Tailored Plasmonic Au@MnO_2 Nanoparticles for Selective Light-Driven Oxidation of 5-Hydroxymethylfurfural

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INTRODUCTION & AIM

- **Sustainable valorization of biomass** is a key pillar of **green chemistry** and circular economy
- **5-Hydroxymethylfurfural (HMF)** is a versatile platform molecule for producing high-value **bioplastics** such as 2,5-furandicarboxylic acid (FDCA)
- Traditional oxidation methods rely on **harsh conditions** (high T, strong oxidants), limiting selectivity and sustainability
- **Plasmonic light-assisted catalysis** with gold nanoparticles (AuNPs) offers mild, tunable oxidation

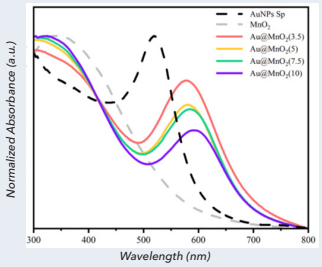
OBJECTIVE: understand how **MnO_2 shell thickness** and **irradiation wavelength** (365 nm vs. 450 nm) control HMF oxidation **selectivity and efficiency**, providing insight into **light-driven biomass valorization**

MATERIALS & METHODS

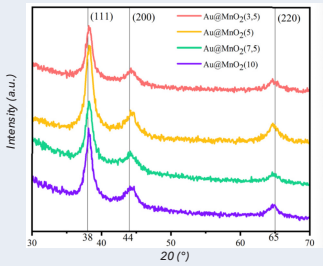
SYNTHESIS

- **Synthesis of NPs:** synthesized via the standard citrate reduction method
- **MnO_2 shells (3.5, 5.0, 7.5, 10.0 nm):** via hydrothermal method with controlled $KMnO_4$ reduction in alkaline medium
- **Deposition on ZrO_2 support**: enhanced dispersibility and catalytic stability, Lewis acidic sites promote selectivity, porous structure improves active-site accessibility

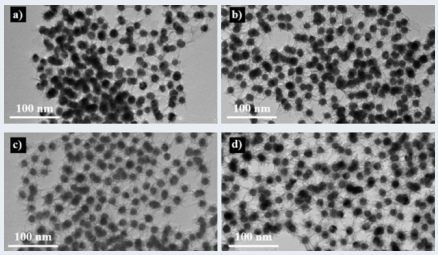
CHARACTERIZATION



UV ViS spectra of Au@MnO_2 core-shell NPs and comparson wit, Au NPs and MnO_2 spectra



X-Ray Powder Diffraction of Au@MnO_2 core-shell NPs



TEM images of Au@MnO_2 with different thicknesses of MnO_2 layers: (a) 3,5 nm, (b) 5 nm, (c) 7,5 nm, and (d) 10 nm

RESULTS & DISCUSSION

CATALYTIC TESTS

- 5 mg catalyst, 25 mM HMF, 3 mol NaOH eq., 4 h, 40 °C
- **LED irradiation:** 365 nm vs. 450 nm
- Control experiments: dark, no base, bare AuNPs

TABLE 1

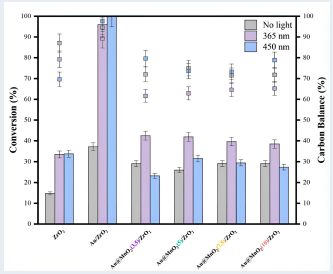
***Blank tests** under various illumination and reaction conditions, **without catalyst**, at ambient temperature and pressure*

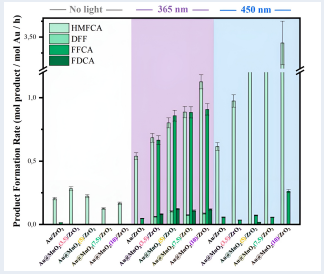
Light (nm)	NaOH	Conv. (%)	Sel. DFF (%)	Sel. HMFCA (%)	Sel. FDCA (%)	C.B. (%)
365	–	62.50	0.00	0.14	0.00	37.72
450	–	1.29	7.28	4.77	0.00	98.92
–	–	4.76	0.00	0.16	0.00	95.46
365	2:1	45.89	0.30	4.27	0.00	58.39
450	2:1	33.48	0.00	4.31	0.00	68.10
–	2:1	11.09	0.00	5.69	0.00	89.60

TABLE 2

*Blank tests under different illumination and reaction conditions using 5 mg **ZrO_2 alone** and 5 mg **unsupported MnO_2 nanomaterials**: (1) nanowires and (2) nanoflowers*

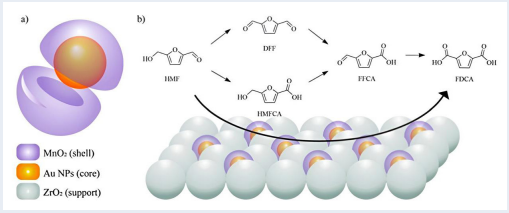
Catalyst	Light (nm)	Conv. (%)	Sel. DFF (%)	Sel. HMFCA (%)	Sel. FFCA (%)	Sel. FDCA (%)	C.B. (%)
ZrO_2	–	14.8	0.00	11.56	0.89	0.00	87.04
ZrO_2	365	33.8	0.00	5.27	4.43	0.48	69.64
ZrO_2	450	33.51	0.00	35.70	2.03	0.40	79.27
MnO_2(1)	365	19.9	0.91	2.02	0.67	0.47	80.91
MnO_2(2)	365	30.46	0.35	0.07	0.32	0.32	69.87





***Conversion** of the 5-HMF and **carbon balance** during the reaction performed under thermal (40°C, no light) and photochemical conditions (365 nm and 450 nm)*

CONDITION	HMF CONVERSION	SELECTIVITY HIGHLIGHTS	CARBON BALANCE
Thermal, dark	30%	Mainly HMFCA	High
365 nm	70%	Higher selectivity for FFCA & FDCA	Moderate
450 nm	60%	Higher selectivity for HMFCA	High



Oxidation pathway of 5-HMF

CONCLUSION & FUTURE DIRECTIONS

- **Au@MnO_2 nanoparticles** successfully merge **plasmonic enhancement** with **catalytic selectivity**
- **Photocatalytic HMF oxidation** is tunable via **light wavelength** and **MnO_2 shell thickness**
- **10 nm MnO_2 shell:** optimal balance of activity, selectivity, and stability

FUTURE DIRECTIONS

- **In situ spectroscopy** to monitor reactive intermediates
- **Extended illumination studies** to assess long-term stability
- Exploration of **other biomass-derived molecules** for sustainable chemical production

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