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Advanced Non-Noble Catalysts for Electrocatalytic Energy Conversion Processes

Jingjing Duan

School of Chemical Engineering

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Abstract

The key renewable-energy technologies, such as fuel cells, metal-air batteries, and water electrolysers, provide sustainable solution to the aggravating energy and environment issues. They can convert chemical energy to electricity or fuel directly with high efficiency and low even zero greenhouse gas emission. However, the commercial success of these techniques has been greatly hampered by the prohibitive cost, low abundance, and limited stability of the state-of-the-art noble-metal electrocatalysts (Pt, IrO_2 or RuO_2) at the anodes and/or cathodes. Therefore, the development of cost-effective, highly active, and durable electrocatalysts is highly desirable for these techniques. This thesis aims to design and fabricate a series of advanced electrocatalysts for oxygen reduction reaction (ORR), hydrogen evolution reaction (HER), and oxygen evolution reaction (OER) which are the cathodic or anodic reactions of fuel cells, metal-air batteries and water electrolysers.

The first part of the thesis focuses on ORR to fabricate a number of low cost transition metal oxides and carbon materials as the alternative to commercial Pt/C. Non-precious metal oxides such as Mn_3O_4 have been studied as Pt substitute due to their earth abundance and environmental compatibility. In addition, heteroatom-doped graphene which combines excellent electrical conductivity, high surface area, and rich active sites, displays good electrocatalytic performance. As a consequence, a hybrid material composed of Mn_3O_4 nanoparticles on nitrogen-doped graphene was firstly synthesized for ORR catalysis. Further, the shape effect of metal oxide nanoparticles (Mn_3O_4) on ORR activity has been examined, based on the fact that the heterogeneous ORR process involving the adsorption of reactants and desorption of products on the exposed facets of nanocrystals.

The second part of thesis is to study HER which is the primary step of sustainable H_2 production from electrochemical water splitting. Other than tuning the chemical composition and nanostructure of electrocatalysts, the HER performance can also be optimized through the manipulation of the electrode architectures. Heteroatom-doped graphene has been investigated as the HER catalyst, but its performance is limited due to the small amount of accessible active sites. In response, we hybridizes heteroatom-doped graphene with a highly active HER catalyst (porous C_3N_4 and $1T-WS_2$) into three dimensional flexible hybrid film, which can be directly utilized as HER catalyst electrodes without substrates or binders. This new category of electrocatalysts can combine the facile HER kinetics and high HER activity. This work offers the possibility to tackle the bottleneck of HER electrocatalyst by tailoring the electrocatalytic performance at atomic scale.

The third part of thesis aims to design a bifunctional electrocatalyst for both HER and OER. The cobalt oxides are known as an efficient OER electrocatalyst, while cobalt phosphides are active HER electrocatalysts. Through adjusting the anion percentage of P and O elements in cobalt phosphoric oxides, we can obtain the optimized bifunctional catalyst for both HER and OER for overall water electrolysis. Moreover, the cation in cobalt phosphoric oxide is modulated by doping different amount of Fe, which can improve its water splitting ability further. As expected, the obtained catalyst electrode has displayed a superior water electrolysis performance, exhibiting the low driving potential and facile reaction kinetics, which might be associated with the three-dimensional conductive network beneficial for the electron and charge transportation, high accessibility of active sites, and the optimum cation and anion percentages.

Thesis Declaration Statement by Author

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