Direct photoelectrochemical oxidation of hydroxymethylfurfural on tungsten trioxide photoanodes†

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Depleting reserves of fossil fuels and growing concerns with atmospheric CO2 levels necessitate the development of non-petroleum derived, renewable fuels and carbon-based building blocks for chemical industries.1 Solar2 and biomass3–6 refineries have been proposed as potential replacements for the current petroleum paradigm, and a key model reaction identified is the oxidation of biomass-derived7–9 2,5-hydroxymethylfurfural (HMF) into 2,5-furandicarboxaldehyde (DFF), furandicarboxylic acid (FDCA), and related intermediates. Quantiﬁcation of the reaction rate constants via a kinetic model gives insight into the modest DFF and FDCA yields (up to 4% and 1%, respectively)—which is due to the formation of by-products—and suggests routes for improvement.

An important target reaction for solar-powered biomass valorization is the conversion of 2,5-hydroxymethylfurfural (HMF) into key monomers for polyester production. Herein, photoanodes of WO3 are demonstrated to directly photo-oxidize HMF in aqueous electrolyte (pH 4) under simulated solar illumination. The addition of 5 mM HMF increases the saturation photocurrent by 26% and suppresses the water oxidation reaction, as determined by rotating ring-disk electrode experiments. Prolonged photoelectrochemical oxidation (64 h) illustrates system robustness and conﬁrms the production of furandicarboxaldehyde (DFF), furandicarboxylic acid (FDCA), and related intermediates. Quantification of the reaction rate constants via a kinetic model gives insight into the modest DFF and FDCA yields (up to 4% and 1%, respectively)—which is due to the formation of by-products—and suggests routes for improvement.

While the photocatalytic oxidation of HMF has been suggested,21–25 the PEC oxidation of HMF to FDCA has been less developed. One recent report uses a BiVO4 photoanode,26 however the approach was severely limited since BiVO4 is incapable of directly performing HMF oxidation. Instead, BiVO4 first oxidizes a redox mediator (2,2,6,6-tetramethylpiperidine-1-oxyl, TEMPO) which then carries out the homogeneous oxidation of HMF in solution. This increases the complexity of product separation, and since TEMPO parasitically absorbs visible light,28 it reduces sunlight harvesting by the photoelectrodes. Moreover, the problematic long-term stability of the TEMPO radical calls into question the practical application of this approach. Thus, the identiﬁcation of a photoanode material that can directly oxidize HMF to FDCA, without redox mediators and selectively over water oxidation in aqueous electrolyte, is needed to advance the ﬁeld.

Herein we demonstrate for the first time that WO3 photoanodes can directly oxidize HMF in aqueous electrolyte under illumination while suppressing the competing water oxidation reaction. Our detailed analysis of the resulting product distribution and reaction kinetics gives important insights into the...
reaction pathways, suggesting routes to further enhance the performance.

Based on the unique PEC properties of WO3, we hypothesized that it could provide advantages toward the direct photo-oxidation of HMF. Specifically, compared to BiVO4, which has a valence band maximum (VBM) at a potential of 2.4 V vs. NHE,27 the VBM of WO3 is considerably more oxidizing at 3.1–3.2 V vs. NHE27 suggesting an increased driving force to overcome the activation energy barrier associated with HMF oxidation. In addition, WO3 also demonstrates poor selectivity for the OER, even in aqueous solution. In fact, WO3 often prefers to oxidize other small molecules, or anions such as MeOH, and Cl–.25,28–31 This can reduce or eliminate competition from water oxidation when operating in aqueous conditions. This strategy has been employed in the past, where WO3 was used to oxidize alcohols photoelectrochemically in aqueous solution.32 Finally, WO3 is easy to prepare and demonstrates stability in acidic aqueous media. These properties are highly desirable for a PEC material if it is to be employed in an H2 producing PEC cell since acidic conditions favour the production of H2 from water.

WO3 photoanodes prepared by the sol–gel method (see ESI† for details) were first examined for HMF oxidation in aqueous electrolyte using linear sweep voltammetry (LSV), and the results were compared to BiVO4 and Fe2O3 (similar photoanode materials, for synthesis see ESI†). Fig. 1a–c shows LSV results in the dark and under simulated 1 Sun illumination, with and without 5 mM HMF in the electrolyte. We note that different pHs were used due to the stability limits of each material, thus the VBM of WO3 is considerably more oxidizing at 3.1 V vs. NHE, a valence band maximum (VBM) at a potential of 2.4 V vs. NHE, and Fe2O3.33

The remarkable ability of WO3 to directly oxidise HMF was confirmed with rotating ring-disk electrode experiments (for Experimental details, and full explanation see ESI and Fig. S1†). Briefly, as seen in Fig. 1d, the ring current observed in the absence of HMF (due to the reduction of the O2 formed at the WO3 disk under illumination, see ESI† for additional discussion) is suppressed when HMF is added despite no significant change in the disk photocurrent, even at highly oxidizing potentials (1.43 V vs. RHE). This confirms that the photocurrent observed with HMF in Fig. 1c is due to HMF oxidation and not water oxidation when 5 mM HMF is present in the electrolyte.

The selectivity towards various HMF oxidation products and the durability of WO3 was next examined via the continuous photo-oxidation of a 5 mM HMF electrolyte (aqueous NaPi buffer pH 4) under simulated solar illumination using a constant applied potential of 0.68 V vs. RHE in a 2-compartment cell (working and counter electrodes separated by a Nafion membrane) in order to eliminate the possibility of reducing oxidized products at the cathode. Larger-area photoelectrodes (ca. 3 cm² vs. 1 cm²) and 3 Suns equivalent illumination were used to maximize the quantity of products formed. The concentration of HMF and the formed products were monitored using HPLC. Fig. 2a shows the evolution of the photocurrent and HMF concentration [HMF], over 64 h (data has been averaged from three independent runs). We note that the measured photocurrent was lower than expected from Fig. 1c due to the increased substrate resistance of the larger area photoanodes.31,34 In addition, the photocurrent decreases from an initial 0.3 to 0.1 mA cm⁻² over 64 h of continuous operation due to the depletion of oxidizable substrate (at the applied potential no photocurrent from the OER was observed in the absence of HMF). Indeed [HMF] decreased to ca. 200 mM. In contrast, only a 12% decrease in [HMF] was observed in a control experiment without WO3 where the 5 mM HMF electrolyte was irradiated for 64 hours (see Fig. S2 and Table S1, ESI†). This small decrease in...
[HMF] results from its photo-decomposition which has been reported previously.\textsuperscript{14,35,36}

We note that no obvious corrosion of the WO\textsubscript{3} photoanode was observed via scanning electron microscopy during extended operation (see Fig. S3, ESI\textsuperscript{†}). This confirms the stability of the anode under these operation conditions.

The detected products formed during the continuous photo-oxidation with WO\textsubscript{3} are shown in Fig. 2b. 2,5-furandicarboxaldehyde (DFF), 5-hydroxymethyl-2-furan-carboxylic acid (HMFCA), 5-formyl-2-furancarboxylic acid (FFCA), and 2,5-furandicarboxylic acid (FDCA) are observed. It appears that DFF and FFCA are the primary products, with DFF being formed first at yields up to 4\% (based on HMF), while FFCA and finally FDCA appear later, as expected from the established oxidation pathways\textsuperscript{37} (Fig. 2c). While the FDCA concentration is still slightly increasing after 64 hours, its yield is quite modest (ca. 25 \textmu M, 0.5\% based on HMF), and raises important questions about the reaction pathways and reaction kinetics occurring during the direct oxidation at the photoanode. Indeed, we note that the amount of consumed HMF is not equivalent to the amount of produced DFF and HMFCA. Moreover, the FDCA production rate appears smaller than the FFCA oxidation rate. This implies that side reactions involving the HMF and the other small molecules is occurring. We note that the formation of macromolecular humin by-products has been previously reported to occur with HMF oxidation.\textsuperscript{38}

Given the relatively complex reaction pathways, the limited yield of FDCA compared to the other products, and the possible production of macromolecular by-products, we next developed a model of the photo-electrochemical oxidation reactions. The set of differential equations describing the evolution of the concentration of the reactants/products and an equation for the photocurrent were solved numerically and fit with pseudo first order reaction rate constants, \( k \)'s, defined in Fig. 2c (see ESI\textsuperscript{†} for full details and explanation). Briefly, we considered that the concentration of photogenerated holes at the WO\textsubscript{3} surface to be in excess, and that mass transfer from the bulk of the electrolyte to the surface of the photoanode to be similar for all components (see Fig. S4 and S5, ESI\textsuperscript{†}). To obtain reasonable rate constant fitting, we accounted for the formation of unknown oxidation by-products, B, by the oxidation of the known products, and the further oxidation of these species (into B\textsuperscript{*}), as shown in Fig. 2c, which is consistent with the formation of macromolecular oxidation products. The simulated photocurrent and product concentrations from the fit model are shown as dashed lines in Fig. 2a and b, and the obtained reaction rate constants (shown in Table 1) with given standard error show a high-quality fit. Moreover, these values give quantitative insight to the oxidation pathways on the WO\textsubscript{3} photoanode. Since the rate constant for DFF production (\( k_{11} \)) is 2.5 times larger than for HMFCA production (\( k_{12} \)), it appears that the oxidation of HMF to DFF is preferred. This result is corroborated by LSV performed with only HMF, DFF, or the diol, 2,5-bis(hydroxymethyl)furan (BHMF), which shows a higher photocurrent for HMF or BHMF compared to DFF, implying that WO\textsubscript{3} reacts faster with the alcohol moiety (see Fig. S6,
Table 1  Pseudo-first order rate constants for oxidation by WO₃ photoanode at 0.68 V vs. RHE (pH 4, 3 Sun illumination), as extracted from model fitting (see reactions Fig. 2c).

| Rate constant* (× 10⁻³ h⁻¹) | Rate constant (× 10⁻³ h⁻¹) |
|-------------------------------|-----------------------------|
| k₁¹ | 5.54 (0.19) | k₉¹ | 30.2 (0.4) |
| k₁₂ | 1.82 (0.05) | k₉₂¹ | 43.5 (7.1) |
| k₂¹ | 64.9 (4.1) | k₈₂² | 0.03 (8.4) |
| k₂₂ | 38.0 (8.5) | k₈₃ | 54.5 (4.3) |
| k₃ | 7.30 (0.39) | k₉₄ | 72.2 (5.9) |
| k₉ | 1.73 (0.27) |

* Standard error from fitting the averaged experimental data in parentheses.

Regarding the formation of unknown by-products, this generally occurs faster than oxidation by the known pathways. For example, the oxidation of HMF to either DFF or HMFCA is 4 times slower than the oxidation of HMF to the likely humin by-products. As an exception, the oxidation of HMFCA to FFCA occurs relatively fast (k₁₂²) compared to its competing oxidation to by-product (k₈₂²). This suggests that FDCA yield may be improved by driving the reaction through the HMFCA pathway. Finally, we note that the desired FDCA product is further oxidized at the WO₃ surface (as verified by LSV, Fig. S7, ESI†), and this by-product reaction appears to occur with the fastest rate constant. Thus, the low FDCA yield is in part due to its quick oxidation with the photogenerated holes at the WO₃ surface. Overall, it is clear that identifying strategies to reduce the rate of the by-product reactions (i.e. by adding a selective surface catalyst) will be needed to further advance the direct PEC production of FDCA.

Conclusions

In summary, we demonstrate the first example of direct PEC oxidation of HMF to DFF and FDCA. The unique reactivity of WO₃, including its known poor selectivity for the OER and stability in aqueous acidic electrolyte are likely contributing factors towards its unique ability to directly photo-oxidize HMF under aqueous conditions, while suppressing the water oxidation reaction. A maximum yield of DFF up to ca. 4% was observed under prolonged operation, and although yields of FDCA remain modest at < 1%, modelling the reaction kinetics suggests that increasing the rate of intermediate HMFCA production and reducing the unwanted oxidation by-products can lead to further improvements. Overall, this demonstration represents an important simplification over previous work and progresses PEC systems towards the scalable and economical production of both solar fuels and valorized biomass products—without requiring the sluggish OER.

Conflicts of interest

There are no conflicts to declare.

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