Electroless plated Ni-B_x films as highly active electrocatalysts for hydrogen production from water over a wide pH range

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Abstract
The performance of electroless plated Ni-B_x films was studied in a wide pH range for the hydrogen evolution reaction (HER). The atomic ratio of B to Ni has great influence on the particle size and the morphology of Ni-B_x materials, and more importantly on the catalytic H_2-evolution property of Ni-B_x films. The film with a B:Ni atomic ratio of 0.54, denoted as Ni-B_{0.54}, displayed the best performance with a current density of 10 mA cm^{-2} at very low overpotentials (\eta) of 45 mV in 0.5 M H_2SO_4, 54 mV in 1.0 M pH 7 phosphate buffer solution (PBS), and 135 mV in 1.0 M KOH, and the catalytic activity maintained over 20-h electrolysis at \eta=100 mV in all tested media of different pH values. The Tafel slopes of the Ni-B_{0.54} film are 43, 77, and 88 mV dec^{-1} in 0.5 M H_2SO_4, 1.0 M neutral PBS, and 1.0 M KOH, respectively. These results show that the combination of earth-abundant nickel and boron elements in an optimal B-to-Ni atomic ratio can provide highly active and stable electrocatalysts for the HER over a wide pH range.

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Introduction
Hydrogen, as a carbon free fuel with high energy density, has been proposed as an ideal energy carrier to substitute traditional fossil fuel and thus to meet the globally rapid...
increasing demand for energy and reduce the discharge of carbon dioxide. A practical and sustainable way to produce hydrogen is electrolysis of water driven by clean electric power that was generated by renewable energy sources such as photovoltaic and wind. To build highly efficient and cost-effective electrolyzers for this purpose, one of the key challenges is to develop supra-active, stable, inexpensive, and scalable electrocatalysts for the two half reactions of water splitting, namely oxygen and hydrogen evolution reactions. Although some noble metals such as Pt are known as the best hydrogen evolving catalysts in acidic solutions, the low abundance and high cost of such precious metals limit their large-scale application. In the past decade, some catalytic materials composed of abundant elements have been developed for the hydrogen evolution reaction (HER) [1,2], mostly Fe [3–7], Co [8–16], Ni [17–23], Mo [24–27], and W-based materials [28–31].

In a commercial application point of view, a clean and easily scaled-up procedure for the preparation of earth-abundant HER catalysts and the compatible reaction conditions of HER catalysts with those required by the oxygen evolution reaction (OER) catalysts are highly desired, in addition to the requirements of high activity, low overpotential, and good stability. Many reported non-noble metal-based catalysts were prepared by using poisonous reagents and harmful gases, processing at high temperature and/or high pressure, or using special equipments or instruments. Scale-up of such preparation procedures is problematic. In another aspect, most of the non-noble metal-based catalysts are limited to being used in specific pH values. For example, molybdenum sulfides function well in strongly acidic aqueous media for the HER [32–36], while amorphous NiMo materials display high activity and good stability in alkaline solution [37–39]. Some earth-abundant HER catalysts, FeP [3,5], CoP [9,14], and CoS [13], exhibit a current density of 10 mA cm\(^{-2}\) at an overpotential lower than 200 mV in neutral buffer solution. There are only a few HER catalysts that function well in aqueous media over a wide pH range [4,15,21,40–43]. The very recently reported NiP\(_2\) catalyst displays a current density of 10 mA cm\(^{-2}\) at 23 mV in 1.0 M H\(_2\)SO\(_4\) solution and at 49 mV in 1.0 M NaOH solution, and more importantly, NiP\(_2\) is stable in both cases, but the preparation of this metal phosphide alloy relies on the solvothermal reaction using octylthioglycolic acid as solvents [21].

Although a huge number of metal phosphides, sulfides, selenides, carbides, and nitriles have been studied as catalysts for the HER [1,2], to the best of our knowledge, only a few examples of metal borides used as electrochemical HER catalysts have been reported in the literatures [44–46]. It is known that Ni-B film is typically used in the electronics industry where low-resistivity coatings are required. Besides, ultrafine Ni-B alloy has been demonstrated as an efficient hydrogenation catalyst [47,48]. With this awareness, we explored the electrocatalytic property of Ni-B\(_x\) films as earth-abundant catalysts for the HER in acidic, neutral, and basic solutions. Here we report the nickel-boron materials containing amorphous Ni-B\(_x\) alloy and crystallized metallic nickel nanoparticles as efficient and robust HER catalysts in water over a wide pH range. The best electrocatalytic performance was observed for the Ni-B\(_{0.54}\) catalytic material, which displayed low overpotentials (\(\eta\)) of 45, 54, and 135 mV in 0.5 M H\(_2\)SO\(_4\), 1.0 M pH 7 phosphate buffer solution (PBS), and 1.0 M KOH medium, respectively, to reach a current density of 10 mA cm\(^{-2}\), and the catalytic activity maintained over 20-h electrolysis, with nearly 100% Faradaic efficiency in the acidic, neutral, and basic aqueous media. This catalyst is among the best performing noble-metal-free catalysts known to date for electrochemical H\(_2\) production over a wide pH range.

**Experimental section**

**Materials**

Compounds NiCl\(_2\)-6H\(_2\)O, NaOH, NaBH\(_4\), and ethanediamine were used as received from J&K Scientific Ltd. The water used for electrolyte solutions was deionized with a Millipore Milliq-Q UF Plus system (15-18 M\(_2\)cm resistivity). T2 copper plate with a thickness of 0.03 mm was purchased from a local company. The plate was cut into 0.5 x 2 cm\(^2\) pieces and used as electroless plating substrates.

**Electroless plating**

The working electrodes were fabricated by an electroless plating method. The salt NiCl\(_2\)-6H\(_2\)O (3.00 g) was dissolved in 25 mL water and the solution was cooled to lower than 10 °C with an ice bath. Ethanediamine aqueous solution (20%, 25 mL) was slowly added into the NiCl\(_2\) solution with stirring, and the color of the mixture was changed from green to dark violet. Compound NaBH\(_4\) (0.21 g) was dissolved in NaOH solution (25 mL) at pH 13.5, which was then combined with the Ni\(^{2+}\) mixture. The electroless plating solution was adjusted to 100 mL at pH 13.5 by 10 M NaOH solution and water.

The Ni-B\(_x\) films were prepared in a conical flask filled with 100 mL electroless plating solution at 90 °C. Prior to use, copper plate (0.5 x 2 cm\(^2\)) was washed with 0.5 M HCl, isopropanol, and deionized water successively. After overnight hanging in the plating solution for 2 h, the copper substrate was modified by an argonette Ni-B\(_x\) film. The as-prepared film was rinsed with water and ethanol successively and dried, which was ready to be used as working electrode for further examination.

**Characterization of the as prepared Ni-B\(_x\) film**

XPS spectra were acquired with a Thermo VG ESCALAB250 surface analysis system using a monochromatized Al K\(_\alpha\) small-spot source and a 500 μm concentric hemispherical energy analyzer. The loading amounts (Table S1) of nickel and boron on the surface of copper plate were determined by ICP-OES on a Perkin Elmer 2000 DV ICP Optical Emission Spectrometer. Powder X-ray diffraction (PXRD) patterns were obtained with a Panalytical Empyrean using Cu K\(_\alpha\) radiation (\(\lambda=1.5405\) Å). Data were collected in Bragg-Brentano mode using 0.5° divergence and scatter slits and a 0.3° receiving slit at a scan rate of 5° min\(^{-1}\). Samples of Ni-B\(_x\) alloy for PXRD were collected by scraping off the Ni-B\(_x\) film from the copper plate. SEM images and EDX spectra were obtained with a NOVA NanoSEM 450 equipped with an EDX
system. Images were obtained with an acceleration voltage of 4–5 kV and EDX spectra were obtained at an acceleration voltage of 12 kV or 20 kV. TEM images and selected area electron diffraction (SAED) patterns were collected on a FEI Tecnai G² F20 S-TWIN transmission electron microscope (TEM) with an acceleration voltage of 200 kV.

Electrochemical measurements

All electrochemical experiments were performed with a CH Instrument 650E potentiostat and a BASi Ag/AgCl reference electrode. Unless otherwise stated, All potentials reported in this manuscript were converted to the SHE or RHE reference scale using $E_{\text{SHE}} = E_{\text{Ag/AgCl}} + 0.205 \text{ V}$, and $E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.205 \text{ V} + 0.059 \text{ pH V}$.

The electrochemical experiments were carried out in a three electrode cell consisting of two compartments separated by a glass tube ($d = 1 \text{ cm}$). The as-prepared Ni-Bx films were limited to 0.5 cm² by using epoxy glue and used as a working electrode. Platinum foil (2 cm²) was purchased from Tjaida and used as counter electrode for electrochemical studies. An iR correction was made in polarization experiments to compensate for the voltage drop between the reference and working electrodes using the software supplied with the CH instrument potentiostat. A typical value of 1.0–2.0 Ω was usually measured for the internal resistance.

Results and discussion

The Ni-Bx electrode was conveniently fabricated by electroless plating with a copper plate as substrate in a pH 13.5 ethanediamine aqueous solution containing NiCl₂·6H₂O and NaBH₄ at 90 °C for 2 h [49]. Such an economical and practical procedure can be easily scaled up. With adjusting the molar ratio of NaBH₄ to NiCl₂ in the plating solution, different Ni-Bx films were fabricated with $x = 0.27$, 0.36, 0.48, and 0.54 on the basis of the analytic data of inductively coupled plasma optical emission spectroscopy (ICP-OES). The loading amounts of nickel and boron elements on the surface of copper plate are given in Table S1. The Ni-Bx film with a B:Ni atomic ratio higher than 0.54 was not obtained by further increasing the molar ratio of NaBH₄ to NiCl₂ in the plating solution.

The as-prepared Ni-Bx films were used as working electrodes for linear sweep voltammetric (LSV) experiments in 0.5 M H₂SO₄, 1.0 M pH 7 PBS, and 1.0 M KOH solution. To make a direct comparison, the LSVs of a Pt foil and a Ni foil were also recorded under the same conditions. The LSVs (Fig. 1a) of Ni-Bx electrodes in 0.5 M H₂SO₄ solution show that as the atomic ratio of B to Ni increases from 0.27 to 0.54 (Table S2) the catalytic current density is apparently enhanced and the overpotential required to generate a current density of 10 mA cm⁻² is positively shifted by 120 mV. A similar tendency was observed from the LSVs recorded in 1.0 M neutral solutions.

![Fig. 1](image_url) LSVs of (a) the as-prepared Ni-Bx films in 0.5 M H₂SO₄ aqueous solution; Ni-B₀.₅₄ film as well as Pt and Ni foils in (b) 0.5 M H₂SO₄, (c) 1.0 M pH 7 PBS, and (d) 1.0 M KOH solutions with a scan rate of 5 mV s⁻¹.
Electroless plated Ni-B_x films as highly active electrocatalysts for hydrogen production from water over a wide

PBS (Fig. S1, Table S3) and in 1.0 M KOH aqueous solution (Fig. S2, Table S4). Among the as-prepared Ni-B_x materials, the Ni-B_0.54 film with an atomic ratio of B:Ni = 0.54 exhibits the highest catalytic activity for the hydrogen production in entire pH range. The overpotentials required to reach the current density of 10 mA cm^{-2} are 45 mV in 0.5 M H_2SO_4, 54 mV in 1.0 M pH 7 PBS, and 135 mV in 1.0 M KOH solution (Fig. S2–d). In comparison, Pt foil displayed the current density of 10 mA cm^{-2} at 29 mV in 0.5 M H_2SO_4, 163 mV in 1.0 M pH 7 PBS, and 165 mV in 1.0 M KOH solution. Nickel foil displayed very low H_2-evolution activity under all test conditions. The overpotentials required by the Ni-B_0.54 film to produce the current densities of 10, 50, and 100 mA cm^{-2} are summarized in Table S5.

Apparently, in acidic solution the catalytic activity of Ni-B_0.54 is slightly inferior to that of Pt foil, but in the neutral PBS the Ni-B_0.54 film is much more active than Pt foil for the HER. The current density of Ni-B_0.54 reached 100 mA cm^{-2} at η=200 mV in the neutral PBS, which is 4-fold of that displayed by Pt foil at the same potential. In 1.0 M KOH solution, the performance of Ni-B_0.54 electrode is similar with Pt foil before −0.97 V vs. SHE and better than Pt foil at more negative potentials. Considering the overpotential required for reaching a certain current density, the Ni-B_0.54 film is among the best noble-metal-free catalysts in 0.5 M H_2SO_4 solution, which display a current density of 10 mA cm^{-2} at η<50 mV, such as FeP [3,5], CoP [11,15], NiMoZn [50], and polypyrrole/MoS_x [51]. The lowest overpotentials so far reported to attain 10 mA cm^{-2} in neutral PBS are 102-125 mV for FeP [3,5], 149-178 mV for CoP [9,14], and 170 mV for CoS [13], which are 48-124 mV larger than the overpotential required by the Ni-B_0.54 film.

Controlled potential electrolysis (CPE) experiments were performed with the Ni-B_0.54 film as working electrode in 0.5 M H_2SO_4, 1.0 M PBS, and 1.0 M KOH aqueous solution at η=100 mV for 120 min. The amount of evolved H_2 determined by GC analysis during the experiment is in good agreement with that calculated from the accumulated charge, suggesting that the Faradaic efficiency for HER by the Ni-B_0.54 film is close to 100% under test conditions (Fig. S3).

The Tafel slope and exchange current density (j_0) are important kinetic indicators to evaluate the inherent property of a new material electrocatalyst. The Ni-B_0.54 film displays a small Tafel slope of 43 mV dec^{-1} in 0.5 M H_2SO_4 in the region of −32 to −88 mV vs. RHE (Fig. 2a). The Tafel slopes of Ni-B_0.54 are 77 mV dec^{-1} in a 1.0 M PBS in the region of −28 to −125 mV vs. RHE and 88 mV dec^{-1} in 1.0 M KOH solution in the region of −102 to −209 mV vs. RHE. The corresponding geometric exchange current densities (j_0) of Ni-B_0.54 in the aforementioned typical acidic, neutral, and basic solutions were calculated to be 0.380, 0.851, and 0.275 mA cm^{-2}, respectively, by applying the extrapolation method to the corresponding Tafel plot. A comparison of the Tafel slopes as well as the exchange

Fig. 2  (a) Tafel slopes of the Ni-B_0.54 film in 0.5 M H_2SO_4, 1.0 M PBS, and 1.0 M KOH aqueous solutions. Plot of the cumulated charge vs. time for the extended CPE experiments with the Ni-B_0.54 electrode in (b) 0.5 M H_2SO_4, (c) 1.0 M pH 7 PBS, and (d) 1.0 M, KOH aqueous solutions at η=100 mV (inset: current density vs. time during the CPE experiment).
current densities of Ni-B_{0.54} and Pt is shown in Fig. S4 and Table S6. The Ni-B_{0.54} film has similar Tafel slopes to Pt foil under the same conditions, while it features apparently higher geometric exchange current density than Pt, that is, 0.380 vs. 0.355 mA cm^{-2} in 0.5 M H_{2}SO_{4}, 0.851 vs. 0.096 mA cm^{-2} in pH 7 PBS, and 0.275 vs. 0.065 mA cm^{-2} in 1.0 M KOH solution, for the j_0 of Ni-B_{0.54} vs. that of Pt.

The stability of the Ni-B_{0.54} film in the aqueous media of different pH values was explored by extended CPE experiments and continuous cyclic potential scanning. As shown in Fig. 2b-d, the Ni-B_{0.54} film affords an essentially linear charge build-up over time and the time dependence of the current density exhibits no loss in activity over 20 h electrolysis experiment at \( \eta = 100 \) mV in the solutions of all tested pH values. The Ni-B_{0.54} film maintained the current densities at 44 mA cm^{-2} in 0.5 M H_{2}SO_{4}, 17.5 mA cm^{-2} in 1.0 M pH 7 PBS, and 4.6 mA cm^{-2} in 1.0 M KOH aqueous solution. The slight increase of current density (about 4.2-5.2%) with electrolysis time extending using Ni-B_{0.54} film in acidic and basic solutions (Insets in Fig. 2b and d) possibly results from the gradual escape of B_{2}O_{3} from the surface of Ni-B_{0.54} film to solution, making more Ni-B_{x} active sites expose to the electrolyte, while in neutral buffer solution the catalytic current keeps constant during long-time CPE experiments (Inset in Fig. 2c). The control CPE experiment showed that only negligible charge was passed when a blank copper or nickel foil was used as working electrode under the same conditions. The polarization curves that were measured for the Ni-B_{0.54} film in 1.0 M neutral PBS before and after 2000 cycles ranging from \(-0.35\) to \(-0.72\) vs. SHE at a scan rate of 100 mV s^{-1} show no noticeable loss in the cathodic currents (Fig. S5). After 20 h CPE experiments, the ICP-OES analyses of the resulting electrolytes show no leaching of nickel from the Ni-B_{0.54} film during the electrolysis of neutral PBS and only a trivial leaching (about 0.17%) of nickel in 1.0 M KOH solution. In contrast, about 0.067 mg nickel (5.2% of the nickel initially loaded on the surface of Ni-B_{0.54} film) was stripped from the Ni-B_{0.54} film during the 20 h electrolysis of 0.5 M H_{2}SO_{4} solution, but the leaching of such a small amount of nickel did not cause a decline in current density (Inset in Fig. 2b). The repeated CPE experiment over the course of 42 h also showed no substantial loss in catalytic current density using the Ni-B_{0.54} film as a working electrode in 0.5 M H_{2}SO_{4} at an overpotential of 100 mV (Fig. S6). All of these results indicate that the Ni-B_{0.54} film is a highly active and robust electrocatalyst for hydrogen production from water over a wide pH range. To date only a few noble-metal-free catalysts are known to function well and stable for the HER in the aqueous media of entire pH range. The representatives are Co-embedded

<table>
<thead>
<tr>
<th>Catalyst (loading: mg cm^{-2})</th>
<th>pH</th>
<th>( \eta ) value at ( j = 10 ) mA cm^{-2}</th>
<th>Stability</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu foilNi-B_{0.54} (loading: 1.40 mg cm^{-2})</td>
<td>0.5 M H_{2}SO_{4}</td>
<td>45 mV</td>
<td>Current kept constant in 20 h CPE at ( \eta = 100 ) mV</td>
<td>This work</td>
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<tr>
<td></td>
<td>1.0 M pH</td>
<td>54 mV</td>
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<td></td>
<td>7 PBS</td>
<td></td>
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<tr>
<td></td>
<td>1.0 M KOH</td>
<td>135 mV</td>
<td>Value kept constant in 10 h CPE at ( \eta = 150 ) mV</td>
<td>[40]</td>
</tr>
<tr>
<td></td>
<td>0.5 M H_{2}SO_{4}</td>
<td>260 mV</td>
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<td></td>
<td>0.1 M pH</td>
<td>( \sim ) 520 mV</td>
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<tr>
<td></td>
<td>7 PBS</td>
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<tr>
<td></td>
<td>1.0 M KOH</td>
<td>( \sim ) 380 mV</td>
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<tr>
<td>C clothiFeP NR arrays (loading: 1.50 mg cm^{-2})</td>
<td>0.5 M H_{2}SO_{4}</td>
<td>58 mV</td>
<td>Current decayed by 18% in 20 h CPE at ( \eta = 150 ) mV</td>
<td>[4]</td>
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<tr>
<td></td>
<td>1 M pH</td>
<td>202 mV</td>
<td></td>
<td>N/A</td>
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<tr>
<td></td>
<td>7 PBS</td>
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<tr>
<td></td>
<td>1.0 M KOH</td>
<td>218 mV</td>
<td>( \eta ) Value changed from 181 to 194 mV in 12 h CPE at ( j = 20 ) mA cm^{-2}</td>
<td>[41]</td>
</tr>
<tr>
<td>Ti foilCoP NRs (loading: 0.31 mg cm^{-2})</td>
<td>0.5 M H_{2}SO_{4}</td>
<td>134 mV</td>
<td>( \eta ) Value changed from 217 to 229 mV in 12 h CPE at ( j = 20 ) mA cm^{-2}</td>
<td>[41]</td>
</tr>
<tr>
<td></td>
<td>1.0 M KOH</td>
<td>150 mV</td>
<td>Current kept constant in 40 h CPE at ( \eta = 91 ) mV</td>
<td>[15]</td>
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<td>0.5 M H_{2}SO_{4}</td>
<td>49 mV</td>
<td>Current decayed apparently in 40 h CPE at ( \eta = 106 ) mV</td>
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<tr>
<td>C clothiCoP (loading: 10.3 mg cm^{-2})</td>
<td>1 M KOH</td>
<td>48 mV</td>
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<tr>
<td>Ni foam/WniP (loading: 1.0 mg cm^{-2})</td>
<td>0.5 M H_{2}SO_{4}</td>
<td>( \sim ) 90 mV</td>
<td>Current density kept constant in 16 h CPE at ( \eta = 10 ) mA cm^{-2}</td>
<td>[21]</td>
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<tr>
<td></td>
<td>1 M KOH</td>
<td>( \sim ) 130 mV</td>
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<tr>
<td>GCPorous Mo_{2}C NRs (N/A)</td>
<td>0.5 M H_{2}SO_{4}</td>
<td>150 mV</td>
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<td>N/A</td>
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<tr>
<td></td>
<td>1 M KOH</td>
<td>150 mV</td>
<td></td>
<td>N/A</td>
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<tr>
<td>Ni_{3}P_{4} (loading: 50 mg pellet in 6 mm diameter)</td>
<td>1 M H_{2}SO_{4}</td>
<td>23 mV</td>
<td></td>
<td>N/A</td>
</tr>
<tr>
<td></td>
<td>1 M NaOH</td>
<td>49 mV</td>
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</table>
Electroless plated Ni-B\(_x\) films as highly active electrocatalysts for hydrogen production from water over a wide range of conditions have been investigated. The Ni-B\(_{0.54}\) films were fabricated by electroless plating with a Cu plate as a substrate for comparison with the Ni-B\(_{0.54}\) electrode. The current curve of the Ni-B\(_{0.54}\) film displayed the highest activity among the as-prepared Ni-B\(_{0.54}\) films, but its catalytic activity is considerably lower than that of Ni-B\(_{0.54}\) at 0.5 M H\(_2\)SO\(_4\) (Fig. S11). These contrast experiments clearly show the advantage of the Ni-B\(_{0.54}\) alloy over the Ni-B\(_{0.54}\) alloy and crystalline metallic nickel with a fcc structure. Furthermore, the high magnification TEM images (Figs. 5c and S16a) of the Ni-B\(_{0.54}\) material scraped off from the copper plate show that the metallic nickel crystals are mainly located in the edge of a nanoparticle to form a 3-4 nm outside layer, which has a tight contact with the bulk amorphous Ni-B\(_{0.54}\) alloy. By comparison of the SAED (Figs. S16b, S18, and S19) and PXRD patterns (Fig. S20) as well as the TEM images (Fig. 5) of Ni-B\(_{0.27}\), Ni-B\(_{0.48}\), and Ni-B\(_{0.54}\), we found that the amount of metallic nickel crystals at the edge of the nanoparticles was increased as the B:Ni atomic ratio was enhanced in the Ni-B\(_{0.54}\) alloy. The as-prepared Ni-B\(_{0.54}\) films were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), energy-dispersive X-ray spectroscopy (EDX), X-ray photoelectron spectroscopy (XPS), powder X-ray diffraction (PXRD), and selected area electron diffraction (SAED), as well as the ICP-OES analysis. The SEM images (Fig. 3) show that the electroless plated Ni-B\(_{0.54}\) film is consist of compact semiglobular nanoparticles together with some homogeneously distributed nanovoids, which are formed by evolution of H\(_2\) in the plating process. The thickness of the film on the surface of a copper foil is about 2 µm (inset in Fig. 3a). The EDX spectrum (Fig. S12) indicates that Ni, B, and O are the principal elemental components of the Ni-B\(_{0.54}\) film. After the Ni-B\(_{0.54}\) film was used for 20 h electrolysis, the SEM images (Fig. S13) show there is no noticeable change in the morphology of the Ni-B\(_{0.54}\) film as compared to that of the film before used.

The XPS (Fig. S14) of the Ni-B\(_{0.54}\) material shows two peaks in the Ni 2p region at 852.8 and 870.2 eV, each with a satellite peak at 859.4 and 874.8 eV (Fig. 4a), respectively, corresponding to the Ni 2p\(_{3/2}\) and 2p\(_{1/2}\) core levels of a Ni\(^{0}\) species [52,53]. The two peaks at 187.8 and 192.4 eV binding energies in the B 1s region are assigned to the two types of B element, most possibly existing in the amorphous Ni-B\(_x\) and B\(_2\)O\(_3\) [53,54]. The atomic percentage of Ni, B, and O on the surface of the Ni-B\(_{0.54}\) film was determined by ICP-OES analysis. On the basis of these experimental observations, we speculate that the B\(_2\)O\(_3\) film contains amorphous Ni-B\(_x\) alloy and crystalline metallic nickel with an fcc structure. The SAED (Fig. S16b) and PXRD patterns (Fig. S17) suggest that the Ni-B\(_{0.54}\) film contains amorphous Ni-B\(_x\) alloy and crystalline metallic nickel with an fcc structure. The atomic percentage of Ni, B, and O on the surface of the Ni-B\(_{0.54}\) film was determined by ICP-OES analysis. The XPS (Fig. S14) of the Ni-B\(_{0.54}\) film shows that the Ni 2p region at 852.8 and 870.2 eV, each with a satellite peak at 859.4 and 874.8 eV (Fig. 4a), respectively, corresponding to the Ni 2p\(_{3/2}\) and 2p\(_{1/2}\) core levels of a Ni\(^{0}\) species [52,53]. The two peaks at 187.8 and 192.4 eV binding energies in the B 1s region are assigned to the two types of B element, most possibly existing in the amorphous Ni-B\(_x\) and B\(_2\)O\(_3\) [53,54].

![Image](https://example.com/image.png)
nickel nanocrystals at the edge of the Ni-B_x particles consequently provides a highly efficient catalyst for the HER in aqueous solutions over entire pH range.

The SEM images of Ni-B_x films in different B:Ni atomic ratios clearly show that the average particle size on the surface of Ni-B_x film is decreased from 2.27 to 0.55 μm with the increase of the B:Ni atomic ratio from 0.27 to 0.54 (Figs. S25 and S26). For the same geometric area, the zoom out of the particle size on the electrode surface means the enlargement of the electrochemically active surface area (EASA). To estimate the EASA and evaluate the influence of EASA on the catalytic activity of Ni-B_x film, the capacitance of the double layer at the solid/liquid interface of a Ni-B_x film and electrolyte was measured in 0.1 M Na_2SO_4. The cyclic voltammograms (Fig. S27) were collected in the Faradaic silent region, where the current response is only due to the charging and off-charging of the double layer. Fig. S28 shows that the capacitance of Ni-B_0.54 is apparently enhanced as the B to Ni atomic ratio increased. Considerable increase of the catalytic activity of Ni-B_0.54 film can be partly attributed to the larger EASA of this film compared with other Ni-B_x films in a lower B:Ni atomic ratio. In addition, on the basis of the capacitances, the EASA of the Ni-B_0.54 electrode is 32.9 and 228.1 times that of Pt and Ni foil (Fig. S29), respectively. Fig. 6 shows the LSVs of j value normalized by EASA against applied potential. The j

Fig. 4 Fitted profiles for (a) Ni 2p and (b) B 1s core level XPS of the Ni-B_0.54 film.

Fig. 5 TEM images of (a) Ni-B_0.27, (b) Ni-B_0.48, and (c) Ni-B_0.54 nanomaterial.

Fig. 6 LSVs of the Ni-B_0.54 film, as well as Pt and Ni foil with j values normalized by EASA, in (a) 0.5 M H_2SO_4, (b) pH 7 PBS (2.0 M), and (c) 1.0 M KOH solution, at a scan rate of 5 mV s\(^{-1}\) (iR-corrected).
(EASA) value of the Ni-B0.54 electrode is higher than that of Ni foil, but lower than that of Pt foil at all test pH values. The results indicate that geometric gain plays an important role in the enhancement of activity of the Ni-B0.54 electrode for the HER.

Recent theoretical calculations and photoelectron spectroscopic studies revealed that the electron transfer in transition metal (Fe, Co, Ni) borides is different depending on the ratio of M to B atom in boron-rich systems (MBx, x &gt; 2) and from B to M atom for metal-rich borides (MBx, x &lt; 2). Other independent calculations for CoB and Co2B suggest that electrons are transferred from Co to B atom in crystalline form and from B to Co atom in amorphous state [55]. In our case, the Ni-B0.54 film consists of amorphous Ni-Bx nanoparticles with metallic nickel nanocrystals decorating at the outside layer of the particles. Therefore, electron transfer occurs from B to Ni atom in the Ni-B0.54 material, making Ni sites of the nickel boride alloy more electropositive. These Ni atom sites with enriched d-band electron density could be active sites for water reduction to hydrogen. The B atom, in addition to electron donating effect, plays a primary role in the superior performance of the Ni-B0.54 material by forming a relatively stable amorphous structure owing to high covalency of Ni-B bond and by ensuring homogeneous dispersion of unsaturated reactive Ni sites [47]. The function of metallic nickel nanocrystals of the Ni-B0.54 material in electrocatalytic H2-evolving reaction is currently not clear, but the experimental evidence has shown that the existence of a small amount of nickel nanocrystals in the amorphous Ni-Bx material can result in decrease of the average particle size of Ni-Bx material, enlargement of EASA, and consequently, in enhancement of catalytic activity. The detailed mechanism for the catalytic H2 generation at the Ni-Bx film needs more computational and spectroscopic studies in the future.

Conclusions

The Ni-Bx electrode was fabricated on the surface of a copper plate by electroless plating method which is a convenient and scalable procedure. The out-layer of amorphous Ni-Bx nanoparticles contains metallic nickel nanocrystals. As the atomic ratio of B to Ni in the film is increased, the size of the Ni-Bx particles considerably decreases and the content of metallic nickel crystals in the out-layer of particles augments, which leads to apparent enlargement of the EASA and thus to significant enhancement of the catalytic activity of Ni-Bx electrode. The highest B-to-Ni atomic ratio of the electroless plated Ni-Bx film is 0.54 under the present preparation conditions. The Ni-B0.54 film exhibited superior activities with onset overpotentials smaller than 40 mV (at j=1 mA cm-2) for the HER in aqueous media of entire pH range, with Faradaic efficiency close to 100%. The catalytic current density reached 100 mA cm-2 at an overpotential of 125 mV in 0.5 M H2SO4, 200 mV in 1.0 M pH 7 PBS, and 220 mV in 1.0 M KOH solution. The current density maintained constant at an applied overpotential of 100 mV for 20 h electrolysis of the Ni-B0.54 film in the three tested solutions of different pH values. These results show that the electroless plated Ni-B0.54 film is an efficient and stable earth-abundant catalyst for the HER over a wide pH range.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.jnanoen.2015.11.020.

References

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