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*Corresponding author

Zheng Yin, Key Laboratory of Auxiliary Chemistry and Technology for Chemical Industry, Ministry of Education, Shaanxi Collaborative Innovation Center of Industrial Auxiliary Chemistry and Technology, College of Chemistry and Chemical Engineering, Shaanxi University of Science and Technology, Xi'an 710021, Xi'an Lanqiao New Energy Technology Co., LTD, Xi'an 710018, P. R. China

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Short Communication

MOF-Derived NiP_x/C Nanocomposites as Bifunctional Electrocatalysts for Enhanced Water Splitting

Jing-Yi Wang[1], Dan-Jiang Tang[1,2], Peng-Wei Zhang[2*] and Zheng Yin[1,2*]

[1]Key Laboratory of Auxiliary Chemistry and Technology for Chemical Industry, Ministry of Education, Shaanxi Collaborative Innovation Center of Industrial Auxiliary Chemistry and Technology, College of Chemistry and Chemical Engineering, Shaanxi University of Science and Technology, Xi'an 710021, P. R. China

[2]Xi'an Lanqiao New Energy Technology Co., LTD, Xi'an 710018, P. R. China

Abstract

MOF-derived transition metal phosphides possess a large specific surface area and excellent electrical conductivity, thereby exposing an abundance of catalytically active sites. In this study, NiP_x/C-400 °C nanocomposites were synthesized via medium-temperature phosphidation using Ni-MOF as a precursor template. The rich catalytic active sites in NiP_x/C-400 °C endow it with superior electrocatalytic performance for both oxygen evolution reaction (OER) and hydrogen evolution reaction (HER). When the electrocatalyst NiP_x/C-400 °C was deposited on nickel foam, it exhibited low overpotentials of 311 mV at 10 mA cm^{-2} for OER and 77 mV at 10 mA cm^{-2} for HER in 1 mol/L KOH solution. Moreover, overall water splitting could be achieved at a cell voltage as low as 1.69 V.

Introduction

With the increasing global energy demand and the serious environmental problems caused by the rapid consumption of fossil fuels, it is of great significance to explore advanced energy storage and conversion technologies [1]. As the key to energy conversion and storage, electrocatalytic reactions require efficient and stable electrocatalysts in the catalytic process to enhance the rate and selectivity in the optimized reaction process [2]. The great challenge is the need for electrocatalysts with sufficient activity to improve the efficiency of electrocatalytic reactions. To date, typical commercial catalysts used for electrocatalytic total hydrolysis are noble metal (Pt, Ru, and Ir) based materials, and the high cost and limited service life associated with these materials have severely hampered their widespread application [3]. The development of efficient, stable and inexpensive electrocatalysts is still the core challenge in the field of photovoltaic/wind power decomposition of water to produce green hydrogen. 3d transition metal elements are abundant, inexpensive and environmentally friendly, and their unique d-electronic grouping structure has brought about a rich variety of electrocatalytic applications, and the design and construction of new types of electrocatalysts based on 3d metals is one of the most promising frontiers of research in the field [4,5]. Transition metal phosphides (TMPs) have unique electrically charged properties and are considered as one of the most promising electrocatalysts for overall water splitting [6-8]. The presence of P elements in TMPs can further improve the catalytic performance by tuning the electronic structure and greatly increasing the catalytic activity. On the one hand, TMPs have good compositional sustainability, which can adjust their electronic structure and optimize the adsorption of intermediates. On the other hand, the multiple active sites derived in TMPs also help to further improve the electrocatalytic performance. Therefore, amorphous TMPs have received increasing attention as ideal electrocatalysts for water decomposition.

As a new type of functional materials, metal-organic skeletons (MOFs) have the advantages of large specific surface area [9,10], tunable crystal structure, and high porosity, which make them widely used in the fields of catalytic reaction, adsorption and separation, and drug delivery [11,12]. However, due to the poor electrical conductivity and structural stability of most of the pristine MOF materials, a large number of researchers have focused on MOF-derived materials such as metal carbides, oxides, phosphides and sulfides. In this paper, Ni-MOF with linear $[Ni_3(COO)_6]$ node was used as a precursor template, and NiP_x/C-400 °C material was prepared by medium temperature phosphorylation. As a result, this MOF-derived NiP_x/C nanocomposites can perform as bifunctional electrocatalysts for enhanced water splitting.

Synthesis Method

Preparation of Ni-MOF

$Ni(NO_3)_2{\cdot}6H_2O$ (0.1 mmol, 0.0290 g), H_3bpt (0.25 mmol, 0.0716 g) were weighed and dissolved in a mixture of DMF (14.0 mL), EtOH (2.0 mL) and H_2O (2.0 mL), and the mixture was stirred for 10 min, and then transferred to a 25 mL high-pressure reactor lined with PTFE. The reaction was carried out in an oven at 140 °C for 48 h. The reactor was then removed and cooled to room temperature, and the product was observed as a light green rod-shaped crystal under a microscope. The obtained product was filtered and washed with DMF for three times, and the crystals were dried at room temperature for subsequent thermal treatment.

Preparation of electrocatalysts

200 mg of NaH_2PO_2 and 10 mg of Ni-MOF (20:1) were placed in the upstream and downstream boats respectively, and the two boats were separated by about 2 cm, and heated to the target temperature of 400 ℃ under N_2 atmosphere at a heating rate of 5 ℃ min^{-1} and held for 3 h. Subsequently, 5 mg of the sample was weighed and grinded in a mortar, and then the grinded sample was transferred to the sample tube, and 970 μL of methanol and 30 μL of naphthol were added into the sample tube and sonicated for 30 min to form a suspension by taking 13~15 μL of the suspension in batches and dropping it onto the foam. Then, 970 μL of methanol and 30 μL of naphthol were added into the sample tube, and ultrasonication was performed for 30 min to make the suspension uniformly dispersed, and 13~15 μL of the suspension was applied to the surface of the nickel foam in batches, and then dried naturally for electrochemical testing.

Results and Discussion

To confirm the structure of the as-synthesized MOFs, PXRD tests were conducted on Ni-MOF. The PXRD spectra (Figure 1a) reveal that the observed peaks of the Ni-MOF are in good agreement with the simulated peaks, although slight discrepancies in peak intensities can be attributed to crystal anisotropy, confirming the successful synthesis of Ni-MOF. After phosphorylation at 400 °C, as illustrated in Figure 1b, the NiP_x/C-400 °C compounds exhibit diffraction peaks at 2θ angles of 40.714°, 44.611°, 47.362°, 54.196°, and 66.371°, corresponding to the (111), (201), (210), (300), and (310) crystallographic planes (PDF#74-1385 for Ni_2P). The presence of these characteristic peaks suggests the formation of the Ni_2P phase, which facilitates further investigation of its properties. Additionally, thermogravimetric analysis (TGA) was performed on Ni-MOF (Figure 1c), revealing that decomposition begins at a phosphatization temperature of 400 °C. This indicates the presence of residual carbon materials, and NiPx/C-400 °C would be a nanocomposite of metal nanoparticles dispersed within amorphous carbon similar to our previous work [13].

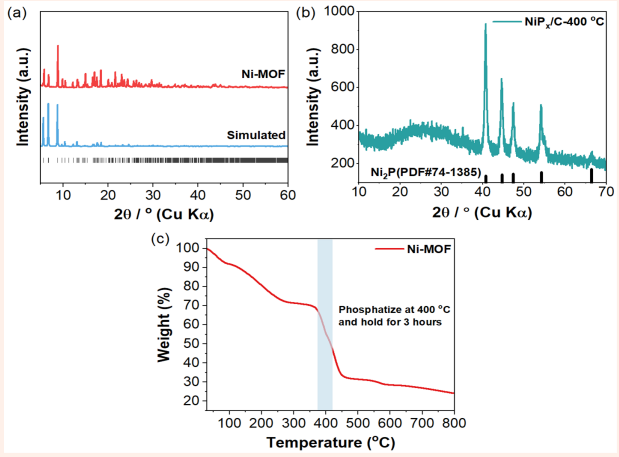

Figure 1: The PXRD spectra of (a) Ni-MOF and (b) NiP_x/C-400 ℃. (c) The TG curve of Ni-MOF under N_2 atmosphere.

Electrochemical properties

Based on the above structural and compositional information, the NiP_x/C-400 °C material was evaluated for its potential as an electrocatalyst for water cracking. The OER and HER properties of the materials were electrochemically tested using a typical three-electrode system in 1.0 M KOH solution at room temperature under alkaline conditions. In the experimental tests, the electrocatalyst loaded on nickel foam was scanned 60 times in the interval of 0-1.6 V using cyclic voltammetry at a rate of 50 mV/s in order to realize the stability of the electrocatalysts for the subsequent electrochemical performance tests in the next step.

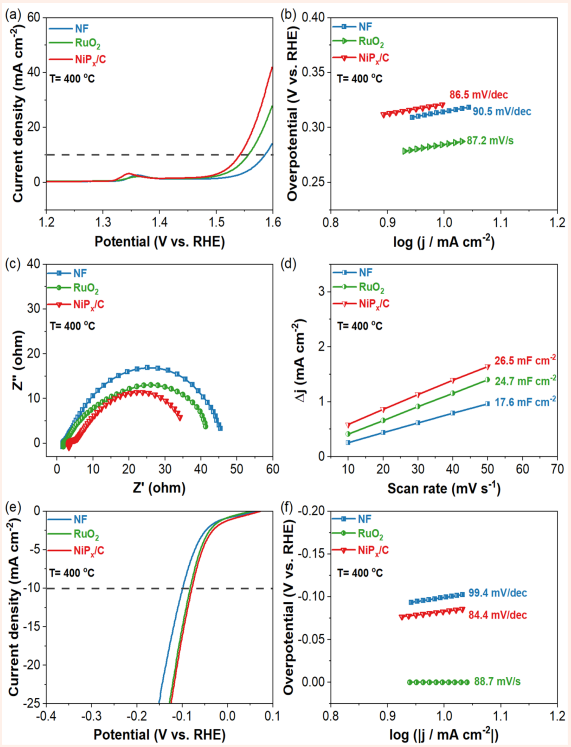

Figure 2: Electrocatalytic performance of NiP_x/C-400 °C in 1 M KOH. (a) LSV curve of OER, (b) corresponding Tafel curve of OER, (c) EIS plot of OER, (d) ECSA value of OER, (e) LSV curve of HER and (f) corresponding Tafel curve of HER.

For the oxygen precipitation reaction (OER), it can be analyzed from the LSV curve (Figure 2a) that the NiP_x/C-400 °C electrode requires only 311 mV overpotential to reach 10 mA cm^{-2}, which is much lower than that of the commercial RuO_2 (326 mV) and Nickel foam (356 mV), and it has a high OER activity. As shown in Figure 2b, the NiP_x/C-400 °C electrode displayed a low Tafel slope of 86.5 mV dec^{-1}, indicating that the fewer electron transfer barriers in the catalytic process, the better the corresponding electrocatalytic activity. In order to further investigate the performance of the electrocatalysts, the electrochemical impedance (EIS) test as well as the electrochemically active area (ECSA) calculated by fitting through the double layer capacitance (Cdl) were performed on the electrocatalyst materials. From the Nyquist diagram (Figure 2c), the resistance of NiP_x/C-400 °C electrode is 33 Ω, and the resistance of RuO_2 and Nickel foam are 40 Ω, and 50 Ω, respectively, and the results show that the NiP_x/C-400 °C electrode has a strong charge transfer capability. In addition, the current densities of the electrocatalysts at different scanning speeds were demonstrated as shown in Figure 2d. The current densities of the electrocatalysts at different scanning speeds are as follows. Among them, the electrochemically active surface area obtained from the fitting of NiP_x/C-400 °C electrode was 26.5 mF cm^{-2}, and the electrochemically active surface areas of RuO_2 and Nickel foam were 24.7 mF cm^{-2} and 17.6 mF cm^{-2}, respectively, and according to the formula ECSA = Cdl / Cs, the higher the value of Cdl, the higher the value of electrocatalytic activity ECSA. It is demonstrated that the NiP_x/C-400 °C material exposes more active sites and improves the catalytic activity, which in turn exhibits excellent electrocatalytic performance. Notably, in addition to the OER activity, the NiP_x/C-400 °C material also has good HER performance in 1.0 M KOH electrolyte. Based on the HER polarization curves and Tafel curves, it can be obtained (Figures 2e and 2f) that the NiP_x/C-400 °C material has a lower overpotential of 77 mV and a smaller Tafel slope of 84.4 mV dec^{-1} at a current density of 10 mA cm^{-2}, which proves that the NiP_x/C-400 °C material also has an excellent electrocatalytic performance in the electrolyte of 1.0 M KOH.

In view of the efficient OER and HER electrocatalytic performances, the NiP_x/C-400 °C material was loaded on two pieces of nickel foam with the same specifications and acted as both cathode and anode during water electrolysis. Compared with bare NF||NF, the NiP_x/C-400 °C material exhibited excellent total hydrolysis performance in 1.0 M KOH electrolyte on the LSV curve at a scan rate of 5 mV s^{-1} (Figure 3a), and the overall hydrolysis was achieved at only 1.69 V. The NiP_x/C-400 °C material was used as the cathode and anode during the water electrolysis. When the current density was 10 mA cm^{-2}, the NiP_x/C-400 °C material was maintained in the overall hydrolysis process at a constant voltage for 20 h (Figure 3b), showing good total hydrolysis stability.

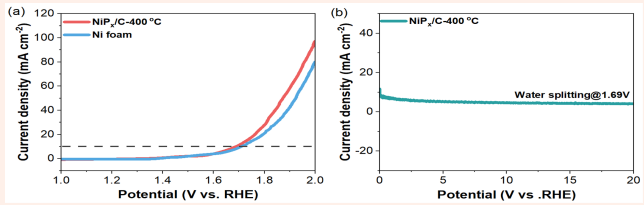

Figure 3: (a) LSV curves and (b) chronocurrent curves for total hydrolysis of NiP_x/C-400 °C.

Conclusion

In summary, a transition metal phosphide NiP_x/C-400 °C electrocatalyst was synthesized using a specific Ni-MOF as a precursor template. Under moderate phosphidation conditions, the linear $[Ni_3(COO)_6]$ nodes transformed into Ni_2P nanoparticles, while the organic linkers were converted into amorphous carbon. This resulted in NiP_x/C nanocomposites with high specific surface area and excellent electrical conductivity, exposing a large number of catalytically active sites. Consequently, the electrocatalytic activity for both OER and HER was significantly enhanced. The NiP_x/C-400 °C electrode demonstrated stable performance, maintaining a current density of 10 mA cm^{-2} for 20 hours at an operating voltage of 1.69 V in a water electrolysis device. This promising performance suggests potential for practical applications. The presented study also offers a novel approach to designing highly efficient bifunctional electrocatalysts for energy-efficient hydrogen production.

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