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Modulating Ni-S Coordination in Ni$_3$S$_2$ to Promote Electrocatalytic Oxidation of 5-Hydroxymethylfurfural at Ampere-Level Current Density

Lan Chen, Zhaohui Yang, Chuanyu Yan, Yijun Yin, Zhimin Xue, Yiting Yao, Shao Wang, Fanfei Sun, Tiancheng Mu

Electricity-driven oxidation of 5-hydroxymethylfurfural (HMF) to 2,5-furandicarboxylic acid (FDCA) is a highly attractive strategy for biomass transformation. However, achieving industrial-grade current densities remains a great challenge. Herein, by modulating water content in the solvothermal system, Ni$_3$S$_2$/NF with stabilized and shorter Ni-S bonds as well as tunable coordination environment of Ni sites was fabricated. The prepared Ni$_3$S$_2$/NF was highly efficient for electrocatalytic oxidation of HMF to produce FDCA, and the FDCA yield and Faraday efficiency could reach 98.8% and 97.6% at the HMF complete conversion. More importantly, an industrial-grade current density of 1000 mA·cm$^{-2}$ could be achieved at the potential of only 1.45 V vs. RHE for HMFOR, and the current density could exceed 500 mA·cm$^{-2}$ with other bio-based compounds as the reactants. The excellent performance of Ni$_3$S$_2$/NF originated from the shorter Ni-S bonds and its better electrochemical properties, which significantly promoted the dehydrogenation step of oxidizing HMF. Besides, the gram-scale FDCA production could be realized on Ni$_3$S$_2$/NF in a MEA reactor. This work provides a robust electrocatalyst with high potentials of practical applications for the electrocatalytic oxidation of biomass-derived compounds.

Introduction

In order to mitigate the environmental problems and energy crisis caused by the overconsumption of fossil resources, there is an urgent need to find alternative resources that should be renewable and abundantly available.[1] Biomass, the world’s most abundant renewable carbon-based resource, is one promising alternative of fossil resources. Generally, biomass can be converted into high-value chemicals,[2] fuel products (e.g., bio-oils),[3] and functional bio-based materials.[4] In this regard, 5-hydroxymethylfurfural (HMF), a highly attractive platform molecule prepared from biomass-based carbohydrates (e.g., cellulose, and glucose),[5] has great potential in the production of high value-added fine chemicals,[7] such as 2,5-furandicarboxylic acid (FDCA), 2,5-furandicarboxaldehyde (DFF), and 2,5-dimethyl furan (DMF), etc. Of these HMF-derived compounds, FDCA has been employed as the renewable monomer for the synthesis of polyethylene 2,5-furandicarboxylate (PEF), which has been considered as an environmentally friendly alternative to petroleum-derived and widely-used polyethylene terephthalate (PET).[8, 9] Therefore, selective conversion of HMF to produce FDCA has become a hotspot in recent years.[10-12] Generally, FDCA could be synthesized from oxidation of HMF via the conventionally thermal catalysis.[13] However, thermal catalysis was usually carried out under harsh reaction conditions (i.e., high temperature, and/or high oxygen pressure).[14, 15] Recently, electrocatalytic oxidation of HMF (HMFOR) for the production of FDCA has been developed, which exhibits inherent advantages such as mild conditions, no need for precious metals and oxidants, as well as environmental friendliness. More importantly, HMFOR has favorable thermodynamic properties compared to OER and can be coupled with different cathodic reduction reactions to obtain various high value-added products (e.g., H$_2$[16, 17] and CO[18]). Currently, the main challenge for HMFOR remains the development of robust catalysts for practical applications. In previous studies, transition metal materials, especially nickel-based catalysts, were the most used electrocatalysts[19] due to Ni sites (by the adsorption of hydroxide or being converted into hydroxide) could promote HMF oxidation by proton-coupled electron transfer processes. HMFOR generally requires a redox mediator as a sacrificial agent (e.g., TEMPO) for the conversion of HMF to FDCA under neutral or weakly acidic conditions.[20, 21] However, the Ni-based catalysts reported in recent articles can efficiently convert HMF to FDCA through an indirect oxidation mechanism without the need of a sacrificial agent.[22] Although many Ni-based catalysts have been developed for HMFOR, the developed catalysts unfortunately underwent
severe and uncontrollable surface reconstruction to form oxides or hydroxides under alkaline conditions, which might result in a significant decrease in catalytic activity.[23] More challengingly, there were only few catalytic systems that could conduct HMFOR under a high concentration of HMF (>50 mM) at industrial-scale current densities (>500 mA cm\(^{-2}\)), and the systems reaching ampere-scale current densities were even less.[24, 25] Therefore, it is highly essential to construct robust and stable nickel-based electrocatalysts to realize HMFOR at high current densities.

The electro-catalytic performance of Ni-based catalysts was significantly affected by the electronic environment of Ni sites. Generally, the orbital hybridization of Ni sites could be modulated by changing the type and ratio of coordination bonds of the active sites, resulting in a delicate regulation of electronic structure.[26, 27] Thus, modifying the coordination structure of Ni sites was a promising strategy to improve the activity of Ni-based catalysts on HMFOR. Besides, the electrochemical performance of the electrodes could also be improved by introducing heteroatoms (e.g., S, N and P) to optimize the electrode surface properties.[28] Poor catalytic efficiency was often obtained due to excessive adsorption of substrates on the electrode surface with a too strong positive electric field.[29] It has reported that the S\(^2-\) anion of good electronegativity could reduce the strength of the positive electric field on the electrode surface, thereby promoting the desorption of the product as well as the adsorption and desorption of the probable intermediates.[30] Additionally, according to the Lewis acid-base theory, there was a M-X coordination (M and X represented the metal and the heteroatom, respectively) formed between the metal and the heteroatom.[31] In this way, the Lewis acid-base electron pair could boost the activation of the catalyst and reduce the reaction potential barrier on the catalytic electrode effectively.[32] Based on the discussions above, robust and stable Ni-based electrocatalytic materials to generate high current densities for HMFOR could be potentially constructed by finely tuning the coordination structure of Ni sites.

In this work, Ni\(_3\)S\(_2\) nanosheets on the surface of nickel foam (NF) was synthesized by a one-step solvothermal method. The synthesized Ni\(_3\)S\(_2\)/NF with shorter Ni-S coordination offered the possibility of sustained and rapid electron transfer during the reaction as well as the deprotonation of HMF, and showed high catalytic efficiency on HMFOR, in which the HMF conversion, the FDCA yield, and the Faraday efficiency (FE) of FDCA could reach close to 100%, 98.8% and 97.6%, respectively. More importantly, an ultra-high current density (1000 mA·cm\(^{-2}\)) could be achieved at the potential of only 1.45 V vs. RHE. The fact of achieving industrial current density and the high stability represented the major breakthrough, thus making the developed catalyst have great potentials in practical applications.

Results and discussion

The desired Ni\(_3\)S\(_2\)/NF was prepared by the one-step solvothermal route as illustrated in Figure 1a, where thioacetamide (TAA) was employed as the sulfur source. The morphology of the prepared Ni\(_3\)S\(_2\)/NF was characterized using field emission scanning electron microscopy (FE-SEM). As shown in Figure S1a and S1b, after the solvothermal process, the NF framework was well maintained, and Ni\(_3\)S\(_2\) nanosheets were arranged neatly on the NF surface to form three-dimensional porous nanospheres (Figures 1b-f). In comparison, the morphology of the Ni\(_3\)S\(_2\)/NF changed from nanospheres to

![Figure 1](image_url)

**Figure 1.** (a) The process of preparing the desired Ni\(_3\)S\(_2\)/NF, (b-d) SEM images of Ni\(_3\)S\(_2\)/NF, (e) TEM image of Ni\(_3\)S\(_2\)/NF, and (f and g) HRTEM images of Ni\(_3\)S\(_2\)/NF.
nanodendrites when water was introduced into the synthetic system, and the size of dendrites became larger with the increase of the introduced water (Figures S2-S5). Transmission electron microscopy (TEM) image showed that the prepared Ni\textsubscript{1-x}S\textsubscript{x}/NF was composed of nanosheets (Figure 1e). Importantly, the NiS\textsubscript{2}/NF had a higher electronic conductivity. Moreover, Raman spectrum was used to identify the molecular vibrational information of functional groups on the electrode surface. The XPS spectra of Ni 2p, S 2p, the electronic interaction between Ni species and S species in the prepared materials could be tuned by the water ratio in the solvothermal system.

With the increase of water proportion in the solvothermal system, the Ni-S bond at 852.3 eV.

More importantly, the binding peaks were observed. Besides, there was an extra peak assigned to S\textsuperscript{2-}/NF-1 showed the characteristic Ni-O bond, S\textsuperscript{2-}/NF-1, S\textsuperscript{2-}/NF with a higher electronic conductivity. Additionally, the ratio of S-O/Ni-S bonds increased from 0 to 1.180 when the water ratio in the solvothermal system increased from 0 to 100% (Table S1), indicating the controllable modification of the material structure by the water ratio in the solvothermal system. The above results indicate that the Ni-S bond could be modulated by adjusting the water ratio in the solvothermal system. Considering the important role of surface species and their electronic state on the electrocatalysis, the electronic states and the surface chemical compositions of the prepared materials were determined by XPS. XPS survey spectra (Figure S6) confirmed the coexistence of Ni, S, and O elements in the obtained materials. In the high-resolution XPS spectra of Ni 2p (Figure 2c), characteristic peaks of Ni\textsuperscript{2+} at 855.7 (Ni\textsuperscript{2+} 2P\textsubscript{3/2}) and 873.7 eV (Ni\textsuperscript{2+} 2P\textsubscript{1/2}) accompanied by oscillating satellite peaks were observed. Besides, there was an extra peak assigned to the Ni-S bond at 852.3 eV.[30, 33] More importantly, the binding energy of Ni 2p increased with the increase of water ratio in the solvothermal system, suggesting that the Ni sites in the Ni\textsubscript{1-x}S\textsubscript{x}/NF were more negatively charged. From the XPS spectra of S 2p, two peaks at 162.1 eV and 163.5 eV, which were assigned to S\textsuperscript{2-} 2P\textsubscript{3/2} and S\textsuperscript{2-} 2P\textsubscript{1/2} respectively, could be observed. Notably, the peak of S 2p in Ni\textsubscript{1-x}S\textsubscript{x}/NF moved towards lower binding energy with the increase of water ratio in the solvothermal system (Figure 2d), implying that S\textsuperscript{2-} in Ni\textsubscript{1-x}S\textsubscript{x}/NF was more negatively charged. Based on the XPS results of Ni 2p and S 2p, the electronic interaction between Ni species and S species in the prepared materials could be tuned by the water ratio in the solvothermal system, and this interaction in Ni\textsubscript{1-x}S\textsubscript{x}/NF was the strongest. Additionally, the ratio of S-O/Ni-S bonds increased from 0 to 1.180 when the water ratio in the solvothermal system increased from 0 to 100% (Table S1), indicating the controllable modification of the material structure by the water ratio in the solvothermal system. With the increase of water proportion in the solvothermal system, water molecules would occupy more Ni-ligand sites,

The fine structure of the prepared Ni\textsubscript{1-x}S\textsubscript{x}/NF was further characterized by X-ray diffraction (XRD), Raman spectrum, and X-ray photoelectron spectroscopy (XPS). As presented in XRD patterns (Figure 2a), both Ni\textsubscript{1-}S\textsubscript{x}/NF and Ni\textsubscript{1-}S\textsubscript{x}/NF-1 showed the characteristic peaks of Ni\textsubscript{1-}S\textsubscript{x} (PDF # 44-1418) and Ni (PDF # 04-0850), while Ni(OH)\textsubscript{2}/NF possessed the characteristic peaks of Ni(OH)\textsubscript{2} (PDF # 38-0715) and Ni (PDF # 04-0850). More importantly, the peak intensity for the Ni\textsubscript{1-}S\textsubscript{x} in Ni\textsubscript{1-}S\textsubscript{x}/NF was greater than that in Ni\textsubscript{1-}S\textsubscript{x}/NF-1, suggesting that Ni\textsubscript{1-}S\textsubscript{x}/NF was more fully Vulcanized and crystallized, which endowed Ni\textsubscript{1-}S\textsubscript{x}/NF with a higher electronic conductivity. Moreover, Raman spectrum was used to identify the molecular vibrational information of functional groups on the electrode surface. In Raman spectra of the prepared electrodes (Figure 2b), the characteristic Ni-S vibrational modes were observed in the range of 100-800 cm\textsuperscript{-1}. The electron microscopy (TEM) image showed that the prepared nanodendrites when water was introduced into the synthetic system, and the size of dendrites became larger with the increase of the introduced water (Figures S2-S5). Transmission electron microscopy (TEM) image showed that the prepared nanodendrites when water was introduced into the synthetic system, and the size of dendrites became larger with the increase of the introduced water (Figures S2-S5).
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potential for HMFOR was lower than that of OER, indicating that voltammetry (CV) at a scan rate of 50 mV·s⁻¹ of 1000 mA cm⁻². Subsequently, the catalytic performance of the prepared electrodes was more favorable in thermodynamics than OER. Ni³⁺ best of our knowledge, this current density was the maximum on Ni(OH)₂ electrodes. Especially, Ni³⁺ investigated. It was observed that the current densities on LSV curves (Figure 3a), a small peak appeared at the potential in 1.0 M KOH solution with and without 50 mM HMF. Before electrochemical testing, the electrodes were activated by cyclic voltammetry (CV) at a scan rate of 50 mV·s⁻¹ (Figure S11). In the LSV curves (Figure 3a), a small peak appeared at the potential of 1.38 V vs. RHE for OER, representing the oxidation of Ni³⁺ to Ni⁴⁺ as well as the adsorption of OH⁻. In comparison, the onset potential for HMFOR was lower than that of OER, indicating that HMFOR was more favorable in thermodynamics than OER. Subsequently, the catalytic performance of the prepared electrodes on HMFOR performance was systematically investigated. It was observed that the current densities on Ni₃S₂/NF, Ni₃S₂/NF-0.4, Ni₃S₂/NF-0.8, Ni₃S₂/NF-1 and Ni(OH)₂/NF decrease continuously (Figures 3b and c), and the tendency was consistent with the content of S-O bond in the electrodes. Especially, Ni₃S₂/NF could achieve a current density of 1000 mA cm⁻² only at the potential of 1.45 V vs. RHE. To the best of our knowledge, this current density was the maximum that could be achieved with non-precious metal electrodes in alkaline electrolyte (Figure 3d and Table S3). To analyze different catalytic performance, Tafel plots for different electrodes was collected (Figure 3e). As expected, Ni₃S₂/NF had the lowest Tafel slope (63.5 mV·dec⁻¹) compared with Ni₃S₂/NF-0.4 (91.43 mV·dec⁻¹), Ni₃S₂/NF-0.8 (98.49 mV·dec⁻¹), Ni₃S₂/NF-1 (103.64 mV·dec⁻¹) and Ni(OH)₂/NF (156.56 mV·dec⁻¹), indicating the superior catalytic kinetics for HMFOR over Ni₃S₂/NF. The lowest Tafel slope of Ni₃S₂/NF was probably caused by the stronger interaction between Ni and S species, which leaded to an optimized electronic configuration, thus enhancing the corresponding charge transfer process. Furthermore, the double layer capacitance (C_dl) was calculated by CV curves in non-Faradic region (Figure S12) to estimate the electrochemically active surface area (ECSA) of the electrodes. Ni₃S₂/NF exhibited the highest ECSA (Figure 3f), which could provide more electrochemically active sites for the HMFOR. Meanwhile, the interfacial charge transfer resistance was investigated based on electrochemical impedance spectroscopy.

Figure 3. Electrochemical performance of the prepared materials. (a) Linear sweep voltammetry (LSV) curves of Ni₃S₂/NF in 1 M KOH with and without 50 mM HMF, (b) LSV curves of Ni₃S₂/NF, Ni₃S₂/NF-0.4, Ni₃S₂/NF-0.8, Ni₃S₂/NF-1 and Ni(OH)₂/NF for HMFOR, (c) Comparison of the current densities of Ni₃S₂/NF, Ni₃S₂/NF-0.4, Ni₃S₂/NF-0.8, Ni₃S₂/NF-1 and Ni(OH)₂/NF at different potentials, (d) Comparison of HMFOR performance with previously reported electrocatalysts, (e) Tafel plots, (f) Change of current density plotted against the scan rate for Ni₃S₂/NF, Ni₃S₂/NF-0.4, Ni₃S₂/NF-0.8, Ni₃S₂/NF-1 and Ni(OH)₂/NF, (g) Nyquist plots, (h) Calculated TOFs, and (i) Potentials for oxidation of different substrates containing hydroxyl and aldehyde groups at 500 mA cm⁻².
the Nyquist plot of Ni$_3$S$_2$/NF in 1 M KOH without HMF was more than five times larger than that after the addition of 50 mM HMF (Figure S14), suggesting that OER had much larger charge transfer resistance ($R_{ct}$) than HMFOR. More importantly, Ni$_3$S$_2$/NF exhibited a smaller $R_{ct}$ value in comparison with Ni$_3$S$_2$/NF-0.4, Ni$_3$S$_2$/NF-0.8, Ni$_3$S$_2$/NF-1 and Ni(OH)$_2$/NF (Figure 3g), indicating a faster charge transfer at the interface of Ni$_3$S$_2$/NF. Generally, most of the reported electrode materials tended to have a larger surface area than the geometry of the substrate electrode, resulting in a bias in the evaluation of apparent versus intrinsic activity.[37-39] To reveal the inherent correlation between structural features and the catalytic activity of different electrodes, the turnover frequency (TOF) was evaluated (Figure 3h), and the number of active sites was estimated by integration of the redox peak because the oxidation process of HMF involved a redox cycle between Ni$^{3+}$ and Ni$^{2+}$ (Figure S15).[40] Based on the results in Figures 3h and S13, Ni$_3$S$_2$/NF not only had more active sites but also possessed the highest TOF. Based on the discussions above, we could deduced that the good performance of Ni$_3$S$_2$/NF probably originated from its high content of Ni-S bonds, which contributed to the exposure of the active sites, thereby enhancing the intrinsic activity of Ni$_3$S$_2$/NF on HMFOR. Encouraged by the excellent electrocatalytic performance of Ni$_3$S$_2$/NF for HMFOR, the electrooxidation of other bio-based compounds containing aldehyde or hydroxyl groups was evaluated. Based on the results in Figures 3i and S16, after adding 50 mM benzaldehyde (BZH), 5-hydroxymethyl furfural acid (HMFCA), 2,5-diformylfuran (DFF), ethylene glycol (EG), glycerol (Gly) and furfural (FF) into 1 M KOH solution, the onset potentials were all lower than OER, indicating that the oxidation of these compounds was more favorable in thermodynamics than OER. More importantly, for the electrooxidation of all the mentioned compounds, Ni$_3$S$_2$/NF could achieve a current density of 500 mA cm$^{-2}$ before the potential of 1.6 V vs. RHE. These results above not only confirmed the outstanding catalytic activity of Ni$_3$S$_2$/NF, but also demonstrated its versatility for the oxidation of diverse substrates.

The reason on the excellent performance of Ni$_3$S$_2$/NF on HMFOR was systematically analyzed. As well-accepted, the adsorption of HMF molecules on the electrode surface played the crucial role of determining the HMFOR performance.[41]

Generally, the open-circuit potentials (OCP) could reflect the capacity of HMF adsorption in Helmholtz layer on the electrode surface. After adding 50 mM HMF in the reaction system, the OCP values of Ni$_3$S$_2$/NF, Ni$_3$S$_2$/NF-1, and Ni(OH)$_2$/NF were 402, 341, and 330 mV, respectively, implying that Ni$_3$S$_2$/NF with robust Ni-S coordination had the strongest adsorption capacity for HMF. Besides, the surface structures of Ni$_3$S$_2$/NF were monitored by potential-dependent operando Raman spectra to reveal the variation of active sites during the reaction. In the control experiments, Ni$_3$S$_2$/NF was used as the working electrode and the surface changes of the electrode were monitored at different potentials in 1 M KOH without or with 50 mM HMF. In general, Ni$^{3+}$-OH was considered to be the active species of both OER and HMFOR.[42] For the OER, the characteristic Raman peaks were observed at 476 and 556 cm$^{-1}$ attributed to bending and stretching vibrations of Ni$^{3+}$-OH when the potential increased to 1.40 V vs. RHE (Figure 4b), matching perfectly with the appearance of an oxidation peak in the potential of 1.35-1.4 V vs. RHE (Figure 3a). In comparison, after adding 50 mM HMF into 1 M KOH solution, the two peaks were not observed until the potential exceeded to 1.45 V vs. RHE, probably resulting from that the generated Ni$^{3+}$-OH before 1.45 V vs. RHE was rapidly consumed. In other words, Ni$^{2+}$ was electrooxidized to form Ni$^{3+}$-OH sites, which would be rapidly consumed by the spontaneous HMFOR through the interaction between Ni$^{3+}$-OH and HMF adsorbed on the electrode, which was independent of the applied potential (Figure 4c). In order to gain more insight into the behavior of catalyst-electrolyte interface, operando EIS were utilized to further analyze the differences between OER and HMFOR.[43] For HMFOR, the $R_{ct}$ of Ni$_3$S$_2$/NF decreased sharply after the potential exceeds 1.3 V vs. RHE and was smaller than that of Ni$_3$S$_2$/NF-1 and Ni(OH)$_2$/NF (Figure 4d), suggesting the faster charge transfer rate of HMFOR on Ni$_3$S$_2$/NF. However, the $R_{ct}$ increased slightly after the potential of 1.45 V vs. RHE, which was attributed to the competition between HMFOR and OER. Besides, the semicircle radius of the Nyquist plot (Figure S17) displayed that the impedance of OER was consistently larger than that of HMFOR, implying the faster charge transfer rate of HMFOR. On the basis of the above discussions, Ni$_3$S$_2$/NF had the highest electrochemical surface area, lowest charge transfer resistance, strongest adsorption capacity for HMF. These advantages could significantly improve the oxidation efficiency of HMF to generate FDCA. Thereby, a much better performance on HMF electrooxidation could be achieved over Ni$_3$S$_2$/NF in comparison with other materials.
frequency region, were attributed to the dehydrogenation of HMF process until the charge reached 580 C (Figure S19), resulting from the current density continually decreased during the electrocatalysis was achieved with a FDCA yield of 98.8% and a Faraday efficiency of 95.6-98.1% varied within a highly narrow range. More importantly, 2.002 g FDCA could be obtained from the continuous consumption of HMF. More importantly, the cycling stability test of the Ni$_3$S$_2$/NF electrode could be recycled for six consecutive electrocatalytic cycles, and the HMF conversion (99.4-99.8%), the FDCA selectivity (97.9-99.6%) and FDCA Faraday efficiency (95.6-98.1%) varied within a highly narrow range. Meanwhile, the used Ni$_3$S$_2$/NF was characterized by SEM, XPS and XRD techniques (Figures S20-S22), and the results showed that the properties of the Ni$_3$S$_2$/NF was very similar with the fresh electrode. Particularly, the XPS spectra of S 2p in the used Ni$_3$S$_2$/NF remained almost devoid of S-O bonds, demonstrating the solidity of Ni-S coordination. These results above confirmed the outstanding stability (both catalytic activity and its structure) of Ni$_3$S$_2$/NF, and its surface was not electrochemically reconfigured to hydroxide or oxyhydroxides as in previously reported work. To further reveal the possibility for the practical application of the Ni$_3$S$_2$/NF, a membrane electrode assembly (MEA) reactor of alkaline electrolysis with Ni$_3$S$_2$/NF was fabricated for the HMFOR. When employing 1 M KOH with 50 mM HMF as the electrolyte, the current density of HMFOR//HER was much higher than that of OER//HER, indicating that substitution of OER for HMFOR was favorable as a mean to reduce energy consumption (Figure 5f).

Figure 5. The chronoamperometric electrolysis measurements of HMFOR by Ni$_3$S$_2$/NF at 1.4 V vs. RHE. (a) The possible pathways of HMF oxidized to FDCA, (b) HPLC chromatogram traces of electrolyte during the electrochemical oxidation of HMF, (c) The concentration changes of HMF and its oxidation products during HMF electrooxidation, (d) HMF conversion, selectivity and FE of FDCA during HMF electrooxidation at the potential of 1.4 V vs. RHE in 6 successive cycles, (e) Schematic representation of the MEA reactor, and (f) LSV curves of Ni$_3$S$_2$/NF in 1 M KOH with and without 50 mM HMF in MEA reactor.

Selectivity of the targeted products was a key aspect of biomass upgrading. As well-known, there were two main pathways in the electrooxidation of HMF due to the co-existence of carbonyl and hydroxyl groups (Figure 5a). In the pathway 1, the aldehyde group on HMF was firstly oxidized to generate 5-hydroxymethyl 2-furan carboxylic acid (HMFCA) as the reaction intermediate. In the pathway 2, 2,5-dicarboxyfuran (DFF) was generated as the reaction intermediate by the preferential oxidation of the hydroxymethyl group on HMF. Subsequently, both HMFCA and DFF were further oxidized to form FFCA, which was ultimately converted to FDCA. To conform the predominant pathway, the concentrations of HMF and the products were monitored by high performance liquid chromatography (HPLC) and quantitatively calculated based on the standard curves (Figure S18). With the prolonging of the electrolysis time, the concentration of HMF gradually decreased and the concentration of FDCA gradually increased, indicating that HMF was successfully converted into FDCA (Figures 5c and d). Simultaneously, HMFCA and FFCA were identified during the electrolysis process, but negligible amounts of DFF could be detected, indicating that the electrooxidation of HMF on Ni$_3$S$_2$/NF mainly proceeded through the pathway 1 (Figure 5a). Finally, nearly complete conversion of HMF was achieved with a FDCA yield of 98.8% and a Faraday efficiency of 97.6% when the charge was accumulated up to 580 C. Additionally, the current density continually decreased during the electrocatalysis process until the charge reached 580 C (Figure S19), resulting from the continuous consumption of HMF.
was more than 99%, which could be proved by HPLC (Figures 5f and S23).

Density functional theory (DFT) calculations was finally used to theoretically uncover the differences in structure as well as reactivity regarding Ni$_3$S$_2$ with robust Ni-S coordination and Ni$_3$S$_2$/NF of being conventionally oxygen-embedded. Based on the experimental results above, the optimal theoretical models for Ni$_3$S$_2$/NF and Ni$_3$S$_2$/NF-1 were constructed (Figures 6a and b), and the density of electronic states (DOS) of these two catalysts were analyzed to obtain the differences in electronic structure (Figure 6b). Compared with Ni$_3$S$_2$/NF-1, Ni$_3$S$_2$/NF had higher TDOS near the Fermi energy, suggesting an enhanced intrinsic conductivity of Ni$_3$S$_2$/NF and thus facilitating the electron transfer in the electrocatalytic process. In order to further demonstrate the bonding strength in both catalysts, the crystal orbital Hamiltonian cloth residence (COHP) was used to quantitatively analyze the Ni-S bond interactions.[47] As shown in Figures 5c, 5d, and S24, the COHP value of Ni-S in Ni$_3$S$_2$/NF was -4.01, which was more negative than that in Ni$_3$S$_2$/NF-1 (-3.06). Besides, DFT Moreover, the behavior of HMFOR on the catalysts was further simulated by the calculations on the HMF dehydrogenation. HMFOR was a stepwise deprotonation process, in which the oxidation of the aldehyde group of HMF in alkaline required hydration to form diol group and then gradual dehydrogenation to generate carboxyl group. The kinetic energy barriers for proton transferred from HMF to Ni$_3$S$_2$/NF surface with adsorbed hydroxyl groups were calculated. As shown in Figures 6f and 6g, HMF was adsorbed on the Ni sites while the absorbed OH acted as a proton transfer receptor, followed by H detached from HMF to combine with OH to generate water. The energy barrier of hydrogen transfer on Ni$_3$S$_2$/NF was 1.35 eV, which was lower than that of Ni$_3$S$_2$/NF-1 (1.59 eV), suggesting that Ni$_3$S$_2$/NF enhanced the deprotonation ability of HMFOR and thus facilitated the oxidation of HMF. All these calculation results were in agreement with the experimental observations for electrocatalytic oxidation of HMF.

![Image](https://i.imgur.com/3.png)

**Figure 6.** (a and b) Theoretical models of Ni$_3$S$_2$/NF and Ni$_3$S$_2$/NF-1, (c) The density of states (DOS) of Ni$_3$S$_2$/NF and Ni$_3$S$_2$/NF-1, (d and e) Crystal Orbital Hamilton Population (−COHP) of Ni-S bonds of Ni$_3$S$_2$/NF and Ni$_3$S$_2$/NF-1 (The bonding and antibonding states of the Ni-S bonding interactions were shown in blue and red, respectively.), (f) Energy changes in the deprotonation process on Ni$_3$S$_2$/NF and Ni$_3$S$_2$/NF-1, and (g) The initial, transition and final states in the deprotonation process.

**Conclusions**

In summary, Ni$_3$S$_2$ nanosheets supported on NF were fabricated directly by a one-step solvothermal method, and the Ni-S coordination in these materials could be controllably tuned by changing the water content in the solvothermal system. The as-prepared materials as electrodes could catalyze electro-oxidation of HMF to produce FDCA. It was observed that the catalytic activity of the obtained electrodes increased with the decrease of the water content in the solvothermal system of preparing the catalysts, and Ni$_3$S$_2$/NF showed the best performance for the reaction with current densities up to 1000 mA·cm$^{-2}$ at a potential of only 1.45 V vs. RHE. The HMF conversion was almost 100% with a FDCA yield of 98.8% and a Faraday efficiency of 97.6% on the Ni$_3$S$_2$/NF. Besides, industrial-scale current densities of 500 mA·cm$^{-2}$ could be also achieved in the electrooxidation of other bio-based compounds, including benzaldehyde, 5-hydroxymethyl furfural, 2,5-diformylfuran, ethylene glycol, glycerol and furfural. Systematic investigations revealed that Ni$_3$S$_2$/NF had higher electronic conductivity, lower charge transfer resistance, and higher electrochemical surface area, which all could promote its catalytic activity.
performance on the HMFOR. More importantly, Ni\textsubscript{S}S\textsubscript{2}/NF could be applied in a MEA reactor, which allowed the gram-scale FDCA production with a purity of more than 99%. We believe that the constructed Ni\textsubscript{S}S\textsubscript{2}/NF has great potential of practical applications for the synthesis of FDCA from electrocatalytic oxidation of HMF.

Author Contributions
Lan Chen: Methodology, investigation, data curation, writing original draft. Zhaohui Yang: Methodology, investigation, writing original draft. Chuanyu Yan: Conceptualization, supervision. Yijun Yin: Methodology, investigation. Zhimin Xue: Conceptualization, Writing - review & editing supervision. Yiting Yao: Methodology, investigation, data curation. Shao Wang: Methodology. Fanfei Sun: Investigation, data curation. Tiancheng Mu: Conceptualization, methodology, supervision.

Conflicts of interest
There are no conflicts to declare.

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Notes and references
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