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SINGAPORE

**NEW METHODS TO SYNTHESIZE NANOSIZED OXIDES FOR
ENERGY STORAGE APPLICATIONS**

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SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

2018

NEW METHODS TO SYNTHESIZE NANOSIZED OXIDES FOR ENERGY STORAGE APPLICATIONS

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SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

A thesis submitted to the Nanyang Technological University
in partial fulfilment of the requirement for the degree of
Doctor of Philosophy

2018

Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research and has not been submitted for a higher degree to any other University or Institution.

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Vincent Ng Ming Hong

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I have reviewed the content and presentation style of this thesis and declare it is free of plagiarism and of sufficient grammatical clarity to be examined. To the best of my knowledge, the research and writing are those of the candidate except as acknowledged in the Author Attribution Statement. I confirm that the investigations were conducted in accord with the ethics policies and integrity standards of Nanyang Technological University and that the research data are presented honestly and without prejudice.

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Authorship Attribution Statement

This thesis contains material from (a) paper(s) published in a/the following peer-reviewed journal(s) where I was the first and/or corresponding author.

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- Dr. Huang and Assoc. Prof. Kong suggested the topic on MXenes and edited the manuscript drafts.
- I wrote the manuscript drafts.
- The manuscript was reviewed, commented and revised together with Assoc. Prof. Zhou, Prof. Lee, Prof. Que and Assoc. Prof. Xu.

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The contributions of the co-authors are as follows:

- Assoc. Prof. Kong provided the initial project direction and edited the manuscript drafts.
- I conducted all the experiments, analyzed the data and wrote the manuscript drafts. The manuscript was commented by Dr. Wang, Dr. Huang, Assoc. Prof. Xu, Prof. Yao, Prof. Zhou and Prof. Que.
- Ms. Wu helped in the synthesis and TGA characterization.
- Dr. Liu and Dr. Zhu advised on the flow of information and presentation of data.

- Dr. Yu provided guidance to the assembly of half-cells in a glovebox and the collection of electrochemical measurement data.

03/08/2018

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Date

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Vincent Ng Ming Hong

Abstract

The proliferation of portable consumer electronics has been built upon the breakthrough in electrode materials for rechargeable electrochemical energy storage — coinciding with the advent of lithium-ion batteries (LIBs) technology. Coupled with the lifestyles of the burgeoning global population becoming more energy intensive, it has evolved into both a technological and societal demand for the development of more cost-efficient and durable batteries. The consensual approach towards tackling intermittency of renewable energy sources and improving the competitiveness of electric vehicles necessitates an energy storage system to reversibly uptake and release greater quantity of charges and to reliably do so at a much faster rate. However, the incumbent graphitic anode material in existing commercialized LIBs is inherently limited in both capacity (energy density) and rate performance (power density).

Combined with its relative abundancy and low cost, the environmentally benign tin (IV) oxide (SnO_2), which possesses alternative Li^+ ions storage mechanisms beyond insertion chemistry and high theoretical gravimetric capacity of 1494 mAh g^{-1} , is one widely studied alternative anode material for LIBs application. Nevertheless, it is generally accepted that further improvement is required to overcome its inherent poor conductivity and rapid structural degradation upon charging/discharging. Over the past years, tremendous progress in dimensional reduction, morphological variations and formation of composites have significantly enhanced electrochemical performance of SnO_2 -based nanostructures. However, most are prepared by complex chemical synthesis which are not feasible for scaling up to industrial production.

Herein, within the context of this thesis, three approaches involving procedures with high practicality are purposefully selected for either the synthesis and modification of SnO_2 to overcome the inadequacies of SnO_2 as LIBs anode material. First, despite the absence of size distribution and morphological uniformity, a multi-faceted SnO_2 -graphite nanocomposite as-fabricated by an industrially compatible high energy mechanical milling

delivers high specific capacity comparable to those by complex chemical synthesis. Second, an unorthodox and counterintuitive approach to post-treat antimony (Sb)-doped SnO_2 in selected acidic etchants for partial dopant removal from SnO_2 lattice has yielded significantly enhanced cyclic stability beyond those of untreated Sb-doped SnO_2 (mere doping) and undoped SnO_2 . Analogous to void engineering by removal of sacrificial phase, this demonstrates the viability of the partial dopant removal and provides a new perspective on incorporating dopant species into semiconducting materials, such as SnO_2 . Third, a hierarchical $\text{Ti}_3\text{C}_2\text{T}_x\text{-SnO}_2\cdot\text{Co}_3\text{O}_4$ architecture with unheralded customizability of packing density was simply assembled by a mature industrial procedure of freeze-drying. The $\text{Ti}_3\text{C}_2\text{T}_x\text{-SnO}_2\cdot\text{Co}_3\text{O}_4$ hybrid anode exhibits exceptional cyclic stability and rate capability, beyond most MXene/transition metal oxide (TMO) that have been reported.

Lay Summary

Changing lifestyles of an ever-growing number of inhabitants pose the conundrum to satisfy the surge in world's energy demand without accelerating emissions in global warming carbon dioxide (CO₂) nor depleting finite resources such as fossil fuels. Coupled with our increased environmental consciousness and the need to sustainably develop for our future generations, a technological shift towards seeking out and consuming alternative renewable energy sources and developing hybrid electric vehicles (HEVs) and electric vehicles (EVs) evidently ensues. High performance electrochemical storage systems are vital in negating intermittency of renewable energy sources and defining the autonomy and competitiveness of these vehicles.

Motivated by the lucrative markets of electric vehicles and energy storage grids for renewable and intermittent sources, lithium-ion batteries (LIBs) — the ubiquitous energy storage in consumer electronics have been intensively investigated. A consensus approach is to develop alternative electrode material to reversibly uptake and release greater quantity of lithium (Li⁺) ions and to reliably do so at a much faster rate than the incumbent graphite (C) anode with a theoretical gravimetric capacity of 372 mAh g⁻¹. Coupled with its relative abundancy and low cost, the environmentally benign tin (IV) oxide (SnO₂), possessing alternative Li⁺ ions storage mechanisms beyond insertion chemistry and high theoretical gravimetric capacity of 1494 mAh g⁻¹, is one widely studied candidate anode material. Nevertheless, it is generally accepted that further improvement is required to overcome its inherent poor conductivity and rapid structural degradation upon charging/discharging.

Over the past years, tremendous progress in dimensional reduction, morphological variations and formation of composites have significantly enhanced electrochemical performance of SnO₂-based nanostructures. However, most are prepared by complex chemical synthesis which are not feasible for scaling up to industrial production. In addition, to date, the critical size and optimal morphology for SnO₂-based anodes remain inconclusive. Herein, one chapter of this thesis is dedicated to assessing if size distribution and morphological uniformity of the SnO₂ component can be neglected without inflicting

too severe a handicap to its overall electrochemical performance. Intriguingly, despite an apparent absence of dimensional and morphological uniformity, a hierarchical structure of polydispersed $\text{SnO}_2\text{-C}$ nanoclusters anchored on thin remnant graphite sheets, by a simple one-step high energy mechanical milling, exhibits comparable electrochemical performance to other binary SnO_2 nanocomposites.

Elemental doping, which involves the addition of dopant species during precursory or synthesis stage, is one straightforward method to improve the electronic properties of semiconducting materials, such as SnO_2 . Another chapter in this thesis is devoted to a seemingly counterintuitive post-synthesis acid treatment of antimony (Sb)-doped SnO_2 , which expectedly results in a reduced Sb dopant concentration, but surprisingly enhanced the cyclic stability beyond those of untreated Sb-doped SnO_2 (mere doping) and undoped SnO_2 . The choice of etchants and duration of immersion are systematically varied. The contributions to such improved electrochemical performance are postulated and discussed in view of circumstantial evidence from materials characterization.

A third chapter in this thesis is committed to the study of a multifaceted $\text{Ti}_3\text{C}_2\text{T}_x\text{-SnO}_2\text{-Co}_3\text{O}_4$ architecture assembled via a simple freeze-drying procedure. This industrially compatible approach offers unheralded customizability of tap/packing density and does not require surfactant(s) nor structurally deteriorate the MXene nanosheets (i.e. oxidize or reduce lateral dimension). Due to the structural design and deliberate combination of components, the reversibility of SnO_2 conversion reaction is greatly enhanced and synergistic Li^+ storage further adds to the high capacity. In this architecture, the percolating $\text{Ti}_3\text{C}_2\text{T}_x$ network holds down the expanding/contracting $\text{SnO}_2\text{-Co}_3\text{O}_4$ nanocubes during lithiation/delithiation, enhancing the retention of structural integrity and overall conductivity of the electrode, respectively. At the same time, these entrapped $\text{SnO}_2\text{-Co}_3\text{O}_4$ nanocubes separate individual $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets and double as conductive contacts between isolated $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets, thereby preserving active surfaces and enriching interfacial interactions. Unprecedentedly, a non-freestanding but compositionally optimized $\text{Ti}_3\text{C}_2\text{T}_x\text{-SnO}_2\text{-Co}_3\text{O}_4$ hybrid anode demonstrates an exceptional cyclic stability and rate capability, beyond most MXene/transition metal oxide (TMO) that have been reported.

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Figure 4.7 (a) Cycling performance of the SnO₂-C8020 nanocomposites, ball milled for 2, 5, 12 and 20 h, cycled between 0.005 and 3.0 V at current density of 200 mA g⁻¹. (b) Cycling performance of SnO₂-20h, SnO₂-C9505-20h, SnO₂-C8812-20h and SnO₂-C8020-20h cycled between 0.005 and 3.0 V at current density of 200 mA g⁻¹. (c) Rate performance of SnO₂-C8020-20h at current densities of 200, 500 and 1000 mA g⁻¹. (d) Cycling performance and Coulombic efficiency of SnO₂-C8020-20h between 0.005 and 3.0 V at current density of 200 mA g⁻¹. (e) Discharge/charge profile of SnO₂-C8020-20h nanocomposite at current density of 200 mA g⁻¹. (f) Cyclic voltammograms of SnO₂-C8020-20h at a scan rate of 0.1 mV·s⁻¹.

Figure 4.8 Electrochemical impedance spectra (EIS) of (a) the samples ball milled for 20 h with varying graphite content and (b) samples, with 20 wt.% graphite, ball milled for differing durations, both before cycling at the amplitude of 10 mV over frequency range from 100 kHz to 10 mHz.

Figure 5.1 (a) XRD (b) XPS survey, and (c) high-resolution XPS spectra of Sn 3d of as-synthesized ATO, ATO-H₂SO₄-2h, ATO-H₂SO₄-4h, ATO-H₂SO₄-6h, and ATO-H₂SO₄-8h. (d) High-resolution XPS spectra of the overlapping Sb 3d and O 1s of as-synthesized ATO.

Figure 5.2 FESEM images of as-synthesized (a) SnO₂, (b) ATO, (c) ATO-H₂SO₄-2h, (d) ATO-H₂SO₄-4h, (e) ATO-H₂SO₄-6h, and (f) ATO-H₂SO₄-8h.

Figure 5.3 TEM images of as-synthesized (a) SnO₂, (b) ATO, (c) ATO-H₂SO₄-2h, (d) ATO-H₂SO₄-4h, (e) ATO-H₂SO₄-6h, and (f) ATO-H₂SO₄-8h.

Figure 5.4 (a) Cycling performance of ATO and ATO after etching in 6 M H₂SO₄ for various duration. (b) Electrochemical impedance spectra (EIS) of ATO and ATO after etching in 6 M H₂SO₄ at the amplitude of 10 mV over frequency range from 100 kHz to 10 mHz.

Figure 5.5 XRD of varyingly etched ATO by (a) 6 M HCl and (b) 6 M HNO₃ at 80 °C, respectively. High-resolution XPS spectra of Sn 3d of varyingly etched ATO by (c) 6 M HCl and (d) 6 M HNO₃ etchant solution, respectively.

Figure 5.6 Cycling performance of as-synthesized ATO and ATO after etching in (a) 6 M HCl and (b) 6 M HNO₃ for various duration. Electrochemical impedance spectra (EIS) of as-synthesized ATO and ATO after etching in (c) 6 M HCl and (d) 6 M HNO₃ for various duration, at the amplitude of 10 mV over frequency range from 100 kHz to 10 mHz.

Figure 6.1 (a) XRD patterns of precursory Ti₃AlC₂, unmodified, vacuum- and freeze-dry HCl/LiF-etched Ti₃C₂T_x. FESEM images of (b) bulk Ti₃AlC₂ at low magnification, (c-d) vacuum-dry HCl/LiF-etched Ti₃C₂T_x at low magnification and high magnification (area enclosed by blue dotted box in (c)), respectively, (e-f) freeze-dry HCl/LiF-etched Ti₃C₂T_x at low magnification and high magnification (area enclosed by orange dotted box in (e)), respectively.

Figure 6.2 (a) Low resolution TEM image of the laterally large and wrinkled architecture made up of freeze-dry HCl/LiF-etched Ti₃C₂T_x (surface modified) nanosheets, and the corresponding EDS mapping of (b) Ti, (c) C, (d) O, (e) S and (f) F.

Figure 6.3 XPS (a) survey of unmodified, vacuum- and freeze-dry HCl/LiF-etched Ti₃C₂T_x, (b) S 2p spectra of freeze-dry HCl/LiF-etched Ti₃C₂T_x, Ti 2p spectra of (c) vacuum-dry HCl/LiF-etched Ti₃C₂T_x and (d) freeze-dry HCl/LiF-etched Ti₃C₂T_x, respectively. (e) Raman spectra and (f) FTIR spectra of unmodified, vacuum- and freeze-dry HCl/LiF-etched Ti₃C₂T_x.

Figure 6.4 (a) Cyclic voltammograms (1st and 2nd cycle) of unmodified (purple), vacuum- (blue) and freeze-dry (orange) HCl/LiF-etched Ti₃C₂T_x at a scan rate of 0.1 mV·s⁻¹. (b) Galvanostatic discharge/charge profile of freeze-dry Ti₃C₂T_x at current density of 100

mA g⁻¹. (c) Cycling performance and Coulombic efficiency of unmodified, vacuum- and freeze-dry HCl/LiF-etched Ti₃C₂T_x between 0.005 and 3.0 V at current density of 100 mA g⁻¹. (d) Electrochemical impedance spectra (EIS) of unmodified, vacuum- and freeze-dry HCl/LiF-etched Ti₃C₂T_x after 100th cycle at the amplitude of 10 mV over frequency range from 100 kHz to 10 mHz.

Figure 6.5 (a) XRD patterns of freeze-dry HCl/LiF-etched Ti₃C₂T_x (grafted with grafting *p*-phenyl-SO₃H), intermediary CoSn(OH)₆, SnO₂·Co₃O₄, and Ti₃C₂T_x-SnO₂·Co₃O₄ (5:5). (☆: Ti₃C₂T_x, #: Co₃O₄, ◇: SnO₂). FESEM images of (b) intermediary CoSn(OH)₆, (c) SnO₂·Co₃O₄ nanocubes, both at 30 000 x magnification. (d) TEM image of SnO₂·Co₃O₄ nanocubes, revealing its porous nature. (e) FESEM image of the Ti₃C₂T_x-SnO₂·Co₃O₄ (5:5) nanocomposite, showing SnO₂·Co₃O₄ nanocubes embedded between Ti₃C₂T_x nanosheet layers. (f) TEM image of Ti₃C₂T_x-SnO₂·Co₃O₄ (5:5), indicating SnO₂·Co₃O₄ nanocubes are uniformly distributed across the surface of Ti₃C₂T_x nanosheet.

Figure 6.6 (a) Low resolution TEM image of the Ti₃C₂T_x-SnO₂·Co₃O₄ (5:5) hybrid, and the corresponding EDS mapping of (b) Sn, (c) Co, (d) Ti, (e) C and (f) O.

Figure 6.7 XPS (a) Sn 3d spectra, (b) Co 2p spectra, and (c) O 1s spectra of Ti₃C₂T_x-SnO₂·Co₃O₄ (5:5) hybrid. (d) N₂ adsorption-desorption isotherms of freeze-dry Ti₃C₂T_x nanosheets (in black), SnO₂·Co₃O₄ nanocubes (in blue) and Ti₃C₂T_x-SnO₂·Co₃O₄ (5:5) hybrid (in orange).

Figure 6.8 (a) Cyclic voltammograms (1st, 2nd and 5th cycle) of the Ti₃C₂T_x-SnO₂·Co₃O₄ (5:5) nanocomposite at a scan rate of 0.1 mV·s⁻¹. (b) Galvanostatic discharge/charge profile of Ti₃C₂T_x-SnO₂·Co₃O₄ (5:5) nanocomposite at current density of 100 mA g⁻¹. (c) Cycling performance and Coulombic efficiency of the surface-modified, freeze-dry Ti₃C₂T_x nanosheets, naked SnO₂·Co₃O₄ nanocubes and the Ti₃C₂T_x-SnO₂·Co₃O₄ (5:5) nanocomposite between 0.005 and 3.0 V at current density of 100 mA g⁻¹. (d) Rate capabilities of the surface-modified, freeze-dry Ti₃C₂T_x nanosheets, bare SnO₂·Co₃O₄

nanocubes and the $\text{Ti}_3\text{C}_2\text{T}_x\text{-SnO}_2\cdot\text{Co}_3\text{O}_4$ (5:5) nanocomposite. (e) Extended cycle behavior of the $\text{Ti}_3\text{C}_2\text{T}_x\text{-SnO}_2\cdot\text{Co}_3\text{O}_4$ (5:5) nanocomposite at current density of 100 mA g^{-1} . (f) Cyclic performance of the $\text{Ti}_3\text{C}_2\text{T}_x\text{-SnO}_2\cdot\text{Co}_3\text{O}_4$ (5:5) nanocomposite at high current density of 1 A g^{-1} .

Figure 6.9 (a) Cycling performance of $\text{Ti}_3\text{C}_2\text{T}_x\text{-SnO}_2\cdot\text{Co}_3\text{O}_4$ nanocomposites with different $\text{Ti}_3\text{C}_2\text{T}_x$ content. (b) Electrochemical impedance spectra (EIS) of various $\text{Ti}_3\text{C}_2\text{T}_x\text{-SnO}_2\cdot\text{Co}_3\text{O}_4$ nanocomposites, after 100th cycles, at the amplitude of 10 mV over frequency range from 100 kHz to 10 mHz. (c) CV curves of $\text{Ti}_3\text{C}_2\text{T}_x\text{-SnO}_2\cdot\text{Co}_3\text{O}_4$ (5:5) nanocomposite at different scan rates from 0.2 to 2.0 mV s^{-1} . (d) Plot of logarithm peak current against logarithm scan rates at different voltages. (e) The capacitive and diffusion-limited contribution ratio in the three cathodic processes of $\text{Ti}_3\text{C}_2\text{T}_x\text{-SnO}_2\cdot\text{Co}_3\text{O}_4$ (5:5) nanocomposite at 0.2 mV s^{-1} scan rate.

Figure 7.1 XRD of (a) $\text{SnO}_2\text{-M-C}$ #1 (all three components are added in at once and ball milled for 20 h) and (b) $\text{SnO}_2\text{-M-C}$ #2 (mixture of SnO_2 and M are first ball milled for 12 h, prior to addition of C and further milled for 8 h); M = Co, Fe, Zn, Mn and $\diamond$: SnO_2 , #: Co, Co_3O_4 , $\star$: Fe, $\gamma\text{-Fe}_2\text{O}_3$, o: Zn, ZnO, x: Mn, $\alpha\text{-MnO}_2$). Rate performance of (c) $\text{SnO}_2\text{-M-C}$ #1 and (d) $\text{SnO}_2\text{-M-C}$ #2.

Figure 7.2 FESEM images of CoSn(OH)_6 formed with increasing concentration of sodium citrate: (a) 0.005 mol, (b) 0.010 mol (as in Chapter 6), (c) 0.015 mol, (d) 0.020 mol in mixture containing 0.010 mol of $\text{SnCl}_4\cdot 5\text{H}_2\text{O}$ and $\text{CoCl}_2\cdot 6\text{H}_2\text{O}$, respectively in 300 mL of DI water and addition of 50 mL of 2 M NaOH (for coprecipitation) and 20 mL of 8 M NaOH (for etching).

Figure 7.3 FESEM images of CoSn(OH)_6 formed with increasing quantity of excess NaOH (for etching): (a) 0.06 mol, (b) 0.12 mol, (c) 0.18 mol, (d) 0.24 mol.

Figure A1 Lattice parameter of undoped SnO_2 , as-synthesized ATO, and variously-etched ATO.

Figure A2 Cyclic voltammograms (1st, 2nd and 3rd cycle) of (a) undoped SnO_2 , (b) as-synthesized $\text{Sb}_{0.17}\text{Sn}_{0.83}\text{O}_2$ (ATO), (c) ATO- H_2SO_4 -8h, (d) ATO-HCl-8h, and (e) ATO- HNO_3 -8h at a scan rate of $0.1 \text{ mV} \cdot \text{s}^{-1}$.

Figure A3 Galvanostatic discharge/charge profiles of (a) undoped SnO_2 , (b) as-synthesized $\text{Sb}_{0.17}\text{Sn}_{0.83}\text{O}_2$ (ATO), (c) ATO- H_2SO_4 -8h, (d) ATO-HCl-8h, and (e) ATO- HNO_3 -8h at current density of 100 mA g^{-1} .

Figure A4 TEM images of (a) ATO-HCl-8h and (b) ATO- HNO_3 -8h.

Figure A5 XPS Ti 2p spectra of $\text{Ti}_3\text{C}_2\text{T}_x\text{-SnO}_2\text{-Co}_3\text{O}_4$ (5:5) nanocomposite.

Figure A6 (a) Cyclic voltammograms (1st, 2nd and 5th cycle) of the $\text{SnO}_2\text{-Co}_3\text{O}_4$ nanocubes at a scan rate of $0.1 \text{ mV} \cdot \text{s}^{-1}$. (b) Galvanostatic discharge/charge profile of the $\text{SnO}_2\text{-Co}_3\text{O}_4$ nanocubes at current density of 100 mA g^{-1} between voltage window of 0.01 to 3.0 V.

Figure A7 (a) XRD and (b-d) FESEM images of $\text{Ti}_3\text{C}_2\text{T}_x\text{-SnO}_2\text{-Co}_3\text{O}_4$ nanocomposite (vary compositions). (b) $\text{Ti}_3\text{C}_2\text{T}_x\text{-SnO}_2\text{-Co}_3\text{O}_4$ (2:8), (c) $\text{Ti}_3\text{C}_2\text{T}_x\text{-SnO}_2\text{-Co}_3\text{O}_4$ (3:7) and (d) $\text{Ti}_3\text{C}_2\text{T}_x\text{-SnO}_2\text{-Co}_3\text{O}_4$ (4:6). It is to be noted that within a frame of FESEM image of $\text{Ti}_3\text{C}_2\text{T}_x\text{-SnO}_2\text{-Co}_3\text{O}_4$ (1:9), there is a noticeably absence of $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheet due to its apparent low statistical distribution, hence its corresponding FESEM is excluded (no significance).

Figure A8 (a-d) CV curves of $\text{Ti}_3\text{C}_2\text{T}_x\text{-SnO}_2\text{-Co}_3\text{O}_4$ nanocomposite (vary compositions) at different scan rates from 0.2 to 2.0 mV s^{-1} .

Abbreviations

2D	Two-dimensional
AIMD	Ab-initio Molecular Dynamic
ATO	Antimony-doped Tin Oxide
BET	Brunauer-Emmett-Teller
BF	Bright Field
CBM	Conduction Band Minimum
CMC	Carboxymethyl Cellulose
CNT	Carbon Nanotube
CV	Cyclic Voltammetry
DEC	Diethyl Carbonate
DF	Dark Field
DFT	Density Functional Theory
DI	Deionized
DMC	Dimethyl Carbonate
DMSO	Dimethyl Sulfoxide
EC	Ethylene Carbonate
EDS	Energy Dispersive X-ray Spectroscopy
EDX	Energy Dispersive X-ray
EIS	Electrochemical Impedance Spectroscopy
EMC	Ethyl Methyl Carbonate

EV	Electric Vehicle
LIB	Lithium-ion Batteries
FTIR	Fourier Transform Infrared Spectroscopy
FTS	Flame-Transport-Synthesis
GNR	Graphene Nanoribbon
HEV	Hybrid Electric Vehicle
HF	Hydrofluoric Acid
HRTEM	High Resolution Transmission Electron Microscopy
ICDD	International Centre for Diffraction Data
JCPDS	Joint Committee for Powder Diffraction Standards
LUMO	Lowest Unoccupied Molecular Orbital
MXene	Layered Transition Metal Carbide and/or Nitride
NMP	N-Methyl-2-Pyrrolidone
NMR	Nuclear Magnetic Resonance
OCV	Open Circuit Voltage
PC	Propylene Carbonate
PVDF	Polyvinylidene Fluoride
rGO	Reduced Graphene Oxide
SAED	Selected Area Electron Diffraction
SEI	Secondary Electron Imaging
SEI	Solid Electrolyte Interphase
SEM	Scanning Electron Microscopy

SSA	Specific Surface Area
TEM	Transmission Electron Microscopy
TGA	Thermogravimetric Analysis
TMAOH	Tetramethylammonium Hydroxide
TMO	Transition Metal Oxide
WC	Tungsten Carbide
XAS	X-ray Absorption Spectroscopy
XPS	X-ray Photoelectron Spectroscopy
XRD	X-ray Diffraction

Chapter 1

Introduction

The inadequacies of graphite anodes in current commercialized lithium-ion batteries (LIBs) are well recognized and have hindered proliferation in high energy and high power applications, such as grid storage and electric vehicles. In this chapter, the theme of this thesis is revealed to revolve around addressing the inadequacies of tin (IV) oxide (SnO_2) as alternative LIB anode. The objectives and scope of three different approaches on the enhancement of SnO_2 covered by this dissertation will be highlighted. As a prelude to the whole thesis, an outline of the content in subsequent chapters is presented. A summary of the novelty/outcome is also included at the end of this chapter.

1.1 Background/Problem Statement

Changing lifestyles of an ever-growing number of inhabitants pose the conundrum to satisfy the surge in world's energy demand without accelerating emissions in global warming carbon dioxide (CO₂) nor depleting finite resources such as fossil fuels.¹ Coupled with our increased environmental consciousness and the need to sustainably develop for our future generations, a technological shift towards seeking out and consuming alternative renewable energy sources and developing low CO₂ emission hybrid electric vehicles (HEVs) and electric vehicles (EVs) evidently ensues.² High performance electrochemical storage systems are decisive in negating intermittency of renewable energy sources, i.e. to reliably store the excess harvested and rapidly deliver when required, and defining the autonomy and competitiveness, i.e. preferably high mileage per recharge and short charging time, of these vehicles.

Motivated by the lucrative markets of electric vehicles and energy storage grids for renewable and intermittent sources, lithium-ion batteries (LIBs) — the ubiquitous energy storage in consumer electronics have been intensively investigated. A consensus approach is to develop alternative electrode material to reversibly uptake and release greater quantity of lithium (Li⁺) ions (high energy density) and to reliably do so at a much faster rate (high power) to replace the graphite (C) anode with theoretical gravimetric capacity of only 372 mAh g⁻¹.³ Figure 1.1 summarizes the various milestones in LIBs' anode development and the general storage properties of the reported anode materials. Coupled with its relative abundance and low cost, the environmentally benign tin (IV) oxide (SnO₂), possessing alternative Li⁺ ions storage mechanisms beyond insertion chemistry and high theoretical gravimetric capacity of 1494 mAh g⁻¹, is one widely studied candidate anode material. Nevertheless, it is generally accepted that further improvement is required to overcome its inherent poor conductivity and rapid structural degradation upon charging/discharging. Preferably, industrial compatible procedures should be integral for the syntheses and modifications of SnO₂-based LIB anodes.

Figure 2.1 Various breakthrough in LIBs' anode development and the general energy storage properties of the reported materials.

Herein, procedures with high practicality are purposefully selected for the synthesis and modification of SnO_2 within the context of this thesis. The hypotheses, measurables and parameters for the three distinct approaches will be elucidated in the following section.

1.2 Hypotheses, Objectives and Scope

Capacity fading in SnO_2 has been largely attributed to pulverization of the active material during reversible reactions, and this gradually leads to failure of the cell. To date, a few methods have been found to be effective in mitigating/alleviating this issue. Morphological tailoring, reduction in particle size and incorporation of carbon phases are some of the most well explored methods. However, most of them involved tedious and complicated preparation process.⁴⁻⁶ Other methods include elemental doping, or the incorporation of a foreign element/matrix into the structure, have also enriched the electrochemical

performance of SnO_2 .⁷ Herein, we propose three different approaches that could help improve the overall performance of tin (IV) oxide-based anode materials for LIBs.

Hypothesis 1 – The Presence of a Carbonaceous Matrix Can Help SnO_2 to Retain High Reversible Li^+ Storage Capacity.

Although tremendous progress has been made with various strategies to synthesize and modify SnO_2 for enhanced electrochemical performances, most chemical syntheses are not translatable to industrial applications.⁸ In addition, to date, the critical size and optimal morphology for SnO_2 -based anodes remain inconclusive. In Chapter 4, to elucidate if dimensional and morphological uniformity in SnO_2 are indispensable for extended cyclic stability, SnO_2 -based binary composites are prepared by a physical top-down approach of high energy mechanical milling. The incorporation of carbonaceous conductive matrix should enhance overall electronic conductivity and prolong structural integrity of SnO_2 anode.

Specific Objective 1.1: To characterize and evaluate electrochemical performance of binary SnO_2 -graphite (C) composite as-prepared by high energy mechanical milling.

Specific Objective 1.2: To correlate observable features, if any, in the SnO_2 -C composite besides dimensional and morphological nonuniformity with deterioration/enhancement of electrochemical performance.

Scope: Planetary ball milling duration is capped at 20 h, for extended period is no longer as effective in the reducing particle size while incurring the cost of high electrical power consumption. As graphite has low density and theoretical capacity, the maximum content of graphite is limited to 20 wt.%.

Hypothesis 2 – Heterogeneous Doping Could Improve Conductivity of SnO_2 By Altering Its Electronic Structure; Incorporated Cationic Dopant in SnO_2 Matrix Can Be Sacrificially Removed to Engineer Defects/Voids and Improve Cyclability.

Many works have been conducted on elemental doping of SnO_2 to improve its electrical conductivity, however, to date none has reported significant breakthrough in improving its cyclic stability.^{7, 9-18} Coupled with numerous precedents of subsequent removal of incorporated sacrificial phase to engineer voids within SnO_2 structures, it may be intuitive to consider if substitutional dopant species may also be selectively removed to achieve a more intricately modified SnO_2 architecture with improved reversible Li^+ storage capacity.

Specific Objective 2.1: To characterize the morphology and antimony (Sb) dopant content before and after acid etching and verify the possibility of complete removal of Sb dopant from SnO_2 matrix by the procedure.

Specific Objective 2.2: To understand and evaluate the effect of etching parameters, such as choice of etchants and etching duration, on the electrochemical performance of Sb-doped SnO_2 (ATO).

Scope: The initial high concentration Sb-dopant in as-synthesized ATO nanoparticles at ~ 18 at.% is intended to accentuate any reduction, even nominal, in Sb concentration by the etching procedure. The benchmark electrochemical performance is arbitrarily set by that of the bare ATO nanoparticles (without post-synthesis acid treatment) and all post-synthesis etched ATO samples are accordingly evaluated.

Hypothesis 3 – The Combination of Highly Conductive $\text{Ti}_3\text{C}_2\text{T}_x$ and High Capacity $\text{SnO}_2 \cdot \text{Co}_3\text{O}_4$ Can Beneficially Complement Each Other and Realize Synergistic Effect.

Hitherto, few works, if any, have fabricated nanostructured $\text{Ti}_3\text{C}_2\text{T}_x/\text{TMO}$ hybrid with customizable packing density or industrially compatible approach. It also remains challenging to achieve homogeneously mixed $\text{Ti}_3\text{C}_2\text{T}_x/\text{TMO}$ powder samples without compromising the morphology or excellent electronic properties of $\text{Ti}_3\text{C}_2\text{T}_x$ component.

Specific Objective 3.1: To verify that both $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets and $\text{SnO}_2 \cdot \text{Co}_3\text{O}_4$ nanocubes

retain their morphologies (survival of nanostructure), i.e. do not succumb to thermal shock due to the introduction of liquid nitrogen (N_2).

Specific Objective 3.2: To demonstrate the importance of homogeneous distribution of $Ti_3C_2T_x$ nanosheets and $SnO_2 \cdot Co_3O_4$ nanocubes to cyclic capacity and rate capability of $Ti_3C_2T_x-SnO_2 \cdot Co_3O_4$ nanocomposite.

Specific Objective 3.3: To understand the various charge mechanism at play in $Ti_3C_2T_x-SnO_2 \cdot Co_3O_4$ nanocomposite via kinetic analysis by cyclic voltammetry (CV), at different scan rates and identify the optimal composition by evaluating electrochemical performance of differently composed $SnO_2 \cdot Co_3O_4$ nanocomposites.

Scope: All the $Ti_3C_2T_x-SnO_2 \cdot Co_3O_4$ nanocomposites are assembled by a facile freeze-drying procedure. As $Ti_3C_2T_x$ nanosheets are highly conductive but inherently limited in Li^+ storage capacity, the content of $Ti_3C_2T_x$ should be minimized. Slurry casting is adopted throughout the preparation of all samples to be evaluated. The comparison between freestanding and non-freestanding and various tap densities are beyond the scope of this study.

1.3 Dissertation Overview

The thesis addresses the scalability for the fabrication of nanostructured SnO_2 -based LIB anode by using industrially compatible methods such as high energy mechanically milling and freeze-drying procedure. The ambiguity between dimensional and morphological uniformity and extended cyclic and rate performance, the seemingly ineffectiveness of conventional doping for enhancement of electrochemical performance and the challenge to assemble a ternary MXene nanocomposite are systematic examined in separate chapters of this thesis.

Chapter 1 provides the research motivation and outlines the three specific research gaps which will be addressed by this thesis. An overview for the design of experiments to verify as-stated hypotheses and the flow of content are also summarized.

Chapter 2 reviews the literature concerning both incumbent and in development LIB anode materials. The two materials of interest are tin (IV) oxide (SnO_2), which possesses high theoretical gravimetric capacity and $\text{Ti}_3\text{C}_2\text{T}_x$ (MXene), which owns exceptional electrical conductivity and rate capability. Various synthetic approaches and strategies for enhancement are collectively summarized and the corresponding research gaps are duly listed.

Chapter 3 elaborates the justifications for the choice of various synthesis procedure and characterization techniques adopted. The underlying principles and limitations of these different characterization tools are elucidated.

Chapter 4 elaborates the fabrication of a binary SnO_2 -graphite nanocomposite by an industrially compatible high energy mechanical milling, the inherent absence of dimensional and morphological uniformity by this physical top-down approach is evaluated to determine if its high energy performance is compromised or can be conditionally tolerable with incorporation of a carbonaceous phase.

Chapter 5 introduces a unique approach of post-synthesis removal of substitutional antimony (Sb) dopant species from a Sb-doped SnO_2 matrix. Unlike previous works on doping of SnO_2 to merely improve electronic properties and Coulombic efficiency, a more intricately modified SnO_2 architecture is achieved with significantly improved cyclic Li^+ capacity.

Chapter 6 demonstrates the assembly of a ternary $\text{Ti}_3\text{C}_2\text{T}_x\text{-SnO}_2\cdot\text{Co}_3\text{O}_4$ nanocomposite with customizable packing density by a simple, industrial mature freeze-drying procedure. Without compromising the morphology or excellent electronic properties of $\text{Ti}_3\text{C}_2\text{T}_x$ component, homogeneously mixed $\text{Ti}_3\text{C}_2\text{T}_x/\text{TMO}$ powder samples are accomplished. Unprecedented cyclic stability and rate capability beyond most MXene/transition metal oxide (TMO) that have been reported, are demonstrated by this non-freestanding, compositionally optimized $\text{Ti}_3\text{C}_2\text{T}_x\text{-SnO}_2\cdot\text{Co}_3\text{O}_4$ hybrid anode.

Chapter 7 draws together the effect and improvement that each engineering approaches bring about in the overall electrochemical performance of SnO_2 as LIB anode. Reconnaissance studies that did not warrant a complete chapter, opportunities and strategies for future work are also included in this chapter.

1.4 Findings and Outcomes/Originality

This research led to several novel outcomes by:

1. Understanding if absence of dimensional and morphological uniformity is critically detrimental to electrochemical performance of SnO_2 or maybe circumstantially ameliorated by inclusion of carbonaceous matrix. An industrially compatible high energy mechanically milling of a mixture of micro-sized SnO_2 and graphite was used as an example to elucidate the aforementioned.
2. Establishing a proof-of-concept for partial removal of substitutional Sb dopant from as a means of incorporation of voids in a Sb-doped SnO_2 matrix via post-synthesis etching. Substantial enhancement in cyclic performance of bare Sb-doped SnO_2 was achieved.

3. Demonstrating the assembly of a ternary $\text{Ti}_3\text{C}_2\text{T}_x\text{-SnO}_2\cdot\text{Co}_3\text{O}_4$ nanocomposite via a simple freeze-drying procedure. Homogeneity, highly customizable tap/packing density of the components and without intervention of surfactant(s) nor structurally deteriorating the MXene nanosheets (i.e. oxidize or reduce lateral dimension) was concomitantly accomplished.

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Chapter 2

Literature Review

The aims of this chapter are firstly to facilitate understanding of lithium-ion battery (LIB) storage and introduce commonly used terminologies, secondly, to review works concerning tin (IV) oxide (SnO_2) as LIB anode, and lastly, to establish suitability and benefits for the incorporation of layered transition metal carbide and/or nitride (MXenes) in hybrid LIB anode. First, functions and typical materials employed in various components in a LIB, fundamental working mechanism of a generic LIB and key figure of merits will be introduced. Second, the various strategies adopted to enhance electrochemical performance SnO_2 as LIB anode and corresponding limitations will be elucidated. Last, the synthesis procedures, subsequent processing and reported electrochemical performance of MXene-based (especially $\text{Ti}_3\text{C}_2\text{T}_x$) nanocomposites will be elaborated in detail.

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2.1 Basics of Lithium-ion Batteries (LIBs): Functions and Material Used for Various Components and Simplified Working Mechanism

A typical lithium-ion battery cell comprises of two electrodes—an anode (negative electrode) and a cathode (positive electrode), a non-aqueous electrolyte and a polymeric separator as illustrated in Figure 2.1.¹ In most typical commercial LIBs, graphite (C) remains the predominant active material for anode, while various metal oxides such as layered lithium cobalt oxide (LiCoO₂), spinel lithium manganese oxide (LiMnO₄) and olivine lithium iron phosphate (LiFePO₄) are prevalent active material choices for cathode. Preparation of an anode/cathode commonly begins with formulating a coalescence slurry by the addition of carbon-based additives (such as carbon black or Super P) and polymeric binder solution (such as PVDF in NMP) to active material in various mass ratios. The electrode manufacture procedure continues with subsequent coating and drying of this slurry onto a copper/aluminum foil (current collector) and completes when the coated current collectors are cut into desired dimension. The electrode (anode/cathode) serves as host material for accommodation of Li⁺ ions between charging (Li⁺ ions moves from cathode to anode) and discharging (vice versa), respectively. Concurrently during discharge, the lithiated graphite anode loses electron (e⁻) while the delithiated Li_{1-x}CoO₂ cathode gains e⁻. The e⁻ flow through an external circuit to deliver current to drive electronic devices until fully discharged and can be elucidated as Equations 2.1 and 2.2, respectively:

Conversely, to charge the secondary battery (LIB), an application of external voltage is necessary to reverse the e⁻ flow, deintercalate Li⁺ from the cathode material, even though thermodynamically unfavorable, and drive Li⁺ back to intercalate into the anode material.² This mechanism of reversible redox reaction leads to the moniker “rocking-chair” battery for LIBs.

These two electrodes are mechanically separated by either a porous polypropylene (PP)/polyethylene (PE) or woven glass fiber separator (possessing high electronic

resistance) to prevent short circuiting whilst allowing unhindered and reversible diffusion of Li^+ ions between the cathode and anode during operation.³ A medium for the Li^+ ions to reversibly shuttle between the electrodes is provided by an electrolyte when both the electrodes and separator are completely immersed in it. The ionically conductive but electronically insulating electrolyte is mainly based on the dissolution of inorganic lithium salts such as lithium hexafluorophosphate (LiPF_6) in a mixture of organic solvents of alkyl carbonates (such as PC, EC, DEC) at various ratios.

As the energy density (a key performance indicator) of LIBs is most sensitive to the specific capacities and operating voltages of electrode materials (both anode and cathode), active materials (of electrode) have understandably been the focus of intensive studies in recent years.^{4, 5} Conventional and economically viable LIBs anode materials, based on intercalation mechanism which store Li^+ ions in stable carbonaceous or transition metal compound frameworks, are already approaching or at their limits (theoretical specific and power capacities).⁶ To achieve a breakthrough in both energy and power density of LIBs, i.e. reversibly absorb and release Li^+ ions in larger quantities and in shorter duration, replacement of existing anode (graphite) seems inevitable. Alternative anode materials (inclusive of pure elements and compounds) should intuitively involve beyond-intercalation chemistries (involving more Li^+/e^- exchange) and minimally remain competitive in terms of cost and sustainability. Comparatively, improvement in any of the other cell components such as separators, binders and formulation of the electrolyte has substantially less direct impact on enhancing the overall electrochemical performance of LIBs.

Figure 2. 1 A schematic representation of the working principles in a typical commercial LIB cell. During charging, an external voltage is applied and Li^+ ions diffuse from lithiated $LiCoO_2$ cathode towards the graphite anode accompanied by concurrent oxidation and reduction of these two electrodes, respectively. During discharging, Li^+ ions exit from lithiated graphite anode and move towards the delithiated $Li_{1-x}CoO_2$ cathode and the e^- flow may be channeled to the external circuit to do work. [Reprinted with permission from Ref. 1. Copyright 2012 The Royal Society of Chemistry].

2.1.1 Key Figures of Merit for LIBs

As above mentioned in previous subsection, the discharging process of electrode material is thermodynamically favorable (may be spontaneous) and is driven by the variance of Gibbs free energy between the formation of products and reactants and can be expressed by Equation 2.3:

$$\Delta G_{rxn}^0 = \sum \Delta G_f^0 (products) - \sum \Delta G_f^0 (reactants) \quad (2.3)$$

where ' ΔG^o_{rxn} ' refers to the change in Gibbs free energy of a reaction at standard conditions and ' ΔG^o_f ' corresponds to the Gibbs free energy of formation at standard conditions. Subsequently, the equilibrium potential or open-circuit potential (V_{OC}) can be derived using Equation 2.4:

$$V_{OC} = \frac{-\Delta G^o_{rxn}}{nF} \quad (2.4)$$

where ' n ' refers to the number of moles of e^- involved in the reversible redox reaction and ' F ' refers to Faraday constant ($96\,485\text{ C mol}^{-1}$). However, the actual functional voltage window of a LIB cell is limited by the operative voltage limit of the electrolyte in the system, the ceiling is constrained by the voltage beyond which electrolyte decomposition or oxygen evolution^{7,8} sets in and the floor is defined by lithium metal plating potential^{5,9}.

The term 'specific capacity' (often accompanied by the unit of mAh g^{-1}) refers to the amount of charge per unit mass an active electrode material can accommodate. An electrode material's theoretical specific capacity (C^{th}) can be derived using Equation 2.5,

$$C^{th} = \frac{nF}{M} \quad (2.5)$$

where ' n ' refers to the number of moles of e^- involved in the reversible redox reaction, ' F ' refers to Faraday constant ($96\,485\text{ C mol}^{-1}$) and ' M ' refers to the molecular mass of the active electrode material. It is an intrinsic characteristic of the material dependent on its structure and redox chemistry. For instance, using the fully intercalated graphite stoichiometry of LiC_6 , whereby for every mole of C_6 there is 1 mole of e^- ($\text{Li}_6\text{C} \leftrightarrow \text{C} + 6\text{Li}^+ + 6e^-$), and M of C_6 is 72 g mol^{-1} , and conversion from C to mAh g^{-1} (given that $1\text{ mAh} = 3.6\text{ C}$), the often quoted theoretical specific capacity of graphite 372 mAh g^{-1} is thus derived by application of Equation 2.5.

The total specific capacity of a LIB (C_T) can be expressed as Equation 2.6,

$$C_T = \frac{1}{\frac{1}{C_A} + \frac{1}{C_C} + \frac{1}{Q_M}} = \frac{C_A C_C C_M}{C_A Q_M + C_C Q_M + C_A C_C} \quad (2.6)$$

where ' C_A ' and ' C_C ' refers to the theoretical specific capacity of anode and cathode, respectively and ' I/Q_M ' is the specific mass of other components in the cell.¹⁰ Taking into account the specific capacity of current state-of-the-art cathode (ca. 200 mAh g⁻¹), to achieve a breakthrough enhancement in LIB capacity, while all other variables (components) remain constant, will necessitate an alternative anode with specific capacity approximately 1000 mAh g⁻¹.

The term 'Coulombic efficiency' (C.E.) of an anode material corresponds to the ratio of its discharging and charging capacity and can be expressed as Equation 2.7,

$$C.E. = \frac{\text{Discharge capacity}}{\text{Charge capacity}} \times 100 \% \quad (2.7)$$

Ideally, a C.E. at 100 % is preferred as it implies total reversibility of all Li⁺ ions storage and extraction within the system/device in use. However, in practicality, due to parasitic side reactions, Li⁺ ions may be irreversibly consumed from the electrolyte and correspondingly C.E. values are usually below 100 %. It is to be noted that C.E. should not be confused with energy efficiency, in which voltage hysteresis governs the latter.

The term 'energy density' or 'specific energy' of an electrode material refers to the multiplication of its voltage by charge per unit volume or mass. Accordingly, the energy storage of an electrode material can be improved by widening the chemical potential difference between the electrodes or/and increasing the specific capacity of either/both electrodes. Energy density is sometimes used interchangeably with specific capacity in some context due to their linear correlation.

The term 'power' corresponds to the rate at which energy is delivered by an electrode material and is affected by both cell design and materials used. The power density or specific power of an electrode material is the multiplication of the current by the operating voltage per unit volume or mass respectively.

Rate capability (C_{rate}) is an expression for current output (flow of electric charge) of an electrode and indicates how rapidly an electrode may be charged and discharged. A rate of $1/n$ C refers to the necessary current to fully discharge a cell in n h, i.e. rate of 2 C is the current necessary to completely discharge a cell in 0.5 h. As current density (expressed in mA g^{-1}) is independent of total capacity, it may be more convenient and often quoted instead of C_{rate} when comparison between different electrode materials is made.¹¹ Due to a combination of limited diffusion kinetics, morphological and structural dependency and the electrode material's inherent redox chemistry, an increase in C_{rate} commonly leads to a decrease in the electrode's specific capacity.¹²

2.1.2 Three Main Electrochemical Reaction Mechanisms for Existing and Alternative Anode Materials and The Advantages/Disadvantages

There are three fundamentally different electrochemical reaction mechanisms that can take place during the charge/discharge process in an operating LIB cell; namely intercalation/deintercalation, alloying/dealloying, and conversion reactions and these are schematically summarized by Figure 2.2.¹² Currently, most commercial cathode and anode materials can be fittingly described using only one (intercalation/deintercalation) mechanism, while proposed alternative anode materials may be classified under a single or a combination of these abovementioned mechanisms. Back in 2005, the first use of conversion/alloying-based anode (amorphous Sn-Co-C) in commercialized LIBs has materialized in Sony's Nexelion battery although, to date, graphitic carbon remains the hitherto anode in most commercialized LIBs.¹³

Intercalation/deintercalation is the reversible insertion and extraction of Li^+ ions into/from the electrode material matrix with minimum alteration to structural properties.¹⁴ Intercalation and deintercalation are observed in most cathode materials (with layered, spinel, olivine or tavorite structures),¹⁵ carbonaceous (graphite, graphene etc.),¹⁶ and titanate (TiO_2)-based anodes (with opened structures).¹⁷ Insertion-based electrode

materials are advantageous for their low cost, small volumetric variation between lithiation and delithiation, stable cyclic stability and safe lithiation potential.^{15, 18} However, materials, which undergo insertion reaction, have inherently limited crystallographic sites available for Li⁺ ions storage and correspondingly low theoretical specific capacity (between 170 to 400 mAh g⁻¹).^{19, 20} For instance, graphite – the most widely adopted intercalation-based anode in commercial LIBs, require six carbon atoms to accommodate a single Li⁺ ion within the basal plane, and this contributes to a theoretical specific capacity of 372 mAh g⁻¹. Prospective alternative intercalation-based anode material such as monoclinic TiO₂ bronze (TiO₂(B)), is structurally more open than other TiO₂ polymorphs, and possesses one-dimensionally infinite channels. Additionally, diffusion of Li⁺ ions in TiO₂(B) follows a pseudocapacitive reaction mechanism (fast) rather than the rather sluggish solid-state diffusion process in both anatase and rutile TiO₂.¹⁷ Consequently, TiO₂(B) exudes its attractiveness as a candidate anode material for fast rechargeable (i.e. high power) LIBs with a vastly superior theoretical capacity (335 mAh g⁻¹) than that of commercialized Li₄Ti₅O₁₂ (175 mAh g⁻¹) and anatase TiO₂ (170 mAh g⁻¹).²⁰ Despite their longevity (excellent cyclic stability) and economic viability, the inherently limited specific capacity of intercalation-based anode materials hinders their development and incorporation in high energy density LIBs for electric vehicles and grid-scale storage.

Alloying/dealloying refers to the reversible formation of a mixture of Li with a Li electrochemically active metallic (M) or semi-metallic element(s)/compound(s). A typical alloying/dealloying reaction can be summarized by Equation 2.8:

Group 14 elements, such as silicon (Si),⁵ germanium (Ge),²¹ and tin (Sn),^{22, 23} are some of the most well-studied alloying/dealloying materials for prospective LIB anode applications. In consideration of cost efficiency, abundancy in supply and low environmental impact, other compatible Li alloying semi-metals such as aluminum (Al),^{24, 25} antimony (Sb),²⁶ and as well as silicon monoxide phase, SiO_x,⁵ have also been extensively investigated. Alloying-based anode materials are advantageous for low operating potential (< 0.7 V vs. Li⁺/Li) and multifold higher specific capacity (between 900 to 4000 mAh g⁻¹) than

intercalation-based anode materials. However, inevitable colossal volumetric variation (ca. 300 %) between lithiation and delithiation leads to rapid structural degradation, unstable solid electrolyte interphase (SEI), consequential rapid capacity fading (due to repeated active material depletion for irreversible SEI formation) and eventual low cyclic lifetime. Si has the highest theoretical gravimetric capacity of ca. 4000 mAh g⁻¹, as it can store up to 4.4 Li⁺ ions per mole of Si. Cyclic Li⁺ ions storage, via alloying/dealloying reactions in Si, can include several phase transition steps and crystalline to amorphous reactions, with spontaneous formation of Li₁₂Si₇, Li₇Si₃, Li₁₃Si₄ and Li₂₂Si₅.²⁷ Ge is another exciting alternative alloying-based anode material, which possesses a high theoretical capacity of ca. 1600 mAh g⁻¹ and two order of magnitude (ca. 400 times) higher Li⁺ ion diffusivity at room temperature than in Si, but its high raw material cost due to scarcity in supply and low cyclic stability due to structural degradation and delamination from current collectors, accumulatively prevent its widespread adoption for LIBs anode application.²⁸

Conversion reaction mechanism refers to reversible electrochemical (replacement redox) reaction, in which a transition metal compound with general composition M_aX_b, where M is a 3d transition metal, X may be O (oxides), S (sulfides), P (phosphides), N (nitrides) etc., is electrochemically destroyed and reduced to its metallic state in nanoscale form and embedded in Li_nX matrix.^{14, 29} A typical conversion reaction can be exemplified by Equation 2.9:

where 'n' refers to the redox number of the anionic complex Xⁿ⁻. The investigation and application of metal (such as cobalt-, iron-, tin-) based oxides as LIBs anode were pioneered by Tarascon *et al.*³⁰ Conversion-based anode materials are promising they can store more than one Li⁺ ions per unit compound thus having higher specific capacity than intercalation-based anode materials. However, like alloying/dealloying-based materials, the large energy density of conversion-based materials is accompanied by concomitantly massive volumetric variation between lithiation and delithiation, making them susceptible to pulverization from repeated rearrangement of particles (deteriorates crystal structure) and loss of electrical contact. The pressure from large volumetric variation can detrimentally induce welding effect that causes agglomeration, consequential increased

diffusion length of Li^+ ions, reduced reversibility of conversion reaction and increased irreversible capacity loss. To ensure active and reversible participation of Li_nX , voltage hysteresis, i.e. large separation of voltage between lithiation and delithiation, may also adversely lower the energy efficiency of the material (potential difference between the two electrodes). For example, although cobalt (II, III) oxide (Co_3O_4) possesses a theoretical specific capacity of 890 mAh g^{-1} , in addition to its low electronic conductivity, limited solid-state lithium diffusivity and formation of unstable SEI (due to associated volumetric variation), its inherently high operating voltage ($> 2.0 \text{ V}$) remains the most challenging obstacle to its practical application in a full cell.²⁹

Figure 2. 2 A schematic illustration of the three different reaction mechanisms which LIB anode materials may undergo between lithiation and delithiation and their associated shortcomings. Inherent voids in the electrode material, metal atoms, lithium atoms are represented by the black, blue and yellow circle, respectively. [Reprinted with permission from Ref. 12. Copyright 2009 The Royal Society of Chemistry].

2.2 Tin (IV) Dioxide, SnO₂, As Prospective LIBs Anode Material

Amongst various transition metal oxides as alternative LIBs anode under investigation, tin (IV) dioxide (SnO₂) remains one of the most intriguing candidate material, because of its relative abundancy, affordability, environmental benignity and high specific (783 or 1494 mAh g⁻¹, depending on the perceived reversibility of the conversion reaction) and volumetric capacity for Li⁺ ions storage.³¹ SnO₂ has a tetragonal rutile crystal structure (i.e. Cassiterite) with P42/mnm space-group symmetry and lattice parameters of 4.737 Å for *a* and *b* and 3.185 Å for *c*. SnO₂ is an intrinsic *n*-type semiconducting oxide due to the presence of intrinsic defects such as tin interstitials and oxygen vacancies. Compared with other Group 14 oxides, SnO₂ possesses superior electrical conductivity due to reversible transition between the stoichiometric Sn⁴⁺ and reduced Sn²⁺, which is made possible by the varied chemical potential of oxygen within the system.³² A two-step lithiation mechanism (conversion-alloying) has been observed in SnO₂ by various ex-situ and in-situ studies.³³⁻³⁶ Firstly, SnO₂ will undergo a conversion reaction, $\text{SnO}_2 + 4\text{Li}^+ + 4\text{e}^- \leftrightarrow \text{Sn} + 2\text{Li}_2\text{O}$, and this accounts for a gravimetric capacity of 711 mAh g⁻¹. Subsequently, Sn formed in the above-mentioned conversion reaction will undergo an alloying reaction with Li⁺ ions, $\text{Sn} + 4.4\text{Li}^+ + 4.4\text{e}^- \leftrightarrow \text{Li}_{4.4}\text{Sn}$, adding a further 783 mAh g⁻¹ towards the overall reversible capacity. Although the alloying/dealloying reaction of Sn has been unanimously observed to be highly reversible, the reversibility of the conversion reaction is, on the contrary, highly dependent on morphology (especially size) and widely perceived to be irrevocable and has been commonly attributed as the source to poor initial Coulombic efficiency of SnO₂.³⁷⁻⁴⁰ However, the adoption of such conversion/alloying-based oxide anode remains hampered by its inherently limited electrical conductivity (semiconducting with a 3.6 eV band gap) and substandard cyclic stability due to pulverization of active material and its loss of electrical contact with the current collector.⁴¹

2.2.1 Progress and Strategies to Improve Electrochemical Performance of SnO₂

Myriad approaches, which may also be extended to other prospective anode materials, have been endeavored to overcome these abovementioned intrinsic inadequacies of SnO₂.^{22, 23, 31, 42, 43} Figure 2.3 summarizes some of the most widely adopted strategies for performance enhancement, and this list is barely exhaustive.¹⁵ Substantial progress to mitigate issues such as low electronic conductivity and Li⁺ ions diffusivity, and mechanical degradation due to recurring large volumetric variation has been achieved with intricate nanomaterials design. Nanosized SnO₂ with different dimensions, morphologies and hierarchical structures have been experimentally synthesized and their correspondingly improved electrochemical performance are well-documented. Nanostructuring shortens the diffusion length of both Li⁺ ions and e⁻ and makes possible rapid charging/discharging of LIBs (enhanced power density).⁴⁴ This phenomenon can be explained using the one-dimension solution of Fick's second law (Equation 2.10),

$$\tau = \frac{L^2}{D} \quad (2.10)$$

where 'τ' refers to characteristic diffusion time constant, 'L' refers to diffusion length and 'D' refers to material dependent diffusion coefficient. However, as ionic and electronic conductivities of active material for LIBs electrodes (not limited to only SnO₂) are normally different, nanosized architectures with dissimilar dimensionalities such as fibers and sheets have been strategically exploited to optimize electrode design.⁴⁵⁻⁴⁸ Additionally, nanoscale electrode materials are reportedly more resistant towards mechanical degradation due to repetitive volume variation.⁴⁹

Figure 2. 3 List of generic strategies towards electrode material improvement for enhanced Li^+ ions storage performance and their motivation: (a) miniaturization of active materials, (b) formation of hierarchical structures/composites, (c) doping and functionalization, (d) morphological tuning, (e) encapsulation or coating of nanostructured electrode architectures, (f) modification of electrolyte's formulation. [Reprinted with permission from Ref. 15. Copyright 2015 Elsevier].

Both chemical and physical synthesis procedures have been explored to realize different nanostructures of SnO_2 . Exquisite morphological control from nanoparticles, nanoboxes,⁵⁰ nanorods, nanotubes, nanowires,⁵¹ nanosheets,⁵² single-shelled, yolk-shelled, and multi-shelled hollow nanostructures has been extensively achieved via wet chemical synthesis routes.⁵³ Morphological evaluation of some SnO_2 nanostructures are as summarized in Figure 2.4. Lou *et al.* has comprehensively reviewed various synthetic approaches for obtaining hollow nanostructures.⁵⁴ Self-templating, in which precursors partake in both morphology-determining and converting into essential components of final products and can involve different mechanisms, such as inside-out Ostwald ripening,⁵⁵ Kirkendall effect,⁵⁶ or galvanic replacement,⁵⁷ has overtaken conventional hard- and soft- templating (simple hollow nanostructures, additional processing for template removal required) as the go-to approach for increasingly complicated hollow nanostructuring. Even with increased complexity in the form of both morphological and chemical compositional configuration of subunits and shell(s) for hollow nanostructures, inherently low (although improved) tap density of hollow structural design for electrodes has limited commercial practicality

despite its overwhelming effective in accommodating volumetric variation.^{53, 54} However, nanostructured SnO₂ alone is insufficient to alleviate all the issues especially intrinsic electronic conductivity of SnO₂ remains low and nanosized SnO₂ self-aggregate readily to reduce the high surface energy, both detrimental to long-term cyclic stability at high rates.⁵⁸ Moreover, scalability of nanostructured SnO₂ remains less than satisfactory as it often involves costly precursors and low throughput yield.⁵⁹

Figure 2. 4 (a-b) TEM images of as-synthesized (template-directed) SnO₂ nanoboxes at low magnification, (c) high-magnification TEM image of a corner of an individual SnO₂ nanobox, showing a well-defined interior and a very thin wall [Reprinted with permission from Ref. 50. Copyright 2011 American Chemistry Society]. (d) Optical image of a macroscopic piece of interconnected SnO₂ prepared by flame-transport-synthesis (FTS) procedure, (e-f) FESEM images of 3D interconnected networks of FTS SnO₂ at different magnifications [Reprinted with permission from Ref. 51. Copyright 2015 John Wiley & Sons, Inc.]. (g) FESEM image of two-dimensional (2D) SnO₂ nanosheets fabricated using graphene oxide (GO) template and removal, (h) TEM of 2D SnO₂ nanosheets at low magnification, (i) HRTEM image of SnO₂ 2D nanosheets, inset is portion of image at even higher magnification; scale bar is equivalent to 1 nm [Reprinted with permission from Ref. 52. Copyright 2017 John Wiley & Sons, Inc.].

Although not as morphologically elegant as bottom-up chemical synthesis approaches, top-down physical approaches offer simplicity, practicality and scalability. Recently, methods such as high energy mechanical milling of SnO_2 , have nonetheless garnered much attention for synthesis of multifaceted nanostructures with outstanding electrochemical performance. By a simple two-step non-reactive ball milling method, Liu *et al.* demonstrated simultaneous dispersing and anchoring SnO_2 onto rigid SiC nanoclusters and concomitantly exfoliating graphite layers and coating around SnO_2 -SiC islands to prepare a ternary nanocomposite SnO_2 -SiC/G.⁶⁰ Interestingly, even in the absence of well-defined morphology for individual SnO_2 particles due to repetitious fracture and cold welding, SnO_2 -SiC/G nanocomposite still retained a reversible capacity of 1351 mAh g^{-1} , after 40 cycles at moderate current density of 100 mA g^{-1} within a voltage window of 0.01–3.0 V. Beyond inherent mixing and refinement of components, this work provides the conceptual framework of incorporation of a secondary/ternary phase to mitigate agglomeration of SnO_2 and enhance reversibility of conversion and alloying reaction as it undergoes destruction of crystal structures and chemical bond formation/breaking. Zhu *et al.* improved upon this simple and scalable approach by systematically incorporating different electrochemically active transition metal (ductile) species, such as copper (Cu),⁶¹ cobalt (Co),⁶² iron (Fe),⁶² and manganese (Mn),^{62, 63} instead of electrochemically inactive SiC. Although SnO_2 -Cu/G nanocomposite retained an unremarkable reversible capacity of 451 mAh g^{-1} , after 80 cycles, it exhibited a much improved initial Coulombic efficiency (C.E.) of 76 %.⁶¹ SnO_2 -Fe/G nanocomposite exhibited an exceptional initial C.E. of 83.2 % (average of seven tested cells), evidently higher than the lowly initial C.E. of 52.4 % for completely irreversible Li_2O formation/conversion reaction or moderate initial C.E. of 76.2 % for partially reversible conversion reaction (reverting of Sn/ Li_2O mixture to SnO).^{40, 62} Comparatively, SnO_2 -Co/G and SnO_2 -Mn/G recorded initial C.E. of 80 % and 77 %, respectively. More importantly, SnO_2 -Fe/G retained a reversible capacity of 1045 mAh g^{-1} after 200 cycles at 100 mA g^{-1} and SnO_2 -Mn/G recorded a reversible capacity of 700 mAh g^{-1} after 1300 cycles at high rate of 2.0 A g^{-1} .⁶² Figure 2.5 summarizes the simplicity of fabrication procedure, morphology of SnO_2 -Fe/G nanocomposites and comparison of different SnO_2 -M/G (M is Fe, Mn) and SnO_2 /G nanocomposites' electrochemical performance. Hitherto, prelithiation of electrode materials has been a standard procedure

in fabrication of commercial LIBs; costly but necessary (for energy density) as surplus of cathode material is required in the assembly process to provide excess Li to be sacrificially depleted to mitigate initial irreversible capacity loss due to consumption of active materials.^{29, 64, 65} Unexpectedly, such simple, cost efficient and, industrially mature method has proven to be a viable alternative towards assimilating a hierarchical structure and resolving both irreversibility and extended cyclic stability issues in conversion-based anodes for high energy LIBs.

Figure 2. 5 (a) Schematic representation of SnO₂-M/G nanocomposite fabrication, (b) FESEM image of as-synthesized SnO₂-Fe/G at low magnification, (c-d) FESEM images of SnO₂-Fe/G at high magnification, showing wide range of size distribution for SnO₂-Fe aggregations with graphite (G) nanosheets distinctively recognized, (e) Comparison of cyclic performance of the SnO₂-Fe/G, SnO₂-Mn/G nanocomposite and SnO₂ milled for 20 h at current density 0.2 and 2.0 A g⁻¹. [Reprinted with permission from Ref. 62. Copyright 2017 John Wiley & Sons, Inc.].

Elemental doping is one mature and straightforward route to enhance electrical conductivity and other properties of semiconductors such as SnO₂. The introduction of selected dopants or a secondary metal oxide phases into host lattice of SnO₂ has widely explored and been demonstrated to bring about improved electrochemical performance for LIBs anode.⁶⁶ Examples of investigated metallic/cationic dopants include antimony (Sb),^{67, 68} iron (Fe),^{69, 70} copper (Cu),⁷⁰ manganese (Mn),⁷⁰ cobalt (Co),⁷⁰⁻⁷³ zinc (Zn),^{70, 73} titanium (Ti),^{70, 74} nickel (Ni),^{70, 75} magnesium (Mg),⁷³ niobium (Nb),⁷⁰ zirconium (Zr),⁷⁰ and molybdenum (Mo)⁷⁶. Both redox inactive (Nb, Ti, Zr) and redox active (Fe, Co, Cu, Zn, Mn, Ni) species were investigated and a continuous hydrothermal procedure, with all parameters kept consistent except choice of dopant, was employed for synthesis of these various doped and undoped SnO₂ nanoparticles in a systematic investigation by Lübke *et al.*⁷⁰ Contrary to most literature, it was revealed that dopants, apart from 9 at.% Co, in fact, brought about negligible impact towards improving Coulombic efficiency, delithiation potential and cyclability. This observation, however, is consistent with other studies about the synergistic effect of Co on improving partial reversibility of the reduction of Li₂O formed during conversion reaction of SnO₂.^{73, 77-81}

Probably due to the lack of effective and accessible fabrication procedures, studies involving anionic doping of SnO₂ for LIBs anode are severely underrepresented.⁸²⁻⁸⁴ Sun *et al.* synthesized fluorine (F)-doped SnO₂@reduced graphene oxide (rGO) nanocomposite by an ethylenediamine (EDA)-mediated hydrothermal procedure with a tin (II) tetrafluoroborate Sn(BF₄)₂ as Sn source. This F-doped SnO₂@rGO retained a reversible capacity of 1277 mAh g⁻¹ after 100 cycles at current density of 100 mA g⁻¹ and heightened rate capability than its undoped counterpart, as illustrated in Figure 2.6 (a-c).⁸² Alternatively, Xu *et al.* prepared a F-doped doped SnO₂/rGO nanocomposite using a combination of sol-gel method and hydrothermal procedure with ammonium fluoride (NH₄F) as source of N dopant. The latter F-doped doped SnO₂/rGO recorded a reversible capacity of 1439 mAh g⁻¹ after 200 cycles at current density of 100 mA g⁻¹ and outstanding discharge capacity of 1148 mAh g⁻¹ at 1.0 A g⁻¹ (rate capability).⁸³ Most recently, using a laser induced pyrolysis process (as detailed in Figure 2.6 (d)), Wang *et al.* synthesized nitrogen (N)-doped (optimized 3 at.%) SnO₂ nanoparticles which exhibited exceptional

capacity retention of 1192 mAh g⁻¹ after 500 cycles at current density of 1.4 A g⁻¹ and rate capability of 522 mAh g⁻¹ at 10 A g⁻¹.⁸⁴ However, it is difficult to accurately isolate and quantify the effect of dopants on SnO₂, as controlled and precise doping at nanoscale remains elusive (challenging to have exactly the same/repeatable dopant concentration in different samples), and concomitant influence on crystal growth processes (variance in morphology and size) and modulated magnetic properties may have indirect implication(s) on measured electrochemical performance.^{85, 86}

Figure 2. 6 (a) Schematic representation of the synthesis parameters involved for the EDA-mediated hydrothermal procedure to prepare F-doped SnO₂@rGO and undoped SnO₂@rGO nanocomposites, Comparison of F-doped SnO₂@rGO and undoped SnO₂@rGO nanocomposites' (b) cyclic performance and their corresponding Coulombic efficiency for 100 cycles at 0.1 A g⁻¹, (c) rate capabilities, respectively [Reprinted with permission from Ref. 82. Copyright 2015 American Chemistry Society]. (d) Schematic representation for the sequences of steps in the laser pyrolysis process to prepare N-doped SnO₂, Comparison of undoped SnO₂, SnO₂+N3% and

SnO₂+N8%'s (e) cyclic performance and their corresponding Coulombic efficiency for 500 cycles at 1.4 A g⁻¹, (f) rate performance between voltage window of 0.01 to 3.00 V vs. Li⁺/Li. [Reprinted with permission from Ref. 84. Copyright 2017 John Wiley & Sons, Inc.].

Hierarchical structures by incorporation of a more conductive or mechanically buffering matrix and/or coating/encapsulation have been demonstrated to be beneficial towards relieving appreciable resistance and undesirable side reactions (lower Coulombic efficiency and short cycle lifespan) due to miniaturization of anode materials. Unconventionally, Liu *et al.* prepared a sandwich structure of SnO₂ layer slotted in between two super-elastic films of Ni-Ti alloy which retained a reversible capacity exceeding 800 mAh g⁻¹ after 300 cycles at 0.2 mA cm⁻². The suppression of Sn coarsening between lithiation/delithiation, improved reversibility of conversion reaction and consequential enhanced electrochemical cyclability has been accredited to this intriguing configuration of electrode materials.⁸⁷ Many works, especially with introduction of carbonaceous materials, such as amorphous carbon,^{88, 89} carbon nanotube (CNT),⁹⁰ and graphene,⁹¹ have indicated positive impact on enhancing overall conductivity and durability (cyclic stability) of SnO₂-based anodes. SnO₂/graphene nanocomposites have indisputably received the most attention amongst the many electrode designs and fabrication strategies.³¹ Graphene, in addition the hype of being the first experimentally synthesized two-dimensional (2D) material, possesses many favorable properties such as outstanding electrical conductivity, large specific surface area (SSA), comparatively high theoretical capacity at 744 mAh g⁻¹, excellent mechanical flexibility and chemical stability.^{31, 92, 93} Lin *et al.* laid down one of the earliest benchmark electrochemical performance for graphene nanoribbons (GNRs)/SnO₂ nanocomposite, which retained reversible capacity of 825 mAh g⁻¹ after 50 cycles at 0.1 A g⁻¹ recorded rate capability of 580 mAh g⁻¹ at 2.0 A g⁻¹.⁹⁴ Many different synthesis approaches including in-situ wet chemistry routes, such as hydrothermal,^{95, 96} solvothermal,⁹⁷ microwave-assisted heating,^{93, 98} supercritical method,⁹⁹ and ex-situ self-assembly routes¹⁰⁰⁻¹⁰² involving/in absence of surfactant have all been extensively reported. Additionally, optimization of structural arrangement (variety), as summarized in Figure 2.7, and compositional makeup (i.e. weight ratio of constituent components) of SnO₂/graphene-based anodes often leave many opportunities for discussion and exploration.¹⁰³ Nevertheless, graphene is intrinsically constrained to the chemistry of

carbon (intercalation mechanism and pseudocapacitance), whilst its excellent conductivity is considerably compromised by modification of redox-active side groups, unresolved restacking issue and lack of economical, environmentally benign and scalable fabrication procedure severely hampered its prospect towards commercialization.^{104, 105}

Figure 2. 7 (a) Schematic representation of six main different morphologies of transitional metal oxide (TMO)/graphene composite electrode materials. Encapsulated refers to single TMO nanoparticle or nanocluster being encapsulated by graphene, mixed refers to mechanical mixture of separately synthesized TMO(s) and graphene, wrapped refers to TMO being wrapped by numerous graphene sheets, anchored refers to TMO being decorated on the graphene surface, sandwiched refers to TMO layer in between two graphene layers and layered refers to alternating TMO and graphene nanosheets, (b) Schematic illustration highlighting probable drawback of graphene of blocking Li^+ ion movement [Reprinted with permission from Ref. 103. Copyright 2014 Springer Nature].

2.3 Layered Transition Metal Carbides and/or Nitrides (MXenes)

In 2011, a new two-dimensional (2D) early transition metal carbide, Ti_3C_2 , was first synthesized by selectively etching the Al atoms in layered hexagonal (space group $\text{P6}_3/\text{mmc}$) ternary carbide, Ti_3AlC_2 , with the use of aqueous hydrofluoric acid (HF) at room temperature (RT).¹⁰⁶ Ti_3AlC_2 is one of the 70-plus different known ternary carbides and nitrides with general chemical composition $\text{M}_{n+1}\text{AX}_n$, where M is an early transition metal, A is primarily a group 13 or 14 (i.e. group IIIA or IVA) element, X is C and/or N, and $n = 1, 2$, or 3 .¹⁰⁷ Additionally, $\text{M}_{n+1}\text{AX}_n$ can also be synthesized with solid solutions of M, A and X atoms, such as $(\text{Mo}_2\text{Ti})\text{AlC}_2$, $\text{Ti}_3(\text{Al}_{0.5}\text{Si}_{0.5})\text{C}_2$ and $\text{Ti}_2\text{Al}(\text{C}_{0.5}\text{N}_{0.5})$, respectively, potentially augmenting the 2D material constellation by quite a large number, when the A layers are selectively extracted, leaving the M_{n+1}X_n layers intact.¹⁰⁸⁻¹¹⁰

These layered hexagonal $\text{M}_{n+1}\text{AX}_n$ phases are composed of two formula units per unit cell, where M layers are nearly closely packed with X atoms filling between the octahedral sites and the M_{n+1}X_n layers are interleaved with layers of A atoms.¹¹¹ These laminated structures have anisotropic properties for the M–X bond which has an assortment of ionic/covalent/metallic characteristics, while the M–A bond is purely metallic in nature. The strong bonds between the layers in $\text{M}_{n+1}\text{AX}_n$ phases, unlike the weak van der Waals interactions present in other layered materials such as graphite and transition metal dichalcogenides (TMDs), are unsurmountable by mere mechanical exfoliation into 2D layers.¹¹² However, by exploiting the varied characteristics and relative strengths between M–X and M–A bonds, the relatively weakly bound and reactive A layers can be selectively etched with suitable chemical(s) leaving behind the chemically more stable closely packed $\text{M}_{n+1}\text{X}_n\text{T}_x$ layers. T_x refers to surface-terminating functional groups such as oxygen (=O), hydroxyl (–OH) or fluorine (–F) that are attached to the surface M atoms after the etching procedure. The thickness of the $\text{M}_{n+1}\text{X}_n\text{T}_x$ is dependent on the value of n . For example, when $n = 1$, the layer will consist of a single block of octahedra, when $n = 2$ and 3 , there will be two and three blocks, respectively. These new materials have been termed as MXenes in recognition of the loss of the A element from the parent $\text{M}_{n+1}\text{AX}_n$ phase and

2D morphology reminiscent of graphene. Figure 2.8 summarizes various MXenes which have either been experimentally synthesized or theoretically modelled.¹¹³

Figure 2. 8 Summary of experimentally and theoretically derived MXenes as reported in literatures [Reprinted with permission from Ref. 113. Copyright 2017 Springer Nature].

2.3.1 Synthesis and Processing of MXenes

The predominant synthesis routes to multi-layered MXenes involve selective removal of the A-element (hitherto limited to only Al) layers from $M_{n+1}AX_n$ phases with either aqueous hydrofluoric acid (HF) etching¹¹⁴ or fluoride-based salt etching (*in situ* formation of HF through the reaction of hydrochloric acid (HCl) and fluoride salt (such as lithium fluoride (LiF),¹¹⁵ ammonium bifluoride (NH_4HF_2),^{116, 117} sodium bifluoride ($NaHF_2$) and potassium bifluoride (KHF_2)¹¹⁸). To varying degree of success, other fluoride salts (such as sodium fluoride (NaF), potassium fluoride (KF), caesium fluoride (CsF), tetrabutylammonium fluoride, calcium fluoride (CaF_2)), could be added in place of LiF into either HCl or sulfuric acid (H_2SO_4) to prepare etchant solution for various multi-

layered MXenes (including Nb₂CT_x,¹¹⁹ Ti₂CT_x,¹²⁰ Cr₂TiC₂T_x,¹²¹ Mo₂TiC₂T_x,¹²¹ Mo₂Ti₂C₃T_x,¹²¹ Mo₂CT_x¹²² and (Nb_{0.8}Zr_{0.2})₄C₃T_x¹²³. Previously, only Al from group 13 and 14 elements, has been successfully removed from M_{n+1}AX_n phases to form MXenes.^{113, 124} Most recently, a breakthrough in the synthesis of Ti₃C₂T_x has been achieved via an oxidant-assisted selective etching (H₂O₂/HF at 40 °C for 45 h) of silicon (Si) from titanium silicon carbide (Ti₃SiC₂)—the most abundant (more cost-efficient than Ti₃AlC₂) M_{n+1}AX_n phase.¹²⁵ Various oxidant-HF etchant solutions (such as (NH₄)₂SO₈/HF, KMnO₄/HF, FeCl₃/HF) have demonstrated preliminary successes for selective etching of Si from Ti₃SiC₂. Thus, more MXenes (new) can be expected to be synthesized by extending this oxidant-assisted selective etching of A-layers (beyond only Al) to existing and growing family of M_{n+1}AX_n.

Interestingly, by extending the modified HF-etching protocol to beyond M_{n+1}AX_n phases, MXenes such as Mo₂CT_x and Zr₃C₂T_x have been synthesized by selective etching of Ga and Al from Mo₂GaC^{126, 127} and Zr₃Al₃C₂,¹²⁸ respectively. This adds to the growing family of HF-etched multi-layered MXenes, which includes Ti₂CT_x, Ta₄C₃T_x, (V_{0.5}Cr_{0.5})₃C₂T_x, (Ti_{0.5}Nb_{0.5})₂CT_x, Ti₃CN_xT_x, Nb₂CT_x, V₂CT_x, Nb₄C₃T_x, Mo₂TiC₂T_x, Mo₂Ti₂C₃T_x, Cr₂TiC₂T_x and (Nb_{0.8}Ti_{0.2})₄C₃T_x.^{120, 123, 129-131} The preferential etching of the M-A bond in M_{n+1}AX_n phases with Al and concurrent surface functionalization can be summarized by Equations 2.11 to 2.13:

Notably, essential etching parameters such as HF concentration (between 3 to 50 %), duration of immersion (from 2 h to a few days) and temperature (from room temperature to 55 °C) necessary to completely convert various parent M_{n+1}AX_n phases into multi-layered MXenes expectedly differ, depending on the M species, structure and lateral size.^{120, 129, 132, 133} Inevitably, different etching conditions will yield MXenes with varied defect concentrations and surface chemistry, and will be discussed later within this subsection.

However, HF-etching is not applicable for synthesis of nitride-based MXenes as more energy may be necessary for extraction of the more strongly bound Al from $\text{Ti}_{n+1}\text{AlN}_n$ than from $\text{Ti}_{n+1}\text{AlC}_n$.¹³⁴ Furthermore, the as-prepared less stable $\text{Ti}_{n+1}\text{N}_n$ could have probably been dissolved in concentrated HF solution.^{114, 135} Instead, a molten-salt assisted synthesis of multi-layered $\text{Ti}_4\text{N}_3\text{T}_x$ has been reported by thermally treating an equal mass of Ti_4AlN_3 powders ($>37\ \mu\text{m}$) and fluoride salt mixture (59 wt.% KF, 29 wt.% LiF and 12 wt.% NaF) at $550\ ^\circ\text{C}$ for 0.5 h in argon (Ar).¹³⁶ Previously, high temperature ($>800\ ^\circ\text{C}$) gaseous halide etching, molten-salt assisted approach or even evaporation of A-layers from $\text{M}_{n+1}\text{AX}_n$ in vacuum has failed to produce MXenes due to limited selectivity of gaseous etchants and preferential formation of cubic phase (at elevated temperature).¹³⁷⁻¹⁴⁰

The synthesis using *in situ* formation of HF by addition of fluoride salt (LiF etc.) to HCl yields laterally large flakes of single/few-layered $\text{Ti}_3\text{C}_2\text{T}_x$ with less defects and consequential enhanced performance in energy storage application.^{115, 141} The concomitant intercalation of Li^+ ions and water increases $\text{Ti}_3\text{C}_2\text{T}_x$ interlayer space and enables delamination to form single/few-layered $\text{Ti}_3\text{C}_2\text{T}_x$ even without additional procedure unlike HF-etched $\text{Ti}_3\text{C}_2\text{T}_x$. Subsequent prolong period of mechanical agitation (such as sonication or shaking) or intercalation of polar organic molecules (such as dimethyl sulfoxide (DMSO), hydrazine, urea,¹⁴² isopropylamine¹⁴³), large organic base molecules (such as tetrabutylammonium hydroxide (TBAOH), choline hydroxide or *n*-butylamine¹⁴⁴), or even various metal cations^{141, 145} may be optional for HCl/LiF-etched $\text{Ti}_3\text{C}_2\text{T}_x$ and other MXenes. Figure 2.9 summarizes the synthesis conditions for the two predominant etching routes to $\text{Ti}_3\text{C}_2\text{T}_x$.¹⁴⁶

Figure 2. 9 Summary of parameters (different etchant concentrations and etching durations) for Ti₃C₂T_x synthesis from Ti₃AlC₂ by either HF and *in situ* HF etching. HF and bifluoride salt route yield mostly multi-layered Ti₃C₂T_x and thus necessitate additional intercalation procedure with large organic molecules such as DMSO or TMAOH to achieve delamination and single/few-layered Ti₃C₂T_x. Due to intercalated Li⁺ and H₂O, spontaneous delamination may be accomplished by the HCl/LiF etchant route, and dependent on the concentration of HCl and LiF in the formulated etchant, with (clay) or without sonication (MILD) [Reprinted with permission from Ref. 146. Copyright 2017 American Chemical Society].

In the synthesis of HCl/LiF-etched Ti₃C₂T_x, a change of the concentration of LiF and HCl in the etchant solution was reported to significantly change the quality (defects), lateral sheet size and ease of delamination.^{147, 148} An increase in molar ratio of LiF: Ti₃AlC₂ from :1 to $\geq 7.5:1$, accompanied by an increase in HCl concentration from 6 to 9 M yielded larger single/few-layered Ti₃C₂T_x with less defects even without the need for sonication.^{105, 147, 148} Figure 2.10 shows the morphological differences in HCl/LiF-etched Ti₃C₂T_x, with concentration of precursors (HCl, LiF, Ti₃AlC₂), as observed under TEM and AFM, respectively.¹⁴⁸ An improved etchant formulation with 9 M HCl/12 M LiF (even higher molar ratio of LiF: Ti₃AlC₂) has been recommended for optimal synthesis of larger flakes of less defective HCl/LiF-etched Ti₃C₂T_x (most desirable for high electronic conductivity).¹⁴⁶

Figure 2. 10 TEM images of $\text{Ti}_3\text{C}_2\text{T}_x$ flakes synthesized with molar ratio LiF to Ti_3AlC_2 (a) 5:1 (Route 1), and (b) 7.5:1 (Route 2), respectively. Small panels in (a) and (b) show HRTEM images and SAED patterns of monolayer 2D crystals of $\text{Ti}_3\text{C}_2\text{T}_x$. AFM images of the $\text{Ti}_3\text{C}_2\text{T}_x$ flakes deposited on Si/SiO₂: (c) Route 1, and (d) Route 2. (e) AFM height profiles measured along the dashed lines in (c). The colors of the height profiles in (e) correspond to the colors of the dashed lines in (c). (f) AFM height profile measured along the dashed line in (d) [Reprinted with permission from Refs. 148 and 124. Copyright 2016 John Wiley & Sons, Inc., and Copyright 2017 The Royal Society of Chemistry, respectively].

As observed from literature, $\text{Ti}_3\text{C}_2\text{T}_x$ is the most widely studied and applied amongst MXenes.^{113, 124, 149} Although there are numerous protocols to derive MXene materials,¹⁴⁶ it is unrealistic to expect one synthesis route to invariantly fulfill the criteria of various applications with different desired properties. Thus, it is inherent to first understand the required properties of MXenes for certain application and then accordingly adopt or adjust synthesis parameters.

Proceeding from colloids of delaminated MXenes, a comprehensive variety of deposition procedures for these solution-processed MXenes has been reported.¹⁴⁶ These methods include alternating vacuum-filtration,^{150, 151} spin coating,¹⁵²⁻¹⁵⁴ spray coating,^{155, 156} painting^{115, 157} or slurry rolling^{105, 151}. Figure 2.11 highlights a few of these approaches to fabricating electronically conductive, freestanding and flexible $\text{Ti}_3\text{C}_2\text{T}_x$ films.¹⁴⁶ More recently, freeze-drying method has been explored as a viable route to alternatively prevent restacking of delaminated MXene nanosheets and attain enhanced electrochemical performances.^{158, 159}

Figure 2. 11 Schematic representation of fabrication methods such as alternating vacuum-filtration (left), spray coating (center), and painting (right) to prepare freestanding and flexible $\text{Ti}_3\text{C}_2\text{T}_x$ film (as depicted by the corresponding digital photographs (below)) [Reprinted with permission from Ref. 146. Copyright 2017 American Chemical Society].

2.3.2 Selected Properties of MXenes for Energy Storage Applications

MXenes are promising materials for energy storage applications. First, MXenes have been experimentally and theoretically demonstrated to be capable hosts (with decent theoretical capacity) for various alkali metal ions, such as Li^+ , Na^+ , K^+ , Ca^{2+} and Al^{3+} , by both adsorption on surface and redox reactions on active sites.^{142, 160-162} Unlike typical diffusion limited battery electrode materials, intercalation of ions in MXenes can paradoxically occur at a high rate, without significantly depreciating their energy storage capacities.¹²⁴ Levi *et al.* explained that this capacitive paradox was made possible by the presence of both shallow and deep cationic adsorption sites, saturated with ions and water molecules.¹⁶³ Moreover, an *in situ* X-ray absorption spectroscopy (XAS) study revealed a continuous change in the oxidation state of Ti during lithiation/delithiation of $\text{Ti}_3\text{C}_2\text{T}_x$, reaffirming pseudocapacitance as the dominant charge storage mechanism.¹⁶⁴ Consequently, the galvanostatic charge-discharge profiles of MXenes in metal-ion batteries are devoid of plateau region (resemblance of capacitive/non-faradic behavior instead).¹¹³ Second, MXenes are endowed with excellent electronic conductivity^{150, 156} (crucial for high power battery electrodes) or can be tuned to semiconducting, depending on the identity of M, X, and T_x .^{106, 113, 120, 152, 165, 166} According to theoretical studies, MXenes sheets with =O terminations are suggested to possess the highest capacity as compared to other surface groups (T_x), while either -OH or -F impedes Li^+ transport.^{164, 167} In addition, the weak van der Waals' forces between T_x which hold exfoliated multi-layered $\text{M}_{n+1}\text{X}_n\text{T}_x$ layers together, may be favorably exploited to achieve delamination and single/few-layered MXene colloid(s).¹⁶⁸ Two independent *ab initio* density function theory (DFT) calculations by Xie *et al.* and Er *et al.* similarly concluded that Li^+ storage capacity of $\text{Ti}_3\text{C}_2\text{T}_x$ was indeed enhanced by a larger interlayer distance.^{161, 169} This reiterates the importance of having dispersed MXene single layers to achieve high LIB anode performance. Last, single/few-layered MXenes possess low diffusion barriers which are favorable for high rate performance, as well as exceptional mechanical properties that are invariant to ion adsorption, which is desirable for cyclic stability.^{113, 124, 170}

2.3.3 Strategies to Enhance MXene's Electrochemical Performance

MXene-based nanocomposites offer the most promise for high-capacity and high-rate electrode materials. In this approach, active material, such as electrochemically active transition metal oxides (TMOs), contributes high energy density and mitigates restacking of MXene layers, and MXene functions as a highly conductive network and confinement against perpetual volumetric variation and agglomeration of TMOs, which deteriorate electrode structural integrity. To achieve synergistic hybridization with substantially enhanced cyclic longevity and fast-charging capability, there are continuous efforts towards the development of various synthesis approaches for assimilating tailored architectures.

In bid to improve the electronic conductivity between layers of HF-etched $\text{Ti}_3\text{C}_2\text{T}_x$ sheets, reduce contact resistance amongst the sheets and increase ion accessibility by preventing restacking, Lin *et al.* grew conductive CNFs to connect the isolated layers. Consequently, this 86.2 wt.% $\text{Ti}_3\text{C}_2\text{T}_x/\text{CNFs}$ retained a reversible capacity of 320 mA h g^{-1} at 1C after 300 cycles and 97 mA h g^{-1} at 100C even after 2900 cycles (Figure 2.12 (b)).¹⁷¹ Alternatively, Ren *et al.* improved ion accessibility by synthesizing porous $\text{Ti}_3\text{C}_2\text{T}_x$ flakes and by incorporating 10 wt.% of MWCNTs as interlayer spacers and conductive agent, the as-prepared porous $\text{Ti}_3\text{C}_2\text{T}_x/\text{MWCNTs}$ retained a reversible capacity of 800 mA h g^{-1} at 160 mA g^{-1} after 350 cycles. This exceptional reversible capacity is presumed to be consequential of more adsorption and storage of Li^+ ions on the edges of pores in this porous $\text{Ti}_3\text{C}_2\text{T}_x/\text{MWCNT}$ composite.¹⁷² Zou *et al.* synthesized a 90 wt.% HF-etched $\text{Ti}_3\text{C}_2/\text{Ag}$ composite, by reducing AgNO_3 in the presence of $\text{Ti}_3\text{C}_2\text{T}_x$. The formation of well-dispersed Ag nanoparticles on the layered $\text{Ti}_3\text{C}_2\text{T}_x$ improved its overall electrical conductivity. This composite electrode recorded a reversible capacity of 310 mA h g^{-1} at 1C (320 mA g^{-1}) after 800 cycles, 260 mA h g^{-1} at 10C after 1000 cycles and 150 mA h g^{-1} at 50C after 5000 cycles. It was inferred that the Ag species had important catalytic roles in increasing more efficient and conductive Ti(III) species from Ti(II) species in the $\text{Ti}_3\text{C}_2/\text{Ag}$ composite after 2000 cycles (discharge–charge), whereas a pristine $\text{Ti}_3\text{C}_2\text{T}_x$ displayed negligible Ti species variation after cycling.¹⁷³

To overcome its inherent moderate gravimetric capacity, Luo *et al.* synthesized a PVP–Sn⁴⁺@Ti₃C₂T_x nanocomposite, which exhibited a synergistic “pillar effect”, whereby spontaneous expansion of anchored Sn when alloying with Li⁺, concurrently pushed the Ti₃C₂T_x interlayers further apart to allow more Li⁺ intercalation. And when evaluated in a half-cell configuration, it retained a reversible capacity of 544 mA h g⁻¹ at 500 mA g⁻¹ after 200 cycles (Figure 2.12 (c)).¹⁷⁴ Zhao *et al.* prepared a freestanding delaminated HCl/LiF etched Ti₃C₂T_x/planar NiCo₂O₄ composite film using three different methods, namely alternating filtration, spray coating and an *in situ* growth process (Figure 2.12 (d)). The former two methods offered the flexibility to fabricate the hybrid films with different mass ratios of NiCo₂O₄ to Ti₃C₂T_x and it was noted that the mechanical properties deteriorate with increasing NiCo₂O₄ content. The *in-situ* growth process, probably catalyzed by Ni and Co cations, induced partial oxidation of Ti₃C₂T_x flakes and resulted in a comparatively reduced conductivity of the hybrid film. It was established that the activated (through pre-cycling at low rates) spray-coated 50 wt.% Ti₃C₂T_x/planar NiCo₂O₄ hybrid film (3 μm) displayed the best performance amongst the three samples as it retained a reversible capacity of ca. 1010 mA h g⁻¹ at 1C after 100 cycles. This performance was attributed to better electrolyte penetration with a higher degree of disorder in arrangement of Ti₃C₂T_x and planar NiCo₂O₄ nanoflakes within the film due to spray coating and a large amount of Ti₃C₂T_x (50 wt.%) to facilitate fast electron and ion transfer.¹⁷⁵

Figure 2.12 (a) Rate performance of the TiO₂/Ti₂CT_x hybrid obtained by partially oxidizing Ti₂CT_x with H₂O₂ (ca. 5 minutes of contact time) at various current densities [Reprinted with permission from Ref. 176. Copyright 2016 The Royal Society of Chemistry]. (b) Cycling stability of Ti₃C₂T_x at 1C and the Ti₃C₂T_x/CNF composite at 1C and 100C. The inset shows the electrochemical impedance spectroscopy (EIS) plots of Ti₃C₂T_x and Ti₃C₂T_x/CNF composite [Reprinted with permission from Ref. 171. Copyright 2015 The Royal Society of Chemistry]. (c) CV curves of PVP-Sn⁴⁺@Ti₃C₂T_x at a scan rate of 0.1 mV s⁻¹ [Reprinted with permission from Ref. 174. Copyright 2016 American Chemical Society]. (d) Schematic representation of approaches for the fabrication of free-standing and flexible Ti₃C₂T_x/TMO hybrid films through sandwich-like assembly by alternating filtration, spray coating methods and an *in situ* growth method [Reprinted with permission from Ref. 175. Copyright 2016 Elsevier].

2.4 Research Gaps

Question # 1: Is the associated absence of well-defined morphology in high energy mechanical activation of SnO₂ not detrimental to overall electrochemical performance?

Both Liu *et al.* and Zhu *et al.* demonstrated exceptional improvement to Coulombic efficiency, cyclic stability and rate capability via simultaneous dispersing and anchoring SnO₂ nanoparticles (ca. 100 nm) onto either rigid SiC or ductile transition metal (such as Cu, Co, Mn, Fe) nanoclusters and concomitantly exfoliating micro sized graphite into layers and coating to prepare ternary SnO₂-based nanocomposites.⁶⁰⁻⁶³ Notably, this was achieved despite non-existence of regular/uniform morphology and size distribution for the final ternary SnO₂-based nanocomposites due to repetitive fracturing and cold welding. This raises the question about the relationship (effect) and necessity of morphological control of final SnO₂ products for enhanced cyclic and rate performance. An intuitive follow-on question is whether micro sized SnO₂ (more cost efficient) can be used in place of nanosized SnO₂ as the precursory powder since high energy mechanical milling inherently brings about concurrent mixing and refinement of the components. These questions are consistent with the fact that, to date, despite tremendous progress in intricate morphological control with nanostructured SnO₂ through chemical syntheses, the ideal or optimal morphology/size for application of SnO₂ as a LIB anode remains inconclusive. Additionally, the influence of effective milling duration, graphite content, and comminution medium in high energy mechanical activation (physical top-down approach, industrially mature, but often overlooked for fabrication of multifaceted nanostructures) has not been well elucidated.

Question # 2: If changing the dopant species in SnO₂ is dated and ineffective in enhancing overall electrochemical performance, what are the other possible adjustments that can be made to improve on the prospects of the works on doping SnO₂?

Elemental doping is one tried and tested method to increase electrical conductivity of SnO₂ (semiconducting). Although many different cation-doped (substitutional) SnO₂-based anodes have been examined, only Co-doped SnO₂ has, across various studies, consistently exhibited noticeable improvement to initial Coulombic efficiency, delithiation potential and cyclic stability.^{66, 70, 73, 77-81} This implies that regardless the choice of cationic species, it is apparently naïve to expect an electrically optimized SnO₂ nanostructure to be the breakthrough solution to resolve cyclic instability and poor rate performance. In addition, precise doping at nanoscale remains elusive and this leads to the question if there can be post-synthesis procedure(s) to rectify/modify the concentration of dopant(s). If so, may the substitutional dopant species then be viewed as a temporary inclusion in the SnO₂ matrix and subsequently removed (partially or completely) via selective etching to achieve possibly new architecture designs for SnO₂-based anodes with introduced defects or lattice vacancies (previously occupied by dopant atoms) to better accommodate volumetric variation between lithiation and delithiation and improve cyclic lifespan.

Question # 3: Since the customizability of tap density and areal mass loading of active materials are limited by current solution-processing of Ti₃C₂T_x/TMO, can there be alternative technique(s) to assemble the nanostructure but with improved packing density?

Based on literatures, fabrication Ti₃C₂T_x/TMO hybrid for battery electrodes has been limited to alternating vacuum filtration, alternating spray coating, rolling, in-situ wet chemistry synthesis, self-assembly in solution or modified layer-by-layer assembly.^{113, 124, 146, 175, 176} Synergistic Ti₃C₂T_x/TMO nanocomposites, with different chemistry and Li⁺ ions storage mechanisms, offer great improvement to specific energy and power density but low mass loading or limited customizability of areal capacity (freestanding films) restricts their commercial practicability.¹⁷⁵ To date, few works, if any, have reported on procedure or attempt to assemble nanostructured Ti₃C₂T_x/TMO hybrid with either customizable packing/tap density or industrially compatible approach beyond solvent-based processing. This raises the question if homogeneously mixed Ti₃C₂T_x/TMO powder samples, not in

the form of freestanding film, can be scalable and prepared without compromising the morphology (sheet size) or excellent electronic properties of $\text{Ti}_3\text{C}_2\text{T}_x$ component. Next, it is intuitive to question the optimal electrochemical performance of $\text{Ti}_3\text{C}_2\text{T}_x/\text{TMO}$ and examine if a variant compositional makeup (less of $\text{Ti}_3\text{C}_2\text{T}_x$ and more of TMO) can bring about enhanced Li^+ storage capability exceeding the sum of its constituent components (synergistic effect) than previously reported.

2.5 Thesis in the Context of the Literature

Firstly, a simple and industrially compatible one-step planetary ball milling of a mixture containing commercially available micro-sized SnO_2 and graphite powders without inert atmosphere is conducted. Deviating from the literature (usually multi-step and under protective atmosphere) and customary use of nano-sized SnO_2 (costly) as starting material, this study is designed to incorporate the randomness of comminution and mixing of components (less costly but larger starting size) by a combination of impact, shear and attrition to intentionally achieve final products without regular morphology (inclusive of SnO_2) nor size distribution. A systematic optimization of milling time and graphite content to develop binary SnO_2 -C nanocomposites with enhanced electrochemical performance for LIBs anode application is experimentally realized.

Secondly, the effect of acid etching on the morphology (size) and dopant concentration on solvothermally synthesized antimony (Sb)-doped SnO_2 is systematically investigated. Typically, the quantitative control/optimization of dopant level in semiconducting SnO_2 is achieved via addition of dopant species during precursory or synthesis stage. Interestingly, and for the first time, a post-synthesis acid treatment of Sb-doped SnO_2 (with a consequential reduction of Sb dopant) is demonstrated to be more effective in improving cyclic stability of Sb-doped SnO_2 as compared to untreated Sb-doped SnO_2 (mere doping) and undoped SnO_2 . The choice of etchants (hydrochloric acid (HCl), nitric acid (HNO_3), sulfuric acid (H_2SO_4)) and duration of immersion in etchants (2, 4, 6, and 8 h) are examined.

The contributions to such improved electrochemical performance are postulated and discussed in view of circumstantial evidence from materials characterization.

Last, but not least, a simple and industrially compatible freeze-drying procedure to fabricate nanostructured $\text{Ti}_3\text{C}_2\text{T}_x\text{-SnO}_2\cdot\text{Co}_3\text{O}_4$ hybrid anode is initiated. Although freeze-drying has been a mainstream procedural processing of 2D graphene to achieve high specific area/exfoliation,¹⁷⁷ few has incorporated this method for the exfoliation of 2D $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets or its associated nanocomposites. and with most work still reliant on solvent-based processing (tedious). Herein, it is hypothesized that with a sufficiently low concentration of $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets and $\text{SnO}_2\cdot\text{Co}_3\text{O}_4$ nanocubes well-dispersed in water and sublimated, the homogeneity of $\text{Ti}_3\text{C}_2\text{T}_x/\text{TMO}$ powder would be comparable or even exceed those achievable via multi-step solvent-based procedure. In addition, the electrochemical performance of $\text{Ti}_3\text{C}_2\text{T}_x\text{-SnO}_2\cdot\text{Co}_3\text{O}_4$ hybrid anodes with varying compositions is evaluated to identify the optimal composition for enhanced Li^+ storage capability exceeding the sum of its constituent components (synergistic effect).

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Chapter 3

Experimental Methodology

The focus of this chapter is to highlight the underlying rationale and principles of various synthesis procedure and characterization techniques adopted in experiments within this thesis. Firstly, the impetus for the choice of precursor and synthesis routes will be presented. Secondly, the working principle of characterization tools and corresponding limitations will be elucidated. Lastly, the fabrication processes, electrochemical evaluation of as-synthesized materials in half-cell configuration for application in lithium-ion batteries will be elaborated in detail.

3.1 Selection of Materials

Both the advantages and limitations of SnO_2 and $\text{Ti}_3\text{C}_2\text{T}_x$ as anode material in LIBs have already been extensively reviewed in the previous chapter, thus they will not be repeated in this chapter. Amongst the many probable strategies to improve the electrochemical performance of SnO_2 , three different engineering principles have been specifically chosen for experimentation and discussion within this dissertation. These three engineering principles are as follows:

- 1) Mechanical ball milling of micron-sized precursors to achieve concomitant downsizing to nanoscale, carbon coating, incorporating voids and conductive graphite network to better buffer strain and improve overall conductivity;
- 2) Elemental doping of tin oxide via solvothermal synthesis and subsequent acid etching to surface modify these as-synthesized antimony-doped tin oxide (ATO) and improve cyclic stability;
- 3) Incorporating highly conductive and pseudocapacitive $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets to CoSnO_3 nanocubes to enhance overall conductivity, cyclic stability and rate performance.

3.2 Selection of Synthesis Methods

The main aim of this thesis is to demonstrate simple and scalable methods to prepare tin-based oxides for application as anode material in LIBs. Factors such as reproducibility, cost of precursors, turnover time, and scalability have been considered when choosing synthesis methods. Taking these factors into consideration, three different methods, namely planetary ball milling, solvothermal synthesis, and co-precipitation are selected for the preparation of modified tin-based oxides.

3.2.1 Working Principle of High Energy Planetary Ball Milling

High energy planetary ball milling is a process in which vials and the supporting disc rotate in opposite directions. Two consequential centrifugal fields alternately act in similar and opposite directions. In the vials, milling balls are accelerated by these two centrifugal forces. At intervals, the milling balls are forced down the inside wall of the vial and grind the powder charge (sample), and in other instances, these milling balls are spontaneously lifted and traveled within the vial before colliding against the opposite inside wall.¹ At the same time, the charge rotates around two axes—the mill axis and the vial axis. Mechanical energy is transferred to the particles, causing deformation, friction, cold weld, fracture, amorphization and so on.² High energy planetary ball milling can also bring about mechanical activation, mechanical coating or induce mechanical alloying/chemical reactions (mechanochemistry), however these are beyond the scope of this thesis dissertation. Simple mechanical milling is an inexpensive alternative approach for producing few-layer graphene from bulk graphite (instead of series of process such as thermal oxidation, expansion, and reduction), as well as for assembling complex hierarchical nanostructures with enhanced properties that may be challenging to achieve via conventional (chemical synthesis) approaches.³⁻⁵

There are several variables which affect the milling efficiency. Substantial particle size reduction occurs with extended milling duration although its effectiveness exponentially decays.⁶ Larger and denser milling balls have comparatively higher impact forces on the sample powders. The milling intensity is generally proportional to the milling speed though beyond certain critical speed, the milling balls will be pinned to the vial wall and not exert any impact on the sample powders. The main advantages of this synthesis method are its simplicity and industrial compatibility. However, several drawbacks are associated with this method. As it is a mechanical top-down approach, ball milled products generally do not have uniform distribution of well-controlled morphology (unlike chemical bottom-up approach) and tend to aggregate with a broad range of particle sizes. It also remains challenging to distinguish if amorphization has indeed occurred in the aggregated, polydisperse ball milled sample with irregular morphologies. There may be probable

contamination due to wear and tear from milling media although it has been presumably kept to minimal as tungsten carbide (high hardness and density) balls and vials are used.

3.2.2 Working Principle of Solvothermal Synthesis

Solvothermal synthesis is a versatile nonaqueous route to produce a wide variety of highly crystalline metal oxide nanostructures with different sizes and morphologies. In a typical procedure, molecular precursors (e.g. metal halides, metal acetates or metal acetylacetonates) are first homogeneously dissolved in an organic solvent (e.g. alcohols, ketones, amines etc.) or in a solvent mixture.⁷ Using either an oil bath, an autoclave or a microwave reactor, this mixture may then be heated to temperatures between 50 to 250 °C and held isothermally over various duration. At the end of the heat treatment, the product can be easily retrieved from the reaction liquid by centrifugation. In a seemingly simple SnCl₄-benzyl alcohol system, there are essentially numerous possibilities to the formation of a metal-oxygen bond.⁷ However, one proposed simplified mechanism for solvothermal synthesis of ATO nanoparticles via ‘benzyl alcohol route’ is S_N1 nucleophilic substitution reaction.⁸ Firstly, it involves the formation of a stable benzyl carbocation intermediate due to probable and effective charge distribution onto the benzyl group by *p*- π conjugation. Next, by nucleophilic substitution with chloride ions, the benzyl carbocation forms benzyl chloride and a metal hydroxide, which will further react to form the metal oxide.

The main advantages to this solvent-based synthesis route are its comparatively low process temperature, and the many possibilities towards controlling and tailoring the particle size, shape, and chemical composition.⁹ The many physio-chemical factors influencing solvothermal reactions are as follows: the chemical and physiochemical properties of solvent and precursors used, the nature of additives, pH value of the reaction medium, the temperature, pressure and dwelling duration the reaction mixture is subjected to, and the associated technologies (e.g. microwave) deployed.¹⁰ However, as the syntheses are performed within closed vessels and under harsh reaction conditions (e.g. high temperature and high pressure), there is still a lack of in-depth understanding of

nanoparticle formation, crystallization mechanisms, and surface chemistry. It is impossible to predict the product morphology from the components of reaction mixture. It also remains challenging to prevent agglomeration of nanoparticles and facilitate dispersion for subsequent processing. Cumulatively, synthesis development generally still depends on empirical know-how of individual research groups rather than generic guidelines and principles, and this may be detrimental to reliable and reproducible scale-up for industrial applications.

3.2.3 Working Principle of Selective Acid Etching

As detailed in Section 2.3.1 Synthesis and Processing of MXenes previously. Although selective partial or complete (if possible) removal of substitutional dopant from a SnO_2 matrix/surface is unprecedented, selective/preferential acidic/basic etching has long been utilized to exploit the discrepancy of reactivity for different components (both metallic and semiconducting; inclusive of elemental and compound) in etchant solutions.¹¹⁻¹³

3.2.4 Working Principle of Freeze-Drying process

Freeze-drying is an industrially mature drying procedure for direct removal of solvents from samples under low vacuum through sublimation. It is especially appropriate for drying heat sensitive specimens, is a well-established approach to maintain microstructures and create porosity and has been a part of mainstream procedural protocol to realize high specific area/exfoliation of 2D graphene-related materials.¹⁴

3.2.5 Working Principle of Co-precipitation

Co-precipitation is a customizable wet chemistry process, in which multiple components are simultaneously precipitated from a designed solution, to synthesize multi-element nanostructures with well controlled stoichiometric composition, varying sizes and

morphologies.¹⁵ In a typical procedure, two or more metal precursors, in the form of highly soluble inorganic salts such as chlorides, nitrates, or carbonates, are added to a solvent (usually water) and stirred to obtain a homogeneous solution. Subsequently, alkaline precipitating agent (e.g. ammonia solution (NH_4OH), sodium hydroxide (NaOH) or sodium bicarbonate (NaHCO_3)) is commonly added to induce precipitation since most precursory salt solutions are coincidentally acidic in nature.¹⁶ Driven by homogeneous nucleation, insoluble mixed nanocrystals are formed. With inclusion of capping agent(s), the aggregation of primary nanocrystals may be alleviated.¹⁷ In some instances, post formation calcination is necessary to obtain the desired phase (especially oxides).

Co-precipitation method for preparation of multi-element (mixed) transition-metal oxides epitomizes procedural simplicity and relatively short reaction times, which are favorable for industrial scale-up. Precipitated products may be further modified, through subsequent addition of caustic solution (selective etching) or excess alkaline solution (converting of parts of precipitate to solute), to form hollow morphologies.¹⁸⁻²¹ However, there are some caveats to be taken into consideration. The requirement of a post formation heat treatment adds to the overall turnover time for the synthesis of mixed metal oxides. This high temperature heat treatment may also lead to poor size control, loss of morphology, phase segregation and/or irreversible hard aggregates of primary nanosized metal oxides.

3.3 Selection of Characterization Techniques

Different characterization techniques were utilized to analyze structural, morphological, compositional and crystallographic properties, as well as effective surface area and porosity determination, of the as-synthesized nanomaterials. The relevant methods are scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), Brunauer-Emmett-Teller (BET) surface area analysis, and thermogravimetric analysis (TGA). Each characterization tool collects a certain limited but specific set of information about the nanomaterials under study. Consequently, a more comprehensive understanding about the samples can only be

achieved through an appropriate combination of probing with different techniques. Electrochemical performance of all samples was evaluated using galvanostatic discharge-charge tests, rate capability characterization, cyclic voltammetry (CV), and electrochemical impedance spectroscopy (EIS).

3.3.1 Working Principle of Scanning Electron Microscopy (SEM)

Scanning electron microscopy (SEM) is one of the essential imaging tools to investigate bulk specimen of nanomaterials at high magnification, with high resolution (resolvable distance >20 nm) and great depth of field. In a typical SEM operation, electrons are first emitted from a thermionic, Schottky or field-emission cathode and then accelerated by application of a voltage difference. Within the SEM column, there are various systems of electromagnetic lenses and apertures to converge the beam of accelerated electrons, as well as a high vacuum environment to minimize scattering. By probing the sample with a focused beam of energetic electrons, a variety of signals is generated by the interaction of electron beam with the surface of the sample.²² More accurately, the energetic electrons penetrate the sample to a certain depth and forms a tear-shaped interaction volume.

Amongst the plethora of emitted signals from elastic and inelastic scattering events, secondary electrons and characteristic X-rays are most commonly collected by different detectors to study topographical information and atomic composition, respectively. Secondary electrons are sensitive to the tilt angle of specimen surface, edges, and shadow contrast due to incomplete collection.²³ In secondary electron imaging (SEI) mode, the fraction secondary electrons with low exit depth, coupled with the strategic placement of an Everhart Thornley detector within the SEM column, cumulatively reveals the topology and morphology of the bulk specimen. In energy dispersive X-ray (EDX) spectroscopy, the specimen is bombarded with electrons accelerated by an even higher accelerating voltage than in SEI mode. An atom from the specimen becomes ionized when an inner shell electron is displaced after colliding with a primary electron, and correspondingly, an outer shell electron will drop into the inner shell to maintain orbital charge. Subsequently, the excited electron will return to its ground state after it emits an X-ray photon. As individual

element has discrete energy states, the emitted X-ray is distinctive and can be detected to identify which elements are present, both qualitatively and quantitatively. The variety of signals from the interaction of electron beam with specimen, interaction volume and the basic components in a SEM have been simplistically summarized and illustrated in Figure 3.1.

Figure 3. 1 Schematic representation of (a) interaction between the high energetic primary electrons and specimen and the different emitted signals from elastic and inelastic scattering events [Image originated from the internet. Copyright @ Wikipedia. Source: https://commons.wikimedia.org/wiki/File:Electron_Interaction_with_Matter.svg], (b) basic components within a typical SEM setup and how the electron beam is focused by series of magnetic lens before interaction with specimen [Image originated from the internet. Copyright @ Wikispace. Source: <http://cellularphysiology.wikispaces.com/scanning+electron+microscope+%28SEM%29>].

In this thesis, SEI mode was used to image the morphologies of various as-synthesized nanomaterials, and to obtain an estimate of particle size distribution and homogeneity of components dispersion within the nanocomposites. Prior to imaging, a thin layer of platinum was coated on samples consisting of poorly conducting metal oxides to minimize surface charging, which will affect the quality of SEM images. SEM analysis was

performed using JEOL JSM-7600F, equipped with a thermal field emission gun operating at 5 kV accelerating voltage.

3.3.2 Working Principle of Transmission Electron Microscopy (TEM)

Transmission electron microscopy (TEM) is another powerful tool to extract morphological, structural, crystallographic information of thin specimen of nanomaterials. In a typical TEM operation, electrons are first emitted from the surface of the cathode within an electron gun. To meet most practical high-resolution requirements, electrons are commonly accelerated with a high accelerating voltage (V_o) of 200 kV to form a high energy electron beam.²⁴ This corroborates well with a shorter wavelength of electrons can greatly enhance resolution of the electron microscope. The direct correlation between accelerating voltage and resolution can be better explained with Equations 3.1 and 3.2.

$$\lambda = \frac{h}{\sqrt{2meV_o}} \quad (3.1)$$

where ' λ ' refers to wavelength of electrons, ' h ' refers to Planck constant, ' m ' refers to mass of electron, and ' eV_o ' refers to energy of electron beam. According to Equation 3.1, a modified de Broglie equation, an application of a high accelerating voltage will reduce the wavelength of electrons. Consequently, this small wavelength of electrons will facilitate a very small resolvable distance (i.e. high resolution) as denoted by Equation 3.2,

$$d = \frac{0.61\lambda}{NA} \quad (3.2)$$

where ' d ' refers to minimum resolvable distance, ' λ ' refers to wavelength of electrons, and ' NA ' refers to numerical aperture. It is essential to operate under a high vacuum environment to minimize energy loss through scattering events.

Within the TEM column, there are series of electromagnetic lenses, such as condenser, objective, intermediate, and projector lenses, to deflect and focus the beam of electrons.²⁵ The condenser lens system governs the beam diameter and convergence of incident beam on a specimen. The focused beam of highly energetic electrons, unlike in SEM, exhibits particle and wave dualism, by both interacting with atoms in the sample and passing

through the thin specimen (usually < 100 nm), though the electrons are, to some extent, scattered. Simultaneously, an intermediate image (first) and diffraction pattern are generated on the image plane and the back-focal plane of the objective lens, respectively.

By varying the electromagnetic strength of the of the intermediate lens system, the TEM can be switched between diffraction mode and imaging mode. In diffraction mode, the intermediate lens focuses the diffraction pattern formed on the back-focal plane of the objective lens, while in imaging mode, the intermediate lens focuses the intermediate image generated on the image plane of the objective lens. Selected area electron diffraction (SAED) and objective apertures are selectively inserted to minimize the scattering and/or to select the diffracted (contribute to diffraction patterns) or non-diffracted beams (contribute to image contrast), respectively, to appear on the plane of the second intermediate image. Within imaging mode, selective exclusion of electron beam would result in different types of final images such as bright field (BF) (only transmitted beam allowed to pass), dark field (DF) (only diffracted beam allowed to pass) and high-resolution TEM (HR-TEM) (phase difference in electron waves). The projector lens system further magnifies the reciprocal space diffraction pattern or the real space image before either is observed on a fluorescent viewing screen. The basic components in a TEM and the electron beam path in either diffraction or imaging mode have been simplistically summarized and illustrated in Figure 3.2.

Figure 3. 2 Schematic representation of basic components and electron beam pathway in a typically TEM in (a) diffraction mode, and (b) imaging mode.

The advantages of TEM method are accompanied by limitations.^{24, 26} At high magnification/resolution, information is only extracted from an extremely small and localized part of the examined specimen at any one time. Consequently, the first and most significant drawback is the limited statistics from sampling. Under TEM, the information from a three-dimensional (3D) specimen is projected as a two-dimensional (2D) image onto the fluorescent screen. The absence of depth sensitivity in TEM images is the second drawback, which increases the likelihood of misinterpretation, due to artifacts.

In this thesis, BF TEM imaging was used to investigate the morphology of ball milled SnO₂, antimony-doped tin oxide (ATO), CoSnO₃, Ti₃C₂T_x and the dispersion state of components within nanocomposites. With dissimilar mass-density (thickness and density) of individual components within the nanocomposites, there will be variation in electron intensity projected onto the image screen. Nanoparticles of SnO₂, ATO, CoSnO₃ with higher atomic mass will scatter the transmitted electrons more strongly than thin graphite layers or Ti₃C₂T_x nanosheets. For instance, ball milled SnO₂ nanoparticles will appear comparatively darker than thin layers of graphite, and CoSnO₃ nanocubes will appear relatively darker than few-layered Ti₃C₂T_x nanosheets. This mass-density contrast is useful

in differentiating various components as well as evaluating the homogeneity of components distribution within as-prepared nanocomposites. TEM analysis was performed using JEOL 2010 UHR TEM, equipped with a lanthanum hexaboride (LaB₆) gun operating at 200 kV accelerating voltage.

3.3.3 Working Principle of X-ray Diffraction (XRD)

X-ray diffraction (XRD) is a well-established tool to extract crystallographic information (such as crystalline phase(s) present, phase composition, lattice parameters, grain size, preferred orientation, atomic arrangement, atomic occupancy (vacancy and interstitial)) from solid samples of interest.^{27, 28} In a typical XRD operation, continuous X-rays with varying wavelengths are first produced by the X-ray tube. The incident beam of X-rays is then passed through series of soller slits, divergence slits, anti-scatter slits and filter to limit the axial divergence, equatorial divergence, height divergence, scattering and the K_β radiation, respectively. Consequently, monochromatic X-rays are irradiated onto the surface of the specimen. As the wavelength of X-rays ($10^{-8} - 10^{-11}$ nm) is comparable to the interplanar distance within crystal lattices, the monochromatic X-rays penetrate the surface and are subsequently scattered by interaction with atomic orbital electrons within the specimen.

The diffracted X-rays can either proceed constructively or destructively. Constructive interference is the superposition of diffracted, but in-phase, X-rays (path length difference equals to an integer multiple of the wavelength). This may be summarized by Equation 3.3 (a derivation from Bragg's Law),

$$n\lambda = 2d \sin \theta \quad (3.3)$$

where 'n' refers to a positive integer representing the order of diffraction peak, 'λ' refers to the wavelength of the incident X-ray, 'd' refers to the crystallographic interplanar spacing of the irradiated sample, and 'θ' refers to diffracted angle. Figure 3.3 illustrates an occurrence of Bragg's diffraction and its corresponding components in the equation, $n\lambda = 2d \sin \theta$. It is indicative that a variance in the atomic configuration will alter the path of

X-ray irradiation reaching a set of parallel lattice planes, resulting in a phase shift of the reflected X-rays. There are different configurations in which diffracted beams can be intercepted and recorded, however for powder XRD, a ‘fixed λ , varying θ ’ approach is typically adopted.²⁸ Some examples of configuration include a stationary X-ray source, coupled with rotating the specimen stage and detector by θ and 2θ , respectively, or a stationary specimen stage is paired with concurrently rotating both the X-ray and detector by θ . The diffracted X-rays (satisfying Bragg’s Law) are then passed through series of soller slits, divergence slits, anti-scatter slits and secondary monochromator before being measured by the detector in terms of count rates (intensity). Consequently, the derived diffraction intensity over a selected range of diffraction angle, 2θ , is presented as an XRD diffractogram.

Figure 3. 3 Schematic illustration of occurrence of Bragg’s diffraction, the path of incident and diffracted X-rays on two adjacent atomic planes, separated by a crystallographic interplanar spacing ‘ d ’.

In this thesis, X-ray powder diffraction (XRD) analysis was conducted to evaluate the crystallinity and phase of intermediates and final products. It is assumed that there are some hkl planes, in some of the many randomly orientated crystals within a powder sample, inadvertently positioned at angles, satisfying Bragg’s condition for coherent scattering.²⁸ The obtained XRD patterns reveal the presence of crystalline phases, and the phases (of SnO_2 , ATO, CoSnO_3 , $\text{Ti}_3\text{C}_2\text{T}_x$) are identified by comparing with a database of powder

diffraction files (the International Centre for Diffraction Data, ICDD— formerly the Joint Committee for Powder Diffraction Standards, JCPDS). However, it remains challenging to characterize amorphous or short-range ordered nanomaterial, such as ball milled graphite in Chapter 4, and especially so with a near-overlapping peak of SnO₂. In Chapter 5 (etching ATO with H₂SO₄, HNO₃, HCl) and Chapter 6 (freeze-dry assembly of Ti₃C₂T_x-SnO₂·Co₃O₄ nanocomposite), XRD analysis was performed using Shimadzu 6000 X-ray diffractometer with Cu K_α radiation ($\lambda=1.5418 \text{ \AA}$).

3.3.4 Working Principle of X-ray Photoelectron Spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS), also known electron spectroscopy for chemical analysis (ESCA), is a surface-sensitive spectroscopic technique to extract elemental composition and chemical state information from the top 10 nm (outer surface) of solid samples. XPS can detect all elements, except H and He, if the element of interest is no less than 0.1 at.%. In a typical XPS operation, highly energetic X-ray photons bombard the surface of the specimen under ultra-high vacuum conditions ($>10^{-9}$ millibar (mbar)). Ultra-high vacuum is necessary to remove adsorbed gases, contaminant from the specimen, to prevent arcing and high voltage breakdown, and to increase the mean free path for electrons and photons. When the massless and neutral package of energy (photon) is adequate to excite an electron in specific bound state(s), it will be completely absorbed by an atom/ion. Consequently, an inner shell/valence electron is ejected from the specimen, generating a photoelectron. There are two sequential de-excitation processes, namely Auger process (emission of Auger electrons) and fluorescence.²⁹ Figure 3.4 (a) and (b) illustrate the photoelectron emission and Auger electron emission, respectively. An initially emitted photoelectron is a core level electron, whereas an Auger electron is a non-core level electron subsequently emitted to conserve energy when an outer shell electron falls to fill the core level vacancy (created by photoelectron emission). Inevitably, some photoelectrons and Auger electrons are inelastically scattered en route to the specimen surface, while unaffected electrons are collected by an electron energy analyzer and will

be reflected on the energy spectra. The basic components in a typical XPS has been simplistically summarized and illustrated in Figure 3.4 (c).

By measuring the kinetic energy (K.E.) of initial emitted electrons, the corresponding binding energy (B.E.) of each of the emitted electrons can be derived by Equation 3.4 (a derivation from Ernest Rutherford's work),

$$B.E._{emitted\ electron} = E_{photon} - (K.E._{emitted\ electron} + \Phi) \quad (3.4)$$

where ' $B.E._{emitted\ electron}$ ' refers to the binding energy of initial emitted electron (not subsequent emitted Auger electron), ' E_{photon} ' refers to the energy of the irradiated X-ray photon, ' $K.E._{emitted\ electron}$ ' refers to the measured kinetic energy of emitted electron, and ' Φ ' refers to the work function of the spectrometer, which is an instrument-dependent constant.³⁰ However, it is to be noted that Equation 3.4 is not applicable to subsequent Auger emissions since the energies of Auger electrons (non-core level electrons) are indifferent to energy of incident X-ray photons.³¹

Figure 3. 4 Schematic illustration of (a) photoelectron emission, (b) Auger electron emission, (c) basic components in a typical XPS Image originated from the internet. Copyright @ LinkedIn Corporation 2018. Source: <https://www.slideshare.net/cynon/xps-3529469>].

There are two key pieces of information which could be derived from the XPS spectra. Firstly, as most elemental core level electron transition occurs at characteristic binding energy, the position and intensity (peak area) of the electron energy spectra may then be used to identify and to favorably/conditionally quantify the concentration of element(s) present, respectively. The quantitative elemental composition of the specimen may be derived from the integrated areas under characteristic peaks and their corresponding relative sensitivity factors (different elements have different values). Secondly, XPS can also reveal the chemical states of the element(s) present within the specimen as there may be a slight shift in the spectra by photoelectron emission, depending on probable change in the atom's oxidation state, chemical bonds or crystal structure. Advantageously, the above information may be obtained with relative ease with minimal sample preparation.

In Chapter 5 and 6, XPS was conducted to identify and analyze the element(s) present and the chemical state of these element(s). A broad survey scan was first performed to collect energy spectra over all accessible energies to account for all the elements present in the specimen. Subsequently, high-resolution narrow scans were performed by only concentrating on photoelectron signals from elements of interest (Sn and Sb). The oxidation state of Sn and Sb species and their relative content within different specimens were investigated. This ensures a thorough quantification of all elements present and a time-efficient data collection. XPS was performed using a Thermo Scientific ESCALab 250Xi, with a monochromatic Al K_{α} (1486.7 eV) X-ray source and under ultra-high vacuum (10^{-9} mbar). The C1s peak at 284.8 eV was used as the reference for spectra calibration of all other elements. Ensuing peak fitting of XPS spectra were conducted using Thermo ScientificTM Advantage Software.

3.3.5 Working Principle of Brunauer-Emmett-Teller (BET) Surface Area Analysis

Due to the inherent complexity of porous structures, to date, there is no single experimental technique to accurately measure the absolute surface area of porous samples. Instead, Brunauer-Emmett-Teller (BET) specific surface area ($\text{m}^2 \text{g}^{-1}$) has been frequently reported.

In a typical adsorption/desorption setup, the specimen is probed with nitrogen (N₂) at 77 K (a default adsorptive for most surface area and pore size analysis) over a range of relative pressures. An automatic analyzer measures the quantity of physically adsorbed N₂ against the variable relative pressure. The Brunauer-Emmett-Teller (BET) theory, although first introduced more than 80 years ago, remains relevant and fundamental to the interpretation of the isotherm data.³² The data are manipulated according to Equation 3.5 (BET adsorption isotherm equation),

$$\frac{1}{[V_a \left(\frac{P_0}{P} - 1 \right)]} = \frac{C-1}{V_m C} \times \frac{P}{P_0} + \frac{1}{V_m C} \quad (3.5)$$

where ' V_a ' refers to the volume of adsorbed gas at standard temperature and pressure (STP), ' P ' refers to equilibrium partial vapor pressure of adsorbate gas at 77 K, ' P_0 ' refers to the saturated pressure of adsorbate gas, ' V_m ' refers to the volume of adsorbed gas forming an apparent monolayer on the specimen surface at STP, and ' C ' refers to an empirical constant related to the enthalpy of adsorbent-adsorbate interactions.³³ Subsequently, volume of monolayered adsorbed gas, V_m , is derived from the intercept of the linear plot of Equation 3.5. BET specific surface area (SSA) can then be calculated by applying Equation 3.6,

$$S = \frac{V_m N_a}{m \times 22400} \quad (3.6)$$

where ' S ' refers to BET specific surface area, ' N_a ' refers to the Avogadro constant, ' m ' refers to mass of test specimen, and ' 22400 ' refers to arbitrary volume occupied by one mole of ideal adsorbate gas at STP.

There are six types (Type I to Type VI) of gas physisorption isotherms and four types (H1 to H4) of hysteresis loops (empirically classified by International Union of Pure and Applied Chemistry (IUPAC)). The shapes of hysteresis loops can accordingly be correlated with the information about specimen surface (porosity, pore size, pore distribution). Interestingly, this gas adsorption technique can provide information about both open and closed pores, however conditionally for the latter if both true and bulk density of specimen are known.

In this thesis, the BET specific surface area ($\text{m}^2 \text{g}^{-1}$) of the samples were determined using Micromeritics TriStar II 3020 surface area analyzer. Before measurement, the samples were purged overnight in vacuum at 120°C to remove previously adsorbed moisture, gases on the surface.

3.3.6 Working Principle of Thermogravimetric Analysis (TGA)

Thermogravimetric analysis (TGA) is one of the most utilized thermal analytical tool to investigate thermal stability, content of selected organic/inorganic components, decomposition mechanism and reaction kinetics of a given specimen.³⁴ It involves designed heating of the sample within an enclosed chamber filled with either nitrogen (pyrolytic environment) or oxygen (oxidative environment). Mass variation, when either a physical or chemical phenomenon occurs, is accurately registered by a micro balance within the system of a thermogravimetric analyzer as a function of temperature or time. Typically, the information from TGA can be presented as either a graph of change in mass (%) against temperature ($^\circ\text{C}$) or a decomposition profile (first derivative TG curve), which is a plot of rate of mass loss ($\text{mg } ^\circ\text{C}^{-1}$) versus temperature ($^\circ\text{C}$). This method advantageously produces highly reproducible data (within the limit of $\pm 1^\circ\text{C}$) and only requires minute quantity of specimen (~ 5 to 20 mg) for each run. However, the tests are destructive in nature.

In this thesis, thermogravimetric analysis was employed in Chapter 4 to quantitatively measure the carbon content and/or SnO_2 content within various hierarchical SnO_2 -graphite nanocomposites. It is assumed that the transition metal oxides exhibit negligible weight variation, and the significant weight loss is contributed by the evaporation of adsorbed water and the oxidation of carbon content to form carbon dioxide/carbon monoxide (CO_2/CO) gas. TGA was performed using thermogravimetric analyzer, TA Instruments Q500, under airflow (oxygen) with a heating rate of $20^\circ\text{C min}^{-1}$ and held isothermally 800°C for 10 min.

3.3.7 Working Principle of Electrochemical Characterizations in a “Half-Cell” Configuration

The electrochemical characterizations of all samples for LIBs anode application were conducted in a “half-cell” configuration (coin cell, CR2032), with lithium (Li) metal foil as the counter negative electrode and the active material to be evaluated as the positive electrode.³⁵ Consequently, the lithiation/delithiation process of the as-synthesized material is considered as discharge/charge reaction, respectively. The electrode preparation process starts from intimately and homogeneously mixing as-synthesized (active) material, carbon black conductive additive (Super P) and carboxymethyl cellulose (CMC) binder in a mass ratio of 8:1:1 to form a water-based slurry with low viscosity. The carbon black additive builds effective conductive networks in the electrode film and the polymeric binder holds the various components together on the current collector. Both are assumed to contribute negligible charge storage to the overall observed capacity. The resulting slurry is coated onto nickel foams (each 0.8 x 0.8 cm), followed by drying overnight at 60 °C in a vacuum oven. This deviates from the modus operandi of averaging mass of blank and coated copper foil mass, assuming uniform density and thickness across the entire sheet of copper foil. Individual pieces of nickel foams are weighed before and after coating (dried) to accurately derive the mass of loaded active material (between 1.0 to 2.0 mg). For drying procedure, excessively high temperature (>80 °C) is avoided to prevent rapid drying, which may fracture the coated sample film. Slurry preparation is a complex multicomponent process, the abovementioned procedure may not be “the best method” but its consistency allows for reliable and reproducible application to all the samples discussed within this thesis.³⁶

CR2032 coin cells were assembled in an Ar-filled glove box. A Celgard 2400 polymeric separator is slotted between the Li foil counter electrode and the working electrode (nickel foam coated with to-be-evaluated material), and all these components are submerged in an electrolyte containing 1 M LiPF₆ and equal volume of ethylene carbonate (EC), ethyl methyl carbonate (EMC), dimethyl carbonate (DMC). The main drawback to the use of coin cells is its difficult disassembly and subsequent retrieval of post-cycled electrode material for post-mortem ex-situ failure studies. The many steps involved can be tedious

and may induce artifact(s) or even damage to-be-investigated post-cycled electrode.

The evaluation in a half-cell configuration enables the study of intrinsic electrochemical properties such as gravimetric and volumetric capacity, and voltages at which lithiation/delithiation occur. However, a half-cell configuration does not provide an accurate assessment of the material for practical application. Although charge consumption due to parasitic reactions during cycling is mostly neglected in a half-cell configuration with surplus Li reserve, this is not realistic for a full-cell (real battery) with limited Li. Any irreversible/undesirable side reaction(s) within a full-cell will deplete the limited Li reservoir and severely compromise the electrochemical performance. Additionally, key figure of merits for actual practical batteries, such as energy and power density, cannot be determined from a single electrode (evaluated material) as in a half-cell configuration (with Li as the reference electrode) as per basic electrochemistry.³⁷

3.3.8 Working Principle of Galvanostatic Discharge/Charge Tests

A galvanostatic discharge/charge test is one of the most well-established procedures to evaluate the electrochemical performance of an electrode material. It involves an application of a constant current to the working electrode, within a selected potential window (mostly 0.01-3.00 V vs. Li^+/Li for the work in this thesis) to discharge and charge a cell. For evaluating a LIB anode material in a “half-cell” configuration, the cycle begins with a discharge process (lithiation) and then vice versa. This method quantitatively measures the specific capacity of as-synthesized material (time taken to fully discharge/charge a cell), evaluates each cycle’s Coulombic efficiency (a ratio of discharge capacity and charge capacity), assesses its cyclic stability (capacity retained after selected number of cycles) and rate capability (electrochemical responses under different current densities). Additionally, the discharge/charge profile provides insight into the probable lithium storage mechanism of the evaluated material. Features such as steep gradients to the redox potential of the material, accompanied by a flat plateau would suggest charge storage by faradic reactions, whereas gradual linear plot without any plateau would suggest

charge storage by adsorption/desorption on the surface (capacitive). In this thesis, galvanostatic discharge/charge tests were performed using Neware battery testing equipment, subjecting the “half-cells” to different current densities across a voltage window of 0.01-3.00 V vs. Li⁺/Li.

3.3.9 Working Principle of Cyclic Voltammetry (CV)

Cyclic voltammetry is a potentiodynamic electrochemical measurement applied to evaluate the redox state(s) and the reversibility of these redox reactions in the working electrode, and to also identify any undesirable side reactions. It measures the electrode response (current generated) to small increment in applied voltage at selected scan rate(s). Specific spikes in measured current across certain potential can indicate occurrence of faradaic electrochemical (redox) reactions, especially at low scan rates (0.1 to 0.2 mV s⁻¹). Good reversibility of these redox reactions may be identified from exact overlapping CV curves in different cycles. In a typical “half-cell” configuration for CV evaluation of an anode material, a single complete CV cycle involves scanning the working electrode in a negative direction from open circuit voltage (OCV) (ca. 3.0 V vs. Li) to the end of a specified discharge potential and reversing the scan as the electrode material is slowly charged back to its initial state.

By increasing scan rates of the potential sweep, the contribution from capacitive and diffusion-limited processes could be quantitatively distinguished. A power law relationship between peak current and scan rate can be expressed by Equation 3.7,

$$\log i_p = b \log v + \log a \quad (3.7)$$

where ‘ i_p ’ refers to peak current, ‘ v ’ refers to the scan rate, ‘ a ’ and ‘ b ’ refer to the adjustable parameters and can be derived from the y-intercept and gradient of the linear plot of Equation 3.7, respectively.³⁸ A b -value of 0.5 and 1.0 would imply majority of charge storage processes are diffusion-limited and capacitive, respectively. The scan rates, in this thesis, were varied at 0.2, 0.4, 0.6, 0.8, 1.0, 2.0 mV s⁻¹ for all samples. All CV measurements were performed using Bio-Logic, VSP, electrochemical workstation.

3.3.10 Working Principle of Electrochemical Impedance Spectroscopy (EIS)

Electrochemical impedance spectroscopy (EIS) is a one of the most widely applied probing technique (non-destructive) for the study of charging/discharging kinetic limitations in electrode materials. It involves an application of a sinusoidal potential (usually 10 to 20 mV) or current perturbation to the assembled “half-cell” over a frequency range (between 1 MHz to 1 mHz), and the electrode material is, to some extent, correspondingly displaced from its prevailing stable state.³⁹ This small deviation induces changes in the transport and reaction mechanisms involving Li^+ ions at varied frequencies.

The collected data is commonly represented by a Nyquist plot. By appropriately fitting an equivalent circuit to the Nyquist plot, the EIS data may be further interpreted to extract constituent electrochemical mechanisms involved in the electrode response. Components in the fitted equivalent circuit may include resistive contributions from both interfacial and material bulk processes, however this requires some theoretical understanding of probable capacitive and resistive processes at the electrode material. Resistive circuit elements can be visually identified from the complex plane (Z'' — Z') in the impedance plots.⁴⁰ A distinct semicircle, at between high to medium frequencies, corresponds to the resistance encountered as Li^+ ions migrate to the surface and film capacitance. Another circle, usually smaller and at medium frequencies, corresponds to charge transfer resistance and interfacial capacitance. An increasingly inclined straight line, at low frequencies, corresponds to Warburg impedance which is indicative of solid state diffusion characteristics. Classical impedance models mostly attribute the delay in full charging (poor rate capability) to limited charge transport, especially Li^+ ions diffusion, however reaction-limited mechanisms may also contribute to the observed tardiness in kinetics.^{39, 41} EIS can provide complementary information about the electrode material to support observations from galvanostatic discharge/charge curves at different current intensities. In addition, EIS data may also be used to correlate electrochemical performance to morphological or compositional effect.

In this thesis, EIS measurements were conducted using Bio-Logic, VSP, electrochemical workstation, with a 10-mV sinusoidal perturbation voltage applied over a frequency range of 100 kHz to 10 mHz.

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Chapter 4

Influence of Effective Milling Duration, Graphite Composition and Comminution Medium in High Energy Mechanical Activation of Hierarchical SnO₂-Graphite Nanocomposite

High energy mechanical milling, although industrially compatible, has hitherto been overlooked for synthesis of multifaceted nanostructures. However, recent work on mechanically ball milled ternary SnO₂ nanocomposites demonstrated outstanding improvement to Coulombic efficiency, cyclic lifespan and rate capability despite apparent absence of uniform morphology and size distribution. Herein this chapter presents the hypothesis that planetary ball milling a mixture of micro sized SnO₂ and graphite powder can facilitate a binary SnO₂-Graphite nanocomposite with desirable electrochemical performances in the absence of uniformity in morphology and size distribution. The effect of milling duration and graphite composition on the Li⁺ ions storage performance of these SnO₂-Graphite nanocomposite anodes was evaluated.

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4.1 Introduction

Our perpetual overreliance on non-renewable energy sources, particularly fossil fuels, and consequential greenhouse gas emission, have the potential to probable irreversible and catastrophic climate changes.^{1, 2} Against this backdrop of increased awareness to embrace sustainable development and urgency to seek alternatives, rigorous investigations of new energy conversion technologies and improved energy storage for green energy sources are well underway. Lithium-ion batteries (LIBs), although the ubiquitous cornerstone of portable consumer electronics era and de facto front-runner incorporated in commercial battery packs for electric vehicles (EVs), still necessitate significant improvement to address inadequacies in energy density, power density and cyclic stability.^{3, 4} At present, graphite — the conventional intercalation-based material, with its inherent limited crystallographic sites available for Li^+ ions storage and low theoretical specific capacity at 372 mAh g^{-1} corresponds to an incompatible anode for high energy density LIBs and its low Li^+ transport rate (10^{-9} to $10^{-7} \text{ cm}^2 \text{ s}^{-1}$) hinders the further development of high power density LIBs.^{5, 6} Numerous metal oxides, have since been explored as alternative anode materials after the first reported nanoscale transition metal oxide anode by Tarascon *et al.*⁷⁻

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Among transition metal oxides, tin (IV) dioxide (SnO_2) is one of the most promising candidate, because of its abundancy, affordability, environmental benignity and high theoretical specific and volumetric capacity for Li^+ ions storage.¹¹ A two-step lithiation mechanism for SnO_2 has been suggested by various ex situ and in situ studies. The conversion reaction, $\text{SnO}_2 + 4\text{Li}^+ + 4\text{e}^- \leftrightarrow \text{Sn} + 2\text{Li}_2\text{O}$, contributes to a gravimetric capacity of 711 mAh g^{-1} , which is followed by an alloying reaction, $\text{Sn} + 4.4\text{Li}^+ + 4.4 \text{e}^- \leftrightarrow \text{Li}_{4.4}\text{Sn}$, adding 783 mAh g^{-1} towards the overall reversible capacity.¹²⁻¹⁵ Although the alloying/dealloying reaction is unanimously observed to be highly reversible, the reversibility of conversion reaction is, on the contrary, highly size dependent and widely conceived to be irrevocable resulting in poor initial Coulombic efficiency.¹⁶⁻¹⁹ Additionally, the adoption of such conversion-alloying based materials is hindered by its limited cyclic

stability, due to pulverization of electrode material induced by the repeatedly large volume variation during lithiation/delithiation.²⁰⁻²³ Dimensional reduction, morphological modifications and composite formation within various conductive carbon buffer matrix are among the most commonly explored routes.^{11, 24, 25} Unfortunately, many of these nanostructures are prepared by complex chemical synthesis methods, which are not feasible to scale up for industrial production.

High energy mechanical milling, although industrially mature, has hitherto been overlooked for synthesis of multifaceted nanostructures. Recently, ternary SnO₂ nanocomposites, such as SnO₂-SiC/G and SnO₂-Fe-G, with excellent performance as LIBs anode, have been prepared by using two-step ball milling activation.²⁶⁻²⁸ SnO₂-SiC/G nanocomposite retained a good reversible capacity of 1351 mAh g⁻¹, after 40 cycles at current density of 100 mAh g⁻¹ within a voltage window of 0.01–3.0 V.²⁶ However, it contains 20 wt.% of SiC, which is electrochemically inactive with Li and does not contribute any reversible capacity. Therefore, the actual specific capacity and energy density of this hybrid nanocomposite are much lower. A SnO₂-Fe-G nanocomposite with outstanding reversible capacity of 1338 mAh g⁻¹ has been prepared by using a two-step planetary ball milling with nanosized SnO₂, in which the effect of electrochemical active transition metal was studied to achieve high initial Coulombic efficiency.²⁸ However, the influence of milling time and graphite content on electrochemical behavior of the SnO₂ nanocomposites has not been well elucidated. Herein, we present a simple and industrially compatible one-step ball milling of pristine commercially available micron-sized SnO₂ and graphite powders. A systematic optimization on the two mentioned parameters was conducted to develop binary SnO₂-C nanocomposites with desired electrochemical performances.

4.2 Materials and Method

Unless otherwise specified, reagents were of analytical grade and were used as received without further purification. Tin (IV) oxide (<10 micron, 99.9 %) and graphite (C) powder (7-10 micron, 99 %) were purchased from Alfa Aesar.

In a typical procedure, SnO₂-C composites were prepared by ball milling micron-sized SnO₂ and graphite powder in atmosphere, with a planetary ball mill (Pulverisette 5, Fritsch) at 200 rpm for 2-20 h. The rotational direction of the bowl and the sun wheel were programmed to change every 20 min after a rest interval of 10 min. The weight ratio of SnO₂:C was systematically varied, i.e., 95:5, 88:12 and 80:20, and different milling durations, i.e., 2, 5, 12 and 20 h, were used. For convenience and consistency in naming the samples, a composite with 95 wt.% SnO₂ that had been ball milled for 2 h will be labeled SnO₂-C9505-2h. Tungsten carbide (WC) lined grinding bowls (250 mL) and tungsten carbide milling balls (10 mm dia.) were used. A ball-to-powder weight ratio of 80:1 was maintained for all samples.

4.2.1 Materials Characterization

X-ray diffraction (XRD) analysis of the samples was carried out by using a Shimadzu powder diffractometer with Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$), at $2\theta = 10\text{-}70^\circ$, with a step size of 0.02° and scan rate of 2° min^{-1} . Morphologies of the samples were characterized by using a field-emission scanning electron microscopy (FESEM, JSM-6340F) operated at 5 kV in secondary electron imaging (SEI) mode. High-resolution transmission electron microscopy (HRTEM) studies were conducted by using transmission electron microscopy (JEM-2010F, JEOL) operated at 200 kV in bright field imaging mode. Brunauer Emmet-Teller (BET) surface area of the samples was estimated from the nitrogen (N₂) adsorption isotherm by using a surface and porosity analyzer (ASAP Tri-star II 3020, Micromeritics) at 77 K. Thermal gravimetric analyses (TGA) was carried out by using thermogravimetric analyzer (Q500, TA Instruments) at a heating rate of $20^\circ \text{C min}^{-1}$ between 30 and 800 °C in air.

4.2.2 Evaluation of Electrochemical Performance

The prepared SnO₂-C nanocomposite powders were mixed with conductive carbon (SP) and binder (sodium carboxymethyl cellulose, CMC) with the weight ratio of 80:10:10 and dissolved in deionized water to form slurry. The slurry was then coated onto nickel foam current collector and dried in a vacuum oven at 70 °C overnight. With pure Li foil as counter/reference electrode, a Celgard 2400 separator and electrolyte of 1M LiPF₆ in ethylene carbonate/dimethyl carbonate (1/1 by volume), CR2032 coin cells were assembled in an Ar-filled glove box. Galvanostatic charge-discharge curves of half-cells cycled within a voltage window between 0.005 and 3.0 V versus Li⁺/Li at different current densities were recorded with a NEWARE battery tester. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) measurements were conducted with an electrochemical workstation (VSP, Bio-Logic). The CV curves were recorded between 0.005 and 3.0 V at a scanning rate of 0.10 mV s⁻¹ and EIS spectra were collected by application of sine wave perturbation voltage with an amplitude of 10 mV over a frequency range of 100 kHz to 10 mHz.

4.3 Results and Discussion

The preparation procedure of SnO₂-C nanocomposites is schematically illustrated in Figure 4.1. The mixtures of SnO₂ and graphite powders were milled for various durations, during which the SnO₂ and graphite were significantly refined and mixed with each other by impact, shear, attrition, compression or a combination of them.²⁹ Planetary ball milling of graphite in the presence of oxygen introduces fractures (decrease in particle size) and stacking defects. Due to the weak van der Waals forces, the graphite layers are easily cleaved by shearing and compression. Exfoliated nanosized graphite platelets were then coated onto the SnO₂ particles. By extending the duration of milling, aggregations of nanostructured SnO₂-C (more brittle) was grafted on the remnant graphitic sheets (less brittle) as expected for a brittle-brittle component system.

Figure 4. 1 A schematic representation illustrating the preparation process of the hierarchical SnO₂-C nanocomposites via high energy ball milling, the presence of dual axes of rotation of the bowl and wheel (plane), respectively, the apparent state of the materials (both precursors and the milling balls) and the features in the SnO₂-C nanocomposite with the best electrochemical performance.

4.3.1 Effect of Milling Duration on the Crystallinity and Morphology of the SnO₂-C Composites

XRD patterns the SnO₂-C8020 composites milled for different time durations are as plotted in Figure 4.2 (a). The diffraction peaks of the SnO₂-C8020 composites match well with that of tetragonal rutile SnO₂ (JCPDS 41-1445) and graphite (JCPDS 41-1487), respectively. Most notably, the (110) plane of SnO₂ overlaps with the (002) plane of graphite at around 26.5 °. Compared to pristine SnO₂, all peaks from SnO₂-C8020-20h sample appear with reduced intensity and broadened, indicative that crystallinity and/or size of SnO₂ and graphite decreases with lengthened milling duration. This also corroborates well with the knowledge that a mechanical method, such as ball milling, can be limitedly effective in reduction of particle size to certain critical values (an inherent limitation of top-down approach), beyond which energy supplied to the particles will only cause defects in the crystal and subsequently amorphization.³⁰ Additionally, by comparing the (110) peak of SnO₂-C8020-20h to that of SnO₂-C8020-12h, the width of these two peaks are almost identical but the former is observed to have at a much reduced intensity.

This may be explained by a probable onset of partial amorphization in the as-prepared sample, in which manifestation of defects is restricted to the crystal surfaces, forming a disordered SnO_2 shell around the crystalline SnO_2 core. The trend of increasing milling time decreases crystallinity and/or size is similarly observed in the other samples with different graphite content, such as SnO_2 -C8812 (Fig. 4.2 (b), SnO_2 -C9505 (Fig. 4.2 (c)) and SnO_2 -C (Fig. 4.2 (d)). Due to the near overlapping (110) peak of SnO_2 and (002) peak of graphite, it is difficult to precisely quantify the extend of graphite structure destroyed by the ball milling. However, it may be assumed that most of the long-range order of graphite has been destroyed by ball milling with WC comminution material, since other diffraction peaks of graphite are not observed.²⁶

Figure 4. 2 XRD patterns of (a) (i) pristine graphite powder, (ii) pristine SnO_2 powder, (iii-vi) the SnO_2 -C8020 nanocomposite prepared with increased milling duration of 2, 5, 12, and 20 h, respectively; (b) SnO_2 -C8812 nanocomposite, (c) SnO_2 -C9505 nanocomposite, and (d) SnO_2 . (i-iv) represents corresponding samples prepared with increased milling duration of 2, 5, 12, and 20 h, respectively.

FESEM images of the pristine sub-micron spherical SnO₂ particles and large micron-sized graphite sheets are shown in Figure 4.3 (a) and (b), respectively. Figure 4.3 (c) shows FESEM image of the SnO₂-C8020-20h composite. It comprises of randomly distributed SnO₂ aggregations and graphite, with irregular shape and reduced size — resultant of repeated fracture and cold weld of particles due to the impact and friction during the planetary ball milling. Remnants of graphite sheets can still be clearly observed within the mixture of disordered carbon and clustered SnO₂. The magnified image in Figure 4.3 (d) further reveals SnO₂-C8020-20h to be an aggregation of varied shape and size of SnO₂ primary particles, with sizes to be less than 100 nm, together with graphite nanosheets (white arrows in Figure 4.3 (d)). Figure 4.3 (e) shows TEM image of the SnO₂-C core-shell structure formed when layers of carbon are continuously peeled from the graphite sheets and crushed by impact from milling balls. Subsequently, these nanosized graphite platelets are densely packed around the SnO₂ agglomerates. This also confirms that SnO₂ nanoparticles are indeed the building block of the polydispersed SnO₂ secondary clusters, as seen in Figure 4.3 (d). With reference to the inset of Figure 4.3 (e), the presence of polycrystalline SnO₂ can be confirmed by the ring-like selected-area electron diffraction (SAED) patterns indexed to be (110), (101) and (211) planes of rutile SnO₂, which is consistent with earlier results from XRD analysis. As seen in Figure 3 (f), the HRTEM image indicates a core made up of (101) SnO₂ plane as identified from its corresponding d-spacing of 0.264 nm and the outer layer comprises of tens of nanometers thick graphite as identified by d-spacing of 0.335 nm, which corresponds to (002) plane of graphite though with mainly disordered fringe, indicating that the graphite coating has lost most of its long-range order, as per discussed earlier in the XRD analysis.

Figure 4. 3 FESEM images of (a) pristine SnO_2 particles prior to ball milling, (b) pristine graphite flakes prior to ball milling, (c) SnO_2 -C8020-20h nanocomposite at 10 000 magnification and (d) SnO_2 -C8020-20h nanocomposite at magnification of 30 000. (e) TEM image of the edge of the SnO_2 -C8020-20h nanocomposite (Inset: SAED pattern). (f) HRTEM image of the SnO_2 -C8020-20h nanocomposite.

The effect of ball milling duration on the dispersion state of SnO_2 and graphite in the as-milled SnO_2 -C nanocomposite was investigated using TEM. Figure 4.4 shows TEM

images of the SnO₂-C8020 nanocomposites milled for different milling durations. Figure 4.4 (a) reveals that the SnO₂-C8020-2h sample is a simple mixture of comparatively large SnO₂ primary particles (> 100 nm) and few thin graphite sheets, because the actual effective milling time is merely 80 minutes, which is too short to sufficiently grind the SnO₂ particles down to nanoscale. For such short duration of milling, the dominant effect on graphite sheets is the shearing of layers along its basal plane accompanied by minimal fractures. Figure 4.4 (b) shows that the SnO₂-C8020-5h sample consists of agglomerates of irregular-shaped SnO₂ nanoparticles (ca. 40-80 nm), with negligible carbon layer coating and smaller than previous thin graphite sheets, which concurs well with Alcantara *et al.*'s observations for short duration ball milling of graphite.³¹ Interestingly, although the size of SnO₂ particles and graphite sheets is slightly reduced when the milling time is increased from 2 h to 5 h, there is a significant increase in BET surface area from $18.27 \text{ m}^2 \text{ g}^{-1}$ (SnO₂-C8020-2h) to $45.43 \text{ m}^2 \text{ g}^{-1}$ (SnO₂-C8020-5h). This suggests that the onset of effective mechanical peeling of thin layers from graphite sheets is between 2 to 5 h of milling, most probably coinciding with the buildup of temperature within the grinding bowls after prolonged milling, which helps to weaken van der Waals' forces between graphite layers. The exfoliation of graphite can be confirmed by the slit-shaped pores associated type H3 hysteresis in isothermals of samples (Figure 4.5 (a)), as well as the lowered oxidation temperature of graphite, due to reduced number of layers, as observed in TGA (Figure 4.5 (b-c)).^{32, 33} As shown in Figure 4.4 (c) and (d), when the milling times are doubled and quadrupled, majority of the observed SnO₂ particles and graphite sheets are smaller and more irregular in shape than those in the samples of SnO₂-C8020-2h and SnO₂-C8020-5h. It is also noted that specific surface area (SSA, which is directly correlated to particle size) of the SnO₂-C nanocomposites does not significantly decrease beyond 12 h of milling (as seen to Table 4.1), suggesting the practical limit of mechanical size reduction has likely been reached. Beyond the critical threshold of particle size reduction, the SnO₂ nanoparticles are deformed plastically rather than fractured, which is accompanied by aggregation due to the increased interparticle cohesion.³⁴ The continued transfer of mechanical energy leads to the accumulation of defects on the comminuted particles and disordering within the crystal structure.

Figure 4. 4 TEM images of the SnO₂-C8020 nanocomposite prepared by ball milling for different time durations: (a) 2 h, (b) 5 h, (c) 12 h, and (d) 20 h.

Figure 4. 5 (a) N₂ adsorption-desorption isotherms of SnO₂-C9505-20h, SnO₂-C8812-20h and SnO₂-C8020-20h. TG of (b) SnO₂-C9505-20h, SnO₂-C8812-20h and SnO₂-C8020-20h, and (c) SnO₂-C8020 prepared by various duration of high energy ball milling.

Table 4. 1 The BET surface area of various SnO₂-C nanocomposites.

	SnO ₂ - C8020-2h	SnO ₂ - C8020-5h	SnO ₂ - C8020-12h	SnO ₂ - C8020-20h	SnO ₂ - C8812-20h	SnO ₂ - C9505-20h
BET surface area/ m² g⁻¹	18.27	45.43	58.47	55.13	35.90	16.04

Figure 4.6 shows FESEM images of various composition of SnO₂-C prepared by ball milling for 20 h. Noticeably, primary particles in all the four samples are expectedly irregular in shapes. As observed in Figure 4.6 (b), there are hardly observable graphite sheets, whereas some remnant graphite sheets can still be observed in Figure 4.6 (c) and (d). As the SnO₂-9505-20h sample has a low graphite content of 5 wt.%, it can be presumed that most of the graphite sheets have been consumed to form somewhat incomplete carbon coating around the severely agglomerated SnO₂ primary particles, as seen in the TEM image (inset) of Figure 4.6 (b). A composition with 5 wt.% of graphite is shown to be explicitly insufficient to adequately coat and disperse the SnO₂ clusters, resulting in poor electrochemical performance as LIBs anode, as will be discussed in more detail later. From the TEM images (insets) in Figure 4.6 (c) and (d), both the SnO₂-8812-20h and SnO₂-8020-20h are observed to have a similar SnO₂-C core-shell structure anchored on remnant graphite sheets. Unlike those in SnO₂-9505-20h, the SnO₂ nanoparticles appear as smaller clusters, which are better dispersed by the graphite sheets. Such a structure is more favorable for electrochemical performance as anode material. The absence of remnant graphite sheets and severe agglomeration in SnO₂-9505-20h agree well with the measured BET surface areas of SnO₂-9505-20h, SnO₂-8812-20h and SnO₂-8020-20h, which are 16.04, 35.90 and 55.13 m² g⁻¹, respectively (as summarized in Table 4.1).

Figure 4. 6 FESEM images of (a) SnO₂-20h, (b) SnO₂-9505-20h, (c) SnO₂-8812-20h and (d) SnO₂-8020-20h. Insets in (b-d) are corresponding HRTEM images.

4.3.2 Evaluation of SnO₂-C Nanocomposites' Electrochemical Performance and Associated Correlation to Features Observed

Figure 4.7 (a) shows the cycling performances of SnO₂-C8020 nanocomposites prepared by different milling duration, which are cycled within a voltage window between 0.005 and 3.0 V at current density 200 mA g⁻¹. Although with identical composition, their varied structures result in vastly different reversible capacities. The 100th cycle specific discharge capacity for SnO₂-C8020-2h, SnO₂-C8020-5h, SnO₂-C8020-12h and SnO₂-C8020-20h are 278, 389, 710 and 725 mAh g⁻¹, respectively (as summarized in Table 4.2).

As discussed above, SnO₂-C8020-2h is a mixture of comparatively large SnO₂ particles (> 100 nm) and few thin graphite sheets (as seen in Figure 4.4 (a)), rapid capacity fading from pulverization and agglomeration of SnO₂ is expectedly not circumvented.²⁵ SnO₂-C8020-5h, a combination of aggregates of irregular-shaped SnO₂ nanoparticles (ca. 40-80 nm) without observable continuous graphite coating and smaller than previous thin graphite

sheets, demonstrates considerable improvement in capacity retention after 80 cycles. Dimensional reduction shortens the diffusion length of SnO₂ and graphite for both Li⁺ and e⁻, significantly improving the rate and efficiency of lithiation/delithiation and e⁻ transport as governed by the one-dimension solution of Fick's second law, $\tau = \frac{L^2}{D}$, where τ refers to characteristic diffusion time constant, L refers to diffusion length and D refers to material dependent diffusion coefficient.³⁵ From the 80th cycle onwards, there is a huge drop-off in reversible capacity, presumably due to the loss of electrical contact caused by the delayed pulverization from the repeated rearrangement of SnO₂ nanoparticles. More importantly, SnO₂-C8020-12h and SnO₂-C8020-20h, having similar SnO₂-C core-shell structure anchored on remnant graphitic nanosheets, retain more than 700 mAh g⁻¹ after 100 cycles. Interestingly, due to the irregularity in morphologies of SnO₂ nanoparticles, unintentional but beneficial internal void space exists within the SnO₂ clusters (as observed in Figure 4.3 (e)) to buffer against the concomitant large volumetric variation during the perpetual charge/discharge process. The exfoliated thin graphite nanoplatelets layer and remnant graphite sheets function as both an electrical pathway as well as a buffer layer to enhance overall electrical conductivity and delay fracture of the SnO₂ nanoparticles, respectively. The marginally improved reversible capacity of SnO₂-C8020-20h at 725 mAh g⁻¹ as compared to that of SnO₂-C8020-12h at 710 mAh g⁻¹ is most likely due to the thin graphite platelets that more firmly wrapped around the SnO₂ nanoparticles via agglomeration as seen in Figure 4.4 (d), which agrees well with the slightly larger measured BET surface area of 57.81 m² g⁻¹ for SnO₂-C8020-12h than 54.27 m² g⁻¹ for SnO₂-C8020-20h.

Figure 4.7 (b) shows the cycling stability curves of SnO₂-C nanocomposites with different graphite content, all prepared by optimized milling time of 20 h. The 100th cycle specific discharge capacities for SnO₂-20h, SnO₂-C9505-20h, SnO₂-C8812-20h and SnO₂-C8020-20h are 361, 507, 650 and 725 mAh g⁻¹, respectively. For SnO₂-C9505-20h, the although low 5 wt.% graphite content still contributes to an incomplete carbon coating around the aggregates of the SnO₂ nanoparticles (as earlier observed in Figure 4.6 (b)), as well as spacer to alleviate the agglomeration from the competing fracture and coalescence events during ball milling, thus leading to a great increase in the reversible capacity from 361

mAh g⁻¹ (bare SnO₂) to 507 mAh g⁻¹. Therefore, increasing the content of graphite (>5 wt.%) in the SnO₂-C nanocomposite is recommended. Comparatively, by increasing the graphite content to 20 wt.%, a more complete carbon coating can be achieved, together with better dispersion of SnO₂ secondary clusters and more remnant graphite sheets for the SnO₂ clusters to anchor onto. As a result, the SnO₂-C8020-20h sample retains the highest reversible capacity amongst the 20 h-milled nanocomposites.

Figure 4.7 (c) demonstrates the rate performance of SnO₂-C8020-20h at various current densities. Reversible discharge capacities of ca. 800 mAh g⁻¹, ca. 700 mAh g⁻¹, and ca. 500 mAh g⁻¹ are recorded at current densities of 200, 500 and 1000 mA g⁻¹, respectively. Meanwhile, when the current density is reverted to 200 mA g⁻¹ after 30 cycles at different rates, the specific discharge capacity reverts to ca. 800 mAh g⁻¹.

Figure 4.7 (d) illustrates cycling stability of SnO₂-C8020-20h tested at 200 mA g⁻¹ for 100 cycles. A stable specific discharge capacity of ca. 725 mAh g⁻¹, with Coulombic efficiency exceeding 97 %, is retained at the end of 100 cycles, which is achieved by the unique architecture of SnO₂-C8020-20h. Interestingly, the concomitant coalescence forms secondary clusters with nanoscale SnO₂ particles and graphite layers as building blocks, reducing the surface area while preserving the advantages of nanostructuring (especially size reduction). As irregularly shaped SnO₂ nanoparticles form clusters, unintentional voids are created that allow the SnO₂ nanostructures to maintain interparticle connection despite cyclic expansion and contraction. The presence of carbon-based coating in the form of exfoliated thin graphite nanoplatelets layer improves electrical conductivity among the SnO₂ nanoparticles and forms a mechanically and chemically stable thin SEI, which notably and expectedly enhances the reversible capacity of SnO₂-C8020-20h.^{36, 37} The observed decay of reversible discharge capacity of SnO₂-C8020-20h is probably related to pulverization of the SnO₂ particles that have not been refined sufficiently in size, thus leading to the loss of electrical connectivity with neighboring particles.

Figure 4.7 (e) shows galvanostatic discharge-charge profiles of the SnO₂-C8020-20h nanocomposite evaluated at 200 mA g⁻¹ for the 1st, 2nd, and 100th cycles. The initial

discharge and charge capacities are 1738 and 1191 mAh g⁻¹, respectively, with the initial Coulombic efficiency to be 68.5 %. Quantitatively, the contributions of the conversion reaction and alloying reaction of SnO₂, as well as the intercalation reaction of graphite, are derived to be 568.8, 626.4, and 74.4 mAh g⁻¹, respectively. The detailed derivation of the capacity contribution is calculated as follow, $C_{\text{theoretical}} = C_{\text{SnO}_2(\text{conversion})} * \text{wt.\% of SnO}_2 + C_{\text{SnO}_2(\text{alloying})} * \text{wt.\% of SnO}_2 + C_{\text{graphite}} * \text{wt.\% of graphite} = 711 * 0.80 + 783 * 0.80 + 372 * 0.20 = 1270 \text{ mAh g}^{-1}$. The contribution of the conversion reaction and alloying reaction of SnO₂, and the intercalation reaction of graphite are 568.8, 626.4, and 74.4 mAh g⁻¹, respectively. Similarly, the theoretical capacity of SnO₂-8812 and theoretical capacity of SnO₂-9505 composites are calculated to be 1359 and 1438 mAh g⁻¹, respectively. Unsurprisingly, for most of pure SnO₂ without graphite samples, it can be noted that the initial discharge capacity is less than that of the theoretical capacity of 1494 mAh g⁻¹ for SnO₂; and exhibit irrecoverable capacity loss, poor Coulombic efficiency, retain discharge capacity close to contribution from only the alloying/dealloying reaction of SnO₂ at 711 mAh g⁻¹ after ca. 20 cycles and decay considerably thereafter. The positive effect of size reduction on cyclic stability is epitomized by SnO₂-20h, which possesses the lowest degree of crystallinity and fractionally more of smaller particles amongst the pure SnO₂ samples, with slightly better reversible discharge capacity at 361 mAh g⁻¹ after 100 cycles. Most noticeably, the reversible capacity is consistently best retained for any of these SnO₂-C nanocomposites, regardless of graphite content, when ball milled for 20 h. The beneficial effect of having a more complete carbon-coating with higher graphite content as well as finer and better dispersed SnO₂ nanoclusters when milled for longer duration is evident in the measured electrochemical performances. However, the exact rationale for the initial discharge capacity exceeding that of the derived theoretical capacity (for instance, 1270 mAh g⁻¹ for SnO₂-C8020-20h) is not clear and beyond the scope of the present study. Severe side reaction on the large surface area of the electrode material with the electrolyte, decomposition of electrolyte, formation of the SEI layer and the incomplete activation of electrode material are probable sources of such excess capacity.^{26, 38} Consequently, the 31.5 % loss of initial capacity for SnO₂-C8020-20h is not truly reflective of the actual Coulombic efficiency of the active material itself. There are two potential plateaus with

different gradients in the initial discharge cycle. The sloping plateau in the range of 0.7-1.0 V corresponds to the formation of SEI layer and conversion reaction between SnO_2 and Li^+ ions, resulting in the synchronous formation of Sn and Li_2O . However, this latter plateau becomes less prominent in the second cycle onwards, indicating that the formation of Li_2O may be partially irreversible and liable to the subsequent drop off in reversible capacity. The second sloping plateau at lower voltage corresponds to the alloying reaction between Sn and Li^+ and associated formation of Li-Sn alloys.

As observed in Figure 4.7 (f), there is an obvious difference between the CV curves of the first and subsequent cycles. A broad cathodic peak at 0.69 V, corresponding to the formation of SEI, is only observed in the first cycle but not subsequent cycles. The reduction peak for SnO_2 to Sn in the conversion reaction, $\text{SnO}_2 + 4\text{Li}^+ + 4\text{e}^- \leftrightarrow \text{Sn} + 2\text{Li}_2\text{O}$, is enveloped within this broad peak. There is another broad reduction peak located at 0.07 V, which envelops the formation of $\text{Li}_{4.4}\text{Sn}$ through the alloying reaction, $\text{Sn} + 4.4\text{Li}^+ + 4.4\text{e}^- \rightarrow \text{Li}_{4.4}\text{Sn}$ and LiC_6 by intercalation reaction, $\text{C} + x\text{Li}^+ + x\text{e}^- \rightarrow \text{Li}_x\text{C}_6$. The four oxidation peaks at about 0.20 V, 0.58 V, 1.30 V and 1.87 V correspond to deintercalation of LiC_6 , $\text{Li}_x\text{C}_6 \rightarrow \text{C} + x\text{Li}^+ + x\text{e}^-$, dealloying reaction of $\text{Li}_{4.4}\text{Sn}$, $\text{Li}_{4.4}\text{Sn} \rightarrow \text{Sn} + 4.4\text{Li}^+ + 4.4\text{e}^-$, sequential conversion reactions of Sn to SnO, $\text{Sn} + \text{Li}_2\text{O} \rightarrow \text{SnO} + 2\text{Li}^+ + 2\text{e}^-$, and SnO to SnO_2 , $\text{SnO} + \text{Li}_2\text{O} \rightarrow \text{Sn} + 4.4\text{Li}^+ + 4.4\text{e}^-$, respectively.^{28,39} The overlapping CV curves of the second and fifth cycles is indicative of the stabilization and reversibility of electrode reactions.

Figure 4. 7 (a) Cycling performance of the SnO₂-C8020 nanocomposites, ball milled for 2, 5, 12 and 20 h, cycled between 0.005 and 3.0 V at current density of 200 mA g⁻¹. (b) Cycling performance of SnO₂-20h, SnO₂-C9505-20h, SnO₂-C8812-20h and SnO₂-C8020-20h cycled between 0.005 and 3.0 V at current density of 200 mA g⁻¹. (c) Rate performance of SnO₂-C8020-20h at current densities of 200, 500 and 1000 mA g⁻¹. (d) Cycling performance and Coulombic efficiency of SnO₂-C8020-20h between 0.005 and 3.0 V at current density of 200 mA g⁻¹. (e) Discharge/charge profile of SnO₂-C8020-20h nanocomposite at current density of 200 mA g⁻¹. (f) Cyclic voltammograms of SnO₂-C8020-20h at a scan rate of 0.1 mV s⁻¹.

Table 4. 2 List of electrochemical performance various SnO₂-C nanocomposites evaluated between 0.005 and 3.0 V at current density 200 mA g⁻¹; (initial discharge capacity/initial charge capacity; 100th cycle discharge capacity).

	2 h	5 h	12 h	20 h
SnO₂	1442/894; 239 (mAh g ⁻¹)	1365/853; 216 (mAh g ⁻¹)	1365/882; 188 (mAh g ⁻¹)	1773/1182; 361 (mAh g ⁻¹)
SnO₂-C9505	1502/1039; 330 (mAh g ⁻¹)	1544/1098; 350 (mAh g ⁻¹)	1517/1096; 350 (mAh g ⁻¹)	2164/1341; 507 (mAh g ⁻¹)
SnO₂-C8812	1626/1085; 244 (mAh g ⁻¹)	1371/954; 277 (mAh g ⁻¹)	1590/1093; 288 (mAh g ⁻¹)	1753/1121; 650 (mAh g ⁻¹)
SnO₂-C8020	1445/947; 278 (mAh g ⁻¹)	1424/997; 389 (mAh g ⁻¹)	1607/1136; 710 (mAh g ⁻¹)	1738/1191; 725 (mAh g ⁻¹)

EIS measurements were carried out to provide further insight into the effect of graphite content and milling duration on electrical conductivity of the SnO₂-C composite electrodes. Figure 4.8 (a) shows Nyquist plots of the SnO₂-C nanocomposites, with different graphite content, which are prepared by 20 h of ball milling. The diameter of the semicircle in the high frequency region shows the charge transfer resistance, indicating the lowest value of SnO₂-C8020-20h when compared with SnO₂-20h, SnO₂-C9505-20h and SnO₂-C8812-20h. Additionally, due to the presence of carbon coating in SnO₂-C9505-20h and SnO₂-C8812-20h (as observed in Insets of Figure 4.6 (b) and (c), respectively), a much improved electrochemical kinetic (smaller semicircle diameter) has been observed as compared to that of SnO₂-20h (largest semicircle diameter). The slanted straight line in the low frequency region corresponds to the Warburg impedance, a characteristic for diffusion of Li⁺ ions into the active material (electrode). A more inclined slope as compared with that of SnO₂-20h, is observed for SnO₂-C9505-20h, SnO₂-C8812-20h and SnO₂-C8020-20h, which is indicative of improved Li⁺ diffusion. Figure 4.8 (b) shows Nyquist plots of SnO₂-C8020 ball milled for various durations. Consistent with the observed electrochemical performance and structural characterizations, SnO₂-C8020-20h expectedly has the lowest charge transfer impedance, amongst the samples with 20 wt.% graphite, as inferred from

the smallest diameter of the semicircle in the high frequency region.

Figure 4. 8 Electrochemical impedance spectra (EIS) of (a) the samples ball milled for 20 h with varying graphite content and (b) samples, with 20 wt.% graphite, ball milled for differing durations, both before cycling at the amplitude of 10 mV over frequency range from 100 kHz to 10 mHz.

4.4 Summary

In summary, the electrochemical performance of nonhomogeneous SnO₂ microstructure can be improved by prolonging the high energy ball milling to obtain a homogeneous surface coating of graphite nanoplatelets layer on the SnO₂ clusters. Fascinatingly, a hierarchical structure of polydispersed SnO₂-C nanoclusters anchored on thin remnant graphite sheets has been experimentally obtained from 20 h of high energy ball milling of a mixture of micro sized SnO₂ with 20 wt.% graphite and it exhibits impressive electrochemical performance, with a retained discharge capacity of 725 mAh g⁻¹ after 100 cycles at current density of 200 mA g⁻¹. This is only made possible by the combination of many unexpected features in the SnO₂-C architecture (although non-uniform), with characteristics of reducing SnO₂ particles to nanoscale that results in enhanced efficiency of Li⁺ diffusion and e⁻ transfer, introduction of carbon coating in the form of nanosized graphite platelets providing a more stable SEI in addition to improved charge transfer pathways along the SnO₂-graphite interface, internal voids within the SnO₂ clusters that help to buffer against the repeated volume variation and the remnant graphite sheets to help maintain the electrode integrity by suppressing SnO₂ aggregation and pulverization. The

effect of milling duration, graphite content, and WC-based comminution medium (ball-to-powder ratio) in this single-step high energy mechanical activation approach has also been systematically evaluated.

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Chapter 5

Significantly Improved Cyclability of Antimony-doped SnO₂ (ATO) After Post-Synthesis Acid Treatment

Heterogeneous doping is a straightforward approach to improve the electronic conductivity of semiconducting SnO₂. However, the incorporation of dopant species has yet to yield significant breakthrough in improving SnO₂'s cyclic stability and rate capability. It is indicative that merely heightening conductivity in SnO₂ is insufficient as the limitations of SnO₂ as LIBs anode extend beyond its intrinsically poor electronic conductivity. Herein this chapter presents the hypothesis that substitutional antimony (Sb) dopant may instead be viewed as a temporary inclusion in the SnO₂ matrix which can be selectively removed to introduce defects and/or lattice vacancies and better accommodate the repeated volumetric variation. The proof-of-concept for this seemingly counterintuitive post-synthesis etching of Sb-doped SnO₂ to enhance SnO₂'s cyclability will be presented in detail.

5.1 Introduction

In the previous chapter, a single-step assembly of high capacity, multifaceted SnO₂-C nanostructure was achieved by high energy mechanical milling a mixture of micro sized SnO₂ and graphite (C) powder. It demonstrates the relevance to identify and incorporate industrial compatible process into the fabrication of SnO₂-based anode for LIBs application. Elemental doping, which involves inclusion of foreign species into a host matrix, is one of the most mature approach (both academically and industrially) to modify the electronic properties of semiconducting materials. In addition to the expectedly enhanced electrical conductivity, some dopant species have been identified to considerably improve Coulombic efficiency of SnO₂, but none has led to substantial breakthrough in its cyclability.¹⁻¹¹ This suggests the somewhat bleak prospects of cationic doping and explains the recent uptake in anionic doping to advance SnO₂-based LIB anode.¹²⁻¹⁴ The key practical question is how to make cost-effective and industrially scalable doping relevant to greatly enhance reversible capacities of SnO₂.

Most recently, Koketsu *et al.* reported a novel approach to introduce high concentration of titanium vacancies (22%) in anatase titanium dioxide (TiO₂) and greatly enhance the electrochemical activity of TiO₂ through aliovalent doping.¹⁵ Other methods such as anion substitution,¹⁶ reducing or oxidizing heat treatments,¹⁷ and equilibrating the oxides in specific pH suspensions¹⁸ have also been successfully with the creation of cation vacancies in various transitional metal oxides (TMOs). The cation vacancies may contribute to additional capacity due to the extra cation intercalation sites but only if it is not offset by the proportional decrease in the quantity of redox-active transition metal centers (reduced overall theoretical capacity).^{19,20} Thus it is essential to moderate the concentration of point defects.

In addition, numerous precedents of defect engineering, such as removal of incorporated sacrificial phase (such as silicon dioxide (SiO₂)) to purposefully incorporate voids within structures, have been demonstrated to effectively counteract pulverization related

deterioration.²¹⁻²³ More encouragingly, the paradigm of selective etching of pure elements to form new materials, morphologies and features has been realized through the recent works on MXenes.²⁴⁻²⁶ Cumulatively, it is thought-provoking to ascertain if substitutional dopant species in semiconducting materials, such as SnO₂, may be selectively removed to achieve a more intricately modified SnO₂ architecture with improved reversible Li⁺ storage capacity.

In this work, as continuation to the intent of adopting synthesis procedures with high scalability and throughput, solvothermal synthesis, coupled with delicate dimensional and morphological control,²⁷ is used to synthesize antimony-doped SnO₂ (ATO). As a proof-of-concept, a post-synthesis acid treatment of ATO is conducted to demonstrate this strategy of improving electrochemical performance through the partial removal of substitutional dopant species in ATO.

5.2 Materials and Method

Unless otherwise specified, reagents were of analytical grade and were used as received without further purification. Tin (IV) chloride (SnCl₄), antimony (III) chloride (SbCl₃), and anhydrous benzyl alcohol were purchased from Sigma-Aldrich. Sulfuric acid (H₂SO₄, 95-97%) and nitric acid (HNO₃, 69%) were purchased from Fluka. Hydrochloric acid (HCl, 37%) was purchased from Merck.

In a typical procedure to prepare Sb-doped SnO₂ (ATO), 0.625 g of SnCl₄ (2.4 mmol), 0.137 g of SbCl₃ (0.6 mmol) were successively added into 40 mL of anhydrous benzyl alcohol under stirring.²⁸ The clear homogenous solution was then transferred to a 45 mL Teflon-lined autoclave and heated in oven at 200 °C for 6 h. The ATO nanoparticles were retrieved, centrifuged and washed several times with deionized (DI) water.

In a typical procedure to prepare 200 mL of 6 M H₂SO₄ etchant solution, 122.578 g of H₂SO₄ (95-97%) was slowly added to 80 mL of DI water in an ice bath and more DI water was added until the meniscus of the solution reaches the line marked on the 200 mL

volumetric flask. The solution was periodically swirled to allow better mixing between the concentrated acid and DI water. Similarly, to prepare 200 mL of 6 M HNO₃ and 6 M HCl etchant solutions, 109.583 g of HNO₃ (69%) and 118.216 g of HCl (37%) were respectively added to separate volumetric flasks, each containing 80 mL of cold DI water. The flasks were swirled and topped up to 200 mL with more DI water.

In a typical post-synthesis etching procedure for the ATO nanoparticles, 0.5 g of ATO nanoparticles were added to 50 mL of 6 M H₂SO₄ etchant solution and the etching proceeded in a closed PP bottle (to avoid evaporation of water, i.e. change of etchant concentration) maintained at 80 °C under continuous stirring. The duration of immersion was varied at 2, 4, 6 and 8 h, respectively. The experiments were repeated with 6 M HCl and 6 M HNO₃ etchant solutions. The varyingly etched ATO nanoparticles were collected via vacuum-filtration through 0.22 µm polyvinylidene fluoride (PVDF) membranes, washed with large quantity of DI water and then dried in air at room temperature.

5.3 Results and Discussion

5.3.1 Effect of Hot Concentrated H₂SO₄ on Sb-dopant Concentration and Electrochemical Performance of ATO

The XRD patterns of as-synthesized ATO nanoparticles and post-synthesis H₂SO₄-etched ATO are as plotted in Figure 5.1 (a). The diffraction peaks of both as-synthesized and etched ATO can be indexed to tetragonal rutile SnO₂ (JCPDS 41-1445). The absence of impurity phases such as antimony (III) oxide (Sb₂O₃) or antimony pentoxide (Sb₂O₅) is indicative that the Sb dopant ions have been successfully incorporated into SnO₂ crystal lattice by solid solution formation with Sb ions substituting Sn ions.²⁸ This is expected as the relative quantity of Sb precursor added to the solvothermal synthesis solution is only 20 at.% (Sn precursor is 80 at.%), which is well below the reported solubility limit of 30 at.% Sb in Sn lattice.²⁹ To confirm if the Sb dopant atoms are in the substitutional or interstitial configuration in the SnO₂ host lattice, the corresponding lattice parameters (*a*

and c) of unetched and variously-etched ATO are derived from their respective XRD plots. A variation of lattice parameters (i.e. change in structure and lattice size) is understandably reflected in a variation of ' 2θ ' (i.e. shift of the XRD peaks). According to Vegard's law,³⁰ the incorporation of Sb by substitution would shrink the host lattice appreciably because the ionic radius of Sb^{5+} (0.65 Å, coordination number CN = 6) is slightly smaller than that of Sn^{4+} (0.71 Å, coordination number CN = 6).³¹ Conversely, if the incorporation of Sb occurs at the interstitial sites between the Sn and O atoms, the SnO_2 lattice should expand instead. Since the calculated lattice parameters of various Sb-doped SnO_2 (both unetched and -etched) are consistently smaller than the JCPDS value of $a = 4.738$ Å and $c = 3.187$ Å for tetragonal rutile SnO_2 , the Sb dopant atoms are implied to be readily incorporated into the SnO_2 host lattice by substitution. The detailed derivation and plots of relevant lattice parameters of these SnO_2 -based samples (Figure A1 (a-c)) have been included in the Appendix. Furthermore, the incorporation of Sb dopant does not incur any change in preferential orientation, with (110), (101) and (221) remaining the three most predominant peaks and this lends credence to the earlier conjecture that Sb dopant ions replace Sn host ions in lattice sites and not at interstitial sites.

Figure 5.1 (b) shows the XPS survey spectra of as-synthesized ATO nanoparticles and post-synthesis H_2SO_4 -etched ATO. In addition to the overlapped characteristic peaks of antimony (Sb 3d) and oxygen (O 1s) at 531.1 eV, there are two other characteristic peaks at 487.1 and 285.0 eV, corresponding to tin (Sn 3d) and carbon (C 1s), respectively. This also reveals that immersing ATO nanoparticles in hot concentrated H_2SO_4 etchant solution even for 8 h is insufficient to completely remove the Sb dopants from SnO_2 lattice. The high-resolution XPS spectra of Sn 3d for various ATO samples, in Figure 5.1 (c), can be deconvoluted into two components, centered at 495.5 and 487.0 eV, for contribution from Sn 3d_{3/2} and Sn 3d_{5/2} orbitals, respectively. Although the gap between the Sn 3d core-level peaks is 8.5 eV (typical of standard SnO_2 spectrum), the peaks are slightly slanted (not upright) thus it is apparent that the Sn species present are not exclusively Sn^{4+} . The slight tilt of Sn 3d peaks to lower energies is indicative of the presence of oxygen vacancies and Sn in a lower oxidation state (than Sn^{4+}) due to n-type doping with Sb.³²

More importantly, the deconvolution of high-resolution XPS spectra of the overlapping Sb 3d and O 1s for as-synthesized ATO, in Figure 5.1 (d), reveals a standalone Sb 3d_{3/2} peak at 540.5 eV and the overlapping Sb 3d_{5/2} and O 1s peaks at 531.1 eV. This standalone Sb 3d_{3/2} peak at 540.5 eV is then used to isolate the Sb 3d_{5/2} peak from the O 1s peaks, because the intensity between the two Sb 3d peaks has a fixed ratio of 1.44.³³ Subsequently, the overlapping Sb 3d_{5/2} and O 1s peaks at 531.1 eV can be deconvoluted into three components. A Gaussian peak at 531.3 eV may be attributed to Sb 3d_{5/2} and two peaks at 531.9 and 531.0 eV, can be ascribed to oxygen vacancies or the oxygen of the adsorbed hydroxyl groups and water on the surface of ATO nanoparticles and the characteristic metal-oxygen bonds within the lattice, respectively. The normalized atomic compositions of the as-synthesized ATO nanoparticles and post-synthesis H₂SO₄-etched ATO are derived by mathematical manipulation involving the area under Sn 3d and Sb 3d peaks and the corresponding atomic sensitivity factor are summarized in Table 5.1. Expectedly, the Sb dopant concentration in ATO comparatively decreases as duration of immersion in etchant increases.

Figure 5. 1 (a) XRD (b) XPS survey, and (c) high-resolution XPS spectra of Sn 3d of as-synthesized ATO, ATO- H_2SO_4 -2h, ATO- H_2SO_4 -4h, ATO- H_2SO_4 -6h, and ATO- H_2SO_4 -8h. (d) High-resolution XPS spectra of the overlapping Sb 3d and O 1s of as-synthesized ATO.

Table 5. 1 Normalized compositions of as-synthesized ATO and ATO immersed in hot 6 M H_2SO_4 for various duration.

	Sn (at.%)	Sb (at.%)
ATO	82.7	17.3
ATO (H_2SO_4 -2h)	84.9	15.1
ATO (H_2SO_4 -4h)	84.9	15.1
ATO (H_2SO_4 -6h)	85.1	14.9
ATO (H_2SO_4 -8h)	85.6	14.4

The FESEM images of as-synthesized undoped SnO_2 , ATO (17.3 at.% Sb) and post-

synthesis H_2SO_4 -etched ATO nanoparticles are as shown in Figure 5.2 (a-f). Generally, the nanoparticles are spherical and approximately 10 nm and there is no obvious reduction in particle size and surface smoothness even after extended period of etching in hot concentrated H_2SO_4 (8 h), which suggests that the SnO_2 lattice is rather resistant to the H_2SO_4 etchant.

Figure 5. 2 FESEM images of as-synthesized (a) SnO_2 , (b) ATO, (c) ATO- H_2SO_4 -2h, (d) ATO- H_2SO_4 -4h, (e) ATO- H_2SO_4 -6h, and (f) ATO- H_2SO_4 -8h.

Figures 5.3 (a-f) depict the TEM images of as-synthesized undoped SnO_2 , ATO (17.3 at.% Sb) and post-synthesis H_2SO_4 -etched ATO nanoparticles and reaffirm earlier observation by FESEM that the morphology remains invariant to Sb doping and H_2SO_4 etching procedure. This also corroborates well with the normalized composition analysis by XPS which indicates the partial removal of Sb dopant but not Sn.

Figure 5. 3 TEM images of as-synthesized (a) SnO_2 , (b) ATO, (c) ATO- H_2SO_4 -2h, (d) ATO- H_2SO_4 -4h, (e) ATO- H_2SO_4 -6h, and (f) ATO- H_2SO_4 -8h.

Conductive carbon and binder were added to the samples of as-synthesized undoped SnO₂, ATO (17.3 at.% Sb) and post-synthesis H₂SO₄-etched ATO nanoparticles and the slurry casted anodes were evaluated by cyclic voltammetry (CV), galvanostatic charge discharge (GCD) method and electrochemical impedance spectroscopy (EIS). Figures A2 (a-c) show the CV curves of as-synthesized undoped SnO₂, ATO (17.3 at.% Sb) and post-synthesis H₂SO₄-etched ATO at scan rate 0.1 mV s⁻¹ within a potential window of 0.005 to 3.0 V, and they expectedly exhibit similar features. In the first cycle, a broad cathodic peak (from around 1.10 V to 0.50 V) envelops peaks corresponding to the reduction of SnO₂ into Sn,^{34, 35} the accompanying formation of Li₂O, the decomposition of electrolyte and formation of SEI.³⁶ There is another broad peak at < 0.25 V which encompasses the formation of Li_{4.4}Sn through the multi-step alloying reaction between Li⁺ and Sn.³⁷ Its corresponding broad anodic peak for the dealloying (oxidation) of Li_{4.4}Sn can be seen at around 0.67 V. The oxidation peak of Sn to SnO₂ is observed at 1.05 V, indicative of the reversibility of the SnO₂ conversion reaction.^{34, 35} The most obvious difference between the initial and subsequent cycles' CV curves is the disappearance of the prominent cathodic peak (from around 1.10 V to 0.50 V) which includes the one-off and irreversible SEI formation and side reactions. Although the electroactive Sb dopant species in various ATO samples should also contribute to the overall capacity via alloying/dealloying mechanism, there are no corresponding distinct redox peaks in the CV scans (Figures A2 (b) and (c)).^{38, 39} This is because the potential, at which the alloying/dealloying of Sb occurs, coincides with that of Sn, therefore the alloying/dealloying peaks of Sn in fact envelop that of Sb. The galvanostatic discharge-charge profiles of as-synthesized undoped SnO₂, Sb_{0.17}Sn_{0.83}O₂ (ATO) and post-synthesis H₂SO₄-etched ATO measured at current density of 100 mA g⁻¹, as shown in Figure A3 (in Appendix), agree well with the corresponding CV results.

Although the undoped SnO₂, as-synthesized Sb_{0.17}Sn_{0.83}O₂ (ATO) and varyingly etched ATO samples exhibit similar CV features and comparable specific discharge capacities in the initial few cycles, they differ significantly in their cyclic stability (Figure 5.4 (a)). The bare and undoped SnO₂ shows the highest of capacity fading and retains a lowly reversible discharge capacity of 247 mAh g⁻¹ after 200 cycles at 100 mA g⁻¹ current density. Comparatively, bare Sb_{0.17}Sn_{0.83}O₂ (ATO) retains an improved discharge capacity of 410

mAh g^{-1} at the end of the 200th cycle. More interestingly, the bare and varyingly etched ATO samples demonstrates enhanced cyclic stability with reversible capacities between 650 to 790 mAh g^{-1} even after 200 cycles. By immersing the as-synthesized ATO nanoparticles in the acidic etchant for longer duration (6 and 8 h), the samples are accompanied by lowered 14.9 and 14.3 at.% Sb, correspondingly higher concentration of cation vacancies in the SnO_2 lattice and improved reversible capacities of 710 and 790 mAh g^{-1} , respectively. Thus, it is postulated that analogous to void space, the consequential cation vacancies due to the partial removal of the substitutional Sb dopant from the SnO_2 lattice (reduced Sb concentration according to XPS analysis) in the varyingly etched ATO samples, can be beneficial for the alleviation of structural degradation from repeated volumetric variation between delithiation/lithiation and improving cyclic stability.

Electrochemical impedance spectroscopy (EIS) measurements were conducted to provide insight into the effect of Sb dopant and cation vacancy concentration on the kinetics of ionic diffusion and charge transfer in as-synthesized undoped SnO_2 , $\text{Sb}_{0.17}\text{Sn}_{0.83}\text{O}_2$ (ATO) and post-synthesis H_2SO_4 -etched ATO. As observed in the Nyquist plots in Figure 5.4 (b), by doping SnO_2 with Sb, the charge transfer resistance (correlated to electrical conductivity but may not necessarily be linear relationship), as inferred from the diameter of the semicircle in the high frequency region, can be drastically reduced. As the Sb dopant concentration is moderately reduced (from 17.3 to 14.4 at.% Sb) by the etching procedure, there is expectedly another round of significant reduction in charge transfer resistance from that of the $\text{Sb}_{0.17}\text{Sn}_{0.83}\text{O}_2$ (ATO) to those of post-synthesis H_2SO_4 -etched ATO samples. This may be explained by the fact that the 17.3 at.% Sb in the as-synthesized ATO exceeds the optimal Sb concentration (at ca. 10 at.%) for highest electrical conductivity, the Sb dopant species predominantly exist as the electron trapping Sb^{3+} rather than the beneficial Sb^{5+} donor species to maintain charge neutrality in the SnO_2 lattice. Consequently, a reduction in excess Sb dopant concentration by etching can understandably improve the electrical conductivity of the ATO nanoparticles.^{39, 40}

Figure 5. 4 (a) Cycling performance of ATO and ATO after etching in 6 M H₂SO₄ for various duration. (b) Electrochemical impedance spectra (EIS) of ATO and ATO after etching in 6 M H₂SO₄ at the amplitude of 10 mV over frequency range from 100 kHz to 10 mHz.

5.3.2 Effect of Hot Concentrated HCl and HNO₃ on Sb-dopant Concentration and Electrochemical Performance of ATO

Instead of the diprotic H₂SO₄ acid, other common mineral and monoprotic acids such as HCl and HNO₃ were also examined as the probable etchants to realize the removal of Sb dopant from the SnO₂ lattice. It is important to note that the efficacy of the etchants for Sb dopant removal is dependent on the anionic species rather than hydrogen ions (H⁺).

The XRD patterns of variously etched ATO by 6 M HCl and 6 M HNO₃ are as plotted in Figures 5.5 (a) and (b), respectively. The diffraction peaks can be well indexed to tetragonal rutile SnO₂ (JCPDS 41-1445) and there is no obvious peak shift nor variation in peak intensity of the ATO samples even when immersed in either acidic etchants for extended period. This may be indicative that crystallite size of ATO remains invariant to both HCl and HNO₃ etching procedure, and this is confirmed by the TEM images of ATO immersed in 6 M HCl and 6 M HNO₃ at 80 °C for extended duration of 8 h (in Figures A4 (a) and (b), respectively), which show spherical nanoparticles, which are approximately 10 nm in diameter. However, it is also noted that ATO nanoparticles etched by HCl (Figure A4 (a)) are rough around the edges (signs of pitting) unlike the smooth ATO nanoparticles etched by HNO₃ (Figure A4 (b)), which is suggestive that 6 M HCl is a comparatively more corrosive etchant than 6 M HNO₃.

The high-resolution XPS spectra of Sn 3d for the varyingly etched ATO samples by concentrated HCl and HNO₃, as shown in Figures 5.5 (c) and (d), can be deconvoluted into two components, centered at 495.5 and 487.0 eV, for contribution from Sn 3d_{3/2} and Sn 3d_{5/2} orbitals, respectively. Like the Sn 3d spectra for ATO samples etched by H₂SO₄ (as shown in Figure 5.1 (c)), the gap between the Sn 3d core-level peaks for ATO samples etched by HCl and HNO₃ is also 8.5 eV. Admissibly, the Sn 3d peaks are slightly asymmetric (tilted) as some Sn species exist in lower oxidation state than Sn⁴⁺ due to n-type doping with Sb.³²

The normalized atomic compositions of the as-synthesized ATO nanoparticles and post-synthesis HCl- and HNO₃-etched ATO are summarized in Table 5.2 and 5.3, respectively. Most notably, monoprotic HCl can reduce the Sb concentration in ATO from 17.3 to 11.4 at.% with 8 h of immersion whereas at identical concentration (6 M), temperature (80 °C) and immersion duration (8 h), monoprotic HNO₃ can only marginally remove Sb dopant from SnO₂ lattice (Sb dopant level only minimally decreases to 16.5 at.% after 8 h of immersion). This reveals that chloride ions (Cl⁻) are the most effective species for etching Sb from SnO₂ lattice followed by sulphate ions (SO₄²⁻) and nitrate ions (NO₃⁻).

Figure 5. 5 XRD of varyingly etched ATO by (a) 6 M HCl and (b) 6 M HNO₃ at 80 °C, respectively. High-resolution XPS spectra of Sn 3d of varyingly etched ATO by (c) 6 M HCl and (d) 6 M HNO₃ etchant solution, respectively.

Table 5. 2 Normalized compositions of as-synthesized ATO and ATO immersed in hot 6 M HCl for various duration.

	Sn (at.%)	Sb (at.%)
ATO	82.7	17.3
ATO (HCl-2h)	85.7	14.3
ATO (HCl-4h)	86.9	13.1
ATO (HCl-6h)	87.4	12.6
ATO (HCl-8h)	88.6	11.4

Table 5. 3 Normalized compositions of as-synthesized ATO and ATO immersed in hot 6 M HNO₃ for various duration.

	Sn (at.%)	Sb (at%)
ATO	82.7	17.3
ATO (HNO₃-2h)	83.0	17.0
ATO (HNO₃-4h)	83.0	17.0
ATO (HNO₃-6h)	83.1	16.9
ATO (HNO₃-8h)	83.5	16.5

The galvanostatic discharge-charge profiles of post-synthesis HCl- and HNO₃-etched ATO measured at current density of 100 mA g⁻¹, as shown in Figures A3 (d) and (e), match well with the corresponding CV results, which are like that of post-synthesis H₂SO₄-etched ATO (Figure A3 (c) in Appendix), and thus will not be elaborated (repeatedly) in detail here.

The cyclic stability of the variously etched (by HCl) ATO samples are as illustrated in Figure 5.6 (a). Coincidentally, the bare ATO which has been etched by HCl for shortest duration of 2 h (14.3 at.% Sb) exhibits the best cyclic stability amongst the HCl etched ATO samples, retaining a reversible discharge capacity of 780 mAh g⁻¹ (comparable to ATO-H₂SO₄-8h, 14.4 at.% Sb) after 200 cycles at 100 mA g⁻¹ current density. As the duration of immersion in HCl extends from 4 h to 8 h, the Sb dopant concentration decreases further from 13.1 to 11.4 at.% while the corresponding reversible capacities (200th cycle) are reduced and vary between 650 to 675 mAh g⁻¹. This notable decrease in reversible capacity is probably due to decrease in redox-active transition metal (Sb) centers (reduced overall theoretical capacity) exceeding the additional capacity brought about by the cation vacancies.^{19, 20} Although the Sb dopant concentration decrement in various ATO samples etched by HNO₃ is seemingly insignificant, they still exhibit significantly enhanced cyclic reversibility with retained discharge capacities between 630 to 670 mAh g⁻¹ at the end of 200 cycles. Although the exact mechanism for this improvement is not

clear, it is reasonable to speculate that there exists some synergistic effect from the excess Sb dopant and defect (Sb and O vacancies) content which combine to endow these variously etched ATO with the exceptional electrochemical stability. Considering the difference in bond dissociation energies of Sn–O ($\Delta H_{f298}^{\circ}=528 \text{ kJmol}^{-1}$) and Sb–O ($\Delta H_{f298}^{\circ}=434 \text{ kJmol}^{-1}$), it is thermodynamically more favorable for the removal of Sb dopant than Sn host atoms when the ATO nanoparticles are immersed in various acidic etchants.⁴¹ Similarly, according to XPS analysis, chloride ions (Cl^{-}) have been identified to be the most effective species for etching Sb from SnO_2 lattice followed by sulphate ions (SO_4^{2-}) and nitrate ions (NO_3^{-}), and this difference may also be explained by thermodynamics. In addition, the wet chemical etching process invariably proceeds from the surface of the spherical ATO nanoparticles and considering the random distribution of Sb dopant atoms within the SnO_2 lattice (i.e. no straightforward channel for etchant molecules to reach the core), a pseudo core-shell structure may be formed. The shell consists of etched ATO with much reduced Sb content and increase in vacancies, and the core is made up of mostly unetched ATO. Consequently, the increase in vacancies on the surface (shell layer) and Sb dopant atoms may exhibit a diluent effect, which combinedly mitigates the formation of large Sn clusters and decreases interparticle strain during the electrochemical discharge/charge process.^{20, 42, 43} Moreover, it is noteworthy that these improved cyclic stabilities of post-synthesis etched ATO samples (mostly exceed 650 mAh g^{-1}) are achieved without further modifications (bare nanoparticles are evaluated without carbon coating or making a composite). This lends further credence to the proposed formation of core-shell structure within these variously etched ATO.

Electrochemical impedance spectroscopy (EIS) measurements were also conducted to provide insight into the effect of Sb dopant removal and cation vacancy concentration on the charge transfer in post-synthesis HCl- and HNO_3 -etched ATO. As observed in Figure 5.6 (c), the diameter of the semicircle for unetched ATO in the high frequency region of Nyquist plot is significantly smaller than that of undoped SnO_2 . This indicates that the successful incorporation of Sb dopants into SnO_2 lattice to form ATO has expectedly reduced charge transfer impedance, which also implies improved electrical conductivity.⁴⁴ According to classical band theory, excess electrons (charge carriers) from a nearby dopant

valence band (particularly Sb^{5+} (Sb 5p) instead of the native Sn^{4+} (Sn 5s, 5p)) can be directly injected into the lowest unoccupied molecular orbital (LUMO) or the conduction band minimum (CBM) of SnO_2 , thereby improving conductivity.⁴⁵⁻⁴⁷ In addition, due to Sb doping in SnO_2 , associated defects such as oxygen vacancies (O 2p) can also effectively create an excess of electrons.⁴⁸ With adequate orbital overlap, delocalization of these electrons from the defect sites may occur and further increase the concentration of conduction electrons at CBM of SnO_2 .^{49, 50} The diameter of the semicircle in the high frequency region from the Nyquist plots in Figure 5.6 (c) also suggests that the charge transfer resistance of ATO-HCl-2h (with 14.3 at.% Sb) is less than that of unetched ATO. This corroborates well with the earlier observation in H_2SO_4 -etched ATO samples, a reduction in excess Sb dopant in as-synthesized ATO (from 17.3 at.% Sb towards 10 at.% for optimal electrical conductivity) by HCl etching may decrease the quantity of the electron trapping Sb^{3+} species and consequently improve the electrical conductivity of ATO-HCl-2h.^{39, 40} However, as orbital overlap between nearest-neighbor cations (both Sb and Sn) contributes to electron conductive pathway, the increasingly more Sb-deficient ATO structures tend to be less conductive than their less defective counterpart.⁵¹ Since the partial removal of Sb dopant from ATO is also accompanied by the formation of Sb and O vacancies (i.e. Schottky defects), the mean free path length of electrons is inevitably reduced due to the electron scattering effect from the increased number of defects which eventually outweighs the increased conductivity conferred by the moderate presence of oxygen vacancies and concomitant recovery to predominance of beneficial Sb^{5+} dopant donor characteristics.^{49, 52-56} This offset and subsequent increased resistivity are evident in the slightly larger diameter of semicircles for ATO-HCl-4h (with 13.1 at.% Sb), ATO-HCl-6h (with 12.6 at.% Sb), and ATO-HCl-8h (with 11.4 at.% Sb), respectively, in the high frequency region than that of unetched ATO in Figure 5.6 (c). This suggests that the post-synthesis etching of ATO in HCl etchant for extended duration (4 h and beyond) can be counterproductive towards enhancing electrical conductivity even though it can supposedly reduce Sb concentrations towards the classically optimal concentration at ca. 10 at.%.

In Figure 5.6 (d), the diameter of the semicircles for all HNO₃-etched ATO samples in the high frequency region from the Nyquist plots are less than that of unetched ATO. This suggests that the charge transfer resistance of all four HNO₃-etched ATO samples are less than that of unetched ATO. As previously mentioned, the unetched ATO sample predominantly possesses electron trapping Sb³⁺ species and exhibits less than classically optimal electrical conductivity due to an excess of Sb dopant concentration. Subsequently, a reduction in excess Sb dopant concentration by HNO₃-etching can understandably improve the electrical conductivity of the ATO nanoparticles with the moderation of oxygen vacancies and concomitant reversal to Sb⁵⁺ dopant donor characteristics.^{39, 40} Interestingly, the slanted straight lines for ATO-HNO₃-6h and ATO-HNO₃-8h in the low frequency region of the Nyquist plots are less inclined than that for as-synthesized ATO, ATO-HNO₃-2h and ATO-HNO₃-4h in Figure 5.6 (d). Combined with earlier observation with H₂SO₄- and HCl-etched ATO samples, there seems to be a deterioration in Li⁺ ions diffusion when the Sb concentration is reduced to between 16.9 to 14.9 at.% from an initial concentration of 17.3 at.%. Consistent with literature,⁵ Sb-doping into SnO₂ lattice brings about minimal enhancement to the characteristic semi-infinite diffusion of the Li⁺ ions in the electrode (Warburg impedance) as indicated by the similarly inclined straight lines for as-synthesized ATO before and after etching in the low frequency region of the Nyquist plots.

Figure 5.6 Cycling performance of as-synthesized ATO and ATO after etching in (a) 6 M HCl and (b) 6 M HNO₃ for various duration. Electrochemical impedance spectra (EIS) of as-synthesized ATO and ATO after etching in (c) 6 M HCl and (d) 6 M HNO₃ for various duration, at the amplitude of 10 mV over frequency range from 100 kHz to 10 mHz.

5.4 Summary

In summary, a post-synthesis acid treatment of as-synthesized Sb_{0.17}Sn_{0.83}O₂ (ATO) has been conducted using different etchant solutions of 6 M H₂SO₄, 6 M HCl and 6 M HNO₃ at 80 °C. Most probably limited by the particulate morphology (inner/core not exposed to the etchant), only partial removal of substitutional dopant species in ATO was realized by the series of experiments with varying etchants and duration of immersion. More importantly, chloride ions (Cl⁻) have been identified to be the most effective species for etching Sb from SnO₂ lattice followed by sulphate ions (SO₄²⁻) and nitrate ions (NO₃⁻). Analogous to the strategy of incorporating void to buffer against repeated volumetric

variation between delithiation/lithiation, the consequential cation vacancies due to the partial removal of the substitutional Sb dopant from the SnO₂ lattice (according to XPS analysis) in the varyingly etched ATO samples, are postulated to be beneficial for the alleviation of structural degradation and extension of cyclic longevity. Coincidentally, both ATO-H₂SO₄-8h and ATO-HCl-2h exhibit the best cyclic performance amongst the evaluated samples with a high discharge capacity of ca. 790 mAh g⁻¹ retained at the end of the 200th cycle at current density 100 mA g⁻¹. It is more remarkable that such excellent cyclic stability has been achieved by bare ATO nanoparticles with ca. 14.4 at.% Sb (reduced from its initial of 17.3 at.% Sb) and similar cation (Sb) vacancies concentration without further modification(s). Herein, only preliminary data supporting the viability of the etching procedure for the partial removal of Sb dopant from SnO₂ lattice has been presented. Optimization of the etchant formulation and parameters will be necessary to improve and extend this method to removal of other dopants and host lattices.

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Chapter 6

Effect of Composition on the Electrochemical Performance of Hybrid Anode Based on $\text{SnO}_2\cdot\text{Co}_3\text{O}_4$ Nanocubes Entrapped in $\text{Ti}_3\text{C}_2\text{T}_x$ Nanosheets by a Simple Freeze-drying Procedure

The integration of nanomaterials with complimentary properties into desired architecture is one effective approach to develop high-performance LIBs anode materials. Hybridization of two-dimensional (2D) $\text{Ti}_3\text{C}_2\text{T}_x$ (MXene), with high electronic conductivity but moderate capacity, and transition metal oxide (TMO), with high capacity but low electrical conductivity, have demonstrated promising electrochemical performances. To date, fabrication of MXene/TMO hybrids has been limited to alternating vacuum-assisted filtration, layer-by-layer spray coating and in-situ wet chemistry synthesis, which may be time-consuming (tedious) and limiting homogeneity of constituents. Herein this chapter presents the hypothesis that freezing a well-mixed solution of $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets and $\text{SnO}_2\cdot\text{Co}_3\text{O}_4$ nanocubes by liquid nitrogen and subsequent sublimation can facilitate a homogeneously mixed $\text{Ti}_3\text{C}_2\text{T}_x$ - $\text{SnO}_2\cdot\text{Co}_3\text{O}_4$ nanocomposite powder. The composition effect on the Li^+ ions storage performance of these $\text{Ti}_3\text{C}_2\text{T}_x$ - $\text{SnO}_2\cdot\text{Co}_3\text{O}_4$ hybrid anodes was evaluated.

6.1 Introduction

In the previous chapter, post-synthesis acid etching of Sb-doped SnO₂ (ATO) was demonstrated to be beneficial towards improving overall electrochemical performance. However, as extensively reviewed in Chapter 2, some intrinsic problems persist in nanostructured SnO₂-based LIBs anode materials.^{1,2} Although SnO₂ exhibits high Li⁺ ions storage capacity due to beyond intercalation mechanism, concomitant partially irreversible phase transformations and ensuing repeated volumetric variation substantially challenge its long-term cyclic stability.³⁻⁶ The structural integrity of electrode may be compromised due to probable pulverization and delamination from the current collector.⁷ To improve the partial reversibility of the reduction of Li₂O formed during conversion reaction of SnO₂, nanocubes of intimately mixed SnO₂ and Co₃O₄, are deliberately selected for this work, to exploit the reported synergistic effect of Co nanoparticles, formed by decomposition of Co₃O₄ during lithiation.⁸

Poor rate performance due to inherently limited electron and ion transport kinetics of SnO₂ may be desirably alleviated by combining with a highly conductive phase, which in some instances, doubled as a buffer matrix to delay mechanical degradation.⁹ Amongst 2D materials beyond graphene, pseudocapacitive Ti₃C₂T_x, the most studied MXene, is one intriguing candidate material to combine with nanostructured SnO₂ and form hybrid architectures which favorably assimilate advantages and shortcomings of constituent components.¹⁰⁻¹³ Ti₃C₂T_x nanosheets embody large specific surface area (double-edged as greater contact area with electrolyte favorably enhances ionic transferal kinetics but undesirably triggers parasitic side reactions and increases irreversible capacity loss due to solid-electrolyte (SEI) formation) with excellent electronic conductivity, mechanical strength, low operating voltage range and low diffusion barriers albeit moderate capacity and issues with restacking of delaminated layers.^{9, 14}

In continuation on the theme of etching in material synthesis (Chapter 5), the procedures to prepare SnO₂·Co₃O₄ nanocubes and few-layered HCl/LiF-etched Ti₃C₂T_x nanosheets

involve alkaline and acid etching, respectively. Polyhedral $\text{CoSn}(\text{OH})_6$ are first prepared by a simple co-precipitation of Sn^{4+} , Co^{2+} and OH^- in the presence of citrate ions.¹⁵ With excess OH^- from addition of concentrated sodium hydroxide (NaOH) solution, soluble $[\text{Co}(\text{OH})_4]^{2-}$ and $[\text{Sn}(\text{OH})_6]^{2-}$ can be formed from amphoteric $\text{CoSn}(\text{OH})_6$ even at room temperature. Essential to the preservation of polyhedral morphology, thermodynamically unstable $[\text{Co}(\text{OH})_4]^{2-}$ species readily oxidize to form a passivating outer layer.¹⁵ With extended exposure to excess OH^- , coupled with continuous excavation of inner material, hollow $\text{CoSn}(\text{OH})_6$ nanocubes may also be formed.¹⁵⁻¹⁸ Interestingly, subsequent heat treatment of $\text{CoSn}(\text{OH})_6$ in air or inert atmosphere (such as N_2 or Ar) will result in either a mixture of crystalline SnO_2 and Co_3O_4 , or amorphous CoSnO_3 , respectively.¹⁵⁻¹⁹

Among the myriad of synthesis conditions and reagents to prepare few-layered $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets from selective etching of the Al atoms in layered hexagonal ternary carbide, Ti_3AlC_2 , one protocol may be advantageous over another depending on the desired properties and intended application.^{11, 20, 21} Counterintuitively, between two of the most mature synthesis routes, the use of HCl/LiF , a comparatively less harsh etchant than concentrated HF (hazardous), produces a higher yield of delaminated $\text{Ti}_3\text{C}_2\text{T}_x$ even without sonication.²²⁻²⁴ A modified minimally intensive layer delamination (MILD) approach was adopted, with a further increase in molar ratio of LiF to Ti_3AlC_2 to 12: 1 instead of 7.5 to 1, in 9 M HCl etchant solution at room temperature for 24 h to favorably obtain large flakes of highly conductive $\text{Ti}_3\text{C}_2\text{T}_x$, which are desired for application in LIBs.^{20, 21} This deviates from the pioneering work reported by Ghidui *et al.* (5 M LiF in 6 M HCl solution at 35 °C for 24 h), which produces laterally smaller flakes of delaminated $\text{Ti}_3\text{C}_2\text{T}_x$ albeit with more defects.²²

Coinciding with the much improved delamination than HF -etched $\text{Ti}_3\text{C}_2\text{T}_x$ even without discretionary intercalation of polar organic molecules (such as dimethyl sulfoxide (DMSO), hydrazine, urea,²⁵ isopropylamine²⁶), or large organic base molecules (such as tetrabutylammonium hydroxide (TBAOH), choline hydroxide or *n*-butylamine²⁷), works on surface modification of HCl/LiF -etched $\text{Ti}_3\text{C}_2\text{T}_x$ remain few and far between. Additionally, thorough removal of solvent(s) and/or intercalant molecules in reported

methods remains challenging. Thus, it is imperative to explore scalable and efficient posttreatment to increase the yield of delaminated HCl/LiF-etched $\text{Ti}_3\text{C}_2\text{T}_x$, to mitigate the undesired restacking of single/few-layered $\text{Ti}_3\text{C}_2\text{T}_x$ (increased lamellar thickness), or to graft functional group(s) (for enhanced surface properties). Cumulatively, the ease of removal of water soluble aryl diazonium salts, improved dispersibility of $\text{Ti}_3\text{C}_2\text{T}_x$ in water (highly relevant to preparation of MXene-based composites), increased interlayer distance, and more surface-active sites after grafting of *p*-phenyl- SO_3H groups, make the use of diazonium salts a promising surface modifying agent for MXenes.²⁸

Based on literatures, current procedures to fabricate $\text{Ti}_3\text{C}_2\text{T}_x/\text{TMO}$ hybrid for battery electrodes have mostly been limited to alternating vacuum filtration, alternating spray coating, rolling, in-situ wet chemistry synthesis, self-assembly in solution or modified layer-by-layer assembly.^{10, 11, 20, 21, 29} Hitherto, few works, if any, have presented the fabrication of nanostructured $\text{Ti}_3\text{C}_2\text{T}_x/\text{TMO}$ hybrid with either customizable packing density or industrially compatible approach beyond solvent-based processing. It also remains challenging to achieve homogeneously mixed $\text{Ti}_3\text{C}_2\text{T}_x/\text{TMO}$ powder samples without compromising the morphology or excellent electronic properties of $\text{Ti}_3\text{C}_2\text{T}_x$ component.

Herein, it is hypothesized that, from a mechanistic perspective, a simple freeze-drying procedure can convert a well-mixed suspension of few-layered $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets and $\text{SnO}_2\cdot\text{Co}_3\text{O}_4$ nanocubes into a well-designed heterostructure of alternating layers of $\text{Ti}_3\text{C}_2\text{T}_x$ and $\text{SnO}_2\cdot\text{Co}_3\text{O}_4$ with outstanding electrochemical performance as LIBs anode. In addition, the electrochemical performance of $\text{Ti}_3\text{C}_2\text{T}_x\text{-SnO}_2\cdot\text{Co}_3\text{O}_4$ hybrid anodes with varying compositions was evaluated to determine if certain combination of $\text{Ti}_3\text{C}_2\text{T}_x$ and $\text{SnO}_2\cdot\text{Co}_3\text{O}_4$ can indeed bring about enhanced Li^+ storage capability exceeding the sum of its constituent components (synergistic effect). This work presents a rational strategy to effectively integrate $\text{Ti}_3\text{C}_2\text{T}_x$ and multiple components into a powdered hybrid, which subsequently offers opportunities to develop alternative approaches for nanostructured electrode materials with increased tap density and improved scalability.

6.2 Materials and Method

Unless otherwise specified, reagents were of analytical grade and were used as received without further purification. Tin (IV) chloride pentahydrate ($\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$), cobalt (II) chloride hexahydrate ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$), sodium citrate tribasic dihydrate ($\text{HOC}(\text{COONa})(\text{CH}_2\text{COONa})_2 \cdot \text{H}_2\text{O}$), sodium hydroxide (NaOH), and sodium nitrite (NaNO_2) were purchased from Sigma-Aldrich. Lithium fluoride (LiF), sulfanilic acid (4- $(\text{H}_2\text{N})\text{C}_6\text{H}_4\text{SO}_3\text{H}$) were purchased from Alfa Aesar. Hydrochloric acid (HCl , 37%) was purchased from Merck. Titanium aluminum carbide (Ti_3AlC_2) was purchased from Beijing Forsman Scientific (China) and passed through a 400-mesh sieve.

In a typical procedure to prepare $\text{CoSn}(\text{OH})_6$ nanocubes, 3.506 g of $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ (10 mmol), 2.379 g of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (10 mmol) and 2.941 g of sodium citrate tribasic dihydrate (10 mmol) were successively added into 300 mL of deionized (DI) water under stirring.^{15-19, 30} 50 mL of 2 M NaOH was added dropwise into the above homogeneous solution over a period of 30 min. Subsequently, 20 mL of 8 M NaOH was poured into the mixture and kept under stirring for another 15 min. The resultant pink $\text{CoSn}(\text{OH})_6$ precipitate was retrieved, centrifuged and washed several times with DI water. The dried $\text{CoSn}(\text{OH})_6$ nanopowder was then annealed in air at 450 °C for 2 h with a heating rate of 2 °C min^{-1} to obtain $\text{SnO}_2 \cdot \text{Co}_3\text{O}_4$ nanocubes.

In a typical fluoride-based salt etchant synthesis of $\text{Ti}_3\text{C}_2\text{T}_x$, an etchant solution was first prepared by adding 3.2 g LiF to 40 mL of 9 M HCl in a polypropylene (PP) bottle, kept under continuous stirring.^{20, 21} After 5 min, 2.0 g of Ti_3AlC_2 was slowly added to the above etchant (9 M HCl /12 M LiF) over a period of 10 min to avoid localized overheating. The etching proceeded in a closed PP bottle (to avoid evaporation of water, i.e. change of etchant concentration) at room temperature for 24 h. The mixture of non-etched Ti_3AlC_2 and exfoliated $\text{Ti}_3\text{C}_2\text{T}_x$ was repeatedly washed with DI water to ~pH 6. The black $\text{Ti}_3\text{C}_2\text{T}_x$ slurry was then decanted from a greyish sediment mixture, containing both non-etched Ti_3AlC_2 and exfoliated $\text{Ti}_3\text{C}_2\text{T}_x$, and collected on a 0.22 μm polyvinylidene fluoride (PVDF) membrane via vacuum filtration. The exfoliated $\text{Ti}_3\text{C}_2\text{T}_x$ is termed as unmodified $\text{Ti}_3\text{C}_2\text{T}_x$.

To further increase the yield of delaminated $\text{Ti}_3\text{C}_2\text{T}_x$ from HCl/LiF -etched $\text{Ti}_3\text{C}_2\text{T}_x$, 1.8 g of the above exfoliated $\text{Ti}_3\text{C}_2\text{T}_x$ (unmodified) was dispersed in 60 mL DI water. A typical diazonium salt solution was prepared by dropwise addition of 36 mL cold (between 0 to 5 °C) solution with 4.8 g of NaNO_2 into a cold mixture containing 12.6 g of sulfanilic acid, 18 mL of concentrated HCl (37%) and 60 mL of DI water and was stirred for 30 min.³¹ The diazonium salt solution was added dropwise to Li^+ intercalated $\text{Ti}_3\text{C}_2\text{T}_x$ dispersion (60 mL), with the temperature (between 0 to 5 °C) and stirring of the mixture kept consistent for a further 4 h.²⁸ The resultant mixture was centrifuged at 4000 rpm for 5 min. The supernatant was discarded, and the sediment was washed with DI water and then centrifuged at 2000 rpm for 30 min. The black suspension was collected and washed via vacuum filtration, and then freeze-dried to obtain delaminated $\text{Ti}_3\text{C}_2\text{T}_x$ nanopowder. To study the effect of drying methods on modified $\text{Ti}_3\text{C}_2\text{T}_x$, sample of modified $\text{Ti}_3\text{C}_2\text{T}_x$ were divided into two portions and each distinctly dried by heating in a vacuum oven (at 80 °C, >12 h, and for simplicity will be labeled as vacuum-dry $\text{Ti}_3\text{C}_2\text{T}_x$) or freeze-drying procedure (first frozen by liquid nitrogen (N_2), followed by sublimation, and for simplicity will be labeled as freeze-dry $\text{Ti}_3\text{C}_2\text{T}_x$), respectively.

To assemble a 50 wt.% $\text{Ti}_3\text{C}_2\text{T}_x$ -50 wt.% $\text{SnO}_2\cdot\text{Co}_3\text{O}_4$ nanocomposite powder, 0.2 g of freeze-dry $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets and 0.2 g of $\text{SnO}_2\cdot\text{Co}_3\text{O}_4$ nanocubes were added to 60 mL of DI water, and maintained stirring for 30 min. This randomly mixed colloidal solution was almost instantaneously frozen by introduction of liquid N_2 , and then transferred and kept in an SRK Systemtechnik GmbH LYO GT2 freeze-dryer (ca. $< 2 \times 10^{-2}$ mbar) for at least 48 h. The water content, including those water molecules in between $\text{Ti}_3\text{C}_2\text{T}_x$ layers, was thoroughly removed via sublimation. The weight ratio of $\text{Ti}_3\text{C}_2\text{T}_x$ to $\text{SnO}_2\cdot\text{Co}_3\text{O}_4$ was systematically varied, i.e., 1:9, 2:8, 3:7, 4:6 in addition to the 5:5 set. The $\text{Ti}_3\text{C}_2\text{T}_x$ - $\text{SnO}_2\cdot\text{Co}_3\text{O}_4$ with different $\text{Ti}_3\text{C}_2\text{T}_x$ contents are correspondingly labeled $\text{Ti}_3\text{C}_2\text{T}_x$ - $\text{SnO}_2\cdot\text{Co}_3\text{O}_4$ (a: b), and (a: b) refers to the weight ratio of $\text{Ti}_3\text{C}_2\text{T}_x$ to $\text{SnO}_2\cdot\text{Co}_3\text{O}_4$.

6.3 Results and Discussion

6.3.1 Effect of Surface Modification and Drying Methods on Morphology and Surface Chemistry of HCl/LiF-etched $\text{Ti}_3\text{C}_2\text{T}_x$

To determine if the conversion of Ti_3AlC_2 to $\text{Ti}_3\text{C}_2\text{T}_x$ was successfully, X-ray diffraction (XRD) analysis of pristine Ti_3AlC_2 , unmodified $\text{Ti}_3\text{C}_2\text{T}_x$, vacuum-dry and freeze-dry samples of HCl/LiF-etched $\text{Ti}_3\text{C}_2\text{T}_x$ was conducted using a Shimadzu powder diffractometer with Cu K_α radiation ($\lambda = 1.5418 \text{ \AA}$), at $2\theta = 5\text{-}70^\circ$, with 0.02° step size and 2° min^{-1} scan rate. As evident in Figure 6.1 (a), the presence of remnant (00 l) peaks (basal planes) while all other Ti_3AlC_2 characteristic peaks have either significantly weakened or completely disappeared confirms that exfoliated $\text{Ti}_3\text{C}_2\text{T}_x$ has indeed been synthesized by the removal of Al, after immersing Ti_3AlC_2 in a 9 M HCl/12 M LiF etchant solution at room temperature for 24 h.^{20, 22, 32} In addition, the (002) peak notably shifts to lower 2θ value in both vacuum- (blue) (centered at 6.6°) and freeze-dry (orange) HCl/LiF-etched $\text{Ti}_3\text{C}_2\text{T}_x$ (centered at 6.8°) than unmodified $\text{Ti}_3\text{C}_2\text{T}_x$. This shift is indicative of the additional increase in distance between $\text{Ti}_3\text{C}_2\text{T}_x$ layers due to the surface modification with aryl diazonium salts and concomitant intercalation of water and Li^+ ions.^{28, 33} The leftward shift of the (00 l) peaks for freeze-dry $\text{Ti}_3\text{C}_2\text{T}_x$ is marginally less than that of vacuum-dry $\text{Ti}_3\text{C}_2\text{T}_x$, which is perhaps indicative of the more thorough removal of water via sublimation in the first and the presence of remnant water in the latter. The comparatively reduced intensity of (002) peak (at 6.8°) in freeze-dry HCl/LiF-etched $\text{Ti}_3\text{C}_2\text{T}_x$ than that of vacuum-dry HCl/LiF-etched $\text{Ti}_3\text{C}_2\text{T}_x$ (at 6.6°) suggests that solidification of intercalated water molecules can further increase c lattice parameter (interlayer distance) and reduce long-range order (periodicity) of the nanosheets (less restacking).³⁴ The absence of peaks from any supposedly unreacted Ti_3AlC_2 in unmodified, vacuum- and freeze-dry $\text{Ti}_3\text{C}_2\text{T}_x$ is a consequence of experimental procedure to decant the black $\text{Ti}_3\text{C}_2\text{T}_x$ slurry from the greyish sediment mixture, containing both non-etched Ti_3AlC_2 and exfoliated $\text{Ti}_3\text{C}_2\text{T}_x$.²⁰ It should not be mistaken as an almost 100 % yield of $\text{Ti}_3\text{C}_2\text{T}_x$ from the synthesis route with HCl/LiF etchant. Although there are no peaks corresponding to crystalline TiO_2 in the diffraction

patterns of unmodified and modified $\text{Ti}_3\text{C}_2\text{T}_x$ samples, further characterizations are to be conducted to ascertain $\text{Ti}_3\text{C}_2\text{T}_x$ is not oxidized (i.e. precipitating amorphous TiO_2) during synthesis nor drying in vacuum oven.

Morphological differences in precursory Ti_3AlC_2 , vacuum-dry and freeze-dry samples of HCl/LiF-etched $\text{Ti}_3\text{C}_2\text{T}_x$ were observed using field-emission scanning electron microscopy (FESEM), JEOL JSM-7600F at 5 kV in secondary electron imaging (SEI) mode. The FESEM image of commercially procured Ti_3AlC_2 , in Figure 6.1 (b), shows a compacted, layered structure, which is typical of a bulk layered ternary carbide, and lateral dimension distribution ranging from hundreds of nanometers to several micrometers.³⁵ The FESEM images of vacuum-dry $\text{Ti}_3\text{C}_2\text{T}_x$, in Figure 6.1 (c) and (d), indicate that the large lateral sheet sizes of the parent Ti_3AlC_2 has been retained, though with apparent gaps (due to removal of Al) between the restacked multi-layered $\text{Ti}_3\text{C}_2\text{T}_x$. The FESEM images of freeze-dry $\text{Ti}_3\text{C}_2\text{T}_x$, in Figure 6.1 (e) and (f), show a highly wrinkled three-dimensional (3D) “fluffy” network of exfoliated nanosheets. This result corroborates well with earlier XRD observation, as well as literature, that the freeze-drying process (solidification of water and subsequent removal by sublimation) may be an effective approach to ameliorate the pronounced restacking of delaminated $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets.^{34, 36}

A typical transmission electron microscopy (TEM) image of freeze-dry $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets is presented in Figure 6.2 (a). Laterally large and crumpled nanosheets of freeze-dry $\text{Ti}_3\text{C}_2\text{T}_x$ are expectedly observed, and the almost transparent edges of these wrinkled nanosheets reiterate their ultrathin nature. The first substantial evidence of successful grafting of functional groups, containing sulfur (S) onto the surface of freeze-dry $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets is revealed by the corresponding energy-dispersive X-ray spectroscopy (EDS) elemental mapping as shown in Figure 6.2 (b-f). Beyond the anticipated and uniform distribution of Ti, C, O, and F, which is indicative of the presence of surface-terminating functional groups on freeze-dry $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets, S signal (in Figure 6.2 (e)) is also detected and this suggests that additional S-containing groups have indeed been grafted.

Figure 6. 1 (a) XRD patterns of precursory Ti_3AlC_2 , unmodified, vacuum- and freeze-dry HCl/LiF-etched $\text{Ti}_3\text{C}_2\text{T}_x$. FESEM images of (b) bulk Ti_3AlC_2 at low magnification, (c-d) vacuum-dry HCl/LiF-etched $\text{Ti}_3\text{C}_2\text{T}_x$ at low magnification and high magnification (area enclosed by blue dotted box in (c)), respectively, (e-f) freeze-dry HCl/LiF-etched $\text{Ti}_3\text{C}_2\text{T}_x$ at low magnification and high magnification (area enclosed by orange dotted box in (e)), respectively.

Figure 6. 2 (a) Low resolution TEM image of the laterally large and wrinkled architecture made up of freeze-dry HCl/LiF-etched $\text{Ti}_3\text{C}_2\text{T}_x$ (surface modified) nanosheets, and the corresponding EDS mapping of (b) Ti, (c) C, (d) O, (e) S and (f) F.

To further characterize the surface chemistry and redox states of species in unmodified, vacuum- and freeze-dry samples of HCl/LiF-etched $\text{Ti}_3\text{C}_2\text{T}_x$, X-ray photoelectron spectroscopy (XPS) was conducted. The binding energies in the XPS spectra are calibrated

with the C 1s photoelectron peak at 284.8 eV as reference. In Figure 6.3 (a), the XPS survey spectra show three characteristic peaks at approximately 531.6, 457.8, and 285.0 eV, corresponding to oxygen 1s (O 1s), titanium 2p (Ti 2p), and carbon 1s (C 1s), respectively. There is an additional characteristic peak at 168 eV, corresponding to sulfur 2p (S 2p), in both vacuum- and freeze-dry HCl/LiF-etched $\text{Ti}_3\text{C}_2\text{T}_x$, which reaffirms successful grafting of S-containing functional groups on the surface of modified (vacuum- and freeze-dry) $\text{Ti}_3\text{C}_2\text{T}_x$.³⁷ The high-resolution XPS spectra of S 2p, in Figure 6.3 (b), can be deconvoluted into two components, centered at 167.8 and 169.0 eV (characteristic energy gap of 1.2 eV between the S 2p core-level peaks), for contribution from S 2p_{3/2} and S 2p_{1/2}, respectively.³⁶ Concurring with the absence of nitrogen 1s (N 1s) signal (presumably liberated as nitrogen gas (N_2)), the reaction between the diazonium salt solution and HCl/LiF-etched $\text{Ti}_3\text{C}_2\text{T}_x$ has most probably grafted phenylsulfonic acid (*p*-phenyl- SO_3H) groups onto the MXene's surface. The reaction mechanism is postulated to first proceed with the formation of reactive aryl radicals via acceptance of e^- (from $\text{Ti}_3\text{C}_2\text{T}_x$) by aryl diazonium salts, which also liberates N_2 in the process. Subsequently, to regain stability (chemical state), the aryl radicals are inclined to favorably couple with the surfaces of nearby $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets.^{36,}

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The Ti 2p XPS spectrum of vacuum- and freeze-dry $\text{Ti}_3\text{C}_2\text{T}_x$ in Figure 6.3 (c) and (d), respectively, reveals the difference in the position of Ti characteristic peaks. Both are almost identical in which there are peaks that can be attributed to Ti-C, Ti^{2+} , and Ti^{3+} , and this agrees well with the literature.³⁹⁻⁴¹ However, for vacuum-dry $\text{Ti}_3\text{C}_2\text{T}_x$ in Figure 6.3 (c), there are deconvoluted peaks at 464.7 and 459.0 eV, which are related to Ti-O, and their relatively high intensity of the peaks seemingly suggests contributions from TiO_2 sp³ and sp¹, respectively, in addition to Ti-O on the surface (surface-terminating functional groups). This points toward the probable occurrence of mild oxidation in $\text{Ti}_3\text{C}_2\text{T}_x$ and associated precipitation of amorphous TiO_2 , even though extended period of heating under vacuum to dry $\text{Ti}_3\text{C}_2\text{T}_x$ has been an integral part of the fabrication procedure in the literature.^{20, 21, 29,}

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Raman spectra of unmodified, vacuum- and freeze-dry samples of HCl/LiF-etched $\text{Ti}_3\text{C}_2\text{T}_x$, are shown in Figure 6.3 (e). All three samples routinely exhibit bands at approximately 200 and 400 cm^{-1} , which corroborates well with characteristic bands of $\text{Ti}_3\text{C}_2\text{T}_x$.³⁴ Compared with unmodified and freeze-dry $\text{Ti}_3\text{C}_2\text{T}_x$ (both are not exposed to heating but by freeze-drying), there is a characteristic peak of TiO_2 at 153 cm^{-1} observed in the Raman spectrum of vacuum-dry $\text{Ti}_3\text{C}_2\text{T}_x$.⁴³ This shows that a simple freeze-drying process can proceed with removal of water but avoid the oxidation of $\text{Ti}_3\text{C}_2\text{T}_x$, which is consistent with earlier characterizations by XRD, FESEM, and XPS. Conversely, although there are no peaks matching crystalline TiO_2 (e.g. at 25° and 44° for anatase phase) in the XRD patterns of vacuum-dry $\text{Ti}_3\text{C}_2\text{T}_x$, both XPS and Raman spectrum reveal presence of TiO_2 (probably amorphous) and the inadequacy of vacuum-drying (concomitant mild oxidation due to prolong exposure to heat) for preparing samples of $\text{Ti}_3\text{C}_2\text{T}_x$.

Fourier transform infrared (FTIR) spectroscopy was conducted to evaluate the changes (if any) in chemical structures after surface modification of $\text{Ti}_3\text{C}_2\text{T}_x$ with aryl diazonium salts. FTIR spectra of the unmodified, vacuum- and freeze-dry $\text{Ti}_3\text{C}_2\text{T}_x$ were recorded in a matrix of potassium bromide (KBr) using a PerkinElmer Frontier infrared spectrometer, and as plotted in Figure 6.2 (f). As compared to unmodified $\text{Ti}_3\text{C}_2\text{T}_x$, the presence of S=O bonds is evident in both vacuum- and freeze-dry $\text{Ti}_3\text{C}_2\text{T}_x$ due to the two characteristic bands at 1125 and 1086 cm^{-1} , and this may be indicative that $-\text{SO}_3\text{H}$ groups were successfully grafted onto the surface of $\text{Ti}_3\text{C}_2\text{T}_x$.^{37, 44, 45} Furthermore, there are another three characteristic bands at 1037, 1159 and 1007 cm^{-1} (but absent in the FTIR spectra of unmodified $\text{Ti}_3\text{C}_2\text{T}_x$), corresponding to S-phenyl and C-H bonds, respectively, which confirms that the actual functional groups grafted are, in fact, *p*-phenyl- SO_3H groups.^{44, 46}

The specific surface areas of unmodified, vacuum- and freeze-dry samples of HCl/LiF-etched $\text{Ti}_3\text{C}_2\text{T}_x$ were further investigated by N_2 adsorption/desorption measurements. As determined by the Brunauer-Emmett-Teller (BET) method, unmodified, freeze- and vacuum-dry $\text{Ti}_3\text{C}_2\text{T}_x$ has surface area of 62.77, 65.83, and 5.27 $\text{m}^2 \text{g}^{-1}$, respectively.⁴⁷ Compared with the vacuum-dry $\text{Ti}_3\text{C}_2\text{T}_x$ sample, the high surface areas of unmodified and freeze-dry $\text{Ti}_3\text{C}_2\text{T}_x$ suggest that a simple freeze-drying procedure can effectively maintain

the “fluffy” microstructure and minimize the restacking of delaminated and crumpled $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets. Consequently, the more opened architectures of unmodified and freeze-dry $\text{Ti}_3\text{C}_2\text{T}_x$ can provide more accessible surfaces for adsorption of Li^+ ions and infiltration of the electrolyte, which are favorable for Li^+ storage performance.³⁴ On the contrary, drying $\text{Ti}_3\text{C}_2\text{T}_x$ at elevated temperature even under vacuum, has been shown to result in mild oxidation and adversely strong bonding between the layers, which are detrimental to the electrical conductivity and redispersion (during subsequent processing), respectively.

Figure 6. 3 XPS (a) survey of unmodified, vacuum- and freeze-dry HCl/LiF-etched $\text{Ti}_3\text{C}_2\text{T}_x$, (b) S 2p spectra of freeze-dry HCl/LiF-etched $\text{Ti}_3\text{C}_2\text{T}_x$, Ti 2p spectra of (c) vacuum-dry HCl/LiF-etched

Ti₃C₂T_x and (d) freeze-dry HCl/LiF-etched Ti₃C₂T_x, respectively. (e) Raman spectra and (f) FTIR spectra of unmodified, vacuum- and freeze-dry HCl/LiF-etched Ti₃C₂T_x.

Zeta potential measurements of unmodified and freeze-dry Ti₃C₂T_x (modified), and SnO₂·Co₃O₄ nanocubes were conducted using Horiba Nano Particle Analyzer SZ-100. The zeta potential of freeze-dry Ti₃C₂T_x was measured to be -32.1 mV when dispersed in DI water (pH ~ 7.0). Comparatively, dispersion of unmodified Ti₃C₂T_x recorded a zeta potential of -23.2 mV under similar conditions. This suggests that grafting *p*-phenyl-SO₃H groups on the surface of Ti₃C₂T_x (freeze-dry Ti₃C₂T_x) can improve its dispersibility in water (> -30 mV, implies strong electrostatic repulsion between Ti₃C₂T_x nanosheets).⁴⁸

6.3.2 Effect of Surface Modification (grafting of *p*-phenyl-SO₃H groups) and Drying Methods (extent of restacking) on Electrochemical Performance of HCl/LiF-etched Ti₃C₂T_x

The impact of grafting *p*-phenyl-SO₃H groups on Ti₃C₂T_x's surface and extent of restacking of delaminated Ti₃C₂T_x nanosheets was evaluated through cyclic voltammetry (CV) and galvanostatic charge discharge (GCD) method. As shown in Figure 6.4 (a), the 1st and 2nd CV curves of unmodified (purple), vacuum- (blue) and freeze-dry (orange) HCl-LiF-etched Ti₃C₂T_x, at scan rate of 0.1 mV s⁻¹, show quasi-rectangular shapes with no obvious redox peaks, which is typical of pseudocapacitive behavior as reported in earlier literatures.^{10, 25, 49-51} Additionally, the enclosed area by the CV curves (directly correlated to Li⁺ storage capacity) can be arranged in the following descending order, freeze-dry Ti₃C₂T_x > unmodified Ti₃C₂T_x > vacuum-dry Ti₃C₂T_x. The comparatively reduced area/capacity of vacuum-dry Ti₃C₂T_x (although grafted with *p*-phenyl-SO₃H groups) is most probably consequential of the compact stacking (restacking) of delaminated Ti₃C₂T_x nanosheets (evidently low SSA of 5.27 m² g⁻¹), which detrimentally limits the diffusion of electrolyte into layered Ti₃C₂T_x electrode as well as available surfaces for capacitive storage of Li⁺ ions. Conversely, by a combination of freeze-drying and surface grafting of *p*-phenyl-SO₃H groups, freeze-dry Ti₃C₂T_x (marginally highest SSA of 65.83 m² g⁻¹) exhibits the highest capacity amongst the three evaluated samples. This can be explained

by the propensity of delaminated $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets (with high surface area/energy) to restack (thus it may be insufficient to only incorporate freeze-drying procedure as exemplified by the unmodified $\text{Ti}_3\text{C}_2\text{T}_x$ (SSA of $62.77 \text{ m}^2 \text{ g}^{-1}$)) and the additional presence of *p*-phenyl- SO_3H groups on the surface helps to separate the stacked $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets. The enclosed area of the CV curves (2nd cycle) is noticeably smaller than that of initial cycle, and the reduction in area (loss in capacity) is significantly larger for samples with high SSA. This irreversible capacity loss may be attributed to the solid-electrolyte interphase layer (SEI) formation as well as parasitic side reactions.^{12, 52, 53} The abovementioned shows both the limitation and benefit to having a large active area for electrode material in LIBs.

The resemblance of capacitive/non-faradic behavior of $\text{Ti}_3\text{C}_2\text{T}_x$ is representatively illustrated by GCD profile of freeze-dry $\text{Ti}_3\text{C}_2\text{T}_x$ in Figure 6.4 (b), in which no apparent plateau region is observed, suggesting fast electron and ion transport.²⁹ The initial discharge capacity of freeze-dry $\text{Ti}_3\text{C}_2\text{T}_x$ was measured to be 405 mAh g^{-1} but with a lowly initial Coulombic efficiency (C.E.) of 45.3 %. This reiterates the drawback of concomitant severe side reactions with large active area of delaminated $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets. The C.E. for subsequent cycles was maintained between 97 to 99 %, which is indicative of the highly stable SEI layer formed, and understandably so as there is minimal structural degradation/variation for pseudocapacitive electrode material. The cyclic performance (at 0.1 A g^{-1} current density and voltage window between 0.005 to 3.0 V) of unmodified, vacuum- and freeze-dry HCl-LiF-etched $\text{Ti}_3\text{C}_2\text{T}_x$ is as plotted in Figure 6.4 (c). The retained reversible capacity of unmodified, vacuum- and freeze-dry $\text{Ti}_3\text{C}_2\text{T}_x$ at the end of 100 cycles is 103, 50, and 140 mAh g^{-1} , respectively. This divergence in electrochemical performance could be reasonably ascribed to the different morphologies and surface chemistries as previously discussed. It is noted that the retained discharge capacity of freeze-dry $\text{Ti}_3\text{C}_2\text{T}_x$ (non-freestanding) is evidently lower than its freestanding counterparts,²⁵ but comparable to those similarly prepared and evaluated via slurry casting.⁵⁴ The electrochemical impedance spectroscopy (EIS) results for the above-mentioned samples are presented as Nyquist plots in Figure 6.4 (d). As inferred from

diameter of the semicircle in the high frequency region, both unmodified and freeze-dry $\text{Ti}_3\text{C}_2\text{T}_x$ demonstrate lower charge transfer resistance at 140 and 125 Ω , respectively, than the mildly oxidized but severely restacked vacuum-dry $\text{Ti}_3\text{C}_2\text{T}_x$ (160 Ω). This corroborates well with morphological and cyclic performance evaluation and reiterates that the tendency to restack and restacking of delaminated $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets are indeed detrimental to electrochemical performance.

Figure 6. 4 (a) Cyclic voltammograms (1st and 2nd cycle) of unmodified (purple), vacuum- (blue) and freeze-dry (orange) HCl/LiF-etched $\text{Ti}_3\text{C}_2\text{T}_x$ at a scan rate of 0.1 $\text{mV}\cdot\text{s}^{-1}$. (b) Galvanostatic discharge/charge profile of freeze-dry $\text{Ti}_3\text{C}_2\text{T}_x$ at current density of 100 mA g^{-1} . (c) Cycling performance and Coulombic efficiency of unmodified, vacuum- and freeze-dry HCl/LiF-etched $\text{Ti}_3\text{C}_2\text{T}_x$ between 0.005 and 3.0 V at current density of 100 mA g^{-1} . (d) Electrochemical impedance spectra (EIS) of unmodified, vacuum- and freeze-dry HCl/LiF-etched $\text{Ti}_3\text{C}_2\text{T}_x$ after 100th cycle at the amplitude of 10 mV over frequency range from 100 kHz to 10 mHz.

Interestingly, a seemingly trivial change of method, for removal of solvent/water during processing of HCl-LiF-etched $\text{Ti}_3\text{C}_2\text{T}_x$ from vacuum-drying to freeze-drying, has been

shown to have substantial influence on the architecture (less restacking) and electrochemical performance (almost doubled). Mild oxidation and undesirable restacking of delaminated $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets may simply be avoided by adopting a freeze-drying procedure instead of vacuum-drying for removal of solvent(s). Coupled with grafting *p*-phenyl- SO_3H , freeze-dry HCl-LiF-etched $\text{Ti}_3\text{C}_2\text{T}_x$ (non-freestanding) retained a stable reversible capacity of 140 mAh g^{-1} , however its inherently moderate gravimetric capacity necessitates combination with at least one other high capacity material (such as TMOs) to have competitive overall capacity for application in high energy density LIBs anode.

6.3.3 Physical Characterization of $\text{CoSn}(\text{OH})_6$, $\text{SnO}_2 \cdot \text{Co}_3\text{O}_4$, and $\text{Ti}_3\text{C}_2\text{T}_x\text{-SnO}_2 \cdot \text{Co}_3\text{O}_4$ (5:5) Nanocomposite

Figure 6.5 (a) shows the XRD patterns of freeze-dry HCl/LiF-etched $\text{Ti}_3\text{C}_2\text{T}_x$ (grafted with grafting *p*-phenyl- SO_3H) nanosheets, intermediary $\text{CoSn}(\text{OH})_6$, annealed $\text{CoSn}(\text{OH})_6$ (held isothermally at 450°C , in air), and $\text{Ti}_3\text{C}_2\text{T}_x\text{-SnO}_2 \cdot \text{Co}_3\text{O}_4$ (5:5) hybrid. Correspondingly, all the peaks can be well indexed to $\text{Ti}_3\text{C}_2\text{T}_x$, $\text{CoSn}(\text{OH})_6$ (JCPDS 13-0356), tetragonal rutile SnO_2 (JCPDS 41-1445) and cubic Co_3O_4 (JCPDS 43-1003), respectively. This reveals that the thermal treatment, in air rather than inert atmosphere, converts $\text{CoSn}(\text{OH})_6$ nanocubes into a combination of SnO_2 and Co_3O_4 .

The FESEM images of $\text{CoSn}(\text{OH})_6$, $\text{SnO}_2 \cdot \text{Co}_3\text{O}_4$, and $\text{Ti}_3\text{C}_2\text{T}_x\text{-SnO}_2 \cdot \text{Co}_3\text{O}_4$ (5:5) nanocomposite are as shown in Figure 6.5 (b), (c), and (e), respectively. As observed in Figure 6.5 (b), the as-synthesized $\text{CoSn}(\text{OH})_6$ has cubic morphology with edge length about 70-100 nm. Figure 6.5 (c) indicates the inheriting of the cubic morphology from precursory $\text{CoSn}(\text{OH})_6$ by the $\text{SnO}_2 \cdot \text{Co}_3\text{O}_4$ mixture albeit some rounding of the edges. The preservation of the cubic morphology is due to the surface passivation of the $\text{CoSn}(\text{OH})_6$ nanocubes by Co (III) species formed from thermodynamically favorable oxidation of $[\text{Co}(\text{OH})_4]^{2-}$ complex in air.¹⁵ Moreover, the relatively more smooth corners for the $\text{SnO}_2 \cdot \text{Co}_3\text{O}_4$ nanocubes are probably due to phase segregation during concomitant dehydration of $\text{CoSn}(\text{OH})_6$ and the formation of SnO_2 and Co_3O_4 .¹⁶ The corresponding

TEM image of the $\text{SnO}_2\cdot\text{Co}_3\text{O}_4$ mixture, in Figure 6.5 (d), further reveals that the $\text{SnO}_2\cdot\text{Co}_3\text{O}_4$ nanocubes are, in fact, rough and porous. This agrees well with the formation of porous precursory $\text{CoSn}(\text{OH})_6$ nanocubes by sequential alkaline etching after fast stoichiometric co-precipitation of Sn^{4+} , Co^{2+} and OH^- in aqueous solution under ambient conditions.^{15, 16, 32}

The FESEM image of $\text{Ti}_3\text{C}_2\text{T}_x\text{-SnO}_2\cdot\text{Co}_3\text{O}_4$ (5:5) nanocomposite is as depicted in Figure 6.5 (e). The $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets are paralleled, with bare $\text{SnO}_2\cdot\text{Co}_3\text{O}_4$ nanocubes slotted in between the layers. The preserved morphologies (in both shapes and sizes) of $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets (although wrinkled) and $\text{SnO}_2\cdot\text{Co}_3\text{O}_4$ nanocubes are indicative that exposure to liquid N_2 (extreme low temperature) does not fragment either constituents. More importantly, it demonstrates the suitability of instantaneous freezing (albeit thermal stress) both $\text{Ti}_3\text{C}_2\text{T}_x$ and $\text{SnO}_2\cdot\text{Co}_3\text{O}_4$ by introducing a cryogenic fluid. It also reiterates the necessity for cryogenic freezing, instead of slow freezing, because probable segregation (undesirable) due to different dispersibility of components in solvent (water) has evidently been avoided. This observation is further supported by TEM imaging of the $\text{Ti}_3\text{C}_2\text{T}_x\text{-SnO}_2\cdot\text{Co}_3\text{O}_4$ (5:5) nanocomposite, as shown in Figure 6.5 (f). Dissimilar from observed nonuniformity in previously reported $\text{Ti}_3\text{C}_2\text{T}_x/\text{TMO}$ hybrids and unresolved difficulty in directing homogeneous distribution of TMOs,¹⁰ the $\text{Ti}_3\text{C}_2\text{T}_x\text{-SnO}_2\cdot\text{Co}_3\text{O}_4$ (5:5) prepared by freeze-drying procedure shows that numerous $\text{SnO}_2\cdot\text{Co}_3\text{O}_4$ nanocubes are uniformly distributed across the surface of a $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheet. This unprecedented homogeneity in the distribution of $\text{SnO}_2\cdot\text{Co}_3\text{O}_4$ nanocubes in between the $\text{Ti}_3\text{C}_2\text{T}_x$ layers dispels the preconception that processing a homogeneously mixed aqueous suspension of $\text{Ti}_3\text{C}_2\text{T}_x$ and TMOs, instead of layer-by-layer procedure, can only lead to randomly mixed $\text{Ti}_3\text{C}_2\text{T}_x/\text{TMO}$. It is also to be noted that this one-step assembly of $\text{Ti}_3\text{C}_2\text{T}_x\text{-SnO}_2\cdot\text{Co}_3\text{O}_4$ heterostructure by freeze-drying is both cost-efficient and industrially compatible.

A typical transmission electron microscopy (TEM) image of $\text{Ti}_3\text{C}_2\text{T}_x\text{-SnO}_2\cdot\text{Co}_3\text{O}_4$ (5:5) is presented in Figure 6.6 (a), which shows minimal overlapping of $\text{SnO}_2\cdot\text{Co}_3\text{O}_4$ nanocubes across the $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheet. The coexistence of $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets and $\text{SnO}_2\cdot\text{Co}_3\text{O}_4$

nanocubes is evident in EDS elemental mapping as shown in Figure 6.6 (b-f). The homogeneous distribution of Sn, Co and O elements within a nanocube is also confirmed by Figure 6.6 (b, c and f), illustrating the proximity of SnO_2 and Co_3O_4 (an advantage of the chemical co-precipitation route chosen) which is not achievable by mere mechanical mixing of heterogeneous powders.

Figure 6. 5 (a) XRD patterns of freeze-dry HCl/LiF-etched $\text{Ti}_3\text{C}_2\text{T}_x$ (grafted with *p*-phenyl- SO_3H), intermediary $\text{CoSn}(\text{OH})_6$, $\text{SnO}_2 \cdot \text{Co}_3\text{O}_4$, and $\text{Ti}_3\text{C}_2\text{T}_x\text{-SnO}_2 \cdot \text{Co}_3\text{O}_4$ (5:5). (☆: $\text{Ti}_3\text{C}_2\text{T}_x$, #: Co_3O_4 , ◇: SnO_2). FESEM images of (b) intermediary $\text{CoSn}(\text{OH})_6$, (c) $\text{SnO}_2 \cdot \text{Co}_3\text{O}_4$ nanocubes, both at 30

000 x magnification. (d) TEM image of $\text{SnO}_2 \cdot \text{Co}_3\text{O}_4$ nanocubes, revealing its porous nature. (e) FESEM image of the $\text{Ti}_3\text{C}_2\text{T}_x\text{-SnO}_2 \cdot \text{Co}_3\text{O}_4$ (5:5) nanocomposite, showing $\text{SnO}_2 \cdot \text{Co}_3\text{O}_4$ nanocubes embedded between $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheet layers. (f) TEM image of $\text{Ti}_3\text{C}_2\text{T}_x\text{-SnO}_2 \cdot \text{Co}_3\text{O}_4$ (5:5), indicating $\text{SnO}_2 \cdot \text{Co}_3\text{O}_4$ nanocubes are uniformly distributed across the surface of $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheet.

Figure 6. 6 (a) Low resolution TEM image of the $\text{Ti}_3\text{C}_2\text{T}_x\text{-SnO}_2 \cdot \text{Co}_3\text{O}_4$ (5:5) hybrid, and the corresponding EDS mapping of (b) Sn, (c) Co, (d) Ti, (e) C and (f) O.

To further characterize the redox states of species and elemental composition in $\text{Ti}_3\text{C}_2\text{T}_x\text{-SnO}_2\cdot\text{Co}_3\text{O}_4$ (5:5) nanocomposite, XPS analyses were conducted. The Ti 2p XPS spectrum of the $\text{Ti}_3\text{C}_2\text{T}_x\text{-SnO}_2\cdot\text{Co}_3\text{O}_4$ (5:5) nanocomposite (Figure A5 in Appendix) is almost identical to that of freeze-dry $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets in Figure 6.3 (d)) with deconvoluted peaks which can be ascribed to Ti-C, Ti^{2+} , and Ti^{3+} . The Sn 3d XPS spectrum of $\text{Ti}_3\text{C}_2\text{T}_x\text{-SnO}_2\cdot\text{Co}_3\text{O}_4$ (5:5) is as plotted in Figure 6.7 (a), with two peaks at 495.2 and 486.7 eV, corresponding to the Sn 3d_{3/2} and 3d_{5/2} orbitals, respectively. Although the gap between the Sn 3d core-level peaks is 8.5 eV, which is typical of standard SnO_2 spectrum, it is apparent that the Sn species present are not exclusively Sn^{4+} . The deconvolution of each of the Sn 3d core-level peaks shows two sets of peaks, suggesting the presence of oxygen vacancies and Sn in a lower oxidation state (Sn^{2+}).⁵⁵ This variance in the SnO_2 component is likely consequential of the relatively low calcination/dehydration temperature (450 °C) in the synthesis procedure and the presence of Co species (Co_3O_4 are formed first at ca. 300 °C) in the atomic mixed $\text{CoSn}(\text{OH})_6$ precursor. Figure 6.7 (b) shows the high-resolution spectra of the Co 2p, which has two spin-orbit doublets, at 781.8 and 797.4 eV, attributed to the Co 2p_{3/2} and Co 2p_{1/2} orbitals and two shakeup satellites eV.^{56, 57} The gap between the Co 2p core-level peaks is 15.6 eV, which is typical of standard Co_3O_4 spectrum and this implies that the Co species are in the form of Co_3O_4 without any aberrations (unlike SnO_2 , 450 °C is a sufficiently high temperature to dehydrate Co complex, form Co_3O_4 phase, and anneal to remove defects).^{58, 59} Figure 6.7 (c) presents the high-resolution spectra of the O 1s, with a third peak at 530.4 eV, corresponding to the characteristic metal-oxygen bonds in SnO_2 and Co_3O_4 crystal lattices in addition to peaks at 531.8 and 533.3 eV, which can be attributed to surface-terminating groups, such as $-\text{O}_x$ and $(-\text{OH})_x$, respectively. In addition, the normalized elemental composition (at.%) between Sn and Co of the porous $\text{SnO}_2\cdot\text{Co}_3\text{O}_4$ nanocube constituent is revealed to be 54.9:45.1, which signifies a slight deviation (due to etching) from the initial stoichiometry (1:1) of the precursory $\text{CoSn}(\text{OH})_6$ nanocubes. This insight leads to an estimated and adjusted ratio of 3.66 mole SnO_2 to 1 mole Co_3O_4 in the final product (porous $\text{SnO}_2\cdot\text{Co}_3\text{O}_4$ nanocubes). Subsequently, the compositional breakdown of the $\text{Ti}_3\text{C}_2\text{T}_x\text{-SnO}_2\cdot\text{Co}_3\text{O}_4$ (5:5) nanocomposite is derived to be 50.0 wt.% $\text{Ti}_3\text{C}_2\text{T}_x$, 34.8 wt.% SnO_2 , and 15.2 wt.% Co_3O_4 .

The microstructure and specific surface area (SSA) of freeze-dry $\text{Ti}_3\text{C}_2\text{T}_x$, $\text{SnO}_2\cdot\text{Co}_3\text{O}_4$ nanocubes and $\text{Ti}_3\text{C}_2\text{T}_x\text{-SnO}_2\cdot\text{Co}_3\text{O}_4$ (5:5) nanocomposite were further investigated by using N_2 adsorption/desorption method and derived by Brunauer-Emmett-Teller (BET) equation. As seen in Figure 6.7 (d), all the three N_2 adsorption/desorption isotherms exhibits typical type IV behavior (suggestive of mesoporous nature) with significant hysteresis characteristics only observed at high relative pressure (0.5-1.0).⁶⁰ Coupled with the slit-shaped pores associated type H3 hysteresis loop and a SSA of $62.77 \text{ m}^2 \text{ g}^{-1}$, it is evident that porous freeze-dry $\text{Ti}_3\text{C}_2\text{T}_x$ is highly delaminated with minimal restacking. The isotherms of the porous $\text{SnO}_2\cdot\text{Co}_3\text{O}_4$ nanocubes, in contrast, are accompanied by a type H4 hysteresis loop and recorded a high SSA of $114.69 \text{ m}^2 \text{ g}^{-1}$. This agrees well with the high porosity of $\text{SnO}_2\cdot\text{Co}_3\text{O}_4$ nanocubes as observed in TEM imaging (Figure 6.5 (d)). Interestingly, the $\text{Ti}_3\text{C}_2\text{T}_x\text{-SnO}_2\cdot\text{Co}_3\text{O}_4$ (5:5) nanocomposite has an SSA of $42.53 \text{ m}^2 \text{ g}^{-1}$, lower than either of the constituents alone, which may be suggestive of the porous $\text{SnO}_2\cdot\text{Co}_3\text{O}_4$ nanocubes entrapped in crumpled $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets instead of existing as a mere mixture of the two components.

Figure 6. 7 XPS (a) Sn 3d spectra, (b) Co 2p spectra, and (c) O 1s spectra of $\text{Ti}_3\text{C}_2\text{T}_x\text{-SnO}_2\cdot\text{Co}_3\text{O}_4$ (5:5) hybrid. (d) N_2 adsorption-desorption isotherms of freeze-dry $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets (in black), $\text{SnO}_2\cdot\text{Co}_3\text{O}_4$ nanocubes (in blue) and $\text{Ti}_3\text{C}_2\text{T}_x\text{-SnO}_2\cdot\text{Co}_3\text{O}_4$ (5:5) hybrid (in orange).

6.3.4 Electrochemical Evaluation of Surface-Modified $\text{Ti}_3\text{C}_2\text{T}_x$, $\text{SnO}_2\cdot\text{Co}_3\text{O}_4$ Nanocubes, and $\text{Ti}_3\text{C}_2\text{T}_x\text{-SnO}_2\cdot\text{Co}_3\text{O}_4$ (5:5) Nanocomposite

The electrochemical performances of the fabricated $\text{Ti}_3\text{C}_2\text{T}_x\text{-SnO}_2\cdot\text{Co}_3\text{O}_4$ (5:5) nanocomposite and its constituents were evaluated. Figure 6.8 (a) shows the CV curves of $\text{Ti}_3\text{C}_2\text{T}_x\text{-SnO}_2\cdot\text{Co}_3\text{O}_4$ (5:5) nanocomposite at scan rate 0.1 mV s^{-1} within a potential window of 0.005 to 3.0 V. In the first cycle, a broad cathodic peak (from around 1.50 V to 0.25 V) envelops peaks corresponding to the reduction of Co_3O_4 ^{61, 62} and SnO_2 ^{63, 64} into Co and Sn, respectively, the accompanying formation of Li_2O , and the decomposition of electrolyte and formation of SEI.⁶⁵ There is another broad peak at $< 0.25 \text{ V}$ which

encompasses the formation of $\text{Li}_{4.4}\text{Sn}$ through the multi-step alloying reaction between Li^+ and Sn .⁶⁶ Its corresponding broad anodic peak for the dealloying (oxidation) of $\text{Li}_{4.4}\text{Sn}$ can be seen at around 0.67 V. The oxidation peak of Sn to SnO_2 is observed at 1.05 V, indicative of the reversibility of the SnO_2 conversion reaction.^{63, 64} The matching oxidation peak of Co to Co_3O_4 can be assigned to the first cycle anodic peak at 2.10 V. Consistent with previous observation of CV curves of freeze-dry $\text{Ti}_3\text{C}_2\text{T}_x$ (an intrinsic pseudocapacitive material), there are no obvious peaks related to the MXene component.

The most obvious difference between the initial and subsequent cycles' CV curves is the disappearance of the broad cathodic peak (from around 1.50 V to 0.25 V) which includes the one-off and irreversible SEI formation and side reactions. These features are similarly present in the CV curves of the bare $\text{SnO}_2\cdot\text{Co}_3\text{O}_4$ nanocubes (Figure A6 (a) in Appendix). In comparison, most of the redox peaks of subsequent cycles in $\text{Ti}_3\text{C}_2\text{T}_x\text{-SnO}_2\cdot\text{Co}_3\text{O}_4$ (5:5) shift towards lower overpotential (but this was not observed in the bare $\text{SnO}_2\cdot\text{Co}_3\text{O}_4$ nanocubes), which suggests the multiple compositional effect of $\text{SnO}_2\cdot\text{Co}_3\text{O}_4$ and structural entrapping of $\text{SnO}_2\cdot\text{Co}_3\text{O}_4$ nanocubes in $\text{Ti}_3\text{C}_2\text{T}_x$ layers have favorably improved overall electronic conductivity and reaction kinetics. More importantly, the peak corresponding to the anodic process, in which Sn converts back to SnO_2 (conversion reaction), remains prominently visible at 1.30 V even after 5 cycles (with no obvious decrease in peak size), demonstrates the beneficial effect of compositional and structural design in maintaining stable and reversible conversion of SnO_2 , which contributes largely to overall Li^+ ions storage capacity. The superimposable CV curves of the subsequent cycles prove the excellent reversibility of $\text{Ti}_3\text{C}_2\text{T}_x\text{-SnO}_2\cdot\text{Co}_3\text{O}_4$ (5:5) anode for Li^+ ions storage.

The redox peaks in the CV curves correspond well to the plateaus in the galvanostatic charge-discharge (GSD) profiles of the $\text{Ti}_3\text{C}_2\text{T}_x\text{-SnO}_2\cdot\text{Co}_3\text{O}_4$ (5:5) nanocomposite, as shown in Figure 6.8 (b), and is distinctly different to that of freeze-dry $\text{Ti}_3\text{C}_2\text{T}_x$ (no plateaus). These distinct features, at different potential regions, represent the alloying and conversion processes, typical of SnO_2 and Co_3O_4 , and are similarly present and more obvious for the GSD profiles of $\text{SnO}_2\cdot\text{Co}_3\text{O}_4$ nanocubes (Figure A6 (b) in Appendix). The

initial discharge and charge capacities for the $\text{Ti}_3\text{C}_2\text{T}_x\text{-SnO}_2\cdot\text{Co}_3\text{O}_4$ (5:5) nanocomposite are 1374 and 845 mAh g^{-1} , respectively. The corresponding initial Coulombic efficiency (C.E.) is derived to be a lowly 61.5 %, though the loss of reversible capacity corroborates well with the large contribution by SEI formation as reflected in the first cycle CV curve. The C.E. for the subsequent cycles are maintained between 97 to 99 %, indicative of the high stability of the SEI formed. Near perfect overlapping of the 2nd and 200th cycle GSD profiles of the $\text{Ti}_3\text{C}_2\text{T}_x\text{-SnO}_2\cdot\text{Co}_3\text{O}_4$ (5:5) nanocomposite suggests excellent reversibility for both the alloying/dealloying reaction and the conversion reactions. More notably, the reversible discharge capacity of the $\text{Ti}_3\text{C}_2\text{T}_x\text{-SnO}_2\cdot\text{Co}_3\text{O}_4$ (5:5) nanocomposite in the 200th cycle could be inferentially separated into contributions from the alloying reaction (0.005 to 1.0 V vs. Li^+/Li), ca. 220 mAh g^{-1} , and the conversion reactions (1.0 to 3.0 V vs. Li^+/Li), ca. 750 mAh g^{-1} , respectively. More accurately, this exceptionally high contribution of ca. 750 mAh g^{-1} exceeds that of the sum of normalized theoretical capacity (considering the compositional breakdown) from conversion reactions of both SnO_2 and Co_3O_4 . Coupled with voltage dependent behavior at potential beyond 1.50 V (gentle nonlinear sloping with no obvious plateaus), it is indicative that there are additional contributions due to pseudocapactive mechanism as the $\text{Ti}_3\text{C}_2\text{T}_x\text{-SnO}_2\cdot\text{Co}_3\text{O}_4$ (5:5) hybrid is repeatedly cycled. On the contrary, the alloying and the conversion reactions in the porous $\text{SnO}_2\cdot\text{Co}_3\text{O}_4$ nanocubes in the 200th cycle contribute to ca. 340 mAh g^{-1} (decreased from an initial ca. 515 mAh g^{-1}) and ca. 300 mAh g^{-1} (decreased from an initial ca. 485 mAh g^{-1}), respectively. The loss in the former (usually highly reversible alloying/dealloying reaction of Sn) is probably ascribed to pulverization and loss of electrical contact due to repetitious volumetric variation and the loss in the latter (partial reversible SnO_2 conversion reaction) is commonly attributed to Sn grain coarsening due to repeated phase transformation, exposing the inadequacy of bare porous $\text{SnO}_2\cdot\text{Co}_3\text{O}_4$ nanocubes.^{6, 7} Consequently, the significantly superior electrochemical performance of the $\text{Ti}_3\text{C}_2\text{T}_x\text{-SnO}_2\cdot\text{Co}_3\text{O}_4$ (5:5) hybrid has rationalized the incorporation of $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets (as mechanical buffer and conductive matrix) into the structural design for enhanced cyclic stability.

The cyclability of freeze-dry $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets, bare $\text{SnO}_2\cdot\text{Co}_3\text{O}_4$ nanocubes, and the $\text{Ti}_3\text{C}_2\text{T}_x\text{-SnO}_2\cdot\text{Co}_3\text{O}_4$ (5:5) nanocomposite are examined in a half-cell configuration at a

modest current density of 100 mA g^{-1} within a voltage window of 0.005 to 3.0 V and their cycling profiles are as shown in Figure 6.8 (c). Expectedly, freeze-dry $\text{Ti}_3\text{C}_2\text{T}_x$ alone delivers a reversible discharge capacity of only 140 mAh g^{-1} after 200 cycles, which can be attributed to its inherently low theoretical capacity. As for the bare $\text{SnO}_2\cdot\text{Co}_3\text{O}_4$ nanocubes, a high initial discharge capacity of 1712 mAh g^{-1} is recorded, although it fades rather steadily to 649 mAh g^{-1} at the end of 200 cycles. The $\text{Ti}_3\text{C}_2\text{T}_x\text{-SnO}_2\cdot\text{Co}_3\text{O}_4$ (5:5) nanocomposite exhibits superior Li^+ ions storage ability with a retained discharge capacity of 965 mAh g^{-1} after 200 cycles. Most interestingly, it first undergoes a capacity fading in the initial 50 cycles and retains merely 548 mAh g^{-1} of reversible capacity. Subsequently, as the electrode becomes activated, the reversible discharge capacity steadily increases back to 965 mAh g^{-1} by the end of 200 cycles, giving rise to a remarkably high capacity retention increment over ca. 175 % with further increase seemingly possible. This fading-reactivation phenomenon has been commonly observed in metal oxide-based, especially Co_3O_4 , anodes.⁶⁷⁻⁷⁰ The initial fading process may be attributed to the decomposition of electrolyte, side reactions with the large surfaces of both constituents, $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets and porous $\text{SnO}_2\cdot\text{Co}_3\text{O}_4$ nanocubes and the instability of SEI layer formed. The reactivation phenomenon, consequential increment in capacity and exceedingly high capacity (beyond the sum of theoretical capacities of various constituents) are probably due to a combination of events. First, the lithiation/delithiation of $\text{SnO}_2\cdot\text{Co}_3\text{O}_4$ nanocubes leaves behind structural defects within the matrix and inevitably adds to more available active sites for interfacial Li^+ ions storage.^{61, 62} Second, the probable pseudocapacitance mechanism due to intrinsically high surface area of $\text{SnO}_2\cdot\text{Co}_3\text{O}_4$ nanocubes, which adds to capacity beyond theoretical values.^{70, 71} Third, the enhanced reversibility of SnO_2 conversion reaction (711 mAh g^{-1}) due to synergistic effect of Co nanoparticles, formed by decomposition of Co_3O_4 during lithiation can contribute to a sizable capacity (depending on the compositional breakdown and extent of reaction reversibility).⁸ Fourth, the surface grafting of *p*-phenyl- SO_3H groups and insertion of $\text{SnO}_2\cdot\text{Co}_3\text{O}_4$ nanocubes between delaminated $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets (prevent restacking) may have induced more surface and edge sites for Li^+ ions storage. Last but not least, reversible formation and decomposition of the organic polymer film have also been attributed to the additional high capacity.^{2, 72}

The rate capability of freeze-dry $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets, bare $\text{SnO}_2\cdot\text{Co}_3\text{O}_4$ nanocubes, and the $\text{Ti}_3\text{C}_2\text{T}_x\text{-SnO}_2\cdot\text{Co}_3\text{O}_4$ nanocomposite (5:5) are compared, as presented in Figure 6.8 (d). Although the rate performance of freeze-dry $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets alone remains stable, the corresponding measured values are rather limited, which are 150, 70, 50, and 20 mAh g^{-1} , at the same set of current densities. The rate performance of porous $\text{SnO}_2\cdot\text{Co}_3\text{O}_4$ nanocubes, by itself, is poor as it only retains reversible capacities of 485, 330, 188, and 85 mAh g^{-1} at the same rates and is unable to immediately and/or completely recover when the applied current density is returned to 0.2 A g^{-1} . This is due to the intrinsically limited electronic and ionic conductivity of bare $\text{SnO}_2\cdot\text{Co}_3\text{O}_4$ nanocubes. Evidently, the $\text{Ti}_3\text{C}_2\text{T}_x\text{-SnO}_2\cdot\text{Co}_3\text{O}_4$ (5:5) nanocomposite delivers the highest and most stable capacities of 945, 730, 639, and 455 mAh g^{-1} at current densities of 0.2, 0.5, 1.0, and 2.0 A g^{-1} , and the capacity recovers immediately to 945 mAh g^{-1} when the current density is returned to 0.2 A g^{-1} . The conclusively superior cyclic and rate performance of the $\text{Ti}_3\text{C}_2\text{T}_x\text{-SnO}_2\cdot\text{Co}_3\text{O}_4$ (5:5) nanocomposite is also well-supported by the EIS results in Figure 6.9 (b). A low charge transfer resistance (R_{ct}) value of 49 Ω is measured for the $\text{Ti}_3\text{C}_2\text{T}_x\text{-SnO}_2\cdot\text{Co}_3\text{O}_4$ (5:5) nanocomposite whereas significantly higher R_{ct} values of 114 and 117 Ω are measured for the separated $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets and $\text{SnO}_2\cdot\text{Co}_3\text{O}_4$ nanocubes, respectively. It is well-established that delaminated and highly conductive $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets, if left alone, are inclined to restack to form compact layered structure with much reduced active surface area. This may, to certain extent, deteriorate e^- and Li^+ ions transportation (sluggish) and result in the deceptively high R_{ct} value of 114 Ω . Hence, it is evident that hybridizing the two components can synergistically enhance overall charge transfer, in which the entrapped $\text{SnO}_2\cdot\text{Co}_3\text{O}_4$ nanocubes in $\text{Ti}_3\text{C}_2\text{T}_x$ layers may prevent the restacking and facilitate charge transfer between individual $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets. Concurrently, the crumpled $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets can serve as both an alternative and more efficient conductive pathway between individual $\text{SnO}_2\cdot\text{Co}_3\text{O}_4$ nanocubes, as well as a buffering matrix to mechanically separate $\text{SnO}_2\cdot\text{Co}_3\text{O}_4$ nanocubes (hold in place and minimize agglomeration). This also lends credence to an earlier conjecture about porous $\text{SnO}_2\cdot\text{Co}_3\text{O}_4$ nanocubes are entrapped in wrinkled $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets as inferred from a significant reduction in SSA.

Additionally, Figure 6.8 (e) confirms that the “temporary hook” feature (fading-reactivation) in the cyclic performance of the $\text{Ti}_3\text{C}_2\text{T}_x\text{-SnO}_2\cdot\text{Co}_3\text{O}_4$ (5:5) nanocomposite (as observed in Figure 6.8 (c)) indeed extends beyond 200 cycles, with a stable reversible capacity of 1159 mAh g^{-1} only achieved after 280 cycles, though the same capacity is retained even after 500 cycles at current density of 0.1 A g^{-1} . The tardiness in capacity recovery (increment) may be due to probable drawback of this mixed $\text{Ti}_3\text{C}_2\text{T}_x\text{-SnO}_2\cdot\text{Co}_3\text{O}_4$ structure in which $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets, to some extent, block direct Li^+ ions path to porous $\text{SnO}_2\cdot\text{Co}_3\text{O}_4$ nanocubes and the complexity of $\text{Ti}_3\text{C}_2\text{T}_x\text{-SnO}_2\cdot\text{Co}_3\text{O}_4$ architecture somewhat delays deep electrolyte penetration. As depicted in Figure 6.8 (f), the cyclic performance of the same $\text{Ti}_3\text{C}_2\text{T}_x\text{-SnO}_2\cdot\text{Co}_3\text{O}_4$ (5:5) nanocomposite at high current density of 1.0 A g^{-1} demonstrates a durable and stable discharge capacity of 720 mAh g^{-1} after 500 cycles, with fewer cycles (128^{th}) to complete the fading-reactivation phenomenon. Thus, it is evident that cycling at higher rates resulted in improved activation process for this multifaceted $\text{Ti}_3\text{C}_2\text{T}_x\text{-SnO}_2\cdot\text{Co}_3\text{O}_4$ nanostructure. Although the intimately mixed phases of SnO_2 and Co_3O_4 within a porous architecture, by itself, have favorably triggered synergistic Li^+ ions storage (multiple composition) and extended cyclic lifespan (more durable towards repeated volumetric variation), without the robust and conductive $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets to physically reinforce, entrap, separate and minimize interparticle agglomeration of individual porous $\text{SnO}_2\cdot\text{Co}_3\text{O}_4$ nanocubes, the fading-reactivation phenomenon is thus notably absent in these bare porous $\text{SnO}_2\cdot\text{Co}_3\text{O}_4$ nanocubes.

Figure 6. 8 (a) Cyclic voltammograms (1st, 2nd and 5th cycle) of the $\text{Ti}_3\text{C}_2\text{T}_x\text{-SnO}_2\cdot\text{Co}_3\text{O}_4$ (5:5) nanocomposite at a scan rate of $0.1 \text{ mV}\cdot\text{s}^{-1}$. (b) Galvanostatic discharge/charge profile of $\text{Ti}_3\text{C}_2\text{T}_x\text{-SnO}_2\cdot\text{Co}_3\text{O}_4$ (5:5) nanocomposite at current density of 100 mA g^{-1} . (c) Cycling performance and Coulombic efficiency of the surface-modified, freeze-dry $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets, naked $\text{SnO}_2\cdot\text{Co}_3\text{O}_4$ nanocubes and the $\text{Ti}_3\text{C}_2\text{T}_x\text{-SnO}_2\cdot\text{Co}_3\text{O}_4$ (5:5) nanocomposite between 0.005 and 3.0 V at current density of 100 mA g^{-1} . (d) Rate capabilities of the surface-modified, freeze-dry $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets, bare $\text{SnO}_2\cdot\text{Co}_3\text{O}_4$ nanocubes and the $\text{Ti}_3\text{C}_2\text{T}_x\text{-SnO}_2\cdot\text{Co}_3\text{O}_4$ (5:5) nanocomposite. (e) Extended cycle behavior of the $\text{Ti}_3\text{C}_2\text{T}_x\text{-SnO}_2\cdot\text{Co}_3\text{O}_4$ (5:5) nanocomposite at current density of 100 mA g^{-1} . (f) Cyclic performance of the $\text{Ti}_3\text{C}_2\text{T}_x\text{-SnO}_2\cdot\text{Co}_3\text{O}_4$ (5:5) nanocomposite at high current density of 1 A g^{-1} .

6.3.5 Evaluation of Composition Effect on the Electrochemical Performance of $\text{Ti}_3\text{C}_2\text{T}_x\text{-SnO}_2\cdot\text{Co}_3\text{O}_4$ Hybrid Anodes

The cyclic stability performance of the $\text{Ti}_3\text{C}_2\text{T}_x\text{-SnO}_2\cdot\text{Co}_3\text{O}_4$ nanocomposites with different $\text{Ti}_3\text{C}_2\text{T}_x$ content is as plotted in Figure 6.9 (a). First, the “temporary hook” feature (fading-reactivation) is present in all the five $\text{Ti}_3\text{C}_2\text{T}_x\text{-SnO}_2\cdot\text{Co}_3\text{O}_4$ nanocomposites, which reaffirms the synergistic effects of the $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets in triggering enhanced electrochemical performance from the $\text{SnO}_2\cdot\text{Co}_3\text{O}_4$ component. Second, with a low (10 wt.%) $\text{Ti}_3\text{C}_2\text{T}_x$ content (highly conductive but low inherent capacity), the $\text{Ti}_3\text{C}_2\text{T}_x\text{-SnO}_2\cdot\text{Co}_3\text{O}_4$ (1:9) nanocomposite should comparatively possess the highest capacity amongst the evaluated samples yet it counterintuitively retains the lowest reversible discharge capacity of 507 mAh g^{-1} at the end of 200th cycle. Interestingly, this implies that the overall capacity of the nanocomposites is not dominated by the capacity (theoretical) contribution of $\text{SnO}_2\cdot\text{Co}_3\text{O}_4$ component. This observation is, however, not an anomaly but is rather consistent with the general inverse correlation between the $\text{SnO}_2\cdot\text{Co}_3\text{O}_4$ content (high theoretical capacity) and retained reversible capacity for all the five $\text{Ti}_3\text{C}_2\text{T}_x\text{-SnO}_2\cdot\text{Co}_3\text{O}_4$ nanocomposites with different $\text{Ti}_3\text{C}_2\text{T}_x$ content. The reason for this may be due to the high density of $\text{Ti}_3\text{C}_2\text{T}_x$, thus requiring a much higher mass ratio to be allocated within the nanocomposite to achieve certain molar ratio (even distribution) between the components (as illustrated by Figure A7 (a-d) in Appendix) and trigger synergistic effect. Morphological evaluation (Figure A7 (b-d) in Appendix) by FESEM reveals that an increase in $\text{Ti}_3\text{C}_2\text{T}_x$ content (layers) is accompanied by a decrease in the number of $\text{SnO}_2\cdot\text{Co}_3\text{O}_4$ nanocubes between two adjacent $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets (i.e. more even distribution of the components). It is observed that only with 30 wt.% $\text{Ti}_3\text{C}_2\text{T}_x$ content and beyond, the $\text{Ti}_3\text{C}_2\text{T}_x\text{-SnO}_2\cdot\text{Co}_3\text{O}_4$ nanocomposites with retained reversible capacity of 764, 850, and 965 mAh g^{-1} , outperform the bare $\text{SnO}_2\cdot\text{Co}_3\text{O}_4$ nanocubes (649 mAh g^{-1}). This agrees well with the corresponding reduced SSA of 98.76, 83.98, and $42.53 \text{ m}^2 \text{ g}^{-1}$ (in Table 6.1) and reiterates the synergistic effects of $\text{SnO}_2\cdot\text{Co}_3\text{O}_4$ nanocubes entrapped in the $\text{Ti}_3\text{C}_2\text{T}_x$ layers to the overall capacity. The optimal composition is identified to be 50 wt.% $\text{Ti}_3\text{C}_2\text{T}_x$ and 50 wt.% $\text{SnO}_2\cdot\text{Co}_3\text{O}_4$.

Table 6. 1 Summary of the BET surface area of $\text{Ti}_3\text{C}_2\text{T}_x\text{-SnO}_2\cdot\text{Co}_3\text{O}_4$ with different $\text{Ti}_3\text{C}_2\text{T}_x$ contents.

	$\text{Ti}_3\text{C}_2\text{T}_x\text{-}$ $\text{SnO}_2\cdot\text{Co}_3\text{O}_4$ (5:5)	$\text{Ti}_3\text{C}_2\text{T}_x\text{-}$ $\text{SnO}_2\cdot\text{Co}_3\text{O}_4$ (4:6)	$\text{Ti}_3\text{C}_2\text{T}_x\text{-}$ $\text{SnO}_2\cdot\text{Co}_3\text{O}_4$ (3:7)	$\text{Ti}_3\text{C}_2\text{T}_x\text{-}$ $\text{SnO}_2\cdot\text{Co}_3\text{O}_4$ (2:8)	$\text{Ti}_3\text{C}_2\text{T}_x\text{-}$ $\text{SnO}_2\cdot\text{Co}_3\text{O}_4$ (1:9)
BET surface area/ $\text{m}^2 \text{g}^{-1}$	42.53	83.98	98.76	99.51	104.15

Electrochemical impedance spectroscopy (EIS) measurements were conducted to provide insight into the compositional effect on the kinetics of ionic diffusion and charge transfer in $\text{Ti}_3\text{C}_2\text{T}_x\text{-SnO}_2\cdot\text{Co}_3\text{O}_4$ nanohybrids. As identified by the diameter of the semicircle at high frequency region of Nyquist plots in Figure 6.9 (b), the $\text{Ti}_3\text{C}_2\text{T}_x\text{-SnO}_2\cdot\text{Co}_3\text{O}_4$ (5:5) nanocomposite exhibits the lowest charge transfer resistance ($R_{\text{ct}} = 49 \Omega$) than those of $\text{Ti}_3\text{C}_2\text{T}_x\text{-SnO}_2\cdot\text{Co}_3\text{O}_4$ with descending order of $\text{Ti}_3\text{C}_2\text{T}_x$ content (67, 74, 76, and 145 Ω , respectively). This implies that there exists a minimal $\text{Ti}_3\text{C}_2\text{T}_x$ concentration ($>10 \text{ wt.}\%$), i.e. electrical percolation threshold, to enhancing overall electrical conductivity of the assembled nanocomposite and 50 wt.% of $\text{Ti}_3\text{C}_2\text{T}_x$ is evidently the optimal amongst the evaluated samples. In addition, $\text{Ti}_3\text{C}_2\text{T}_x\text{-SnO}_2\cdot\text{Co}_3\text{O}_4$ nanocomposites with at least 30 wt.% $\text{Ti}_3\text{C}_2\text{T}_x$ show a more inclined (steeper) slope at the low frequency region in their respective Nyquist plots, indicative of significantly reduced Warburg impedance for diffusion of Li^+ ions into the active material (electrode). The Warburg factor (σ_w) of $\text{Ti}_3\text{C}_2\text{T}_x\text{-SnO}_2\cdot\text{Co}_3\text{O}_4$ (5:5) ($\sigma_w = 17.7$) is over three times less than that of $\text{Ti}_3\text{C}_2\text{T}_x\text{-SnO}_2\cdot\text{Co}_3\text{O}_4$ (1:9) ($\sigma_w = 59.4$). It corresponds to an order of magnitude higher Li^+ diffusion rate in $\text{Ti}_3\text{C}_2\text{T}_x\text{-SnO}_2\cdot\text{Co}_3\text{O}_4$ (5:5) than in $\text{Ti}_3\text{C}_2\text{T}_x\text{-SnO}_2\cdot\text{Co}_3\text{O}_4$ (1:9) as the Li^+ diffusion coefficient (D) is inversely proportional to the square of σ_w in Equation 6.1,

$$D = \frac{R^2 T^2}{2A^2 n^4 F^4 C^2 \sigma_w^2} \quad (6.1)$$

where ' R ' refer to universal gas constant, ' T ' refers to the absolute temperature, ' A ' refers to the area of electrode, ' n ' refers to the number of e^- participating in reactions, ' F ' refers to the Faraday constant, and ' C ' refers to the concentration of Li^+ ions in the electrolyte

($10^{-3} \text{ mol cm}^{-3}$).^{54, 73} The significantly enhanced ionic diffusion and charge transfer kinetics may be ascribed to shortened diffusion pathway of nanostructured components (both $\text{Ti}_3\text{C}_2\text{T}_x$ and $\text{SnO}_2 \cdot \text{Co}_3\text{O}_4$), the 2D $\text{Ti}_3\text{C}_2\text{T}_x$ networks functioning as a more efficient and conductive (both electronic and ionic) pathway between individual $\text{SnO}_2 \cdot \text{Co}_3\text{O}_4$ nanocubes and concurrently, the entrapped $\text{SnO}_2 \cdot \text{Co}_3\text{O}_4$ nanocubes mitigating the $\text{Ti}_3\text{C}_2\text{T}_x$ restacking issue and facilitating charge transfer between isolated $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets. These results help explain why $\text{Ti}_3\text{C}_2\text{T}_x\text{-SnO}_2 \cdot \text{Co}_3\text{O}_4$ (5:5) nanocomposite exhibits the best electrochemical performance.

Electrochemical kinetic studies were conducted via CV measurements at dissimilar scan rates from 0.2 to 2.0 mV s^{-1} to differentiate the contribution from diffusion-limited alloying/dealloying and conversion reactions, and surface-limited pseudocapacitance in various $\text{Ti}_3\text{C}_2\text{T}_x\text{-SnO}_2 \cdot \text{Co}_3\text{O}_4$ nanocomposites. Figure 6.9 (c) and Figure A8 (a-d) illustrate the electrochemical response of the $\text{Ti}_3\text{C}_2\text{T}_x\text{-SnO}_2 \cdot \text{Co}_3\text{O}_4$ nanocomposites, in the order of decreasing $\text{Ti}_3\text{C}_2\text{T}_x$ content, when subjected to increasing scan rates. Consistent across all the five samples, there was slight distortion and redox peak shifts as the scan rates were increased. The concomitant increase in polarization is expectedly reflected by the associated gradual widening of the potential difference between corresponding pairs of anodic and cathodic peaks.

The power law relationship between peak current and scan rate can be expressed by Equation 6.2,

$$\log i_p = b \log v + \log a \quad (6.2)$$

where ' i_p ' refers to peak current, ' v ' refers to the scan rate, ' a ' and ' b ' refer to the empirical constants which can be derived from the y-intercept and gradient of the linear plot of Equation 6.2, respectively.⁷⁴ A b -value of 0.5 and 1.0 would imply that the majority of Li^+ storage processes are either diffusion-controlled or pseudocapacitive, respectively. Correspondingly, as illustrated in Figure 6.9 (d), by plotting $\log i_p$ against $\log v$ at various oxidation and reduction stages, the b -values of $\text{Ti}_3\text{C}_2\text{T}_x\text{-SnO}_2 \cdot \text{Co}_3\text{O}_4$ (5:5) are determined to be between 0.55 and 0.91, implying a combination of diffusion-limited and surface-limited

(pseudocapacitive) processes for both alloying/dealloying and conversion reactions. More notably, the conversion reactions of SnO₂ (red-b and oxi-b with b -values ~ 0.9) exhibit dominant rapid surface kinetics (pseudocapacitance). Interestingly, the additional pseudocapacitive behavior corroborates well with the observed substantial Li⁺ storage contribution (extra) from beyond conventional diffusion-limited alloying/dealloying and conversion reactions. This helps to explain the exceptional rate capability and reversible capacity of Ti₃C₂T_x-SnO₂·Co₃O₄ (5:5) anode at 965 (200th cycle) or 1159 mAh g⁻¹ (500th cycle) far exceeding its normalized capacity of 815 mAh g⁻¹ (based on compositional breakdown).

Furthermore, the ratio of capacitive and diffusion-limited contribution can be quantitatively derived from relationship between current response and the sum of capacitive and diffusion-limited contributions as elucidated by Equation 6.3,

$$i(V) = k_1 v + k_2 v^{1/2} \quad (6.3)$$

where ' $i(V)$ ' refers to the current response to a certain potential, ' $k_1 v$ ' refers to the capacitive contribution and ' $k_2 v^{1/2}$ ' refers to the diffusion-limited contribution. As summarized in Figure 6.9 (e), for the Ti₃C₂T_x-SnO₂·Co₃O₄ (5:5) anode at a scan rate of 0.2 mV s⁻¹, the ratio of capacitive contribution in reduction of Co₃O₄ to Co (red-c), reduction of SnO₂ to Sn (red-b) and alloying of Sn with Li⁺ (red-a) is derived to be 6.0, 68.6, and 64.6 %, respectively. Interestingly, the Li⁺ storage behavior of the SnO₂ component is again revealed to have a high proportion of capacitive contribution whereas that of the Co₃O₄ component is dominated by diffusional contribution at low scan rates. Generally, the proportion of capacitive contribution progressively increases with the increase in scan rates. The high capacitive contribution assures rapid discharging-charging, and agrees well with the outstanding rate capability, EIS result and exceptional reversible capacity.

Figure 6. 9 (a) Cycling performance of $\text{Ti}_3\text{C}_2\text{T}_x\text{-SnO}_2\cdot\text{Co}_3\text{O}_4$ nanocomposites with different $\text{Ti}_3\text{C}_2\text{T}_x$ content. (b) Electrochemical impedance spectra (EIS) of various $\text{Ti}_3\text{C}_2\text{T}_x\text{-SnO}_2\cdot\text{Co}_3\text{O}_4$ nanocomposites, after 100th cycles, at the amplitude of 10 mV over frequency range from 100 kHz to 10 mHz. (c) CV curves of $\text{Ti}_3\text{C}_2\text{T}_x\text{-SnO}_2\cdot\text{Co}_3\text{O}_4$ (5:5) nanocomposite at different scan rates from 0.2 to 2.0 mV s^{-1} . (d) Plot of logarithm peak current against logarithm scan rates at different voltages. (e) The capacitive and diffusion-limited contribution ratio in the three cathodic processes of $\text{Ti}_3\text{C}_2\text{T}_x\text{-SnO}_2\cdot\text{Co}_3\text{O}_4$ (5:5) nanocomposite at 0.2 mV s^{-1} scan rate.

6.4 Summary

In summary, an environmentally benign and scalable approach to graft *p*-phenyl-SO₃H groups and assemble a Ti₃C₂T_x-SnO₂·Co₃O₄ nanocomposite has been presented. By a combination of surface modification, conscious selection of components and freeze-drying procedure, it is evident that the consequential hierarchical Ti₃C₂T_x-SnO₂·Co₃O₄ architecture efficaciously triggers synergistic Li⁺ storage and improves the reversible conversion of SnO₂. Unprecedentedly, this non-freestanding Ti₃C₂T_x-SnO₂·Co₃O₄ (5:5) hybrid anode demonstrates an exceptional reversible capacity of 1160 mAh g⁻¹ after 500 cycles at 100 mA g⁻¹ and outstanding rate capability of 720 mAh g⁻¹ after 500 cycles at 1.0 A g⁻¹. In this approach, beyond the obvious shortened Li⁺ diffusion pathways and more active sites on nanostructured components, the 2D layered Ti₃C₂T_x prevents agglomeration of SnO₂·Co₃O₄ nanocubes during lithiation/delithiation, provides a robust and conductive network that buffers against recurring volumetric variation of the SnO₂·Co₃O₄ nanocubes and maintains overall structural and electrical integrity of the nanocomposite anode. The porous SnO₂·Co₃O₄ nanocubes, in turn, mitigate the restacking of delaminated Ti₃C₂T_x during assembly and cycling, and double as conductive contacts between isolated Ti₃C₂T_x nanosheets, thereby preserving active surfaces and enriching interfacial interactions. Moreover, this strategy of assembling MXene/TMOs via freeze-drying is simple, industrially compatible, highly customizable tap/packing density as the quantity of components may be easily varied and can proceed without intervention of surfactant(s) nor structurally deteriorate the MXene nanosheets (i.e. oxidize or reduce lateral dimension).

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Chapter 7

Implications/Impact/Outstanding Questions

As the final chapter in this thesis, it is only fitting that the experimental results from the three distinctly different approaches to improve the electrochemical performance of SnO_2 are briefly summarized. More importantly, the extent to which the outcomes prove the relevance of dimensional and morphological uniformity to electrochemical performance, the viability of partial dopant removal from SnO_2 matrix and homogeneous distribution of components with noticeably different morphologies (i.e. $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets and $\text{SnO}_2\cdot\text{Co}_3\text{O}_4$ nanocubes) will be adequately addressed. Some reconnaissance studies that did not warrant a complete chapter, as well as opportunities and recommendations for future work, are also included within this chapter.

7.1 Summary and Implications of Results

The impetus for the three proposed methods is to improve SnO_2 and move it closer to commercialization. Instead of the relentless chase for even higher reversible capacity of SnO_2 -based anodes (i.e. approaching its theoretical capacity and moving beyond) by more complex chemical synthesis, multistep processing, or coupling with new materials, it is also important to consider incorporating economical and scalable synthesis processes with high practicality. Methods with obvious limitations but offer simplicity, practicality and scalability are intentionally revisited to hopefully provide some new insights.

7.1.1 Outcome of Hypothesis 1

The presence of a carbonaceous matrix can affirmatively help SnO_2 , with apparent absence of dimensional and morphological uniformity, to retain high reversible Li^+ storage capacity.

In Chapter 4, high energy mechanical milling/planetary ball milling, which satisfies industrial scalability and non-uniformity in dimension/morphology of as-prepared samples, is used to prepare binary SnO_2 -graphite (C) composites. A set of control experiments, in which only SnO_2 is comminuted, confirms that extending the milling period can substantially reduce particle size but is limitedly beneficial for improving cyclic performance. Expectedly, reduced particle size of SnO_2 may enhance the efficiency of Li^+ diffusion and e^- transfer, though this alone is insufficient to mitigate the many shortcomings of SnO_2 . More importantly, with the inclusion of graphite into the comminution mixture, a hierarchical structure of polydispersed SnO_2 -C nanoclusters anchored on thin remnant graphite sheets is experimentally obtained from 20 h of high energy mechanical milling. The obvious absence of dimensional and morphological uniformity is seemingly inconsequential as it retains a discharge capacity of 725 mAh g^{-1} after 100 cycles at current density of 200 mA g^{-1} , comparable to many fabricated by chemical synthesis with well-defined size and shape. This dispels the notion that morphological inhomogeneity and

agglomeration of particles are antithesis of excellent cyclic and rate capability of SnO_2 -based anodes. However, this is only made possible by the combination of many unexpected features in a sample by the simple mechanical approach. Carbon coating in the form of nanosized graphite platelets provides a more stable SEI and efficient charge transfer pathways along the SnO_2 interface, unintended internal voids within the secondary SnO_2 clusters help to buffer against the repeated volume variation and the remnant graphite sheets help maintain the electrode integrity by suppressing SnO_2 aggregation and pulverization. The much-maligned and often-overlooked mechanical approach has been shown to competently assemble a multifaceted nanostructure in a single step. This work is also timely and corroborates well with the upward trend in adopting processes with excellent industrial compatibility.

Although the series of experiments can neither confirm nor deny the criticality of dimensional and morphological uniformity to electrochemical performance of SnO_2 , the incorporation of graphite has affirmatively improved the reversible Li^+ storage capacity of SnO_2 .

7.1.2 Outcome of Hypothesis 2

The incorporated Sb dopant in SnO_2 lattice can indeed be partially removed to engineer defects/voids and improve cyclability.

In Chapter 5, it was verified (by XPS analysis) that substitutional antimony (Sb) dopant species can be partially removed from SnO_2 matrix by immersion in hot acidic etchant solution. This seemingly counterintuitive decrease of Sb dopant concentration in Sb-doped SnO_2 (ATO) surprisingly exhibits substantial enhancement in reversible Li^+ storage capacity exceeding those of untreated Sb-doped SnO_2 (mere doping) and undoped SnO_2 . For the first time, substitutional dopant species, instead of incorporated sacrificial phase (foreign), are selectively removed to achieve a more intricately modified SnO_2 architecture. It is postulated that a novel ATO core-shell structure has been formed in which both core and shell are made of the same component (SnO_2) but with distinct differential in Sb

content from the core (highest) to the shell (lowest). Consequentially, the SnO_2 shell with more Sb dopant removed has a higher concentration of vacancies/defects and this may favorably contribute to buffering against the repeatedly large volumetric change between lithiation/delithiation. This work may be a breath of fresh air in the otherwise stagnant approach with elemental doping of SnO_2 , which expectedly improves its electrical conductivity, but none has reported significant breakthrough in cyclic stability.

Unlike the mature protocols which allow complete removal of foreign sacrificial phase (such as silicon dioxide (SiO_2)) from the structure, this proof-of-concept work on post-synthesis etching of ATO has only partial success with dopant removal albeit substantial enhancement in cyclic performance is achieved.

7.1.3 Outcome of Hypothesis 3

The combination of highly conductive $\text{Ti}_3\text{C}_2\text{T}_x$ and high capacity $\text{SnO}_2\cdot\text{Co}_3\text{O}_4$ can indeed complement each other and realize synergistic effect.

In Chapter 6, an unprecedented assembly of a ternary $\text{Ti}_3\text{C}_2\text{T}_x\text{-SnO}_2\cdot\text{Co}_3\text{O}_4$ nanocomposite by a simple freeze-drying procedure was presented. Homogeneity, highly customizable tap/packing density of the components and without intervention of surfactant(s) nor structurally compromising the MXene nanosheets (i.e. oxidize or reduce lateral dimension) was concomitantly accomplished. In this approach, beyond the obvious shortened Li^+ diffusion pathways and more active sites on nanostructured components, the 2D layered $\text{Ti}_3\text{C}_2\text{T}_x$ prevents agglomeration of $\text{SnO}_2\cdot\text{Co}_3\text{O}_4$ nanocubes during lithiation/delithiation, provides a robust and conductive network that buffers against recurring volumetric variation of the $\text{SnO}_2\cdot\text{Co}_3\text{O}_4$ nanocubes and maintains overall structural and electrical integrity of the nanocomposite anode. The porous $\text{SnO}_2\cdot\text{Co}_3\text{O}_4$ nanocubes, in turn, mitigate the restacking of delaminated $\text{Ti}_3\text{C}_2\text{T}_x$ during assembly and cycling, and double as conductive contacts between isolated $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets, thereby preserving active surfaces and enriching interfacial interactions. Counterintuitively, as the proportion of high capacity $\text{SnO}_2\cdot\text{Co}_3\text{O}_4$ nanocubes increases, the overall reversible capacity decreases. It is

apparent that electrochemical performance of $\text{Ti}_3\text{C}_2\text{T}_x\text{-SnO}_2\cdot\text{Co}_3\text{O}_4$ nanocomposites are not simply a sum of its constituents. This brings forth the importance of homogenous spatial distribution to the eventual electrochemical performance of the nanocomposites. Hitherto, fabrication of $\text{Ti}_3\text{C}_2\text{T}_x/\text{TMO}$ hybrids have been limited to alternating vacuum filtration, alternating spray coating, rolling, in-situ wet chemistry synthesis, self-assembly in solution or modified layer-by-layer assembly.¹⁻⁵ This work demonstrates that a homogeneously mixed $\text{Ti}_3\text{C}_2\text{T}_x/\text{TMO}$ powder can be obtained, beyond the means of mere mechanical mixing, and presents the possibility to mechanically press and compact the powders to increase tap density and achieve high areal loading of active material (critical for practical application).

Evidently, the hierarchical architecture of non-freestanding but compositionally optimized $\text{Ti}_3\text{C}_2\text{T}_x\text{-SnO}_2\cdot\text{Co}_3\text{O}_4$ (5:5) hybrid anode improves reversible conversion of SnO_2 and triggers synergistic Li^+ storage, which combinedly contribute to an exceptional reversible capacity of 1160 mAh g^{-1} after 500 cycles at 100 mA g^{-1} and outstanding rate capability of 720 mAh g^{-1} after 500 cycles at 1.0 A g^{-1} , outperforming most MXene/transition metal oxide (TMO) that have been reported.

7.2 Reconnaissance Works

This section will include some interesting studies, which did not warrant a complete chapter but showed promising preliminary results, that may contribute to future research on SnO_2 .

7.2.1 Preliminary Results on Ternary $\text{SnO}_2\text{-M-C}$ Composites by High Energy Mechanical Milling

As a continuation work from the high energy mechanical milled binary $\text{SnO}_2\text{-graphite}$ composites in Chapter 4, it is intuitive to add a third component, preferably electroactive and ductile, to improve the overall conductivity and further separate the SnO_2 clusters.⁶⁻⁹ Cobalt (Co), iron (Fe), zinc (Zn) and manganese (Mn) are the candidates for the third

component (M). A mass ratio of 6.2: 1.8: 2 is adopted for SnO₂-M-C mixture to be comminuted. Consistent with the previous study in Chapter 4, the rotational direction of the bowl and the sun wheel were set to change every 20 min after a rest interval of 10 min. A ball-to-powder weight ratio of 80:1 was maintained for all samples. SnO₂-M-C #1 refers to the series in which all three components are added into the grinding bowls and milled for 20 h, while SnO₂-M-C #2 refers to another series in which SnO₂ and M are first added and milled for 12 h prior to addition of graphite and continue with another 8 h of mechanical milling.

Since the mechanical milling is conducted in air (and not under inert atmosphere), it is expected that the metallic species of Co, Fe, Zn and Mn will slightly oxidize even in the presence of a good reducing agent — graphite. In addition, the highly activated metallic species after extended period of mechanical milling also readily ignite and oxidize during the retrieval of as-milled powders in air. As shown by the XRD analysis of SnO₂-M-C #1 and #2 in Figure 7.1 (a) and (b), respectively, peaks of Co₃O₄ (JCPDS 42-1467), γ -Fe₂O₃ (JCPDS 39-1346), ZnO (JCPDS 36-1451) and α -MnO₂ (JCPDS 44-0144) are correspondingly observed in addition to peaks of tetragonal rutile SnO₂ (JCPDS 41-1445). Further characterizations such as EDS and XPS should be conducted to ascertain the composition difference, if any, between the sets of SnO₂-M-C #1 and SnO₂-M-C #2.

Interestingly, with similar compositional makeup in SnO₂-M-C #1 and SnO₂-M-C #2 (i.e. main component SnO₂ is 62 wt.%) and 20 h of accumulated mechanical milling, the rate performance of SnO₂-M-C #1 and SnO₂-M-C #2 vastly differ except SnO₂-Zn-C. Both SnO₂-Zn-C #1 and #2 exhibit reversible capacities of ca. 690, 550, 480, and 380 mAh g⁻¹ at current density of 0.2, 0.5, 1.0 and 2.0 A g⁻¹, respectively. In comparison, the set of SnO₂-M-C #2 constantly outperforms that of SnO₂-M-C #1 (for M = Co, Fe, Mn) at the same increasing current densities. Amongst the four tested samples in each set, both SnO₂-Mn-C #1 and #2 demonstrate the best rate performance. Beyond the obvious difference in chemical composition of the electrode materials, the localized morphological features,

spatial distribution of the various phases and overall conductivity of the composites require more attention and understanding.

Figure 7. 1 XRD of (a) SnO₂-M-C #1 (all three components are added in at once and ball milled for 20 h) and (b) SnO₂-M-C #2 (mixture of SnO₂ and M are first ball milled for 12 h, prior to addition of C and further milled for 8 h); M = Co, Fe, Zn, Mn and ◇: SnO₂, #: Co, Co₃O₄, ☆: Fe, γ-Fe₂O₃, o: Zn, ZnO, x: Mn, α-MnO₂). Rate performance of (c) SnO₂-M-C #1 and (d) SnO₂-M-C #2.

7.2.2 Synthesis Parameters Affecting Particle Size, Particle Size Distribution and Morphology of CoSn(OH)₆

Although the formation mechanism of CoSn(OH)₆ nanocubes has been well elucidated in literatures,¹⁰⁻¹⁴ the effects of varying synthesis parameters such as concentration of sodium citrate and concentration of excess NaOH (for etching) on the particle size, particle size

distribution and morphology of $\text{CoSn}(\text{OH})_6$ are not well understood. Herein, the concentration of sodium citrate is varied from 0.005 to 0.020 mol in the synthesis of $\text{CoSn}(\text{OH})_6$. As observed in Figure 7.2 (a), when 0.005 mol of sodium citrate is used, both the size and size distribution of $\text{CoSn}(\text{OH})_6$ nanocubes have increased as compared to Figure 7.2 (b) when 0.010 mol sodium citrate is used (as reported in Chapter 6). This suggests that it is insufficient to uniformly moderate the growth of $\text{CoSn}(\text{OH})_6$ nanocubes with 0.005 mol of sodium citrate surfactant. There is no observable difference when the quantity of sodium citrate added increases from 0.010 mol to 0.015 mol. However, when the 0.020 mol is used, there is noticeable distortion (rod-shaped) in the morphology of $\text{CoSn}(\text{OH})_6$. This indicates that the excessive surfactant (i.e. sodium citrate) can cause a change to a different morphology. In summary, it is not possible to synthesize smaller $\text{CoSn}(\text{OH})_6$ nanocubes by simply increasing or decreasing quantity of sodium citrate used.

Figure 7. 2 FESEM images of CoSn(OH)_6 formed with increasing concentration of sodium citrate: (a) 0.005 mol, (b) 0.010 mol (as in Chapter 6), (c) 0.015 mol, (d) 0.020 mol in mixture containing 0.010 mol of $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ and $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, respectively in 300 mL of DI water and addition of 50 mL of 2 M NaOH (for coprecipitation) and 20 mL of 8 M NaOH (for etching).

As shown in Figures 7.3 (a-d), it is observed that size of CoSn(OH)_6 nanocubes remain invariant even as the quantity of the excess NaOH is increased from 0.06 mol to 0.24 mol. This corroborates well with the proposed formation of a passivating outer layer by oxidation of the unstable $[\text{Co(OH)}_4]^{2-}$ species.¹⁰ Since hollow CoSn(OH)_6 nanocubes are formed with extended period of immersion in excess OH^- ,¹⁰⁻¹³ a more dilute precursory solution of $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ and $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ for coprecipitation remains the only route to synthesize smaller CoSn(OH)_6 nanocubes.

Figure 7. 3 FESEM images of CoSn(OH)_6 formed with increasing quantity of excess NaOH (for etching): (a) 0.06 mol, (b) 0.12 mol, (c) 0.18 mol, (d) 0.24 mol.

7.3 Outstanding Questions and Recommendations for Future Work

Question # 1: Is it possible to completely remove dopant and provide more substantial evidence to support the claim about partial removal of Sb dopant from ATO?

In Chapter 5, XPS analysis reveals the partial removal of Sb from ATO by the decrease in at.% Sb in ATO after the etching procedure. According to TEM analysis, particle size of ATO remains invariant to extended etching procedure (72 h of immersion). However, due to the proximity of Sn and Sb in the periodic table and particulate morphology of ATO nanoparticles, it is challenging to obtain useful elemental and morphological information by TEM to further substantiate the claim about partial removal of Sb from ATO. An EDX

line-scan and elemental mapping of a single post-synthesis etched ATO nanoparticle (approximately 10 nm) did not produce enough signals for the instrument to resolve the quantity of Sn to that of Sb.

Recently, Zhao *et al.*¹⁵ and Ayman *et al.*¹⁶ have reported wet synthesis of ultrathin metal oxide nanosheets by adopting a 2D graphene oxide template. It could be interesting if the etching procedures in Chapter 5 were repeated on thin ATO nanosheets with comparable Sb concentration (at.%). Subsequently, aberration-corrected TEM may be used to characterize the thin ATO nanosheets and gain insight into how Sb dopant atoms are distributed within the as-synthesized SnO₂ crystal lattice (i.e. any periodicity in the substituent) and ascertain if only Sb dopant atoms have been removed by the etching procedure (i.e. increase in lattice vacancies). Additionally, atomic force microscopy (AFM) can also be used to measure the thickness and morphology (size and features such as potholes etc.) of the as-synthesized and etched ATO nanosheets to verify if SnO₂ is concomitantly removed by the etching procedure.

Further investigation may also be extended to variables such as choice of dopant, concentration of dopant and formulation of milder etchant solution to improve on the practicality of the procedure.

Question # 2: How defect chemistry and chemical homogeneity of Sb-doped SnO₂ contribute to the excellent cyclic properties examined?

Density functional theory (DFT) study (i.e. first principles calculations) of defective Sb-doped SnO₂ may be conducted to calculate defect formation energy and identify vacancy defects (sites) that are likely to form during the post-synthesis etching procedure. Calculated Li⁺ adsorption energy and diffusion barrier values may also reveal favorable site(s) for Li⁺ storage and ease of Li⁺ mobility across Sb-doped SnO₂, respectively. Ab-initio molecular dynamic (AIMD) simulations can also be conducted to reveal the stability of various Li⁺ accommodation sites and derive the corresponding theoretical capacity of defective Sb-doped SnO₂. Accumulatively, these can aid in explaining the origin of the

exceptional cyclic performance for post-synthesis etched and defective Sb-doped SnO₂ as compared to pristine Sb-doped SnO₂.

To achieve deeper insight into the physics and chemistry of as-synthesized defective Sb-doped SnO₂ anode materials under real-time operating conditions, operando analysis of battery reactions, in addition to ex situ characterizations, is desired.¹⁷ This is because the state of electrode material within an operating battery (non-equilibrium or fast-transient process, e.g. short-lived intermediate species) is mostly different from what is observed once the cell is disassembled (although ex situ measurements are simple, sample preparation and transferal may also introduce unintended contamination, artifacts etc. which are not true reaction products).¹⁸⁻²⁰ Essentially, the *sine qua non* condition for an operando characterization is continuous data collecting from an operating cell to quantify non-equilibrium phenomena/species.^{21, 22} The importance of the design of in situ cells to successful in situ measurements is not to be understated, as a poorly design in situ cell can introduce artifacts and interfere with the signals of interest. Fortunately, many relevant and specific in situ cell designs for various operando analysis have been reported in recent literatures and more effort may also be devoted to improving cell designs.^{20, 23-26}

In view of the complexity and concomitant physical/chemical phenomena occurring in a working LIB cell, a combination of several characterization techniques (both in situ and ex situ) to extract complimentary information for deciphering the contribution(s) to the excellent electrochemical performance of these defective Sb-doped SnO₂. The myriad of operando techniques for LIB research, including, but not limited to, X-ray diffraction (XRD), X-ray absorption spectroscopy (XAS), X-ray photoelectron spectroscopy (XPS), X-ray fluorescence (XRF), atomic force microscopy (AFM), transmission electron microscopy (TEM), Raman spectroscopy, Fourier transform infrared spectroscopy (FTIR), and nuclear magnetic resonance spectroscopy (NMR).^{17, 19} The details on the procedures to data acquisition, data processing software and data fitting for individual techniques are well elaborated in the literature.^{17, 19, 27-32} As individual technique only provides fragmented information about the different physical/chemical variation occurring within the samples at varying time and spatial scales,¹⁹ it is crucial to understand the desired analysis and

derive at some appropriate combination of techniques.

Question # 3: Can the excellent electrochemical performance of $\text{Ti}_3\text{C}_2\text{T}_x\text{-SnO}_2\cdot\text{Co}_3\text{O}_4$ at low mass loading be repeatable at high mass loading and/or in a full cell configuration?

The excellent gravimetric capacity of $\text{Ti}_3\text{C}_2\text{T}_x\text{-SnO}_2\cdot\text{Co}_3\text{O}_4$ (5:5) at low mass loading ($< 2 \text{ mg cm}^{-2}$) when evaluated in half-cell configurations may not truly reflect electrode performance. Even though gravimetric capacity is the most adopted and reported electrochemical property in research papers, this simplistic calculated value only considers the mass of the electroactive material but neglects other passive components such as the current collector, conductive carbon and polymeric binder which make up the entirety of electrode.³³ Electrochemical performance at low mass loading/tap density (thin film) is vastly different to that at high packing density (practical thick electrode) because thicker electrodes require considerably higher ion diffusivity and electron conductivity.³⁴ Although it may be more than a matter of scaling, it is still pertinent to mechanically compact the loose $\text{Ti}_3\text{C}_2\text{T}_x\text{-SnO}_2\cdot\text{Co}_3\text{O}_4$ (5:5) nanopowder into freestanding electrodes with varied mass loading or thickness at given geometric area and evaluate their respective electrochemical performance. This should help identify if further adjustment(s) to the $\text{Ti}_3\text{C}_2\text{T}_x\text{-SnO}_2\cdot\text{Co}_3\text{O}_4$ (5:5) hybrid electrode design/architecture is necessary. It may also be meaningful to explore formation of varied size secondary clusters with the $\text{Ti}_3\text{C}_2\text{T}_x\text{-SnO}_2\cdot\text{Co}_3\text{O}_4$ (5:5) nanopowder to improve packing efficiency and preferably increase areal capacity. A carbon coating may also be considered to build a conductive protective layer to reduce undesired high SSA associated side reactions, improve Coulombic efficiency and hold together the different components in the composite electrode.

To realize commercialization, it is essential to evaluate the anode in a full-cell configuration with actual cathode material such as $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$. Although prelithiation of anode material is a necessary and established protocol in the assembly of commercial LIBs, it may be purposefully to investigate alternative procedure to offset the initial irreversible loss of capacity. The most mature approach involves retrieval

(disassembly) of an electrochemically reduced anode material from a half-cell configuration prior to full-cell assembly. Another approach under development involves direct contact between the anode material and Li foil while immersed in electrolyte to induce SEI formation (long turnover time).

Question # 4: Why is there always excess and irreversible capacity in the initial discharge and an increase in capacity after some cycles of charging and discharging?

The often-low Coulombic efficiency for the initial cycle of LIBs anode is consequential of a very high first discharge capacity exceeding the theoretical specific capacity and a first charge capacity close to its theoretical capacity. Most literatures attribute the inconsistent but excessive capacity contribution to electrolyte decomposition, SEI formation or side reactions however few works have investigated the source(s) to the extra irreversible capacity. It can be timely and meaningful to conduct in situ and/or operando measurements to better understand this phenomenon.³⁵

Recently, Goodenough *et al.* has also reported a work on a battery with rising capacity however the phenomenon remains not well understood.³⁶ In Chapter 6, a similar trend of increasing capacity while being cycled is observed in across the different $\text{Ti}_3\text{C}_2\text{T}_x\text{-SnO}_2\cdot\text{Co}_3\text{O}_4$ (varying composition) half-cells, thus it is affirmatively not an erroneous anomaly. This presents an interesting opportunity for further investigations to study the interfaces and identify the cause(s)/source(s) to the observed phenomenon. However, it may prove challenging as $\text{SnO}_2\cdot\text{Co}_3\text{O}_4$, by itself, when cycled does not exhibit capacity increment and the complexity to concurrently characterize the multi-component $\text{Ti}_3\text{C}_2\text{T}_x\text{-SnO}_2\cdot\text{Co}_3\text{O}_4$ and accurately decipher their corresponding contributions.

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APPENDIX

By measuring the ' 2θ ' values from (110) and (101) peaks, the crystallographic interplanar spacing of each irradiated sample, ' d ', may be calculated from Equation 3.3,

$$n\lambda = 2d\sin\theta \quad (3.3)$$

where ' n ' refers to a positive integer representing the order of diffraction peak, ' λ ' refers to the wavelength of the incident X-ray, ' d ' refers to the crystallographic interplanar spacing of the irradiated sample, and ' θ ' refers to diffracted angle.

The lattice parameters ' a ' and ' c ' of these tetragonal undoped SnO_2 and Sb-doped SnO_2 (both unetched and -etched) structures can be determined by Equation A1.1,

$$\frac{l}{d^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2} \quad (\text{A1.1})$$

Figure A 1 Lattice parameter of undoped SnO_2 , as-synthesized ATO, and variously-etched ATO.

Figure A 2 Cyclic voltammograms (1st, 2nd and 3rd cycle) of (a) undoped SnO₂, (b) as-synthesized Sb_{0.17}Sn_{0.83}O₂ (ATO), (c) ATO-H₂SO₄-8h, (d) ATO-HCl-8h, and (e) ATO-HNO₃-8h at a scan rate of 0.1 mV·s⁻¹.

Figure A 3 Galvanostatic discharge/charge profiles of (a) undoped SnO_2 , (b) as-synthesized $\text{Sb}_{0.17}\text{Sn}_{0.83}\text{O}_2$ (ATO), (c) ATO- H_2SO_4 -8h, (d) ATO-HCl-8h, and (e) ATO- HNO_3 -8h at current density of 100 mA g^{-1} .

Figure A 4 TEM images of (a) ATO-HCl-8h and (b) ATO-HNO₃-8h.

Figure A 5 XPS Ti 2p spectra of $\text{Ti}_3\text{C}_2\text{T}_x\text{-SnO}_2\cdot\text{Co}_3\text{O}_4$ (5:5) nanocomposite.

Figure A 6 (a) Cyclic voltammograms (1st, 2nd and 5th cycle) of the $\text{SnO}_2 \cdot \text{Co}_3\text{O}_4$ nanocubes at a scan rate of $0.1 \text{ mV} \cdot \text{s}^{-1}$. (b) Galvanostatic discharge/charge profile of the $\text{SnO}_2 \cdot \text{Co}_3\text{O}_4$ nanocubes at current density of 100 mA g^{-1} between voltage window of 0.01 to 3.0 V.

Figure A 7 (a) XRD and (b-d) FESEM images of $\text{Ti}_3\text{C}_2\text{T}_x\text{-SnO}_2\cdot\text{Co}_3\text{O}_4$ nanocomposite (vary compositions). (b) $\text{Ti}_3\text{C}_2\text{T}_x\text{-SnO}_2\cdot\text{Co}_3\text{O}_4$ (2:8), (c) $\text{Ti}_3\text{C}_2\text{T}_x\text{-SnO}_2\cdot\text{Co}_3\text{O}_4$ (3:7) and (d) $\text{Ti}_3\text{C}_2\text{T}_x\text{-SnO}_2\cdot\text{Co}_3\text{O}_4$ (4:6). It is to be noted that within a frame of FESEM image of $\text{Ti}_3\text{C}_2\text{T}_x\text{-SnO}_2\cdot\text{Co}_3\text{O}_4$ (1:9), there is a noticeably absence of $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheet due to its apparent low statistical distribution, hence its corresponding FESEM is excluded (no significance).

Figure A 8 (a-d) CV curves of $\text{Ti}_3\text{C}_2\text{T}_x\text{-SnO}_2\cdot\text{Co}_3\text{O}_4$ nanocomposite (vary compositions) at different scan rates from 0.2 to 2.0 mV s^{-1} .