Monometallic phosphide catalyst of Ni$_2$P for Hydrogen production in acidic Solution

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Abstract. Nowadays, it is particularly important to develop efficient hydrogen evolution catalyst in the process of water electrolysis. In this paper, a monometallic phosphide ($\text{Ni}_2\text{P@C}$) was synthesized through a simple one-step calcination and phosphorization process, which was a high efficient catalyst for hydrogen evolution reaction. $\text{Ni}_2\text{P@C}$ exhibits satisfactory activity with a low overpotential of 215 mV and small Tafel slope of 105 mV dec$^{-1}$ at the current density of 10 mA cm$^{-2}$. In addition, the catalyst displayed favorable stability for 16 h when current density maintained at 10 mA cm$^{-2}$. This work provides reference for monometallic phosphates as catalyst for hydrogen evolution.

1. Introduction

Hydrogen production by water decomposition is an efficient and environmentally friendly method, which has been widely studied$^{[1-3]}$. As we all know, platinum (Pt) is the most effective catalyst for hydrogen evolution reaction (HER)$^{[4]}$. But, due to the high consumption and scarcity, it is restricted in the actual hydrogen production process$^{[5]}$. Therefore, a great deal of researches focus on the development of effective, environmentally friendly and low consumption hydrogen catalysts. In recent years, phosphates have been drawing much attention on account of their tunable electronic structures$^{[6]}$. Thereinto, nickel phosphides have been used as hydrogen evolution catalysts because of the unique electronic structures and low consumption$^{[3]}$. For instance, Yang and co-workers used one-pot hot-solution colloidal synthetic method to prepare Ni$_{12}$P$_5$/CNT for HER with low overpotential of 129 mV when the current density attained 10 mA cm$^{-2}$$^{[7]}$. Another example, Pan and co-workers synthesized Ni$_3$P nanoparticles for HER with the small Tafel slope of 81 mV dec$^{-1}$ and low initial overpotential of 70 mV$^{[8]}$.

In our work, a high-efficiency hydrogen evolution catalyst was synthesized via simple high-temperature calcination and phosphorization process. Thereinto, we used polyaniline (PANI) as carbon source and nitrogen source. As we all know, polyaniline is a kind of conductive polymer and has a large
number of lone pair electrons on the N atoms \cite{9}. Therefore, we synthesized carbon-coated nickle phosphide nanoparticles (Ni₂P@C) by the coordination of the Ni²⁺ and N atoms on polyaniline. Ni₂P@C exhibited excellent catalytic activity and high durability.

2. Experimental and characterization

2.1. Synthesis of Ni₂P@C

Polyaniline was synthesized according to reference \cite{10}. In detail, 12.5 mg nickel acetate and 100 mg PANI were mixed and dissolved in a mixture of N, N-Dimethylformamide (DMF) and water. Above the solution was heated to boiling and the solvent was removed. The resulting precursor was calcined at 950 °C with 5 °C min⁻¹ for 2 h under the Ar. In addition, we used sodium hypophosphate as a source of phosphorus.

2.2. Characterization

Characterization methods: Powder X-ray diffraction (PXRD), transmission electron microscopy (TEM), energy dispersive X-ray detector (EDS), Raman, X-ray photoelectron spectroscopy (XPS), N₂ adsorption.

3. Results and discussion

The XRD spectrum of Ni₂P@C is shown in Figure 1a, characteristic peak at 40.6°, 44.4°, 47.2°, 53.9°, 66.3° and 75.1° are corresponding to the Ni₂P (PDF#03-0953) plane of (111), (201), (300), (310) and (400). As sketched in TEM and HRTEM images (Figure 1b and c), the catalyst of Ni₂P@C were carbon coated nanoparticles. Thereinto, in Figure 1c, the lattice spacing was 0.22 nm, which is coincident with the (111) of Ni₂P (PDF#03-0953). In addition, the mapping images (Figure 1d-h) show that C, N, P and Ni elements were uniformly distributed in Ni₂P@C. Figure 2a shows the Raman spectra of Ni₂P@C, respectively, the D band and G band were based in 1354 and 1590 cm⁻¹ with the peak’s intensity ratio of 0.906 (I_D/I_G). Thereinto, the D band and G band originated form a defect in the carbon lattice and the graphite carbon respectively. XPS diagram was tested to further realize the electronic structure of Ni₂P@C. Figure 2b is the Ni 2p spectrogram, it can be seen the peak at 857.3 eV in accord with Ni–P bond, which demonstrated the Ni₂P was successfully synthesized. The peaks of 862.9 eV and 876.3 eV are characteristic peaks of Ni 2P₃/2 and Ni 2P₁/2 for Ni₂P \cite{11}. According to N₂ adsorption diagram (Figure 2c), the large Brunauer–Emmett–Teller (BET) specific surface area of Ni₂P@C was 269.9 m²/g, and the pore diameter was 2.47 nm, which was proved to be mesoporous catalyst.
Hydrogen evolution performance measurement was executed with a three-electrode system in acidic solution. The polarization curves and Tafel slope of PC, Ni2P@C and Pt/C are shown in Figure 3a and b. Ni2P@C exhibits desirable catalytic effect with the Tafel slope of 105 mV dec⁻¹ and overpotential of 215 mV at a current density of 10 mA cm⁻². Figure 3c shows the double layer capacitance (Cdl) of Ni2P@C. The Cdl value of Ni2P@C is 60.5 mF cm⁻², which indicates that Ni2P@C possessing a large catalytic active surface area. Likewise, electrochemical impedance spectroscopy (EIS) was measured at the overpotential of 200 mV. The results are shown in figure 3d, the impedance value of Ni2P@C is much smaller than PC, which indicates that Ni2P@C has a fast-catalytic kinetics. Eventually, the durability was tested by cyclic voltammetry (CV) and chronoamperometry. As shown in figure 3e, the Ni2P@C was stable within 16 h, indicating that the catalyst has improving stability.

In conclusion, we have successfully synthesized the Ni2P@C hydrogen evolution catalyst through a simple process of high temperature calcination and phosphating. Furthermore, Raman, XPS, N2 adsorption and hydrogen evolution performance test proved that the catalyst shows satisfactory catalytic
effect (overpotential of 215 mV at current density of 10 mA cm\(^{-2}\) and Tafel slope of 105 mV dec\(^{-1}\)) and stability (16 h) in 0.5 M \(\text{H}_2\text{SO}_4\). This work provides a universal method for the synthesis of monometallic phosphide hydrogen evolution catalyst (\(\text{Ni}_2\text{P}@\text{C}\)) by using polyaniline as carbon and nitrogen source.

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**References**

[1] Zhang, L., Qi, Y.Y., Sun, L., Chen, G.J., Wang, L.X., Zhang, M.S., Zeng, D.J., Chen, Y.N., Wang, X.G., Xu, K.W., Ma, F. (2020) Facile route of nitrogen doping in nickel cobalt phosphide for highly efficient hydrogen evolution in both acid and alkaline electrolytes. Applied Surface Science., 512: 145715.

[2] Wang, X.G., Li, W., Xiong, D.H., Petrovykh, D.Y., Liu, L.F. (2016) Bifunctional Nickel Phosphate Nanocatalysts Supported on Carbon Fiber Paper for Highly Efficient and Stable Overall Water Splitting. Adv. Funct. Mater., 26: 4067–4077.

[3] Hu, C., Lv, C., Liu, S., Shi, Y., Song, J.F., Zhang, Z., Cai, J.G., Watanabe, A. (2020) Nickel Phospide Electro catalysts for Hydrogen Evolution Reaction. Catalysts., 10: 188.

[4] Pu, Z.H., Ya, X., Amiu, I.S., Tu, Z.K., Liu, X.B., Lia, W.Q., Mu, S.C. (2016) Ultrasmall tungsten phospide nanoparticles embedded in nitrogen-doped carbon as a highly active and stable hydrogen-evolution electrocatalyst. J. Mater. Chem. A., 4: 15327.

[5] Zhou, J., Dou, Y.B., Wu, X.Q., Zhou, A., Shu, L., Li, J.R. (2020) Alkali-Etched Ni(II)-Based Metal–Organic Framework Nanosheet Arrays for Electrocatalytic Overall Water Splitting. Small., 1906564.

[6] Zhang, H.J., Maijenburg, A.W., Li, X.P., Schweizer, S.L., Wehrspohn, R.B. (2020) Bifunctional Heterostructured Transition Metal Phosphides for Efficient Electrochemical Water Splitting. Adv. Funct. Mater., 2003261.

[7] Wang, C.D., Ding, T., Sun, Y., Zhou, X.L., Liu, Y., Yang, Q. (2015) \(\text{Ni}_12\text{P}_5\) nanoparticles decorated on carbon nanotubes with enhanced electrocatalytic and lithium storage properties. Nanoscale., 7(45): 19241-9.

[8] Lin, Y., Pa, Y., Zhang, J. (2017) In-situ grown of \(\text{Ni}_3\text{P}\) nanoparticles on 2D black phosphorus as a novel hybrid catalyst for hydrogen evolution. International Journal of Hydrogen Energy., 42: 7951-7956.

[9] Feng, J.X., Tong, S.Y., Tong, Y.X., Li, G.R. (2018) Correction to “Pt-like Hydrogen Evolution Electrocatalysis on PANI/CoP Hybrid Nanowires by Weakening the Shackles of Hydrogen Ions on the Surfaces of Catalysts. J. Am. Chem. Soc., 140(15): 5118–5126.

[10] Wei, X., Yin, Z.L., Lyu, K.J., Li, Z., Gong, J., Wang, G.W., Xiao, L., Lu, J.T., Zhuang, L. (2020) Highly Selective Reduction of \(\text{CO}_2\) to \(\text{C}_2\text{H}_4\) Hydrocarbons at Copper/Polyaniline Interfaces. ACS Catal., 10: 4103–4111.

[11] Bian, J.L., Song, Z.Y., Li, X.L., Zhang, Y.Z., Cheng, C.W. (2020) Nickel iron phospide ultrathin nanosheets anchored on nitrogen-doped carbon nanoflake arrays as a bifunctional catalyst for efficient overall water splitting. Nanoscale., 12(15): 8443-8452.