials and Method

6.2.1 Products preparation method

ELP16 was expressed and purified using the same method as described in Chapter 5. Purified ELP16 was dissolved in cold DI H_2O . Soluble precursors $\text{LiH}_2\text{PO}_4/\text{NaH}_2\text{PO}_4$ and NH_4VO_3 were dissolved in 60 °C DI H_2O with stirring to achieve a concentration of 0.3 M and 0.2 M respectively. The LVP/NVP precursors were cooled on ice, and added to the ELP16 solution with vigorous stirring on ice. The final concentration of ELP16 in the mixture was 7.5% wt/vol, and 125 mM, 187.5 mM for NH_4VO_3 and MH_2PO_4 respectively. The mixture was then kept stagnant for 1 h, and subsequently frozen in liquid nitrogen before lyophilization. The resulting sample was annealed at 750 °C for 10 h under argon atmosphere. Minute amounts of HNO_3 acid were added to NVP precursors' solution before mixing with ELP16 to avoid precipitation at low temperature. Products characterization was performed as described in previous chapters.

6.2.2 Electrochemical measurement

LVP or NVP, carbon nanotubes, PVDF were mixed in NMP solvent in the ratio of 8:1:1, and then pasted onto the aluminum foils. The mass loading in electrodes was around 1.0 mg cm^{-2} . For LVP LIB cells, lithium foils were used as anodes and the same electrolyte was used as described in chapter 3. For NVP SIB cells, sodium foils were used as anodes and the same electrolyte solution was used as described in chapter 5. All cells were tested using the same tester with previously described in the voltage ranges of 3.0 – 4.3 V vs. Li^+/Li for LVP and 2.5 – 3.8 V vs. Na^+/Na for NVP.

6.3 Results and Discussion

The annealed products were subjected to XRD to determine their chemical compositions. Figure 6.1 shows the XRD spectra of the as-annealed samples (Figure 6.1), confirming the presence of well-crystallized $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ (JCPDF no. 04-012-2044) and $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ (JCPDF no. 96-222-5133) separately. The Al peaks was from the sample holder. There were no detectable impurity phases, indicating that we had successfully obtained pure crystalline $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ and $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ respectively.

Figure 6.1 XRD patterns of as-synthesized (a) LVP and (b) NVP.

Figures 6.2 a – c show the FESEM images of the as-synthesized 3D LVP foam. From the image, it was clear that the annealed product consisted of a nanofibrous porous network structure. FESEM images at higher magnifications (Figure 6.2b) also revealed that the micropores were around 3 μm in diameter. The surfaces of the nanofibers were completely covered by LVP nanoparticles (Figure 6.2c). TEM images at low magnifications (Figure 6.3) show the interconnected fibrous carbon matrix with LVP nanoparticles, confirming the formation of the aerogel structure. Figure 6.2d shows the TEM image of the nanofibers. LVP nanoparticles with diameters of about 100 – 200 nm were found to be embedded within the carbon matrix. Under higher magnifications (Figure 6.2e), it was clear that the LVP nanoparticles were encased by an amorphous carbon shell of around 5 nm thick, with the observed lattice spacing of 3.65 Å corresponding to the (211) plane of LVP. The carbon shell was probably from the pyrolysis of ELP16. The ELP16 scaffold was degraded into carbon matter during the annealing step, resulting

in the carbon coating outside LVP nanoparticles and formation of a 3D conductive carbon porous matrix. This carbon matrix allowed the LVP nanoparticles to nucleate and grow at high temperatures without aggregation. The overall carbon content derived from the recombinant ELP16 matter was determined by dissolving the as-synthesized product in hot concentrated HCl and weighing the residual carbon. It was found that it contained about 22 wt% carbon. XPS analysis of the as-synthesized LVP shown in Figure 6.4 indicates that there isn't any N doping in the carbon matrix. BET results of the product (Figure 6.5) indicated that large amount of mesopores existed within the fibrous carbon matrix, with a specific surface area of $106.3 \text{ m}^2 \text{ g}^{-1}$ and a narrow pore size distribution centered at 4 nm. Here, we conclude that hierarchically 3D foams with carbon coated LVP nanoparticles embedded in micro/meso-porous carbon aerogels (abbreviated as LVP@C/CAs) were indeed obtained.

Figure 6.2 (a – c) FESEM images of as-synthesized LVP 3D foams at various magnifications; (d) TEM image showing the presence of LVP nanoparticles embedded within a carbon matrix; (e) measured lattice spacing (0.367 nm) of the crystals corresponding to (211) plane of the LVP.

Figure 6.3 TEM images of as-synthesized LVP, showing inter-connected fibrous carbon matrix.

Figure 6.4 XPS analysis of as-synthesized LVP, showing none peak of element N.

Figure 6.5 Nitrogen adsorption and desorption isotherms at 77 K for as-synthesized LVP@C/CAs, with inserts showing pore size distributions.

Figures 6.6a - c show the FESEM images of the annealed NVP 3D foams. The morphologies of the foams were similar to that of the LVP@C/CAs 3D foams shown in Figure 6.2a - c. The NVP 3D foams also consisted of a nanofibrous micro-porous network, covered by NVP nano-particles. TEM images at low magnifications (Figure 6.7) also show similar aerogel structure as found in LVP@C/CAs. Figure 6.6d is a TEM image of the fibers, clearly showing the presence of NVP nanocrystallites embedded within a carbon matrix. The NVP nanoparticles with diameters less than 200 nm, and were also encased by an amorphous carbon shell of around 5 nm thick, with the measured lattice spacing of 4.42 Å corresponding to the (104) plane of NVP (Figure 6.6e). BET results (Figure 6.8) indicated that the specific surface area of the NVP 3D foams is 131.9 m² g⁻¹ and the pore size distribution is centered at 3 nm. Here, we demonstrated that micro/meso-porous NVP 3D foams with nanostructure (abbreviated as NVP@C/CAs) could also successfully fabricated *via* the same strategy, indicating the generality of our approach.

Figure 6.6 (a – c) FESEM images of as-synthesized NVP 3D foams at various magnifications; (d) TEM image showing the presence of NVP nanoparticles embedded within a carbon matrix; (e) measured lattice spacing (0.442 nm) of the crystals corresponding to (104) plane of the NVP.

Figure 6.7 TEM images of as-synthesized NVP@C/CAs at low magnification, showing inter-

connected fibrous carbon matrix.

Figure 6.8 Nitrogen adsorption and desorption isotherms at 77 K for as-synthesized NVP@C/CAs, with inserts showing pore size distributions.

To understand the mechanisms involved in the synthesis process, four separate mixtures containing (1) ELP16 and both precursors, (2) ELP16 and LiH_2PO_4 , (3) ELP16 and NH_4VO_3 , and (4) ELP16 only were prepared at 4 °C and freeze dried. Dried samples were examined under FESEM. For ELP16 and both precursors, ELP16/ LiH_2PO_4 and ELP16/ NH_4VO_3 mixtures, we were able to obtain 3D foams with similar fibrous porous structures (Figure 6.9a - c). However, in the absence of either LiH_2PO_4 or NH_4VO_3 , we were unable to obtain 3D foam, but rather chunks of dense ELP16 fragments lacking the fibrous, porous structure (Figure 6.9d). In addition, the sample collapsed into fine powder after annealing. Taken together, it is likely that interactions between LiH_2PO_4 , NH_4VO_3 and ELP16 facilitated the formation of the nanofibrous network.

Figure 6.9 FESEM images of (a) ELP16 and both precursors, (b) ELP16 and LiH_2PO_4 , (c) ELP16 and NH_4VO_3 mixtures, and (d) ELP16 only obtained after freeze drying, with insets showing the corresponding FESEM images at higher magnifications.

Our FTIR results shown in Figure 6.10 revealed shifts in the characteristic peaks for P-O stretching (*i.e.*, from 1079 cm^{-1} to 1050 cm^{-1}) and V-O-V stretching (from 942 cm^{-1} to 967 cm^{-1}) when LVP precursors were mixed with ELP16.^{186,187} Both results suggest that there were indeed interactions between H_2PO_4^- ions and ELP16 as well as between VO_3^- ions and ELP16. There were also shifts in peaks for C-NH₂ stretching (from 1234 cm^{-1} to 1260 cm^{-1}).¹⁸⁸ Therefore, the interactions between H_2PO_4^- ions and ELP16 were likely due to hydrogen bonding between P-O-H and H-N-H, since there are 16 lysine residues (and hence 16 amine groups) per ELP16 molecule. The hydrogen bonding reduced the polarity of P-O bond and resulted in the shifts of P-O stretching peaks. On the other hand, interactions between VO_3^- ions and ELP16 could be due to the formation of dative bonds from the vacant electron orbits of VO_3^- and the lone pairs of the -NH₂ on ELP16. Both interactions contributed to the shift of characteristic peak for C-NH₂ stretching to higher wavenumbers by increasing the polarity of C-N bond. Therefore, the possible mechanisms

involved is proposed as shown in Figure 6.11. In pure ELP16 solutions, there exists hydrophobic forces stemming from the presence of hydrophobic residues along the ELP16 backbone. These hydrophobic force coacervate the ELP16 molecules together. Meanwhile, an electrostatic repulsion force also exists between dissociated $-\text{NH}_2$ groups on the lysine residues. This electrostatic repulsion force acts to disperse the ELP16 molecules. When the both forces cancel each other (as in the case of ELP16 only mixtures), nanofibers could not be formed. However, when LVP or NVP precursors are present, H_2PO_4^- and/or VO_3^- ions could bind to the $-\text{NH}_2$ groups in ELP16 and act as crosslinkers between two adjacent ELP16 molecules. These interactions are further strengthened by the formation of hydrogen bonding or/and dative bonding, thereby enhancing the association of adjacent ELP16 molecules while reducing the dispersive effects of the electrostatic repulsion. Hence, interactions between the H_2PO_4^- and VO_3^- ions and ELP16 drive the formation of ELP16 bundles. In addition, the recruitment of H_2PO_4^- and VO_3^- ions on the ELP16 backbone also contributed to an overall negative charge on the surface of the ELP16 bundles, and further facilitated the recruitment of M^+ ions. During annealing, the N atoms combined both phosphates and vanadium, and acted as nucleating centers for the formation of LVP or NVP nanoparticles. Meanwhile, ELP16 is degraded into carbon matter, resulting in carbon-enveloped LVP or NVP NPs dispersed within a 3D conductive carbon aerogel network. We also noted that the freeze drying of sample taken directly from 4 °C was critical to preserve the integrity of the structure, without which the micro-pore network could not be maintained (Figure 6.12).

Figure 6.10 FTIR spectra of LVP precursors (curve a), ELP16 + LVP precursors (curve b), and

ELP16 (curve c). The shifts in P-O stretching, V-O-V stretching, and C-NH₂ stretching peaks are indicated.

Figure 6.11 Schematic illustrating the mechanisms in the synthesis of MVP 3D foams using recombinant ELP16 proteins.

Figure 6.12 FESEM image of ELP16+ LVP precursor solution placed at room temperature for 1 h, followed by freeze drying. No fibrous structures were observed.

The electrochemical performance of MVP 3D foams were examined by galvanostatic cycling in CR2032 coin-type cells. Metallic lithium and sodium foils were used as the counter electrodes for LVP and NVP cathodes respectively. Figures 6.13a - b show the initial charge-discharge voltage characteristics of the LVP and NVP cathodes at a rate of 1C, respectively. Insets

in Figure 6.13a - b are their corresponding cycling performances. A rate of $n\text{C}$ corresponds to a full charge or discharge in $1/n$ hour. Here, 1C equals to the current density of 133 mA g^{-1} for LVP and 118 mA g^{-1} for NVP, respectively. The redox plateau potentials of $\text{V}^{3+}/\text{V}^{4+}$ are clearly observed at around 3.6, 3.7 and 4.1 V (vs. Li^+/Li) for LVP and $\sim 3.4\text{ V}$ (vs. Na^+/Na) for NVP, corresponding to two lithium or sodium extraction/insertion, *i.e.*, $\text{M}_3\text{V}_2(\text{PO}_4)_3 \leftrightarrow \text{MV}_2(\text{PO}_4)_3$ ($\text{M} = \text{Li}$ and Na). The potential hysteresis was found to be less than 0.06 V, thereby implying an excellent reversibility for Li/Na ions removal and uptake. As a result, at 1C, initial discharge capacities of up to 129 and 112 mA h g^{-1} with Coulombic efficiencies (calculated from the discharge capacity/charge capacity) of 98% and 97% were achieved for LVP and NVP cathodes respectively. Both efficiencies were nearly equivalent to their theoretical values. It was noted here that the capacity contribution from the carbon is negligible in the voltage ranges of 3.0 – 4.3 V (vs. Li^+/Li) and 2.5 – 3.8 V (vs. Na^+/Na), and hence, only the masses of active LVP and NVP were included when calculating the specific capacities. In addition, a near perfect capacity retention ($\sim 99.5\%$) was observed for both types of cathodes during 100 cycles (insets in Figure 6.13a - b).

Figure 6.13 Initial charge-discharge voltage profiles of (a) LVP and (b) NVP cathodes at 1C. Insets show the corresponding cycling performances for each material.

The key advantage of our 3D MVP cathodes is their excellent ultrafast charging / discharging performances, which are highly desirable for high-power LIB/SIB applications such as HEVs and EVs. The discharge voltage profiles of LVP and NVP obtained at discharge rates from 5 C to 200 C are shown in Figures 6.14a - b, respectively. The discharge capacities of LVP were found to be 121, 112, 105, 91 and 79 mA h g^{-1} at discharge rates of 5, 10, 20, 50 and 100 C

(Figure 6.14a). More significantly, the LVP 3D foam cathodes were able to achieve a capacity of 66 mA h g^{-1} ($\sim 50\%$ of its theoretical capacity), even at an ultrahigh rate of 200 C (which corresponded to a time of 18 s to fully discharge). This performance is nearly one order of magnitude larger than materials used in current battery cathodes. Likewise, the 3D NVP cathodes were also able to deliver reversible capacities of $109, 104, 99, 87, 73$ and 51 mA h g^{-1} at rates of $5, 10, 20, 50, 100$ and 200C (Figure 6.14b). Both materials synthesized in this work demonstrated ultrafast discharging properties, far superior than most state-of-the-art LVP and NVP cathodes reported in the literature (see Table 6.1 and 6.2). Our MVP cathodes also exhibit outstanding long-term high rate cycling performances. From Figure 6.14c, there were no obvious capacity losses for LVP and NVP cathodes over 1000 cycles at a rate of 100C .

Finally, to evaluate the possible applications of our LVP and NVP 3D foams as cathode materials, we calculated their power and energy densities based on the weight of cathode materials, working voltages and capacities at various rates. Figure 6.14d shows the Ragone plot for our materials, compared to current advanced LIB and NIB cathodes (normalized to the weight of cathode materials). The LVP cathodes prepared in this work were able to achieve a specific energy density of 450 Wh kg^{-1} at a power density of 2.2 kW kg^{-1} , while maintaining an energy density of 205 Wh kg^{-1} at an ultrahigh power density of 41 kW kg^{-1} . Similarly, the NVP cathodes prepared in this work were able to achieve gravimetric energies of 350 and 147 Wh kg^{-1} at specific powers of 1.8 and 30 kW kg^{-1} respectively. Notably, the maximum specific power densities achieved by our MVP cathodes are significantly higher than the current state-of-the-art active materials such as $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$,¹⁸⁹ CNT/FePO_4 nanowires,⁸ LiFePO_4/C ,¹⁹⁰ LVP/C thin film,¹⁹¹ $\text{Na}_3\text{Ni}_2\text{SbO}_6$,¹⁹² and NVP/graphene .¹⁹³ Hence, we envisioned that the LVP and NVP 3D foams developed in this work have tremendous potential for use in demanding energy storage applications such as HEVs and EVs.

Figure 6.14 Galvanostatic discharging profiles of (a) LVP and (b) NVP cathodes at current rates of 5 C to 200 C (their discharge capacities versus C rates are summarized in the insets). (c) Cycling stability of LVP and NVP at 100 C. (d) Ragone plots of our 3D MVP cathodes, compared with some advanced active materials of $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ (up triangles), CNT/ FePO_4 nanowires (down triangles), LiFePO_4/C (diamonds), LVP/C thin film (right triangles), $\text{Na}_3\text{Ni}_2\text{SbO}_6$ (hexagons), NVP/graphene (stars).

Table 6.1 A comparison of our LVP@C/CAs to previously reported LVP cathodes in the voltage range of 3.0-4.3 V vs. Li^+/Li .

	10 C	20 C	50 C	100 C	200 C
Our LVP@C/CAs	112	105	91	79	66
Ref.¹⁹⁴				66	
Ref.¹⁹⁵	108				
Ref.¹⁹⁶		90 (15 C)			
Ref.¹⁹⁷		47			
Ref.¹⁹⁸	105				
Ref.¹⁹⁹	74				
Ref.²⁰⁰		83			
Ref.²⁰¹			85		
Ref.²⁰²			87 (30 C)		

* The unit is mAh g^{-1} **Table 6.2** A comparison of our NVP@C/CAs to previously reported NVP cathodes in the voltage range of 2.5-3.8 V vs. Na^+/Na .

	10 C	20 C	50 C	100 C	200 C
Our NVP@C/CAs	104	99	87	73	51
Ref.¹⁸⁴					44
Ref.²⁰³	81 (5 C)				
Ref.²⁰⁴	95 (5 C)				
Ref.²⁰⁵	45				
Ref.²⁰⁶	39	20			
Ref.¹⁹³	83	74	60 (30 C)		

* The unit is mAh g^{-1}

Plausible mechanisms enabling ultrafast charge/discharge properties of 3D LVP and NVP cathodes are illustrated as below. (i) It is well known that nanoscale materials have exceptionally short ion (Li^+ and Na^+) transport lengths, leading to a short time constant t for ion diffusion. Taking the estimated values of ion diffusivity D ($\sim 10^{-10} \text{ cm}^2 \text{ s}^{-1}$ for LVP and $\sim 10^{-11} \text{ cm}^2 \text{ s}^{-1}$ for NVP),^{207,208} the time t for Li^+ and Na^+ to diffuse over 100 nm (average particle size, L) is estimated to be 1 and 10 s for LVP and NVP respectively, computed using the equation $t = L^2/D$. Thus, the limiting factor in the improvement of charge/discharge rate is the delivery of ions and electrons to the surface of our monodispersed LVP and NVP nanoparticles rather than solid-state ion transport. (ii) Large surface area of electrodes ($106.3 \text{ m}^2 \text{ g}^{-1}$ for LVP@C/CAs, $131.9 \text{ m}^2 \text{ g}^{-1}$ for NVP@C/CAs) permits high contact area with the electrolytes (see Figure 6.5 and Figure 6.8 for BET measurements). (iii) The 3D interconnected electrolyte-filled pore networks provide fast transport channels for the conductive ions. (iv) The 3D nanoporous carbon monolith combined with the carbon-coating on the nanocrystals can further act as the electrolyte reservoir and as the electronic conductor. The carbon matrix allows fast migration of both Li^+/Na^+ and e^- to the active sites of each LVP/NVP nanoparticle. Therefore, favorable transport characteristics of the unique hierarchical structure with an efficiently mixed conducting 3D network are assumed to lead to the overall excellent power performance.

6.4 Conclusion

Metal vanadium phosphates have been explored as promising materials for cathodes in metal-ion batteries. However, their low conductivities limit their widespread use in applications where ultrahigh power capabilities are required, without significant loss in energy over time. In this work, we report a novel synthesis approach to prepare nanostructured MVP 3D foams *via* assembly of recombinant elastin-like polypeptides (ELP16) proteins. We showed that we were able to obtain 3D fibrous, macro-porous LVP and NVP foams, that displayed exceptional rate cycling capabilities and energy densities, far superior than current advanced active materials used for state-of-the-art battery technologies.

Chapter 7: Conclusions and Outlook

7.1 Conclusions

Biological routes offer an alternative, green strategy for the preparation of novel nanomaterials with micro-features. The body of work addresses our key hypotheses, by collectively demonstrating the feasibility of applying bio-inspired synthesis routes towards the preparation of nanostructured functional materials for LIBs and SIBs.

In chapter 3, we first showed that magnetotactic bacteria can be successfully used to assist the synthesis of carbon-coated Fe_3O_4 1D chains. The Fe_3O_4 1D chains were applied as anode materials in lithium ion batteries, and found to exhibit enhanced electrochemical performance, with discharge capacities of 947, 857, 757, 615, 518, 388, 282 mA h g^{-1} at 0.2, 0.5, 1, 3, 5, 8 and 10 C respectively for lithium ion battery. To demonstrate the generality of using bacteria to synthesize nanomaterials with a more complex stoichiometric chemistry, we utilized *E. coli* bacteria for the preparation of lithium metal phosphates (LiMPO_4). In chapter 4, we utilized a genetically modified *E.coli* bacteria strain that could acquire phosphate from its surroundings. The bacteria cell body was used as a template for reacting with Li and Fe precursors before subjected to annealing. The as-annealed products consisted of well-crystallized LiFePO_4 nanoparticles, encapsulated by a thin layer of amorphous carbon. The discharge capacities of the as-synthesized LiFePO_4/C nanocomposite electrodes were found to be 145.6, 130.6, 117.8, and 92.3 mA h g^{-1} at discharge rates of 0.1, 0.5, 1 and 5 C respectively for lithium ion battery. Taken together, both works demonstrated that bacteria-assisted synthesis is a promising and facile strategy to fabricate novel micro-structured nanomaterials with enhanced electrochemical performance.

While bacteria-assisted approaches can yield nanomaterials with complex chemistries, there is little control over the macroscopic structure of the resulting material. In order to prepare 3D hierarchical inter-connected structures, an alternative template is needed. In chapter 5, polypeptides were explored as a potential template due to their tunable physical and chemical properties. Since polypeptides have almost limitless design of sequence through genetic engineering, it is possible to control the molecular recruitment of metallic ions by engineering specific interactions between the metal and the polypeptides. Elastin-like polypeptides (ELPs)

have widely studied for their ability to form 3D structures via self-assembly or by chemical crosslinking. In chapter 5, we constructed ELPs bearing metal-binding motifs (ELP16-His), with amino sequence of [(VPGIG)₂VPGKG(VPGIG)₂]₁₆HHHHHH. To construct a 3D scaffold, ELP-His was chemically cross-linked at room temperature and freeze dried. The crosslinked scaffold were then rinsed in iron nitrate or cobalt nitrate solution. Metallic precursors interact specifically with the hexahistidine tag (His-tag) dispersed throughout the 3D gel matrix, creating nucleation sites for the growth of metal oxide nanoparticles. After annealing in air at 300 °C for 30 min, Fe₃O₄ or Co₃O₄ nanoparticles around 5 nm encapsulated uniformly in 3D porous carbon microspheres were obtained. The as-synthesized Fe₃O₄@C electrode delivered specific charge capacities of 510, 425, 330, 246 and 163 mA h g⁻¹ at 0.2, 0.5, 1, 2 and 5 A g⁻¹ respectively for SIBs.

To increase the surface areas of the 3D network, self-assembly of ELPs was utilized instead. In chapter 6, synthesis of nanomaterials with more complex stoichiometries was also attempted. Here, ELP16 [(VPGIG)₂VPGKG(VPGIG)₂]₁₆ was mixed with LiH₂PO₄ / NaH₂PO₄ and NH₄VO₃ at 4 °C, followed by freezing drying and annealing. Li₃V₂(PO₄)₃ and Na₃V₂(PO₄)₃ nanostructures supported on hierarchically porous 3D aerogel composed of inter-connected fibrous carbon were obtained. The as-synthesized Li₃V₂(PO₄)₃ and Na₃V₂(PO₄)₃ were about 100 – 200 nm with a layer of carbon coating. The 3D Li₃V₂(PO₄)₃ / Na₃V₂(PO₄)₃ foams showed ultrahigh capacity at ultrafast charging/discharging properties and excellent cycle performance as cathodes for Li/Na secondary battery. The discharge capacities of Li₃V₂(PO₄)₃ were found to be 121, 112, 105, 91 and 79 mA h g⁻¹ at discharge rates of 5, 10, 20, 50 and 100 C. The 3D Na₃V₂(PO₄)₃ cathodes were also able to deliver reversible capacities of 109, 104, 99, 87, 73 and 51 mA h g⁻¹ at rates of 5, 10, 20, 50, 100 and 200 C.

In conclusion, the above four works demonstrate that biological templates including bacteria and polypeptides are promising for directing the building of various micro/nano structures of functional materials under mild conditions. The as-synthesized products exhibit superior performance in LIBs or SIBs.

7.2 Outlook

The future research work is recommended in the following aspects:

(1) As the Chapter 5 demonstrated, amino sequence with specific binding with iron / cobalt cations could be inserted into the ELP16 chain through genetic engineering. As such, the adsorption position of the cation is limited to the C-terminus of the protein backbone. It is thus beneficial to genetically engineer one or two more amino sequences that have specific binding with other metal cations such as Ti and Mn into the ELP16 chain next to his-tag. Mixed metal oxides embedded uniformly in a carbon matrix are expected to be obtained at comparatively lower annealing temperatures than the current methods.

(2) It is suggested to conduct full cell studies of the as-synthesized $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ and $\text{Na}_3\text{V}_2(\text{PO}_4)_3$. By varying anode materials such as graphite and lithium titanium oxide to yield optimized specific capacities, working voltage, and cycling stabilities.

(3) Other sequences of polypeptides with aimed properties are suggested to be designed and produced through recombinant protein technology to direct the formation of other micro/nano structures (such as hollow spheres and nanotubes) of functional materials.

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List of Publications

1. **Y.P. Zhou**, W.P. Sun, X.H. Rui, Y. Zhou, W.J. Ng, Q. Yan*, E. Fong*, Biochemistry-Derived Porous Carbon-Encapsulated Metal Oxide Nanocrystals for Enhanced Sodium Storage. *Nano Energy*, **21**, 71-79 (2016);
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