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Mn-doped NiP_2 nanosheets as an efficient electrocatalyst for enhanced hydrogen evolution reaction at all pH values

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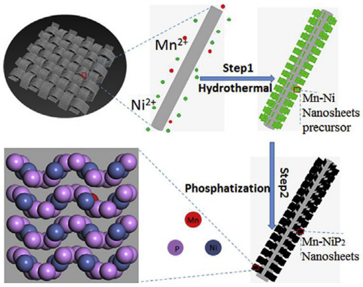
HIGHLIGHTS

- Mn-NiP_2 NSs was synthesized by high temperature toptactic phosphidation route.
- Mn-NiP_2 NSs delivers higher catalytic activities for HER at all pH values.
- The catalytic performances for Mn-NiP_2 NSs were explored by DFT calculations.

GRAPHICAL ABSTRACT



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ABSTRACT

Developing stable and high-efficiency hydrogen generation electrocatalysts, particularly for the cathode hydrogen evolution reaction (HER), is an urgent challenge in energy conversion technologies. In this work, we have successfully synthesized Mn-doped NiP_2 nanosheets on carbon cloth (Mn-NiP_2 NSs/CC), which behaves as a higher efficient three dimensional HER electrocatalyst with better stability at all pH values than pure NiP_2. Electrochemical tests demonstrate that the catalytic activity of NiP_2 is enhanced by Mn doping. In 0.5 M H_2SO_4, this Mn − NiP_2 NSs/CC catalyst drives 10 mA cm^{-2} at an overpotential of 69 mV, which is 20 mV smaller than pure NiP_2. To achieve the same current density, it demands overpotentials of 97 and 107 mV in 1.0 M KOH and phosphate-buffered saline (PBS), respectively. Compared with pure NiP_2, higher HER electrocatalytic performance for Mn − NiP_2 NSs/CC can be attributed to its lower thermo-neutral hydrogen adsorption free energy, which is supported by density functional theory calculations.

1. Introduction

Nowadays, increased concern over environmental pollution and depletion of energy have putted forward an urgent demand for finding pollution-free and sustainable energy to alternate fossil oil. Hydrogen, as a high energy density and zero emission of greenhouse gas, is considered as an ideal candidate [1–5]. H_2 can be produced on a broad scale by electrolysis water splitting, but it is prerequisite that a high-effective electrocatalyst for HER is for affording a high current at a low overpotential [2,6,7]. Pt is the most active and stable catalyst under strongly acidic conditions, which is widely used in water electrolysis, but suffers from scarcity and high cost limits [8–12]. What's more, microbial and alkaline electrolysis cells require HER catalysts working in neutral and alkaline media, respectively. Therefore, to produce hydrogen economically and efficiently, it is required to develop low-cost and highly active catalysts for HER over the entire pH range [1,3,7,12].

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Ni has emerged as a high electrocatalytic active non-noble metal for HER and there has been a significant development in Ni-based HER electrocatalysts [7,13–22]. Recently, transition metal phosphides (TMPs) prepared by phosphating metal oxides, as a semi-metal, possess good electrical conductivity, exhibit high efficiency of electrochemical water splitting [7,23–25]. Within all the TMPs, Ni phosphides have received a wide spread attention for HER electrocatalysis on large scale PH because of their high activity and corrosion resistance [5,7]. It is noted that electrocatalytic active is largely relied on the hydrogen adsorption energy and kinetic energy barrier of HER pathway, which could be effected by atom type or crystal phase exposed on the catalyst surface. Relevant efforts have been paid on enhancing electrocatalytic performance by substituting other transition metals such as Co, Mo, Fe [26–28]. Besides, Sun et al. reported that Mn substitution of Co in CoP possesses an excellent HER performance by lowering the energy barrier [29]. Through the above analysis, proper amount of doping with heteroatoms can help reduce hydrogen adsorption energy and kinetic energy barrier, and mixed TMPs also exhibit higher electrocatalytic HER activity than pure TMPs. However, the effect of Mn atoms on the transition metal poly-phosphides toward HER performance has never been investigated.

In this study, we present our recent finding that Mn-doped NiP_2 nanosheets on carbon cloth, as a high efficient and robust monolithic three dimensional HER electrocatalyst superior to NiP_2 nanosheets over the wide range of pH 0–14. Our experiments demonstrated that only 69, 97, and 107 mV of over-potentials are demanded for $Mn-NiP_2$ NSs/CC to achieve 10 $mA\,cm^{-2}$ in 0.5 M H_2SO_4, 1.0 M KOH, and 1.0 M PBS, respectively. DFT calculations provided a strong proof that Mn doping can weaken the bonds between surface and H atoms, resulting in lower thermo-neutral hydrogen adsorption free energy (ΔGH^*).

2. Experimental

2.1. Materials

CC was provided by Shanghai Dongli Corp. $Ni(NO_3)_2{\cdot}6H_2O$, $MnSO_4{\cdot}3H_2O$, NH_4F, and urea were purchased from Tianjin Fuchen Chemical Reagent Factory. KOH, H_2SO_4, ethanol, NaH_2PO_4, and Na_2HPO_4 were purchased from Beijing Chemical Corp. Hydrochloric acid was purchased from Shanghai Aladdin Biochemical Technology. All reagents were not further purified. The water was treated using a Millipore system in all experiments.

2.2. Preparation of NiP_2 NSs/CC and $Mn-NiP_2$ NSs/CC

First, Mn-doped $Ni(OH)_2$ Nanosheets precursor (Mn-Ni NSs precursor) were synthesized in a typical procedure, $Ni(NO_3)_2{\cdot}6H_2O$ (4 mmol), $MnSO_4{\cdot}H_2O$ (0.2 mmol), NH_4F(16 mmol) and $CO(NH_2)_2$ (20 mmol) were dissolved in 72 mL of distilled water and stirred for 0.5 h to form a transparent and uniform solution. Prior to utilization, CC (about 3 cm × 2.5 cm) was carefully cleaned using ultrasound method in concentrated HNO_3 solution for 1 h in order to remove the surface dirt, and then washed by ethanol and deionized water for 30 min, respectively, which ensures that CC was well cleaned. The precursor solution and the CC were putted into a 25 mL Teflon-lined stainless-steel autoclave, and maintained at 100 °C for 8 h, then cooled to room temperature naturally. The Mn-Ni NSs precursor was taken out and swilled with water repeatedly before dried at 60 °C for 6 h. To prepare $Mn-NiP_2$ NSs/CC, Mn-Ni Nanosheets precursor and 20 mg red phosphorus were sealed in a quartz tube at 10^{-4} Pa, and then it was heat treated at 550 °C for 2 h. The reaction products were thoroughly washed with deionized water, ethanol and dried under 40 °C for 60 min at last. The mass loading of the $Mn-NiP_2$ NSs catalyst was approximately 4.4 $mg\,cm^{-2}$, determined by using a high precision microbalance (Mettler Toledo ML104, 0.1 mg resolution). For searching for an optimum condition, $Mn-NiP_2$ nanosheets on CC with different Mn doping concentrations have also been prepared.

2.3. Characterization

X-ray powder diffraction (XRD) patterns was measured using X-ray diffractometer (Rigaku D/max 2500) operating at 40 kV and 50 mA using Cu Kα radiation. The morphologies and structures of samples were measured by making use of transmission electron microscopy (TEM, FEI TECNAI G2 F20) and Field emission scanning electron microscopy (FE-SEM, TESCAN MIRA3) with an energy dispersive X-ray spectrometer (EDS). X-ray photoelectron spectroscopy (XPS) was performed by using Thermo ESCALAB 250Xi (Thermo) with an Al Kα (1486.6 eV) to probe the surface chemical compositions.

2.4. Electrochemical measurements

Electrochemical catalytic performance were performed using an electrochemical workstation (CH Instruments, Shanghai, China) at 25 °C, by using a standard three-electrode cell system, in which graphite rod was used as the counter electrode, saturated calomel electrode (SCE) (in alkaline solution) and Ag/AgCl (in acidic and neutral medium) as the reference electrode. Polarization LSV data was tested at the scan rate of 2 $mV\,s^{-1}$. The iR correction was conducted by a bundled software of the electrochemical workstation. In this work, only LSVs and Tafel plots were iR corrected. The long-term durability test was performed using continuous cyclic voltammetry and the time dependency of polarization currents during electrolysis process was tested at constant voltage. Electrochemical impedance measurements was probed in different potentiostatic modes in the frequency of 0.1 Hz–10^5 Hz.

2.5. DFT calculations

DFT calculations were performed using the Vienna ab initio simulation package (VASP). We used the PBE functional for the exchange-correlation energy and projector augmented wave (PAW) potentials. The kinetic energy cutoff was set to 450 eV. The ionic relaxation was performed until the force on each atom is less than 0.02 eV/Å. The k-points meshes was 3 × 3 × 1 by using Monkhorst-Pack method [24,30]. Our calculations manifested that the surface energies (E_{surf}) of (111), (101), (011), (110), (100), (001), and (010) facets are 0.059, 0.069, 0.069, 0.069, 0.069, 0.047, 0.047, 0.047 $J\,m^{-2}$, respectively. Here, Esurf = (E_{total}/N - E_{bulk})/S, in which S, E_{bulk} and E_{total} are the surface area, the energy of bulk NiP_2 and the energy of the model used in our calculations, respectively. As the surface of (100) have a lowest energy, which means that it is thermodynamically most stable, so we chose the (100) facet to interpret the HER mechanism in our model. A vacuum must be considered to avoid undesired interactions between images, we chose at least 15 Å vacuum along the z axis in our model. A supercell containing 15 Å vacuum space and a four-layered (2 × 2) NiP_2 (100) slab was used to evaluate the performance of electrocatalytic hydrogen produce. The free energy change for H adsorption on (2 × 2) NiP_2 (100) surface was calculated as follows, which is proposed by Norskov and coworkers [30]:

$$\Delta GH^* = E_{total} - E_{surf} - EH_2/2 + \Delta EZPE - T\Delta S$$

where E_{total} is the total energy for the adsorption state, E_{surf} is the energy of pure surface, E_{H2} is the energy of H_2 in gas phase, ΔEZPE is the zero-point energy change and ΔS is the entropy change.

3. Results and discussion

As shown in Scheme 1, $Mn-NiP_2$ NSs/CC electrode was prepared by the following two steps: (1) Mn-Ni NSs precursor was prepared by hydrothermal synthesis on CC; (2) Mn-Ni NSs precursor was phosphided by red phosphorus to form $Mn-NiP_2$ nanosheets. The colour of CC turns