The Synthesis and Application of Highly Efficient Catalysts for Electrochemical Water Splitting

A thesis presented for the award of the degree of Doctor of Philosophy

From

University of Technology Sydney

Faculty of Science

By Yufei Zhao, B. Eng.

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DEDICATION

This thesis is dedicated to my beloved husband, my parents and my sisters

CERTIFICATION

I, Yufei Zhao, declare that the work in this thesis has not previously been submitted for a degree nor has it been submitted as part of requirements for a degree except as fully acknowledged within the text.

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

This thesis is the result of a research candidature conducted jointly with Beijing Institute of Technology as part of a collaborative Doctoral degree.

Yufei Zhao

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Yufei Zhao

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LIST OF ABBRIEVIATIONS

Abbreviation	Full name
a.u.	Arbitrary unit
nm	Nanometer
cm	Centimeter
LSV	Linear sweep voltammetry
CV	Cyclic voltammetry
EIS	Electrochemical impedance spectroscopy
RRDE	Rotating ring-disk electrode
GC	Glassy carbon electrode
RHE	Reversible hydrogen electrode
GC	Glassy carbon electrode
Eq.	Equation
JCPDS	Joint committee on powder diffraction standards
SAED	Selected area electron diffraction
SEM	Scanning electron microscopy
TEM	Transmission electron microscopy
XPS	X-ray photoelectron spectroscopy
BET	Brunauer Emmett Teller
TGA	Thermogravimetric analysis
XRD	X-ray diffraction
FT-IR	Fourier transform inferior red spectroscopy
DMF	Dimethylformamide
DMDMS	Dimethoxydimethylsilane
TEOS	Tetraethyl orthosilicate
CTAB	Hexadecyl trimethyl ammonium bromide
OCP	Open circuit potential
HER	Hydrogen evolution reaction
OER	Oxygen evolution reaction

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ABSTRACT

Hydrogen (H_2) is an abundant and renewable clean fuel that is regarded as a promising energy carrier to replace fossil fuels in the future. Electrocatalytic water splitting to produce H_2 seems to be one of the cleanest and most sustainable methods for large-scale H_2 production. The catalysts are of extreme significance for the electrochemical performances of water splitting.

The composite of layered MoS_2 nanosheets supported on a 3D graphene aerogel network (GA-MoS_2) has been synthesized by two-step hydrothermal method. The flexible graphene sheets partially overlap in 3D space to form an interconnected porous microstructure, which greatly prevents serious restacking of graphene, and further provides large surface area for growing MoS_2 nanosheets. GA-MoS_2 maintains an excellent porous structure and assembles with MoS_2 nanosheets around the edge of the pores, providing relatively large amounts of exposed edge sites for hydrogen evolution. The 3D structure of the catalyst can also supply efficient conducting network for rapid electronic transport during the electrocatalytic process, offsetting the poor intrinsic conductivity of MoS_2, facilitating fast electron transfer. Therefore, GA-MoS_2 exhibits high catalytic performance and strong stability for electrocatalytic HER application.

Graphene-Co_3O_4 composite with a unique sandwich-architecture is successfully synthesized and applies as an efficient electrocatalyst towards OER. The graphene nanosheets act as a binder to link neighboring Co_3O_4 particles together and Co_3O_4 nanocrystals are homogeneously attached on both sides of graphene nanosheets. The existence of graphene highly increases the conductivity of the composite. The obtained composite shows enhanced

catalytic activities in both alkaline and neutral electrolytes. The current density of 10 mA cm^{-2} has been achieved at the overpotential of 313 mV in 1 M KOH and 498 mV in phosphate buffer solution, respectively. Furthermore, there is no obvious current density decay after the stability test.

An active catalyst composed of porous graphene and cobalt oxide (PGE–CoO) has been synthesized, demonstrating high porosity, large specific surface area and fast charge transport kinetics. The catalyst also exhibits excellent electrochemical performance towards OER with a low onset potential (504 mV *vs*. Ag/AgCl) and high catalytic current density (overpotential of 348 mV for 10 mA cm^{-2}). The enhanced catalytic activity could be ascribed to porous structure, high electroactive surface area and strong chemical coupling between graphene and CoO nanoparticles. Moreover, CoO nanoparticles are wrapped by the porous graphene, inhibiting the corrosion phenomenon, thus this OER catalyst also shows good stability in the alkaline solution. The high performance and strong durability suggest that the porous structured composite is favorable and promising for water splitting.

We develop ultrathin $CoMn_2O_4$ nanosheets with abundant oxygen vacancies vertically aligned on cobalt and nitrogen co-functionalized carbon nanofibers ($CoMn_2O_4$-CoNC) as an efficient OER catalyst by a facial spontaneous redox reaction. The inner CoNC serves as sacrificed template and high conductive substrate to provide fast electronic transportation, and the aligned ultrathin nanosheets rich in oxygen vacancies act as active sites. Benefiting from the collaborative advantages of high effective surface areas, fast charge transfer kinetics and strong synergistic coupled effect, $CoMn_2O_4$-CoNC composite exhibits excellent catalytic activity and good durability for

water oxidation, reaching 10 mA cm^{-2} at an overpotential of 307 mV.

Fe_3C nanoparticles encapsulated at the tip of nitrogen-enriched carbon nanotubes (NCNTs) is investigated as catalyst for OER, which are aligned on one dimensional (1D) nitrogen doped carbon nanofibers (Fe_3C@NCNTs-NCNFs) by a scalable electrospinning technique, as a high performance OER catalyst. The unique 3D hierarchical architecture of Fe_3C@NCNTs-NCNFs leads to highly exposed active sites, enhanced electron transfer properties and strong synergistic coupled effects. Fe_3C@NCNTs-NCNFs exhibits outstanding catalytic performance with a high current density (10 mA cm^{-2} at an overpotential of 284 mV), a low Tafel slope (56 mV dec^{-1}), a low charge transfer resistance and strong durability in 1 M KOH solution.

We report the successful synthesis of cobalt nanoparticle embedded porous nitrogen doped carbon nanofibers (Co-PNCNFs) by a facile and scalable electrospinning technology. The electrospun Co-PNCNF composite exhibits a low onset potential of 1.45 V (vs. RHE) along with high current density (overpotential of 285 mV for 10 mA cm^{-2}) towards OER. The exceptional performance could be ascribed to the bi-functionalized CNFs with nitrogen doping and cobalt encapsulation, which can convert the inert carbon into active sites. Moreover, the porous structure and synergistic effect further provide a highly effective surface area and facilitate a fast electron transfer pathway for the OER process. Interestingly, the Co-PNCNF composite also displays the capability for the hydrogen evolution reaction (HER) in alkaline solution. A water electrolyzer cell fabricated by applying Co-PNCNFs as both anode and cathode electrocatalysts in alkaline solution can achieve a high current density of 10 mA cm^{-2} at a voltage of 1.66 V.