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Blending Fe_3O_4 into a Ni/NiO composite for efficient and stable bifunctional electrocatalyst

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ABSTRACT

As a promising strategy for clean energy production, electrochemical water splitting requires high-efficient, well-stable, and earth-abundant electrocatalysts to realize its practical application. Herein, we report a heterogeneous Fe_3O_4-blended Ni/NiO composite fabricated through a salt-template method as highly active bifunctional catalysts for both oxygen evolution reaction (OER) and hydrogen evolution reaction (HER). To reach a current density of 10 mA cm^{-2}, the Ni/NiO/Fe_3O_4 requires low overpotential of 258 mV for OER in alkaline media and 206 mV for HER in acidic media, respectively, much lower than those of Ni/NiO, Fe_3O_4 and other Ni-based oxides. The excellent electrocatalytic performance can be ascribed to the enhanced charge-transfer kinetics between Ni and Fe sites and improved active sites resulted from the large nano-interface between Ni compounds and Fe_3O_4. This work provides a new method to design high-performance non-noble metal Ni-based electrocatalysts by incorporating Fe-doping and nano-interface-fabrication together, which can also be applied to develop other novel hybrid electrocatalysts for practical application.

1. Introduction

Electrochemical water splitting involving cathodic two-electron hydrogen evolution reaction (HER) and anodic four-electron oxygen evolution reaction (OER) is a promising way to generate hydrogen thus supply clean and renewable energy [1,2]. For high-efficiency electrocatalytic hydrogen generation, both the OER and HER processes have to occur with fast rate. The HER is a relatively thermodynamics-facile reaction and can be catalysed by many efficient electrocatalysts at low overpotential [3,4]. However, the slow kinetics of OER with large reaction barriers often leads to high overpotentials causing the energy expenditures [5,6]. To rationally design a high-efficient electrocatalyst toward OER, it is necessary to lower the overpotential, accelerate the reaction kinetics, and enhance the specific activity, thus improve the energy utilization. To this end, efficient OER electrocatalysts have been studied to accelerate the water oxidation reaction, but the most active compounds are based on the scare and expensive IrO_2 and RuO_2 severely restricting their large-scale applications [7,8]. Therefore, it would be desirable to develop efficient earth-abundant and low-cost electrocatalysts for high-rate water oxidation.

Among nonprecious electrocatalysts, Ni-based complexes have gained great interest because of their low-cost nature and excellent electrocatalytic properties for HER and OER [9–11]. However, most of them still suffer from large overpotential for good OER activity, and their catalytic properties and long-term stability are required to be further improved. Recent studies demonstrated that the addition of Fe, even in trace amount, was thought to greatly improve the OER and HER activity of Ni-based compounds due to the enhanced conductivity and strong synergistic effect in alkaline solutions though the accurate mechanisms and structural characteristics are not yet fully understood [12–14]. In addition to the trace-doping, artificially fabricating the interface of two non-noble metal oxides/sulfides nanoparticle electrocatalysts is recently a novel method to improve their OER and HER capability due to the much faster charge-transfer kinetics resulting from the large interface and the synergetic effects between the different metal

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atoms as well as vacancies at the interface region [15–17]. For example, Zhu et al. reported that Co_9S_8@MoS_2 core-shell architecture could act as a bifunctional catalyst for both OER and HER [18]. The synergetic effects of the nano-interface generated between the Co_9S_8 core and the MoS_2 shell benefit the strong electron transfer between Co and Mo atoms, causing the superior electrocatalytic properties. Zhang and co-workers found that TiO_2 drove from NiTi layered double hydroxides precursors can stabilize the NiO nanosheets, and the hybrid nanostructure can be used as high-performance catalyst for OER [19]. In their results, intrinsic Ni^{3+} and Ti^{3+} sites, and the plentiful nano-interfaces act synergistically to promote charge-transfer between NiO and TiO_2 and reduce the H_2O adsorption energy, thus improving the OER properties. Guo's group designed NiO/CoN porous nanowires with both oxygen vacancies and a strongly interconnected nano-interface between NiO and CoN domains for promoting the electrocatalytic performance and stability for OER [20]. All above-mentioned research suggest that reasonable design of the nano-interface existed in heterostructured metal oxides or sulphides could be an efficient way to develop high-active OER and HER catalysts.

Herein, inspired by Fe-doping that could greatly improve the OER and HER activity of Ni-based compounds and heterostructured composites with abundant interfaces that facilitate charge separation and transfer, we designed a novel and low-cost Ni/NiO/Fe_3O_4 composite catalyst for high-rate water oxidation by composing Fe_3O_4 into Ni/NiO electrocatalyst. As expected, the introduction of Fe_3O_4 could largely enhance the charge transfer between Ni and Fe sites, and supply more active sites for OER and HER due to the interface effects between Ni compounds and Fe_3O_4. This strategy reveals the essence of the synergetic effects in heterostructured composites, and provide guidance for the design of highly active non-noble metallic catalysts for efficient water splitting.

2. Experimental section

2.1. Materials

$FeCl_3 \cdot 6H_2O$ (99%), $NiCl_2 \cdot 6H_2O$ (99%), sodium oleate (82%, anhydrous), sodium sulphate (99%, anhydrous), and potassium hydroxide (KOH) were purchased from Aladdin Ltd. (Shanghai, China). Nafion (5 wt%) was purchased from Sigma-Aldrich. All the reagents were used without any purification.

2.2. Preparation of Ni/NiO/Fe_3O_4, Ni/NiO and Fe_3O_4 catalysts

The catalysts are prepared using a salt-template method. For Ni/NiO/Fe_3O_4, 0.144 g of $NiCl_2 \cdot 6H_2O$ and 0.24 g of $FeCl_3 \cdot 6H_2O$ were dissolved in 1 ml water to obtain a yellowish clear solution. 1.83 g of sodium oleate was later added into the yellowish clear solution, and the mixture was vortexed until there is an even coating of the yellowish solution on the sodium oleate. The mixture was then baked in the oven at 80 °C for 3 h to obtain the metal-oleate complex. After baking for 3 h, the mixture was later grinded with 10 g of Na_2SO_4 for at least 10 min to obtain even coating of metal-oleate complex. The metal-oleate complex coated Na_2SO_4 was then calcinated at a ramping rate of 5 °C min^{-1} to 600 °C for 3 h in N_2 environment. The calcinated sample was washed with water and ethanol for several times before collecting the dried sample by freeze-drying. The preparation of Ni/NiO and Fe_3O_4 catalysts are similar with the synthesis of Ni/NiO/Fe_3O_4 except without addition of $FeCl_3 \cdot 9H_2O$ and $NiCl_2 \cdot 4H_2O$, respectively.

2.3. Electrochemical measurements

Catalyst inks are prepared by dispersing 4 mg of the as-prepared Ni/NiO/Fe_3O_4 (Ni/NiO or Fe_3O_4) catalyst and 1 mg acetylene black in a mixture of 175 μl ethanol and 47.5 μl Nafion and then sonicated for 30 min to form a homogeneous ink. A specific volume of the ink was dropped onto the glassy carbon electrode to a form a thin film with a loading of 0.5 mg/cm^2. The resulting electrodes were dried in air under ambient conditions for at least 30 min. Electrocatalytic performance such as cyclic voltammetry (CV), LSV and chronopotentiometry are performed on a Gamry Reference 3000 electrochemical instrument using a three-electrode electrochemical system in 1 M KOH solution for OER and 0.5 M H_2SO_4 solution for HER. Specifically, catalysts coated on glassy carbon electrode, Pt wire and Ag/AgCl (in saturated KCl solution) are used as the working electrodes, counter electrode, and the reference electrode, respectively. All potentials are referred to the reversible hydrogen electrode by adding a value of $(0.196 + 0.059 \times \text{pH})$ V. LSVs are measured at a scan rate of 2 mV s^{-1}. Tafel slopes are calculated based on the LSV curves by plotting the potential against log(j), where j is the current density. Chronopotentiometry measurements are carried out at a current density of 50 mA cm^{-2} for OER and −10 mA cm^{-2} for HER. The electrochemical impedance spectroscopy (EIS) was measured using AC impedance spectroscopy over a frequence range of 0.01 Hz−10000 Hz at overpotentials of 370 mV for OER and 300 mV for HER.

2.4. Characterizations

The catalysts are characterized by X-ray diffraction pattern (XRD, X′ Pert PRO, PANalytical B.V., the Netherlands). The scanning electron microscope (SEM) images of the catalysts are obtained with a JEOL JSM 6700F electron microscope. The morphology and structures are examined using the transmission electron microscope (TEM) and HRTEM (Philips Tecnai F20). The chemical compositions of the prepared catalysts are acquired using a Kratos Axis ULTRA X-ray photoelectron spectrometer. The energy scale was calibrated to the C 1s peak maximum at 284.5 eV.

2.5. Double layer capacitance (C_{dl}) measurements

The electrochemically active surface areas of the catalysts are compared on a relative scale using the capacitance of the electrochemical double layer (C_{dl}) on the electrode-electrolyte interface. This comparison is validated, as ECSA is proportion to C_{dl}, which assumes that the measured current at the non-Faradaic region (i_c) is due to the charging of the double-layer capacitor. Thus, the current i_c is proportional to the scan rate ν: $i_c = \upsilon C_{dl}$. To estimate the C_{dl}, the catalysts are loaded on the glassy carbon electrode using the procedure described above. CV measurements with different scan rates from 10 to 50 mV s^{-1} are carried out in the potential region of 0.2−0.3 V *vs* Ag/AgCl (the non-Faradaic region) for OER and −0.2 to −0.1 V *vs* Ag/AgCl for HER.

2.6. Calculation

During OER and HER process, a constant potential of 1.54 and −0.28 V vs. RHE were applied to the electrodes and the volume of the evolved gas was recorded using the gas buret. Thus the Faradaic efficiency can be calculated as:

$$\text{Faradaic efficiency} = \frac{n\ (\text{experimental})}{n\ (\text{theoretical})} \times 100$$

where n (experimental) is the number of moles of the evolved gas (O_2 or H_2) form the experiment. n (theoretical) is the number of moles of the gas produced theoretically, which can be calculated using the following equation: