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Morphological and structure dual modulation of cobalt-based layer double hydroxides by Ni doping and 2-methylimidazole inducting as bifunctional electrocatalysts for overall water splitting

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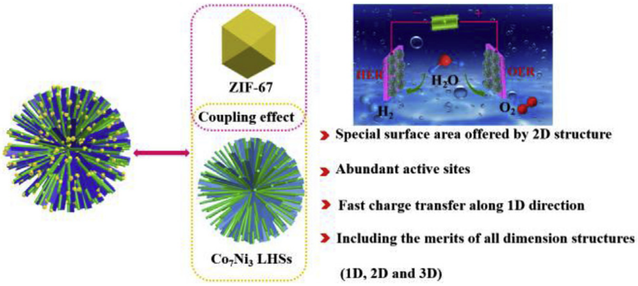
HIGHLIGHTS

- The addition of Ni can simultaneously tun structure and morphology of composite.
- 3D microsphere inherits the merits of all dimension structures (1D, 2D and 3D).
- The Co_7Ni_3 LHSs@ZIF-67/NFF exhibits the highest electrocatalytic activity.

GRAPHICAL ABSTRACT



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ABSTRACT

Developing bifunctional electrocatalysts of high-efficiency and new structures for overall water splitting are highly desirable and ongoing challenge. Herein, Co_xNi_{10-x} layer double hydroxide salts with controllable structure and morphology induced by 2-methylimidazole to derive ZIF-67 on Ni/Fe foam is reported. The as-prepared 3D Co_xNi_{10-x} layer double hydroxide microspheres are constructed by self-assembly of 2D nanoflake and 1D nanorod with ZIF-67 particles due to the double influence of Ni and 2-methylimidazole. It is discovered that the Ni and 2-methylimidazole can simultaneously modulate morphology and structure of Co_xNi_{10-x} layer double hydroxide to distinctly increase the electrochemical active surface area for exposing more accessible active sites. Notably, the 3D microsphere heterogeneous catalysis of the self-assembly combines the merits of low dimensions (1D and 2D) materials, providing high structural void porosity and fast charge transport channels. Particularly, the Co_7Ni_3 layer double hydroxide salts@ZIF-67/Ni/Fe foam exhibits the highest electrocatalytic activity with the lower overpotentials of 260 and 165 mV toward oxygen evolution reaction and hydrogen evolution reaction at current density of 10 mA cm^{-2}, respectively. The outstanding activity originates from the strong electronic coupling between the 3D microsphere and ZIF-67. This work can bring a new prospect for fabricating highly-active and new structure electrocatalysts.

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1. Introduction

With the increasing concerns on severe environmental problem and the consumption of rapid fossil fuel, there are more and more requirements to develop renewable and sustainable energy sources [1–4]. Electrolytic water splitting into hydrogen and oxygen is considered as the most promising technology because of its great advantage of hydrogen production and carbon-free emissions [5–7]. However, a substantial energy will be consumed in the process of the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER), which greatly limits the practical applications of this technology [8,9]. Therefore, it is imperative to develop low-cost and highly active electrocatalysts. Currently, precious metal Pt-based and Ir/RuO_2-based materials are widely studied as the most efficient electrocatalysts for HER and OER, respectively. Nevertheless, their scarcities, high cost and unsatisfactory durability pose limitations to their practical utilization [10,11]. In these regards, design of low-expensive, high-efficiency and earth-abundant catalysts for water electrolysis is still a clear challenge.

Over the past decades, more and more researchers have focused on the development of low-cost materials, such as transition metals [12,13], transition metal oxides [14,15], carbon materials [16,17], LDH [18] and Co-based materials [19,20]. Among them, especial the Co-based materials due to low cost-efficiency, environmental benignity, earth abundance and promising OER and HER performances, have been recognized as candidate for application in water electrolysis. To improve the OER and HER performances of Co-based materials, a feasible approach is to design new materials with enhanced catalytic behaviors. In this respect, many Co-based materials including oxides [21], nitrides [22], (oxy)hydroxides [23] and sulfides [24] have been prepared and explored as water electrolysis. However, the electrocatalytic activity of most reported Co-based catalysts are still lower than that exhibited by precious metals, and many densified efforts still need to be urgently performed in this field. Thus, it is necessary to design a new structure catalyst with highly efficient electrocatalytic activity for HER and OER in the same electrolyte.

Compared to the constructed synergistic composites, the low-dimensional (1D and 2D) materials are multifunction for catalysis than their bulk counterparts in catalytic field due to intrinsic features, such as nearly all of the atoms being exposed on the surface, high surface-to-volume ratios, specific physical, chemical and electronic properties and excellent charge-transport abilities [25]. Nevertheless, the major defect of the low-dimensional materials is the insufficient number of internal spaces and local electrons properties, inhibiting the electronic transmission characteristics [26]. In contrast to this, the 3D material contains the merits of materials of all dimensions. For example, the large open spaces can ensure easier mass transmission and stronger electronic coupling, and that provide more surface sites [27]. Although many electrocatalysts are developed in the form of powders with 3D structure, they are often measured by coating them on the conductive substrate (glass carbon or Ni foam, etc.) with polymeric binders, resulting in the depressed conductivity and the decreased active sites, which are negative for the reaction of OER and HER. Meanwhile, the powder is prone to peel off from substrate in the process of electrolysis water, which greatly deteriorates their stability. In view of this situation, designing the 3D microsphere structure composed with 1D and 2D nanosized materials on the porous and conductive substrates may be a valid method to develop highly active and durable electrode materials for overall water splitting.

Inspired by the above discussion, herein, we report a unique Co-based 3D microsphere frameworks tuned with different Ni content on the Ni/Fe foam (NFF), and they are further induced by the 2-methylimidazole to derive ZIF-67 particles (Scheme 1). This synthesis strategy discovers that the Ni dopants can simultaneously modulate the nanosheet morphology (2D to 3D) and significantly increase the electrochemical active sites. Besides, the Ni-Co layer double hydroxide salts (LHSs) further induced by 2-methylimidazole derives Co-MOF nanoparticles. Surprisingly, some of Co-based 2D nanosheets evolve into 1D nanorods due to the impact of the Ni dopants and 2-methylimidazole induction. Afterwards, the 1D nanorods and 2D nanosheets with ZIF-67 particles form typical 3D microsphere morphology by self-assembly and perfect integration, which inherit the merits of all dimension structures (1D, 2D and 3D). As a result, the 3D microsphere with high void porosity and network structure can provide facile mass diffusion and charge transport within the framework. Remarkably, among of the fabricated catalysts, the optimized Co_7Ni_3 LHSs@ZIF-67/NFF electrode exhibits superior HER and OER performances in 1.0 M KOH alkaline solution with low overpotentials of 165 and 260 mV to reach 10 mA cm^{-2}, respectively, which outperform based-noble metal catalysts. We anticipate that this work will bring a surprising perspective for fabricating nanocatalysts with new structure, which implies at an emerging strategy to obtain high-performance electrocatalysts.

2. Experimental section

2.1. Synthesis of the precursor Co_xNi_{10-x} LHSs on Ni/Fe foam (NFF) substrate

Typically, a piece of NFF foam (1 cm^2) was cleaned by ultrasonic treatment in acetone, ethanol, HCl (2 M), and deionized water solution, respectively, which would remove the surface oil stains and oxide layer. And then, $Co(NO_3)_2{\cdot}6H_2O$ (10 mmol) and $Ni(NO_3)_2{\cdot}6H_2O$ (10 mmol) with various Co^{2+}/Ni^{2+} weight ratios of 10:0, 7:3, 5:5, 3:7, and 0:10, containing urea (40 mmol) were dissolved in 40 mL deionized water. Subsequently, the mixture was transferred into a Teflon-lined stainless steel autoclave and the NFF was immersed into the precursor mixture solution. The autoclave was sealed and heated at 120 °C for 12 h. The obtained product was collected and washed with ethanol and deionized water for several times. Finally, the as-prepared materials were dried at 60 °C for 12 h.

2.2. The preparation of Co_xNi_{10-x} LHSs@ZIF-67/NFF derivatives

The Co_xNi_{10-x} LHSs @ZIF-67/NFF derivatives were carried out by the following method. 2-methylimidazole (30 mmol) was dissolved in 40 mL methanol solution, and then the as-prepared Co_xNi_{10-x} LHSs/NFF was directly immersed into the above solution at room temperature for 6 h. The resulting Co_xNi_{10-x}LHSs@ZIF-67/NFF derivatives were washed with ethanol and deionized water about 3 times to eliminate residual organic matter, and dried in vacuum at 60 °C for 12 h.

2.3. Characterization

The crystalline structures of the samples were measured through using X-ray difractometer (XRD, Rigaku). The morphology of nanocomposite catalyst was characterized by Field-emission scanning electron microscope (FESEM, JEOL, Japan). The transmission electron microscopy system (TEM, Model JEM-2100 JEOL Japan) was used to measure the microstructure of the products. The chemical bonding states of samples were identified by X-ray photoelectron spectroscopy (XPS, VG, Scientific) and FT-IR spectrometer (Nicolet 6700). The electrochemical measurements were carried out in a conventional three-electrode system, Hg/HgO electrode as reference electrode, Pt plate as counter electrode and prepared samples as working electrode.

2.4. Electrochemical measurements

The electrochemical properties experiments were performed by electrochemical workstation with a three-electrode mode (Model CHI750E, Shanghai Chenhua Instrument Co., Ltd.). The $Co(OH)_2$@ZIF-67/NFF, Co_7Ni_3 LHSs @ZIF-67/NFF, Co_5Ni_5 LHSs@ZIF-67/NFF, Co_3Ni_7 LHSs@ZIF-67/NFF and $Ni(OH)_2$/NFF catalysts were directly used as the working electrode, thus Hg/HgO electrode and platinum plate were the