Design of Highly Efficient Non-Noble Electrocatalysts for Water Reduction and Oxidation

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By

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CERTIFICATE OF ORIGINAL AUTHORSHIP

I, Xingxing Yu, certify that the work presented in this thesis has not previously been submitted for a degree nor has been submitted as part of requirements for a degree except as fully acknowledged within the text.

I also certify that the thesis has been written by me. Any help that I have received in my research work and the preparation of the thesis itself has been acknowledged. In addition, I certify that all information sources and literature used are indicated in the thesis.

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DEDICATION

This thesis is dedicated to my family. Thank you all very much for your love and support.

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RESEARCH PUBLICATIONS

1. **X. Yu**, Z. Yu, X. Zhang, Y. Zheng, Y. Duan, Q. Gao, R. Wu, B. Sun, M. Gao, G. Wang, S. Yu, "Superaerophobic" Nickel Phosphide Nanoarray Catalyst for Efficient Hydrogen Evolution at Ultrahigh Current Densities, ***J. Am. Chem. Soc*.., 2019**, 141, 18, 7537-7543.

2. **X. Yu**, Z. Yu, X. Zhang, P. Li, B. Sun, X. Gao, K. Yan, H. Liu, Y. Duan, M. Gao, G. Wang, S. Yu, Highly Disordered Cobalt Oxide Nanostructure Induced by Sulfur Incorporation for Efficient Overall Water Splitting, ***Nano Energy*, 2020**, 71, 104652.

3. X. Zhang, S. Hu, Y. Zheng, R. Wu, F. Gao, P. Yang, Z. Niu, C. Gu, **X. Yu**, X. Zheng, C. Ma, X. Zheng, J. Zhu, M. Gao, S. Yu, Polymorphic Cobalt Diselenide as Extremely Stable Electrocatalyst in Acidic Media via a Phase-mixing Strategy, ***Nat. Commun.*, 2019**, 5338.

4. P. Yang, X. Zhang, F. Gao, Y. Zheng, Z. Niu, **X. Yu**, R. Liu, Z. Wu, S. Qi, L. Chi, Y. Duan, T. Ma, X. Zheng, J. Zhu, H. Wang, R. Gao, S. Yu, Protecting Copper Oxidation State via Intermediate Confinement for Selective CO_2 Electroreduction to C^{2+} Fuels, ***J. Am. Chem. Soc*.., 2020**, 142, 13, 6400-6408.

TABLES OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

ABSTRACT

To satisfy the increasing energy demand and solve the global warming issue, renewable clean energy sources were in the urgent requirement. Hydrogen energy was regarded as the most potential clean energy suppliers. Electrocatalytic water splitting as one of the most promising approach for hydrogen production, has been rapidly blossomed. Tremendous efforts have been devoted into the electrocatalysts' development. However, the design of highly efficient non-noble electrocatalysts for large-scale hydrogen production was still a tough challenge. In the doctoral work, a series of non-noble metal electrocatalysts were prepared and investigated.

In the first project, we prepared the "superaerophobic" Ni_2P nanoarray catalyst grown on a nickel foam substrate. The Ni_2P catalysts demonstrate an outstanding electrocatalytic activity and stability in alkaline electrolyte. Their high catalytic activities can be attributed to the favorable electron transfer, superior intrinsic activity and the intimate connection between the nanoarrays and their substrate. Moreover, the unique "superaerophobic" surface feature of the Ni_2P nanoarrays enables a remarkable capability to withstand internal and external forces and timely release the in-situ generated vigorous H_2 bubbles at large current densities (such as > 1000 mA cm^{-2}). Our results highlight that an aerophobic structure is essential to catalyze large-scale gas evolution.

The second project concentrates on tuning the internal structure of nanomaterials to boost their intrinsic catalytic properties. We reported an incorporation of sulfur ion into crystalline cobalt oxide (S-CoO_x) to create structural disorder via a facile room-temperature ion exchange strategy. Compared with its crystalline form, the disorder in S-CoO_x catalyst endows it remarkable catalytic activities for hydrogen evolution reaction (HER) and oxygen evolution reaction (OER). The water electrolyser adopting S-CoO_x as cathode and anode requires mere 1.63 V to reach 10 mA cm^{-2} in 1 M KOH. Charaterizations and analysis demonstrate that the enhanced electrocatalytic properties could be attributed to increased low oxygen coordination, more defect sites and modified electron densities characteristics. This work provides the new insight on designing structural disordered catalysts for energy storage areas.

In this thesis, the two projects are both about the design of the freestanding and three-dimensional materials. Their advantages could be concluded into two aspects. One is the more effective electron and mass transfer pathway, providing the effective intrinsic catalyst properties. Other is the solid connection, guaranteeing their stabilities even at the high current densities. These findings spotlight the usage of freestanding catalysts in the energy storage and conversion devices.