



Article Mild and Fast Construction of Ni-Based Electrodes for Industrial-Grade Water Splitting

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Abstract: Achieving high–efficiency and stable hydrogen evolution from water splitting is a great challenge. Herein, a facilely prepared two–dimenssional self–supported catalytic electrode with excellent stability is constructed for large–scale hydrogen production from alkaline simulated seawater. The bifunctional catalytic electrode is prepared by a fast and mild one–step of sodium borohydride etching on a nickel foam (NF) substrate without adding other additives (NF@NiB_x–3h). The overpotential of the hydrogen/oxygen evolution reaction (HER/OER) in alkaline–simulated seawater at 10 mA cm⁻² is 96 mV and 261 mV. At 200 mA cm⁻², the NF@NiB_x–3h electrode shows good stability over 7 days throughout the water splitting process due to the corrosion resistance of the NF substrate, and strong adhesion between the Ni–B active material and the substrate. This work demonstrates a novel strategy for fabricating catalytic electrodes with high–performance, low cost and excellent stability.

Keywords: mild and fast construction; chemical etching; HER; OER; industrial-grade water splitting

1. Introduction

Hydrogen (H₂) has received significant attention as a renewable fuel in order to reduce the consumption of fossil fuels and mitigate global warming [1–4]. Currently, H₂ is primarily produced industrially through the conversion of natural gas, steam and coal, which inevitably releases greenhouse gases. Amongst the various methods of hydrogen production, water splitting is considered an ideal high purity way to produce hydrogen and driven by the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) processes, which is important for global clean energy deployment and ecological protection [5–11]. The development of low–cost, stable and high–performance electrocatalysts is key to advancing the technology [12–14]. However, the slow electrochemical kinetics of HER and OER inevitably hinder the energy conversion efficiency of water splitting [15,16]. As a central part of water electrolysis, the mechanism of HER, although having different origins in acid or neutral/alkaline, can be divided into two parts: the Volmer step, the Heyrovsky step or the Tafel step, respectively. The four–electron transfer step of the OER process is more complicated compared to HER in different pH solutions. Therefore, suitable HER and OER catalysts are necessary to assist low–energy hydrogen production [17,18].

Noble metallic-based (Pt, Ir and Ru, etc.) catalysts are considered for high performance. However, they are largely limited by their high price and poor stability [19–22]. Therefore, the transition to cheaper alternatives with lower energy costs is the way forward for global implementation [23,24]. Due to their unique electron distribution and abundance of earth elements, various families of transition metal-based materials (Ni, Mn, Co, Mo, Fe and V, etc.) have received considerable attention in the synthesis of advanced catalysts [25,26]. Many non-precious metal-based catalysts exhibit not only Pt-like HER activity, but also OER activity for bifunctional performance, especially in alkaline solutions,



Citation: Lu, Z.; Liang, R.; Shao, Y.; Hao, W. Mild and Fast Construction of Ni-Based Electrodes for Industrial-Grade Water Splitting. *Inorganics* **2023**, *11*, 170. https:// doi.org/10.3390/inorganics11040170

Academic Editor: Francis Verpoort

Received: 6 March 2023 Revised: 2 April 2023 Accepted: 14 April 2023 Published: 17 April 2023



Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). offering brighter prospects for applications in terms of optimisation of energy utilisation efficiency [27–29]. Among the studied catalysts, transition metal borides (TMBs), particularly Ni–based metal borides, have been investigated with superior catalytic performance and stability for HE and, OER, owing to their outstanding electrical conductivity, rich active sites and adjustable metal–boron stoichiometric ratios [30,31]. At present, the fabrication of Ni–based materials relies on hydrothermal (solvothermal) methods, electrochemical deposition, high–powered ball milling techniques, electrodeposition, etc [32,33]. The preparation of electrodes by a mild method, which does not require additional energy and exploits the chemical properties of each component, has attracted a wide range of interest from researchers. Thus, nowadays, the question of how to obtain catalysts under mild conditions has become unavoidable.

Based on the above considerations, a self–supported NF@NiB electrode is etched by mild one–step boration method, which has the following advantages: (1) NiB material is fabricated by rapid and mild etching in situ; (2) conductive NiB growing on NF can realize fast mass–transfer and electron–transfer; (3) the nanosphere can achieve stable catalysis under corrosive conditions. Therefore, NF@NiB electrode shows excellent catalytic performance. Surprisingly, NF@NiB also stably catalyzes in alkaline harsh electrolyte for about 7 days. This work proposes an economically feasible, rapid and simple strategy to construct efficient and ultra–stable NiB catalytic electrodes, which points the way to the future rapid and gentle preparation of catalytic electrodes.

2. Experimental Materials and Methods

2.1. Chemicals and Materials

Ethanol (C₂H₅OH, AR, Anhydrous, 99.7%), platinum (Pt/C), sodium borohydride (NaBH₄, AR), and potassium hydroxide (KOH, AR) were purchased from Aladdin; sodium chloride (NaCl, 99.9%) and 1.0 mol L⁻¹ nitric acid [HNO₃, AR, 65–68%, Greagent] were used to remove impurities such as surface grease and activate the NF. Nickel foam was purchased from Shanghai Zhengyang Foam Co. Water was purified ultrapure water (18 M Ω cm). Nafion [5 wt% perfluorinated resin, Sigma–Aldrich] was used as a polymerization binder to deposit platinum carbon (5% Pt/C) powder on the NF substrate. All chemicals were used as received and all reagents were used directly for this experiment without further processing.

2.2. Electrode Characterization

Rigaku D/MAX 2550 was used for X-ray diffraction analysis and Zeiss Gemini 300 magnetic field was used for scanning electron microscopy (SEM) with an acceleration voltage of 10 kV. The energy dispersive X-ray spectrometer (EDS, FEI Tecnai F20) and the electrochemical workstation (CHI 760E) were from Shanghai Chenhua Instruments Co., Ltd. Henghui DC power supply (PLD–3010) and X-ray photoelectron spectroscopy data acquisition were on Thermo Science K–Alpha, and the X-ray photoelectron spectrometer used a micro–focused monochromatic Al–K α X-ray source.

2.3. Preparation of NF@NiB Catalytic Electrode

The 1 \times 0.5 cm NF was sonicated with anhydrous ethanol (C₂H₅OH) for 5 min to eliminate the grease and impurities on the surface of NF, and then activated with 1 M HNO₃ for 2 min. The treated NF was reacted directly into 0.5 M NaBH₄ solution for different times (1 h, 3 h and 5 h) to obtain NF@NiB catalytic electrodes (please note that NF@NiB stands for NF@NiB_x-3h unless otherwise stated).

2.4. Electrochemical Measurements

Linear scanning voltammetry (LSV), cyclic voltammetry (CV) and electrochemical impedance (EIS) and electrochemical measurements were performed in alkaline–simulated seawater solution (1.0 M KOH + 0.5 M NaCl) using the Shanghai Chenhua CHI–760E three–electrode system electrochemical workstation with NF@NiB electrode, carbon rod and Hg/HgCl₂ as working electrode, counter electrode and reference electrode. All po-

tential values were calibrated to the reversible hydrogen electrode (RHE) according to the Nernst equation:

$$E_{RHE} = E\left(\frac{Hg}{Hg_2Cl_2}\right) + 0.05916 \times pH + 0.241(298K)$$
(1)

In addition, the Tafel equation was used to assess the reaction kinetics from the Tafel graphs:

$$\eta = b \times \log|j| + a \tag{2}$$

where η is the overpotential (mV), *b* is the Tafel slope (mV·dec⁻¹), *j* is the current density (mA·cm⁻²) and *a* is the exchange current density.

LSV curves were obtained for HER, OER and overall water splitting (OWS) potentials (*iR* corrected) scanned from 0.07 V–0.53 V (vs. RHE), 1.07 V–1.87 V (vs. RHE) and 1.00 V–1.80 V, respectively, at a scan rate of 5 mV s⁻¹.

CV measurements were performed in the potential region 0.07–0.17 V for HER (vs. RHE) and 1.22 V–1.32 V for OER (vs. RHE) at scan rates of 30, 50, 70, 90 and 110 mVs⁻¹ to calculate the double layer capacitance (C_{dl}).

The charge transfer resistance (R_{ct}) of the material was determined using electrical impedance spectroscopy (EIS) at an open circuit potential range of 10^5 –1 Hz and an amplitude of 5 mV.

Long-term stability of HER, OER and OWS in alkaline-simulated seawater was estimated by PLD-3010 chronopotentiometric methods at initial current responses of 200 mA cm^{-2} .

The turnover frequency (TOF) value is used to characterize the number of hydrogen and oxygen molecules formed on each active site on the catalyst surface per unit time. In this work, TOF is calculated by the following formula [34,35]:

$$TOF = \frac{i}{n \times N \times F} \tag{3}$$

where *i* is current (A), *n* is the number of electrons consumed to produce each H_2/O_2 (2/4) molecule, *N* is the number of active sites, and *F* is Faraday's constant (96,485.33 C mol⁻¹).

Faradaic efficiency (FE): the amount of gas generated during the experiment was collected by the drainage gas collection method, with NF@NiB electrodes as the anode and cathode. The FE value can be calculated during the OWS process by the following formula [36]:

$$F = e \times N_A \tag{4}$$

$$n = \frac{N}{N_A} = \frac{V}{V_m} \tag{5}$$

$$Q = j \times A \times t \tag{6}$$

From the above formula,

$$V_{H_2} = \frac{11.2 \times j \times A \times t}{96,485.33} \tag{7}$$

$$V_{H_2} = \frac{11.2 \times j \times A \times t}{96,485.33} \tag{8}$$

where *n* is the number of moles of H₂/O₂, *F* is the Faraday constant (96485.33 C mol⁻¹), *N* is the particle number, *V* is the H₂/O₂ volume, *j* is equal to 100 mA cm⁻² achieved by Henghui PLD–3010, *A* is the exposed area of NF@NiB electrode and *t* is OWS time. Finally, the actual measured ratio of H₂ to O₂ is compared with the theoretical value of 2:1 to obtain the Faraday efficiency.

3. Results

3.1. Characterization of NF@NiB

In this paper, the surface of foam nickel (NF) was boronized at 298 K by soaking in sodium borohydride (NaBH₄) to prepare the NF@NiB electrode to achieve efficient and stable catalytic hydrogen production. The crystal structure transition of NiB was investigated with XRD. The XRD pattern in Figure 1a showed that the diffraction peaks all belonged to Ni (JCPDS#04-0850). The XRD diffraction peaks of NF@NiB did not change significantly compared to bare NF, which may be due to the amorphous nature of NiB [37]. The diffraction peaks of B do not appear because only a small amount of NiB was generated. The sample was further characterised by SEM and the results were shown in Figure 1b,c. Compared with Bare NF, NiB catalytic material was grown on the NF surface. The prepared catalytic materials have a homogeneous nanoparticle morphology with a particle size of approximately 3-4 µm. From Figure 1d-g, it can be seen that there were Ni, O and B elements uniformly distributed on the surface of the NF@NiB catalytic electrode, which proved that NiB was successfully grown on NF, and the O element on the electrode surface might come from the adsorbed O_2 in the air, and NiB is also easily oxidized in air. Figure 1h showed the high-resolution XPS spectra of Ni 2p in NF@NiB with Ni-B bond located at 852.87 eV, while the peak corresponding to metallic Ni⁰ (852.70 eV) appeared in the bare NF. The characteristic peaks of Ni^{2+} in the oxidation state were located at 855.18 eV and 872.67 eV, and the peaks at 860.80 eV and 878.58 eV belonged to the satellite peaks. It was clear that the Ni–B bond of Ni 2p3/2 had a significant positive shifted relative to Ni⁰ (852.68 eV) of Bare NF, which could be attributed to the loss of electrons from Ni due to the introduction of B, indicating that the introduction of B could modulate the electronic structure of the catalyst. Figure 1i showed the B 1s spectrum of NF@NiB catalyst, which consisted mainly of two peaks: Ni-B bond (189.19 eV) and B-O bond (191.48 eV). The high–resolution o1s spectrum shown in Figure 1j was split into three parts, 530.40 eV corresponding to the M–O bond, 531.15 eV corresponding to the M–OH bond and 535.37 eV corresponding to the H_2O . The Raman spectra shown in Figure S1 (Supporting Information) indicate that bending vibrations of water molecules are detected at 1610 cm⁻¹, intermediates of hydrated nickel are detected around 840 cm⁻¹ and transition metal hydroxides are detected near 470 and 560 cm^{-1} [38,39].



Figure 1. (a) XRD patterns of Bare NF and NF@NiB. (b–c) SEM images of NF@NiB at low and high magnifications. (d–g) Elemental mappings for NF@NiB–3h. The high–resolution XPS spectras Ni 2p (h), B1s (i), O1s (j) of NF@NiB.

3.2. Electrochemical Analysis

3.2.1. HER and OER Electrochemical Measurements of NF@NiB Electrode

The overpotential (η) required for a current density of 10 mA cm⁻² (η_{10}) is commonly used as a measure of HER and OER catalytic activity. It was notable that the HER catalytic activity of NF@NiB $_x$ -3h was significantly stronger than that of the other comparison electrodes (Figure 2a). It was observed that the η_{10} = 96 mV of NF@NiB_x-3h was much smaller than that of NF@NiB_x-1h ($\eta_{10} = 209 \text{ mV}$), NF@NiB_x-5h ($\eta_{10} = 145 \text{ mV}$) and NF@Pt/C ($\eta_{10} = 155$ mV). Bare NF as a conductive substrate was inactive at 10 mA cm⁻² of 327 mV and did not contribute much to the overpotential. Thus, NF@NiB_x-3h had the lowest overpotential, indicating the best catalytic activity for hydrogen precipitation. As shown in Figure S2 (Supporting Information), we also performed the HER with 1.0 M KOH; NF@NiB_x-3h also showed excellent HER catalytic activity. To further analyze the electrochemical performance, the Tafel slope was estimated as shown in Figure 2b. Compared to Bare NF (121.46 mV dec⁻¹), NF@NiB_x – 1h (123.82 mV dec⁻¹), NF@NiB_x – 5h (119.37 mV dec⁻¹) and NF@Pt/C (135.12 mV dec⁻¹), NF@NiB_x-3h has the smallest Tafel slope of 113.87 mV dec $^{-1}$. Lower Tafel slope compared to other catalysts indicates a more rapid kinetic in the HER process. In addition, electrochemical impedance spectroscopy (EIS) testing allows a more in-depth study of HER reaction kinetics (Figure 2c). The smallest R_{ct} value of NF@NiB_x-3h indicated that the NiB modification gave Bare NF a lower R_{ct} and a quicker electron transfer rate The C_{dl} values in Figure 2d can be obtained by CV techniques in the non-faradaic interval (Figure S3, Supporting Information), with C_{dl} values of 19.2 mF cm⁻² and 12.6 mF cm⁻² for NF@NiBx-3h and Bare NF, respectively, implying that the introduction of NiB significantly increases the number of active sites and electrochemical regions of the material. As shown in Figure S4 (Supporting Information), the CV method is used to study the TOFs of NF@NiB and Bare NF electrodes for HER. The electrodes were tested in 1.0 M KOH + 0.5 M NaCl and the range was 0.02 to 0.12 V (vs. RHE). The total number of active atoms is proportional to the range of potential regions measured [34,35]. In Figure S4c (Supporting Information), the polarization curves were normalized by the active sites, denoted by TOFs and the TOFs of NF@NiB electrode at -150 mV were 1.89 s⁻¹ in alkaline media, which was higher than Bare NF (TOF = 5.67 s^{-1}). Probably, the higher TOF value of HER process was due to the B doping, which increased the catalytic activity of HER. Figure 2e showed the stability of the electrode tested by chronopotentiometry at 200 mA cm⁻². It could be clearly observed that the OWS performance degradation is less than 8% after 170 h, indicating that NF@NiB catalytic electrode has excellent catalytic stability. Meantime, the XRD spectra tested after stabilisation also indicated a stable structure (Figure S5, Supporting Information).



Figure 2. HER performance in 1 M KOH + 0.5 M NaCl solution: (a) LSV curves; (b) Tafel slopes; (c) Nyquist plots; (d) C_{dl} values; (e) Chronopotentiometric measurement of HER at 200 mA·cm⁻².

Characterisation of the electrochemical properties of the OER process was similar to that of the HER process. Notably, the OER catalytic activity of NF@NiBx-3h was significantly stronger than that of the other comparator electrodes (Figure 3a). It was observed that the $\eta_{10} = 261 \text{ mV}$ of NF@NiB_x-3h was smaller than that of NF@NiB_x-1h $(\eta_{10} = 346 \text{ mV})$, NF@NiB_x-5h ($\eta_{10} = 306 \text{ mV}$), and higher than for commercial NF@IrO₂ (η_{10} = 164 mV). Bare NF as a conductive substrate was inactive at 10 mA cm⁻² of 351 mV and did not contribute much to the overpotential. Thus, NF@NiB_x-3h has low overpotential, indicating good catalytic activity for OER. As shown in Figure S7 (Supporting Information), we also performed the OER with 1.0 M KOH; NF@NiB_x-3h also showed excellent OER catalytic activity. To further characterize the electrochemical properties, the Tafel slope of the OER process was estimated, as shown in Figure 3b. Compared to Bare NF (98.25 mV dec⁻¹), NF@NiBx-1h (63.21 mV dec⁻¹), NF@NiBx-5h (108.13 mV dec⁻¹) and NF@Pt/C (114.23 mV dec⁻¹), NF@NiBx-3h had a smaller Tafel slope of 49.39 mV dec⁻¹. Lower Tafel slope compared to other catalysts indicates a more rapid kinetic. In the EIS test of the OER process (Figure 3c), NF@NiB_x-3h also had the smallest R_{ct} value, indicating a lower charge transfer resistance and a quicker electron transfer rate. The C_{dl} values in Figure 3d could be obtained by CV techniques in the non-faradaic interval (Figure S3, Supporting Information), with C_{dl} values of 19.5 mF cm⁻² and 12.5 mF cm⁻² for NF@NiBx-3h and Bare NF, respectively. This meant that the insertion of NiB significantly increased the number of active sites and electrochemical regions of the material. Same as the HER process, TOF of OER used CV method to study in 1.0 M KOH + 0.5 M NaCl solution, and the range of potential is from -0.06 to 0.04 V (vs. RHE), as shown in Figure S4d,e (Supporting Information). The number of active sites is equal to the charge of the oxidation peak divided by the charge per electron, $N = Q_S/Q_E$ [40,41]. The TOF of NF@NiB electrode (1.89 s⁻¹) was larger than Bare NF (0.46 s⁻¹) electrodes at 1.60 V in 1.0 M KOH + 0.5 M solution, indicating that the NiB material own high active. Figure 3e shows the stability of the electrode tested by chrono-potentiometry at a constant current density of 200 mA cm^{-2} . It could be observed that the OWS performance degradation is less than 8% after 170 h, indicating that NF@NiB catalytic electrode has excellent catalytic stability and the XRD spectra and SEM images indicated a stable structure (Figures S5 and S6, Supporting Information).



Figure 3. OER performance in 1 M KOH + 0.5 M NaCl solution: (a) LSV curves; (b) Tafel slopes; (c) Nyquist plots; (d) C_{dl} values; (e) Chronopotentiometric measurement of OER at the current density of 200 mA·cm⁻².

3.2.2. OWS Electrochemical Measurements of NF@NiB Electrode

Inspired by the excellent bifunctional activity, NF@NiB electrode was used as anode and cathode electrodes to manipulate the OWS in an electrolyzer with 1.0 M KOH + 0.5 M NaCl. As shown in Figure 4a, (–) NF@NiB | | NF@NiB (+) reached 10 mA cm⁻² at a

relatively low cell voltage of 1.637 V, which was much lower than (–) Bare NF | |Bare NF (+) (1.808 V), and slightly higher than the commercial cell (–) NF@Pt/C | NF@IrO₂ (+) (1.604 V) at the same measurement conditions. As shown in Figure S8 (Supporting Information), we also performed the OWS in 1.0 M KOH; NF@NiB | NF@NiB also showed excellent OWS catalytic activity. In addition, the (–) NF@NiB | NF@NiB (+) water electrolyzer exhibited excellent stability in the OWS reaction (Figure 4b). It was evident that after 170 h of electrolysis at 200 mA cm⁻² current density, the (–) NF@NiB | NF@NiB | NF@NiB (+) electrolyzer still kept 96.1% of its initial voltage. A comparison of the experimentally measured actual gas volume ratio with the theoretical calculated H₂ and O₂ volumes ratio via the chronopotentiometric method, shows that the volume ratio of H₂ and O₂ generated was close to 2:1 and the Faraday efficiency was close to 100%. On the other hand, the voltage of NF@NiB at 10 mA cm⁻² was comparable to most previously reported electrolytes assembled from boron–based or nickel–based electrocatalysts (Figure 4d, Table S1, Supporting Information).



Figure 4. (a) LSV curves of OWS for NF@NiB||NF@NiB, Bare NF||Bare NF and NF@Pt/C||NF@IrO₂ in a two-electrode system. (b) Chronoamperometric curve of NF@NiB in 1.0 M KOH + 0.5 M NaCl. (c) Theoretically calculated and experimentally measured gas volumes relative to time for NF@NiB||NF@NiB. (d) Comparing the OWS performance of NF@NiB||NF@NiB with state-of-the-art transition metal-based bifunctional electrocatalysts.

4. Conclusions

In summary, we have developed a convenient, cost-effective and efficient way to construct bifunctional self-supporting electrocatalysts, which were directly doped with boron on a nickel foam substrate and grown in situ to form NF@NiB bifunctional catalytic electrodes for water splitting. The pretreated NF was directly placed into sodium borohydride solution to trigger chemical etching, which can effectively form a binary NiB catalyst. The comprehensive experiments fully verified the excellent catalytic performance of NF@NiB as well as the outstanding corrosion resistance. Specifically, NF@NiB exhibited overpotentials of 96 and 261 mV at 10 mA cm⁻². More notably, they provided a current density of 200 mA cm⁻² for OWS with a stable long cycle of no less than 7 days. This work opens up new possibilities for the development of novel water splitting devices based on nickel or other transition metals.

Supplementary Materials: The following supporting information can be downloaded at: https:// www.mdpi.com/article/10.3390/inorganics11040170/s1. Figure S1: Raman spectrum of NF@NiBx and Bare NF electrodes at 532 nm excitation; Figure S2: LSV curves of NF@NiBx and Bare NF electrodes for HER in 1 M KOH solution; Figure S3: CV curves within a non-faradaic reaction region of 0.02~0.12 V (vs. RHE) at different scan rates toward HER for NF@NiB (a) and Bare NF (c); -0.06~0.04 V (vs. RHE) at different scan rates toward OER for NF@NiB (b) and Bare NF (d); Figure S4: (a,b) CV curves of NF@NiB and Bare NF for HER in 1.0 M KOH + 0.5 M NaCl with a scan rate of 50 mV s-1; (d, e) CV curves of NF@NiB and Bare NF for OER in 1.0 M KOH + 0.5 M NaCl with a scan rate of 50 mV s-1; (c,f) The calculated TOFs curves for HER and OER; Figure S5: XRD spectra of NF@NiBx after HER and OER stability measurements; Figure S6: SEM images of NF@NiB after HER (a) and OER(b) stability tests; Figure S7: LSV curves of NF@NiBx and Bare NF electrodes for OER in 1 M KOH solution; Figure S8: LSV curves of NF@NiBx and Bare NF electrodes for 0 M KOH solution; Table S1: Comparison of overall water splitting performance of NF@NiB electrode with state-of-the-art nickel and boron series catalysts under alkaline conditions [10,11,26,42–55].

Author Contributions: Z.L. and R.L. contributed equally to this work. Z.L. and R.L.: methodology, investigation, formal analysis, data curation, writing—original draft. Y.S.: methodology, investigation. W.H.: conceptualization, methodology, writing—review and editing, supervision, funding acquisition. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by "the National Natural Science Foundation of China, grant number 22109098", "The Natural Science Foundation of Shanghai (23ZR1443900)" and "The Shanghai Sailing Program (20YF1432300)" and "Shanghai Engineering Research Center for Food Rapid Detection was funded by 19DZ2251300".

Data Availability Statement: Not applicable.

Acknowledgments: The authors acknowledge the funding support from the National Natural Science Foundation of China (Grant No.22109098), the Natural Science Foundation of Shanghai (23ZR1443900), and the Shanghai Sailing Program (Grant No. 20YF1432300), Shanghai Engineering Research Center for Food Rapid Detection (19DZ2251300). The authors would like to thank Yuwei Zhou for the scanning electron microscope images and grazing—incident XRD analysis from Shiyanjia Lab ("www.shiyanjia.com (accessed on 3 Mar. 2023)").

Conflicts of Interest: The authors declare no conflict of interest.

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