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NiMn layered double hydroxide nanosheets/$NiCo_2O_4$ nanowires with surface rich high valence state metal oxide as an efficient electrocatalyst for oxygen evolution reaction

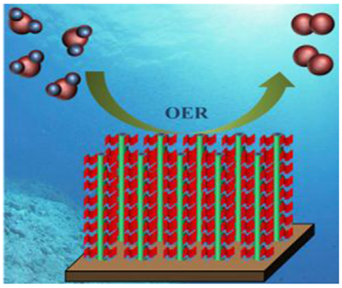
Liting Yang[a], Lin Chen[b], Dawen Yang[a], Xu Yu[a], Huaiguo Xue[a], Ligang Feng[a,*]

[a] *School of Chemistry and Chemical Engineering, Yangzhou University, Yangzhou 225002, PR China*
[b] *Department of Physics Chalmers University of Technology, SE-412 96 Göteborg, Sweden*

HIGHLIGHTS

- NiMn LDH/$NiCo_2O_4$ nanowires nanocomposite is efficient for OER.
- Catalytic performance is linked to the higher content of high valence Ni and Mn oxide.
- OER performance outperforms noble IrO_2 catalyst.
- Rate determining step on the nanocomposite electrode is changed.

GRAPHICAL ABSTRACT



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ABSTRACT

High valence transition metal oxide is significant for anode catalyst of proton membrane water electrolysis technique. Herein, we demonstrate NiMn layered double hydroxide nanosheets/$NiCo_2O_4$ nanowires hierarchical nanocomposite catalyst with surface rich high valence metal oxide as an efficient catalyst for oxygen evolution reaction. A low overpotential of 310 mV is needed to drive a 10 mA cm^{-2} with a Tafel slope of 99 mV dec^{-1}, and a remarkable stability during 8 h is demonstrated in a chronoamperometry test. Theoretical calculation displays the change in the rate-determining step on the nanocomposite electrode in comparison to $NiCo_2O_4$ nanowires alone. It is found high valence Ni and Mn oxide in the catalyst system can efficiently facilitate the charge transport across the electrode/electrolyte interface. The enhanced electrical conductivity, more accessible active sites and synergistic effects between NiMn layered double hydroxide nanosheets and $NiCo_2O_4$ nanowires can account for the excellent oxygen evolution reaction. The catalytic performance is comparable to most of the best non-noble catalysts and IrO_2 noble catalyst, indicating the promising applications in water-splitting technology. It is an important step in the development of hierarchical nanocomposites by surface valence state tuning as an alternative to noble metals for oxygen evolution reaction.

1. Introduction

Limited availability of fossil fuels and the associated environmental pollution as urgent concerns have seriously hindered human society development, and scientific experts from all over the globe are stimulated to explore alternative clean energy technology [1–3]. Hydrogen, which is regarded as an ideal energy carrier due to its high energy density and environmental friendliness, has captured increasing

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[*] Corresponding author.
E-mail addresses: ligang.feng@yzu.edu.cn, fenglg11@gmail.com (L. Feng).

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attention in the past few years [4–7]. Electrochemical water splitting that can decompose water into hydrogen and oxygen has been considered as a sustainable method to generate hydrogen among numerous energy technologies [8–10]. Nevertheless, oxygen evolution reaction (OER), a half-reaction of the electrolysis process, substantially determines the overall efficiency of water splitting. The sluggish kinetics and high overpotential for the reaction thus impede the large-scale commercialization. To date, most of the state-of-the-art OER catalysts that can tremendously improve the reaction kinetics and reduce the overpotential, are noble metal oxides such as IrO_2 and RuO_2 [11,12]. However, their high cost, scarcity and poor resources indubitably as the major bottlenecks hinder their large-scale implementation. Therefore, the exploitation of highly active and low-cost electrocatalysts for OER has attracted an interest in the field of clean and regenerated energy [13–15].

Recently, a large number of cost-effective catalysts have been fabricated in an attempt to improve the reaction kinetics and reduce the overpotential such as transition metal oxides [16,17], carbon-based materials [18–20], perovskites [21], layered double hydroxides [22] and so on. Of particular note, layered double hydroxide (LDH), a kind of multi-metal clay material consisting of divalent metals, trivalent metals and charge-balancing anions in the interspace, has emerged out among the candidate materials. Advantages of its unique structure make it have strong potential applications in the electrochemical energy catalysis reaction, such as high redox activities, versatility, tunable composition, and low cost. It has been concluded that LDHs based on 3D transition-metals had superior catalytic activity. Diaz-Morales et al. have demonstrated that NiFe, NiCr and NiMn LDHs exhibited notable performance compared to IrO_2 nanoparticles [23]. However, the conductivity of LDHs was relatively inferior, inevitably becoming a limiting factor in transferring electron and influencing the enhancement of the OER performance [24]. In order to further improve the catalytic performance, hierarchical nanocomposites based on the LDHs have been proposed such as NiMn LDH nanosheet arrays grown on KCu_7S_4 microwires [25], NiFe LDH ultrathin sheets of several atomic layers grown on $NiCo_2O_4$ nanowire arrays [26] and core-shell catalyst of Cu@NiFe LDH supported on Cu foam [27] etc. Recently, $NiCo_2O_4$ has emerged out in the field of OER for its excellent electrical conductivity, low cost, fairly low overpotential and great corrosion-resistivity in alkaline solution. In addition, benefiting from the dual contribution of nickel and cobalt, the $NiCo_2O_4$ has rich redox chemistry, making it an outstanding electrocatalyst for OER [28].

The OER is a complex process involving 4 electrons in the reaction and the catalytic mechanism is still a classic problem of current physical electrochemistry [15,29]. To realize the water oxidation to final oxygen, a multistep process is necessary to complete the 4 electrons reaction in which different intermediates are generated on the electrode surface. Hence different pathways for the OER are proposed and high valence state of the active metal oxide sites formation is regarded as a significant step during the reaction [30–32]. High valence state of metal oxide species with lower coordination number and larger H_2O molecules adsorption energy was proposed as the active catalytic sites for OER through inducing deprotonation of OOH species to produce O_2. By thermal annealing of the mixture of melamine and metal precursors, NiO/Co_3O_4@NC was synthesized and demonstrated highly efficient catalytic ability for water oxidation reaction due to high valence state of Co oxide [33]. However, the fabrication of high valence state of the active metal oxide sites is still out of control.

Inspired by the above reports, we focused our concern on hierarchical nanocomposites that can integrate advantages of different components in order to maximize the catalytic performance. In the current study, NiMn LDH nanosheets were grown on $NiCo_2O_4$ nanowires to form a novel hierarchical nanocomposite as a promising OER catalyst. Morphology of NiMn LDH nanosheets/$NiCo_2O_4$ nanowires (denoted as NiMn LDH/$NiCo_2O_4$) was observed by transmission electron microscopy and surface rich high valence Ni and Mn oxide was revealed by X-ray photoelectron spectroscopy. As expected, the hierarchical nanocomposites retained excellent mechanical integrity to ensure fast electron transportation and exhibited excellent OER performance. A low overpotential of ca. 310 mV was needed to drive the current density of 10 mA cm^{-2} for NiMn LDH/$NiCo_2O_4$ nanocomposites. It also displayed an outstanding stability for 8 h without obvious degradation at 1.65 V (vs. RHE). Theoretical calculation displayed the change in the rate-determining step on the nanocomposite and a low overpotential was both found in the theoretical and experimental results. The enhanced activity can be attributed to the synergistic effects between NiMn LDH nanosheets and $NiCo_2O_4$ nanowires in terms of the improved electrical conductivity, more accessible high valence active sites, rapid charge transfer kinetics in a hierarchical structure.

2. Experiments

2.1. Catalyst preparation

Synthesis of $NiCo_2O_4$ nanowires on Ni foam. The size of the Ni foam used in the synthesis process was 1 cm*3 cm with a thickness of 1.5 mm. $NiCo_2O_4$ nanowires on Ni foam were synthesized through a hydrothermal method followed by thermal annealing at high temperature. First of all, the Ni foam was cleaned in acetone and 1.0 M HCl solution under ultrasonication conditions for 10 min and then rinsed repeatedly with ethanol and water to remove the nickel oxide. Secondly, 10 mmol $CoCl_2$•$6H_2O$, 5 mmol $NiCl_2$•$6H_2O$, and 15 mmol urea were dissolved in 75 mL of water and magnetically stirred for 30 min to form a homogeneous pink solution. And then the solution was transferred to a stainless Teflon-lined autoclave with the inner volume of 100 mL, and a piece of the cleaned Ni foam was immersed in the solution. Finally, the autoclave was sealed and placed in an electric oven at a temperature of 120 °C for 6 h. When the temperature naturally cooled down to room temperature, the as-obtained nanocomposites were washed with water and ethanol for several times to remove the residual ingredients. Finally, $NiCo_2O_4$ nanowires on Ni foam were obtained by the thermal annealing at 400 °C in an air atmosphere for 3 h to realize the transformation from the NiCo precursor to $NiCo_2O_4$.

Synthesis of NiMn LDH/$NiCo_2O_4$ nanocomposites. 9 mmol of $Ni(NO_3)_2$•$6H_2O$, 3 mmol of $Mn(NO_3)_2$•$4H_2O$, 20 mmol of urea, and 1 mmol of $Na_3C_6H_5O_7$•$2H_2O$ were dissolved in 100 ml of water and stirred for 30 min to make a homogeneous solution. Subsequently, the as-obtained $NiCo_2O_4$ nanowires on Ni foam were immersed in the solution, and then the mixture was transferred to a 150 mL of autoclave and hydrothermally treated at 150 °C for 48 h to grow NiMn LDH nanosheets on the $NiCo_2O_4$ nanowires. After the solution was cooled down to room temperature, the products were washed using distilled water and ethanol and dried in an oven at 60 °C overnight to finally obtain the NiMn LDH/$NiCo_2O_4$ nanocomposites. For comparison purposes, the growth of $NiCo_2O_4$ nanowires on Ni foam was also synthesized as the control sample by hydrothermal and thermal annealing.

2.2. Characterization

The X-ray diffraction (XRD) was measured by a Bruker AXS D8 ADVANCE X-ray diffractometer with Cu-Ka radiation ($\alpha = 0.15148$ nm) operating at 30.0 kV and 20.0 mA. The sweep range was from 10° to 80° and the sweep speed was $5^{\circ}min^{-1}$. X-ray photoelectron spectroscopy (XPS) analysis which was employed to probe the elemental composition and chemical valence states of the nanocomposite was performed on an X-ray photoelectron spectrometer (Thermo Scientific ESCALAB 250Xi). The morphologies of the catalysts were observed by scanning electron microscopy (FESEM, Hitachi, S-4800 II, Japan) and transmission electron microscopy (TEM, Philips, TECNAI 12, Holland). High-resolution TEM (HRTEM) images and energy dispersive X-ray spectroscopy (EDS) mapping were captured on the Tecnai G2 F30 transmission electron microscope (acceleration