

Applications of Carbon Nanomaterials and Silicon-based Hybrid Composites in Lithium-ion Batteries

Applications of Carbon Nanomaterials and Silicon-based Hybrid Composites in Lithium-ion Batteries

By

Chang-Seop Lee, Angelica Martino
and Ruye Cong

Cambridge
Scholars
Publishing



Applications of Carbon Nanomaterials and Silicon-based Hybrid
Composites in Lithium-ion Batteries

By Chang-Seop Lee, Angelica Martino and Ruye Cong

This book first published 2024

Cambridge Scholars Publishing

Lady Stephenson Library, Newcastle upon Tyne, NE6 2PA, UK

British Library Cataloguing in Publication Data

A catalogue record for this book is available from the British Library

Copyright © 2024 by Chang-Seop Lee, Angelica Martino and Ruye Cong

All rights for this book reserved. No part of this book may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means, electronic, mechanical, photocopying, recording or otherwise, without the prior permission of the copyright owner.

ISBN (10): 1-0364-0035-2

ISBN (13): 978-1-0364-0035-4

TABLE OF CONTENTS

List of Illustrations	xii
List of Tables	xxix
Preface	xxxiii
Chapter 1	1
Introduction	
1. Lithium–ion batteries (LIBs) as an efficient energy storage system (ESS)	
1.1. Working principle of the LIBs	
1.2. Components of the conventional LIB	
1.3. Limitations of the current LIBs	
2. Silicon (Si) as an alternative to graphite anodes	
2.1. Properties of Si	
2.2. Related literature on utilizing the pure Si as anodes	
2.3. Challenges of the pure Si anodes	
2.4. Structural regulation of Si	
3. Utilization of diverse carbon nanomaterials to address Si challenges	
3.1. Related literature on Si and carbon nanomaterials hybrid LIB anodes	
3.2. Properties of carbon nanomaterials	
3.3. Carbon nanomaterials classified according to structure	
4. Three-dimensional graphite	
4.1. Structure and properties of graphite	
4.2. Synthetic routes to prepare graphite	
4.3. Graphite in Si-based LIB systems	
5. Two-dimensional graphene	
5.1. Structure and properties of graphene	
5.2. Synthetic routes to prepare graphene	
5.2.1. Chemical exfoliation by a modified Hummers method	
5.2.2. Electrochemical exfoliation method	
5.2.3. Graphene prepared via the CVD method	
5.3. Graphene in Si-based LIB systems	
6. One-dimensional CNFs	

6.1. Structure and properties of CNFs	
6.2. Synthetic routes to prepare CNFs	
6.2.1. CNFs prepared via the CVD route	
6.2.2. CNFs prepared via electrospinning	
6.3. CNFs in Si-based LIB systems	
7. Zero-dimensional Graphene quantum dots (GQDs)	
7.1. Structure and properties of GQDs	
7.2. Synthetic routes to prepare GQDs	
7.2.1. Top-down synthetic routes	
7.2.2. Bottom-up synthetic routes	
7.3. GQDs in Si-based LIB systems	
Acknowledgement	
Section References	

Section I: Silicon in Graphene and Carbon Nanofibers Hybrids

Chapter 2	76
LIBs based on Mechanical Mixing of Graphene, Carbon Nanofibers and Silicon	
Overview	
1. Introduction	
2. Experimental methods	
2.1. Synthesis of CNFs	
2.2. Preparation of Si/CNF/rGO and Si/rGO composites	
3. Analyses	
3.1. Structure and morphology	
3.2. Morphology and composition	
3.3. Crystalline structure	
3.4. Defect quantity	
3.5. Surface chemical states	
3.6. Thermal stability	
4. Electrochemical performance	
4.1. Cyclic voltammetry	
4.2. The effect of graphene and CNFs on Si/CNF/rGO cycling performance	
4.3. The effect of graphene and CNFs on Si/CNF/rGO electronic conductivity	
4.4. Volume expansion of electrode surface after delithiation cycles	
5. Summary	
6. Acknowledgement	

Chapter 3 99

LIBs based on Nitrogen-Doped Graphene, Carbon Nanofibers and Silicon
Overview

1. Introduction
2. Experimental methods
3. Analyses
 - 3.1. Structure and morphology
 - 3.2. Morphology and composition
 - 3.3. Crystalline structure
 - 3.4. Defect quantity
 - 3.5. Surface chemical states
 - 3.6. Chemical species
 - 3.7. Thermal stability
4. Electrochemical performance
 - 4.1. Cyclic voltammetry
 - 4.2. Cycling performance at low-current densities
 - 4.3. Coulombic efficiency of hybrids
 - 4.4. Rate capability
 - 4.5. SEI formation and chemical reaction kinetics
 - 4.6. Volume expansion of electrodes at lithiated states
5. Summary
6. Acknowledgments

Chapter 4 126

Carbon-coated Silicon in Nitrogen-doped Graphene
and Carbon Nanofibers

Overview

1. Introduction
2. Experimental methods
 - 2.1. Preparation of transition metal precursors
 - 2.2. Preparation of CVD-assisted CNFs
 - 2.3. Preparation of NG/C@Si/CNF hybrids
3. Analyses
 - 3.1. Structure and morphology
 - 3.2. Morphology and composition
 - 3.3. Crystalline structure
 - 3.4. Degree of graphitization
 - 3.5. Chemical states and chemical shift
 - 3.6. Chemical groups
 - 3.7. Thermal stability
4. Electrochemical performance

- 4.1. Rate capability
- 4.2. Cyclic voltammetry
- 4.3. Galvanostic charge and discharge profiles
- 4.4. Cycling performance
- 4.5. Volume expansion at lithiated states
- 4.6. Charge transfer kinetics
- 4.7. Formation of mechanically stable SEI
- 4.8. Li^+ storage mechanism
- 5. Summary
- 6. Acknowledgement
- Section References

Section II: Silicon in Graphene Quantum Dots and Carbon Nanomaterials

Chapter 5	176
-----------------	-----

Preparation of Graphene Quantum Dots, Carbon Nanofibers and Carbon Nanotubes

Overview

- 1. Introduction
- 2. Experimental methods
 - 2.1. Fabrication of OH-GQDs
 - 2.2. Preparation of positively charged SiNPs
 - 2.3. Preparation of GQD/SiNP composite
 - 2.4. Preparation of Si, GQD, CNF and CNT composites
- 3. Analyses
 - 3.1. Structure and morphology of OH-GQDs
 - 3.2. Elemental states
 - 3.3. Chemical species
 - 3.4. Structure and morphology of hybrids
 - 3.5. Crystalline structure
 - 3.6. Chemical states and chemical shift
 - 3.7. Degree of graphitization
- 4. Summary
- 5. Acknowledgement

Chapter 6	192
-----------------	-----

LIBs based on Graphene Quantum Dots, Graphene and Silicon

Overview

- 1. Introduction
- 2. Experimental methods

- 2.1. Fabrication of OH-GQDs
 - 2.2. Electrostatic assembly of composite hybrids
 - 2.3. Dual surface modifications of SiNP into SiOH and PDDA@SiOH
 - 2.4. Synergistic effects of OH-GQD and GO
 3. Analyses
 - 3.1. Evidence of successful Si surface modifications
 - 3.1.1. Surface and morphology
 - 3.1.2. Zeta potential values supporting Si surface modification
 - 3.1.3. Chemical species in surface-modified Si
 - 3.1.4. Surface chemical states of surface-modified Si
 - 3.2. Characterization of the fabricated OH-GQD
 - 3.2.1. Structure and morphology
 - 3.2.2. Crystalline structure
 - 3.2.3. Degree of graphitization
 - 3.2.4. Hydroxyl functionalization
 - 3.3. Characterization of the fabricated hybrid composites
 - 3.3.1. Structure and morphology
 - 3.3.2. Mechanism of Si surface modification and electrostatic assembly of hybrids
 - 3.3.3. OH-GQD in composite hybrids and coating efficiency
 - 3.3.4. Crystalline structure of composite hybrids
 - 3.3.5. Degree of graphitization and defect quantity
 - 3.3.6. Surface chemical states and chemical shifts
 - 3.3.7. Chemical bonds
 - 3.3.8. Thermal stability
 - 3.3.9. Shielding effect of OH-GQDs
 4. Electrochemical performance
 - 4.1. Cyclic voltammetry
 - 4.2. Cycling performance
 - 4.3. Rate performance
 - 4.4. Comparison of coulombic efficiency and rate capability over literature
 - 4.5. Synergistic effects influencing electrochemical performance
 - 4.6. Li^+ storage mechanism
 - 4.7. SEI formation and charge-transfer kinetics
 - 4.8. Volume expansion of hybrids at lithiated states
 - 4.9. Crystalline structure of hybrids at lithiated states
 5. Summary
 6. Acknowledgement
- Section References

Section III: Silicon in One-Dimensional Carbon

Chapter 7	256
LIBs based on Directly-Grown Carbon Nanofibers on Transition Metal-Coated Silicon	
Overview	
1. Introduction	
2. Experimental methods	
2.1. Fabrication of Ni@Si composites	
2.2. Synthesis of Ni@Si/CNFs composites	
3. Analyses	
3.1. Structure and morphology	
3.2. Effect of Ni concentration to coating efficiency	
3.3. Elemental composition of CVD-grown CNFs in Ni@Si/CNFs hybrids	
3.4. Quantitative analysis of CNFs content in Ni@Si/CNFs hybrids	
3.5. Crystalline structure of Ni@Si/CNFs hybrids	
3.6. Crystalline structure of Ni@Si/CNFs hybrids	
4. Electrochemical performance	
4.1. Initial Coulombic efficiency	
4.2. Cycling performance	
4.3. Cyclic voltammetry	
4.4. Stable SEI formation and charge transfer kinetics	
4.5. Rate capability	
5. Summary	
6. Acknowledgement	
Section References	

Section IV: Core-shell and Yolk-shell Silica-coated Silicon with Polymeric Carbon Coating

Chapter 8	286
LIBs based on Core-shell and Yolk-shell Silica-coated Silicon with Polydopamine Carbon Shell	
Overview	
1. Introduction	
2. Experimental methods	
2.1. Fabrication of core shell PDA-PEI@PVP-SiO ₂ @Si composites	

- 2.2. Fabrication of yolk shell PDA-PEI@PVP-SiO₂@Si composites
 - 3. Analyses
 - 3.1. Role of APTES in the synthesis of SiO₂@Si shells
 - 3.2. Multifaceted effects of proposed modified Stöber via hydrothermal treatment
 - 3.2.1. Maintaining crystallinity of Si active material
 - 3.2.2. Polymeric coating efficiency
 - 3.3. Significance of PVP K30 surface protection during NaOH etching
 - 3.4. Characteristics of representative core shell and yolk shell hybrids
 - 3.4.1. Surface composition
 - 3.4.2. Defect quantity and degree of graphitization
 - 3.4.3. Thermal stability
 - 4. Electrochemical performance
 - 4.1. Cyclic voltammetry
 - 4.2. Cycling performance and Coulombic efficiency
 - 4.3. Rate capability
 - 4.4. Factors affecting cycling and rate performance
 - 4.5. Li⁺ diffusion and storage mechanisms
 - 4.6. Stable SEI formation
 - 5. Summary
 - 6. Acknowledgement
- Section References

Index	336
-------------	-----

LIST OF ILLUSTRATIONS

- Fig. 1-1.** Schematic of the operational mechanism of the LIB
- Fig. 1-2.** Schematic illustrating the detrimental effects of the severe volume expansion of Si particles—inducing the formation of cracks, generation of a thick and unstable SEI film, and pulverization of Si morphology upon repeated cycling.
- Fig. 1-3.** Crystal lattice structure of graphite illustrating the ABA stacking of its layers. The covalently bonded hexagonal planes exhibit weak van der Waals forces across the planes.
- Fig. 1-4.** Flow chart illustrating the general manufacturing process of the bulk artificial graphite
- Fig. 1-5.** The hexagonal lattice of graphene showing a unit cell. (a) Carbon atoms represented by A and B appear as triangular sublattices, while a_1 and a_2 represent lattice unit vectors. (b) The first Brillouin zone (BZ) of graphene showing symmetry point.
- Fig. 1-6.** Zigzag and armchair edge structure of monolayer graphene nanoribbons
- Fig. 1-7.** Organosulfates present in graphene oxide prepared via the Hummers method
- Fig. 1-8.** Schematic illustrating the chemical evolutions from graphitic system to oxidized domains of cleaved graphene layer
- Fig. 1-9.** Preparation of graphene oxide based on an improved Hummers method

- Fig. 1-10.** Schematic showing the thermal reduction of graphene oxide prepared via the Hummers method and conversion into reduced graphene oxide
- Fig. 1-11.** Experimental set-up the IL-assisted graphite anode exfoliation via electrochemical routes
- Fig. 1-12.** Schematic showing the mechanism for producing few-layer graphene from the exfoliation of graphite, wherein the intercalation at graphite edges leads to exfoliation, and graphene is obtained via ultrasonication
- Fig. 1-13.** Schematic of the proposed exfoliation mechanism highlighting the role of peroxide ions in the intercalation of ions between graphite layers to form graphene sheets
- Fig. 1-14.** Schematic of the electrochemical set-up using a HOPG electrode dipped in acidic electrolyte solution
- Fig. 1-15.** Schematic of a multiple electrochemical exfoliation (MEE) using a vertical cell configuration.
- Fig. 1-16.** Representative schematic of (a) a thermal CVD set-up and (b) a PECVD system for graphene synthesis.
- Fig. 1-17.** Diagram showing the general growth mechanism of CVD-assisted graphene synthesis
- Fig. 1-18.** Schematic of the reduction of graphene oxide to reduced graphene oxide.
- Fig. 1-19.** Schematic of the structure of N-doped reduced graphene oxide.
- Fig. 1-20.** Representation of CNFs structure according to the angle of the graphene stack with respect to fiber axis

- Fig. 1-21.** The structure of CNFs.
- Fig. 1-22.** Process diagram for the synthesis of CNFs via CVD.
- Fig. 1-23.** Schematic of a typical setup for electrospinning
- Fig. 1-24.** Typical edge conformational pattern of GQDs: (a) armchair, (b) zigzag, and (c) a combination of both.
- Fig. 2-1.** Process for preparing the catalysts and the synthesis of carbon nanofibers.
- Fig. 2-2.** Preparation process of Si/CNF/rGO and Si/rGO composite films.
- Fig. 2-3.** SEM images of the (a–c) Si/rGO and (d–f) Si:CNF/rGO=1:1 composites.
- Fig. 2-4.** TEM images of (a–c) Si/rGO, (d–f) Si:CNF/rGO=1:1 composites. High-resolution TEM images of (g) Si/rGO and (h) Si:CNF/rGO=1:1 composites.
- Fig. 2-5.** X-ray diffraction patterns of Si/CNF/rGO, Si/CNFs, CNFs, Si/rGO, Si, rGO, and GO.
- Fig. 2-6.** Raman spectra of the Si/CNF/rGO composite, CNFs, Si/rGO composite, rGO, and GO.
- Fig. 2-7.** C 1 s XPS spectra of (a) Si/GO, (b) Si/CNFs/GO, (c) Si/rGO, and (d) Si/CNF/rGO. (e) Si 2p XPS spectrum of Si/CNF/rGO.
- Fig. 2-8.** TGA curves of the Si/rGO, Si:CNF/rGO=3:2, Si:CNF/rGO=1:1, and Si:CNF/rGO=2:3 samples.
- Fig. 2-9.** TGA curves of the Si:CNF/rGO =1:1 composite.
- Fig. 2-10.** Cyclic voltammetry curves of the synthesized Si/CNF/rGO=1:1 composite in the initial five cycles.

- Fig. 2-11.** Cycling performances of the synthesized Si/rGO and Si/CNF/rGO=1:1, 2:3, and 3:2 composite electrodes at a current density of $0.1 \text{ A} \cdot \text{g}^{-1}$.
- Fig. 2-12.** Cycling performances of the synthesized (a) Si/rGO, (b) Si:CNF/rGO = 3:2, (c) Si:CNF/rGO = 2:3, and (d) Si:CNF/rGO = 1:1 composite electrodes at a current density of $0.1 \text{ A} \cdot \text{g}^{-1}$.
- Fig. 2-13.** (a) Nyquist plots and electrochemical impedance spectra of the Si:CNF/rGO=1:1, 3:2, and 2:3 and Si/ rGO composite anodes before cycling. (b) Nyquist plots and electrochemical impedance spectra of the Si:CNF/ rGO=1:1, 3:2, and 2:3, and Si/rGO composites anode after cycling. EIS curves of the (c) Si/rGO composites anode and (d) Si:CNF/rGO=1:1 composite anode after the 50th and 100th cycles.
- Fig. 2-14.** Nyquist plots and electrochemical impedance spectra of the (a) Si:CNF/rGO = 2:3 and (b) Si:CNF/rGO = 3:2 anodes after 50 and 100 cycles.
- Fig. 2-15.** SEM images of the surface of (a–c) Si/CNF/rGO electrodes before the first cycle and (d–f) after 100th cycles at a current density of $100 \text{ mA} \cdot \text{g}^{-1}$.
- Fig. 3-1.** Schematic diagram of the preparation process of Si/N-doped rGO/CNF and Si/N-doped rGO composite material.
- Fig. 3-2.** SEM images of the (a–c) Si@N-doped rGO and (d, e) Si@N-doped rGO/CNF composites and the EDS result of Si@N-doped rGO/CNF.
- Fig. 3-3.** TEM images of (a, b) Si@N-doped rGO, (c, d) Si@N-doped rGO/CNF composites, (e) High-resolution TEM images of Si@N-doped rGO/ CNF composites, (f) Selected Area Electron Diffraction (SAED) pattern of Si.

- Fig. 3-4.** The EDS mapping of the Si, N, C, O elements on the surface of the Si@N-doped rGO/CNF composite.
- Fig. 3-5.** X-ray diffraction patterns of GO, rGO, CNF, Si, Si@N-doped rGO, and Si@N-doped rGO/CNF.
- Fig. 3-6.** Raman spectra of the GO, rGO, CNF, Si@APTES/N-doped GO, Si/rGO, Si@N-doped rGO, and Si@N-doped rGO/CNF.
- Fig. 3-7.** Survey XPS spectra of Si@APTES, Si@APTES/N-doped GO, Si@APTES/N-doped GO/CNF, Si@N-doped rGO, and Si@N-doped rGO/CNF.
- Fig. 3-8.** Si 2p XPS spectra of Si, Si-OH, Si@APTES, Si@APTES/N-doped GO, Si@APTES/N-doped GO/CNF, Si@N-doped rGO and Si@N-doped rGO/CNF.
- Fig. 3-9.** C 1s XPS spectra of Si-OH, Si@APTES, Si@APTES/N-doped GO/CNF and Si@N-doped rGO/CNF.
- Fig. 3-10.** N 1s XPS spectra of Si@APTES and Si@N-doped rGO/CNF.
- Fig. 3-11.** FT-IR spectra of Si, Si@OH, and Si@APTES.
- Fig. 3-12.** FT-IR spectra of GO and Si@APTES/N-doped GO and Si@APTES/N-doped GO/CNF.
- Fig. 3-13.** TGA curves of the pure nano-Si, Si@N-doped rGO, and Si@N-doped rGO/CNF composite material.
- Fig. 3-14.** Cyclic voltammetry curves of the synthesized (a) Si@N-doped rGO and (b) Si@N-doped rGO/CNF electrodes in the initial five cycles.
- Fig. 3-15.** Cycling performances of the synthesized Si/CNF/rGO, Si@N-doped rGO, and Si@N-doped rGO/CNF composite electrodes at a current density of $0.1 \text{ A} \cdot \text{g}^{-1}$.

- Fig. 3-16.** Charging and discharging cycle performance and Coulomb efficiency of Si@N-doped rGO and Si@N-doped rGO/CNF electrodes.
- Fig. 3-17.** Rate performances of Si@N-doped rGO and Si@N-doped rGO/CNF electrodes under different current densities.
- Fig. 3-18.** Nyquist plots and electrochemical impedance spectra of the Si/CNF/rGO, Si@N-doped rGO, and Si@N-doped rGO/CNF composite electrodes (a) before and (b) after 100 cycles.
- Fig. 3-19.** SEM images of the surface of (a–c) Si/rGO/CNF, Si@N-doped rGO, and Si@N-doped rGO/CNF electrodes before the first cycle. SEM images of the surface of (d–f) Si/rGO/CNF, Si@N-doped rGO, and Si@N-doped rGO/CNF electrodes after the 100th cycle at a current density of 0.1 A g⁻¹.
- Fig. 4-1.** Proposed process for preparing the catalysts and synthesis of carbon nanofibers (CNFs).
- Fig. 4-2.** Schematic diagram for the preparation process of NG/C@Si/CNF composite material.
- Fig. 4-3.** Schematic diagram of the chemical reaction process of the melamine formaldehyde resin (MFR) formed by the polymerization of formaldehyde and melamine.
- Fig. 4-4.** SEM images of the (a, b) NG/C@Si, (c, d) G@Si/CNF, and (e, f) NG/C@Si/CNF composites.
- Fig. 4-5.** Representative TEM images of (a, b) NG/C@Si, (c, d) G@Si/CNF and (e, f) NG/C@Si/CNF composites, (g) HRTEM images of NG/C@Si/CNF composites, and (h) SAED pattern of Si.
- Fig. 4-6.** EDS mapping of the Si, N, C, and O elements on the surface of the NG/C@Si/CNF composite.

- Fig. 4-7.** XRD patterns of Si, GO, rGO, CNF, NG/C@Si/CNF, NG/C@Si, and G@Si/CNF.
- Fig. 4-8.** Raman spectra of Si, GO, rGO, CNF, NG/C@Si/CNF, NG/C@Si, and G@Si/CNF.
- Fig. 4-9.** (a) Survey XPS spectra of NG/C@Si/CNF, G@Si/CNF, and NG/C@Si. (b) Si 2p XPS spectrum of NG/C@Si/CNF, (c) C 1s XPS spectrum of NG/C@Si/CNF, (d) N 1s XPS spectrum of NG/C@Si/CNF.
- Fig. 4-10.** Representative Si 2p XPS spectra of (a) Si-OH, (b) Si-NH₂, (c) GO/MFR@Si/CNF, and (d) NG/C@Si/CNF.
- Fig. 4-11.** FT-IR spectra of pure nano-Si, Si-OH, Si-NH₂, GO, and NG/C@Si/CNF.
- Fig. 4-12.** TGA curves of pure nano-Si, G@Si/CNF, NG/C@Si, and NG/C@Si/CNF composite materials.
- Fig. 4-13.** Rate performances of the G@Si/CNF, NG/C@Si, and NG/C@Si/CNF electrodes under different current densities.
- Fig. 4-14.** CV curves of the NG/C@Si/CNF electrode in the initial five cycles.
- Fig. 4-15.** Cyclic voltammetry curves of the (a) G@Si/CNF and (b) NG/C@Si composite electrode in the initial five cycles.
- Fig. 4-16.** The charge and discharge profiles of the NG/C@Si/CNF composite electrode
- Fig. 4-17.** The charge and discharge profiles of (a) G@Si/CNF and (b) NG/C@Si composite electrode.

- Fig. 4-18.** Cycling performances of the G@Si/CNF, NG/C@Si, and NG/C@Si/CNF composite electrodes at a current density of 0.1 A g⁻¹.
- Fig. 4-19.** The cycling performances of the synthesized (a) G@Si/CNF and (b) NG/C@Si composite electrode at a current density of 0.1 A g⁻¹.
- Fig. 4-20.** Charging and discharging cycle performance and Coulombic efficiency of the NG/C@Si/CNF composite electrode at a current density of 0.1 A g⁻¹.
- Fig. 4-21.** Representative SEM images from cross section view of the (a) NG/C@Si/CNF, (b) G@Si/CNF, and (c) NG/C@Si electrodes before the first cycle and (d, e, f) after 100 lithiation/delithiation cycles at a current density of 0.1 A g⁻¹, respectively.
- Fig. 4-22.** Nyquist plots and electrochemical impedance spectra of the G@Si/CNF, NG/C@Si, and NG/C@Si/CNF composite electrodes (a) before cycling.
- Fig. 4-23.** Nyquist plots and electrochemical impedance spectra of the G@Si/CNF, NG/C@Si, and NG/C@Si/CNF composite electrodes (a) after 100 lithiation/delithiation cycles.
- Fig. 4-24.** Representative SEM images from surface view of (a) NG/C@Si/CNF, (b) G@Si/CNF and (c) NG/C@Si electrodes before the first cycle and (d, e, f) after 100 lithiation/delithiation cycles at a current density of 0.1 A g⁻¹, respectively.
- Fig. 5-1.** OH-GQDs synthesis and irradiation with 365 nm UV light.
- Fig. 5-2.** Synthesis process of GQD/SiNP/CNFs and GQD/SiNP/CNTs composites.

- Fig. 5-3.** TEM images of synthesized OH-GQDs at different scales at (a) 10 nm, and (b, c) at 2 nm magnification.
- Fig. 5-4.** XPS spectrum of synthesized OH-GQDs.
- Fig. 5-5.** FT-IR spectrum of synthesized OH-GQDs.
- Fig. 5-6.** FT-IR spectra of GQD/SiNP composites (a) before annealing at 450 °C and (b) after annealing at 450 °C.
- Fig. 5-7.** SEM images at 2 μm scale (a) CNFs, (b) GQD/SiNP/ CNFs composite, (c) CNTs, and (d) GQD/SiNP/CNTs composite.
- Fig. 5-8.** TEM images at different scales (a–c) GQD/SiNP/CNFs composite and (d–f) GQD/SiNP/CNTs composite. Scales are (a) and (d) at 100 nm, (b) and (e) at 50 nm, and (c) and (f) at 20 nm.
- Fig. 5-9.** XRD patterns of (a) GQD/SiNP/CNTs composite, (b) GQD/ SiNP/CNFs composite, (c) CNTs, (d) CNFs, (e) OH-GQDs, and (f) SiNPs.
- Fig. 5-10.** XPS spectra of (a–c) GQD/SiNP/CNFs, (d–f) GQD/SiNP/CNTs composites. (a), (d) survey spectra of GQD/SiNP/CNFs and GQD/SiNP/CNTs composites (50,000 counts s⁻¹), (b), (e) C 1s hyperfine spectra of GQD/SiNP/CNFs and GQD/SiNP/CNTs composites (10,000 counts/s), (c), (f) Si 2p hyperfine spectra of GQD/SiNP/CNFs and GQD/SiNP/CNTs composites (100 counts s⁻¹).
- Fig. 5-11.** Raman spectra of GQD/SiNP/CNFs (black) and GQD/SiNP/ CNTs (red) composites.
- Fig. 6-1.** Schematic representation of the fabrication process of OH-GQD@Si/rGO.

- Fig. 6-2.** SEM images of pure SiNP (a), SiOH following piranha treatment, and (c) EDS of PDDA@SiOH after PDDA modification
- Fig. 6-3.** Structural formula of PDDA.
- Fig. 6-4.** FTIR results comparing (a) SiNP and SiOH against (b) PDDA@SiOH.
- Fig. 6-5.** XPS high-resolution (a) Cl 2p and (b) N 1s spectra of PDDA@SiOH.
- Fig. 6-6.** TEM images of (a–d) fabricated OH-GQD at various magnifications.
- Fig. 6-7.** Height distribution profile of fabricated OH-GQDs.
- Fig. 6-8.** XRD pattern of OH-GQD in comparison with GO and rGO.
- Fig. 6-9.** Raman spectra of OH-GQD in comparison with GO and rGO.
- Fig. 6-10.** FT-IR result of fabricated OH-GQDs.
- Fig. 6-11.** XPS high-resolution (a) O 1s and (b) C 1s spectra of OH-GQDs.
- Fig. 6-12.** SEM images of (a–c) 0.2OH-GQD@Si/0.2rGO-1 and (d–f) 0.3OH-GQD@Si/0.1rGO-2 at different magnifications.
- Fig. 6-13.** Zeta potential values of SiOH, PDDA@SiOH, OH-GQD, OH-GQD@PDDA@SiOH, GO, and OH-GQD@PDDA@SiOH/GO showing distinct opposing charges of particles.
- Fig. 6-14.** Zeta potential values of PDDA@SiOH, OH-GQD, and GO at different pH concentrations.
- Fig. 6-15.** TEM images of (a, c, e) 0.2OH-GQD@Si/0.2rGO-1 and (b, d, f) 0.3OH-

GQD@Si/0.1rGO-2 at different magnifications demonstrating individual lattice spacing assigned to (e, f) Si, OH-GQD, and rGO. High crystallinity was verified by the (g) SAED image and representative (h inset) FFT pattern of 0.3OH-GQD@Si/0.1rGO-2.

- Fig. 6-16.** XRD patterns of GO, rGO, OH-GQD, Si, 0.2OH-GQD@Si/0.2rGO-1, and 0.3OH-GQD@Si/0.1rGO-2.
- Fig. 6-17.** JCPDS Face-centered cubic Si crystal.
- Fig. 6-18.** Cubic carbon oxide crystal (Reference code 98-002-6962).
- Fig. 6-19.** Raman spectra of GO, rGO, OH-GQD, 0.2OH-GQD@Si/0.2rGO-1 and 0.3OH-GQD@Si/0.1rGO-2, including corresponding spectra before thermal annealing/reduction.
- Fig. 6-20.** Gaussian–Lorentzian model fitting and parameters for (a) GO, (b) rGO and (c) OH-GQD samples.
- Fig. 6-21.** Gaussian–Lorentzian model fitting and parameters for (a) OH-GQD@Si/GO-1, (b) OH-GQD@Si/rGO-1, (c) OH-GQD@Si/GO-2, and (d) OH-GQD@Si/rGO-2.
- Fig. 6-22.** XPS survey spectra of the composites.
- Fig. 6-23.** XPS High-resolution (a, d) C 1s, (b, e) O 1s, and (c, f) N 1s spectra of 0.2OH-GQD@Si/0.2rGO-1 and 0.3OH-GQD@Si/0.1rGO-2 composites, respectively.
- Fig. 6-24.** FTIR spectra of the various OH-GQD@Si/rGO samples.

- Fig. 6-25.** FT-IR showing the conversion of GO into rGO via thermal reduction.
- Fig. 6-26.** TGA/DTA curves of (a) 0.2OH-GQD@Si/0.2rGO-1 and (b) 0.3OH-GQD@Si/0.1rGO-2 composites.
- Fig. 6-27.** CV profiles of (a) 0.2OH-GQD@Si/0.2rGO-1 and (b) 0.3OH-GQD@Si/0.1rGO-2 electrodes during initial five cycles.
- Fig. 6-28.** (a) Cycling performance of 0.3OH-GQD@Si/0.1rGO-2 and 0.2OH-GQD@Si/0.2rGO-1 with corresponding (b, c) Galvanostatic charge and discharge profiles at a current density of 100 mA g⁻¹, respectively.
- Fig. 6-29.** (a) Rate performance of 0.3OH-GQD@Si/0.1rGO-2 and 0.2OH-GQD@Si/0.2rGO-1 with corresponding (b, c) Galvanostatic charge and discharge profiles at different current densities, respectively.
- Fig. 6-30.** (a) Charge and discharge capacities of 0.2OH-GQD@Si/0.2rGO-1 and 0.3OH-GQD@Si/0.1rGO-2 with corresponding CE at a current density of 100 mA g⁻¹. (b) The rate capability of 0.3OH-GQD@Si/0.1rGO-2 composite compared to prior works.
- Fig. 6-31.** Nyquist plots and electrochemical impedance spectra of 0.2OH-GQD@Si/0.2rGO-1 and 0.3OH-GQD@Si/0.1rGO-2 (a) before cycling and (b) after the 30th cycle.
- Fig. 6-32.** SEM images showing the surface of the (a–b) 0.2OH-GQD/0.2rGO-1 and (c–d) 0.3OH-GQD/0.1rGO-2 electrodes before and (e–f, g–h) after 50 lithiation/delithiation cycles at a current density of 100 mA g⁻¹, respectively.
- Fig. 6-33.** SEM images showing the cross-sectional view of the 0.2OH-GQD@Si/0.2rGO-1 and 0.3OH-

GQD@Si/0.1rGO-2 electrodes (a, b) before and (c, d) after 50 cycles, respectively.

Fig. 6-34. XRD thin film analysis of the 0.2OH-GQD/0.2rGO-1 and 0.3OH-GQD/0.1rGO-2 electrodes before and after 50 lithiation/delithiation cycles.

Fig. 6-35. JCPDS of a cubic copper crystal (Reference code 01-070-3039).

Fig. 6-36. JCPDS of a cubic silicon carbide crystal (Reference code 98-018-2362).

Fig. 7-1. (a) Schematic diagram of the transition metal@Si composites synthesized by reacting hexahydrate metal ions with ammonia water; (b) process for the synthesis of Ni@Si/CNFs composites.

Fig. 7-2. TEM images of transition metal-coated Si nanoparticles with (a, b) 0.01 M $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ solution and (c, d) 0.01 M $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ solution; TEM images of transition metal-coated Si nanoparticles with (e, f) 0.01 M $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ solution and (g, h) 0.1 M $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ solution.

Fig. 7-3. SEM images of the (a, b) 0.01 M Ni@Si composites, (c, d) 0.01 M-Ni@Si/CNFs composites, (e, f) 0.02 M Ni@Si composites, and (g, h) 0.02 M-Ni@Si/CNFs composites.

Fig. 7-4. TGA curves of the 0.01 M-Ni@Si/CNFs composites and 0.02 M-Ni@Si/CNFs composites.

Fig. 7-5. XRD patterns of the synthesized Ni@Si/CNFs composites and pure Si.

Fig. 7-6. Raman spectra of Si, CNFs, 0.01 M-Ni@Si/CNFs and 0.02 M-Ni@Si/CNFs composites.

- Fig. 7-7.** Voltage profiles of the (a) 0.01 M-Ni@Si/CNFs and (b) 0.02 M-Ni@Si/CNFs electrodes for the first and second discharge–charge cycle.
- Fig. 7-8.** Cycle performances of the synthesized (a) 0.01 M-Ni@Si/CNFs electrodes and (b) 0.02 M-Ni@Si/CNFs electrodes for 100 cycles.
- Fig. 7-9.** CV profiles of (a) 0.01 M-Ni@Si/CNFs and (b) 0.02 M-Ni@Si/CNFs electrodes during initial five cycles.
- Fig. 7-10.** Nyquist plots and electrochemical impedance spectra of 0.01 M-Ni@Si/CNFs and 0.02 M-Ni@Si/CNFs (a) before cycling and (b) after the 30th cycle.
- Fig. 7-11.** Rate performance of 0.01 M-Ni@Si/CNFs and 0.02 M-Ni@Si/CNFs composites.
- Fig. 7-12.** Galvanostatic charge and discharge profiles of (a) 0.01 M-Ni@Si/CNFs and (b) 0.02 M-Ni@Si/CNFs at different current densities.
- Fig. 8-1.** Schematic representation of the fabrication process of core shell and yolk shell PDA-PEI@PVP-SiO₂@Si composites.
- Fig. 8-2.** FE-SEM images of (a) TEOS-derived SiO₂@Si and (b) APTES/TEOS-derived SiO₂@Si via catalyst-free Stöber route synthesis at room temperature.
- Fig. 8-3.** FE-SEM image of (a) pure Si nanoparticles. (b) FT-IR result comparing pure Si nanoparticles and Si-OH after piranha solution pre-treatment.
- Fig. 8-4.** TEM images of (a–d) TEOS-derived SiO₂@Si and (e–h) APTES/TEOS-derived SiO₂@Si nanoparticles after a catalyst-free, sol-gel synthesis at room temperature.

- Fig. 8-5.** (a) Formation of siloxane networks from piranha-treated Si-OH using APTES. (b) Hydrolysis and (c) condensation reaction mechanism of TEOS showing formation of siloxane bridges.
- Fig. 8-6.** XPS high resolution (a, d) Si 2p, (b, e) O 1s, and (c, f) C 1s scans of (a–c) TEOS-SiO₂@Si and (d–f) APTES/TEOS-SiO₂@Si samples. The insets at (c) and (f) shows the Si-C peaks within respective samples.
- Fig. 8-7.** XRD patterns of core shell and yolk shell PDA-PEI@PVP-SiO₂@Si composites fabricated from hydrothermally assisted modified Stöber (HT) compared with the control group fabricated conventional sol-gel reaction at room temperature (RT), before and after pyrolysis, and after NaOH etching processes.
- Fig. 8-8.** XRD patterns of (a) Si and (b) TEOS-derived SiO₂@Si and APTES/TEOS-derived SiO₂@Si.
- Fig. 8-9.** XRD reference peaks for face-centered cubic Si crystal (Reference code 98-065-2265).
- Fig. 8-10.** FE-SEM images of (a, c, e) composite samples prepared via RT and (b, d, f) HT before and after pyrolysis and NaOH etching of SiO₂ template.
- Fig. 8-11.** TEM images showing carbon crosslinking from PEI and PDA carbon coating efficiency in (a, b) composite samples prepared via traditional SiO₂ sol-gel synthesis reaction and carbon coating at room temperature and (c, d) composite samples prepared via hydrothermal treatment at 140 °C for 24 h.
- Fig. 8-12.** FTIR spectra of APTES/TEOS-SiO₂@Si, PVP-SiO₂@Si, HT-PDA-PEI@PVP-SiO₂@Si, core shell PDA-PEI@PVP-SiO₂@Si and yolk shell

PDA-PEI@PVP-SiO₂@Si samples with PVP K30-surface protection.

- Fig. 8-13.** TEM images of composite samples fabricated via hydrothermal treatment of APTES/TEOS-SiO₂@Si seeds (a, b) with and (c, d) without PVP K30 surface protection after NaOH etching.
- Fig. 8-14.** XPS high resolution (a) Si 2p, (b) O 1s, (c) C 1s, and (d) N 1s scans of APTES/TEOS-SiO₂@Si after PVP K30 polymer loading via proposed hydrothermal route. The inset in Figure (c) shows the different carbon atoms in the PVP K30 molecular structure.
- Fig. 8-15.** XPS high-resolution (a, e) Si 2p, (b, f) O 1s, (c, g) C 1s, and (d, h) N 1s scans of (a–d) core shell PDA-PEI@SiO₂@Si and (e–h) yolk shell PDA-PEI@SiO₂@Si composite samples.
- Fig. 8-16.** Illustration of the two possible reaction mechanisms showing the formation of PDA-PEI carbon crosslinks.
- Fig. 8-17.** XPS high-resolution (a, e) Si 2p, (b, f) O 1s, (c, g) C 1s, and (d, h) N 1s scans of (a–d) core shell PDA@SiO₂@Si and (e–h) yolk shell PDA-PEI@PVP-SiO₂@Si composite samples.
- Fig. 8-18.** Raman spectra of (a) TEOS-SiO₂@Si, (b) APTES/TEOS-SiO₂@Si, (c) PVP-SiO₂@Si, (d) core shell PDA@SiO₂@Si, (e) yolk shell PDA-PEI@SiO₂@Si, (f) yolk shell PDA-PEI@PVP-SiO₂@Si, and (g) core shell PDA-PEI@SiO₂@Si samples.
- Fig. 8-19.** Raman peak fitting of (a) core shell PDA@SiO₂@Si, (b) yolk shell PDA-PEI@SiO₂@Si, (c) yolk shell PDA-PEI@PVP-SiO₂@Si, and (d) core shell PDA-PEI@SiO₂@Si composite samples.

- Fig. 8-20.** (a) TG curves of (a) core shell PDA@SiO₂@Si, (b) yolk shell PDA-PEI@PVP-SiO₂@Si, (c) yolk shell PDA-PEI@SiO₂@Si, and (d) core shell PDA-PEI@SiO₂@Si samples. (b) TG-DTA and DTG curves of representative composite yolk shell PDA-PEI@PVP-SiO₂@Si sample. (c) DTG curves of core shell PDA@SiO₂@Si sample and (d) other composites.
- Fig. 8-21.** CV profiles of (a) core shell PDA@SiO₂@Si in RT, (b) core shell PDA@SiO₂@Si in HT, (c) yolk shell PDA-PEI@PVP-SiO₂@Si in HT, and (d) yolk shell PDA-PEI@SiO₂@Si in HT during the initial five cycles.
- Fig. 8-22.** CV scans of core shell PDA-PEI@TEOS-SiO₂@Si composite fabricated via RT using TEOS as precursor solution.
- Fig. 8-23.** (a) Cycling performance of composite samples with (b) galvanostic charge and discharge profiles of representative yolk shell PDA-PEI@PVP-SiO₂@Si composite sample via HT. (c) The corresponding CE values of composite samples at 0.1 A g⁻¹ over 100 lithiation/delithiation cycles.
- Fig. 8-24.** Rate performance of representative composite samples.
- Fig. 8-25.** Nyquist plots and electrochemical impedance spectra of the fabricated composites (a) before cycling and (b) after 100 lithiation/delithiation cycles.

LIST OF TABLES

- Table 1-1.** Characteristics of cathode in LIBs.
- Table 1-2.** Types and characteristics of anode materials in lithium secondary batteries.
- Table 1-3.** Types and characteristics of electrolytes in LIBs.
- Table 1-4.** Types and characteristics of LIBs separators.
- Table 1-5.** A summary of the crystal structure, unit cell volume, and volume per Si atom in various Li–Si systems.
- Table 1-6.** Characteristics of the biphasic reactions of various Li–Si systems during Si lithiation.
- Table 1-7.** Classification of carbon fibers according to mechanical properties
- Table 2-1.** EDX spectral results of the Si:CNF/rGO = 1:1, 3:2, and 2:3 composites.
- Table 2-2.** Raman spectroscopy results of the GO, rGO, CNFs, Si/rGO, and Si/CNF/rGO samples.
- Table 2-3.** Discharge capacity, coulomb efficiency, and capacity retention rate of the Si/rGO and Si:CNF/rGO = 1:1, 3:2, and 2:3 composite electrodes.
- Table 2-4.** R_{CT} and R_{SEI} values calculated from the EIS spectra.
- Table 3-1.** Raman spectroscopy results of the GO, rGO, CNFs, Si/rGO, and Si/CNF/rGO samples.

- Table 3-2.** Discharge capacity, Coulombic efficiency, and capacity retention rate of the Si/CNF/rGO, Si@N-doped rGO and Si@N-doped rGO/CNF composite electrodes.
- Table 4-1.** Raman spectroscopy results for the GO, rGO, CNFs, NG/C@Si/CNF, G@Si/CNF, and NG/C@Si samples.
- Table 4-2.** Discharge capacity, Coulomb efficiency, and capacity retention rate of the NG/C@Si/CNF, G@Si/CNF, and NG/C@Si composite electrodes.
- Table 5-1.** EDS analysis results of GQD/SiNP/CNFs and GQD/SiNP/ CNTs composites.
- Table 6-1.** Zeta potential values of different samples at two different diluted concentrations.
- Table 6-2.** Determination of IEP and optimum pH range for electrostatic assembly of PDDA@SiOH, OH-GQD and GO at half of the recommended dilution concentration according to particle size.
- Table 6-3.** Peak list for a Si crystal (JCPDS 27-1402).
- Table 6-4.** Peak list for a cubic carbon oxide crystal (Reference code 98-002-6962).
- Table 6-5.** The I_D/I_G values of the samples calculated by the ratio of the D band peak area to the G band peak area using Gaussian-Lorentzian curve fitting model.
- Table 6-6.** Summary of phase transformations in SiNP during cycling.
- Table 6-7.** Comparison of fitted parameters obtained from Nyquist plots for 0.2OH-GQD@Si/0.2rGO-1 and 0.3OH-GQD@Si/0.1rGO-2 composite anodes.