Facile Route Fabrication of Steam Exploded Poplar Loaded with Non-metal Doped Ni-Fe Nanoparticles: Catalytic Activities in 4-nitrophenol Reduction and Electrocatalytic Reaction

Cheng Pan (✉ ch_pan1018@hbut.edu.cn)

Hubei University of Technology

Guangying Yang

Hubei University of Technology

Haitao Yang

Hubei University of Technology

Research Article

Keywords: Steam exploded poplar, Ni-Fe nanoparticles, Catalytic hydrogenation

Posted Date: July 12th, 2021

DOI: <https://doi.org/10.21203/rs.3.rs-611719/v1>

License: © ⓘ This work is licensed under a Creative Commons Attribution 4.0 International License.

[Read Full License](#)

Abstract

A simple and effective method for the preparation of non-metallic ion-doped nickel-supported catalyst is reported. Using economical and recyclable fiber raw materials as carriers, nickel-supported catalysts are prepared by adsorption and reduction at room temperature. The nanoparticles dispersedly anchored on a rational support can efficiently inhibit the aggregation and thus enhance the catalytic activity. For the model catalytic hydrogenation of 4-NP by NaBH_4 , the N-B-Ni₂P/SEP and N-B-NiFeP/SEP catalysts exhibited much better catalytic performances than other catalysts recently reported in terms of the catalytic activity (reaction completed within 5 min), reaction rate constant (1.617 and 0.765 min^{-1}) and the activity factor K (539 and $255 \text{ min}^{-1} \cdot \text{g}^{-1}$), respectively. The catalyst showed activities for electrocatalytic HER and OER under ambient conditions. In general, the reported preparation method of nickel-supported catalyst is convenient, economical and environmentally friendly, which is in line with many green chemistry and sustainable development principles and widely available starting materials.

Introduction

The energy crisis and environmental pollution require clean and renewable energy to replace fossil fuels widely used by electricity. As an alternative energy carrier, hydrogen is becoming an important part of the future energy system because of its high energy density and environment-friendly. In recent years, hydrogen production by hydrolysis is an economical and feasible method. At present, the development of catalysts to improve hydrolysis efficiency is an urgent problem to be solved, so a variety of rare earth-rich non-precious metal catalysts have been developed. it contains transition metal compounds such as sulfides, phosphates, carbides, nitrides, oxides and selenides to solve the problem. The addition of non-metallic elements (O, S or N) to the transition metal-based electrocatalyst can also adjust the kinetics of the reaction and improve its catalytic activity. (Xu K et al. 2017; Hao J.H et al. 2017; Anjum MAR et al. 2018)

Nickel-supported catalysts have attracted wide attention in the hydrogenation, oxygen reduction and olefin oxidation of nitrobenzene and nitrophenol because of their low price and excellent catalytic performance. In order to facilitate the recovery of catalysts, nickel particles are usually dispersed on solid matrix to prepare heterogeneous nickel catalysts. Therefore, various materials are used as carriers, including silica, alumina, titanium dioxide, zirconia, magnesia, carbon and so on. Among them, porous carbon carrier is the most commonly used economic carrier, and carbon-based carriers such as cellulose paper with chemical deposition of metallic nickel particles on the surface (Sahasrabudhe A et al. 2018), nickel based mesoporous carbons (Yang Y et al. 2014), In-situ preparation of Ru nanoclusters and porous carbon (Ding R et al. 2020) have many advantages over other carriers because of their chemical inertia and good stability. Compared with other carbon materials, the advantages of carbonized fiber obtained from biomass include easier availability, easier regeneration and lower cost (Lai C et al. 2019).

Meanwhile, as the emphasis of technology is gradually shifting towards green synthetic strategy, the utilization of nontoxic, renewable and environmentally benign chemicals are required (C. Zhou et al. 2018;

Ming YuKuo et al. 2019). How to design high-value products with long life, reusability, cost-effectiveness and high efficiency is particularly important. The products of agricultural, industrial or forestry wastes are complex and difficult to separate, so how to transform them into specific products of a specific nature and complexity is particularly critical. How to transform it into a specific product of a specific nature and complexity is particularly critical. Other complex factors include excessive chemicals accumulated during the use of the product, natural aging, the recycling process itself and the flow of materials and products associated with it (Kümmerer K et al. 2020). Steam explosion is an optional pretreatment technology in the field of biomass conversion. The particle sizes of different types of agricultural wastes are different after steam blasting. In the process of steam explosion treatment of biomass raw materials, a large amount of water vapor permeates into biomass raw materials and forms hydrogen bonds with some hydroxyl groups on the cellulose molecular chain. At the same time, the condition of high temperature and high pressure aggravates the fracture of hydrogen bond in cellulose, releases new hydroxyl groups, increases the specific surface area of cellulose and increases the adsorption capacity of blasting products. Lignocellulose is an ideal carbon source for the preparation of carbon carriers because of its renewability and rich hydroxyl groups. In the process of preparation, it is of great significance to try to embed nickel nanoparticles directly into carbon materials to prepare "embedded" catalysts.

Here, we report a simple and effective method for the preparation of non-metallic ion-doped nickel-supported catalyst. using economical and recyclable fiber raw materials as carriers, nickel-supported catalysts are prepared by adsorption and reduction at room temperature. among them, non-metallic ions and Ni-Fe metal particles are highly dispersed. The nanoparticles dispersedly anchored on a rational support can efficiently inhibit the aggregation and thus enhance the catalytic activity. (Fu Y.K et al. 2019) Non-metallic ion-doped nickel-supported catalysts have catalytic activity and durability, and can be used in various catalytic reactions, such as electrochemical reaction, 4-nitrophenol reduction and so on. In general, the reported preparation method of nickel-supported catalyst is convenient, economical and environmentally friendly, which is in line with many green chemistry and sustainable development principles and widely available starting materials.

Experimental

Materials

Poplar was steam exploded at 213°C for 5 min. The compositional analysis of steam exploded poplar (SEP) on a dry basis was carried out. Analytical grade hydrogen sodium borohydride (NaBH_4), 4-nitrophenol (4-NP), were procured from Sigma-Aldrich (Shanghai, China). Nickel nitrate hexahydrate, Iron nitrate nonahydrate, ethanol, were analytical grade and procured from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). All chemicals were used without further purification.

Nickel Supported Catalyst Preparation

Steam-exploded poplar (SEP) prepared at 213°C for 5 min by steam explosion. 2g steam-exploded poplar (SEP) and Nickel nitrate hexahydrate (5mmol) were dispersed to 100 mL of deionized water for 15 minutes under ultrasonic treatment, and stirred for 40 minutes to completely dissolve. After completion of Ni^{2+} and SEP, 5 mL of NaBH_4 (0.5 mol/L) solution was added, and the boron-containing metal oxide was grown vertically in situ in SEP at room temperature. The resulting product was collected by centrifugation and washing with deionized water and ethanol, and then dried in vacuo to dry overnight. The carbon material was hereafter referred to as N-B-Ni/SEP. Thereafter, the obtained product was used to pyrolyze the feedstock as follows: the precursor and 200 mg NaH_2PO_2 will be prepared in both ends of the porcelain. Temperature was increased at a rate of 5°C/min under nitrogen protection, and the N-B-Ni/SEP was held for 1.5 hours at 350°C, followed by cooling to room temperature inside the furnace. The carbon material was hereafter referred to as N-B-Ni₂P/SEP. N-B-NiFeP/SEP was prepared by adding Nickel nitrate hexahydrate (5mmol) and Iron nitrate nonahydrate (5mmol), under the same conditions.

Characterization

The Fourier transform infrared spectrometer (Karlrsuebrook, Germany) used KBr pellet technology to measure FT-IR. The ZEISS Merlin roller was observed by scanning electron microscope (SEM) under 10kV voltage. Energy dispersive spectroscopy (EDS) was used to determine the element composition. The crystal structure of the sample was analyzed by Ultima IV X-ray diffractometer. The working voltage of the X-ray diffractometer was 40 kV, and the current density was 30 mA. X-ray photoelectron spectroscopy (XPS) analysis was carried out by using ESCALAB 250 analyzer (Thermo Science) and monochromatic Al Ka X-ray source. The adsorption-desorption isotherm of nitrogen was determined by BELSORP-mini II instrument and Brunauer-Emmett-Teller (BET) method. The UV-vis absorption spectra were recorded via a UV-2900 spectrophotometer (Hitachi, Japan). Inductive coupling plasma emission spectrometer (ICP-OES) was carried out by using PerkinElmer 8300 analyzer.

Catalytic Reduction Of 4-np

The reduction of 4-nitrophenol (4-NP) was carried out in a quartz cuvette and monitored using UV-vis spectroscopy (Hitachi UV-2900) at room temperature. For comparison, the aqueous 4-NP solution (0.01 M) was prepared and measured prior to monitoring the change of absorption. Then a total of 25 μL of aqueous 4-NP solution was mixed with 2.5 ml of a fresh NaBH_4 (0.01 M) solution. Subsequently, a given amount of nickel catalyst was added to start the reaction, and the UV spectrometry was employed to in situ monitor the reduction by measuring the absorbance of the solution at 400 nm over time.

Electrochemical Characterization

The electrochemical measurement was carried out at room temperature using a three-electrode device using CHI760E electrochemical workstation. The glassy carbon electrode was the working electrode

(opposite electrode) and the Ag/AgCl electrode is the reference electrode. The linear sweep voltammogram (LSV) was recorded at the scanning rate of 5mV/s in 1.0M KOH electrolyte for OER, and in 0.5M H₂SO₄ for HER. The scanning range was 1.0-1.8vs.RHE. The linear sweep voltammetry curve was obtained by the scanning rate of 5mV/s, and the linear sweep voltammetry curve was corrected by 90% IR compensation method. According to the Nernst equation ($E_{RHE} = E_{Ag/AgCl} + 0.059 \cdot pH + 0.197$), the measured potential was converted into the corresponding reversible hydrogen electrode potential. The current density (J) was normalized to the geometric surface area, and the measured potential E_{Appl} (vs.Ag/AgCl) was converted into reversible hydrogen electrode (RHE). The overpotential (η) of OER when the current density was 10mA/cm² is calculated by using the equation ($\eta = E_{RHE} - 1.23V$). The overpotential (η) of HER when the current density was 10mA/cm² is calculated by using the equation ($\eta = E_{RHE}$). According to the Tafel equation ($\eta = a + b \cdot \log(J)$) to calculate the Tafel slope (b), Tafel slope could be obtained by fitting the linear part of the Tafel curve. (Cao Y.Q et al. 2020; Lan K et al. 2019)

Results And Discussion

Characterizations

The FTIR analyzer was used to identify the functional groups on the Catalyst samples and SEP surface, which are shown in Fig. 1. The FTIR spectra showed strong absorption at 3421 cm⁻¹, which was due to stretching of the phenolic and aliphatic hydroxyl groups. Peaks at around 2921 cm⁻¹ that were related to the C-H functional group changed after the nickel-supported catalyst samples were prepared by SEP. The results showed that there were chemical interactions and ion changes between OH, C-H, C=O, and heavy metal ions in the bio-adsorption process of nickel (Foroutan F et al. 2019). The FT-IR spectrum of N-B-Ni₂P/SEP, N-B-NiFeP/SEP and N-B-NiFeP/SEP-1 confirmed the existence of NO₃⁻ and OH⁻ group in the Nickel iron load catalyst (Fig. 1). The bands at 1596, 1363 and 777 cm⁻¹ were characteristic vibration for H₂O, -NO₃⁻ and Metal-O (M-O) (Lee S et al. 2019; H Yang et al. 2019), respectively, which proved again that the NiFe was formed on SEP. Compared with blank SEP, the change of absorption peak at 777 cm⁻¹ indicated that metal particles are attached to the surface of SEP. while the weak peaks at 1112 cm⁻¹ is characteristic of the C-N stretching mode. (Coates J. 2006) The absorption peaks of repeatedly used catalysts at 777 cm⁻¹ was not lowered, indicating that the catalytic process did not affect the transition metal particles on the surface of the carrier.

The morphology and microstructural information of the N-B-NiFeP/SEP and N, B-Ni₂P/SEP were systematically studied using electron microscopy techniques. (Xiao C.L et al. 2016) The closely packed

NiFe coating deposited at room temperature did not change the fiber structure of steam-exploded poplar (Fig. 2a-b). It can be seen from nickel-plated iron or nickel scanning electron microscope (SEM) that there are a large number of voids in the bracket. SEM images (Fig. 2a-b) show the growth of NiFe layer Ni-P vertically arranged nano-thin sheets, with interconnected macroporous morphology, will not hinder the underlying macroporous structure. This interesting morphology is beneficial to electrocatalysis because it

provides a large number of exposed catalytic active sites and enables electrons to travel rapidly along vertical nanoflakes. Energy dispersive X-ray (EDX) spectroscopy was used to further characterize the elemental composition and distribution of the Nmai-B-talk NiFeP-hand EDS samples by EDS surface scan (Fig. 2d-g). The results show that Ni, Fe, P, B and N are uniformly distributed in the sample, and the atomic ratio is 1.28 (Ni): 1.21 (Fe). It is further confirmed that B and N atoms have been successfully entered into SEP. The above results further prove that the NMagi B talk NiFeP hand SEP is successfully realized by introducing zero valent NMagi B atoms.

The detailed structural features of the obtained sample were firstly investigated by X-ray diffraction (XRD). All the diffraction peaks can be ascribed to hexagonal Ni_2P (JCPDS card No. 03-065-1989) without any peaks for impurities, suggesting the N-B- Ni_2P /SEP precursor was successfully converted into nickel phosphide/SEP. (Pinilla J.L et al. 2016; Sun Y.Q et al. 2020). The diffraction pattern for PC has a broad peak at 26, which were characteristic of the (002) plane of graphitic carbon (Fig. 3).

Compared with N-B- Ni_2P /SEP, the four diffraction peaks of Ni_2P in the XRD spectrum of Fe-doped catalyst (N-B-NiFeP/SEP) shift to a larger diffraction angle with the doping of Fe, indicating that Fe atoms enter the Ni lattice to form Fe-Ni alloy. The intensity of the diffraction peaks of 111, 201, 210 and 300 of Ni decreases with the doping of Fe, indicating that the doping of Fe will affect the crystallinity of the alloy particles.

The average crystallite size was determined to be about 10.78 nm for N-B-NiFeP/SEP, and 17.97 nm for N-B- Ni_2P /SEP from the (111) reflection by utilizing Scherrer's equation relating the coherently scattering domains with Bragg peak widths: $D = k\lambda/B \cos(\theta)$, in which $k = 0.89$ for spherical particles and B is the full angular width at half-maximum of the peak in radians. On the basis of these results, we come to the conclusion that the metal particles can be well dispersed on the surface of the fiber, and the doping of Fe will affect the crystallinity of the alloy particles. The above results showed that the addition of Ni could effectively promote the miniaturization of Fe grains (Mansouriieh N et al. 2016). The XRD pattern of NiFe/Ni-P electrode (Fig. 3) further confirms the amorphous nature of NiFe catalyst layer as no new peaks are observed besides those from the catalyst. In fact, it has been proposed that amorphous NiFe electrocatalysts are much more active than their crystalline counterparts due to their structural flexibility and a high density of co-ordinatively unsaturated sites that help in the adsorption of oxidized intermediates.

Table 1
Catalysts composition determined by ICP-MS and XPS

Catalysts	Fe loading (wt%)	Ni loading (wt%)	Fe:Ni (molar ratio)	FeNi loading (wt%)	
N-B-NiFeP/SEP (1:1)	15.58	17.19	1:1.05	32.77	ICP-MS
N-B-Ni ₂ P/SEP	/	27.71	/	27.71	
N-B-NiFeP/SEP (1:1)	14.84	11.14	1:0.75	25.98	XPS
N-B-Ni ₂ P/SEP	/	13.88	/	13.88	

The XPS survey scan spectrum (Fig. 4a) clearly confirmed that all Ni, Fe, B, P, N, O, and C elements were in the samples. According to XPS analysis, the contents of Ni and Fe in N-B-NiFeP/SEP were measured to be 11.14 and 14.84 wt% (Table 1), respectively. The molar ratio and actual total loading content of Fe and Ni in the N-B-NiFeP/SEP and N-B-Ni₂P/SEP catalysts were further determined by ICP-MS, as shown in Table 1. The results are in good agreement with the theoretical molar ratio, indicating that the Ni and Fe metal particles are uniformly dispersed on the steam explosion poplar carrier. It should be pointed out that Ni and Fe loading of N-B-NiFeP/SEP from ICP-OES (17.19 and 15.58 wt%) analysis is much higher than the outmost surface Ni and Fe content (11.14 and 14.84 wt%) measured by XPS. This result helps us to conclude that the tiny Ni and Fe are embedded in the carbon fiber instead of anchored on the surface. (Ding R et al. 2020) This phenomenon is more obvious in the nickel content of the N-B-Ni₂P/SEP.

The high-resolution spectra of the Ni 2p region showed two peaks, 2p_{3/2} (856.82 eV) and 2p_{1/2} (874.47 eV) correspond to the Ni²⁺ derived from the oxidation of the Ni₂P surface, respectively (with corresponding shakeup satellite peaks at 862.26 and 880.03 eV) (Ding Y et al. 2020). The Fe 2p spectrum (Fig. 4h) could be fitted into two separate peaks at 711.76 and 724.68 eV corresponding to the spin-orbit states of Fe 2p_{3/2} and Fe 2p_{1/2}, respectively. This also confirms that Fe predominantly exists in the Fe³⁺ state. As shown in Fig. 4g, compared with N-B-Ni₂P/SEP, the negative shift of Ni2p indicates a decrease in the number of electrons at Fe site and the accumulation of electrons around the Ni site (Jiao S.L et al. 2019). These changes in electron accumulation changed the distribution of electrons, thus changing the local electronic structure of the metal position.

The XPS spectrum (Fig. 4c) for O 1s of samples can be deconvoluted into two peaks at binding energies of 531.08 and 532.08 eV, which were attributed to surface adsorbed water (-OH) and C-O species (oxygen vacancies), respectively. The oxygen vacancies indicate a defect site with low oxygen coordination, which decrease the barrier for the adsorption of OH⁻ and promotes OER. In particular, N-B-NiFeP/SEP and N-B-Ni₂P/SEP had a clear difference area of oxygen vacancies due to Fe metal ions (29.49% : 51.62%). (Xu W.J et al. 2018; Kim S.H et al. 2020)

As shown in Fig. 4b, the four components of C1s spectrum (284.77, 286.36, 288.49 and 291.54 eV) were attributed to sp² C-C, sp³ C-C, C-O and carboxylic groups, respectively. In the high-resolution XPS spectra of P 2p exhibits three contributions, P 2p_{3/2} and P 2p_{1/2}, located at respectively 129.49 and 130.46 eV (Fig. 4e), which can be assigned to Ni₂P, and the peak at 133.72 eV can be caused by oxidized P species.

The B 1s spectrum (Fig. 4f) clearly evidences the presence of three chemical environments for phosphorus atoms (B-O, B-C, and B-Ni). The existence of B³⁺ in N-B-NiFeP/SEP and N-B-Ni₂P/SEP catalyst is evidenced by the peak at 192.05 eV (Fig. 4f), which can be attributed to borate species surface oxidation. Compared with N-B-Ni₂P/SEP, the peak intensity at 191.16 eV of N-B-NiFeP/SEP that corresponds to B-C bonds was higher, which indicated that some C atoms in carbon fiber are replaced by B atoms. Pleasantly, the peak at 187.66 eV can be attributed to B(0) in the Ni-B bonds, which matches well with the previous literature. This result suggests that there are abundant zero valent B atoms in the N-B-NiFeP/SEP and N-B-Ni₂P/SEP after N₂ treatment.

As for the high-resolution N 1s spectrum, in addition to the characteristics related to pyrrolic-N (402.07 eV) and pyridinic-N (400.00 eV), a characteristic peak with a 397.10 eV binding energy is observed in the N regions, that is ascribed to metal-nitrogen bonds, indicating zero valent N(0) atoms in the N-B-NiFeP/SEP and N, B-Ni₂P/SEP (Fig. 4d). The presence of N dopant in the sample will inherently improve the interaction ability with the reactants and produce a higher positive charge density on its adjacent carbon atoms, which may also contribute to the high activity of the sample. (Sun Y.Q et al. 2020) Therefore, the above results indicate that the zero valent N, B atoms were successfully doped into N, B-Ni₂P/SEP and N-B-NiFeP/SEP.

The crystallization and graphitization degree of carbonized steam exploded poplar support on nickel-supported catalyst and Ni-Fe bimetallic catalyst were studied by Raman spectroscopy. In general, the I_D/I_G ratio less than one is ideal. As shown in Fig. 5, the carbon fiber carriers have high quality and crystallinity, the peak intensity ratio (I_D/I_G) is less than one, and the carbon samples show two distinct bands. The first band is the well-known D band, located at 1363cm⁻¹, attributed to disorder in the carbon structure, such as defects in the carbon structure or amorphous carbon. (M.S.Dresselhaus et al. 2002; Awadallah A.E et al. 2013) On the other hand, the vibration of sp² carbon atoms in the graphitization region forms the G band located in 1589 cm⁻¹. (Buthainah Ali et al. 2017; Allaedini G et al. 2015) Generally, the ratio of D-band strength to G-band strength I_D/I_G is used to reflect the degree of graphitization. The I_D/I_G ratio of N-B-NiFeP/SEP is 0.89, which indicates that a large number of defects and irregular structures have been introduced into the carbon fiber carrier. The I_D/I_G ratio was further increased to 0.95 for N-B-Ni₂P/SEP, representing the enhanced number of structural defects, increased localized sp³ defects in sp² framework, high electrical conductivity.

The specific surface area and porosity of the obtained materials have been investigated by N₂ adsorption-desorption experiments. In the curves of N-B-NiFeP/SEP and N-B-Ni₂P/SEP (Fig. 6a), the type IV adsorption branches were corresponding to the mesoporous structure. According to IUPAC

classification, the isotherms (Fig. 6) of the mixed oxides were classified as type IV with an H3 hysteresis loop, suggesting the existence of mesoporous materials with an incision-like pore geometry. The specific surface area of N-B-NiFeP/SEP and N-B-Ni₂P/SEP were calculated to be 55.44 and 57.18 m²·g⁻¹, respectively. The pore size distributions are shown in Fig. 6b. The average pore size of N-B-NiFeP/SEP was about 11.86 nm, while those of N-B-Ni₂P/SEP was around 8.42 nm. It was clear that N-B-NiFeP/SEP and N-B-Ni₂P/SEP were mainly composed of micropores and mesopores around 10 nm. As shown in Fig. 6d, the average pore widths of three samples follow the order of N-B-NiFeP/SEP > N-B-Ni₂P/SEP and the pore volumes of N-B-NiFeP/SEP and N-B-Ni₂P/SEP were 0.19 and 0.11 cm³·g⁻¹, respectively. The pore structure of materials played an important and even decisive role in many properties of materials. Carbon materials as carriers, their porous properties were conducive to the diffusion of substrates and products, and can expose more active sites, thus improving the overall activity of the catalyst.

Catalytic Performance

3.2.1 Oxygen evolution reaction

The electrocatalytic OER performance of N-B-NiFeP/SEP and N-B-Ni₂P/SEP were studied in O₂-saturated 1 M KOH. The linear sweep voltammograms (LSVs) data (Fig. 7a-b) was recorded with the scan rate of 5 mV·s⁻¹. N-B-Ni₂P/SEP showed that the Ni²⁺/Ni³⁺ was oxidized in the potential range of 1.35–1.5 V (all potentials were versus reversible hydrogen electrode (RHE)) (Fig. 7b). The existence of the oxidation peak indicated that the insufficient oxidation may not form a fully protected NiO shell outside the Ni nanoparticles, leading to corrosion of metal Ni and the formation of NiOOH during OER in alkaline solution (Sivanantham A et al. 2016). The curves of polarization (Fig. 7a-b) showed that the N-B-NiFeP/SEP exhibited excellent OER performance with a overpotential of 395mV at 10 mA·cm⁻² and 488mV at 30 mA·cm⁻² current density, compared to N-B-Ni₂P/SEP (431 and 579 mV).

In addition, to investigate the kinetics of these catalysts, the Tafel slopes obtained from the LSV polarization curves were shown in Fig. 7c. The Tafel slope of N-B-NiFeP/SEP (101 mV dec⁻¹) was considerably smaller than those of N-B-Ni₂P/SEP (151 mV dec⁻¹), confirming its faster OER kinetics. According to our research results, it can be concluded that the synergetic effect of Ni-Fe bimetal load and carbon carrier played an important role in facilitating the kinetics of OER (Li Y.Y et al. 2020; Jiang J et al. 2018; Yue S et al. 2019).

3.2.2 Hydrogen evolution reaction

To assess the electrocatalytic HER activity of the N-B-NiFeP/SEP and N-B-Ni₂P/SEP, the related electrochemical measurements were performed using a three-electrode system. Figure 7d showed the polarization curves of the N-B-NiFeP/SEP and N-B-Ni₂P/SEP in N₂-saturated 0.5 M H₂SO₄ solution. In comparison to N-B-Ni₂P/SEP, which shows a η₁₀ value of 397 mV, the N-B-NiFeP/SEP requires 392 mV to

reach 10 mA cm^{-2} , which means that the Fe trace in N-B-NiFeP/SEP do not contribute to the electrochemical activities and remain as mere spectator species. Tafel slopes were drawn to evaluate HER kinetics (Fig. 7e). The Tafel slope is 122 mV dec^{-1} for N-B-NiFeP/SEP, which is much smaller than that N-B-Ni₂P/SEP (119 mV dec^{-1}). In the study of the mechanism of electrocatalytic hydrogen evolution in acidic media, it is generally believed that the reaction process is divided into the following three steps: the first step is the electrochemical reaction process, the second step is the electrochemical desorption process, and the third step is the compound desorption process. The general hydrogen evolution reaction mechanism includes at least an electrochemical process and a desorption process, so it can be divided into Volmer-Heyrovsky mechanism or Volmer-Tafel mechanism according to different rate steps. As can be seen from the diagram, the Tafel slope of the N-B-NiFeP/SEP and N-B-Ni₂P/SEP is 122 and 119 mV dec^{-1} , respectively. So the hydrogen evolution process of the catalyst in acidic medium is a slow discharge mechanism, and the Volmer reaction process is a rate control step, which is Volmer-Heyrovsky mechanism (B.E. Conway et al. 2002; Li D.J et al. 2014; Yanguang Li et al. 2011).

3.2.3 Catalytic activity for 4-NP hydrogenation as a model reaction

Removal of 4-nitrophenol (4-NP) from wastewater is of significant importance in view of environment protection since 4-NP is a prevalent contaminant produced in industry and agriculture (Choi S et al. 2019; Ding R et al. 2020). It is known that 4-aminophenol (4-AP) is very useful and important in many applications including analgesic and antipyretic drugs, photographic developer, corrosion inhibitor and anticorrosion-lubricant. The reduction of 4-NP to 4-AP has been extensively used as a benchmark system to evaluate the catalytic activity of metal NPs (Guohui Chang et al. 2012; Yang Y et al. 2014).

Therefore, the reduction of 4-NP toward 4aminophenol (4-AP) in the presence of NaBH₄ was selected as a model reaction to further confirm the generality of N-B-NiFeP/SEP and N-B-Ni₂P/SEP. As shown in Fig. 8a, the adsorption peak of 4-NP was red-shifted from 317 to 400 nm immediately upon the addition of NaBH₄ solution which corresponds to a color change from light yellow to yellow green, due to the formation of the 4-nitrophenolate ion under alkaline conditions. When catalyst was added, the intensity of characteristic peak at 400 nm quickly declined. The reduction of 4-NP was completed within 10 min over 3 mg N-B-Ni₂P/SEP and N-B-NiFeP/SEP (Fig. 8c). Considering that the reductant concentration is much higher than that of 4-NP ($C_{\text{NaBH}_4}/C_{4\text{-NP}} = 100$) in the reaction mixture, the pseudo-first-order rate kinetics with respect to 4-NP concentration could be used to evaluate the catalytic rate. The reaction kinetics can be described as $-\ln(C_t/C_0) = kt$, where k is the rate constant at a given temperature and t is the reaction time. C_0 and C_t are the 4-NP concentration at the beginning and at time t , respectively. As expected, a good linear correlation of $\ln(C_t/C_0)$ vs. reaction time t was obtained (Fig. 8b), whereby the kinetic rate constant k was estimated to be 1.617 ($R^2 = 0.99$) and 0.765 ($R^2 = 0.99$) min^{-1} for N-B-Ni₂P/SEP and N-B-NiFeP/SEP. To compare different catalysts, we calculated the ratio of rate constant K over total weight of nickel catalyst, where $K = k/m$. Thus the activity factor K was calculated to be 539 and 255 $\text{min}^{-1} \cdot \text{g}^{-1}$ for

N-B-Ni₂P/SEP and N-B-NiFeP/SEP, respectively. It is clear that N-B-Ni₂P/SEP shows the largest activity factor.

The excellent catalytic performances of N-B-Ni₂P/SEP for 4-nitrophenol reduction can be contributed to the following featured advantages. From the point of view of catalysis, steam explosion poplar is an ideal substrate for the growth of active catalyst layer. Because there are abundant coordination hydroxyl groups and epoxy functional groups on the cellulose microfiber, the ultra-fine and clean metal nanoparticles formed in situ are uniformly dispersed on the surface of the carrier rather than embedded in the carrier. Together, these two functions can lead to stronger binding and faster mass transfer kinetics.

Conclusions

In summary, using economical and recyclable fiber raw materials as carriers, nickel-supported catalysts are prepared by adsorption and reduction at room temperature. For the model catalytic hydrogenation of 4-NP by NaBH₄, the N-B-Ni₂P/SEP and N-B-NiFeP/SEP catalysts exhibited much better catalytic performances than other catalysts recently reported in terms of the catalytic activity (reaction completed within 5 min) and reaction rate constant (1.617 and 0.765 min⁻¹). The catalyst showed activities for electrocatalytic HER and OER under ambient conditions. In general, the reported preparation method of nickel-supported catalyst is convenient, economical and environmentally friendly, which is in line with many green chemistry and sustainable development principles and widely available starting materials.

Declarations

Ethical statement

I certify that this manuscript is original and has not been published and will not be submitted elsewhere for publication while being considered by Cellulose. And the study is not split up into several parts to increase the quantity of submissions and submitted to various journals or to one journal over time. No data have been fabricated or manipulated (including images) to support your conclusions. No data, text, or theories by others are presented as if they were our own.

The submission has been received explicitly from all co-authors. And authors whose names appear on the submission have contributed sufficiently to the scientific work and therefore share collective responsibility and accountability for the results.

The authors declare that they have no conflict of interest.

This article does not contain any studies with human participants or animals performed by any of the authors. Informed consent was obtained from all individual participants included in the study.

Acknowledgements

The authors are grateful for the support of the National Nature Science Foundation of China (NSFC, No. 21978074).

References

1. Awadallah A.E, Aboul-Enein A.A, Aboul-Gheit A.K. (2013). Various nickel doping in commercial Ni-Mo/Al₂O₃ as catalysts for natural gas decomposition to CO_x-free hydrogen production, *Renwable Energy* 57:671-678. 10.1016/j.renene.2013.02.024
2. Allaedini G, Aminayi P, Tasirin S.M. (2015). The Effect of Alumina and Magnesia Supported Germanium Nanoparticles on the Growth of Carbon Nanotubes in the Chemical Vapor Deposition Method, *Journal of Nanomaterials* 2015:1-6. 10.1155/2015/961231
3. Anjum MAR, Okyay MS, Kim M, et al. (2018). Bifunctional sulfur-doped cobalt phosphide electrocatalyst outperforms all-noble-metal electrocatalysts in alkaline electrolyzer for overall water splitting, *Nano Energy* 53: 286-295. 10.1016/j.nanoen.2018.08.064
4. B.E. Conway, B.V. Tilak. (2002). Interfacial processes involving electrocatalytic evolution and oxidation of H₂, and the role of chemisorbed H, *Electrochimica Acta* 47(22): 3571–3594. 10.1016/S0013-4686(02)00329-8
5. Buthainah Ali, Dayang R. A. Biak, Sapuan S. M, et al. (2017). Preparation of Carbon Nanotubes via Chemical Technique (Modified Staudenmaier Method). *Nanoscience & Nanotechnology-Asia* 7(1): 113–122. 10.2174/2210681206666160711161421
6. Coates J. (2006). Interpretation of Infrared Spectra, A Practical Approach. *Encyclopedia of analytical chemistry* 331. 10.1002/9780470027318.a5606
7. C. Zhou, C. Lai, C. Zhang, et al. (2018). Semiconductor/boron nitride composites: synthesis, properties, and photocatalysis applications, *Applied Catalysis B: Environmental* 238: 6-18. 10.1016/j.apcatb.2018.07.011
8. Choi S, Oh M. (2019). Well-arranged and confined incorporation of PdCo nanoparticles within a hollow and porous metal-organic framework for superior catalytic activity, *Angewandte Chemie International Edition* 58(3): 866–871. 10.1002/anie.201812827
9. Cao Y.Q, Zhang H, Ji S.F, et al. (2020). Adsorption Site Regulation to Guide Atomic Design of Ni-Ga Catalysts for Acetylene Semi-Hydrogenation, *Angewandte Chemie-International Edition* 59(28):11647-11652. 10.1002/anie.202004966
10. Ding Y, Miao BQ, Li SN, et al. (2020). Benzylamine oxidation boosted electrochemical water-splitting: Hydrogen and benzonitrile co-production at ultra-thin Ni₂P nanomeshes grown on nickel foam, *Applied Catalysis B-Environmental* 268(118393). 10.1016/j.apcatb.2019.118393
11. Ding R, Chen Q, Luo Q, et al. (2020). Salt template-assisted in situ construction of Ru nanoclusters and porous carbon: excellent catalysts toward hydrogen evolution, ammonia-borane hydrolysis, and 4-nitrophenol reduction, *Green Chemistry* 22(3): 835-842. 10.1039/c9gc03986d

12. Fu Y.K, Qin L, Huang D.L, et al. (2019). Chitosan functionalized activated coke for Au nanoparticles anchoring: Green synthesis and catalytic activities in hydrogenation of nitrophenols and azo dyes, *Applied Catalysis B-Environmental* 255. 10.1016/j.apcatb.2019.05.042
13. Foroutan F, Carta D, McGuire J, et al. (2019). Antibacterial copper-doped calcium phosphate glasses for bone tissue regeneration, *ACS Biomaterials Science & Engineering* 5: 6054–6062. 10.1021/acsbiomaterials.9b01291
14. Guohui Chang, Yonglan Luo, Wenbo Lu, et al. (2012). Ag nanoparticles decorated polyaniline nanofibers: synthesis, characterization, and applications toward catalytic reduction of 4-nitrophenol and electrochemical detection of H₂O₂ and glucose, *Catalysis Science & Technology*, 2(4): 800-806. 10.1039/c2cy00454b
15. Hao J.H, Yang W.S, Peng Z, et al. (2017). A Nitrogen Doping Method for CoS₂ Electrocatalysts with Enhanced Water Oxidation Performance, *ACS Catalysis* 7(6):4214-4220. 10.1021/acscatal.7b00792
16. H Yang, C Wang, Y Zhang, Q Wang. (2019). Green synthesis of NiFe LDH/Ni foam at room temperature for highly efficient electrocatalytic oxygen evolution reaction, *Science China Materials* 62(5):681-689. 10.1007/s40843-018-9356-1
17. Jiang J, Sun F.F, Zhou S, et al. (2018). Atomic-level insight into super-efficient electrocatalytic oxygen evolution on iron and vanadium co-doped nickel (oxy)hydroxide, *Nature Communications* 9(2885). 10.1038/s41467-018-05341-y
18. Jiao S.L, Yao Z.Y, Li M.F, et al. (2019). Accelerating oxygen evolution electrocatalysis of two-dimensional NiFe layered double hydroxide nanosheets via space-confined amorphization, *Nanoscale* 11(40):18894-18899. 10.1039/c9nr07465a
19. Kümmerer K, Clark J.H, Zuin V.G. (2020). Rethinking chemistry for a circular economy, *Science* 367(6476): 369-370. 10.1126/science.aba4979
20. Kim S.H, Park Y.S, Kim C, et al. (2020). Self-assembly of Ni-Fe layered double hydroxide at room temperature for oxygen evolution reaction, *Energy Reports* 6: 248-254. 10.1016/j.egyr.2020.10.007
21. Li D.J, Maiti U.N, Lim J, et al. (2014). Molybdenum Sulfide/N-Doped CNT Forest Hybrid Catalysts for High-Performance Hydrogen Evolution Reaction, *Nano Letters* 14(3): 1228-1233. 10.1021/nl404108a
22. Lai C, Zhang M, Li B, et al. (2019). Fabrication of CuS/BiVO₄ (040) binary heterojunction photocatalysts with enhanced photocatalytic activity for Ciprofloxacin degradation and mechanism insight. *Chemical Engineering Journal* 358: 891-902. 10.1016/j.cej.2018.10.072
23. Lan K, Li J, Zhu Y, et al. (2019). Morphology engineering of CoSe₂ as efficient electrocatalyst for water splitting, *Journal of colloid and interface science* 539:646-653. 10.1016/j.jcis.2018.12.044
24. Lee S, Cho HS, Cho WC, et al. (2019). Operational durability of three-dimensional Ni-Fe layered double hydroxide electrocatalyst for water oxidation, *Electrochimica Acta* 315: 94-101. 10.1016/j.electacta.2019.05.088
25. Li Y.Y, Huang J.W, Rao G.F, et al. (2020). Enhanced water oxidation activity of 3D porous carbon by incorporation of heterogeneous Ni/NiO nanoparticles, *Applied Surface Science* 530. 10.1016/j.apsusc.2020.147192

26. M.S.Dresselhaus, G Dresselhaus, A.Jorio, et al. (2002). Raman spectroscopy on isolated single wall carbon nanotubes, *Carbon* 40(12): 2043–2061. 10.1016/S0008-6223(02)00066-0
27. Mansouriieh N, Sohrabi MR, Khosravi M. (2016). Adsorption kinetics and thermodynamics of organophosphorus profenofos pesticide onto Fe/Ni bimetallic nanoparticles, *International Journal of Environmental Science and Technology* 13(5):1393-1404. 10.1007/s13762-016-0960-0
28. Ming YuKuo, Chih FengHsiao, Yi HsuanChiu, et al. (2019). Au@Cu₂O core@shell nanocrystals as dual-functional catalysts for sustainable environmental applications, *Applied Catalysis B: Environmental* 242: 499-506. 10.1016/j.apcatb.2018.09.075
29. Pinilla J.L, de Llobet S, Moliner R, et al. (2016). Ni-Co bimetallic catalysts for the simultaneous production of carbon nanofibres and syngas through biogas decomposition, *Applied Catalysis B-Environmental* 200: 255-264. 10.1016/j.apcatb.2016.07.015
30. Sivanantham A, Ganesan P, Shanmugam S. (2016). Hierarchical NiCo₂S₄ Nanowire Arrays Supported on Ni Foam: An Efficient and Durable Bifunctional Electrocatalyst for Oxygen and Hydrogen Evolution Reactions, *Advanced Functional Materials* 26(26):4661-4672. 10.1002/adfm.201600566
31. Sahasrabudhe A, Dixit H, Majee R, et al. (2018). Value added transformation of ubiquitous substrates into highly efficient and flexible electrodes for water splitting, *Nature Communications* 9(2014). 10.1038/s41467-018-04358-7
32. Sun Y.Q, Xu K, Zhao Z.H, et al. (2020). Strongly coupled dual zerovalent nonmetal doped nickel phosphide Nanoparticles/N, B-graphene hybrid for pH-Universal hydrogen evolution catalysis, *Applied Catalysis B-Environmental* 278(119284). 10.1016/j.apcatb.2020.119284
33. Xiao C.L, Li Y.B, Lu X.Y, et al. (2016). Bifunctional Porous NiFe/NiCo₂O₄/Ni Foam Electrodes with Triple Hierarchy and Double Synergies for Efficient Whole Cell Water Splitting, *Advanced Functional Materials* 26(20):3515-3523. 10.1002/adfm.201505302
34. Xu K, Ding H, Zhang MX, et al. (2017). Regulating Water-Reduction Kinetics in Cobalt Phosphide for Enhancing HER Catalytic Activity in Alkaline Solution, *Advanced Materials* 29(28). 10.1002/adma.201606980
35. Xu W.J, Lyu F.L, Bai Y.C, et al. (2018). Porous cobalt oxide nanoplates enriched with oxygen vacancies for oxygen evolution reaction, *Nano Energy* 43:110-116. 10.1016/j.nanoen.2017.11.022
36. Yanguang Li, Hailiang Wang, Liming Xie, et al. (2011). MoS₂ nanoparticles grown on graphene: an advanced catalyst for the hydrogen evolution reaction, *J. Am. Chem. Soc* 133(19): 7296-7299. 10.1021/ja201269b
37. Yang Y, Ren Y, Sun CJ, Hao SJ. (2014). Facile route fabrication of nickel based mesoporous carbons with high catalytic performance towards 4-nitrophenol reduction, *Green Chemistry* 16(4): 2273-2280. 10.1039/c3gc42121j
38. Yue S, Wang S.S, Jiao Q.Z, et al. (2019). Preparation of Yolk-Shell-Structured CoFe_{1-x}P with Enhanced OER Performance, *Chemsuschem* 12(19):4461-4470. 10.1002/cssc.201901604

Figures

Figure 1

FT-IR spectra of SEP, N-B-Ni₂P/SEP, N-B-NiFeP/SEP and N-B-NiFeP/SEP-1

Figure 2

Morphology, structure and chemical composition analyses of N-B-NiFeP/SEP and N, B-Ni₂P/SEP. (a) SEM images of N-B-NiFeP/SEP, (b) SEM images of N, B-Ni₂P/SEP, (c-j) EDS of N-B-NiFeP/SEP

Figure 3

XRD spectra of N-B-NiFeP/SEP and N-B-Ni₂P/SEP.

Figure 4

(a) XPS survey spectrum and (b-h) high-resolution XPS spectra of C1s, O1s, N1s, P2p, B1s, Ni2p, Fe2p of N-B-NiFeP/SEP and N-B-Ni₂P/SEP

Figure 5

Raman spectra of N-B-NiFeP/SEP and N-B-Ni₂P/SEP.

Figure 6

N₂ adsorption-desorption curves (a), pore distribution curve (b), specific surface area (c), Pore volume and pore diameter (d) of N-B-NiFeP/SEP and N-B-Ni₂P/SEP.

Figure 7

Electrochemical performance in acid and basic solution. (a) polarization curves for OER. (a) polarization curves (1.3-1.5 V) for OER. (c) Tafel plots for OER. (d) polarization curves for HER. (e) Tafel plots for HER. (f) Overpotential for HER and OER.

Figure 8

(a) UV-vis spectra of 4-nitrophenol before and after adding NaBH₄ solution, (b) the reduction of 4-nitrophenol in aqueous solution recorded with time using 3.0 mg N-B-NiFeP/SEP and N-B-Ni₂P/SEP, (c) the relationship between $\ln(C_t/C_0)$ and reaction time (t).

Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- [scheme1.png](#)