UNIVERSITY OF TECHNOLOGY SYDNEY

TRANSITION METAL-BASED CATALYSTS FOR ELECTROCHEMICAL WATER SPLITTING

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Thesis submitted in fulfilment of the requirements for the degree of

Doctor of Philosophy

under the supervision of Prof. Bruce Ni

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February 2022

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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ACKNOWLEDGEMENTS

I acknowledge and thank all those who guided, supported, and encouraged me throughout my Ph.D. study. First and foremost, my sincere gratitude to my supervisor, Professor Bruce Ni, whose insight, formidable wisdom, and expertise make me complete this thesis. Without his endless guidance and constant encouragement, I cannot finish my research under the influence of the COVID-19. Also, deep thanks are extended to my co-supervisor Dr. Yiwen Liu, who gave me a lot of guidance.

Special thanks to Prof. Hong Chen and all the group members at Southern University of Science and Technology for their assistance. Their contributions to my research are deeply appreciated. I feel very lucky to have the chance to study with such creative and energetic young people.

I am thankful to all the researchers I have worked with on this journey. I would like to thank Dr. Dawei Su from the School of Mathematical and Physical Sciences at UTS; Prof. Shaobin Wang and Dr. Xiaoguang Duan from the University of Adelaide; Prof. Hong Chen, Dr. Renji Zheng, Dr. Wenfei Wei, Ranhao Wang, Jing Li, and Wensong Zou at Southern University of Science and Technology; Yinhong Song at Wuhan Textile University; Prof. Grzegorz Lota and Dr. Małgorzata Graś at Poznan University of Technology for their strong support for my doctoral research.

I would like to thank my colleagues and friends in UTS, Dr. Derek Hao, Lan Wu, Xiaoqing Liu, Dr. Wei Wei, Dr. Teng Bao, Huan Liu, Zehao Zhang, Chen Wang, Dr. Jiantao Li, Dr. Lei Zheng, Dr. Wenkui Dong, Dr. Yuanyao Ye, Dr. Jiawei Ren, Dr. Dongle Cheng, Dr. Huan Li, Dr. Bentuo Xu, Haoding Xu, Fulin Qu, Yayong Li, Bing Zhang, and Irdis Ibrahim, we had a happy time in Sydney. I would like to thank Dr. Md Johir and Dr. Nirenkumar Pathak, their kind help and support are essential to my laboratory work. Moreover, I want to acknowledge the support from administrative and academic staff from the School of Civil and Environmental Engineering and Graduate Research School.

My deepest love and thanks to my family. I appreciate my father Xinchun Chen, my mother Meihua Lv, my brother Yaoyong Chen, my sister-in-low Rihong Chen, my lovely niece Yanqi Chen and nephew Yuqi Chen for their unconditional support and love. My deepest love and thanks to my wife Duo Zhang for her companionship and love. Without their continuing support and encouragement, I would not achieve my goals during my Ph.D. study.

Finally, financial supports provided by UTS, China Scholarship Council, and the Australian Research Council are gratefully acknowledged.

RESEARCH PUBLICATIONS

Publications included in this thesis

1. **Chen, Z.**, Wei, W., & Ni, B. J. (2021). Cost-effective catalysts for renewable hydrogen production via electrochemical water splitting: Recent advances. *Current Opinion in Green and Sustainable Chemistry*, 27, 100398. (**Chapter 2**)
2. **Chen, Z.**, Duan, X., Wei, W., Wang, S., & Ni, B. J. (2019). Recent advances in transition metal-based electrocatalysts for alkaline hydrogen evolution. *Journal of Materials Chemistry A*, 7(25), 14971-15005. (**Chapter 2**)
3. **Chen, Z.**, Duan, X., Wei, W., Wang, S., Zhang, Z., & Ni, B. J. (2020). Boride-based electrocatalysts: Emerging candidates for water splitting. *Nano Research*, 13(2), 293-314. (**Chapter 2**)
4. **Chen, Z.**, Zheng, R., Graś, M., Wei, W., Lota, G., Chen, H., & Ni, B. J. (2021). Tuning electronic property and surface reconstruction of amorphous iron borides via W, P co-doping for highly efficient oxygen evolution. *Applied Catalysis B: Environmental*, 288, 120037. (**Chapter 4**)
5. **Chen, Z.**, Ibrahim, I., Hao, D., Liu, X., Wu, L., Wei, W., Su, D., & Ni, B. J. (2020). Controllable design of nanoworm-like nickel sulfides for efficient electrochemical water splitting in alkaline media. *Materials Today Energy*, 18, 100573. (**Chapter 5**)
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1. **Chen, Z.**, Zheng, R., Wei, W., Wei, W., Ni, B. J., & Chen, H. (2022).

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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
η	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

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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 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 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.