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PHOTO- AND ELECTRO-CATALYTIC OXIDATION OF BIOMASS DERIVED 5-HYDROXYMETHYLFURFURAL TO 2,5-DIFORMYLFURAN OR 2,5-FURANDICARBOXYLIC ACID

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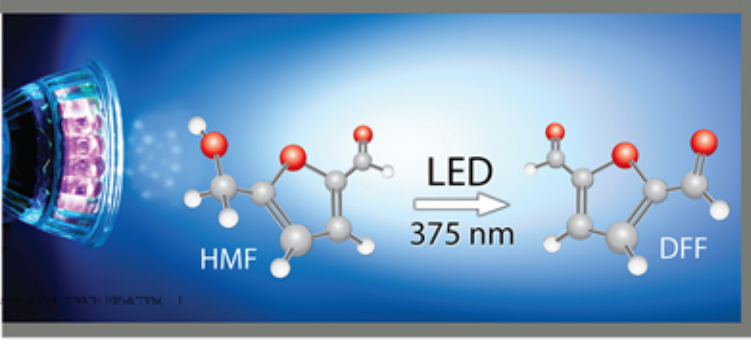


SYNOPSIS

Selective catalytic oxidation is a promising candidate for the valorization of chemicals derived from lignocellulosic biomass. 5-hydroxymethylfurfural (HMF) is a well-known biomass derived furan compound, an important raw material for the generation of other furan derivatives. Partial oxidation of HMF can lead to 5-diformyl furan (DFF), which can be used as a precursor for the bio-oriented synthesis of pharmaceuticals, antifungal agent, organic conductor, and bio-polymer. In this study (***D. A. Giannakoudakis et al, App. Cat. B, 2019, 256, 117803***), light assisted selective oxidation of HMF to DFF at ambient conditions has been carried out using nanostructured manganese oxide as a catalyst.

Synthesis & Characterizations

Synthesis: ultra-slow controlled precipitation

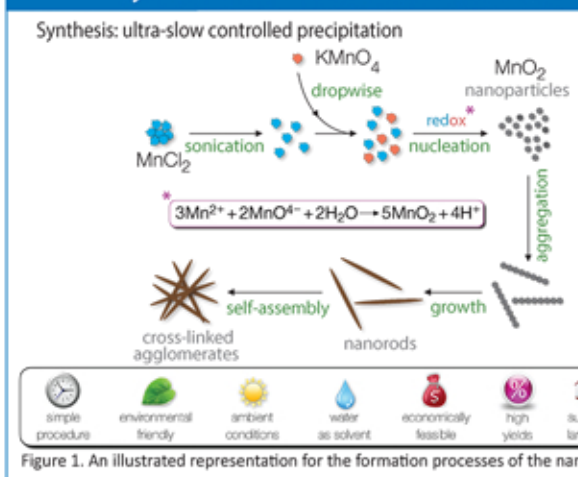


Figure 1. An illustrated representation for the formation processes of the nanocatalyst.

Characterizations outcomes

- body-centered tetragonal α-MnO_2
- surface area: 38.5 m^2/g
- total pore volume: 0.336 cm^3/g
- thermally stable up to 400 °C
- cross-linked uniform nanorods
- diam.: 10-55 nm
- length: 150-1500 nm

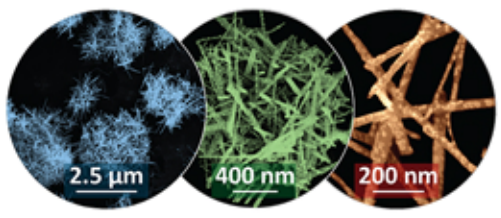


Figure 2. SEM images of the nanocatalyst at different magnifications.

Photoreactor & resusability

- ambient conditions (temperature control by air flow)
- low energy UV emittion (375 nm)
- 18 InGaN single LED chip (max 200 mW each)

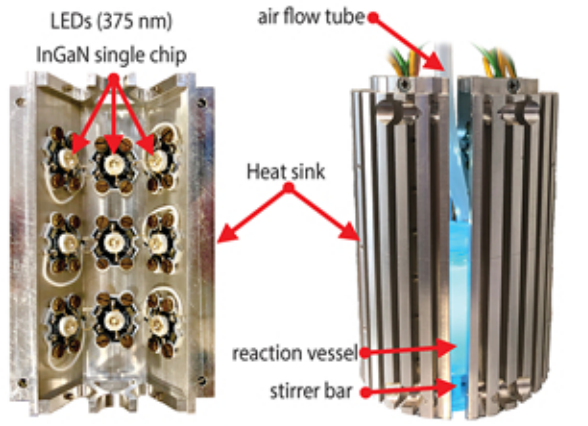
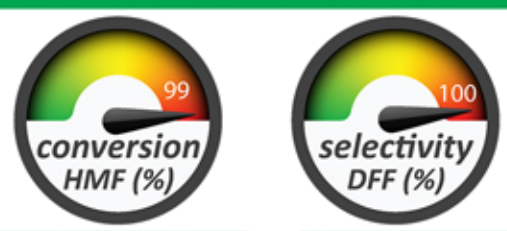


Figure 5. Photos of the homemade LED photo-reactor; on the left the interior array of the LEDs and on the right the running experimental setup.

Characterizations of the spent samples

- the strucural and surface chemistry features did not change
- negligible adsorption
- no Mn leaching

Photo-asssited oxidation results



- ambient conditions (23-39 °C, 1 atm)
- solvents: water or acetonitrile
- additive free (no oxidant or gas purging)
- photo-assisted heteregeneous thermo-catalysis
- light ehnance the conversion rate (0.120 mmol/min)

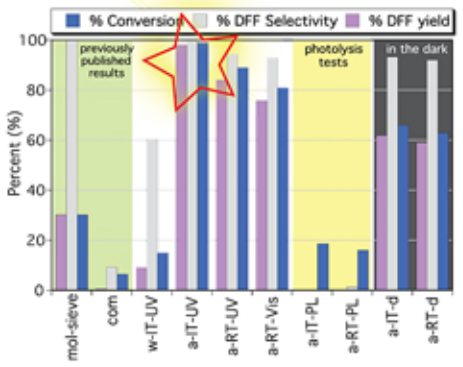
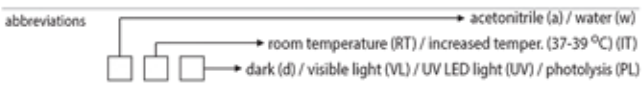


Figure 3. HMF conversion, DFF yield & selectivity under different reaction conditions; previous literature results with MnO_2 materials are included for comparison.



MECHANISTIC INSIGHTS

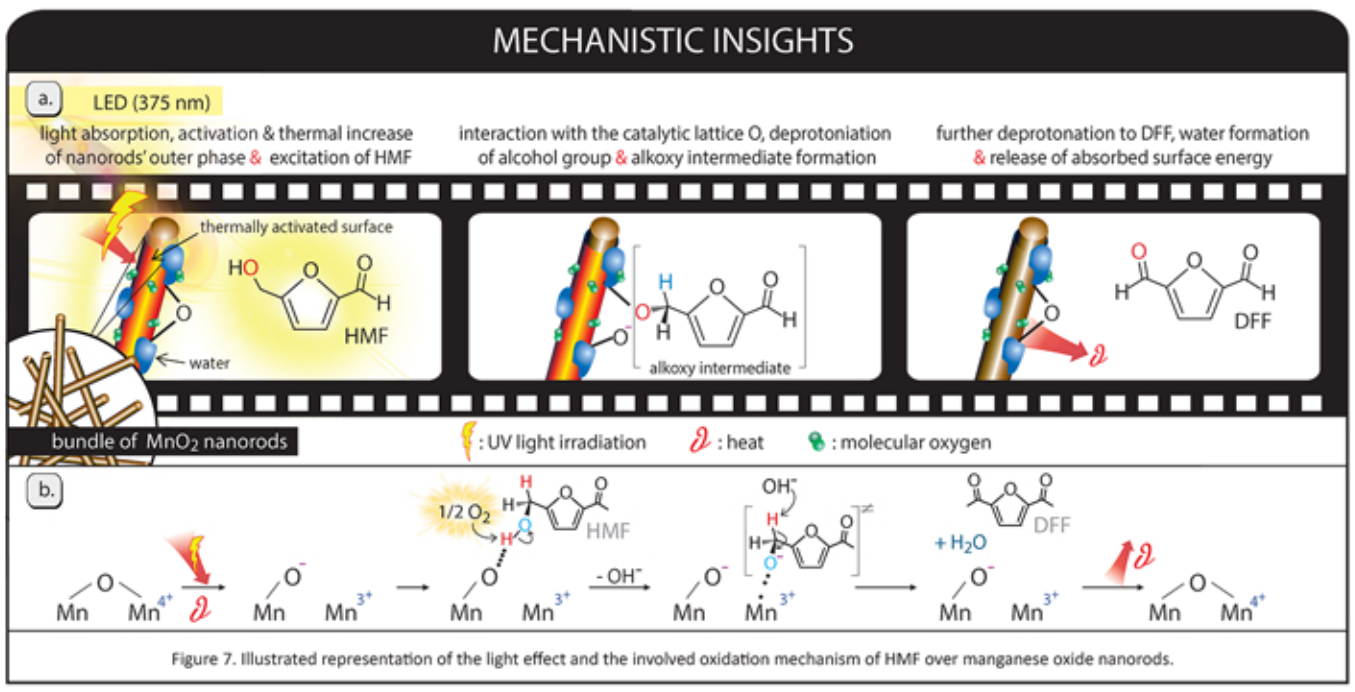


Figure 7. Illustrated representation of the light effect and the involved oxidation mechanism of HMF over manganese oxide nanorods.

CONCLUSIONS

A Controlled precipitation led to MnO_2 nanorods of 10 to 55 nm in diameter.
The nanostructured material is thermaly stable and absorb light in the entire UV-Vis range.

B The nano-material acts as a perfect and stable photo-assisted thermo-catalyst.
100 % HMF conversion & DFF selectivity at ambient conditions without additives.

C Mechanistic key aspects of HMF Oxidation:
1) Mn^{4+} <--> Mn^{3+} redox cycle
2) contibution of molecular oxygen
3) lattive O involvement
4) formation of an alkoxy intermediate

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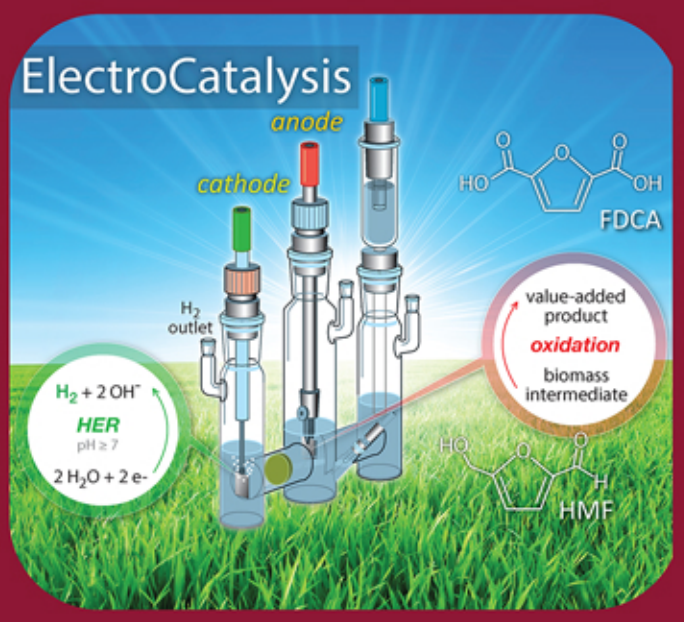

images from the literature

ElectoCatalytic Oxidation (ECO)

In highly basic environment (pH>13), almost 100% HMF conversion and FDCA yield can be achieved. Also possible to achieve moderate high FDCA selectivity at strongly acidic environment (pH=1).