

学 位 論 文 の 要 旨

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学位論文題目	Developing highly efficient and durable electrocatalysts for water splitting over a wide pH range (幅広い pH 領域で高い耐久性を持つ高性能水電解用電極触媒の開発)		
<p>学位論文要旨</p> <p>Water splitting is a promising process to convert water to hydrogen energy and other chemicals via renewable energy, in which two half-cell reactions, i.e., oxygen evolution reactions (OER) and hydrogen evolution reactions (HER), occur simultaneously. Comparing with the two-electron transfer reaction of HER, the OER is a four-electron transfer reaction, which is more kinetically sluggish. Therefore, the OER always governs the overall electrochemical water splitting efficiency. To date, Iridium dioxide (IrO₂) and ruthenium dioxide (RuO₂) is state-of-the-art OER electrocatalysts with low overpotential and Tafel slope while platinum (Pt) and Pt-based alloys are the state-of-the-art HER electrocatalysts. However, their scarcity and high price limit their industrial applications. This study focuses on developing earth-abundant and low-cost transition metal-based nanostructured electrocatalysts for highly efficient and durable water splitting over a wide pH range.</p> <p>Firstly, Ni-Fe layer double hydroxide (LDH) based OER electrocatalysts were developed. To improve the OER performance, NiO@NiFe-LDH electrocatalysts with a core@shell structure were decorated on a three-dimensional (3D) mesoporous nickel foam (NF) by a two-step hydrothermal synthesis process followed by and a calcination step. Due to the 3D rational configuration with highly active sites, the obtained composite electrode showed high performance for OER, which needed a low apparent overpotential of 265 mV to afford the standard current density of 10 mA cm⁻². In addition, the NiO@NiFe-LDH coated electrode was further treated in an organic solution via ultrasound for <i>in situ</i> intercalations of the NiFe-LDH to provide larger channels for ion transportation and gas diffusion. As a result, the charge transition resistance was obviously reduced and the apparent activity, as well as the long-term stability, were improved. The optimized NiO@NiFe-LDH composite exhibited excellent long-term stability in 50 h even at high current densities of 50 and 100 mA cm⁻², and meanwhile, the required apparent overpotential of OER for sustaining the standard current density (10 mA cm⁻²) was reduced from 265 to 210 mV.</p> <p>Secondly, to develop HER electrocatalysts with high efficiency, long-term stability, and low-cost for the large-scale and effective application of renewable energy, a binder-free NiCoP-carbon nanocomposite (denoted as NiCoP-C(TPA)) film with unique nanostructure was successfully coated on the electrode for the first time by deposition of a terephthalic acid-induced NiCo bimetallic compound</p>			

precursor film on the NF with a hydrothermal synthesis method followed by a calcination process in Ar atmosphere and continuous phosphorization treatment with NaH_2PO_2 . In the obtained NiCoP-C(TPA) electrocatalyst, bimetallic phosphide nanoparticles were well combined with graphite carbon. It is found that the bimetallic NiCo alloy was also formed in the carbonization process, which affected the performance of the final catalyst. As a result, the NiCoP-C(TPA) electrocatalyst had much higher activity than the monometallic phosphides of NiP-C(TPA)/NF and CoP-C(TPA)/NF, and the NiCoP-C(TPA)/NF electrode exhibited an overpotential as low as 78 mV at the standard current density of 10 mA cm^{-2} with a small Tafel slope of 73.4 mV dec^{-1} , a faradic efficiency of $\sim 94\%$ and long-term stability at high current density in the alkaline electrolyte. Meanwhile, the NiCoP-C(TPA)/NF electrode also exhibited superior HER performance in the acidic electrolyte with an overpotential of $94 \text{ mV}@10 \text{ mA cm}^{-2}$, a Tafel slope of 81.1 mV dec^{-1} , and long-term stability although a relatively high overpotential of $248 \text{ mV}@10 \text{ mA cm}^{-2}$ with a high Tafel slope of $112.5 \text{ mV dec}^{-1}$ was obtained in the neutral electrolyte. It is expected to provide a novel synthesis method by using organic solid acid to derive high-performance bimetallic phosphide-based electrocatalysts with special nanostructure for HER in the water-splitting process.

Lastly, the bifunctional electrocatalysts for the overall water splitting were developed, in which combining oxides with bimetallic elements was considered as an efficient route to modify the electronic distribution for improving the intrinsic activity of electrocatalysts, and further engineering the defect structure and adjusting the valence state could provide more adsorption sites as well as active sites for the decomposition of the reactants and/or intermediates. NiMnO_x nanosheets with rich defects were electrochemically deposited on the surface of $\text{Cu}(\text{OH})_2$ nanowires followed by a thermal treatment process to form a CuO_x nanowires @ NiMnO_x nanosheets ($\text{CuO}_x \text{ NWs}@ \text{NiMnO}_x \text{ NSs}$) electrocatalyst with core-shell configuration. Structure characterizations indicated that NiMnO_x nanosheet had numerous vacancies with scattered defects and dislocations with partial cracking of the inert basal planes, resulting in extra active edge sites and coordination-unsaturated spinel crystal. As such, the valence states of Ni and Mn elements became unstable in the defect-modified NiMnO_x materials under the applied potential. Comparing with the initial NiMnO_x , more Ni^{3+} and Mn^{4+} were formed during the oxygen evolution reaction (OER) whereas they were converted to Ni^{2+} and Mn^{3+} during the hydrogen evolution reaction (HER). These controllable valence state changes of metal elements endowed the NiMnO_x to have a high ability for catalyzing overall water electrolysis. As a result, the $\text{CuO}_x \text{ NWs}@ \text{NiMnO}_x \text{ NSs}$ bifunctional electrocatalysts exhibited high performances in both HER and OER in alkaline electrolytes. Meanwhile, by using the same electrocatalysts in the neutral electrolyte, the overpotentials@ 10 mA cm^{-2} was also as low as 80.7 and 390 mV with Tafel slopes of 77.6 and $101.6 \text{ mV dce}^{-1}$ for HER and OER, respectively. A two-electrode overall water electrolysis system using this bifunctional electrocatalyst exhibited low cell voltages of 1.62 and 1.75V in the alkaline and neutral electrolytes respectively at the standard current density of 10 mA cm^{-2} with long-term stability, indicating that this $\text{CuO}_x \text{ NWs}@ \text{NiMnO}_x \text{ NSs}$ core@shell-type material should be an effective bifunctional electrocatalyst in both alkaline and neutral pH media.