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博士論文審査報告書

Doctor Thesis Screening Results Reports

論 文 題 目

Thesis Theme

Design of Nanoporous Transition Metal Sulfides
for Electrochemical Water Splitting

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Coupling electrochemical reactions to renewable energy sources (e.g. solar, wind, geothermal, etc.) is a realistic pathway toward a closed-loop economy where energy and materials can be recycled indefinitely without any of the negative side effects of fossil fuels. Electrochemical water splitting is a reliable method to transform water into oxygen and hydrogen fuels. However, electrochemical water splitting method tends to rely on expensive precious metal catalysts like platinum (Pt) which limits its scalability as a viable energy supply technology. This thesis describes the design of nanoporous transition metal sulfide electrodes for efficient electrochemical water splitting. Transition metal sulfides have unique physical and chemical properties that enable them to catalyze the full water splitting reaction from the hydrogen evolution reaction (HER) to the oxygen evolution reaction (OER) in a bifunctional electrode setup. In addition, these transition metal sulfide materials are far more Earth-abundant and can generate hydrogen at a lower economic cost.

Chapter 1 introduces recent developments in the application of transition metal sulfides in electrochemical water splitting.

Chapter 2 describes the preparation of a bifunctional electrocatalyst for both HER and OER. A metal-organic framework called ZIF-67 is used as a morphological template and cobalt precursor. This work creates a hollow core-shell heterostructure composed of inner Co_3S_4 and outer MoS_2 using a hydrothermal process. The Co_3S_4 is an efficient OER catalyst that has poor stability, while the MoS_2 is a good HER catalyst with poor OER performance. The synergistic and protective effects between the core of Co_3S_4 and shell of MoS_2 allow these $\text{Co}_3\text{S}_4@\text{MoS}_2$ materials to have outstanding bifunctional catalytic performances for both HER and OER in acidic and alkaline media. The strategy developed here opens new avenues in the design and fabrication of highly effective bifunctional electrocatalysts.

Chapter 3 demonstrates the synthesis of a hollow cubic $\text{Co}_3\text{S}_4@\text{MoS}_2$ bifunctional catalyst using a Co-Fe Prussian blue analogue (PBA) precursor. The hollow Co_3S_4 nanoboxes are formed initially based on an ion exchange reaction between $\text{Fe}(\text{CN})_6^{3-}$ of Co-Fe PBA and S^{2-} . Subsequently, MoS_2 nanosheets are grown on the surface of the Co_3S_4 nanoboxes. Again this work demonstrates the strong synergistic effects fostered by the combination of MoS_2 and Co_3S_4 , providing more evidence that this material system generates enhanced bifunctional catalytic performance. Consequently, the $\text{Co}_3\text{S}_4@\text{MoS}_2$ shows a low cell voltage of 1.58 V when it is used as both cathodic and anodic electrodes in a water splitting electrolyzer. This approach is widely applicable to other PBAs with different compositions. Well-designed architectures with optimal

compositions will improve the performance of these electrodes in practical applications.

Chapter 4 extends the above synthetic strategy to generate hollow heterometallic phosphide nanocubes *via* one-step phosphidization of trimetallic NiCoFe PBA. Modulating the Ni content in the PBA precursors enables various heterometallic phosphides with different morphologies and compositions to be synthesized. There is an optimal composition that exhibits increased active sites and improves electrical conductivity, which makes it a good catalyst for both HER and OER. This work highlights a new strategy for preparing low-cost, efficient, and stable catalysts for overall water splitting.

Chapter 5 describes the preparation of mesoporous metal sulfides. Polystyrene-*block*-poly(acrylic acid) (PS-*b*-PAA) polymer micelles are used as pore-directing agents and as sacrificial templates. The electrostatic interactions between negatively charged micelles and positively charged metal species play a critical role in the formation of mesostructured precursor. Dithiooxamide (DTO, $\text{NH}_2\text{C}(\text{S})\text{C}(\text{S})\text{NH}_2$) is added to the synthetic process so that it combines with the cationic metal (*e.g.*, Zn^{2+} , Co^{2+} , Ni^{2+}) by strong covalent bonding and with the Mo source by electrostatic interactions, respectively. Calcination of this material generates spherical CoMo sulfides containing mesopores. The mesoporous network promotes diffusion of reactants and products within the spheres, leading to enhanced catalytic kinetics for both the HER and OER.

Chapter 6 extends the soft-templating method described earlier for the construction of mesoporous N-doped carbon containing ultrafine molybdenum carbide (Mo_2C) nanoparticles. Another amphiphilic diblock copolymer polystyrene-*block*-polyethylene oxide (PS-*b*-PEO) is used as the pore-forming agent. The complexation between dopamine hydrochloride (DA, $(\text{HO})_2\text{C}_6\text{H}_3\text{CH}_2\text{CH}_2\text{NH}_2\cdot\text{HCl}$) and the Mo source on the PS-*b*-PEO micelles results in the formation of mesostructured precursor. After carbonization of the precursor under N_2 atmosphere, mesoporous $\text{Mo}_2\text{C}/\text{N}$ -doped carbon is obtained with high surface area. In this catalyst, the Mo_2C is responsible for enhancing oxygen reduction reaction (ORR) performance, while the N-doped carbon matrix can help to further improve the conductivity and prevent the aggregation of the Mo_2C nanoparticles. This chapter shows the wide applicability of the polymeric micelle strategy to generate various kinds of mesoporous materials with different electrocatalytic properties.

Chapter 7 describes the general conclusions of the thesis and proposes future prospects. Highly efficient bifunctional electrocatalysts for water splitting are obtained through various strategies, including morphological

control, construction of heterostructures, and heteroatom doping. Perhaps more importantly, the strategies developed in this thesis will provide a general route to synthesize other kinds of efficient electrocatalysts for energy storage and conversion systems in the future. Therefore, we believe this work is sufficient to warrant a degree of Doctor of Engineering.

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