Ni₂P/CoP loading on Porous carbon matrix for hydrogen evolution

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Abstract. Due to high specific surface and plentiful of porosity, 3D porous carbon matrix has shown enormous potential for catalyst supporters. Hydrogen was thought as the next-generation clean energy to substitute the fossil fuel. Metal phosphides has been investigated and exhibited a good catalytic performance for hydrogen evolution reaction (HER). In this work, we prepared Ni₂P/CoP loading on Porous carbon matrix through a facile method. The mixture of nickel nitrate, cobalt nitrate and chitosan was ball-milled, then was carbonized under N₂ atmosphere at 900°C with NH₄HPO₂. The as-obtained materials were characterized by X-Ray diffraction (XRD), SEM and Raman spectrums. Also the electrochemical performance for HER was test using electrochemical workstation. The result shown that this catalysts presented a low overpotential at 10 mA cm⁻², which was 270 mV.

1 Introduction

Because of eco-friendly, clean and renewable advantages, hydrogen had been widely investigated to develop the application [1]. The traditional method was the coal production and methanol synthesis process production [2]. This method was high-cost and environmental pollution. And the purity was very poor for application. Recently, the electrochemical catalysts and photocatalysts had sprung up to catalyze the water split for hydrogen production [3]. Water could provide the plentiful of sources and the efficient was very high. The electrocatalysts could improve the reaction process and reduce the reaction free energy for HER. The traditional catalysts were noble metal compounds, such as Pt / C, the unique electron structure could facilitate the adsorption of intermediate H^{*} and form H-H for hydrogen evolution.

Due to high-cost and scarce natural resource, the demand for electrocatalysts for HER was hindered. To develop eco-friendly and plentiful resource had become a research hotspot. The transition metal compounds, such as such as Chalcogenides [4-6], carbides [7-10], and phosphides [11-13], had played a vital role to catalyze the hydrogen production. This aforementioned compounds exhibited a good conductivity, abundant of active sites and low overpotentials for the reaction process. Zhang et al. had prepared mesoporous FeP Film for hydrogen evolution [1]. The high proportion of mesopore contributed the more active sites and excellent electron transfer, which was beneficial for a high catalytic performance for HER. The overpotentials at a

current density of 10 mA cm⁻² was low to 65 mV, which was superior to the nanoparticle-stacked disordered porous structure. Meanwhile, several strategies had been adopted to construct multimetal compounds to form the interface, which accelerated the electron transfer and the desorption of intermediate H^{*}. MoP nanosheets with Mn-doped for hydrogen production were reported by Mu and coworkers [2]. Mn(CH₃COO)₂·4H₂O and MoO₃ were used as the precursors, NaH₂PO₂ could phosphorize the metal compounds. The Mn doping optimizes the electronic configuration of MoP, leading to lower charge transfer resistance and higher intrinsic activity. Herein, we prepared Ni₂P/CoP loading on Porous carbon matrix through a facile method using Ni(NO₃)₂, Co(NO₃)₂, chitosan and NH₄HPO₂ as precursors. The as-obtained materials had a high specific surface and a interconnect structure. The unique structure provided abundant of exposure active sites for catalytic behavior. The overpotential was 270 mV at a current density of 10 mA cm⁻².

2 Materials and methods

Materials: Ni(NO₃)₂, Co(NO₃)₂, chitosan and NH₄HPO₂ were purchased from Aladdin Co. Ltd. All reagents were of analytical reagent (AR) grade and were used without further treatment.

Preparation of catalysts:

Ni(NO₃)₂, Co(NO₃)₂, chitosan and NH₄HPO₂ were mixed using ball-milling for 4h, then the mixture were carbonization under N₂ atmosphere at 900°C to obtain a black materials, which was denoted as Ni₂P/CoP/CN.

Characterization:

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The as-prepared materials were characterized by an ASAP 2420 surface-area analyzer (Micromeritics, USA) with the Brunauer–Emmett–Teller (BET) method, X-ray diffractometry with CuK α radiation ($\lambda = 1.54 \text{ \AA}$), scanning electron microscopy and Raman spectrums.

HER electrochemical test:

The electrochemical performance was investigated through electrochemical workstation, LSV curves and tafel slopes were obtained. Potentials were referred to as the reversible hydrogen electrode (RHE), $E \text{ (vs. RHE)} = E \text{ (vs. SCE)} + 0.224 \text{ V}$, the electrolyte was 1.0M KOH.

3 Result and discussion

Figure 1 (a) N₂ adsorption/desorption curves; (b) pore size distribution curves

Table 1 Porous properties of as-obtained catalysts

Entry	S_{BET} (m ² g ⁻¹)	S_{micro} (m ² g ⁻¹)
Ni ₂ P/CN	510	401
CoP/CN	524	387
Ni ₂ P/CoP/CN	602	462

The microstructure properties were obtained through BET analysis and the corresponding results were shown in Figure 1 and Table 1. Obviously, the adsorption/desorption curves presented a similar hysteresis loops in Figure 1a, indicating the presence of mesopore structure. It was seen there was a rise up at the

$P/P_0 < 0.01$, which was caused by the micropore structure. As observed in Figure 1b, all the samples exhibited a approximate pore size, which was 3-7 nm. This porous structure was beneficial for the electron transfer and reduced the resistance for reaction process. The specific surface area was listed in Table 1. Compared with Ni₂P/CN and CoP/CN, Ni₂P/CoP/CN shown a larger specific surface area, which could provide plentiful of active sites for catalytic reaction.

Figure 2 SEM images of different samples(a: Ni₂P/CN; b: CoP/CN; c: Ni₂P/CoP/CN)

The porous morphology was observed through SEM and the images were presented in Figure 2. Clearly, a large of clusters of polymer particle were seen, which was formed in the carbonization process. The chitosan polymerized and aggregated to form the aforementioned particles. Meanwhile, the 3D interconnected porous structure also was obtained, which provided plentiful exposure active sites for hydrogen production reaction.

And the interconnected pathway could facilitate the ions and electron transfer for HER.

Figure 3 XRD pattern of Ni₂P/CoP/CN

The crystal structure was investigated through XRD and the pattern was shown in Figure 3. As seen in Figure 3, the peaks at 40.83°, 44.85°, 48.3° and 55.4° were corresponding to CoP (PDF No.00-054-0413), and the peaks located at 40.7°, 44.6°, 47.3° and 54.1° were assigned to Ni₂P (PDF No.01-089-4864). The aforementioned analysis verified that Ni₂P/CoP loading on Porous carbon matrix was successfully prepared through the aforementioned method.

Figure 4 Raman spectrum of Ni₂P/CoP/CN

The Raman spectrum was used to analyze the graphitization degrees. The lower graphitization degree, the better conductivity. As shown in Figure 4, two peaks at 1370 cm⁻¹ and 1590 cm⁻¹ was corresponding to graphite carbon (G line) and amorphous carbon (D line). And the ratio of I_D / I_G could declar the graphitization degree. The ratio of I_D / I_G was 1.12, which was low, indicating Ni₂P/CoP/CN had a good conductivity for electron transfer.

The electrochemical performance for hydrogen evolution reaction was tested and the corresponding results were presented in Figure 5. LSV curves shown that all the samples had a low overpotentials at a current density of 10 mA cm⁻², which was 310 mV (CoP/CN), 290 mV (Ni₂P/CN) and 270 mV (Ni₂P/CoP/CN), respectively. Ni₂P/CoP/CN exhibited a superior catalytic behavior, which was attributed to the porous structure and good conductivity. The porous structure could provide more exposure active sites and the good conductivity accelerated the electron transfer for HER. Compared with

others, Ni₂P/CoP/CN also had a smaller tafel slope value, 60 mV dec⁻¹, indicating Ni₂P/CoP/CN executed a good reaction kinetics for HER. The HER performance parameters were listed in Table 2. As shown in Table 2, the onset potential of Ni₂P/CoP/CN was smaller than others, indicated Ni₂P/CoP/CN had a good catalytic behavior for hydrogen evolution reaction. The stability of Ni₂P/CoP/CN was obtained and the result was presented in Figure 6. Compared with the first test, the 1000th test proved the catalyst exhibited an excellent stability for HER.

Figure 5 (a) LSV curves; (b) Tafel slopes

Table 2 HER Performance of as-obtained catalysts

Entry	E _{onset} (mV)	Ts (mV dec ⁻¹)
Ni ₂ P/CN	190	60
CoP/CN	210	74
Ni ₂ P/CoP/CN	180	70

Figure 6 LSV curves for 1st and 1000th

4 Conclusion

In summary, Ni₂P/CoP loading on Porous carbon matrix was prepared through a facile method. Chitosan was used as the carbon source, Ni(NO₃)₂, Co(NO₃)₂ and NH₄HPO₄ were adopted to obtain Ni₂P and CoP. The as-prepared materials exhibited a 3D interconnected structure, which benefited the electron transfer and provided more exposure active sites for reaction. Ni₂P/CoP/CN presented a low overpotential at a current density of 10 mA cm⁻², the tafel slope was 60 mV dec⁻¹, which was superior to previous reports.

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