

Influence of electrolyte and pH value on the photoelectrochemical oxidation of 5-hydroxymethylfurfural using mesoporous tungsten oxide photoanodes

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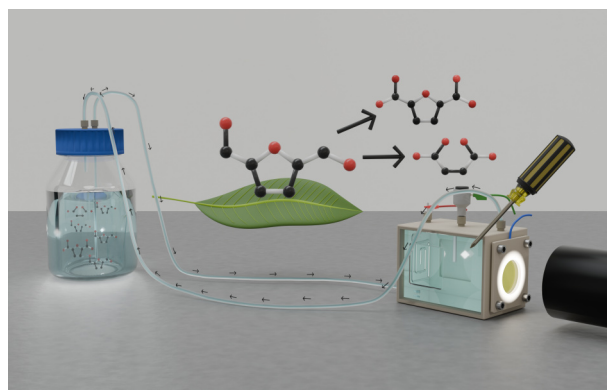


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ABSTRACT: Photoelectrochemical (PEC) water splitting is a promising strategy for providing clean, sustainable fuel. However, its efficiency is limited by the high overpotential and sluggish kinetics of the oxygen evolution reaction. To improve oxidation kinetics and produce a higher-value product, it is possible to oxidize organic molecules instead. One such molecule is 5-hydroxymethylfurfural (HMF), which can be converted into the high-value platform chemical 2,5-furandicarboxylic acid (FDCA). In this study, we used porous tungsten oxide (WO₃) photoanodes to oxidize HMF photoelectrochemically. Our work focuses on electrolyte selection for this conversion reaction, and we therefore conducted a detailed reproducible study. Furthermore, we carried out a mechanistic investigation and studied the capability of oxidizing the reaction intermediates to support our electrolyte choice. Using the most suitable electrolytes in a self-designed flow-cell setup enabled us to produce FDCA (0.02 mM) for the first time using WO₃ photoanodes under AM 1.5 G illumination. Due to the identification of the side products maleic acid and formic acid, this work also provides knowledge for further optimization of PEC HMF oxidation.



KEYWORDS: 5-hydroxymethylfurfural, WO₃, photoelectrochemical, organic oxidation

1 Introduction

The modern world faces two major problems: the climate crisis and the rising global energy demand. Addressing both simultaneously requires utilizing renewable energy sources. Because these sources are available only periodically, storing renewable energy in the form of chemical energy is essential. Solar energy is the most abundant energy source on Earth, so utilizing it plays a key role in achieving climate-neutral energy production¹. One possible approach to store its energy is the conversion into hydrogen using photoelectrochemical (PEC) water splitting^{2, 3}. Since it was first introduced by Fujishima and Honda in 1972, it is a frequently investigated mild, simple and effective method to utilize solar energy^{4, 5}, although its efficiency is limited by the slow kinetics and the high overpotential of the oxygen evolution reaction (OER). In

addition, the economic value of oxygen is rather low. Here, oxidation reactions for value-added products are an interesting alternative, which exhibit usually accelerated kinetics compared to OER^{6–8}.

One such example is the oxidation of 5-hydroxymethylfurfural (HMF). This bio-derived platform chemical can be obtained from lignocellulosic biomass, like woods, grasses, and agricultural residues^{9, 10}. By oxidizing HMF, 2,5-furandicarboxylic acid (FDCA) can be obtained, which serves as a monomer for the production of bio-based polyesters, polyamides and polyurethanes^{11, 12}. One specific example with a good gas barrier performance, recyclability and favorable mechanical properties is polyethylene furanoate (PEF). Therefore, it is considered as a candidate to replace fossil-based polyethylene terephthalate (PET)^{13–15}.

Oxidation of HMF to FDCA can proceed via two different pathways (Scheme 1). Path I, which is preferentially followed in non-strong alkaline media (pH < 13), starts with an alcohol oxidation towards the intermediate 2,5-diformylfuran (DFF). Path II in contrast begins with a conversion of the formyl group to form 5-hydroxymethyl-2-furancarboxylic acid (HMFCa). This pathway is preferred in strong alkaline media (pH ≥ 13). In both cases, the first intermediate is converted into 5-formyl-2-furancarboxylic acid (FFCA), which can be further oxidized to FDCA^{10, 16–19}.

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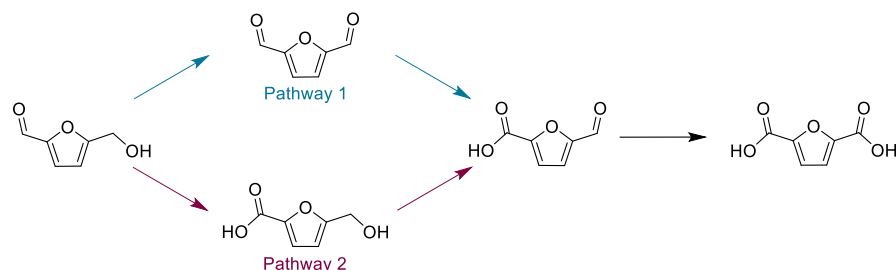
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Scheme 1. Schematic illustration of the two possible pathways for the oxidation of HMF towards FDCA.

Photoelectrochemical oxidation of HMF was first reported by *Cha et al.* using a BiVO_4 photoelectrode. An indirect oxidation path, using 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) as a redox mediator, was chosen in that work²⁰. When applying this mechanism, the potential which was applied to the PEC cell was used to oxidize the redox mediator. The mediator, which is present in the oxidized state, then oxidizes the functional groups of HMF^{10, 21–23}.

In contrast, in direct oxidation conditions, the applied potential drives the substrate oxidation. It directly facilitates the substrate oxidation by promoting the adsorption of OH^- onto the electrode, which enables the formation of highly reactive oxygen species involved in the oxidation. Furthermore, the rapid removal of electrons deposited into the surface of the electrode is facilitated by the applied potential^{23–25}. A semiconductor which is able to convert HMF into FDCA over a direct pathway is WO_3 . This was shown by *Lhermitte et al.* applying a 0.1 M NaPi electrolyte with a pH value of 4 under 3 suns illumination²⁶.

Due to its suitable band gap for visible light absorption (2.5–2.8 eV), WO_3 is a widely used semiconductor in PEC^{27–29}. Other advantages are its good hole diffusion length (~ 150 nm) and high charge carrier mobility ($12 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$) in comparison to other commonly applied semiconductors like $\alpha\text{-Fe}_2\text{O}_3$, BiVO_4 , SnO and ZnO^{30–36}. While exhibiting a sufficient charge carrier lifetime (1–9 ns), it is also highly stable in acidic electrolytes (pH ≤ 4). Furthermore, it is resistant against photocorrosion and is non-toxic. However, its solar to hydrogen efficiency is limited to a value of 5.8% by its band gap^{33, 37, 38}. Due to the lower Gibbs free energy requirements, substituting water oxidation with the conversion of HMF into FDCA, can enhance the conversion efficiency of solar energy into chemical energy in PEC cells with a WO_3 photoanode^{1, 6}.

Nevertheless, to date, only incomplete conversion of HMF was observed applying direct PEC oxidation with WO_3 photoanodes using AM 1.5 G illumination³⁹. This low FDCA yield is attributed to the low selectivity in comparison to competing reactions⁴⁰. A well-known possibility to enhance the performance of photoelectrochemical cells is to optimize the composition of the electrolyte. Studies have shown that the selection of the right anion as well as the cation can boost the efficiency^{41–45}. This also applies for the oxidation of organic compounds. *Kong et al.* demonstrated that the electrolyte significantly influences the selectivity and conversion rate in the PEC oxidation of glycerol using BiVO_4 photoanodes⁴⁶. Therefore, finding the most suitable electrolyte for HMF oxidation could be a promising strategy to enhance its selectivity and performance towards FDCA formation.

Since no studies have investigated how electrolyte selection influences PEC oxidation of HMF using mesoporous WO_3 photoanodes, we systematically compared different electrolytes to identify the most suitable one for this reaction. Sodium perchlorate (NaClO_4), sodium nitrate (NaNO_3), and sodium and potassium

sulfate (Na_2SO_4 and K_2SO_4) were examined for their ability to oxidize HMF in comparison to buffer systems such as sodium and potassium phosphate (NaPi and KPi) and sodium acetate. Additionally, their corresponding acids were applied as electrolytes. Moreover, by comparing their photocurrents and performing advanced photoelectrochemical characterization, deeper insights into the reaction mechanism were gained. Additionally, we quantitatively identified multiple side products of HMF oxidation by applying nuclear magnetic resonance (NMR) spectroscopy. One of these products is the valuable platform chemical maleic acid (MA), of which 0.72 mM was produced in a 72-hour chronoamperometric measurement under AM 1.5 G illumination. For this measurement, a 0.1 M K_2SO_4 electrolyte with the addition of TEMPO was used. Using the K_2SO_4 electrolyte without a redox mediator yielded 0.02 mM of FDCA at pH 3 and 6 throughout the reaction.

2 Methods

2.1 Materials

Acetone (Fisher Scientific, $\geq 99.8\%$), ethanol (VWR, $\geq 99.93\%$), 2,5-diformylfuran (abcr, 98%), di-potassium hydrogen phosphate (Gruessing, 99%), furan-2,5-dicarboxylic acid (abcr, 98%), 5-hydroxymethyl-2-furaldehyde (Sigma-Aldrich, 99%), 5-formyl-2-furancarboxylic acid (abcr, 95%), 5-(hydroxymethyl)-2-furoic acid (abcr, 97%), orthophosphoric acid (Fisher Scientific, 85.5%), perchloric acid (Sigma-Aldrich 70%), Pluronic P123 (Aldrich, $31,000 \text{ g} \cdot \text{mol}^{-1}$), potassium dihydrogen phosphate (Gruessing, 99%), potassium sulfate (Gruessing, 99%), 2-propanol (VWR, $\geq 99.5\%$), sodium nitrate (Gruessing, 99.5%), sodium perchlorate (Sigma-Aldrich, $\geq 99.9\%$), sodium sulfate (Carl Roth, $\geq 99\%$), sulfuric acid (Fisher Scientific, $\geq 95\%$) tetrahydrofuran (THF) (Fisher Scientific, $\geq 99.8\%$) and WCl_6 (abcr, 99.9%) were used without further purification. Fluorine doped tin oxide (FTO) substrates (Pilkington TEC 8 glass with a resistance of $8 \Omega \text{ mm}^{-2}$) were purchased from XOP-Glass. The substrates were cleaned using an ultrasonic bath in ethanol, acetone and isopropanol, followed by ultrapure water for 30 min each. After this treatment, the FTOs were dried using nitrogen.

2.2 Synthesis of mesoporous WO_3 photoanodes

The synthesis was performed according to our previous research^{47, 48}. To obtain the precursor solution 0.225 g Pluronic P123 was dissolved in a mixture of 10 mL EtOH and 3.36 mL THF. While stirring the solution, 2.25 g of WCl_6 was added at once. The sol-gel solution was stirred for 1 h and underwent a color change from orange-brown to turquoise-blue in the meantime. During this period, the screw-cap bottle in which the reaction was carried out was kept closed.

Once the gelation process is finished, the solution was applied onto FTO substrates, using a dip-coating technique. A dipping speed of $162 \text{ mm} \cdot \text{min}^{-1}$ and a dwell time of 3 s were chosen. After each coating step, the photoanode was dried on a heating plate at 150°C (2 min) followed by an annealing step at 300°C (2 min). This cycle was performed 5 and 15 times, respectively. During the coating step, the backside was covered with Kapton tape which was removed prior to the drying step. After finishing the dip-coating, the photoanodes were calcined at 550°C for 30 min in air. The heating rate was set to $10^\circ\text{C} \cdot \text{min}^{-1}$.

2.3 Electrolyte preparation

The electrolytes were all prepared in a concentration of 0.1 M and their pH was adjusted to the desired value with the respective 0.1 M acid. All applied electrolytes and the respective pH value are displayed in Table S1. For measuring the pH value, a pH 3110 SET (purchased from WTW) was applied.

2.4 Electrochemical (EC) and PEC measurements

Unless otherwise stated, electrodes employed for EC and PEC measurements were synthesized by applying 5 dip-coating cycles.

Cyclic voltammetry (CV) and linear sweep voltammetry (LSV) measurements were acquired with a Parstat 3000A-DX potentiostat. VersaStudio was the software used to acquire data.

The CV measurements were conducted in a range from $-0.4 V_{\text{RHE}}$ to $2.2 V_{\text{RHE}}$ with a scan speed of $50 \text{ mV} \cdot \text{s}^{-1}$. The starting value was set to $0 V_{\text{RHE}}$ and 2 cycles were performed in each measurement.

For LSV measurements, a Quantum Design LOT sun simulator, equipped with a 300 W Xe lamp and an AM 1.5 G filter, was utilized as a light source. The power of the incident radiation reaching the cell was set to $100 \text{ mW} \cdot \text{cm}^{-2}$. A range from $1.6 V_{\text{RHE}}$ to $0.3 V_{\text{RHE}}$ and a scan speed of $10 \text{ mV} \cdot \text{s}^{-1}$ were chosen for the LSV measurements. During all experiments, the photoanodes were illuminated from the back side. For the electrolyte study, 4 samples of each electrolyte and pH value were measured to ensure the reproducibility of those results. For the mean onset potential and photocurrent response, the average value of all 4 measurements was calculated.

EC and PEC measurements for the determination of the oxidation capabilities of WO_3 photoanodes regarding HMF were conducted in a self-constructed electrochemical cell with a volume of 90 mL and an irradiation window of 1 cm^2 . In this cell a Pt-wire was applied as the counter electrode and a Mini HydroxFlex electrode (Gaskatel) served as the reference electrode.

For the electrolyte and the oxidation intermediate study, a PEC cell from Zahner was applied. It has an irradiation window of 1 cm^2 and uses a three-electrode setup with a Pt-wire as the counter electrode. As the reference electrode, a Mini-HydroFlex electrode from Gaskatel was employed, while the WO_3 photoanodes served as working electrode.

To acquire incident photon-to-current efficiency (IPCE) measurements and electrochemical impedance spectra (EIS), a Zahner PP211 workstation was employed. To record the data ThalesXTS 5.6.0 software was used. The measurements were performed in the same Zahner cell, equipped with a Pt-wire as a counter and an Ag/AgCl as reference electrode.

For the IPCE measurements, the samples were illuminated from the backside with a distance of 1 mm using a Zahner TLS 03 light source. All those measurements were acquired in a wavelength

range from 300 to 800 nm. The illumination time was set to 10 s, the frequency to 100 mHz and the counts to 5.

EIS was conducted by applying a frequency between 50 mHz and 800 kHz. Furthermore, an amplitude of 20 mV was used, and the samples were illuminated by simulated sunlight from the backside during the measurements.

The charge carrier injection efficiency P_{inj} and the charge carrier separation efficiency P_{sep} were calculated according to Dotan *et al.*⁴⁹. Therefore, LSV measurements were performed directly after adding 0.1 M H_2O_2 as a hole scavenger into the respective electrolyte. For the calculation of the separation and injection efficiency of the charge carriers, Eqs. (1) and (2) were applied.

$$J_{\text{H}_2\text{O}} = J_{\text{abs}} \times P_{\text{sep}} \times P_{\text{inj}} \quad (1)$$

$$J_{\text{H}_2\text{O}_2} = J_{\text{abs}} \times P_{\text{sep}} \quad (2)$$

The value of J_{abs} (theoretical maximum photocurrent density) was chosen as $4 \text{ mA} \cdot \text{cm}^{-2}$ according to Wang *et al.*⁵⁰. Additionally, J_{abs} was calculated using the band gap of the applied semiconductors. Their band gap of 2.71 eV leads to a maximum photocurrent density of $3.87 \text{ mA} \cdot \text{cm}^{-2}$. Other values contributing to these equations are $J_{\text{H}_2\text{O}}$ (photocurrent density in water) and $J_{\text{H}_2\text{O}_2}$ (photocurrent density with the sacrificial agent).

For long-term measurements, electrodes fabricated by applying 15 cycles and a custom-made flow-cell setup were used. This flow-cell has a cell volume of 80 mL and an irradiation window of 1 cm^2 . It is equipped with a Pt-wire as the counter electrode and a Mini HydroxFlex as the reference electrode. To pump the electrolyte through the cell, a Cole-Palmer Ismatec Reglo ICC peristaltic pump with 2 channels was utilized. During those measurements, a constant potential of $0.95 V_{\text{RHE}}$ was applied and AM 1.5 illumination was utilized. As a starting volume 120 mL was chosen. For the analysis of the products, a sample was taken every 8 h from the storage vessel.

2.5 Quantification of organic products

For the analysis of the oxidation products, quantitative ^1H -NMR measurements were performed. Those measurements were acquired using a Bruker Advance III HD with a frequency of 500 MHz and a field strength of 11.7 T. It was equipped with a 5 mm CryoProbeTM Prodigy BBO 500 S2 and a SampleXpress (60 samples) autosampler. For data analysis, the software Topspin 3.2 pl 7 was applied. The quantitative ^1H NMR spectra were acquired using water suppression mode with potassium hydrogen phthalate as an internal standard. A number of 64 scans with a delay of 5 s were performed. For the calibration of the spectra, the signal of the solvent ($\text{DMSO}-d_6$) was utilized. For the product identification and quantification, spectra and calibration curves of the pure reference substances were acquired.

Reversed phase ultra-performance liquid chromatography-mass spectrometry (RP-UPLC-MS) was performed on an ACQUITY™ UPLC®-system that was coupled with a Single Quadrupole mass spectrometer equipped with an ESI-ion source working in positive mode and a diodearray-detector (200–300 nm). The NUCLEODUR C18 HTEC column was purchased from Macherey-Nagel and had a particle size of $5 \mu\text{m}$, a pore size of $100 \text{ \AA}$, a diameter of 2.0 mm, and a length of 250 mm. The Acquity UPLC® BEH C18 column was purchased from WATERS and had a particle size of $1.7 \mu\text{m}$, a pore size of $130 \text{ \AA}$, a diameter of 2.1 mm, and a length of 50 mm.

For the analysis, 200 μL of the sample was dissolved in 1 mL of MeOH. They were injected using the Partial Loop with Needle Overfill-mode using an auto sampler. The analysis was performed in acetonitrile + 0.1% formic acid and water. To separate the sample components, the following gradient was applied: $\text{H}_2\text{O}:\text{MeCN}+0.1\%$ FA = 90:10 {Start}, 90:10 $\rightarrow$ 70:30 {6 min}, 70:30 {2 min}, 70:30 $\rightarrow$ 10:90 {2 min}, 10:90 $\rightarrow$ 90:10 {1 min} at 0.5 mL/min.

For the calculation of the Faradaic efficiency (FE) of the products, Eq. (3) was applied.

$$FE = \frac{N \times n \times F}{Q_{\text{total}}} \quad (3)$$

Here N represents the number of moles of product formed throughout the reaction and n is the number of e^- , which are required for 1 mol of product formation. The Faradaic constant is represented by F and the total charge passed during the reaction by Q_{total} ⁵¹. While it is assumed that $2 e^-$ are required for the formation of DFF and HMFCFA, $4 e^-$ are needed to generate FFCA. According to the literature, the evolution of FDCA requires $6 e^-$ ⁵². To calculate the FE for the formation of formic acid, a process which requires $2 e^-$ is assumed⁵³. Regarding the oxidation of HMF towards maleic acid, the literature only provides the oxidation of furfural, which requires $8 e^-$. Since HMF possesses an additional hydroxymethyl group compared to furfural, it is assumed that the cleavage of it requires 2 additional electrons⁵⁴.

2.6 Photoanode characterization

To determine the layer thickness of the photoanodes, a stylus profilometer was used. For this purpose, a DekTak Pro from Bruker was applied. The device was equipped with a $12.5 \mu\text{m}$ stylus and Vision 64 was the software utilized for data acquisition. For the measurements, a stylus force of 3 mg, a length of $2000 \mu\text{m}$, and a duration of 25 s was selected.

For the analysis of the crystal structure and phase of the WO_3 , X-ray diffraction (XRD) was performed. A Rigaku SmartLab diffractometer with a HyPix-3000 high energy resolution 2D HPAD detector was applied at 20°C and atmospheric conditions. The diffractograms were acquired in a range from 10° to 70° (2θ) with a step width of 0.04° and a scan speed of $10^\circ\cdot\text{min}^{-1}$. A voltage of 45 kV and a current of 20 mA were applied at the rotating anode, which emitted copper K α radiation with a wavelength of $\lambda = 1.54178 \text{ \AA}$. For the measurements, grazing incidence XRD (GI-XRD) was applied.

Raman spectra were acquired using a Horiba Jobin Yvon Raman spectrometer, equipped with an Olympus BX41 microscope. To deliver the incident radiation, a He-Ne-laser with a wavelength of $\lambda = 633 \text{ nm}$ and a power of 11.5 mW was applied. The spectral measurements range was set between 50 and 2000 cm^{-1} . An accumulation number of 20 and an exposure time of 2 s were chosen. To record the spectra, the LabSpec software was applied.

Ultraviolet-visible (UV-Vis) spectroscopy was carried out using a Perkin Elmer Lambda 750 spectrometer with a 100 mm Ulbricht sphere and an InGaAs detector. The spectra were obtained between 200 and 800 nm with a step of 1 nm. The corresponding reflectance spectra were converted into pseudo-absorption using the Kubelka–Munk function (Eq.4).

$$F(R_\infty) = \frac{(1 - R_\infty)^2}{2R_\infty} = \frac{R}{S} \quad (4)$$

In this equation, R_∞ stands for the reflection at an infinitely thick sample. The coefficients K and S correspond to the absorption and

scattering^{55, 56}. To determine the band gap, the Tauc-plot method was applied. Therefore, $[F(R_\infty)\cdot h\nu]^{1/n}$ is plotted against the energy of the incident photons. Here, h expresses the Planck constant and ν is the wavelength. The exponent $1/n$ describes the nature of the band gap. While $n = 1/2$ is used for a direct allowed transition, $n = 2$ corresponds to an indirect allowed transition^{57–59}.

For the acquisition of IR spectra, an Alpha II diffuse reflectance infrared Fourier transform (DRIFT) spectrometer from Bruker was utilized. The spectra were measured with a resolution of 4 cm^{-1} in a range from 4000 to 350 cm^{-1} performing 24 scans per measurement. The spectroscopy software OPUS from Bruker was applied.

For the acquisition X-ray photoelectron spectroscopy (XPS) measurements, a Physical Electronics PHI VersaProbe II scanning XPS microprobe was applied. Its beam voltage was set to 15 kV and the beam was adjusted to a power of 50 W and a diameter of $200 \mu\text{m}$. The surveys were measured using an energy pass at 224 eV, a step size of 0.4 eV, and a holding time of 50 ms per step. Two cycles were performed for those measurements. To acquire the high-resolution spectra, 12 cycles were performed with a pass energy of 26 eV, a step width of 0.1 eV, and a holding time of 50 ms. For the evaluation of the data, the CASA XPS 2.3.25 software was used. To acquire the measurements, the WO_3 photoanodes were cut into small pieces, which were then utilized for the analysis.

3 Results and discussion

3.1 Electrolyte study

WO_3 photoanodes were prepared and characterized according to our previous work^{47, 48}. Additionally, the layer thickness of the photoanodes was determined using a stylus profilometer. Using this method, the film thickness of the samples synthesized with 5 dip-coating cycles was determined to $1.927 \pm 0.051 \mu\text{m}$. In contrast to that, after 15 dip coating cycles, samples exhibit a thickness of $5.779 \pm 0.262 \mu\text{m}$.

In a previous report by Lhermitte *et al.*, it was shown that HMF can be converted via direct oxidation mechanism using WO_3 photoanodes⁶⁰. Here, it was first investigated if mesoporous WO_3 electrodes prepared using a templated sol-gel dip-coating process are as well suitable for this oxidation. CV and LSV measurements were performed in a 0.1 M sodium phosphate (NaPi) electrolyte with a pH value of 4. This electrolyte was chosen since it was applied in literature before⁶⁰. When the measurements were performed using a Pt-wire as the working electrode (WE), no HMF oxidation can be observed (Fig. 1a and Supplementary Fig. S1a). The only processes occurring are the hydrogen evolution reaction (HER) below a potential of 0 V_{RHE} . The OER has an onset potential of $1.7 \text{ V}_{\text{RHE}}$, which does not change upon the addition of 5 mM HMF. The maximum current increases even faster when HMF is not present in the solution. This does not change upon application of WO_3 as a WE (Supplementary Fig. S1b).

When the electrodes are illuminated with simulated sunlight, the photocurrent onset changes upon the addition of 5 mM HMF. While it is located at $0.7 \text{ V}_{\text{RHE}}$ in the NaPi electrolyte, the presence of HMF causes a decrease in the onset potential to $0.5 \text{ V}_{\text{RHE}}$. The photocurrent at $1.23 \text{ V}_{\text{RHE}}$ on the other hand is increased from 0.97 to $1.41 \text{ mA}\cdot\text{cm}^{-2}$ (Fig. 1b). Those results allow the assumption that mesoporous WO_3 electrodes are able to oxidize HMF. When the light is periodically switched on and off during LSV measurements, the curves exhibit photocurrent transients (Supplementary Fig. S2).

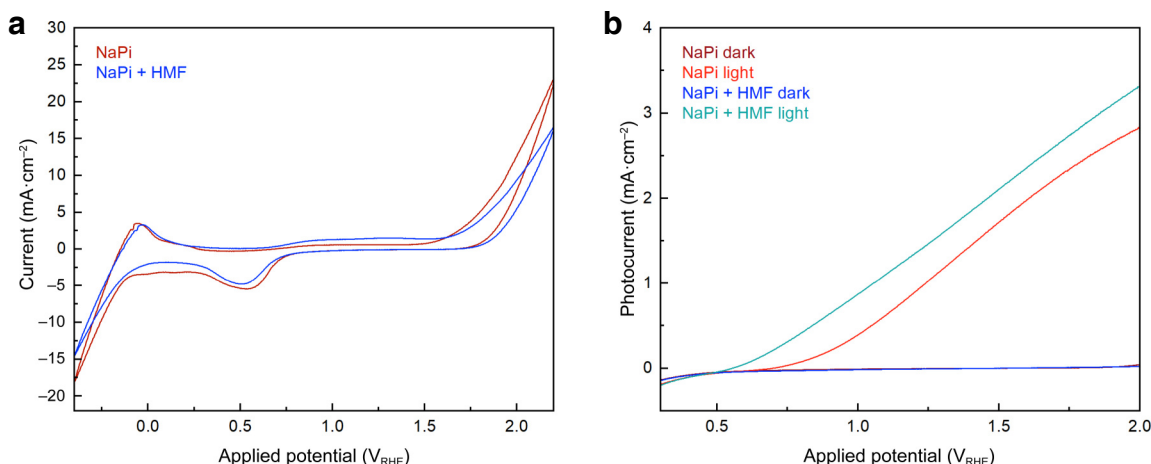


Fig. 1. CV and LSV measurements. **a**, Cyclic voltammetry measurements with Pt wire as WE; **b**, LSV measurements of WO_3 as WEs in the dark and under illumination.

The absence of spikes indicates a good interfacial charge transfer efficiency between the electrode and the electrolyte^{30, 60}. Adding HMF to the solution does not change the transients, which means that the transfer efficiencies are not influenced. In addition to that, it was shown in literature that HMF is stable in a wide range of pH values and undergoes only minor degradation under AM 1.5 G illumination^{26, 61}.

Now that the ability of the WO_3 electrodes to oxidize HMF was shown, in the next step the influence of the electrolyte selection was investigated. Therefore, NaPi, KPi, Na_2SO_4 , K_2SO_4 , NaClO_4 , NaNO_3 , and Na-acetate were first compared regarding their PEC water splitting abilities in the absence of HMF. Each electrolyte is applied in a concentration of 0.1 M at pH values of 2, 3, 4, 5, and 6. Furthermore, the respective acids H_2SO_4 , HClO_4 , HNO_3 , and H_3PO_4 were also investigated in a 0.1 M concentration. To ensure reproducibility, four electrodes were measured for each electrolyte and pH value. When comparing the photocurrent mean values of the different electrolytes, it can be recognized that the pH does not significantly influence the water splitting performance in most cases (Supplementary Figs. S3–S40 and Tables S2–S9). Only when NaNO_3 and Na-acetate are applied, a trend can be recognized. While the photocurrent decreases with an increasing pH in the case of NaNO_3 , the opposite trend can be observed for sodium acetate. If this electrolyte is used with a pH of 5 or 6, it is among the best performing electrolytes (Fig. 2a). If a potential between 0.6 and 1.1 V_{RHE} is applied, the acetate electrolyte is yielding a significantly higher photocurrent than the other electrolytes (Fig. 2b). This could be attributed to a weaker adsorption of the acetate anions on the electrode surface in comparison to the other electrolytes, enabling a more efficient transfer of the photogenerated holes⁶². Using Na_2SO_4 and K_2SO_4 , the electrodes exhibit a very high performance over the entire investigated pH range, which is only surpassed by some of the acids in terms of photocurrent values. As it is expected from the literature, H_2SO_4 is the best performing electrolyte regarding PEC water splitting^{63, 64}.

After the LSV measurement, which were used to compare PEC water oxidation in the different electrolytes, 5 mM of HMF were added to the solutions. To evaluate the suitability of the electrolytes for this oxidation reaction, the photocurrent curves measured without HMF were subtracted from the curves measured after adding HMF. The resulting traces are referred to as the photocurrent difference (Δj). These traces represent the net change

in photocurrent upon the addition of HMF and serve as an indicator of the system's response to the addition of HMF. All difference functions exhibit a maximum at a certain applied potential, which is referred to as Δj_{max} . This maximum reflects the potential where the addition of HMF exerts the strongest influence on the photoelectrochemical processes. The decay of Δj at potentials higher than the maximum can be attributed to mass-transport limitations occurring in the system. Furthermore, with an increasing potential, the competition with the OER for active surface sites increases. The magnitude of Δj and the position Δj_{max} are utilized as comparative parameters for evaluating the influence of the different electrolytes on the system's photoelectrochemical response (Figs. 3a and 3c).

Upon the comparison of the photocurrent differences, it can be recognized that HClO_4 shows the highest PEC response for HMF addition with $1.04 \pm 0.02 \text{ mA}\cdot\text{cm}^{-2}$, followed by H_2SO_4 (Fig. 3b). After those acids, Na_2SO_4 , K_2SO_4 , and NaClO_4 also exhibit good currents, which are not significantly influenced by the pH value of the electrolyte. Among them, Δj of $0.95 \pm 0.01 \text{ mA}\cdot\text{cm}^{-2}$ obtained for K_2SO_4 with a pH 3 is the highest (Fig. 3a). For all electrolytes, the photocurrent differences are distributed narrowly around a mean value ($\leq \pm 0.04$), indicating a good reproducibility of those results.

The PEC response on the presence of HMF of the other electrolytes is influenced by the pH value. For NaPi, KPi, and NaNO_3 , an increase of the pH results in a decrease of Δj , while it results in an increase upon the utilization of sodium acetate. However, those electrolytes exhibit a significantly lower response to HMF addition over the whole pH range. Additionally, their variations are slightly larger.

The applied potential at which the Δj_{max} is located lies between 0.94 and 1.05 V_{RHE} for most electrolytes (Fig. 3d). Only when NaPi (pH 5, 6) and Na-acetate (pH 6) are employed, it is located below this range. NaNO_3 requires the highest applied potential for the maximum HMF influence, with all maxima (except in a pH 2) being located above 1.1 V_{RHE} . Therefore, its application for HMF oxidation is not energetically favorable. The variations of the applied potential at which the maximum difference is located displays small errors ($< 10\%$). Evaluating the results of this electrolyte study, HClO_4 , H_2SO_4 , NaClO_4 , and both sulfate electrolytes can be identified as the most promising candidates for further investigation of PEC HMF oxidation over mesoporous

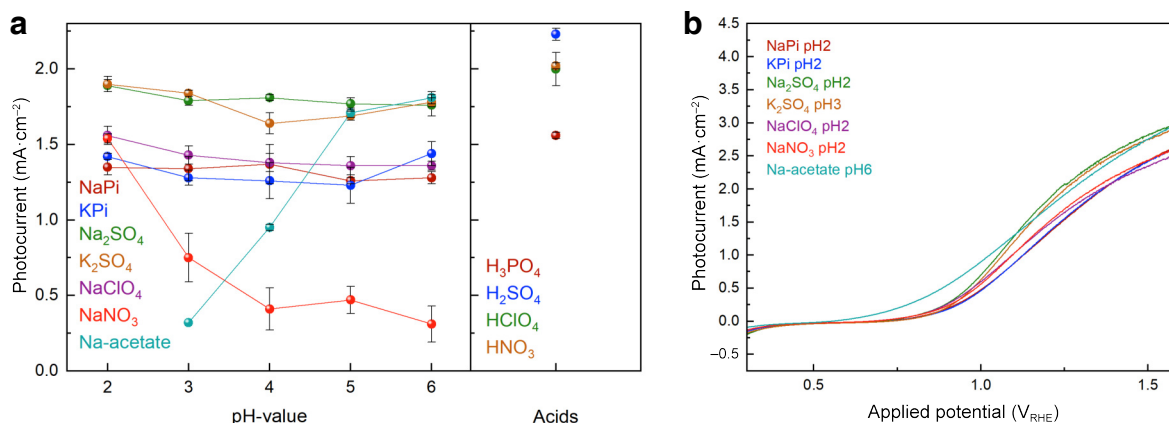


Fig. 2. Photocurrent measurements of mesoporous WO_3 photoanodes in various electrolytes and in the respective acids in the absence of HMF at $1.23 \text{ V}_{\text{RHE}}$: a, Photocurrent mean values with error bars; b, LSV measurements of the best pH values of the respective electrolytes.

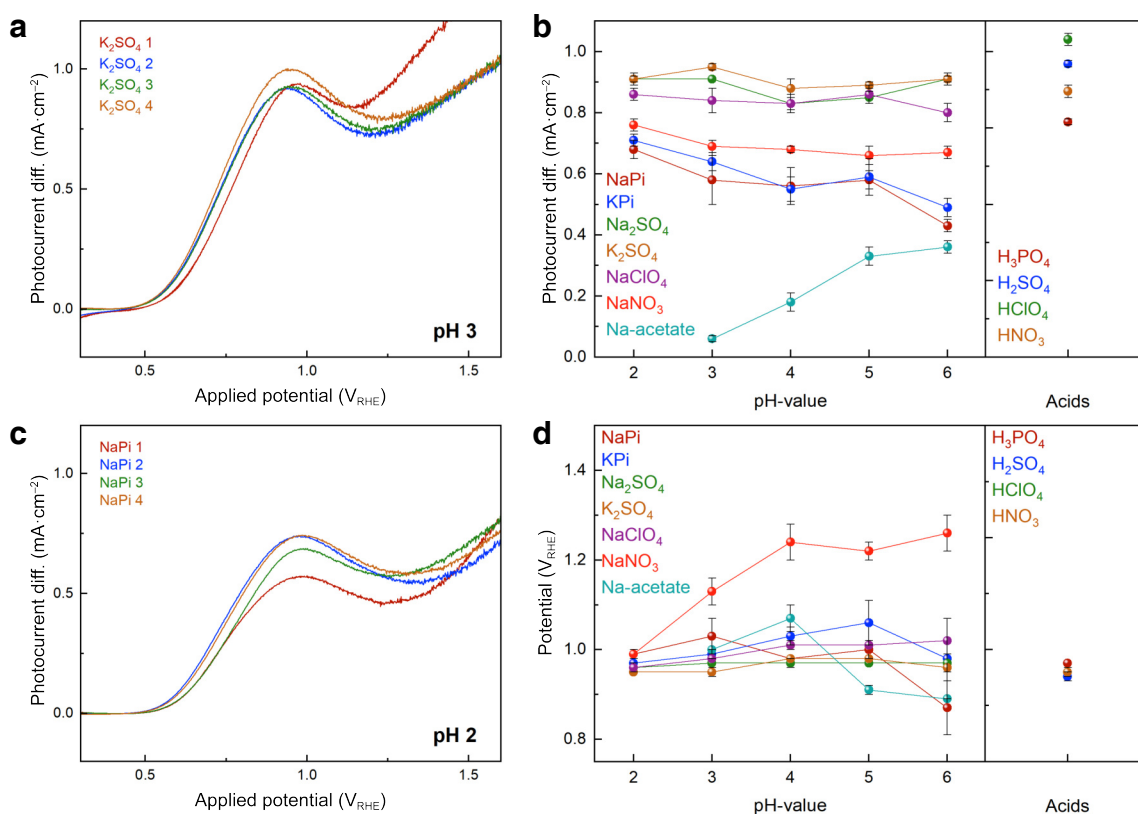


Fig. 3. PEC measurements electrolyte study. a, Photocurrent difference curves of WO_3 photoanodes measured in K_2SO_4 (pH 3); b, overview over the average maximum values of the photocurrent differences; c, Photocurrent difference curves of WO_3 photoanodes measured in NaPi (pH 2); d, overview over the average position of the photocurrent maximum.

WO_3 photoanodes, since they exhibit the most pronounced PEC response.

Besides applying Δj_{max} for comparing the suitability of the different electrolytes, the photocurrent onset potential in the presence and absence of HMF can also be utilized (Supplementary Figs. S41–S44 and Tables S10–S14). The electrolyte composition in general does not majorly influence the onset potential. It varies between 0.46 and $0.52 \text{ V}_{\text{RHE}}$ in most of the electrolytes. Only when utilizing KPi and NaNO_3 the onset potential exceeds values of $0.55 \text{ V}_{\text{RHE}}$. Regarding the change in the onset potential caused by the addition of HMF, the largest value can be obtained under the application of K_2SO_4 . This difference corresponds to a value of

0.2 V and does not change upon pH increase. Those observations also indicate that the HMF oxidation should be favored most when K_2SO_4 is chosen as an electrolyte.

3.2 Mechanistic investigation

To gain mechanistic insights into PEC HMF oxidation, IPCE and impedance measurements were performed. During those measurements, the potential was applied at which the photocurrent difference reached its maximum value (Table S15). For calculating the charge carrier injection and charge carrier transfer efficiency, LSV measurements were recorded utilizing H_2O_2 as a sacrificial agent. Those measurements were conducted for every electrolyte at

the pH value which exhibited the best HMF oxidation performance. While this pH is 3 for K_2SO_4 and 6 for sodium acetate, for the other electrolytes, a value of 2 is derived to be the most suitable pH for HMF conversion.

Analysis of the IPCE data shows a shape similar to the absorption spectra of the photoanodes (Fig. 4, and Supplementary Figs. S45 and S46). For all samples, it reaches its maximum value at 368 nm. Above 480 nm no photons can be utilized, due to the absorption edge of WO_3 being located at this wavelength^{65, 66}. The quantity of interest for those measurements is the improvement of the efficiency caused by the addition of HMF. Therefore, consistent with the LSV measurements, the difference between the maximum IPCE values of the measurement with and without the presence of HMF was taken into account.

These values reflect the enhancement of the charge transfer kinetics due to the addition of HMF into the PEC system. Among them, nitric acid exhibits the highest value, with an IPCE improvement of 30.1% (Table S16). Excluding the acids, the largest IPCE difference is achieved in sodium sulfate (24.3%) and potassium sulfate (22.1%) electrolytes the largest difference is achieved. Although the value for sodium acetate is larger than expected based on the values of Δj , the IPCE differences exhibit a similar trend to that observed for Δj . According to these results, applying acids, especially HClO_4 and HNO_3 could be beneficial for HMF oxidation.

For a better evaluation of the different electrolytes, LSV measurements applying 0.1 M H_2O_2 as a sacrificial agent were conducted (Supplementary Figs. S47–S49 and Table S17). Based on those results, the charge carrier injection P_{inj} and separation efficiency P_{sep} were calculated. Since P_{sep} was calculated using the photocurrent yielded by adding a hole scavenger and the theoretical maximum photocurrent of WO_3 , it does not directly show the HMF oxidation capabilities of WO_3 in the respective electrolyte. However, they display the effective fraction of holes not recombining with electrons in the bulk. Although, it should be noted that the photocurrent which is influenced by the potential distribution and the surface kinetics of the scavenger is utilized for its calculation. For this reason, the value of P_{sep} is influenced by the electrolyte choice. Therefore, P_{sep} represents the amount of holes reaching the electrode/electrolyte interface at a certain applied potential⁴⁹.

Utilizing a value of $4.0 \text{ mA}\cdot\text{cm}^{-2}$, which is usually assumed to be the theoretical maximum photocurrent for WO_3 photoanodes is only valid for electrodes with a band gap of 2.70 eV. For this reason, the maximum photocurrent was calculated from the average band gap of the utilized photoanodes (2.71 eV) resulting in a value of $3.87 \text{ mA}\cdot\text{cm}^{-2}$. A comparison of the values of P_{sep} calculated from the two different photocurrent maximum values exhibits that the values are slightly higher when the value calculated from the measured band gap is utilized (Supplementary Fig. S50, Tables S17

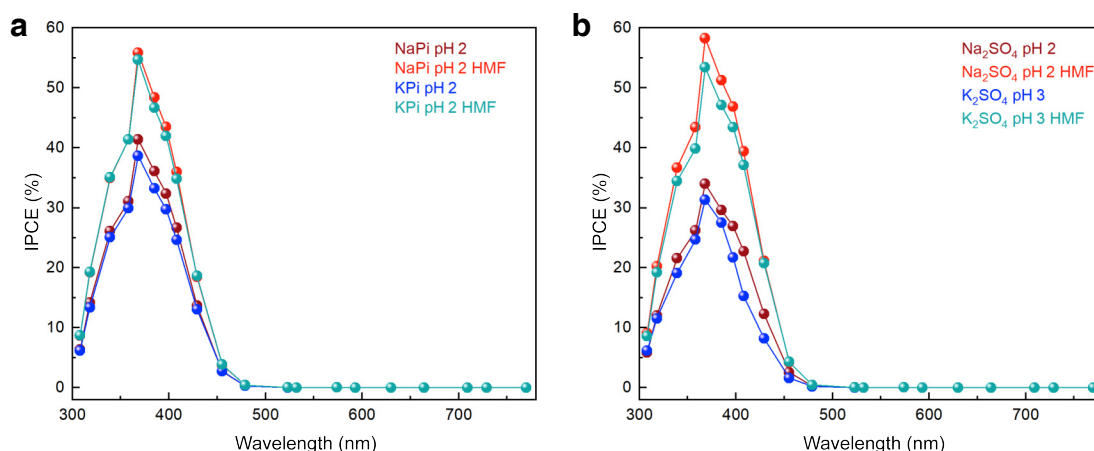


Fig. 4. IPCE measurements. a, b, IPCE spectra of WO_3 photoanodes measured in NaPi and KPi (a), and Na_2SO_4 and K_2SO_4 (b) with and without adding 5 mM HMF; for the measurements, the potential, where the photocurrent difference maximum is located was applied.

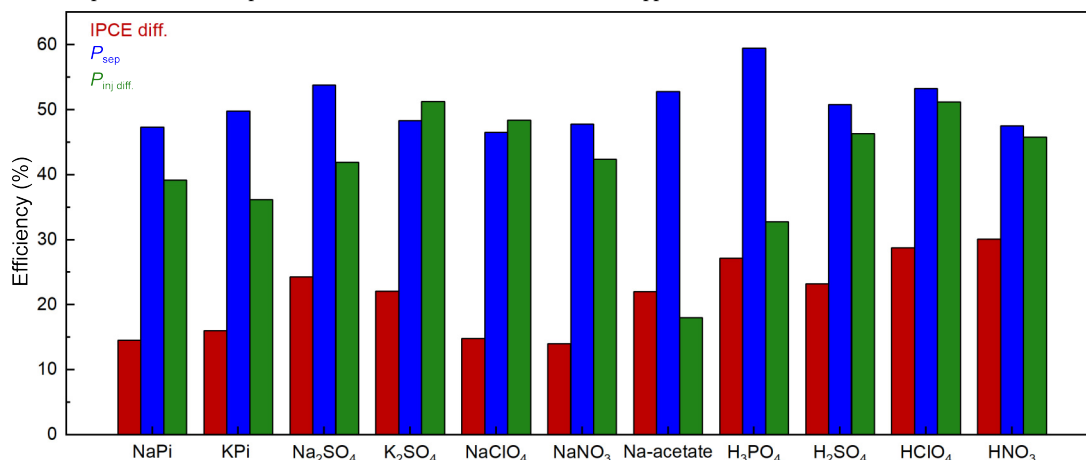


Fig. 5. IPCE and charge carrier efficiencies. Values of the IPCE difference, the charge separation efficiency, and the difference in charge carrier injection efficiency ($P_{\text{inj, diff}}$) determined between measurements in the absence and presence of HMF in the electrolyte.

and S18). Among all electrolytes, H_3PO_4 exhibits the best charge separation efficiency of 59.5%, while the lowest one was observed for NaClO_4 (46.5%) (Fig. 5). Whereas H_2SO_4 and HClO_4 already emerged as promising candidates in the LSV measurements, they also show good separation efficiencies of 50.8% and 53.3%. K_2SO_4 also exhibited a promising photocurrent response towards HMF oxidation in the aforementioned measurements. However, its charge separation efficiency is moderate in comparison to the other electrolytes. Adding HMF into K_2SO_4 (pH 3) increases the charge carrier injection efficiency significantly (Fig. 5). While P_{inj} is 20.2% when only water oxidation takes place, it increases to 71.5% in the presence of HMF. The difference between those values (51.3%) corresponds to the share of holes which do not recombine with electrons at surface traps and are therefore injected into the electrolyte, making them available for HMF oxidation. If $P_{\text{inj diff}}$ is compared to Δj , nearly the same trend can be observed.

With a value of 51.2%, the second highest difference is obtained using HClO_4 , followed by NaClO_4 (48.4%) and H_2SO_4 (46.3%). Upon the application of Na_2SO_4 and H_3PO_4 , $P_{\text{inj diff}}$ is lower than expected according to this trend. The lowest improvement regarding the charge carrier injection efficiency can be obtained for sodium acetate.

To gain deeper insights into the charge transfer mechanism, impedance spectra were recorded under AM 1.5 G illumination. Again, measurements in the presence and absence of 5 mM HMF were compared (Supplementary Figs. S51–S53, Table S19). When the differences between both phosphate (Fig. 6a) and sulfate (Fig. 6b) were evaluated, a few aspects have to be discussed. At first, the electrolyte resistance is more than two times larger in the phosphate electrolytes (higher than 60 Ω) in comparison to the sulfate containing ones (around 30 Ω). Besides that, a slightly lower electrolyte resistance can be observed for the electrolytes containing potassium as a cation. Overall, the electrolyte resistance is lowest for HNO_3 (9.9 Ω), H_2SO_4 (19.8 Ω), and HClO_4 (23.6 Ω), followed by the two sulfate-containing electrolytes (Na_2SO_4 and K_2SO_4). Those values are only slightly affected by the addition of HMF.

Since it is influenced by the presence of HMF, the resistance across the WO_3 /electrolyte interface is also of significance. It can be recognized that upon the addition of HMF, this resistance increases in most cases. In the K_2SO_4 electrolyte, the resistance at the semiconductor/electrolyte interface rises from 151 Ω , which corresponds to the lowest value of all electrolytes, to 210 Ω .

Another electrolyte which shows also a low resistance at the WO_3 /electrolyte interface is HClO_4 . A significantly decreasing resistance can only be observed in the case of H_2SO_4 . If this electrolyte is utilized, the resistance at the semiconductor/electrolyte interface amounts 200 Ω in the absence of HMF and 183 Ω after its addition. Comparing the resistance values at the WO_3 /electrolyte interface with those of $P_{\text{inj diff}}$ a similar trend can be observed. The electrolytes exhibiting the highest difference of P_{inj} also show a large resistance at the semiconductor/electrolyte interface. Therefore, it is assumed that in those electrolytes the overall charge transfer is hindered by an enhanced adsorption of the large HMF molecules at the electrode surface. This causes a blocking of the active reaction centers for water oxidation. On the other hand, HMF molecules probably act as a hole scavenger and are thereby enhancing the charge carrier injection efficiency^{39,67}.

Overall, the conducted electrolyte study, together with the mechanistic investigations, allows the conclusion that K_2SO_4 (pH 3) and HClO_4 are the most suitable electrolytes for PEC HMF oxidation. Adding HMF into them results in the highest photocurrent enhancement among all tested candidates (1.04 $\text{mA}\cdot\text{cm}^{-2}$ for HClO_4 and 0.95 $\text{mA}\cdot\text{cm}^{-2}$ for K_2SO_4). Furthermore, their maximum photocurrent difference was observed at a relatively low potential of 0.95 V_{RHE} , compared to the other electrolytes. Although H_2SO_4 yields good results for those values as well, $P_{\text{inj diff}}$ (46.3%) is lower. In contrast, the $P_{\text{inj diff}}$ values for HClO_4 (51.2%) and K_2SO_4 (51.3%) are significantly higher. Regarding IPCE difference spectroscopy of the three electrolytes show comparable results. Impedance spectroscopy allows the assumption that in the presence of HMF the charge transfer between the electrode and the electrolyte is least hindered. Additionally, it exhibits a low electrolyte resistance, which indicates a good ionic conductivity. Therefore, K_2SO_4 is considered to be the most suitable electrolyte.

3.3 Oxidation intermediate study

To investigate the suitability of the different electrolytes for the targeted conversion of HMF into FDCA, further LSV measurements were performed. These measurements aimed to demonstrate the photoelectrochemical response of mesoporous WO_3 photoanodes to each potential reaction intermediate (Scheme 1). Therefore, HMF and its possible oxidation intermediates, DFF,

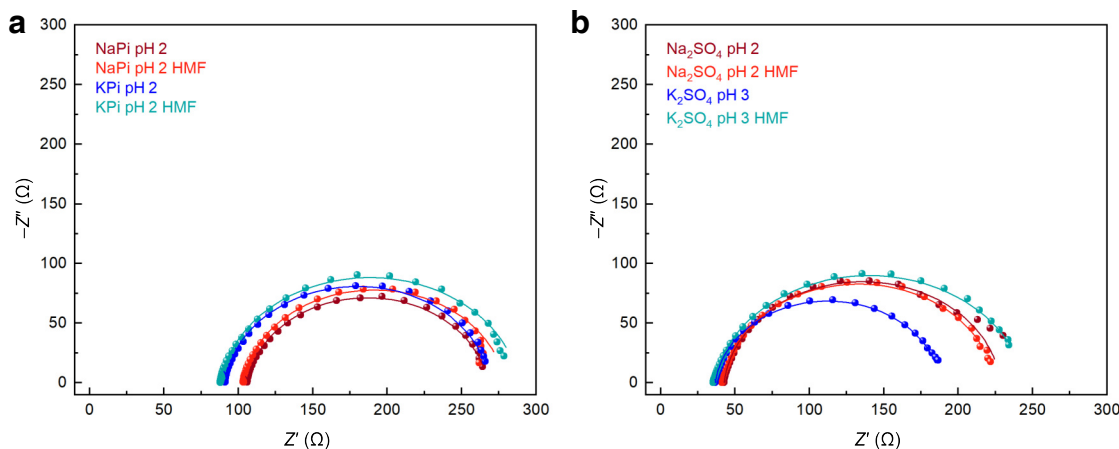


Fig. 6. Impedance spectra: a, NaPi and KPi; b, Na_2SO_4 and K_2SO_4 acquired under AM 1.5 G illumination and the application of the potential at which the maximum photocurrent difference is located. These values are 0.99 V_{RHE} (NaPi pH2), 0.97 V_{RHE} (KPi pH 2), 0.96 V_{RHE} (Na_2SO_4 pH 2), and 0.95 V_{RHE} (K_2SO_4 pH 3).

HMFA, and FFCA, were added into each electrolyte one after another. Like in the electrolyte study, the difference between the photocurrent curves measured without adding the organic substance are subtracted from the ones acquired after their addition. Furthermore, the potential at which $\Delta j_{\max}$ is located was monitored (Fig. 7, and Supplementary Figs. S54–S95 and Tables S20–S35).

An evaluation of $\Delta j_{\max}$ shows that the highest values are yielded for HMF in most cases. After the first oxidation step, DFF and HMFA are the two possible intermediates. With the exception of pH 2, in sodium-containing electrolytes a lower $\Delta j_{\max}$ is exhibited in the presence of DFF compared to HMFA. Since the pathway with DFF as an intermediate is preferentially chosen in pH values below 13, it should be advantageous to use an acid or a potassium-containing electrolyte^{10,68}. Under their application, DFF exhibits the same or even a slightly higher $\Delta j_{\max}$ compared to HMFA in most cases.

These measurements also indicate that the PEC response of the system towards FFCA is the least pronounced, suggesting that this step represents the kinetic bottleneck for the HMF oxidation. The value of Δj is the lowest when FFCA is added for all electrolytes displayed in Fig. 7. The electrolyte which seems to be the most suitable for that oxidation step is NaNO_3 at a pH higher than 2. Using NaNO_3 at pH 4, the photocurrent improves by $1.12 \text{ mA}\cdot\text{cm}^{-2}$ upon FFCA addition. Although, the applied potential at which $\Delta j_{\max}$ is reached is the highest for this electrolyte.

When this applied potential was analyzed for the other electrolytes, it can be observed that it does not depend on the intermediate which is added into the electrolyte. In contrast, the pH value influences the location of the photocurrent difference maximum in every electrolyte. If K_2SO_4 is applied, the maximum is located at $0.94 \text{ V}_{\text{RHE}}$ at a pH of 2 and at $0.97 \text{ V}_{\text{RHE}}$ at pH 5. This corresponds to the lowest distribution.

In general, the potential where $\Delta j_{\max}$ is located increases with an increasing pH value in the other electrolytes. Ranging from 0.92 to $0.96 \text{ V}_{\text{RHE}}$, the acids require the lowest applied potential to reach $\Delta j_{\max}$. Only when K_2SO_4 (pH 2, 3, 4, and 6) and Na-acetate (pH 5 and 6) are utilized, the maxima are also located in this range. According to these results, the oxidation of HMF to FDCA should be possible with all the investigated electrolytes. However, the step of oxidizing the intermediate FFCA towards FDCA is probably the most challenging one. This study on intermediate oxidation also

shows that the three most promising electrolytes for PEC HMF oxidation using mesoporous WO_3 photoanodes are HClO_4 , H_2SO_4 , and K_2SO_4 (pH 3). Those results are in line with the ones of the electrolyte study above.

Combining the results of the electrolyte and intermediate study indicates that K_2SO_4 is the most suitable electrolyte for HMF oxidation. This can be attributed to the highest ionic conductivity of sulfate-containing electrolytes in comparison to the alternatives⁶⁹. This can also be confirmed by the electrolyte resistance data gained from EIS measurements. Furthermore, sulfate-based electrolytes are known to promote side reactions that compete with the OER, especially at low pH values. Using perchlorate and phosphate electrolytes in contrast, the water oxidation is favored over competing reactions. Small ions are able to block the active sites, which explains the lower suitability of sodium-containing electrolytes for the HMF oxidation⁴². Although nitrate containing electrolytes seem to be the most suitable ones for glycerol oxidation using BiVO_4 photoanodes⁴⁶, this is not the case for WO_3 . This discrepancy can be attributed to the higher oxidation power of WO_3 compared to BiVO_4 . For this reason, a direct hole-mediated oxidation is possible, which favors the application of sulfate electrolytes^{45,70,71}.

3.4 Photoelectrochemical long-term conversion of HMF

To investigate HMF conversion using WO_3 photoanodes over a long time, measurements for 72 h using a flow cell setup were performed. Therefore, a one-compartment PEC cell was designed, which is connected via a peristaltic pump to an electrolyte reservoir with an overall volume of 80 ml. The pump is used to circulate the electrolyte from the reservoir through the cell (Fig. 8). One advantage of using such a PEC flow cell is the improved mass transfer due to the transport of the oxidation product away from the electrode. Furthermore, the setup can be easily optimized by for example changing the electrode distance and is advantageous for scaling up^{72–75}. To investigate the influence of the flow speed through the cell on the photocurrent, LSV scans with different rates were performed (Supplementary Figs. S96 and S97).

Measurements conducted with and without adding HMF prove that the HMF oxidation is independent of the flow rate. For the long-term measurements, HClO_4 , K_2SO_4 (pH 3 and 6) and K_2SO_4 (pH 3) + TEMPO were chosen and investigated.

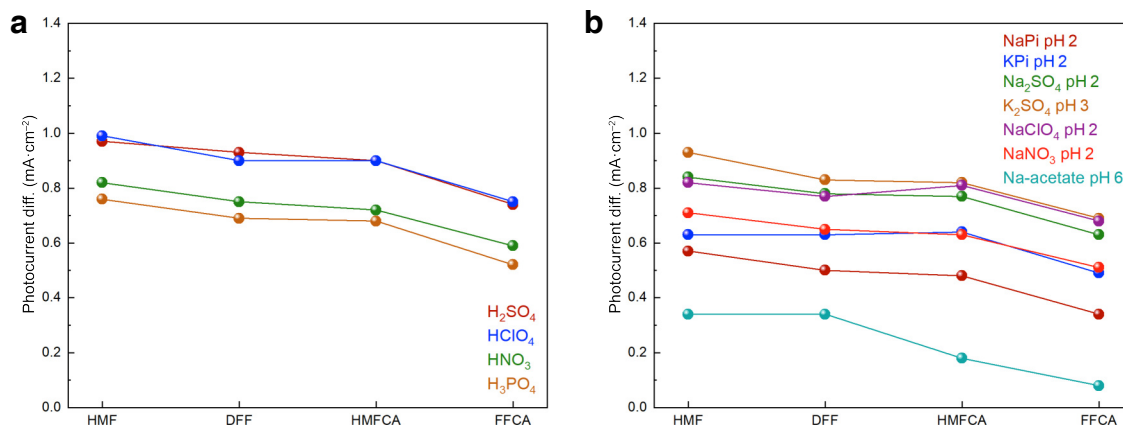


Fig. 7. Maximum photocurrent differences of a) all acids and b) all other electrolytes applied at the pH values which were evaluated as the best in the electrolyte study before. The differences were calculated between LSV measurements performed in the absence and presence of HMF or its oxidation intermediates DFF, HMFA and FFCA.

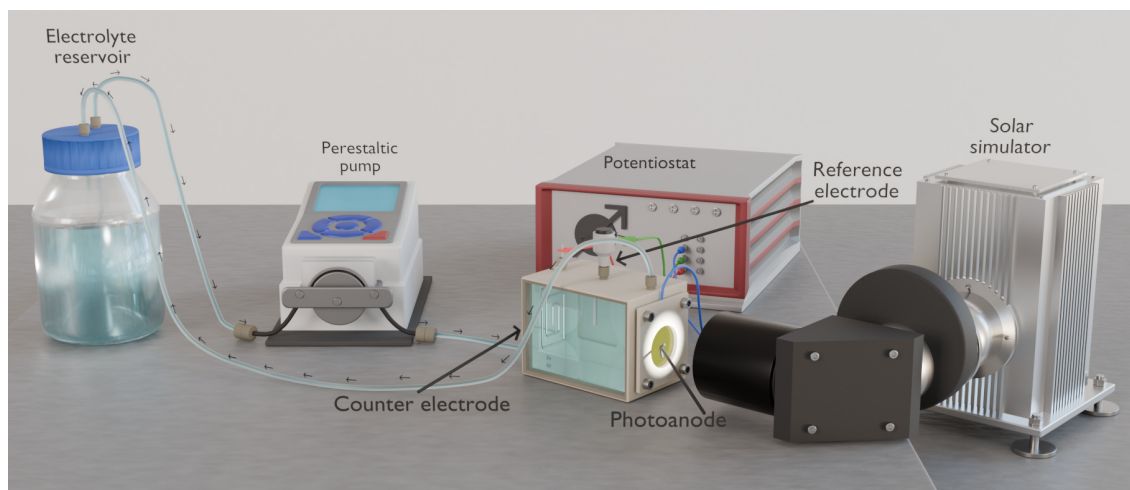


Fig. 8. Schematic illustration of the designed flow cell setup, which was applied for long-term measurements.

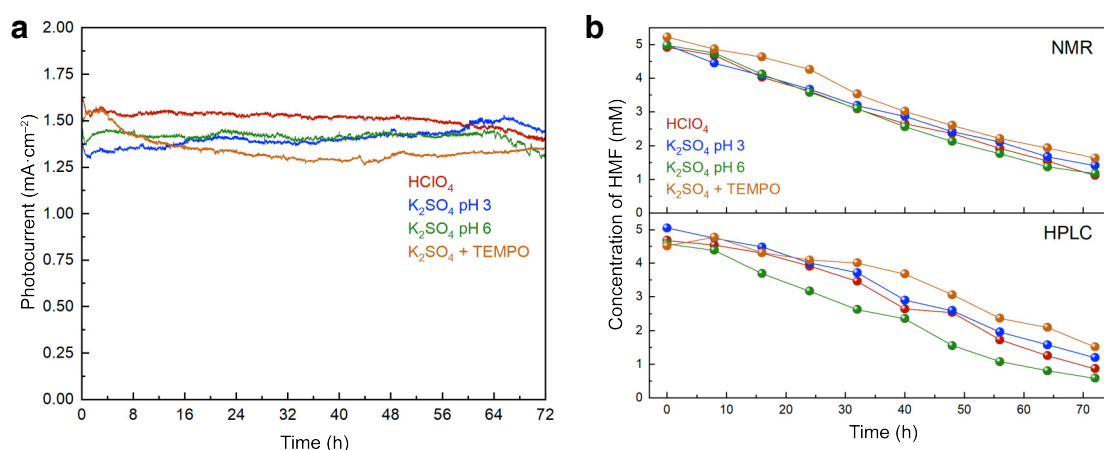


Fig. 9. Long-term measurements and analysis of HMF conversion. **a**, Photocurrents over time of the long-term measurements performed under AM 1.5 G illumination and at an applied potential of $0.95\text{ V}_{\text{RHE}}$ to photoelectrochemically oxidize HMF in a flow cell setup; **b**, HMF consumption over the reaction time monitored by quantitative NMR spectroscopy and UPLC-MS measurements.

Upon investigating the photocurrent values, a very high stability of the mesoporous WO_3 photoanodes can be recognized (Fig. 9a). While in K_2SO_4 (pH 3), 95% of the initial photocurrent remains after 72 h, 90% remains for the measurement conducted in $\text{K}_2\text{SO}_4 + \text{TEMPO}$ (Table S36). In the other chronoamperometric measurements the observed stability is also much higher than expected according to previous reports^{47,48}.

The HMF consumption over time was monitored using quantitative NMR spectroscopy (Fig. 9b and Tables S37–S40). Under the application of HClO_4 , the highest conversion of HMF (3.81 mM) within 72 h can be observed. While in this case, 77% of the starting material are oxidized, the HMF consumption is only slightly lower in the other electrolytes. Using K_2SO_4 at pH 3, the lowest amount of HMF is converted throughout the reaction time of 72 h with 3.58 mM.

Besides NMR spectroscopy, the concentration was also monitored using UPLC-MS (Table S41). For all measurements, except the one where TEMPO was added, these two techniques exhibit a maximum deviation of 0.2 mM regarding HMF consumption. However, the absolute concentration determined via UPLC differs slightly from the one obtained from NMR spectra. This might be attributed to an incomplete extraction of HMF into the organic phase due to its high water solubility⁷⁶.

Analyzing the product distribution, it can be recognized that formic acid (FA) and maleic acid (MA) are the main products (Fig. 10a, and Supplementary Fig. S98a and Tables S37–S40). The presence of those compounds indicates that ring-opening and C–C bond cleavage is occurring. The opening of the furan ring during catalytic HMF oxidation in low pH values was also observed in previous reports⁷⁷.

Using HClO_4 , a concentration of 0.7 mM FA can be monitored after 72 h reaction time. This corresponds to a Faradaic efficiency of 4.13%, which is higher than in all other electrolytes (Tables S43–S45). Under these conditions almost no MA is formed. Upon the utilization of K_2SO_4 (pH 3), 0.11 mM MA and 0.47 mM FA are produced throughout the reaction. The calculation of the FE of those products yields values of 2.98% (FA) and 3.49% (MA). An elevation of the pH to 6 leads to an increased formation of MA (0.47 mM), while almost the same amount of FA is formed (0.42 mM). Those products are obtained with a FE of 14.82% (MA) and 2.65% (FA). Adding TEMPO into the solution, the reaction proceeds over an indirect pathway, which was shown by electrochemical measurements (Supplementary Fig. S99). This leads to a further increase of the MA production (0.72 mM, 23.89%), while FA formation almost remains constant (0.36 mM, 2.39% FE).

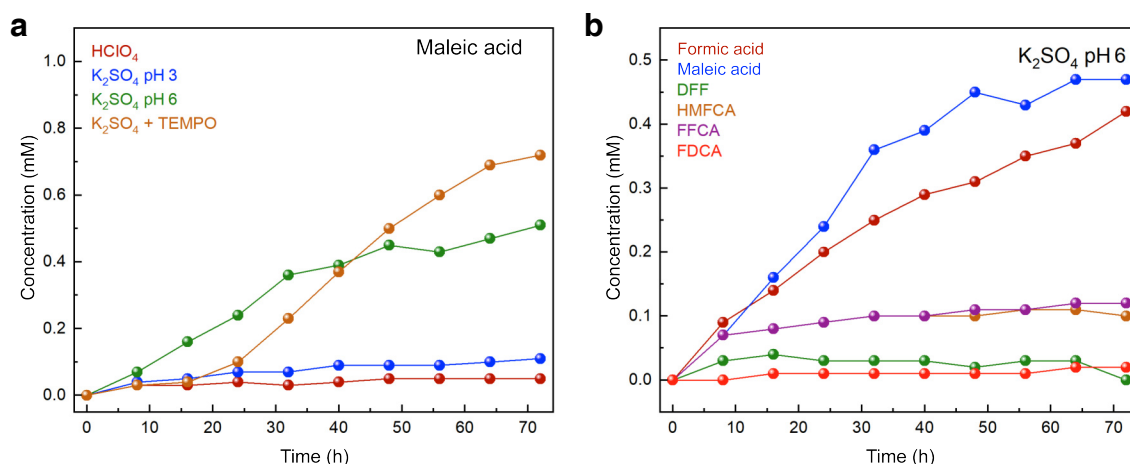


Fig. 10. Product analysis. a, Product evolution of maleic acid (MA) during long-term measurements in different electrolytes; b, evolution of the different products under the application of K_2SO_4 (pH 6) electrolyte.

The final product of HMF oxidation, FDCA, was only obtained when using K_2SO_4 at pH 3 and 6 as the electrolyte (Fig. 10b, and Supplementary Fig. S98b). In those electrolytes, an amount of 0.02 mM was detected, which corresponds to an FE of 0.38% across both pH environments. Besides that, DFF and HMFA are present in the solution, which indicates that the reaction proceeds over both possible pathways. These intermediates are produced with a higher FE than FDCA (Supplementary Tables S43–S45). The same can be observed when TEMPO is added to the K_2SO_4 electrolyte (pH 3); the intermediates are the same as when it is not present. In contrast, only DFF is formed if HClO_4 is used as the electrolyte, meaning that the reaction proceeds only over one pathway. In the sulfate electrolytes, the concentration of DFF is relatively constant and stays below 0.05 mM in both pH values.

Therefore, a relatively fast oxidation of DFF towards FFCA can be assumed. In contrast, the concentration of HMFA slowly increases to a value above 0.1 mM. This shows that the oxidation of HMFA seems to be slower than its production. FFCA, which is the second intermediate along the reaction pathway, accumulates as well over time, reaching a concentration of 0.15 mM (pH 3) and 0.12 mM (pH 6). Based on these results, the assumption can be made that the conversion of FFCA into FDCA is the slowest reaction step in this catalytic system.

Upon further analysis of the NMR spectra, another disubstituted furan species can be detected. According to the NMR data and literature, this could be 5-dihydroxymethylfuran-2-carboxylic acid (Supplementary Scheme S1), which is a known intermediate in the HMF oxidation^{78–80}. Besides the species mentioned, further unidentified side products are present in the electrolyte. Those results exhibit that PEC oxidation of HMF using mesoporous WO_3 photoanodes mainly leads to the formation of formic acid, when electrolytes with low pH values are applied. This C–C cleavage is the result of an overoxidation which shows that those conditions are probably too harsh for the selective oxidation towards FDCA. If the pH value is increased or an indirect mechanism is chosen, the product distribution shifts towards maleic acid. Although it is not the desired product of this oxidation, it is a high value chemical, which is applied as a raw material for the fabrication of lubricant additives, unsaturated polymer resins, surface coatings, plasticizers, copolymers, and agricultural chemicals⁸¹. Overall, 23% of the initial HMF is converted into products with a higher value than oxygen. Those results give rise to the conclusion that further optimization of

the system regarding the onset potential and the application of cocatalysts could improve its conversion and selectivity even more.

Additionally, the results of the intermediate study must be revisited again after the analysis of the products. The discussion in this study is based on the assumption that the increase of the photocurrent response represents the current utilized for the oxidation of the respective intermediate. Although, the product analysis shows that a significant share of the photocurrent goes into the formation of FA and MA. Nevertheless, these results allow an estimation of which intermediate exhibits the least photocurrent response and is therefore the bottleneck of the reaction in the respective electrolyte and pH value.

To analyze if the WO_3 photoanodes change during HMF oxidation, they were characterized after the catalytic reaction. Therefore, XRD, DRIFT, UV–Vis, and XPS measurements were carried out and compared to characterizations performed prior to HMF conversion. The diffractograms exhibit no structural changes regarding the WO_3 photoanodes (Supplementary Fig. S100). After the long-term measurements, they are still present in a monoclinic crystal structure (ref: 01-072-1465). The Raman spectra acquired after the long-term measurement exhibit broad signals in the range from 1100 to 2000 cm^{-1} (Supplementary Fig. S101a). They originate from the amorphous glass substrate and are an indication for a slight dissolution of the WO_3 photoanode. Further information can be gathered by investigating the DRIFT spectra of the films (Supplementary Fig. S101b). Those spectra of the samples measured in K_2SO_4 and $\text{K}_2\text{SO}_4 + \text{TEMPO}$ exhibit a signal of formic acid, which is located at 1724 cm^{-1} . This indicates the adsorption of this product at the photoanode surface. Besides that, the signals occurring at 1268, 1225, and 993 cm^{-1} show the presence of maleic acid on the porous structure. Furthermore, HMF can also be identified at the surface. The presence of those acidic compounds could be responsible for the increase of the photoanode stability, which was observed in the presence of HMF in the solution. Additionally, the UV–Vis spectra (Supplementary Fig. S102) show an increase of the absorption below 550 nm for the photoanodes after the long-term measurements in K_2SO_4 . The photoanode, which was measured in $\text{K}_2\text{SO}_4 + \text{TEMPO}$ exhibits an increased absorption in the range between 200 and 350 nm, while the one utilized for the experiment in HClO_4 exhibits no changes. Those results are in line with the DRIFT spectra, where no adsorption of

an organic compound can be notified for the sample measured in HClO_4 .

To further analyze the photoanodes, XPS spectra were acquired before and after the long-term measurements (Supplementary Figs. S103 and S104). Those spectra exhibit no changes regarding the oxidation state of tungsten, which proves the high stability of the electrodes. One parameter, which is changing is the Si content on the sample. This signal originates from photoelectrons escaping the substrate through the porous WO_3 layer. The intensity change of the O 1s signals is also connected to that. Due to the fact that those changes are relatively small, it can be assumed that the film thickness differs between the measured points. Additionally, the amount of carbon being present on the surface is increased after the PEC measurement, which can be attributed to the adsorption of MA, FA, and HMF at the surface of the electrodes, according to DRIFT measurements.

4 Conclusions

In our work, the formation of FDCA from PEC oxidation of HMF under 1 sun AM 1.5 G illumination was demonstrated for the first time using mesoporous WO_3 photoanodes. By selecting the most suitable electrolyte and respective pH value, it was possible to produce 0.02 mM FDCA after 72 h under an application of 0.95 V_{RHE} in a 0.1 M K_2SO_4 electrolyte at pH 3 or 6. The electrolyte was chosen due to the results of a thorough electrolyte study. In this study, the photocurrent response with HMF being present in the solution was investigated for multiple electrolytes and pH values. Throughout the measurements, reproducibility of the results was shown. Deeper insights into the PEC oxidation of HMF were provided and a study on the oxidation capabilities of mesoporous WO_3 towards the intermediates of HMF oxidation was carried out. Following those studies, chronoamperometric measurements were performed in a newly designed flow-cell PEC setup using the electrolytes that showed the best performance. Under their utilization, a conversion of 77% of the initial HMF was achieved. By the application of quantitative NMR spectroscopy, the most important side product was found to be maleic acid. Although it is not the desired product, it is still of high value, and the present study provided the information that a ring-opening side reaction can occur during PEC HMF oxidation using WO_3 photoanodes. Over the measurement time of 72 h, an amount of 0.72 mM maleic acid was produced, when an indirect reaction mechanism utilizing TEMPO was applied. The information gained throughout this study exhibit that from the applied electrolytes, K_2SO_4 and HClO_4 are the most suitable ones for PEC HMF oxidation with mesoporous WO_3 photoanodes. Furthermore, it was shown that overoxidation seems to be an important issue in this catalytic system. Based on the gained knowledge, an optimization of the applied potential and the application of cocatalysts to provide milder oxidation conditions could further increase the performance regarding HMF conversion to the desired product FDCA.

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Data availability

The data that support the findings of this study are available from the corresponding author.

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Author contributions

L. M. M. has prepared all the samples and performed the material characterizations and photoelectrochemical measurements. Furthermore, he performed the NMR measurements and analyzed the data. I. B. conducted the UPLC analysis to monitor the HMF concentration in the long-term measurements. J. W. conducted and analyzed the XPS measurements. L. M. M. and R. M. together wrote the final manuscript, IB, JW and FH edited the manuscript. F. H. and R. M. acquired the funding.

Competing interests

There are no conflicts of interest to declare.

Use of AI statement

None.

Additional information

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