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Facile construction of ultrafine nickel-zinc oxyphosphide nanosheets as high-performance electrocatalysts for oxygen evolution reaction

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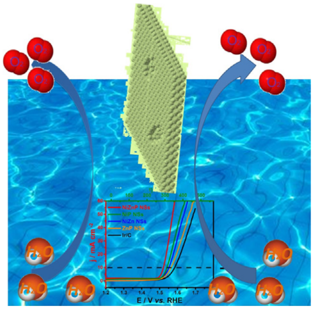
GRAPHICAL ABSTRACT



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ABSTRACT

Realizing the synthesis of highly efficient electrocatalysts for water splitting is generally regarded as a significant section in the field of renewable energy conversion and storage but still an intriguing challenge. Here, a series of transition metal oxyphosphides with ultrafine nanosheet structure have been successfully created as high-performance electrocatalysts for oxygen evolution reaction (OER). Taking advantages of the abundant surface defects, modified electronic effects, as well as the high surface active areas, we herein successfully construct a novel class of highly-efficient electrocatalysts, and the resultant NiZn oxyphosphide nanosheets (NiZnP NSs) can exhibit relatively low overpotentials of 290 and 332 mV to achieve the current densities of 10 and 50 mA cm^{-2} for OER, respectively, outperforming most of non-noble metal electrocatalysts. More impressively, such NiZnP NSs can also retain high catalytic activity with negligible composition and structure variations after long-term electrochemical test. This work provides prospects to construct highly efficient, earth abundant, and ultra-durable two-dimensional (2D) electrocatalysts for water splitting.

1. Introduction

Increasing energy shortage and environmental issues have stimulated more researches on the development of renewable energy [1–3]. Hydrogen, as a clean and renewable energy source, is generally regarded as one of the most potential alternatives to traditional fossil fuels [4,5]. Electrochemical water splitting is an efficient strategy for the production of hydrogen in large quantities, which consists of two main reactions including anodic OER and cathodic hydrogen evolution reaction (HER) [6–8]. In terms of these two half reaction, OER is the bottleneck due to the typical four electron process for the formation of O—O bond, leading to the sluggish reaction kinetics [9–11]. Accordingly, to address this issue, designing and engineering highly active electrocatalysts are crucially needed. Update, extensive research attentions have been focused on the design and development of platinum group metals (PGMs) such as Pt-, Ir-, and Ru-based materials because of their

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intrinsic electrochemical properties [12–14]. However, some drawbacks regarding exorbitant price and scarcity, as well as poor durability greatly hinder their practical applications in water splitting [15–17]. Consequently, the design and development of highly efficient PGM-free electrocatalysts are significant for the extensive application of hydrogen energy.

In recent years, transition-metal-based materials have been demonstrated to be alternative electrocatalysts for OER [18–20]. Among them, multicomponent nickel-based materials have appealed increasing attentions because of their outstanding electrocatalytic performances in OER [21,22]. And the high performances of nickel-based electrocatalysts are primarily ascribed to abundant active sites on nickel surface [23–26]. Although intensive efforts have been dedicated to improving the electrocatalytic performances of Ni-based electrocatalysts, the relatively low active areas in alkaline media remains a big problem that limiting the exposed active sites and poor mass transfer, resulting in unsatisfactory electrocatalytic performances in OER [27,28]. Therefore, it is necessary to engineer the Ni-based electrocatalysts with more surface active sites [29,30].

In general, the active sites of Ni-based catalysts can be increased via many strategies. On one hand, the phosphorization of metals is also generally considered as a favorable approach for achieving the desirable electrocatalytic performances [31,32]. In essential, the doping of P atom can modify the binding energy between hydrogen and metal, resulting in the optimal Gibbs free energy for water splitting [33,34]. On the other hand, extensive studies have reported that the electrochemical properties of catalysts are also greatly depended on their structure, shape, and size [35–38]. Therefore, the construction of well-defined structure can facilitate the mass diffusion/transport of OH^- ions and further increase the utilization efficiency of catalytic active sites, promoting and releasing the gas bubbles, as well as boosting the electron transport, which is efficient for the substantial enhancement of electrocatalytic performances [39,40]. More significantly, the 2D NSs with abundant oxygen vacancies can also greatly enhance the electronic conductivity and facilitate the adsorption of H_2O on the nearby active sites [41].

With the aim of synthesizing high-performance OER electrocatalysts, herein we propose a simple and efficient method for the synthesis of well-defined NiZnP NSs as high-efficiency electrocatalysts towards OER. The earth-abundant NiZnP NSs were realized by co-reducing $NiCl_2{\cdot}6H_2O$, $Zn(NO_3)_2{\cdot}6H_2O$, and NaH_2PO_2 at ambient temperature, enabling the generation of rich oxygen vacancies assisted by $NaBH_4$ and polyvinylpyrrolidone (PVP). Significantly, the 2D NiZnP NSs display outstanding electrocatalytic performances towards OER with a relatively low overpotential of 290 mV to achieve the current density of 10 mA cm^{-2} in 1 M KOH solution, much lower than that of Ir/C catalysts, suggestive of its promising properties for practical OER applications.

2. Experimental section

2.1. Chemicals and materials

Potassium hydroxide (KOH, analytical reagent), nickel chloride ($NiCl_2{\cdot}6H_2O$, analytical reagent), zinc nitrate ($Zn(NO_3)_2{\cdot}6H_2O$, analytical reagent), 100 mg Polyvinylpyrrolidone (PVP, 8000 K) sodium hypophosphite (NaH_2PO_2, analytical reagent), potassium hydroxide (KOH, analytical reagent), and sodium borohydride ($NaBH_4$) were all purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). All the chemicals were used as received without further purification. The water (18 MΩ cm^{-1}) used in all experiments were prepared by passing through an ultra-pure purification system (Aqua Solutions).

2.2. Synthesis of NiZnP NSs

The preparations of 2D NiZnP NSs can be realized based on the co-reduction of $NiCl_2{\cdot}6H_2O$, $Zn(NO_3)_2{\cdot}6H_2O$, and NaH_2PO_2 using $NaBH_4$ as reducing agent at ambient temperature, where selecting PVP as protecting agent. In the standard synthesis of 2D NiZnP NSs, 100 mg PVP were dissolved into 10 mL deionized water to form a homogeneous solution. Then, 10 mM $NiCl_2{\cdot}6H_2O$, 10 mM $Zn(NO_3)_2{\cdot}6H_2O$, and 3 mM NaH_2PO_2 were added into above solution in sequence. After that, 2 mL freshly prepared (0.5 M) $NaBH_4$ solution was then dropped into above solution under violently stirring. For comparison, the NiZn, NiP, and ZnP NSs were also prepared using the same method while without the addition of NaH_2PO_2, $Zn(NO_3)_2{\cdot}6H_2O$, and $NiCl_2{\cdot}6H_2O$, respectively. The products were collected by centrifugation and washed several times with the mixture of ethanol and acetone.

2.3. Characterization

Energy dispersive X-ray (EDX) patterns were acquired by using a XL30 ESEM FEG scanning electron microscope at an accelerating voltage of 20 kV. Low-magnification transmission electron microscope (TEM) was conducted on a HITACHI HT7700 TEM at an acceleration voltage of 120 kV. The samples were prepared by dropping cyclohexane dispersion of samples onto carbon-coated copper TEM grids using pipettes and dried under ambient condition. X-ray photoelectron spectroscopy spectra (XPS) were conducted on a Thermo Scientific ESCALAB 250 XI X-ray photoelectron spectrometer. Powder X-ray diffraction (PXRD) patterns were collected on X'Pert-Pro MPD diffractometer (Netherlands PANalytical) with a Cu Kα X-ray source ($\lambda = 1.540598$ Å).

2.4. Electrochemical measurements

All electrochemical measurements were conducted by a standard three-electrode cell which consisted of a glassy-carbon electrode (GCE) (diameter: 3 mm, area: 0.07 cm^2), a Ag/AgCl electrode, and a carbon rod as the working, reference, and counter electrode, respectively. The polarization curves were acquired using linear sweep voltammetry (LSV) for OER in 1 M KOH solution at the sweeping rate of 5 mV/s. iR drop was compensated at 95% for OER using the CHI 760E electrochemistry workstation. The Tafel plots were derived from the OER polarization curves and constructed by the Tafel equation. The long-term stability test for NiZnP NSs was carried out by chronopotentiometric (CP) measurements. Besides, the LSV after successive 3000 cycle CV was also performed to evaluate its durability. Moreover, we have also conducted the electrochemical impedance spectroscopy (EIS) at the potential of 1.6 V to study the electrical conductivity of electrocatalysts. Notably, all the potentials measured were calibrated to reverse hydrogen electrode (RHE) and the state-of-the-art Ir/C were also employed as the baseline catalysts for all the electrochemical measurements.

3. Results and discussion

The synthesis of NiZnP NSs was performed by a facile phosphorization processing by employing $NaBH_4$ to co-reduce all the precursors under air atmosphere. The morphology, composition, and structure of the as-prepared NiZnP NSs were characterized by TEM, EDX, and PXRD. Fig. 1 showed the typical TEM images, EDX and XRD patterns of the NiZnP nanomaterials. As is shown in Fig. 1a–d, the as-prepared NiZnP nanomaterials showed a typical 2D microstructure, which included abundant self-assembled curly nanosheets, suggesting the successful production of 2D nanosheet