Rapid Synthesis of Nickel Boride/Graphene by Microwave Thermal Shock and its Application in Hydrogen Evolution Reaction

Shuai Wang, Rui Zhao and Weidong Xue*
School of Materials and Energy, University of Electronic Science and Technology of China, Chengdu 610054, China.
*Corresponding author email: xuewd@uestc.edu.cn

Abstract. The urgent demand for sustainable and clean energy has promoted the development of water splitting. Herein, metal borides assisted synthesis of graphene-based material (Ni-B/G) has been carried out by facile and fast microwave heating method and applied to hydrogen evolution reaction (HER) in alkaline solution. The Ni-B combining with 2D graphene give rise to highly efficient HER performance with low overpotential of 187 mV at current density of 10 mA cm$^{-2}$. In addition, it exhibits good stability and retains 76% of current density after continuous oxygen release. The excellent performance is ascribed to the synergetic effect of Ni-B and graphene. The Ni-B not only acts as initiator to adsorb microwave energy but also works as active centre of catalyst. The high conductivity and large specific area of graphene offer accessible contact between electrolyte and intermediates. Therefore, Ni-B/G indicates a promising candidate for HER in alkaline media.

1. Introduction
With the development of modernization, the issues of air pollution and global warming are more and more serious over the world. The demand for alternative sustainable and clean energy to fossil fuels is urgent.[1] Electrochemical water splitting has been regarded as an efficient strategy for acquiring clean energy, which generates H$_2$ and O$_2$ without pollutant release at cathode and anode, respectively.[2] Up to date, Pt based materials are known as the state-of-the-art catalyst for HER. However, their high cost and scarcity hinder the mass production and practical application.[3]

As well known, numerous studies have focused on graphene over the fields of energy storage and conversion, medical science, and military industry due to its unique 2D structure and excellent mechanical performance.[4-6] In electrocatalysis, graphene is generally used as substrate for accessible reaction site and fast charge transfer because of the large specific surface areas and good conductivity, etc. Indeed, a good catalyst requires not only conductivity but also dexterous adsorption/desorption effect. Bare graphene is inadequate to outstanding electrocatalysis performance with regard to composite materials among transition metal based sulfides, phosphides and nitrides, etc. To address these issues, some groups have proposed that constructing graphene-based heterostructure materials is expected to exhibit good HER behaviour.[7, 8] On the other hand, though the synthesis methods of graphene are various including chemical vapor deposition, pyrolysis, mechanical exfoliation and chemical reduction, etc., complex operation process, and high temperature lead to additional costs, and high safety factor.[9] Therefore, a facile and fast method is needed to acquire graphene-based catalyst with highly efficiency.

Currently, transition metal borides (TMBs) have been considered as one kind of promising catalysts in electrocatalysis due to the facile preparation and high activity.[10] The intensive attention
on TMBs results from the special "revise electron transfer" mechanism according to Pauli principle.[11] That is to say, the negativity of B is larger than that of most of transition metals, however, electron donation in TMBs transfers from B atom to transition metal atoms.[12] The "revise electron transfer" mechanism gives rise to electron enrichment of transition metal atoms, which lead to an electronic interaction.

Herein, we have developed the graphene-based composite catalyst (Ni-B/G) via Ni-B assisted microwave shock. Ni-B/G show low Tafel slope of 148 mV dec\(^{-1}\) and overpotential of 187 mV at current density of 10 mA cm\(^{-2}\). Ni-B is first used as initiator for the exfoliation of pristine graphite oxide and simultaneously serves as electrocatalytic active center in the following HER process. Furthermore, the synthesis period only undergoes 10 s, which is facile and feasible for scale-up production. Finally, the electronic enrichment of Ni atom and the conductive graphene ensure the high activity and stability. This work gives a clue to the utilization of metal borides to fast and large-scale fabrication of graphene-based composite with good HER performance.

2. Experimental Section

2.1 Synthesis of Ni-B Alloy
Ni-B alloy was synthesized via a chemical reduction method. Typically, 2 mmol of Ni(NO\(_3\))\(_2\) 6H\(_2\)O was dissolved in 100 mL distilled water. 6 mmol of NaBH\(_4\) was dispersed in 10 mL distilled water and dropwise added to the above solution accompanied by the generations of bubbles and black precipitates under strongly magnetic stirring. After few minutes, the sample was collected as Ni-B alloy.

2.2 Synthesis of Ni-B/G Materials
300 mg of Ni-B alloy was used as initiator and fully mixed with 300 mg of graphite oxide by physical stirring in a glass bottle. Subsequently, the mixture was putted into a microwave oven and reacted at 1000 W for 10 s. After that, the sample was collected as Ni-B/G. For the control sample, acetylene black (AB) was used as initiator instead of Ni-B alloy following the similar process and collected as AB/G.

2.3 Characterizations
The morphology and element composition of AB/G and Ni-B/G were obtained by scanning electron microscope (SEM, Carl Zeiss AG, Germany) equipped with energy dispersive X-ray (EDX) analytical system. The phase of Ni-B/G was identified by powder diffractometer (XRD, X’ Pert PRO, Netherlands) with Cu K\(_\alpha\) radiation (k = 1.54 Å). The surface chemical state was conducted by X-ray photoelectron spectrometer (XPS, Thermo Scientific, USA) with Al K\(_\alpha\).

2.4 Electrochemical Measurements
The HER performance was performed by CHI 760E workstation with the three-electrode system, including the graphite rod, Hg/HgO and the loaded Ni foam. The loading amount of active material was 2.0 mg cm\(^{-2}\). Polarization curve was obtained by linear sweep voltammetry (LSV) at a scan rate of 1 mV s\(^{-1}\) in 1.0 M KOH solution. All the potential value was calibrated to RHE. Tafel slope was derived from linear part of polarization curve. The double-layer capacitance (C\(_d\)) was estimated to explore the electrochemical active surface areas at different scan rates of 10-100 mV s\(^{-1}\). Electrochemical impedance spectroscopy (EIS) was measured from 10\(^6\) to 10\(^3\) Hz with an amplitude potential of 5 mV. Stability was evaluated by i-t test at the constant potential of -0.187 V.

3. Results and Discussion

3.1 Morphology and Structure Analysis of Ni-B/G
Ni-B and graphite oxide are mixed by physical stirring before microwave thermal shock. It is worth noting that the grinding mixture leads to unsatisfied graphene product due to the undesirable energy absorption. Here, the Ni-B alloy is used as initiator via microwave synthesis process. As discovered on
Figure 1, the broad peak centered at approximately 45° is assigned to Ni-B alloy, suggesting its amorphous structure. After high-temperature shock, amorphous Ni-B alloy results in crystallinity. The peaks at 44.41°, 51.77° and 76.33° are ascribed to the (111), (200) and (230) planes of Ni. The peaks at 42.45°, 46.03° and 49.15° belong to NiB, which is consistent with the JCPDS No. 481223. The peak at 24.6° is indexed to (002) plane of graphene, suggesting the successfully fabrication of Ni-B/G composite.[13] The morphologies of Ni-B/G and AB/G are investigated by SEM images (Figure 2a and b). Figure 2a shows the loose and multilayer nanosheets of Ni-B/G with element composition of Ni, B, C, and O with corresponding content in inset. Figure 2b displays graphene nanosheets/ acetylene black nanoparticle heterostructure of AB/G. The EDX spectrum (Figure 2d) exhibits only C and O elements except for Si element, which belongs to the silicon substrate.

The surface chemical composition and electronic state of Ni-B/G are characterized by XPS. As shown in Figure 2a, the XPS survey illustrates the Ni, C, O and B elements. The amounts of Ni and B elements are much lower than those of C and O elements which are consistent with EDX results. The high-resolution C 1s spectra give rise to B-C (283.99 eV), C-C/C=C (285.07 eV) and O-C=O (289.09 eV), suggesting that B doped with carbon during microwave thermal shock process.[14] The high-resolution Ni 2p spectra indicate the oxidation state of nickel in Ni-B/G. The peaks at 856.15 and 859.39 eV are ascribed to the Ni 2p3/2 accompanied with two satellite (Sat.) peaks at 862.41 and 865.69 eV. The peaks at 874.36, 878.21 and 881.04 eV are assigned to the Ni 2p1/2 and corresponding
two satellite peaks, respectively.[15] As shown in Figure 3d, the peak centered at 191.88 eV belongs to boride oxide in Ni-B due to its exposure to air in synthesis process. As a result, the positive shift of binding energy compared to pure B (187.1 eV) indicates an electronic interaction, which is facilitate to electrocatalytic HER.[16]

![Figure 3](image.png)

**Figure 3.** (a) XPS survey spectrum, high-resolution spectra of (b) C 1s, (c) Ni 2p and (d) B 1s of Ni-B/G

### 3.2 HER Performance

The electrochemical performances of as-prepared materials are all tested in 1.0 M KOH solution using the three-electrode system. The polarization curves shown in Figure 4a are obtained by LSV method at scan rate of 1 mV s$^{-1}$. Bare NF exhibits poor electroactivity in both overpotential and current density. As expected, the commercial Pt/C electrode shows outstanding performance with lowest overpotential and highest current density. Ni-B/G gives rise to promising HER behaviour with overpotential of 187 mV at the current density of 10 mA cm$^{-2}$. As for AB/G, it needs 251 mV of overpotential to drive the same current density.
Figure 4. (a) Polarization curves, (b) Tafel plots, (c) activity comparison, (d) estimated $C_{dl}$ values, (e) EIS of AB/G and Ni-B/G, (f) stability test of Ni-B/G in 1.0 M KOH solution.

Tafel slope is a key parameter to investigate kinetics of as-prepared electrodes. The Tafel values locate at three regions of $\sim$30, 40-120, and above 120 $\text{mV} \text{dec}^{-1}$ relating to Tafel, Heyrovsky and Volmer reaction step, respectively. As observed on Figure 4b, Pt/C is the typical Tafel process. As for AB/G and Ni-B/G, they undergo the Heyrovsky-Volmer reaction process. However, Ni-B/G shows lower Tafel slope of 148 $\text{mV} \text{dec}^{-1}$ than that of AC/G (186 $\text{mV} \text{dec}^{-1}$). Detailed, the comparison of HER performance of bare NF, AB/G, Ni-B/G and Pt/C is presented in Figure 4c. The poor activity for AB/G may result in barren active centres and areas as confirmed by the $C_{dl}$ values (Figure 4d). The large CdI value for Ni-B/G suggests large electrochemical active sites for H* intermediate.

To further investigate the kinetics of AB/G and Ni-B/G, EIS method is performed at overpotential of 176 mV in the frequency range of $10^5$-$10^4$ Hz. The small semicircle in high frequency region corresponds to low charge transfer resistance ($R_c$). As found in Figure 4e, Ni-B/G shows lower $R_c$ than that of AB/G, suggesting the faster HER process. Stability of catalyst is also a significant parameter for evaluating the practice application. Figure 4f delivers a stable current density of Ni-B/G for 25000 s. The current density remains 76% after 6 h of continuous oxygen release. The results suggest that Ni-B/G is a promising candidate for HER in alkaline media.

4. Conclusions
In this work, Ni-B/G materials have been prepared via Ni-B assisted fast microwave method. The as-prepared Ni-B/G materials exhibit low overpotential of 187 mV at current density of 10 mA cm$^{-2}$, low Tafel slope of 148 mV dec$^{-1}$ and good stability. Compared to AB/G, Ni-B/G shows favorable HER performance resulting from the electronic interaction and synergetic effect between Ni-B and graphene, where Ni-B materials are first used as initiator and active center simultaneously. This work provides a glimmer of light to the fast construction of metal borides/graphene catalyst for HER process.
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6. References
[1] Sheng WC, Zhuang ZB, Gao MR, Zheng J, Chen JGG, Yan YS 2015 Nature Commun. 6 5848.
[2] Tian XY, Zhao PC, Sheng WC 2019 Adv. Mater. 31 1808066.
[3] Hu CL, Zhang L, Gong JL 2019 Energy Environ. Sci. 12 2620-2645.
[4] Kucinskis G, Bajars G, Kleperis J 2013 J. Power Sources 240 66-79.
[5] Li SS, Sun JR, Guan JQ 2021 Chinese J. Catal. 42 511-556.
[6] Tang XH, Debliquy M, Lahem D, Yan YY, Raskin JP 2021 Sensors 21 1443.
[7] Shuang F, Aifantis KE 2021 Carbon 172 50-70.
[8] Ibrahim A, Klopopinska A, Horvat K, Hamid ZA 2021 Polymers 13 2869.
[9] Coros M, Pogacean F, Magerusan L, Socaci C, Pruneanu S 2019 Front. Mater. Sci. 13 23-32.
[10] Chunduri A, Gupta S, Bapat O, Bhide A, Fernandes R, Patel MK, Bambole V, Miotello A, Patel N 2019 Appl. Catal. B Environ. 259 118051.
[11] Li JH, Chen H, Liu YP, Gao RQ, Zou XX 2019 J. Mater. Chem. A 7 5288-5294.
[12] Jiang B, Song H, Kang YQ, Wang SY, Wang Q, Zhou X, Kani KY, Guo YN, Ye JH, Li HX, Sakka Y, Henzie J, Yamauchi Y 2020 Chem. Sci. 11 791-796.
[13] Fei HL, Dong JC, Wan CZ, Zhao ZP, Xu X, Lin ZY, Wang YL, Liu HT, Zang KT, Luo J, Zhao SL, Hu W, Yan WS, Shakir I, Huang Y, Duan XF 2018 Adv. Mater. 30 1802146.
[14] Wang C, Guo ZY, Shen W, Xu QJ, Liu HM, Wang YG 2014 Adv. Mater. 24 5511-5521.
[15] Peng LS, Shen JJ, Zheng XQ, Xiang R, Deng MM, Mao ZX, Feng ZP, Zhang L, Li L, Wei ZD 2019 J. Catal. 369 345-351.
[16] Han PY, Tan T, Wu F, Cai P, Cheng GZ, Luo W 2020 Chinese Chem. Lett. 31 2469-2472.