1. Introduction

Energy depletion and environmental pollution caused by the excessive use of fossil fuels has triggered rapid development of sustainable energy sources from the aspects of fundamental research and industrial applications. Hydrogen is one of the most promising candidates, due to its high calorific value and facile storage in the form of water. For hydrogen production, water electrolysis has been recognized as a prospective approach because of its mild operating conditions and a clean reaction process. However, large-scale hydrogen production from water electrolysis is restricted by the sluggish and rate-determining oxygen evolution half-reaction (OER). The high costs and scarcity of catalysts (e.g., IrO2 and RuO2) as well as potential explosion of the mixture of O2 and H2 have thus stimulated many novel strategies to realize cheap and efficient hydrogen production.

Instead of design and synthesis of the OER electrocatalyst as those mostly reported, we replace the OER with a thermodynamically and kinetically favorable oxidation half-reaction to achieve cheap and efficient hydrogen production. The electrooxidation of an important but widely existed biomass derivative of 5-hydroxymethylfurfural (HMF) into 2,5-furandicarboxylic acid (FDCA) is expected to be a perfect anodic half-reaction since six electrons that are involved during this oxidation reaction are possibly utilized for the cathodic hydrogen production. In such a case, the overall reaction is expressed as:

\[ \text{HMF} + \text{H}_2\text{O} \rightarrow \text{FDCA} + \text{H}_2 \]  

(1)

instead of

\[ \text{H}_2\text{O} \rightarrow \text{O}_2 + \text{H}_2 \]  

(2)

For the overall reaction (1), the calculated Gibbs free energy at room temperature \((\Delta_G^{298k})\) and the standard reaction potential \((E^\circ)\) are only 65.62 kJ mol\(^{-1}\) and 0.113 V (vs normal hydrogen electrode, NHE), respectively. They are much smaller than those \((\Delta_G^{298k} = 237219 \text{ kJ mol}^{-1} \text{ and } E^\circ = 1.23 \text{ V vs NHE})\) of the overall reaction (2), respectively. Furthermore, FDCA is an important precursor to produce polymers, pharmaceuticals, and fine chemicals. Consequently, in a two-chamber system the simultaneous production of two value-added chemicals—FDCA on the anode and hydrogen on the cathode can be realized to achieve sustainable energy development. Notably, various metal sulfides, phosphides, borides, oxides, and hydroxides have been frequently utilized for the HMF electrooxidation, although their intrinsic redox potentials, conductivities, and stability affected strongly such an oxidation reaction. Moreover, the identity of...
the active catalytic sites in these catalysts still remains controversial.[9] On the other hand, construction of fine architectures and modulation of electronic structures of electrocatalysts are recognized as the most effective ways to improve catalytic performance of electrocatalysts. In this study, transition metal layered double hydroxides (LDH) are thus selected since they have compositions similar to natural hydroxylite minerals. They are composed of positively-charged mixed metal hydroxide layers, where water and anions are inserted.[9] In other words, they own unique 2D morphology, large specific surface areas, and adjustable composition.[9] The LDHs with bimetallic or trimetallic components are perfect candidates for catalytic applications. For example, the CoFe LDH catalysts exhibited promising ability toward water splitting at lower potentials. The easy Co(OH)2/CoOOH conversion and synergistic effect between Co and Fe were believed as the driving force.[11] Therefore, it is expected to obtain enhanced electrocatalytic performance once multiple reaction centers (e.g., Fe, Co, and Fe metal species) are combined. To construct such catalysts, we combine CoFe LDH with NiFe LDH (Figure S1, Supporting Information). A hierarchical and fine nanostructure is expected to be obtained, which will increase the exposure of active sites, promote the mass transfer, adjust the electronic structure of active species, and eventually enable its superior electrocatalytic performance.

Different from previous reports that individually focused on the performance improvement of the HMF electrooxidation or hydrogen production on different optimized catalysts,[12] we couple in this work the anodic HMF electrooxidation reaction with a cathodic hydrogen production in a two-chamber system. Namely, the sluggish OER during water electrolysis is replaced with the thermodynamically favorable HMF electrooxidation reaction, as shown in Equation (1). Such a novel overall system is thus expected to achieve simultaneous production of value-added chemicals and clean hydrogen. Moreover, the mechanisms of the HMF electrooxidation reactions on the hierarchical CoFe@NiFe composite will be revealed by means of operando techniques (e.g., in situ Raman spectroscopy and in situ infrared spectroscopy). This kind of identification and detection of active species and reaction pathways in such systems unfortunately remains indistinct so far. In more detail, the effect of the applied potential on the reaction pathways of the HMF electrooxidation, the function (e.g., as catalytic species center) and contribution of metal centers (namely Fe+3, Co+3, and Ni+3) during the HMF electrooxidation will be clarified and illustrated.

2. Results and Discussion

2.1. Anodic Half-Reaction: Electrooxidation of HMF into FDCA with 100% Selectivity

Electrocatalytic performance of the used catalysts was first evaluated. From the linear sweep voltammograms (LSVs) recorded in 1 m KOH with and without 10 mM HMF (Figure 1a), one can see that the potentials of 1.311 and 1.338 V are required for the CoFe@NiFe and CoFe LDH catalysts to reach a current density of 10 mA cm⁻² in 1 m KOH + 10 mM HMF, respectively. In 1 m KOH, they are 1.351 and 1.374 V, respectively. Under an identical potential, the current density on the CoFe@NiFe catalyst in 1 m KOH + 10 mM HMF is higher than that in 1 m KOH (Figure 1b).

The Tafel slopes (Figure 1c) of the CoFe@NiFe catalyst with and without HMF are 82.8 and 60.5 mV dec⁻¹, respectively. In contrast, they are 90.2 and 83.3 mV dec⁻¹ for the CoFe LDH catalyst, respectively. Their electrochemical double-layer capacitances (Figure 1d), calculated from their cyclic voltammograms in 10 mM HMF + 1 m KOH within the non-Faradaic potential region (Figure S2, Supporting Information), are 1.36 and 0.88 mF cm⁻², respectively. In 1 m KOH, they are 0.375 and 0.302 mF cm⁻², respectively. The Nyquist plot (Figure S3, Supporting Information) of the CoFe@NiFe catalyst exhibits a smaller diameter of the semicircle, revealing its lower charge transfer resistances than the CoFe LDH catalyst. These results show that the HMF electrooxidation occurs more easily than OER on both catalysts. The CoFe@NiFe catalyst is thus more beneficial to the HMF electrooxidation than the CoFe LDH catalyst. This is because the CoFe LDH catalyst is composed of uniformly distributed, vertically aligned, and smooth nanosheets (Figure 1e), while the surface of the CoFe@NiFe catalyst is rough (Figure 1f) since a NiFe nanosheet with a thickness of 6 nm is coated on the surface of the CoFe nanosheets (Figure S4, Supporting Information). Such hierarchical nanosheets formed on the nanosheets construct an ordered array structure, leading to a much enhanced surface area. More active sites are then expected to be available. Promoted electron transfer and/or rapid penetration of the reactants are more likely to occur on the CoFe@NiFe catalyst.

Chronoamperometric curves of the HMF electrooxidation on the CoFe@NiFe catalyst were then recorded at constant potentials in a separated two-chamber electrochemical cell. From recorded chronoamperometric curves at different applied potentials (Figure S5, Supporting Information) and those (Figure S6, Supporting Information) where the 100%-conversion of HMF is achieved, the full conversion of HMF is sluggish when low potentials (e.g., 1.34 and 1.36 V) are applied. The typical chronoamperometric curves of the CoFe@NiFe catalyst in 1 m KOH without (blue curve) and with (red curve) 10 mM HMF are shown in Figure 2a when a potential of 1.40 V and an electrolysis time of 210 min are applied. The oxidation current density (red curve) is reduced gradually in accompany with the decline of the HMF concentration. However, it is always higher than that (3–5 mA cm⁻², blue line) in the KOH solution. Under the same applied potentials (Figure 2b), the current densities in the KOH + HMF solution (red columns) are much higher than those in the KOH solution (blue columns). Compared with a lower potential range (e.g., from 1.38 to 1.50 V) in the KOH + HMF solution (red columns), higher potentials (e.g., from 1.48 to 1.70 V) are required in the KOH solution (blue columns) when similar initial current densities are reached (Figure 2c).

In this context, a higher potential is required to transport the same number of electrons to the cathode and further to produce hydrogen in the KOH solution. For example, the required time is 288 min at 1.38 V for the complete conversion of HMF (Figure 2d), which is shortened to 63 min at 1.50 V. Meanwhile, the charge consumption is increased from 160 to 360 C. However, to completely convert 30 mL of 10 mM HMF into FDCA, the required charge is only 174 C (Supporting Information). Consequently, an increase of the applied potential results in the occurrence of competitive OER, which is unfortunately not favorable for the HMF conversion into FDCA.

The change of the HMF concentration and as-generated products were determined by use of high-performance liquid
chromatography (HPLC) when the potentials of 1.34 (Figure 3a), 1.40 (Figure 3b), and 1.50 (Figure 3c) V are applied. They are also compared with those obtained at other potentials (Figure S7, Supporting Information). Clearly, there exist huge differences with respect to the charges required to fully oxidize HMF into different products as well as selectivity, yields, and Faradaic efficiencies of these conversion reactions. When a potential of 1.34 V is applied, 5-hydroxymethyl-2-furancarboxylic acid (HMFCA) is the main intermediate in the initial process, leading to the relative low selectivity to produce FDCA. When a charge of 140 C is passed, HMF is fully converted. The main product is FDCA with its yield or selectivity of 61.36% and a Faradaic efficiency of 75.71%. Once a potential of 1.40 V is applied, FDCA is the main product. The yields of other intermediates are maintained below 10%. When a theoretical charge of 174 C is passed, HMF is fully converted to FDCA with the selectivity of nearly 100% after the electrolysis for 210 min. No other intermediates are found. Consequently, the application of a potential of 1.40 V can make HMF selectively and fully convert into FDCA (e.g., with a Faradaic efficiency close to 100%). Note that the conversion of HMF into FDCA is hindered with an increase of the applied potential, due to the competitive OER. Taking the potential of 1.5 V as an example, a charge of 360 C is needed to fully convert HMF into FDCA, much higher than 174 C. Although the yield or selectivity of FDCA is 97.03%, related Faradaic efficiency is only 46.82%. Compared with other catalysts (Table S1, Supporting Information), the CoFe@NiFe LDH catalyst exhibits superior performance of the HMF electrooxidation into FDCA.

2.2. Cathodic Half-Reaction: Efficient Hydrogen Production Coupled with Electrooxidation of HMF into FDCA

The amount of hydrogen produced in the cathode of a two-chamber system was detected with gas chromatography (GC).
At 1.40 V, the amount of produced hydrogen in the HMF\( + \)KOH solution is 468.03 \( \mu \text{mol h}^{-1} \), 18.07 times higher than that (25.9 \( \mu \text{mol h}^{-1} \)) obtained in the KOH solution. Therefore, the replacement of OER with the HMF electrooxidation reaction effectively promotes hydrogen production. The hydrogen production rates in the HMF + KOH solution and related Faradaic efficiencies at different potentials were then compared (Figure S8, Supporting Information). At the potentials of 1.38 and 1.50 V, the hydrogen production rates in the first 1 h are varied from 61.91 to 1782.38 \( \mu \text{mol h}^{-1} \) together with an increased Faradaic efficiency from 46.82% to 99.8%. The change in hydrogen production rates as a function of the transferred charges at 1.34 (Figure 4a), 1.40 (Figure 4b), and 1.50 (Figure 4c) V were then analyzed, where the electrooxidation reactions of HMF into DFF (brown columns) or HMFCA (purple columns), FFCA (red columns), and FDCA (blue columns) as well as the effect of the OER (black columns) on the hydrogen production were taken into account. The amounts of hydrogen produced at these potentials are approximately same as those theoretical ones when the given charges are passed. For example, when a theoretical charge of 174 C is passed at 1.40 V, an amount of 901 \( \mu \text{mol cm}^{-2} \) hydrogen is produced when all involved electrons are transferred immediately to the cathode (supporting information). Note that the contribution of hydrogen production from different HMF electrooxidation reactions is changed significantly as the applied potential is altered. At 1.34 V, hydrogen production is mainly attributed to the generation of FDCA together with an incomplete HMF oxidation into HMFCA. When the potential is up to 1.50 V, the competitive reaction OER occurs significantly and thus hydrogen production from water electrolysis almost occupies in the whole electrooxidation process. In order to avoid the participation of the competitive OER during the HMF electrooxidation, a potential of 1.40 V was selected, where HMF can be fully converted into FDCA with 100% selectivity. Moreover, this oxidation reaction offers six electrons, which can be utilized for efficient hydrogen production.

The performance of this integrated overall reaction was checked (Table S2, Supporting Information). As expected, a potential of 1.40 V is optimal for the HMF electrooxidation into FDCA on the CoFe@NiFe catalyst with respect to the yield, selectivity, and Faradaic efficiency of FDCA production. The energy consumed \( (E_c) \), frequently used to describe the energy consumption for the production of 1 kg hydrogen, was then calculated at a potential range of 1.34–1.50 V. The \( E_c \) values fall in the range of 35.89–40.14 kWh kg\(^{-1}\) in 1 m KOH + 10 mm HMF solution. In contrast, the \( E_c \) values in 1 m KOH solution are changed from 37.52 to 45.45 kWh kg\(^{-1}\). Consequently, the addition of HMF into the KOH solution effectively promotes hydrogen production and reduces the energy consumption on the cathode. The integrated overall reaction proposed in the Equation (1) is successfully realized and is thus promising for hydrogen production at an industrial scale.
Figure 3. Variation of conversion ratios of HMF (full squares), 2,5-diformylfuran (DFF, open stars), HMFCA (open upward-pointing triangles), 5-formyl-2-furan-carboxylic acid (FFCA, open downward-pointing triangles), and FDCA (open dots) with consumed charges in the anodic chamber at the potentials of a) 1.34, b) 1.40, and c) 1.50 V. The applied reaction time in (a–c) is 3167, 210, and 63 min, respectively.

Figure 4. Coupled hydrogen production rates as a function of the consumed charges when the potentials of a) 1.34, b) 1.40, c) 1.50 V are applied. The red circles are the amounts of hydrogen detected by GC. The black solid lines are theoretical amounts of generated hydrogen according to transferred charges during the HMF electrooxidation. The brown, purple, red, and blue columns denote for the amounts of generated hydrogen when the HMF is electrooxidized into DFF or HMFCA, FFCA, and FDCA, respectively. The black one is denoted when the OER is involved. The applied reaction time in (a–c) is 3167, 210, and 63 min, respectively.
2.3. Clarification of Reaction Mechanism of the Integrated Overall Reaction

To clarify the reaction mechanism of this overall reaction, the CoFe@NiFe and CoFe LDH catalysts were characterized by different techniques. In their X-ray diffraction patterns (Figure S9a, Supporting Information), two diffraction patterns at 22.9° and 33.5° confirm the successful electrodeposition of NiFe on the surface of the CoFe LDH catalyst.[14] In their Raman spectra (Figure S9b, Supporting Information), characteristic peaks of metal–oxygen vibrations are located at 451 and 532 cm⁻¹; the bending vibrations of hydroxyl groups are located at 983 and 1055 cm⁻¹.[15] Their FT-IR spectra (Figure S9c, Supporting Information) feature a broad absorption peak at 3346 cm⁻¹, originating from the tensile vibration of water molecules in the interlayer.[16] The peak at 749 cm⁻¹ in the CoFe LDH catalyst and the peak at 609 cm⁻¹ in the CoFe@NiFe catalyst stem from the lattice vibration modes of Fe–O, Co–O, or Ni–O.[16]

The element composition and surface valence of the CoFe LDH and CoFe@NiFe catalysts were determined by X-ray photoelectron spectroscopy (XPS). In the Fe 2p XPS spectrum of the CoFe LDH catalyst (Figure S10a, Supporting Information), the peaks centered at 710.7 and 722.5 eV are attributed to Fe²⁺ 2p₁/₂ and Fe³⁺ 2p₁/₂, respectively. The peaks centered at 715.0 and 725.5 eV result from Fe²⁺ 2p₃/₂ and Fe³⁺ 2p₃/₂, respectively. Differently, in the Fe 2p XPS spectrum of CoFe@NiFe catalyst, related Fe²⁺ peaks appear at 711.2 and 724.8 eV. The Fe³⁺ peak is located at 714.3 and 7276 eV. Compared with those in the Fe 2p XPS spectrum of CoFe LDH catalyst, the shifts of Fe²⁺ and Fe³⁺ in the Fe 2p XPS spectrum of the CoFe@NiFe catalyst indicate the interaction between NiFe and CoFe. In the Co 2p XPS spectrum of the CoFe LDH catalyst (Figure S10b, Supporting Information), the peaks centered at 780.7 and 795.8 eV are attributed to Co 2p₃/₂ and Co 2p₁/₂ of Co²⁺, respectively. The peaks centered at 785.7 and 802.9 eV are satellite peaks. In the Co 2p XPS spectrum of the CoFe@NiFe catalyst, related Co²⁺ peaks appear at 781.2 and 796.7 eV, showing positive shifts when compared with those in the Co 2p XPS spectrum of the CoFe LDH catalyst. These results indicate the variation of electronic structure of the Co species after electrochemical deposition of NiFe on the CoFe LDH catalyst. For comparison, the NiFe LDH catalyst was directly electrodeposited on the Ni foam (NF). In the Ni 2p XPS spectrum of this catalyst (Figure S10c, Supporting Information), the Ni 2p₁/₂ and Ni 2p₃/₂ peaks are centered at 856.4 and 873.9 eV, respectively. In contrast, these two peaks shift negatively to 856.0 and 873.6 eV in the Ni 2p XPS spectrum of the CoFe@NiFe catalyst. These shifts confirm again the existence of electrodeposited NiFe as well as their interaction with the CoFe LDH catalyst. The valence states of O in the CoFe LDH and CoFe@NiFe catalysts were also analyzed (Figure S10d, Supporting Information). In the O 1s XPS spectrum of the CoFe LDH catalyst, the peak centered at 529.5 eV belongs to oxygen in the lattice of M–O–M. The characteristic XPS peak of surface adsorbed oxygen OH⁻ is shown at 531.6 eV, which originates from the bond of M–OH or the defective sites with a low oxygen coordination, namely from the oxidoxydride (MOO₄). In the O 1s XPS spectrum of the CoFe@NiFe catalyst, the peak contents of M–OH are increased obviously, although no significant changes of their peak positions (531.4 eV for M–O–M, 529.6 eV for M–OH) are noticed. Therefore, more oxyhydroxides are formed in the CoFe@NiFe catalyst when compared to the CoFe LDH catalyst.

The local electronic structures and atomic environment of the CoFe@NiFe catalyst were further investigated with X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) spectroscopy.[18] From the XANES spectra at the Co K-edge of CoFe@NiFe, Co foil, CoO, and CoOOH (Figure S11a, Supporting Information), one can tell that the species with a higher oxidation state generally has a higher absorption threshold position. The average Co valence state in the CoFe@NiFe catalyst is +2.21 from the fitted Co K-edge XANES spectra (Figure S11b, Supporting Information). In its Co-edge Fourier-transformed k⁴-weighted EXAFS spectra (Figure S11c, Supporting Information), two dominant peaks appear at about 1.5 and 2.3 Å, which are assigned to Co–O and Co–metal coordination, respectively.[19] Meanwhile, the XANES spectra at the Fe K-edge of the CoFe@NiFe catalyst (Figure S11d, Supporting Information), recorded along with Fe foil, Fe₂O₃, and Fe₃O₄, exhibit that the evaluated average Fe valence state from fitted average oxidation states curves is +2.88 (Figure S11e, Supporting Information). The Fourier-transformed k⁴-weighted EXAFS spectra of Fe species in the CoFe@NiFe catalyst (Figure S11f, Supporting Information) show that the radial positions of the Fe–O and Fe–metal scattering peaks match well with those of standard Fe₂O₃. Consequently, the atomic environment of Fe is closer to an oxidation state of +3 in these catalysts.[20]

To examine the changes of these valence states and active species, the XPS spectra of the CoFe@NiFe catalyst were recorded after the HMF electrooxidation at 1.40 V. In the Fe 2p XPS spectrum of a used CoFe@NiFe catalyst (Figure 5a), the peaks appeared at 711.6 and 725.3 eV are assigned to 2p₃/₂ and 2p₁/₂ of Fe²⁺, respectively. The peaks appeared at 714.6 and 7276 eV belong to 2p₁/₂ and 2p₃/₂ of Fe³⁺, respectively. The positive shift of about 0.4 eV and an increased content of trivalent Fe when compared with a fresh CoFe@NiFe catalyst confirm that the Fe²⁺ species is partially oxidized to the Fe³⁺ species during the HMF electrooxidation. In the Co 2p XPS spectrum of a used CoFe@NiFe catalyst (Figure 5b), the peaks at 781.7 and 797.2 eV result from 2p₁/₂ and 2p₃/₂ of Co²⁺, respectively. A positive shift of 0.5 eV is found in comparison with a fresh CoFe@NiFe catalyst. In the Ni 2p XPS spectrum of a used CoFe@NiFe catalyst (Figure 5c), the peaks at 856.5 and 874.1 eV can be attributed to Ni 2p₁/₂ and Ni 2p₃/₂, respectively. A positive shift of about 0.5 eV is seen when compared with the corresponding Ni 2p peaks of a fresh CoFe@NiFe catalyst, namely before its application for the HMF electrooxidation reaction. In O 1s XPS spectrum of a used CoFe@NiFe catalyst (Figure 5d), the M–O–M peak at 529.2 eV stems from lattice oxygen. The M–OH or defect sites with a low oxygen coordination peak correspond to oxyhydroxides, which appears at 531.1 eV. Compared with the O 1s XPS spectrum of a fresh CoFe@NiFe catalyst, the peak content of 531.3 eV increases somehow, indicating more oxyhydroxides are formed during the HMF electrooxidation. In conclusion, the valence states of Fe, Co, and Ni are increased to some degrees and more oxyhydroxides are formed after the HMF electrooxidation. The high-valence Fe, Co, and Ni species are the active species during the HMF electrooxidation.[21]
The change of the open-circuit potential of a CoFe@NiFe catalyst coated electrode was studied since it reflects the variation of electrochemical properties at the electrode-solution interface.\cite{22} An open-circuit potential test (OCPT) was then conducted immediately after a chronoamperometric test was carried out on a CoFe@NiFe catalyst coated electrode at 1.40 V. Due to a time delay, the initial OCP ($E_{ocpt}$) is 1.35 V (Figure 6a). It can be assigned to electrochemically generated M$_{3}^{+}$ (M = Fe, Co, and Ni) species, while an $E_{ocpt}$ of 0.7 V results from M$_{2}^{+}$ (M = Fe, Co, and Ni) species. In the KOH solution, the lifetime of M$_{3}^{+}$ to M$_{2}^{+}$ is found to be 1800 s, which is shortened to 700 s after the addition of 10 mM HMF. In other words, M$_{3}^{+}$ species are the active catalytic species during the HMF oxidation into FDCA, as confirmed from XPS measurements.

The catalytic species of the HMF electrooxidation into FDCA in 1 M KOH on the CoFe@NiFe catalyst were then revealed under different potentials by means of in situ Raman spectroscopy (Figure 6b). The peaks of Ni species dominate the recorded Raman spectra. This is because NiFe is densely electrodeposited on the outer layer of the CoFe@NiFe catalyst. When a potential of 1.30 V is applied, characteristic Raman peaks of bivalent M$_{2}^{+}$ are seen at 457 and 530 cm$^{-1}$. When the applied potential is increased to 1.35 V, new characteristic peaks are noticed at 553 and 472 cm$^{-1}$, resulting from the generation of trivalent Ni$_{3}^{+}$. At 1.40 V, the characteristic peak at 457 cm$^{-1}$ shifts to 472 cm$^{-1}$. The intensity of the peak at 533 cm$^{-1}$ becomes higher than that at 530 cm$^{-1}$, indicating that Ni$_{3}^{+}$ is the dominant species at 1.40 V. Differently, the characteristic peak at 553 cm$^{-1}$ does not appear in the in situ Raman spectra of the CoFe@NiFe catalyst in 1 M KOH + 10 mM HMF (Figure 6c) until a potential of 1.40 V is applied. Namely, the M$_{3}^{+}$ species is only dominant when the applied potential is higher than 1.40 V, although a small amount of the Ni$_{3}^{+}$ species is still available. Subsequently, in situ Raman spectra were recorded at 1.40 V in 1 M KOH with an electrolysis time of 20 min, where the variation of the peaks at 553 and 472 cm$^{-1}$ was investigated as a function of the concentration of the added HMF (Figure 6d). After HMF is added, two characteristic Raman peaks of Ni$_{3}^{+}$ species gradually disappear, and only those of M$_{2}^{+}$ species remain.

To illustrate the catalytic function of Fe$_{3}^{3+}$, Co$_{3}^{3+}$, and Ni$_{3}^{3+}$ species inside the CoFe@NiFe catalyst during the HMF electrooxidation, the catalysts of CoFe LDH, NiFe LDH, and FeOOH have been synthesized. As control experiments, their performance toward the HMF electrooxidation was further studied by use of linear sweep voltammetry, chronoamperometry, and in situ Raman spectroscopy. From their LSVs (Figure S12a, Supporting Information), one can see that the CoFe@NiFe catalyst exhibits the lowest onset potential (1.28 V) among these catalysts. The NiFe LDH catalyst possesses a comparable current density with the CoFe@NiFe catalyst at 1.50 V. It exhibits higher current densities when the potential is higher than 1.50 V (Figure S12b, Supporting Information). The CoFe LDH catalyst shows similar onset potential as the CoFe@NiFe catalyst. Unfortunately, its current density remains always lower than that on the CoFe@NiFe catalyst during the HMF electrooxidation process. On the FeOOH catalyst, the oxidation current is inconspicuously increased after the addition of HMF and the application of a potential of 1.50 V. Therefore, the FeOOH catalyst has limited...
catalytic activity toward the HMF electrooxidation. Moreover, chronoamperometric curves of the HMF electrooxidation on these catalysts were recorded at 1.40 V (Figure S12c, Supporting Information). The current densities follow the order of CoFe@NiFe > NiFe LDH > CoFe LDH > FeOOH. In addition, in situ Raman spectra of these catalysts were recorded in 1 m KOH with the application of a potential of 1.40 V for 60 min (Figure S12d, Supporting Information). The CoFe@NiFe catalyst possesses the highest trivalent Ni$^{3+}$ peak densities at 472 and 553 cm$^{-1}$. The NiFe LDH catalyst shows a slightly lower Ni$^{3+}$ peak density than the CoFe@NiFe catalyst. In this context, the Ni$^{3+}$ species inside the CoFe@NiFe catalyst plays a dominant role for the HMF electrooxidation. A small peak located at 508 cm$^{-1}$ appears in the Raman spectrum of the CoFe LDH catalyst. It can be assigned to CoOOH,[23] an indication of the involvement of the Co$^{3+}$ species during the HMF electrooxidation. An inconspicuous peak at 690 cm$^{-1}$ appears in the Raman spectrum of the FeOOH catalyst, belonging to the features of FeOOH.[24] Consequently, inside the CoFe@NiFe catalyst the Ni$^{3+}$ species has higher catalytic activity than the Co$^{3+}$ species, although the Co$^{3+}$ species effectively lowers the onset of the HMF electrooxidation reaction. The Fe$^{3+}$ species displays very limited catalytic activity toward the HMF electrooxidation. The HMF electrooxidation process on the CoFe@NiFe catalyst is assumed as follows. The
$\text{M}^{2+}$ species is first electrooxidized to the $\text{M}^{3+}$ species in the presence of water, followed by the HMF electrooxidation with aid of the $\text{M}^{3+}$ species, leading to the generation of FDCA and the regeneration of the $\text{M}^{2+}$ species.\cite{afmjournal}

It is known that several electrons and steps involved during the HMF oxidation into FDCA (Figure S13, Supporting Information).\cite{afmjournal} Based on the results obtained from HPLC measurements under different potentials, one can conclude that the formation of FDCA follows two pathways during the HMF electrooxidation reaction on the CoFe@NiFe catalyst, namely the HMFCA-pathway and the DFF-pathway. Such pathways are strongly affected and eventually determined by the applied potentials. For example, with the application of a potential of 1.34 V, the main intermediate is HMFCA in the initial process and its yield reaches as high as 30%. Meanwhile, the yield of DFF is low enough to be negligible. In this regard, the HMFCA-pathway is the dominant way at low potentials during the HMF electrooxidation on the CoFe@NiFe catalyst. When the applied potential is increased, the yield of DFF begins to increase, while the yield of HMFCA is reduced. For example, the application of a potential of 1.40 V results in the generation of both HMFCA and DFF. However, their yields are below 10% and no significant difference is found for them. When the potential is higher than 1.50 V, the yield of DFF reaches up to 13%, while the yield of HMFCA is always low in the whole electrolysis process. In this context, the DFF-pathway is the main route at high potentials during the HMF electrooxidation on the CoFe@NiFe catalyst.

To testify these steps, the in situ infrared spectra of HMF electrooxidation on the CoFe@NiFe catalyst were recorded at different potentials and with an electrolysis time of 5 min (Figure 6e) as well as with different electrolysis time but at a fixed applied potential of 1.40 V (Figure 6f). Besides selected vibration in the in situ infrared spectra (Table S3, Supporting Information), three characteristic peaks appear at 1384, 1407, and 1508 cm$^{-1}$ when a low potential (e.g., from 1.10 to 1.30 V) is applied. They are assigned to the oxidation products of HMFCA, FFCA, and DFF, respectively. The peak at 1384 cm$^{-1}$ is attributed to HMFCA. Its intensity is gradually reduced when the applied potential is increased, which is consistent with the results from the HPLC measurements. At 1.40 V, the characteristic peaks of FDCA appear at 1214 and 1353 cm$^{-1}$. Meanwhile, the characteristic peaks of FFCA are noticed at 1276, 1562, and 1592 cm$^{-1}$. In this regard, the formation of FDCA on the CoFe@NiFe catalyst during the HMF electrooxidation follows as expected two pathways (Figure S13, Supporting Information). When a longer electrolysis time is applied at 1.40 V, the downward peaks are presented at 1027, 1191, and 1295 cm$^{-1}$, an indication of the HMF consumption. In contrast, the upward peaks at 1272 and 1407 cm$^{-1}$ suggest the formation of FFCA. The upward peaks at 1214, 1353, and 1384 cm$^{-1}$ as well as the gray region from 1620–1720 cm$^{-1}$ hint the formation of FDCA. It has to point out that the spectra recorded at higher potentials and with longer electrolysis times contain both FFCA and FDCA.\cite{afmjournal} This is due to the low diffusion-controlled mass transfer, which makes it difficult to let HMF completely convert to FDCA.

To get deeper insight into the proposed overall reaction, the effect of water on the HMF electrooxidation on the CoFe@NiFe catalyst was assessed (Figure S14, Supporting Information).\cite{afmjournal} A series of LSVs were recorded in the solutions of: i) acetonitrile + 0.1 M tetrabutylamyl hexafluoroantimonate, ii) i) + 10 mM HMF, iii): i) + water, iv): i) + 10 mM HMF + water. The LSVs in the solutions (i,ii) are almost the same in a Faradaic-silent region before 2.0 V. In the solution (iii), water oxidation current appears at around 1.40 V. In the solution (iv), obvious oxidation current is seen at 1.20 V. These experiments confirm the involvement of water in the HMF electrooxidation reaction. Water serves as the oxygen source during the HMF electrooxidation.

3. Conclusion

On a hierarchical CoFe@NiFe catalyst, one biomass derivative HMF is electrochemically oxidized into value-added chemicals under atmospheric pressure and at room temperature. At 1.40 V, the HMF can be fully converted into FDCA with 100% selectivity and a Faradaic efficiency of 99.8%. The active species and two pathways for the HMF electrooxidation into FDCA on the CoFe@NiFe catalyst have been revealed by operando techniques. Since the reaction involves six electrons, it is utilized as the anodic half-reaction to replace the OER and further coupled to boost hydrogen production. In summary, the integrated overall reaction is useful for the electrooxidation of biomass or biomass derivatives to value-added chemicals with high selectivity and meanwhile for hydrogen production with high Faradaic efficiencies. It is thus a new strategy to produce clean energy materials from sustainable sources and with cost-effective catalysts, and eventually to solve current challenges of energy depletion and environmental pollution for sustainable energy development.

4. Experimental Section

**Synthesis of the Catalysts of CoFe@NiFe and CoFe LDH, NiFe LDH, and FeO(OH):** The reported methods were adopted after some modifications.\cite{afmjournal}

A NF was first treated and cleaned in dilute hydrochloric acid, acetone, and deionized water with aid of a sonication bath. Meanwhile, a 30 mL aqueous solution was prepared, consisting of 0.5 mmol or 201.99 mg Fe(NO$_3$)$_3$·9H$_2$O, 1.5 mmol or 436.55 mg Co(NO$_3$)$_2$·6H$_2$O, 10 mmol or 600.6 mg urea, and 4 mmol or 148.16 mg NH$_4$F. The mixed solution was then transferred into a 50 mL Teflon-lined stainless steel autoclave, where the treated NF was placed and heated to 120 °C for 6 h. The autoclave was then cooled down to room temperature. Subsequently, the treated NF was washed using ethanol and deionized water copiously. It was then dried at 60 °C for 10 h. In this way, the CoFe LDH catalyst was produced. The coating of the CoFe LDH with electrodeposited NiFe nanosheets led to the generation of the CoFe@NiFe catalyst. Such an electrodeposition process was performed in the electrolyte of 0.15 M Ni(NO$_3$)$_2$·6H$_2$O and 0.15 M FeSO$_4$·7H$_2$O. A three-electrode system was employed, the as-prepared CoFe LDH catalyst coated electrode was used as the working electrode. The counter and reference electrodes were a Pt wire and an Ag/AgCl electrode, respectively. The applied deposition potential and time were −1.0 V (vs Ag/AgCl) and 200 s, respectively. The NiFe LDH catalyst was electrochemically deposited on the NF in the solution of 0.15 M Ni(NO$_3$)$_2$ and 0.15 M FeSO$_4$ for 200 s. The procedure to prepare the FeO(OH) catalyst was similar as that of the NiFe LDH catalyst, except that the electrolyte was 0.15 M FeSO$_4$ and the used working electrode was carbon paper.

**Electrochemical Measurements:** The electrochemical measurements were carried out on a Chenhua CH1660 electrochemical workstation at...
room temperature in a three-electrode system, where the as-prepared catalyst (1 cm × 1 cm) was used as working electrode. The counter and reference electrodes were a Pt wire and an Ag/AgCl electrode, respectively. The electrode potential measured by an Ag/AgCl reference electrode was recalculated with a reversible hydrogen electrode (RHE) according to the Nernst equation:

\[ E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.059 \log \frac{p_{\text{H}_2}}{0.197} \]  

(Product Determination: For product analysis, the electrolysis was conducted at different potentials in a two-chamber reaction that was equipped with a three-electrode system. The working, reference, and counter electrodes were the as-prepared catalyst (1 cm × 1 cm), an Ag/AgCl electrode, and a Pt sheet (2 cm × 2 cm), respectively. In a two-chamber reactor, the HMF electrooxidation occurred on the as-prepared catalyst in the anodic chamber, while hydrogen production happened on a Pt sheet in the cathodic chamber. Note that two chambers were separated with a proton exchange membrane. The used electrolyte was 1 M KOH solution containing 35 mL 10 mM HMF. To analyze HMF and its oxidation products as well as to calculate the corresponding Faradaic efficiencies, the substances presented in the solution during the chronoamperometric tests were detected by use of UPLC (extended C18 column, 4.6 mm × 1150 mm; UV detector wavelength: 261/265 nm). The mobile phase was 90% ammonium formate together with 10% methanol. The flow rate was 1 mL min⁻¹. Prior to applying a constant potential, 10 µL analyte was mixed with 490 L was then injected into the HPLC. The substances were analyzed qualitatively and quantitatively when different potentials were applied during the chronoamperometric tests. The amount of hydrogen produced during the electrolysis.

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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**Conflict of Interest**

The authors declare no conflict of interest.

**Data Availability Statement**

Research data are not shared.

**Keywords**

biomass derivatives, efficient hydrogen production, half-reactions, operando techniques, overall reaction, selective electrooxidation

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