Uniform Loading of Nickel Phosphide Nanoparticles in Hierarchical Carbonized Wood Channel for Efficient Electrocatalytic Hydrogen Evolution

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The development of self-supporting high-efficiency catalysts is a major challenge for the efficient production of H₂ via water splitting. In this manuscript, a freestanding Ni₂P-Ni₁₂P₅/carbonized wood (CW) composite electrode was prepared by a simple hydrothermal method and high-temperature calcination using pine wood with uniform channel as support and a large number of hydroxyl groups as nucleation center. The morphology and structural characteristics indicated that the Ni₂P and Ni₁₂P₅ nanoparticles were uniformly distributed within the hierarchical porous structure of the CW. In acid media, the as-prepared Ni₂P-Ni₁₂P₅/CW exhibits an excellent catalytic activity with a low overpotential of 151 mV at 10 mA cm⁻² and a reasonably good long-term stability.

1. Introduction

In order to realize the sustainable development of human society in the future, how to develop and utilize economic new clean energy has become a main research direction in energy area in the 21st century [1–4]. Direct electrochemical water splitting under room temperature and pressure by using electrocatalyst seems to represent one of the most sustainable and clean strategies for H₂ production. [5, 6]. The best well-known electrocatalytic catalyst for hydrogen evolution reaction (HER) is the precious metal platinum, which has high cost and limited reserves. Therefore, many researchers are paying great attention to the development of high-efficiency, cheap, and environmental-friendly HER catalysts.

Nickel phosphide, which is characterized by high activity, low cost, and earth-abundant, is considered to be one of the most potential alternative HER catalysts for Pt [7–10]. Nevertheless, there is still plenty of scope for improvement in preparation ways and performance. For example, in the traditional process of synthesizing nickel phosphide [11–13], PH₃ gas released through phosphatization reaction is a highly toxic substance, which will seriously pollute the environment. Moreover, the poor conductivity of metal phosphide makes electron transport difficult, which is usually improved by the addition of conductive carbon [14, 15] or metallic element [16, 17].

Wood is a cheap, biodegradable biomass material with well-aligned channels in the growth direction. After proper physical and chemical treatment, they can be derived into wood-based micro/nanomaterials with controllable structure and adjustable performance. These features make them promising materials for numerous applications including energy conversion, wastewater treatments, and microwave absorption [18–20]. At present, wood trunk in electrocatalysis area is still in its infancy, but very promising. A large number of studies have shown that the original channel structure can be maintained after the wood is carbonized at high temperature [21–23]. The resulting carbonized wood-
(CW-) based composites with a certain amount of graphitized carbon have good electrical conductivity, which is conducive to rapid electron transmission along the channel directions. Besides, they can be used directly as a self-standing electrode [24] and provides a strong combination between active substances and CW, leading to enhanced electron transport and stability over the long-term operation. However, it is not easy to load nanoparticles evenly in wood channels.

In this work, we selected the pine wood with uniform and regular channels as raw material and synthesized a Ni3P-Ni12P5/CW heterostructure composite through alkali treatment, hydrothermal reaction, and high-temperature calcination successively. Different from the traditional nongreen preparation method of transition metal phosphides with sodium phosphite or PH3 gas as the phosphorus source, the nontoxic NaH2PO4 was employed as the phosphorus source and the Ni-P-O precursor was loaded into the wood channel by a simple hydrothermal method. Then, the resulting Ni-P-O wood composites were calcined in an inert gas at a high temperature to obtain a self-standing, additive-free Ni2P-Ni12P5/CW electrode. The reason for the uniform loading of the active nanoparticles in the wood channels is that the abundant hydroxyl groups in the wood tracheid wall can act as the nucleation center of precursors. Impressively, the as-developed self-standing Ni3P-Ni12P5/CW electrode shows an excellent catalytic performance toward HER.

2. Materials and Methods

2.1. Materials. The pine wood was purchased from Chenzhou city, Hunan province, China. The reagents, including NaH2PO4·2H2O, Ni(NO3)2·6H2O, NH4OH (≥28%), Na2CO3, H2SO4, NaOH, and Na2SO3, were purchased from Sinopharm Chemical Reagent Co., Ltd. Organic solvents, including ethylene glycol (AR) and absolute ethyl alcohol (AR), were obtained from Sigma Chemistry Co. Ltd. The deionized water was used to make up all mixed solutions and throughout the experiments.

2.2. Pretreatment of Pine Wood Slices. The pine wood slices were cut into chips with a size of 2 × 2 × 0.2 cm along the radial direction by a coping saw. The obtained wood slices were immersed in a mixed solution of NaOH (1 M) and Na2SO3 (1 M) with the volume ratio of 1 : 1 at 80 °C for 24 h and then washed the slices with ethanol and deionized (DI) water in an ultrasonic cleaner for 20 min to remove soluble inorganic salts and other trace elements. Finally, the pine wood slices were dried at 80 °C for 24 h in vacuum.

2.3. Preparation of Ni3P-Ni12P5/CW Composite Electrode. The preparation process of the Ni3P-Ni12P5/CW composite materials is shown schematically in Figure 1. Firstly, the Ni-P-O/wood composites were synthesized by a facile one-pot hydrothermal method. Typically, ethylene glycol (10 mL), NH4OH (10 mL), an aqueous solution of Ni(NO3)2 (5 mL, 1 M), an aqueous solution of NaH2PO4 (7.5 mL, 1 M), and an aqueous solution of Na2CO3 (5 mL, 1 M) were mixed step by step under vigorous stirring. During this process, it takes two minutes to add the next solution. The reaction solution was rapidly stirred in ambient air for 5 min after the last substance is added. Secondly, the above solution was transferred into a 50 mL Teflon-lined autoclave, and a piece of wood substrate was immersed into the reaction solution, which was maintained at 150 °C for 24 h in an electric oven to produce Ni-P-O/wood composite precursors. From the XRD pattern in Figure 2(a), we can see the Ni-P-O/wood composite was constituted of ammonium nickel phosphate and nickel phosphate. In this process, because of the abundance of hydroxyl group in the wood channels, it can be served as nucleation for Ni-P-O growth and finally make the Ni-P-O uniform and stable load on the wood channels. This nucleation mechanism was also mentioned in our previous work [25, 26]. After the equipment cooled down to room temperature naturally, the wood slice was fetched out and ultrasonically cleaned using distilled water and ethanol several times in order to remove the product on the surface. After that, the wood slice loaded with Ni-P-O was dried in vacuum at 80 °C overnight. Finally, the Ni-P-O/wood was converted to Ni3P-Ni12P5/CW after calcining in Ar atmosphere at 800 °C for 200 min. The digital photograph of Ni-P-O/wood and Ni3P-Ni12P5/CW composites in Figure 2(b) shows the volume of wood block materials has shrunk and the particle has successfully loaded onto the surface of the wood after calcination at high temperature.

2.4. Characterization. The morphologies and elemental analysis of the Ni3P-Ni12P5/CW material were characterized using a scanning electron microscope (SEM, JSM-7800F, JEOL) equipped with an energy dispersive spectrometer (EDS). The crystal structures and phase characterization of them were measured by an X-ray diffractometer (X’Pert PRO, PANalytical) in the range of 5–90° (2θ). The specific surface area and pore distribution were examined using nitrogen adsorption and desorption isotherms on an automatic surface area and porosity analyzer (ASAP 2460, Micromeritics). The degree of graphitization of CW was conducted on a LabRAM HR Evolution (HORIBA Jobin Yvon SAS).

2.5. HER Experiments. All electrochemical tests were performed on CHI 760E chemical workstation (CH Instruments, Inc., Shanghai) using a typical three-electrode setup, with the graphite rod, saturated calomel electrode, and self-standing Ni3P-Ni12P5/CW acting as the counter, reference, and working electrode, respectively. Linear sweep voltammetry (LSV) was performed on a solution of 0.5 M H2SO4 with a scan rate of 5 mV·s−1. All potentials measured were calibrated to RHE using the following equation: \( E (\text{RHE}) = E (\text{SCE}) + 0.059 \times \text{pH} + 0.242 \). All experiments were carried out at room temperature (∼25°C).
3. Results and Discussion

3.1. Phase, Morphology, Chemical Composition, and Structure
Study of Ni2P-Ni12P5/CW

3.1.1. XRD. At first, the crystal structure of the as-prepared products was characterized by the XRD patterns as shown in Figure 3. The samples show a set of obvious peaks at 40.7°, 44.6°, 47.4°, 55.0°, and 74.8°, corresponding to (111), (201), (300), (211), and (400) of Ni2P (JCPDS: 74–1385), respectively, suggesting the end-products containing hexagonal Ni2P. Previous research studies have shown that Ni2P is one of the best catalysts for HER. In addition, the samples also include another phase, which can be indexed to the tetragonal Ni12P5 (JCPDS: 22–1190). The diffraction peaks of both Ni2P and Ni12P5 were sharp and intense, indicating their highly crystalline nature. Besides, we can see a broad peak at 23.4° and a weak peak at 26.4° in the pattern, which can be ascribed to the amorphous and graphitized carbon features of the CW block. These results indicate the obtained product is a composite material composed of Ni2P, Ni12P5, and CW.

3.1.2. SEM and EDS. Figure 4 shows some typical SEM images. From Figure 4(a), we can see clearly many straight channels along the growth direction of pine tree and the straight channels have different diameters and numerous small channels around the big channels. Figures 4(b) and 4(c) reveal that the Ni2P-Ni12P5 nanoparticles are evenly dispersed in the CW’s channels, and the size of nanoparticle is about 80 nm. Furthermore, the EDS data from Figure 5 demonstrate that the Ni2P-Ni12P5/CW electrode mainly consists of Ni, P, and C elements. The trace amount of O element may be due to the material’s exposure to the air. And the corresponding quantitative analysis of elements shows the atom ration of P/Ni = 1/3. After calculation, the molar ratio of Ni3P to Ni12P5 is about 1/7.
3.1.3. Raman Spectrum and Surface Area Study of Ni₂P-Ni₁₂P₅/CW. The Raman spectroscopy of the CW slice loading Ni₂P-Ni₁₂P₅ nanoparticles is presented in Figure 6(a). In the spectra, there are two characteristic bands: D band at around 1340 cm⁻¹ and G band at about 1590 cm⁻¹, respectively, match well with amorphous and graphitized carbons. In theory, when the temperature of calcination reaches 800°C, some of the carbon in CW slice will be converted to graphitized carbon. As expected, the \( I_D/I_G \) ratio is about 1.05, which suggests good crystallization of the Ni₂P-Ni₁₂P₅/CW obtained after 800°C annealing. Nitrogen absorption/desorption analysis was applied to investigate the Brunauer–Emmett–Teller (BET) surface area and pore diameter of the Ni₂P-Ni₁₂P₅/CW samples. From Figure 6(b), we can see the BET surface area of the Ni₂P-Ni₁₂P₅/CW is about 112.7 m²·g⁻¹. And this material has hierarchical pore structure, as shown in Figure 6(c).

3.2. Electrochemical Performance Study of Ni₂P-Ni₁₂P₅/CW. The HER catalytic activity of the integrated Ni₂P-Ni₁₂P₅/CW electrode is evaluated in 0.5 M H₂SO₄ solution using a three-electrode cell. And using the acid corrosion method, the load mass of the active substances of the Ni₂P-Ni₁₂P₅/CW electrode could be calculated to be about 0.36 mg·cm⁻².

Figure 4: SEM images of Ni₂P-Ni₁₂P₅/CW at different magnifications.

Figure 5: EDS spectra and element content analysis table of Ni₂P-Ni₁₂P₅/CW.

Figure 6: (a) Raman spectrum and (b, c) nitrogen adsorption-desorption isotherm of the prepared Ni₂P-Ni₁₂P₅/CW.
Ni$_2$P$_5$/CW electrode. As expected, the Ni$_2$P-Ni$_{12}$P$_5$/CW electrode exhibits a good HER activity and achieved a current density of 10 mA cm$^{-2}$ at a low overpotential of 151 mV. Further insight into the catalytic activity of Ni$_2$P-Ni$_{12}$P$_5$/CW is obtained by extracting the slopes from the Tafel plots in Figure 7(b). The calculated value of Tafel slopes is about 79 mV dec$^{-1}$, which suggests that HER on Ni$_2$P-Ni$_{12}$P$_5$/CW occurs via a Volmer–Heyrovsky mechanism. In addition, the Ni$_2$P-Ni$_{12}$P$_5$/CW electrode also exhibits strong durability in strong acid media (Figure 7(c)). Based on the above discussion and experimental results, the reasons for the superior properties of Ni$_2$P-Ni$_{12}$P$_5$/CW can be ascribed to the following points. Firstly, abundant channels in the CW provide a large specific surface area, facilitating electrolyte infiltration. Secondly, the graphitized carbon of the Ni$_2$P-Ni$_{12}$P$_5$/CW has excellent electrical conductivity, which is conducive to rapid electron transport. Thirdly, this self-supporting electrode of Ni$_2$P-Ni$_{12}$P$_5$/CW allows electrons to move quickly between the electrode and the active material.

4. Conclusions

In this work, we chose a cheap biomass material pine wood as the raw material and introduced Ni-P-O precursors by a hydrothermal method using a large number of hydroxyl groups in the wood channel as the nucleation center. After a high-temperature calcination process, a self-supporting Ni$_2$P-Ni$_{12}$P$_5$/CW electrode with Ni$_2$P-Ni$_{12}$P$_5$ nanoparticles evenly dispersed in the CW channels was obtained. With the highly porous feature, large surface area, good electrical conductivity, extended electronic structure, and preeminent structural stabilization of CW, the Ni$_2$P-Ni$_{12}$P$_5$/CW electrode exhibits excellent HER activity and stability.

Data Availability

The data used to support the findings of this study are included within the article.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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References

[1] U.S. Energy Information Administration, *International Energy Outlook*, U.S. Energy Information Administration, Washington, D.C., USA, 2016.
[2] British Petroleum, “Statistical review of world energy,” British Petroleum, London, UK, 2017.
[3] B. Dunn, H. Kamath, and J.-M. Tarascon, “Electrical energy storage for the grid: a battery of choices,” *Science*, vol. 334, no. 6058, pp. 928–935, 2011.
[4] W. Li, J. Liu, and D. Zhao, “Mesoporous materials for energy conversion and storage devices,” *Nature Reviews Materials*, vol. 1, p. 16023, 2016.
[5] L. Rößner and M. Armbärtst, “Electrochemical energy conversion on intermetallic compounds: a review,” *ACS Catalysis*, vol. 9, no. 3, pp. 2018–2062, 2019.
[6] D. A. Henckel, M. Henckel-Olivia, O. M. Lenz, K. M. Krishnan, and B. M. Cossairt, “Improved HER catalysis through facile, aqueous electrochemical activation of nanoscale WSe$_2$,” *Nano Letters*, vol. 18, no. 4, pp. 2329–2335, 2018.
[7] C. Cossairt, R. Zhang, and W. Lu, “Energy-saving electrolytic hydrogen generation: Ni$_2$P nanorarrays as a high-performance non-noble-metal electrocatalyst,” *Angewandte Chemie*, vol. 129, no. 3, pp. 860–864, 2017.
[8] J. Sun, Y. Chen, Z. Ren et al., “Self-supported NiS nanoparticle-coupled Ni$_2$P nanoflake array architecture: an advanced catalyst for electrochemical hydrogen evolution,” *ChemElectroChem*, vol. 4, pp. 1–9, 2017.
[9] H. Wen, L.-Y. Gan, H.-B. Dai et al., “In situ grown Ni phosphide nanowire array on Ni foam as a high-performance catalyst for hydrazine electrooxidation,” *Applied Catalysis B: Environmental*, vol. 241, pp. 292–298, 2019.
[10] R. Zhang, P. A. Russo, M. Feist, P. Amsalem, N. Koch, and N. Pinna, “Synthesis of nickel phosphate electrocatalysts from hybrid metal phosphonates,” *ACS Applied Materials & Interfaces*, vol. 9, no. 16, pp. 14013–14022, 2017.
[11] L.-A. Stern, L. Feng, F. Song, and X. Hu, “Ni2P as a Janus catalyst for water splitting: the oxygen evolution activity of Ni2P nanoparticles,” *Energy & Environmental Science*, vol. 8, no. 8, pp. 2347–2351, 2015.

[12] A. Dutta, A. K. Samantara, S. K. Dutta, B. K. Jena, and N. Pradhan, “Surface-oxidized dicobalt phosphide nanoneedles as a nonprecious, durable, and efficient OER catalyst,” *ACS Energy Letters*, vol. 1, no. 1, pp. 169–174, 2016.

[13] J. Chang, L. Liang, C. Li et al., “Ultrathin cobalt phosphide nanosheets as efficient bifunctional catalysts for a water electrolysis cell and the origin of cell performance degradation,” *Green Chemistry*, vol. 18, no. 8, pp. 2287–2295, 2016.

[14] Y. Li, P. Cai, S. Ci, and Z. Wen, “Strongly coupled 3D nanohybrids with Ni2P/carbon nanosheets as pH-universal hydrogen evolution reaction electrocatalysts,” *ChemElectroChem*, vol. 4, no. 2, pp. 340–344, 2017.

[15] J. Chang, Y. Xiao, M. Xiao, J. Ge, C. Liu, and W. Xing, “Surface oxidized cobalt-phosphide nanorods as an advanced oxygen evolution catalyst in alkaline solution,” *ACS Catalysis*, vol. 5, no. 11, pp. 6874–6878, 2015.

[16] Y. Lian, H. Sun, X. Wang et al., “Carved nanoframes of cobalt-iron bimetal phosphide as a bifunctional electrocatalyst for efficient overall water splitting,” *Chemical Science*, vol. 10, no. 2, pp. 464–474, 2019.

[17] Q. Sun, M. Zhou, Y. Shen et al., “Hierarchical nanoporous Ni(Cu) alloy anchored on amorphous NiFeP as efficient bifunctional electrocatalysts for hydrogen evolution and hydrazine oxidation,” *Journal of Catalysis*, vol. 373, pp. 180–189, 2019.

[18] Y. Wang, G. Sun, J. Dai et al., “A high-performance, low-tortuosity wood-carbon monolith reactor,” *Advanced Materials*, vol. 29, no. 2, p. 1604257, 2017.

[19] L. A. Berglund and I. Burgert, “Bioinspired wood nanotechnology for functional materials,” *Advanced Materials*, vol. 30, no. 19, p. 1704285, 2018.

[20] J. Song, C. Chen, S. Zhu et al., “Processing bulk natural wood into a high-performance structural material,” *Nature*, vol. 554, no. 7691, pp. 224–228, 2018.

[21] Y. Li, M. Cheng, E. Jungstedt, B. Xu, L. Sun, and L. Berglund, “Optically transparent wood substrate for perovskite solar cells,” *ACS Sustainable Chemistry & Engineering*, vol. 7, no. 6, pp. 6061–6067, 2019.

[22] S. Zhang, C. Wu, W. Wu et al., “High performance flexible supercapacitors based on porous wood carbon slices derived from Chinese fir wood scraps,” *Journal of Power Sources*, vol. 424, pp. 1–7, 2019.

[23] Q. W. Jiang, G. R. Li, F. Wang, and X. P. Gao, “Highly ordered mesoporous carbon arrays from natural wood materials as counter electrode for dye-sensitized solar cells,” *Electrochemistry Communications*, vol. 12, no. 7, pp. 924–927, 2010.

[24] H. S. Yaddanapudi, K. Tian, S. Teng, and A. Tiwari, “Facile preparation of nickel/carbonized wood nanocomposite for environmentally friendly supercapacitor electrodes,” *Scientific Reports*, vol. 6, p. 33659, 2016.

[25] Y. Bai, H. Zhang, L. Fang, L. Liu, H. Qiu, and Y. Wang, “Novel peapod array of Ni2P@graphitized carbon fiber composites growing on Ti substrate: a superior material for Li-ion batteries and the hydrogen evolution reaction,” *Journal of Materials Chemistry A*, vol. 3, no. 10, pp. 5434–5441, 2015.

[26] Y. Bai, L. Fang, H. Xu, X. Gu, H. Zhang, and Y. Wang, “Strengthened synergistic effect of metallic MxPy (M=Co, Ni, and Cu) and carbon layer via peapod-like architecture for both hydrogen and oxygen evolution reactions,” *Small*, vol. 13, no. 16, p. 1603718, 2017.