

Preparation of amorphous NiP-based catalysts for hydrogen evolution reactions

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Abstract: Amorphous alloy NiP and its carbon composite catalysts NiP/C and NiP/reduced graphene oxide (RGO) were successfully one-pot synthesized using NaH₂PO₂ and NiSO₄ as phosphorus and nickel source, respectively. The electrocatalysts were characterized with transmission electron microscope (TEM), X-ray diffraction spectrometer (XRD), inductively coupled plasma analysis (ICP) and thermogravimetric analysis (TG), respectively. The hydrogen evolution reactions (HER) performance of the electrocatalysts was evaluated with a linear sweep voltammetry method in both acidic and alkaline solution. Among them, NiP/RGO electrocatalyst exhibited 89.0 mV onset overpotential and Tafel slope 135.1 mV/decade in acidic solution, as well as 116.1 mV onset overpotential and Tafel slope 122.4 mV/decade in alkaline solution with excellent long-term stability. Results indicated that the NiP/RGO was a very active catalyst.

Keywords: hydrogen evolution reaction; NiP/RGO; overpotential; Tafel slope

Hydrogen, as a clean renewable energy source, has become one of the promising alternatives to carbon-based fuels^[1,2]. Electrochemical splitting water by using renewable wind and solar power to produce hydrogen has attracted a great deal of attention recently^[3]. However, it heavily relies on the efficiency of the cathode electrocatalyst to minimize the overpotential during the hydrogen evolution reaction (HER)^[4–6]. Although a few precious metals such as Pt, have exhibited high catalytic activity for HER, their excessive price and lack of abundance limit their application industrially. A possible replacement for Pt catalysts are Mo, W, Ni-based materials, such as metal alloys, borides, carbides, nitrides, sulfides, selenides^[4,5] and even metal free catalysts^[6], which have shown promise for HER in both acidic and alkaline media. In particular, transition metal phosphide nanostructured crystalline materials with structural and electronic analogies to the active site of hydrogenase have been identified as active HER catalysts because they can merge the activity of hydrogenase with the stability of a heterogeneous catalyst^[7–9]. Especially Lewis and Schaak reported the preparation of nanostructured crystalline metal phosphides *ca.* Ni₂P as an efficient electrocatalyst for HER^[7]. After that, different preparation methods of crystalline nickel phosphides^[9–12] and their composite catalysts incorporating other materials eg. carbon

nanotube^[13], carbon nanospheres^[14,15], nitrogen-doped graphene^[16], Fe^[17], etc. were comprehensively reported. However, the preparation process involved high temperature decomposition of a phosphine which could liberate phosphorus, so this reaction should be considered as highly corrosive and flammable^[8]. On the other hand, amorphous alloy NiP was extensively used for hydrodesulfurization (HDS) catalyst^[18–20], and which was also shown to be an active HER catalyst^[21,22]. That is, both HDS and the HER rely on the catalyst to reversibly bind H₂, with H₂ dissociating to produce H₂S in HDS and with protons bound to the catalyst to promote the formation of H₂ in the HER, suggesting that other materials that are known HDS catalysts may also provide active electrocatalysts for the HER. In our previous work, amorphous alloy NiP and its carbon composite catalysts NiP/C and NiP/RGO were successfully synthesized by a facile solution process and exhibited superior HER performance. Carbon materials were introduced to improve the conductivity of amorphous alloy NiP. This work will provide an alternative method of preparing NiP carbon composite catalysts as well as a new non-noble metal electrocatalyst for hydrogen evolution reaction.

1 Experimental

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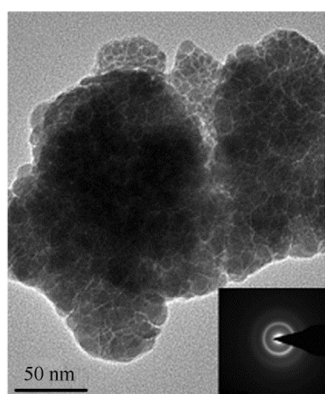


Fig. 1 TEM of NiP, composite electrocatalysts, the insert shows the diffraction pattern and the amorphous nature of the nanoparticles

Amorphous alloy NiP based catalysts NiP/RGO and NiP/C(NiP/acetylene black containing NiP 20% (w/w) abbreviated as NiP/C-20%; 80% (w/w) abbreviated as NiP/C-80%, respectively) were prepared. All chemicals used in the experiments were of analytical grade and used without further purification. 20 g $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, 20 g $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$, 20 g $\text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O}$, 33.3 g $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$ and 5 mL (2 mg/L) graphene oxide (prepared with our previous work)^[23] or acetylene black (0.15 g and 2.40 g) were dispersed into 250 mL deionized water, respectively. The solution rigorously stirred at 60°C for 1 h. After adding 1, 2 drops of NaBH_4 solution (2 mol/L), the stock solution turned to black color with evolution of hydrogen bubbles. When the reaction was completely finished, the black precipitation (NiP/RGO and NiP/C catalysts) was filtered from the stock solution and extensively washed by deionized water, acetone and anhydrous alcohol, respectively. Then the as-prepared NiP/RGO and NiP/C catalysts were dried at 60°C for use. The procedure of pure amorphous alloy was same to the preparation of NiP/RGO only without RGO. The transmission electron microscopy (TEM) images were carried out with a FEI Tecnai (G2 f20 s-twin 200 kV) microscope. The compositions of the as-prepared samples were analyzed by inductively coupled plasma analysis (ICP Varian 720). X-ray powder diffraction (XRD) was performed using a Bruker D8-advance X-ray diffractometer with graphite-monochromatized $\text{Cu } K\alpha$ radiation. Thermogravimetric analysis (TGA) was carried out at a heating rate of 10 K/min on a Netzsch TG 209 in N_2 atmosphere at a flow rate of 40 cm^3/min . 5 mg of amorphous alloy NiP based catalysts was mixed with 625 μL DI water and 125 μL nafion in a 5 mL vial. The mixture was sonicated for 60 min in ultrasonic instrument. Then 10 μL of the suspended solution was dropped on a 3 mm diameter glassy carbon (GC) electrode (0.07 cm^2). Finally, the electrode was dried under a 300 W infrared lamp for at least 0.5 h.

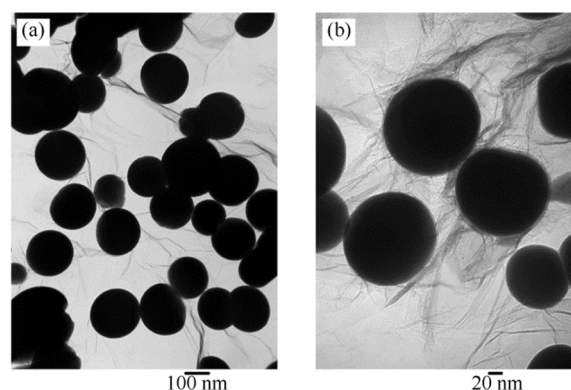


Fig. 2 TEMs of NiP/RGO composite electrocatalysts

The HER performance of as-prepared catalysts was studied with an electrochemical workstation (Zahner Zennium CIMPS-1, Germany) using linear sweep voltammetry (LSV) in N_2 -saturated 0.5 mol/L H_2SO_4 and 1 mol/L NaOH solutions at 10 mV/s, respectively. The electrolytic cell was controlled at 25°C with a circular water bath system to avoid the influence of temperature. A three-electrode configuration consisting of GC working electrode, Pt wire counter electrode and reference electrode was used. The reference electrode was Ag/AgCl electrode in acid solutions, and Hg/HgO (1 mol/L NaOH electrolyte) in alkaline solutions, respectively. The potentials in previous work were versus the reversible hydrogen electrode (RHE) obtained from calibration equations: $E(\text{RHE}) = -0.059 \times \text{pH}$ vs. $E(\text{NHE})$, $E(\text{Hg}/\text{HgO}) = 0.098$ vs. $E(\text{NHE})$. The stability of the catalysts was studied at scan rate (50 mV/s) for 500 cycles.

2 Results and discussion

Morphology of the as-prepared catalysts was determined using the TEM images. Although exhibiting very small size around several nanometers, the TEM images of pure NiP prepared without any support show the morphology of the serious aggregations of NiP particles. As shown in Figure 1, the diameter of the aggregations is around 500 nm, and the SAED patterns indicate the amorphous structure of NiP samples, see the insert of Figure 1. By comparing with the TEM images of NiP/RGO and NiP catalyst, the particles of NiP/RGO show the shape of spheres and the sizes range from 100 nm to 200 nm. As shown in Figure 2, the size decreases sharply from aggregation state to about 100 nm. With the introduction of acetylene black, the particles of the NiP/C also show the shape of spheres, seen in Figure 3. When the loading of NiP is comparatively low, ca. 20%, the sphere NiP catalyst showed few and scattered, and the size of NiP becomes only 30–40 nm. When the loading of NiP is high, ca. 80%, the size of NiP/C-80% increased quickly from 30–40 nm to about 100 nm.

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