Effect of nickel phosphide nanoparticles crystallization on hydrogen evolution reaction catalytic performance

Ya-qiong CHEN$^{1,2}$, Jin-feng ZHANG$^{1,2}$, Lei WAN$^{1,2}$, Wen-bin HU$^{1,2,3,4}$, Lei LIU$^{1,2}$, Cheng ZHONG$^{3,4}$, Yi-da DENG$^{3,4}$

1. School of Materials Science and Engineering, Shanghai Jiao Tong University, Shanghai 200240, China;
2. State Key Laboratory of Metal Matrix Composites, Shanghai Jiao Tong University, Shanghai 200240, China;
3. School of Materials Science and Engineering, Tianjin University, Tianjin 300072, China;
4. Key Laboratory of Advanced Ceramics and Machining Technology (Ministry of Education), and Tianjin Key Laboratory of Composite and Functional Materials, Tianjin University, Tianjin 300072, China

Received 15 December 2015; accepted 3 May 2016

Abstract: In order to investigate the effect of nickel phosphide nanoparticles’ (Ni–P NPs) crystallization on hydrogen evolution reaction (HER) catalytic performance, amorphous Ni–P NPs and crystalline Ni$_5$P$_5$ were synthesized by a simple and low-cost autocatalytic reduction method and heat treatment process. The result of electrochemical tests shows that crystalline Ni$_5$P$_5$ has much higher HER catalytic activity than the amorphous one. X-ray diffraction, transmission electron microscopy and X-ray photoelectron spectroscopy revealed that Ni–P bond formed during crystallization, making Ni positively charged and P negatively charged. This charged nature of Ni$_5$P$_5$ is similar to [NiFe] hydrogenase and its analogous, which make the removal of H$_2$ less energy-cost.

Key words: hydrogen evolution reaction; nickel phosphide nanoparticles; Ni$_5$P$_5$; catalyst; crystallization

1 Introduction

With the decreasing reserves-to-production ratio of traditional fossil fuels and increasingly serious environment issues of pollution [1–3], a numerous researches concerning the development and utilization of renewable clean energy have been conducted [4–8]. It is widely considered that hydrogen is a promising energy carrier because of its larger storage density and longer storage time [9,10]. Among all kinds of hydrogen production methods, water electrolysis is a clean, simple and fast way to produce hydrogen on large scale [11]. According to the volcano plot described by TRASATTI [12] and NØRSKOV et al [13,14], the hydrogen evolution reaction (HER) catalytic performance is related to the binding strength between the metal surface and the absorbed hydrogen (M-Hads). Unfortunately, the best electrocatalyst for HER is some noble metals, such as Pt, which have optimal binding strength but cannot be used on large scale due to their high price and low store in earth. Therefore, finding an inexpensive and abundant catalyst could facilitate the industrialization of hydrogen production. Many related researches have been conducted [15–18].

In recent years, metal phosphide nanoparticles as HER electrocatalyst have received a lot of concern because of its excellent catalytic activity [19–23]. Among all these metal phosphides, it has been demonstrated that crystalline nickel phosphide nanoparticles (Ni–P NPs) have superior electrocatalytic performance for HER. POPCZUN et al [24] proved that the hexagonal structure Ni$_5$P exhibits extraordinary HER catalytic activity because of its large surface area and exposed (0 0 1) active facets. Additionally, HUANG et al [25] reported that Ni$_5$P$_5$ is a promising HER catalyst both in electrolysis and photoelectrolysis. PAN et al [22] compared the electrocatalytic properties of nickel phosphides with different phases and demonstrated that the crystalline phase is very important to electrocatalytic performance.

These reported researches suggested that the morphology and phases of Ni–P NPs play important roles in their HER catalytic performance. However, some
other important factors, such as crystallization effect and particles size effect, have not been studied. MAO et al [26] demonstrated that the crystallinity plays an important role in the capacitor performance. JOO et al [27] proved that optimal crystallinity of TiO$_2$ would enhance its catalytic activity. Thus, we think that it is significant to investigate the effect of Ni–P NPs’ crystallinity on HER performance. In this work, Ni–P NPs with different crystallinities were prepared by a simple and low-cost method. And the effect of crystallization of Ni–P NPs was systematically investigated for HER catalytic performance.

2 Experimental

2.1 Chemicals and materials

Nickel sulfate (NiSO$_4$·6H$_2$O), sodium hypophosphite (NaH$_2$PO$_2$·H$_2$O), sodium hydroxide (NaOH) were purchased from the National Chemical Reagent Ltd., Shanghai, China. All chemicals were analytical grade and used without further purification. Solutions of NiSO$_4$ (2 mol/L), NaOH (4 mol/L), NaH$_2$PO$_2$ (4 mol/L) were prepared by dissolving certain quantities of these chemicals in deionized water, respectively.

2.2 Synthesis of Ni–P NPs

An autocatalytic reduction method was used to prepare Ni–P nanoparticles [28]. Firstly, all the needed reagents were preheated to 90 °C. Second, together 15 mL NiSO$_4$ solution, 7.5 mL NaH$_2$PO$_2$ solution and 22.5 mL deionized water were mixed together, then the mixture was constantly stirred violently and kept it at 90 °C. After stirring for 5 min, 30 mL NaOH solution and 50 mL NaH$_2$PO$_2$ solution were added to the mixture. Then, the dark-gray powder dispersion liquid would be obtained in 5 min. Finally, the dispersion was washed repeatedly with deionized water 6 times and the fully-washed powers were dried in vacuum furnace at 100 °C for 6 h.

2.3 Preparation of crystalline Ni–P NPs

Heat treatment was applied to crystallizing synthesized Ni–P NPs. The heat treatment temperature was set at 350 °C, which is above crystallization temperature of synthesized Ni–P NPs according to the differential scanning calorimetry (DSC) and thermogravimetry (TG), as shown in Fig. 1. The samples were heat treated from 20 to 350 °C with a heating rate of 10 °C/min. In order to obtain samples with different crystallinities, the samples were kept at 350 °C for different periods of time. The heat treating condition is in an oven full of 5%H$_2$/Ar [24].

2.4 Characterization

XRD was performed by D/max-IIA X-ray diffractometer with Cu K$_\alpha$ (λ=1.54 Å) as irradiation source. The samples were scanned from 10° to 90° in 2θ with scan rate of 10 °/min. The morphology of samples was investigated by a field-emission transmission electron microscopy (JEM-2100F) with set working voltage of 200 kV. And the TEM samples were prepared by dispersing various Ni–P NPs in ethanol and depositing the dispersion liquid into a carbon copper grid. The crystallization temperature was characterized by DSC/TGA curves which were obtained by a Pyris 1 TGA Thermo Gravimetric. Besides, XPS data were obtained by testing the samples in a Kratos AXIS Ultra X-ray photoelectron spectrooscope with an incident radiation of Monochromatic Al KR X-ray at 150 W.

Fig. 1 DSC and TG curves of synthesized Ni–P NPs

2.5 Preparation of working electrodes

Different Ni–P catalysts and commercial Pt/C catalyst (Johnson Matthey, Hispec 3000, 20%) were prepared as electrode material. Catalyst (7 mg) and Nafton solution (2%, 100 μL) were dispersed in ethanol (1 mL) by ultrasonication, and a homogeneous ink would be formed. Then, 7 μL of catalyst ink was loaded onto a glass carbon electrode (GCE, 2.5 mm in diameter).

2.6 Electrochemical measurements

Electrochemical measurements were performed using an electrochemical workstation (CHI 660D) in a typical three-electrode glass cell. The catalysts deposited glassy carbon electrode served as the working electrode, a platinum foil and Ag/AgCl with saturated KCl were used as the counter and reference electrode, respectively. The electrolyte was oxygen-free 0.5 mol/L H$_2$SO$_4$ solutions, which is achieved by bubbling N$_2$ for 20 min before the experiments.

Catalytic activity to HER was analyzed by means of cyclic voltammetry (CV), linear sweep voltammetry (LSV) and potentiostatic electrolysis. CV curves were...
scanned at a scan rate of 50 mV/s without accounting for uncompensated resistance. 1000 potential cycles of CV were carried out for the stability test. The LSV was conducted at a scan rate of 10 mV/s after a certain number of CV scan cycles. Potentiostatic electrolysis was carried out at 0.12 V vs RHE.

3 Results and discussion

3.1 Morphology and structure

X-ray diffraction (XRD) patterns of the before and after heat treated Ni–P NPs are shown in Fig. 2. Before heat treatment, only a single broad profile was found in the XRD pattern, indicating that the synthesized nanoparticles are amorphous. After heat treatment at 350 °C for 30 min, some peaks appeared, which means that crystallization occurred at this temperature. With increasing heat treatment time, more keen-edged peaks corresponding to Ni₁₂P₅ appeared and the peaks were largely enhanced until heat treatment for 100 min. This means that the crystallinity of Ni–P NPs would increase with increasing heat treatment time. The samples heat treated at 350 °C for 180 min show perfect peaks characteristics of tetragonal Ni₁₂P₅ phase (PDF No. 22–1190). The peaks at 2θ values of 20.3°, 29.2°, 32.7°, 35.8°, 38.4°, 41.3°, 41.7°, 44.4°, 47.0°, 49.0°, 54.0°, 56.2°, 60.1°, 68.6°, 74.0° and 74.8° correspond to the (1 0 1), (2 2 0), (3 1 0), (3 0 1), (1 1 2), (2 0 2), (4 0 0), (3 3 0), (4 2 0), (3 1 2), (5 1 0), (5 0 1), (4 2 2), (6 2 0), (5 3 2) and (0 0 4) crystalline phases, respectively. With further increase of heat treatment time, the crystal phase will not be changed.

Figures 3(a) and (b) present transmission electron microscope (TEM) images of the amorphous Ni–P NPs.

![Fig. 2 XRD patterns of Ni–P NPs with different heat treatment time](image)

![Fig. 3 TEM images (a, b) of amorphous nickel phosphide nanoparticles with inset size distribution pattern, TEM image (c) and HRTEM image (d) of well crystallized Ni₁₂P₅ nanoparticles with FFT pattern](image)
The amorphous Ni–P NPs exhibited the polydisperse channeled nanosphere morphology with average diameter of about 40.44 nm. After being heat treated at 350 °C for 100 min, the regular nanospheres transformed to some bigger irregular particles within nanoscale dimension (Fig. 3(c)), which may be due to the high temperature during the heat treatment. From the high resolution transmission electron microscope (HRTEM) image (Fig. 3(d)) of well crystallized Ni$_{12}$P$_{5}$, clear lattice fringes were observed, and the interplane distance was calculated according to the single-dimensional fast Fourier transform (FFT) pattern, which is 0.186 nm. This interplane distance corresponds to the (3 1 2) crystallinity phase of Ni$_{12}$P$_{5}$, which demonstrates that the 100 min heat treated sample, Ni$_{12}$P$_{5}$, is single crystalline.

### 3.2 Electrocatalytic properties

In order to test electrocatalytic performance, amorphous Ni–P NPs, various crystalline Ni–P NPs with different heat treatment time and commercial Pt/C catalyst (20%) were deposited on glass carbon electrode (GCE). Because of the high temperature during synthesis, amorphous and crystalline Ni–P NPs might have oxides on their surface. Thus, all the electrochemical tests would start after the 50th cyclic voltammetric (CV) sweeps, which will help to remove oxide from the electrode surface [29].

The HER catalytic performance of electrodes was judged by the overpotential required to reach an operating current density, which is determined by both its Tafel slope and onset potential [30]. Figure 4 displays the typical polarization curves of various electrodes and bare GCE in 0.5 mol/L H$_2$SO$_4$. For comparison, the amount of samples loaded on GCE was fixed at 0.25 mg/cm$^2$. As expected, bare GCE showed negligible current in the given potential range. Thus, it is apparent that the cathodic current in that potential range was largely attributed to the catalytic activity of various Ni–P catalysts and commercial Pt/C catalyst. The onset potentials is the potential at which catalytic current is first observed, and we defined it on the basis of 5 mA/cm$^2$. According to Fig. 4, the onset potentials for amorphous sample, 30 min treated sample, 70 min treated sample and 100 min treated sample were 330, 155, 79 and 68 mV, respectively. Clearly, the amorphous sample had the largest onset potential. And after crystallization, the onset potential largely decreased, indicating that the catalytic performance was enhanced. When the current density reached 30 mA/cm$^2$, the potentials required for amorphous sample, 30 min treated sample, 70 min treated sample and 100 min treated sample were 492, 235, 158 and 140 mV, respectively.

The kinetic behavior of the various Ni–P NPs in 0.5 mol/L H$_2$SO$_4$ at 30 °C was studied by Tafel plots, as shown in Fig. 5. By fitting the linear part of the Tafel plots to Tafel equation, Tafel slope could be obtained. The Tafel slopes of samples heat-treated for 30, 70 and 100 min were 85, 60 and 46 mA/dec, respectively. This means that the HER rates were determined by both Heyrovsky and Tafel reactions. And the samples heat-treated for 100 min had the smallest Tafel slope, demonstrating that its catalytic activity for HER is excellent.

![Figure 4 Polarization curves of various Ni–P NPs, commercial Pt/C and bare GCE](image)

![Figure 5 Tafel plots of samples heat treated for 30, 70 and 100 min](image)

Apparently, the HER catalytic performance of crystalline Ni–P NPs is much better than that of the amorphous one. After heat treatment, the electrocatalytic performance of Ni–P NPs was largely enhanced, which will increase with the increased crystallinity. The hydrogen evolution activity data for the tested catalysts and several recently reported Ni–P catalysts were compared in Table 1.

To further demonstrate the high electrocatalytic performance of well crystallized Ni$_{12}$P$_{5}$, the accelerated degradation studies of 100 min treated sample (Ni$_{12}$P$_{5}$) have been conducted. The linear sweep voltammetry
(LSV) curves were tested after different cyclic voltammetric (CV) sweeps (Fig. 6(a)), and the long-term stability of Ni$_2$P$_3$ was also evaluated by electrolysis at a fixed potential (vs RHE) of 120 mV (Fig. 6(b)). It is obvious that the LSV curves after the 200th cycle, 600th cycle, and 1000th cycle were very close and Ni$_2$P$_3$ can remain catalytic current density of 18 mA/cm$^2$ over 10000 s. Therefore, it indicates that the well crystallized Ni$_2$P$_3$ has a good stability in acid condition.

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Summary and comparison of HER catalysis data</th>
</tr>
</thead>
<tbody>
<tr>
<td>Catalyst</td>
<td>Loading amount/ potential $^1$</td>
</tr>
<tr>
<td>Amorphous</td>
<td>(mg cm$^{-2}$)</td>
</tr>
<tr>
<td>30 min sample</td>
<td>0.25</td>
</tr>
<tr>
<td>70 min sample</td>
<td>0.25</td>
</tr>
<tr>
<td>100 min sample</td>
<td>0.25</td>
</tr>
<tr>
<td>Pt/C</td>
<td>0.25</td>
</tr>
<tr>
<td>Ni$_2$P$_3$ [24]</td>
<td>1.00</td>
</tr>
<tr>
<td>Ni$_3$P$_4$ [22]</td>
<td>0.20</td>
</tr>
<tr>
<td>Ni$_2$P$_3$ [25]</td>
<td>1.00</td>
</tr>
</tbody>
</table>

$^1$ defined on the basis of 5 mA/cm$^2$; $^2$ required potential to reach current density listed

3.3 X-ray photoelectron spectroscopy

In order to investigate the effect of crystallization, X-ray photoelectron spectroscopy (XPS) was conducted to amorphous Ni–P NPs and well crystallized Ni$_2$P$_3$. The XPS spectra of the Ni 2p and P 2p regions in amorphous Ni–P NPs and well crystallized Ni$_2$P$_3$ are shown in Fig. 7. In Ni 2p region (Figs. 7(a) and (c)), three peaks at Ni 2p$_{3/2}$ energy level were found. The peaks at 853.1/853.0 eV are close to the peaks of Ni with zero valence state [31], thus it can be speculated that it corresponds to the weakly positive charged Ni ($\text{Ni}^{3+}$) in Ni$_2$P$_3$ [25]. And comparing contribution at around 853 eV, the intensity of Ni$_{3+}$ in Ni$_2$P$_3$ is much larger than that in amorphous Ni–P NPs, indicating only a few of Ni$_2$P$_3$ species formed in Ni–P NPs, which may be due to the high temperature during synthesis procedure. The peaks at 856.0/856.8 eV correspond to Ni$^{2+}$ species due to a superficial passivation, and the 860.2/861.5 eV is the broad shake-up satellite due to the presence of Ni$^{2+}$ species [32]. The remaining peaks at Ni 2p$_{1/2}$ energy level (870.5/870.3, 875.4/875.1 and 879.0/880.0 eV) were the Ni 2p$_{1/2}$ doublets of the prior bands. As to P 2p spectrum (Figs. 7(b) and (d)), the peaks at 129.6/129.5 eV are assigned to weakly negative charged P ($P^{−}$) in phosphide, and 133.5/133.4 eV corresponds to surface phosphate due to the superficial oxidation [33]. Similarly, the intensity of P$^{−}$ in crystalline Ni$_2$P$_3$ is much larger than that in amorphous Ni–P NPs. In Fig. 7(d), two peaks at 130.3 and 134.3 eV are the doublets P 2p$_3/2$–2p$_1/2$ with a separation of 0.84 eV. By comparing XPS spectra of amorphous and crystalline Ni–P NPs, we can see that much more Ni$_2$P$_3$ formed during crystallization, which means that partial electron transfer occurred from P to Ni, making Ni positively charged.

![Fig. 6 LSV curves of well crystallized Ni$_2$P$_3$ after 200, 400, 600, 800 and 1000 cycles (a) and time-dependent current density curve of Ni$_2$P$_3$ heat treated for 10000 s (b)](image)

3.4 Discussion

The HER in acid solution is thought to involve three steps [34,35]:

Volmer step: $\text{H}^+ + e^- \rightarrow \text{H}_2^*$

Heyrovsky step: $\text{H}_2^* + \text{H}_2 \rightarrow \text{H}_3^*$

Tafel step: $2\text{H}_2^* \rightarrow \text{H}_2 + 2^*$

where "**" represents a free active site, and "$\text{H}^*$" represents the hydrogen bonded to this site. A good HER catalyst should have the ability to trap protons, bond the atomic hydrogen strongly, and desorb $\text{H}_2$ as well [19].

As reported, amorphous Ni–P electrodes for HER are active only with low phosphorus content (to 3%) [36]. When phosphorus content is high, it would strongly bound hydrogen, resulting in the high energy cost for the
Fig. 7 XPS spectra of synthesized NPs (a, b) and Ni$_{12}$P$_5$ (c, d): (a, c) Ni 2p region; (b, d) P 2p region

removal of $\text{H}_2$ and the high overvoltage for $\text{H}_2$ evolution [13,19,36]. In our study, the phosphorus content of amorphous Ni–P NPs is about 18%, therefore we speculate that its poor HER catalytic activity can be related to its strong bond with hydrogen.

From the XPS spectra, it is clear that electron transfer occurred from P to Ni during crystallization. Ni in Ni$_{12}$P$_5$ has a very small positive charge, and P has a very small negative charge. This property is very familiar to [NiFe] hydrogenase and its molecular analogues, which have high HER catalytic activity [37,38]. Hydrogenase and its analogues have hydride acceptor site (positively charged Ni in [Ni(PS3*)(CO)]$^-$ and [Ni(PNP)$_{2}$]$^{2+}$) to moderately bond the hydrogen, and proton acceptor site (negatively charged S in [Ni(PS3*)(CO)]$^-$ and N in [Ni(PNP)$_{2}$]$^{2+}$) to strongly trap the protons [19,39,40]. These two sites work co-ordinately, resulting to its HER catalytic activity. Besides, Ni$_2$P has also been proved to be a highly active catalyst for HER because of its similar properties to [NiFe] hydrogenase [19,22,24]. Thus, it is reasonable to speculate that the high HER catalytic performance of crystalline Ni$_{12}$P$_5$ is related to the similar charged nature. After crystallization, Ni–P bond formed in Ni$_{12}$P$_5$ and it has a weak “ligand effect”, which make Ni hollow sites strong hydride acceptors [41], and negatively charged P can trap protons just like [NiFe] hydrogenase and its analogues. And according to Ref. [19] P occupied Ni hollow sites, making the removal of H$_2$ less energy-cost.

4 Conclusions

1) Amorphous Ni–P NPs and well crystallized Ni$_{12}$P$_5$ were successfully synthesized by autocatalytic reduction method and heat treatment process.

2) The electrochemical tests results show that the amorphous Ni–P NPs have poor HER catalytic activity, while crystalline Ni–P NPs are highly active HER catalysts.

3) During crystallization, electron transfer occurred from P to Ni, P occupied Ni hollow sites and Ni–P bond formed, which make the charged nature of Ni$_{12}$P$_5$ similar to [NiFe] hydrogenase and its analogous. This property makes the removal of H$_2$ less energy-cost and is very beneficial to HER catalytic activity.

References

[1] WIGLEY T M, RICHELS R, EDMONDS J A. Economic and environmental choices in the stabilization of atmospheric CO$_2$


