

# **TRANSITION METAL- BASED CATALYSTS FOR ELECTROCHEMICAL WATER SPLITTING**

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under the supervision of Prof. Bruce Ni

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## **CERTIFICATION OF ORIGINAL AUTHORSHIP**

I, Zhijie Chen declare that this thesis, is submitted in fulfilment of the requirements for the award of Doctor of Philosophy, in the Faculty of Engineering and Information Technology at the University of Technology Sydney. This thesis is wholly my own work unless otherwise referenced or acknowledged.

In addition, I certify that all information sources and literature used are indicated in the thesis. This document has not been submitted for qualifications at any other academic institution. This research is supported by the Australian Government Research Training Program.

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# TABLE OF CONTENTS

<b>TITLE PAGE</b>	
<b>CERTIFICATION OF ORIGINAL AUTHORSHIP</b> .....	i
<b>ACKNOWLEDGEMENTS</b> .....	ii
<b>RESEARCH PUBLICATIONS</b> .....	iv
<b>TABLE OF CONTENTS</b> .....	vii
<b>LIST OF ABBREVIATIONS/SYMBOLS</b> .....	xi
<b>LIST OF TABLES</b> .....	xii
<b>LIST OF FIGURES</b> .....	xiii
<b>ABSTRACT</b> .....	xx
<b>CHAPTER 1 Introduction</b> .....	1
1.1.Research background .....	2
1.2.Objectives and scope of the research .....	3
1.3.Research significance .....	4
1.4.Organization of the thesis.....	4
<b>CHAPTER 2 Literature review</b> .....	8
2.1. Hydrogen energy and electrochemistry of water splitting .....	9
2.2. Key parameters for catalyst evaluation .....	10
2.3. Transition metal-based electrocatalysts for water splitting.....	12
2.3.1. Transition metal sulfides.....	13
2.3.2. Transition metal borides .....	18
2.4. Conclusions .....	39
<b>CHAPTER 3 Experimental methods</b> .....	40
3.1.Introduction .....	41



3.2.Experimental materials.....	41
3.3.Catalyst preparation .....	41
3.4.Materials characterization .....	42
3.4.1. X-ray diffraction .....	42
3.4.2. Scanning electron microscopy .....	43
3.4.3. X-ray photoelectron spectroscopy .....	43
3.4.4. Transmission electron microscopy .....	43
3.4.5. Inductively coupled plasma spectroscopy .....	43
3.4.6. Raman spectroscopy .....	44
3.4.7. Fourier-transform infrared spectroscopy .....	44
3.4.8. N <sub>2</sub> sorption/desorption measurement.....	45
3.4.9. Vibrating sample magnetometer measurement.....	45
3.5.Electrochemical techniques.....	45
3.5.1. Electrode preparation .....	45
3.5.2. Cyclic voltammetry.....	45
3.5.3. Linear sweep voltammetry.....	46
3.5.4. Electrochemical impedance spectroscopy .....	46
3.5.5. Chronopotentiometry and chronoamperometry test .....	46
3.6.Computational methods .....	46
<b>CHAPTER 4 Tuning electronic property and surface reconstruction of amorphous iron borides via W-P co-doping for highly efficient oxygen evolution .....</b>	<b>48</b>
4.1 Introduction .....	49
4.2.Experimental section.....	51
4.2.1.Catalyst synthesis.....	51
4.2.2.Material characterization .....	52
4.2.3.Electrochemical tests .....	53

4.2.4. Computational methods .....	53
4.3. Results and discussion.....	53
4.3.1. Synthesis and characterization .....	53
4.3.2. Electrochemical performance .....	57
4.3.3. Understanding the enhanced OER activity of W, P-FeB.....	63
4.4. Conclusions .....	71

**CHAPTER 5 Controllable design of nanoworm-like nickel sulfides for efficient electrochemical water splitting in alkaline media .....**

5.1. Introduction .....	74
5.2. Experimental section .....	75
5.2.1. Material synthesis .....	75
5.2.2. Structural characterization .....	76
5.2.3. Electrochemical tests .....	76
5.3. Results and discussion.....	76
5.3.1. Material characterizations .....	76
5.3.2. Electrocatalytic performance .....	80
5.4. Conclusions .....	85

**CHAPTER 6 Integrating high-efficiency oxygen evolution catalysts featuring accelerated surface reconstruction from waste printed circuit boards via a boriding recycling strategy .....**

6.1. Introduction .....	87
6.2. Experimental Methods .....	90
6.2.1. Catalyst synthesis.....	90
6.2.2. Physical and chemical characterization .....	91
6.2.3. Electrochemical tests .....	91
6.3. Results and Discussion.....	91

6.3.1.Catalyst synthesis and structural characterizations.....	91
6.3.2.Electrocatalytic performance of FNCSBs.....	98
6.3.3.Elucidation of the structure-activity correlations.....	106
6.4.Conclusions .....	110
<b>CHAPTER 7 Recycling spent water treatment adsorbents for efficient electrocatalytic water oxidation reaction .....</b>	<b>112</b>
7.1.Introduction .....	113
7.2.Experimental section.....	115
7.2.1.Conversion of spent adsorbents to electrocatalysts .....	115
7.2.2.Physical and chemical characterization .....	117
7.2.3.Electrochemical tests .....	117
7.3.Results and discussion.....	117
7.3.1.Conversion of spent adsorbents into borides/SA.....	117
7.3.2.Characterizations of synthesized borides/SA.....	121
7.3.3.Electrochemical properties of borides/SA .....	127
7.4.Conclusions .....	134
<b>CHAPTER 8 Conclusions and recommendations.....</b>	<b>136</b>
8.1. Conclusions .....	137
8.2. Recommendations .....	139
<b>REFERENCES .....</b>	<b>141</b>
<b>APPENDIX .....</b>	<b>163</b>

## LIST OF ABBREVIATIONS/SYMBOLS

Abbreviations /Symbols	Description
CA	Chronoamperometry
$C_{dl}$	Double-layer capacitance
CP	Chronopotentiometry
CV	Cyclic voltammetry
$j$	Current density
DFT	Density functional theory
ECSA	Electrochemical surface area
EDS	Energy-dispersive X-ray spectroscopy
EIS	Electrochemical impedance spectroscopy
EWS	Electrochemical water splitting
FTIR	Fourier-transform infrared spectroscopy
HRTEM	High-resolution transmission electron microscopy
HER	Hydrogen evolution reaction
ICP-MS	Inductively coupled plasma mass spectrometry
ICP-OES	Inductively coupled plasma optical emission spectroscopy
LSV	Linear sweep voltammetry
NF	Nickel foam
OER	Oxygen evolution reaction
OWS	Overall water splitting
$\eta$	Overpotential
SAED	Selected area electron diffraction
TEM	Transmission electron microscopy
TMB	Transition metal borides
TMS	Transition metal sulfides
VSM	Vibrating sample magnetometer
WPCBs	Waste printed circuit boards
XRD	X-ray diffraction
XPS	X-ray photoelectron spectroscopy

## LIST OF TABLES

<b>Table 4.1</b>	A summary of the property of OER for recently reported electrocatalysts supported on nickel foam.....	58
<b>Table 4.2</b>	Calculated charge transfer resistance ( $R_{ct}$ ) and solution resistance ( $R_s$ ) (in Ohm, $\Omega$ ) of the materials deposited on NF obtained from the Nyquist plot during the EIS experiments.....	62
<b>Table 6.1</b>	The metal ion concentrations in leachate precursors.....	93
<b>Table 6.2</b>	A summary of base metal recovery from WPCBs with state-of-the-art techniques.....	94
<b>Table 6.3</b>	A summary of the OER properties of FNCSB-4 and the recently documented waste-derived OER catalysts.....	100
<b>Table 6.4</b>	A summary of the OER properties of the recently documented TM-based nanocatalysts, as well as a group of noble metal catalysts.....	102
<b>Table 6.5</b>	Calculated charge transfer resistance ( $R_{ct}$ ) and solution resistance ( $R_s$ ) (in Ohm, $\Omega$ ) of the materials deposited on NF obtained from the Nyquist plot during the EIS experiments.....	104
<b>Table 7.1</b>	Characters of industrial wastewater.....	116
<b>Table 7.2</b>	Elemental composition of the biochar.....	124
<b>Table 7.3</b>	A summary of the recently documented TM-based and biochar-bearing OER catalysts.....	129
<b>Table 7.4</b>	Calculated charge transfer resistance ( $R_{ct}$ ) and solution resistance ( $R_s$ ) (in Ohm, $\Omega$ ) of the materials deposited on NF obtained from the Nyquist plot during the EIS experiments.....	132

## LIST OF FIGURES

- Figure 2.1** A sustainable pathway for the circulation of the hydrogen economy by combining renewable energy and water splitting.....9
- Figure 2.2** Scheme of water electrolyzers and the possible reaction pathways in basic and acidic solutions.....10
- Figure 2.3** (a) Schematic of the preparation of Ni<sub>3</sub>S<sub>2</sub>/NF and N-doped Ni<sub>3</sub>S<sub>2</sub>/NF. (b) HER polarization curves of the pristine (black) and N-doped Ni<sub>3</sub>S<sub>2</sub>/NF (red). (c) Tafel plots of the pristine and N-doped Ni<sub>3</sub>S<sub>2</sub>/NF. (d) Reaction energy of H adsorption,  $\Delta G_{H^*}$ , displayed for sites present before (black lines) and after treatment (red lines). (e) Scheme for the preparation of Co<sub>3</sub>S<sub>4</sub> PNS<sub>vac</sub>. (f) EPR spectra of Co<sub>3</sub>S<sub>4</sub> PNS<sub>vac</sub> and Co<sub>3</sub>S<sub>4</sub> NS. (g) The mass activity of different samples as a function of  $\eta$ . (h) The adsorption energies ( $\Delta E_{ads}$ ) and (i) the activation energy barriers of an H<sub>2</sub>O molecule on three models surfaces.....16
- Figure 2.4** (a) Schematic illustration of the microstructure of Cu NDs/Ni<sub>3</sub>S<sub>2</sub> NTs-CFs. (b) HRTEM image of Cu/Ni<sub>3</sub>S<sub>2</sub> border. (c) LSV curves and (d) Tafel plots of Cu NDs/Ni<sub>3</sub>S<sub>2</sub> NTs-CFs, Ni<sub>3</sub>S<sub>2</sub> NTs-CFs, Cu NDs-CFs, and CFs. (e) The calculated adsorption free energy changes of H<sub>2</sub>O on Cu/Ni<sub>3</sub>S<sub>2</sub>, Ni<sub>3</sub>S<sub>2</sub>, and Cu. (f) H adsorption free energy profiles of Cu NDs/Ni<sub>3</sub>S<sub>2</sub> hybrid, Ni<sub>3</sub>S<sub>2</sub>, and Cu. (g) Schematic of hydrogen evolution process on Cu/Ni<sub>3</sub>S<sub>2</sub>. (h) HRTEM images of NiCo<sub>2</sub>S<sub>4</sub>/Ni<sub>3</sub>S<sub>2</sub>/NF. (i) Schematic illustration of 3D NiCo<sub>2</sub>S<sub>4</sub>/Ni<sub>3</sub>S<sub>2</sub>/NF. (j) Polarization curves and (k) the corresponding Tafel slopes of NiCo<sub>2</sub>S<sub>4</sub>/Ni<sub>3</sub>S<sub>2</sub>/NF, NiCo-LDH/NF, NiCo<sub>2</sub>S<sub>4</sub>/NF, Ni<sub>3</sub>S<sub>2</sub>/NF, and bare Ni foam.....18
- Figure 2.5** (a) Schematic illustration of the synthesis of VCNB via self-templated ion exchange method combined with atomic layer deposition. (b) TEM image of VCNB. The inset shows an enlarged image of the marked region. (c) EDX images for Co, V, Ni, and B in VCNB. Partial DOS (PDOS) plots for (d) VCNB and (e) possible charge transfer procedure in VCNB.....21

<b>Figure 2.6</b>	(a) XRD patterns of amorphous metal borides annealed at different temperatures. (b) Polarization curves of CNBO-NS and their annealed samples at different temperatures. (c) Influence of annealing temperature on the crystal structure of $\text{Co}_2\text{B}$ . (d) HRTEM image of $\text{Co}_2\text{B}$ -500. The inset shows the SAED pattern of the square marked region. (e) HRTEM image of $\text{Co}_2\text{B}$ -500. The inset shows the unit cell structure of $\text{Co}_2\text{B}$ . (f) LSVs of $\text{Co}_2\text{B}$ and $\text{Co}_2\text{B}$ annealed at 500 °C and 1000 °C. (g) Effect of annealing temperature on the OER activity. (h) XANES and (i) EXAFS spectra of $\text{Co}_2\text{B}$ , $\text{Co}_2\text{B}$ -500 and references of CoO and Co foils.....29
<b>Figure 2.7</b>	XPS analysis: (a) Ni 2p and (b) B 1s core-level spectra of $\text{Ni}_x\text{B}$ minimally exposed to air (i) and after prolonged air exposure (ii). (c) O 1s spectra of $\text{Ni}_x\text{B}$ -300 before and after the electrochemical activation. (d) XPS spectra of B 1s of the $\text{NiB}_{0.45}/\text{Cu}$ before and after OER process. (e) HRTEM image of a $\text{NiB}_{0.45}$ NP after used for OER electrolysis. (f) surface sensitive TEY XAS spectra at the Ni L-edge for the $\text{NiB}_{0.45}$ film before and after OER electrolysis. (g) TEM image and (h) HRTEM image of the post-HER CoB catalyst, and the inset in (h) shows the SAED pattern. (i) XPS spectra of Co 2p of the CoB/NF, annealed CoB/NF, post-OER and post-HER CoB/NF catalysts.....33
<b>Figure 4.1</b>	Schematic illustration for the synthesis of W, P-FeB by a facile $\text{NaBH}_4$ chemical reduction process.....53
<b>Figure 4.2</b>	Microscopic measurements of W, P-FeB. (a) SEM image of W, P-FeB. (b) High-resolution SEM image of W, P-FeB. (c) EDS mapping of W, P-FeB. (d) TEM image of W, P-FeB. (e) HRTEM image of W, P-FeB (the inset shows the corresponding SAED pattern).....54
<b>Figure 4.3</b>	XRD patterns of FeB, P-FeB, W-FeB, and W, P-FeB.....55
<b>Figure 4.4</b>	(a) XPS survey spectrum, (b) Fe 2p, (c) W 4f, (d) B 1s, (e) P 2p, and (f) O 1s XPS spectra of W, P-FeB. M in (d) and (f) means metal.....57

- Figure 4.5** (a) LSV curves of as-prepared catalysts in 1.0 M KOH. (b) Comparison of  $\eta_{10}$ ,  $\eta_{50}$ , and  $\eta_{100}$  of as-prepared catalysts. (c) The effect of Fe/W feeds ratio on the  $\eta$ . (d) The effect of B/P feed ratio on the  $\eta$ . (e) Tafel plots of as-prepared catalysts. (f) Comparison of  $\eta$  and Tafel slope of OER between W, P-FeB and reported iron boride-based catalysts.....60
- Figure 4.6** (a) Cyclic voltammograms of W, P-FeB at different scan rates. (b) Scan rate dependence of  $j$  for as-prepared catalysts and the IrO<sub>2</sub> catalyst at 1.15 V vs. RHE. (c) Nyquist plots of as-prepared catalysts and the IrO<sub>2</sub> catalyst at 1.5 V vs. RHE. (d) Chronoamperometric curve of W, P-FeB at 1.458 V vs. RHE.....61
- Figure 4.7** (a) LSV curves of W, P-FeB before and after the CA test in 1 M KOH. (b) Chronoamperometric curve of the IrO<sub>2</sub> catalyst at 1.498 V vs. RHE.....63
- Figure 4.8** (a) ECSA values of W, P-FeB, W-FeB, P-FeB, FeB, and the IrO<sub>2</sub> catalyst. (b) LSV curves normalized with respect to ECSA for W, P-FeB, W -FeB, P-FeB, FeB, and the IrO<sub>2</sub> catalyst. (c-g) High-resolution XPS scans of W, P-FeB in the (c) Fe 2p, (d) W 4f, (e) O 1s, (f) B 1s, and (g) P 2p regions before and after the OER test. (h) The dissolved ion concentrations in electrolytes during the 25 h OER test. (i) HRTEM image of W, P-FeB after the OER test.....66
- Figure 4.9** (a) XRD patterns of the post-OER W, P-FeB sample and bare NF. (b) Raman spectra of W, P-FeB before and after the OER test....68
- Figure 4.10** The structural diagrams of FeOOH (a) and W-doped FeOOH (b). The charge population of FeOOH (c) and W-doped FeOOH (d)...69
- Figure 4.11** DFT simulations of OER. (a) Calculated electron density differences of FeOOH and W-doped FeOOH (red and blue colors denote electron accumulation and depletion, respectively; the labelled Fe atom is the selected active site for the free-energy calculation). (b) Computed DOS for FeOOH and W-doped FeOOH (the  $E_F$  is set to be zero). (c) Reaction free-energy diagrams for OER on FeOOH and W-doped FeOOH at zero potential ( $U = 0$ ); the potential limiting steps and the  $\eta$  are also given. (d) Calculated free-



	energy landscapes for OER on W-doped FeOOH in alkaline solution at various potentials.....	70
<b>Figure 4.12</b>	Illustration of the proposed mechanism for OER activity enhancement.....	71
<b>Figure 5.1</b>	Schematic of the formation of NiS-NW/NF and NiS-NP/NF.....	77
<b>Figure 5.2</b>	(a) SEM image of NiS-NW/NF, (b) SEM image of NiS-NP/NF, (c) SEM-EDS mapping of NiS-NW/NF, (d) XRD patterns of NiS-NW/NF, NiS-NP/NF and bare Nickel foam, (e) HRTEM image of NiS-NW/NF.....	78
<b>Figure 5.3</b>	(a) XPS survey spectrum, (b) Ni 2p, and (c) S 2p XPS spectra of NiS-NW/NF.....	79
<b>Figure 5.4</b>	(a) LSV curves of the OER performance of Ni foam, NiS-NW/NF, NiS-NP/NF, and IrO <sub>2</sub> /NF in 1.0 M KOH. (b) Comparison of $\eta_{100}$ , $\eta_{200}$ , and $\eta_{400}$ of NiS-NW/NF, NiS-NP/NF, and IrO <sub>2</sub> /NF. (c) Tafel plots of Ni foam, NiS-NW/NF, NiS-NP/NF, and IrO <sub>2</sub> /NF. (d) Comparison of $\eta$ and Tafel slope of OER between the NiS-NW/NF and reported nickel sulfide-based catalysts.....	81
<b>Figure 5.5</b>	(a-c) Cyclic voltammograms of NiS-NW/NF, NiS-NW/NF, and nickel foam at different scan rates. (d) Scan rate dependence of $j$ for NiS-NW/NF, NiS-NW/NF, and nickel foam at 1.15 V vs. RHE, (e) Nyquist plots at the open circuit potential, (f) Amperometric i-t curve of NiS-NW/NF at 1.5 V versus RHE.....	82
<b>Figure 5.6</b>	XPS spectra of (a) Ni 2P and (b) S 2p in NiS-NW/NF before and after OER tests.....	83
<b>Figure 5.7</b>	(a) LSV curves of the HER performance of NiS-NW/NF, NiS-NW/NF, nickel foam, and 20 wt % Pt/C, (b) corresponding Tafel plots. (c) Amperometric i-t curve of NiS-NW/NF for HER at an $\eta$ of 190 mV. (d) LSV curve of water electrolysis using NiS-NW/NF or NiS-NW/NF as both HER and OER electrocatalysts in a two-electrode configuration, (e) Amperometric i-t curve of NiS-NW/NF for water splitting at an applied potential of 1.563 V.....	84
<b>Figure 6.1</b>	Schematic illustration of the boriding recycling process. (a) Schematic illustration showing the synthesis of electrocatalysts for	

	OER from the waste leachates of WPCBs via a facile boriding recycling process. (b) Photographs of the WPCB leachates before and after the boriding reaction. (c) Recovery rates of Fe, Cu, Ni, and Sn via the boriding recycling process for FNCSB-4.....91
<b>Figure 6.2</b>	Microscopic characterization of FNCSB-4. (a, b) SEM images. (c) TEM bright-field image. (d) HRTEM image and (e) corresponding SAED pattern. (f) TEM EDS mapping.....96
<b>Figure 6.3</b>	XRD and XPS characterizations of FNCSB-4. (a) XRD pattern. (b) XPS survey of FNCSB-4. (c-h) High-resolution XPS spectra of B 1s, Sn 3d, Cu 2p, Ni 2p, Fe 2p, and O 1s for FNCSB-4.....98
<b>Figure 6.4</b>	OER performance of FNCSBs. (a) LSV curves of FNCSBs, the RuO <sub>2</sub> catalyst, and bare NF. (b) $\eta_{10}$ , and the current densities at 1.50 V vs. RHE of FNCSBs and the RuO <sub>2</sub> catalyst. (c) Tafel plots of FNCSBs and the RuO <sub>2</sub> catalyst. (d) OER activity comparison graph showing the Tafel slope with $\eta_{10}$ for FNCSB-4 and reported state-of-the-art TM-based electrocatalysts, as well as noble metal-containing catalysts (listed in Table 6.3).....99
<b>Figure 6.5</b>	(a) Nyquist plots of FNCSBs and NF at 1.5 V vs. RHE, and the inset shows an enlarged part of the Nyquist plots. (b) ECSA normalized LSV curves for FNCSBs, and ECSA values of FNCSBs (inset). (c) Linear relationship between the $\eta$ at the ECSA normalized current density of 3 mA cm <sup>-2</sup> and the (Fe + Ni) ratio in FNCSBs of all FNCSBs. (d) Chronopotentiometry curve of FNCSB-4 at the $j_{10}$ for 24 h.....105
<b>Figure 6.6</b>	Post-OER characterizations of FNCSB-4. (a) TEM and (b) HRTEM images of FNCSB-4 after the OER test. High-resolution XPS scans in the (c) Ni 2p, (d) Fe 2p, (e) Cu 2p, (f) O 1s, (g) B1s, and (h) Sn 3d regions of FNCSB-4 before and after the OER stability test...108
<b>Figure 6.7</b>	Surface evolution process of FNCSB-4 during OER. (a) B and Sn leaching in electrolytes during the 12 h OER test. (b) LSV curves of pristine FNCSB-4, CV activated FNCSB-4, and post-OER FNCSB-4 in 1.0 M KOH. (c) Difference in current density ( $\Delta j = (j_a - j_c)/2$ ) plots against scan rate of FNCSB-4 before and after OER test, and

	the inset shows the ECSA values. (d) Illustration of the proposed surface evolution process and the mechanism for the enhanced OER activity of FNCSB-4.....	110
<b>Figure 7.1</b>	Schematic of the design of heterostructured OER electrocatalysts from spent biochar adsorbents.....	117
<b>Figure 7.2</b>	(a) Industrial process of spent adsorbents treatment. (b) General strategy of converting biochar based heavy metal contaminated spent adsorbents into OER electrocatalysts, and the multiple merits of multimetal borides/SA as electrocatalysts for OER.....	119
<b>Figure 7.3</b>	(a) An image of magnetic separation of metal boride/biochar heterostructures from reaction solution. (b) conversion efficiency of NiCuB/SA and NiCuFeB/SA reaction system.....	120
<b>Figure 7.4</b>	XPS spectra of (a) C 1s, (b) N1s and (c) O 1s for biochar before and after metal ions adsorption, (d) Fe 2p, (e) Ni 2p, and (f) Cu 2p spectra for post-adsorption biochar.....	122
<b>Figure 7.5</b>	(a) N <sub>2</sub> adsorption-desorption isotherms of the biochar, (b) corresponding pore distribution of the biochar based on a method of Barrett-Joyner-Halenda (BJH).....	123
<b>Figure 7.6</b>	Microscopic characterization of the as-converted NiCuFeB/SA. (a) TEM image. (b) HRTEM image, and the inset is the corresponding SAED pattern. (c) EDS mapping.....	123
<b>Figure 7.7</b>	(a) XRD patterns of NiCuFeB/SA, NiCuB/SA, and SA. XPS spectra of NiCuFeB/SA: (b) survey (c) B 1s, (d) C 1s, (e) N 1s, (f) O 1s, (g) Ni 2p, (h) Fe 2p, and (i) Cu 2p.....	125
<b>Figure 7.8</b>	FTIR spectrum of SA.....	127
<b>Figure 7.9</b>	OER performance of catalysts. (a) LSV curves and (b) Tafel plots of the catalysts in 1.0 M KOH. (c) Comparison of $\eta_{100}$ , $\eta_{10}$ , and Tafel slopes of NiCuB/SA, NiCuFeB/SA, and the RuO <sub>2</sub> catalyst. (d) LSV curves real wastewater-based NiCuFeB/SA and simulated wastewater-based NiCuFeB/SA. (e) OER activity comparison graph showing the Tafel slope with $\eta_{10}$ for NiCuFeB/SA and reported the state-of-the-art TM-based electrocatalysts, as well as biochar-based heterostructured catalysts.....	127

<b>Figure 7.10</b>	(a) Nyquist plots of NiCuB/SA, NiCuFeB/SA, and NF at 1.5 V vs. RHE, and the inset shows an enlarged part of the Nyquist plots. (b) The difference in current density ( $\Delta j = (j_a - j_c)/2$ ) plots against scan rate of as-prepared catalysts. (c) LSV curves normalized with ECSA of NiCuB/SA, NiCuFeB/SA, and NF, and the inset shows ECSA values. (d) LSV curves of NiCuFeB/SA before and after the OER test, and the inset shows the chronoamperometric curve of NiCuFeB/SA at 1.485 V vs. RHE.....	131
<b>Figure 7.11</b>	(a) TEM and (b) HRTEM images of NiCuFeB/SA after the OER test.....	133
<b>Figure 7.12</b>	High-resolution XPS scans of NiCuFeB/SA in (a) Fe 2p, (b) Cu 2p, (c) Ni 2p, and (d) B 1s regions after the OER test.....	134

## ABSTRACT

Electrocatalytic water splitting (EWS) is a promising route to produce green hydrogen, which is centrally hindered by the anodic oxygen evolution reaction (OER) due to its sluggish kinetics. To advance the OER process, substantial efforts have been put into exploring high-performance catalysts. Recently, transition metal-based sulfide (TMS) and boride (TMB) catalysts have attracted enormous attention, while the design of novel TMSs/TMBs with high cost-effectiveness is an ongoing challenge. Hence, in this thesis, useful catalyst design strategies are developed for the construction of cost-effective TMS/TMB electrocatalysts.

The P and W dual-doping strategy was first used to design OER electrocatalysts from FeB with accelerated surface reconstruction and regulated intrinsic activity of evolved FeOOH. The obtained catalyst demonstrates an excellent OER activity (an overpotential of 209 mV to achieve  $10 \text{ mA cm}^{-2}$ ), surpassing most boride-based catalysts. Specifically, anion etching facilitates surface reconstruction and W doping enhances intrinsic catalytic activity. Moreover, the hierarchical structure and amorphous features also benefit OER. This study provides a powerful strategy to construct efficient OER catalysts.

A morphology control strategy was then performed to construct nickel sulfides for overall water splitting (OWS). By taking advantage of small size, large electrochemical surface area, and good conductivity, the nanoworm-like nickel sulfides exhibit better performance for OWS than the nanoplate-like analogues. This study provides a facile strategy to design sulfide-based electrocatalysts for diverse applications.

Designing catalysts from wastes can further enhance catalysts' cost-effectiveness. Herein, a boriding method is developed to turn waste printed circuit boards into OER catalysts (FeNiCuSnBs). High metal recovery rates ( $> 99\%$ ) are attained, and the optimal FNCSB-4 attains  $10 \text{ mA cm}^{-2}$  at an overpotential of 199 mV. The in-depth study suggests that the superior OER performance arises from accelerated surface self-reconstruction by B/Sn co-etching, and the newly formed multimetal (oxy)hydroxides are OER active species.

The boriding strategy was further implemented to convert spent adsorbents into heterostructural OER catalysts (NiCuFeB/SA) which outperforms many state-of-the-art catalysts. Comprehensive analyses suggest the high catalytic efficiency mainly attributed to the porous biochar confined well-dispersed metallic borides and the *in situ* evolved metal (oxy)hydroxides.

This thesis has realized the design of cost-effective TMS and TMB-based electrocatalysts for EWS, which provides guidelines for further design of novel catalysts for advanced electrochemical applications from earth abundant resources. In addition, the boriding strategy presented here may open up a new avenue to design functional materials from wastes.