

# SELECTIVE SUN-DRIVEN OXIDATION OF CELLULOSIC BIOMASS DERIVATIVES FOR THE SYNTHESIS OF ADDED VALUE CHEMICALS

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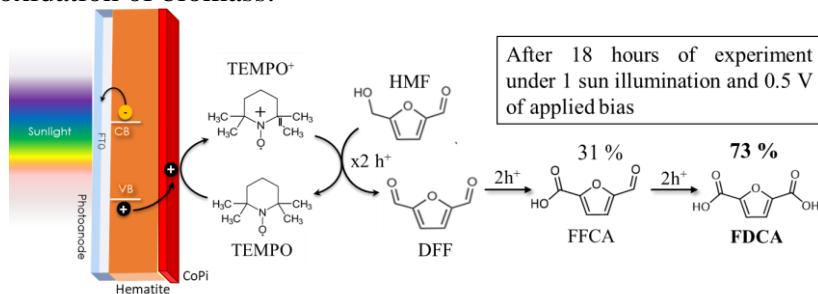
## ABSTRACT

Sun-driven oxidative chemistry aimed at the preparation of high-value chemicals of industrial/pharmaceutical interest is one of the most interesting applications of photoelectrosynthetic cells. Semiconductor-based devices can be exploited to promote different redox processes and, among them, transformations of organic molecules for the synthesis of high-value products under less drastic conditions than traditional organic synthesis methods. In particular, hematite ( $\alpha\text{-Fe}_2\text{O}_3$ ) is an n-type semiconductor that exhibits the target characteristics of a photoanodic material for oxidation reactions, with a band gap of 2.1 eV, which allows for visible-light absorption, stability in aqueous basic environment and environmental compatibility and benignity [1].

Hematite photoelectrodes are able to oxidize biomass and have been used by us in HMF photo-electro oxidation into FDCA driven by Cobalt phosphate-modified Ti: $\text{Fe}_2\text{O}_3$  photoanodes. Electrochemical impedance spectroscopy allowed us to extract and compare charge transfer dynamics in Ti: $\text{Fe}_2\text{O}_3$  for water and HMF oxidation<sup>[2]</sup>. It's been observed that, when hematite electrodes are modified with a Cobalt (III) oxide catalyst with coordinated phosphate (CoPi)<sup>[3]</sup>, photogenerated holes accumulates preferentially on CoPi surface rather than on hematite superficial states. Moreover, adding TEMPO to the electrolyte mixture, which is a redox mediator that starts the reaction, the ability of the catalyst to accumulate charges decreases, meaning that charge transfer processes become faster, and demonstrating that, compared with water oxidation, CoPi is selective toward TEMPO-mediated oxidation of biomass.

Because of the competition with OER, a full conversion of HMF to FDCA is not completely achieved. However, the presence of CoPi on the hematite surface enhances the selectivity towards FDCA, increasing the reaction yield from 50 % to 73% of conversion into the target product.

The reaction it's been conducted in basic aqueous conditions at room temperature, under sunlight illumination with the application of a low bias, milder and environmentally friendly conditions with respect to the traditional industrial production processes of FDCA.



**Figure 1.** Mechanism and reaction yield of HMF photo-oxidation driven by Ti: $\text{Fe}_2\text{O}_3$  electrodes modified with CoPi catalyst.

## REFERENCES

- [1] F.E. Osterloh, Solar Energy for Fuels, (2015) 105-142
- [2] P. Dias et al., Nano Energy 38 (2017) 218–231
- [3] J. Chadderdon et al., ChemElectroChem, 6, (2019), 3387–3392