Supporting Information.Tailored plasmonic gold nanoparticles coated with manganese oxide for selective light-driven oxidation of 5-hydroxymethylfurfural.

Table S1 Volumes of 10 mM $KMnO_4$ and $Na_2C_2O_4$ solutions used for achieving different thicknesses of MnO_2 over the Au nanoparticles (15 nm).

Nominal MnO_2 overlayer (nm)	3.5	5.0	7.5	10.0
Volume of 10.0 mM $KMnO_4$ (μL)	164.5	270.0	523.1	855.0
Volume of 10.0 mM $Na_2C_2O_4$ (μL)	32.9	50.0	101.6	171.0

Table S2 Volumes required to obtain 1% weight loading in 50 mg of ZrO_2.

Au@MnO_2 shell thickness (nm)	Volume (mL)	Mass Au (g)	Mass MnO_2 (g)	Total (g)
10.0	1.055	0.252	0.248	0.500
7.5	1.307	0.312	0.188	0.500
5.0	1.597	0.382	0.118	0.500
3.5	1.760	0.421	0.079	0.500

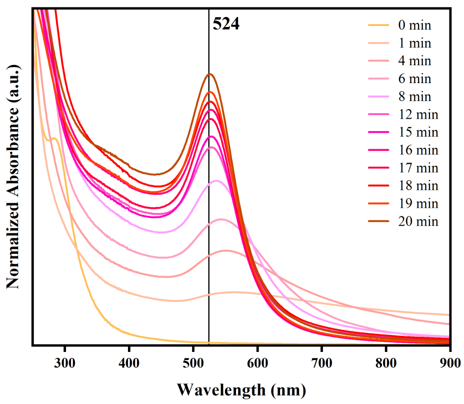


Fig. S1 Time-dependent UV–Vis absorbance monitoring of gold nanoparticle formation following the addition of sodium citrate.

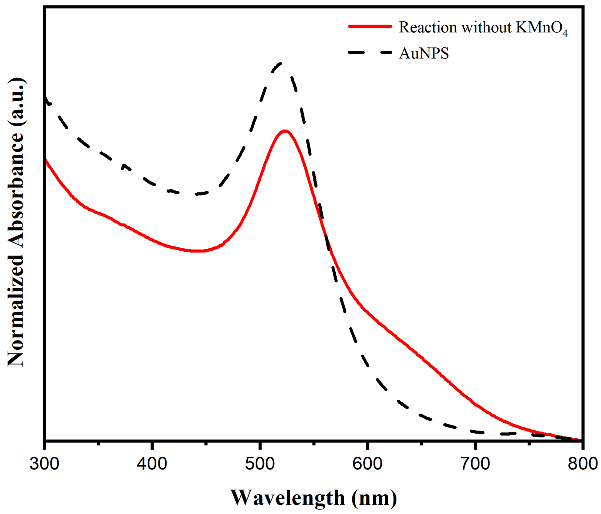


Fig. S2 Control test without $KMnO_4$. The spectrum is normalized for the extinction at the top of the LSPR band.

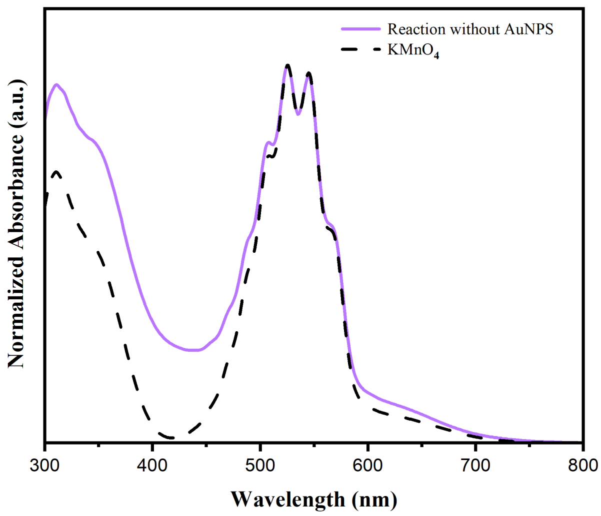


Fig. S3 Control test without Au NPs. The spectrum is normalized for the extinction at the top of the LSPR band.

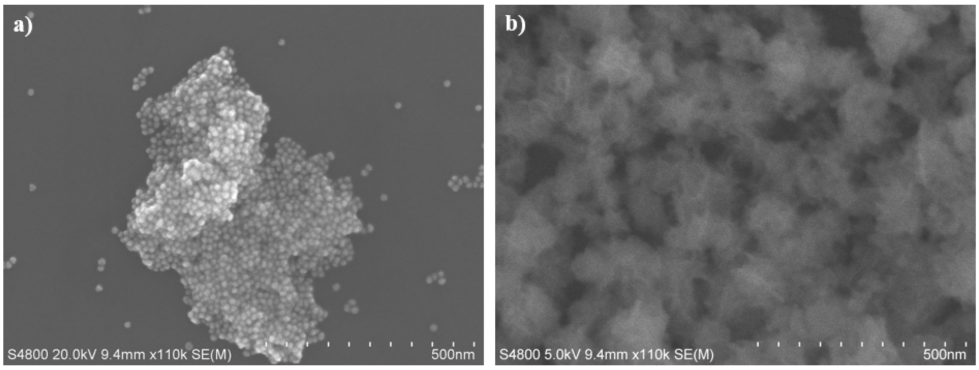


Fig. S4 (a) SEM images from the control experiment without the use of $KMnO_4$ (b) SEM images from the control experiment without the use of AuNPs.

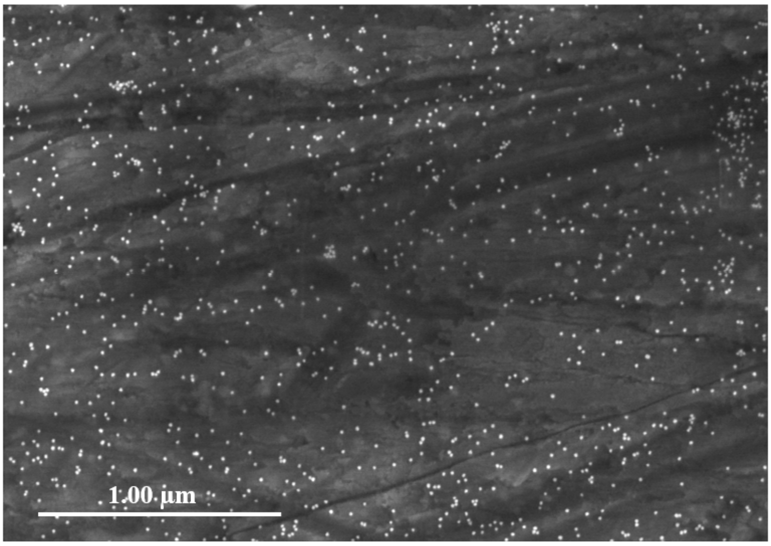


Fig. S5 SEM images of AuSp NPs.

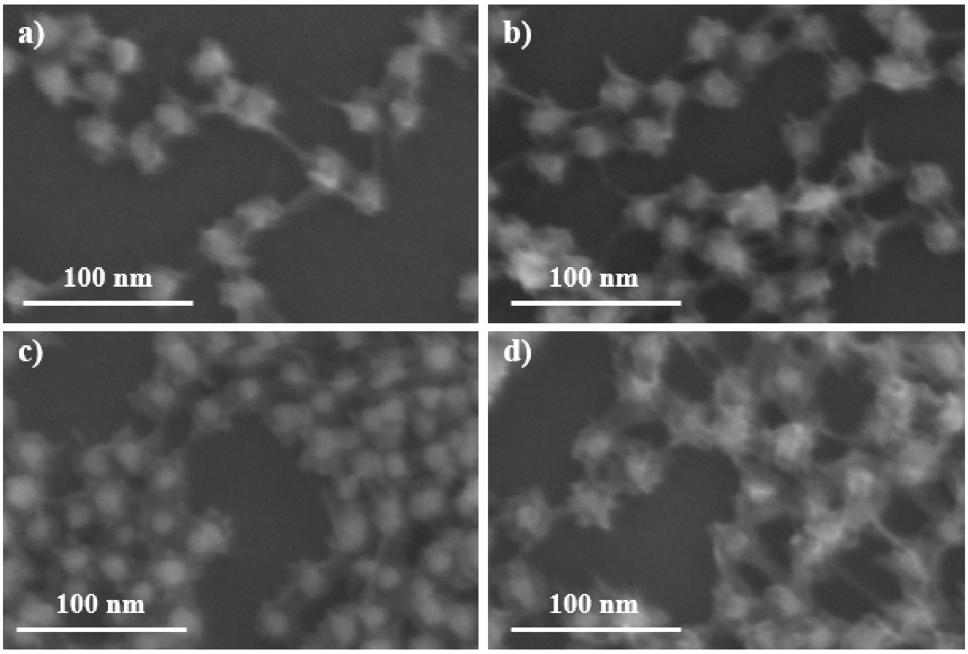


Fig. S6 (a) SEM images of Au@MnO_2 with a 3.5 nm thick layer (b) SEM images of Au@MnO_2 with a 5 nm thick layer (c) SEM images of Au@MnO_2 with a 7.5 nm thick layer (d) SEM images of Au@MnO_2 with a 10 nm thick layer.

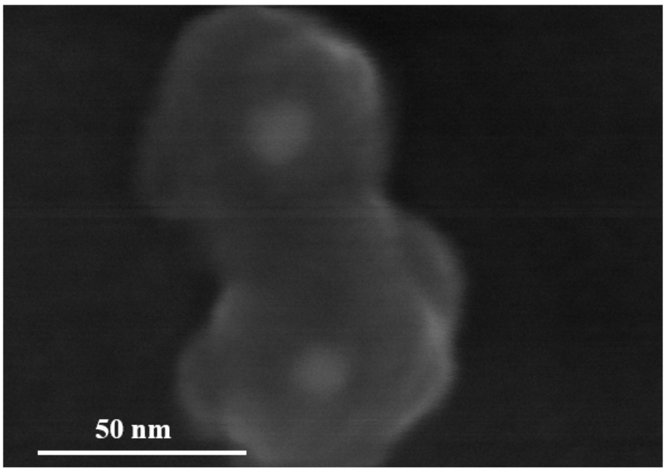
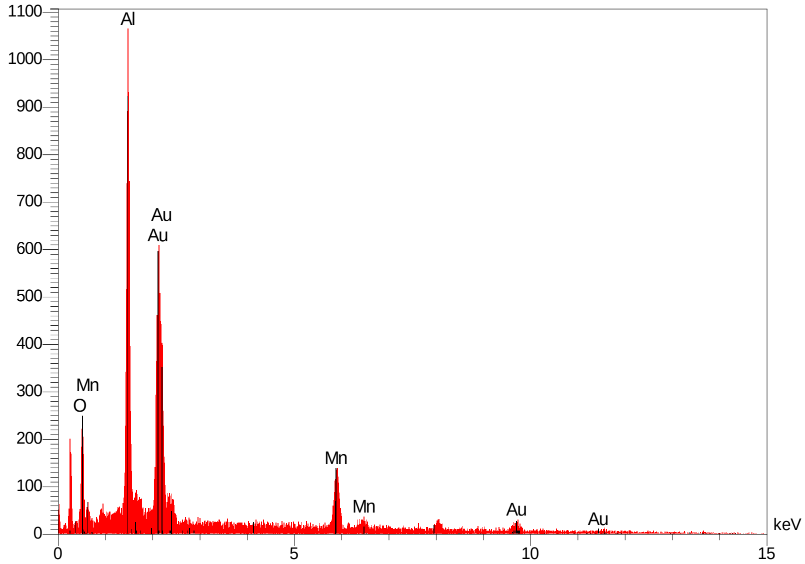


Fig. S7 SEM images of Au@MnO_2 (10 nm) after one year in aqueous solution.



Elt	Ligne	Int	Erreur	K	Kr	P%	A%	ZAF	Formule	Ox%	Pk/Bg
O	Ka	35.0	2.3836	0.0667	0.0490	14.58	45.27	0.3358		0.00	18.44
Al	Ka	192.9	6.2976	0.1617	0.1187	16.04	29.54	0.7402		0.00	27.40
Mn	Ka	37.0	0.7376	0.1620	0.1190	11.78	10.66	1.0097		0.00	9.14
Au	La	4.3	0.4984	0.6096	0.4477	57.60	14.53	0.7772		0.00	3.00
				1.0000	0.7343	100.00	100.00			0.00	

Fig. S8 Results of the EDX analysis showing the detected elements.

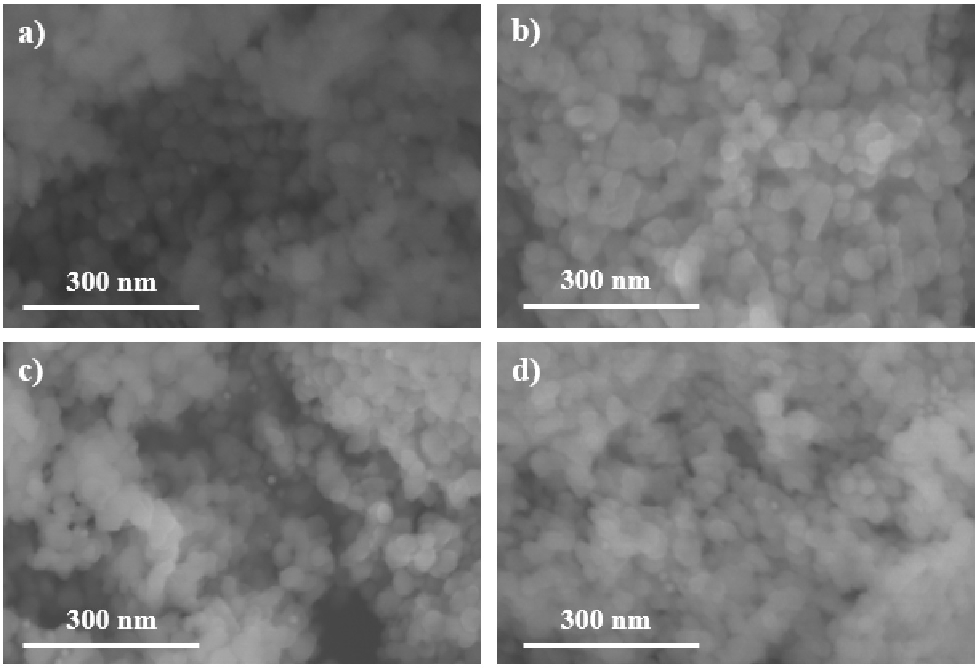


Fig. S9 (a) SEM images of Au@MnO_2 with a 10 nm thick layer on ZrO_2 (b) SEM images of Au@MnO_2 with a 7.5 nm thick layer on ZrO_2 (c) SEM images of Au@MnO_2 with a 5 nm thick layer on ZrO_2 (d) SEM images of Au@MnO_2 with a 3.5 nm thick layer on ZrO_2.

Table S3 Comparison of Au/MnO_2 and Au@MnO_2 systems for the oxidation of HMF under various reaction conditions. HMF/Au represents the molar ratio, T the temperature, t the reaction time, C the conversion, S the selectivity, and r the product formation rate. The results for Au@MnO_2 were obtained under irradiation at 365 nm UV light.

Catalyst	HMF/Au	Solvent	T (°C)	t (h)	C (%)	S_{HMFCA} (%)	r_{HMFCA}	S_{DFF} (%)	r_{DFF}	S_{FFCA} (%)	r_{FFCA}	S_{FDCA} (%)	r_{FDCA}	C.B. (%)	Ref
Au/MnO_2	20.82	Water	100	12	75.7	1.40	0.01	-	-	0.10	0.00	68.70	0.29	70.2	[1]
Au/MnO_2	9.33	Water	100	12	99.0	3.20	0.00	-	-	0.40	0.00	94.10	0.01	97.7	[1]
Au/MnO_2 microsphere	458.06	DMF	120	8	82.0	-	-	99.00	10.20	-	-	-	-	-	[2]
Au/MnO_2 blocky	458.06	DMF	120	8	72.0	-	-	99.00	15.87	-	-	-	-	-	[2]
Au/MnO_2 wire	458.06	DMF	120	8	57.0	-	-	99.00	24.37	-	-	-	-	-	[2]
Au/MnO_2 microsphere	-	DMF	90	6	29.0	-	-	-	-	-	-	-	-	-	[3]
Au@MnO_2 10 nm	657.34	Water	RT	4	38.5	4.85	4.90	0.38	0.38	3.92	3.96	0.51	0.52	65.2	
Au@MnO_2 7.5 nm	516.04	Water	RT	4	39.6	4.73	3.68	0.40	0.31	4.72	3.68	0.59	0.46	64.5	This work
Au@MnO_2 5 nm	433.63	Water	RT	4	41.9	4.82	3.04	0.63	0.40	5.16	3.25	0.74	0.47	62.9	This work
Au@MnO_2 3.5 nm	393.46	Water	RT	4	42.5	4.47	2.53	0.40	0.23	4.35	2.46	0.53	0.30	61.7	This work

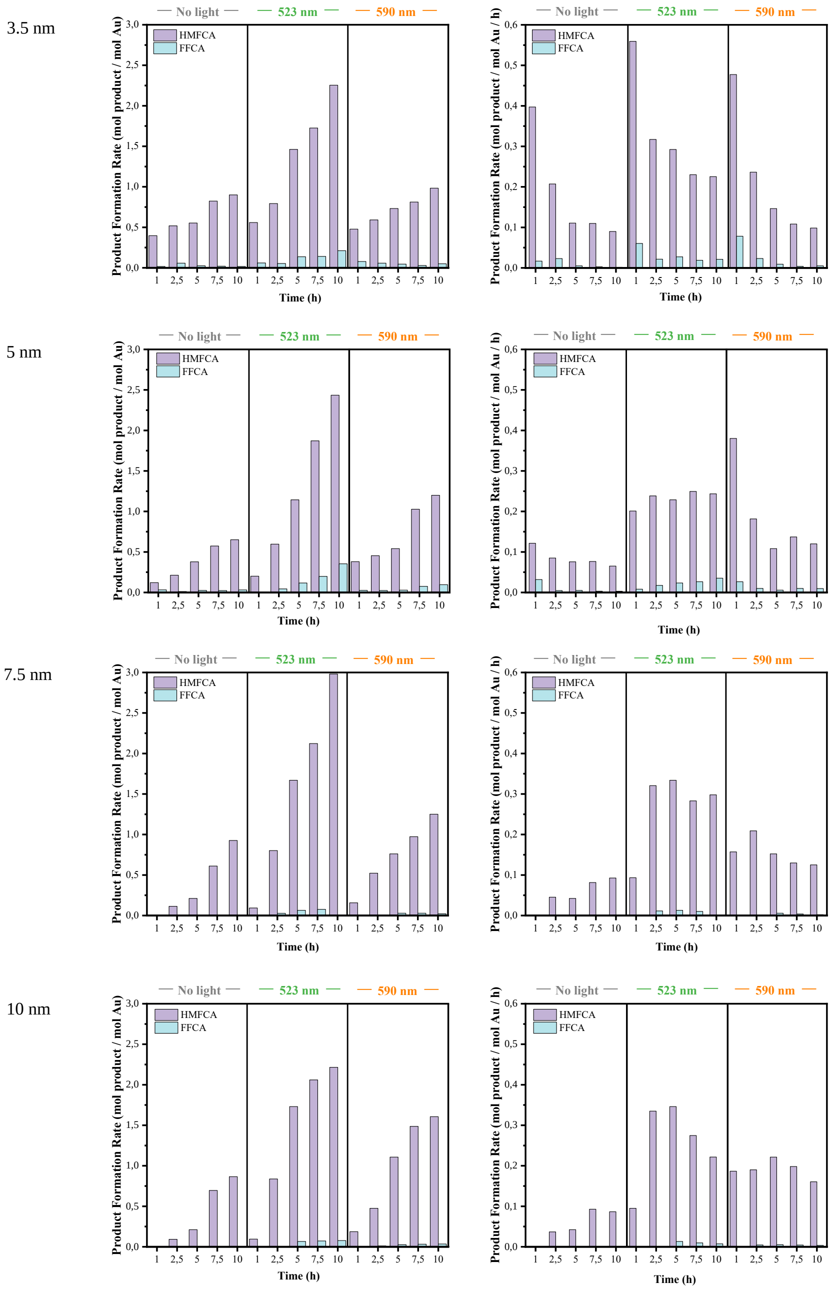


Fig. S10 Evolution of the reaction over time under thermal (40°C, no light) and photochemical conditions (365 nm and 450 nm illumination) as a function of the catalyst used. Formation rates of HMFCA and FFCA during 10 h of reaction using 5 mg of catalyst with 25 mM HMF. The graphs on the right correspond to cumulative histograms, to be compared with the graphs on the left showing the hourly conversion of HMF into HMFCA and FFCA.

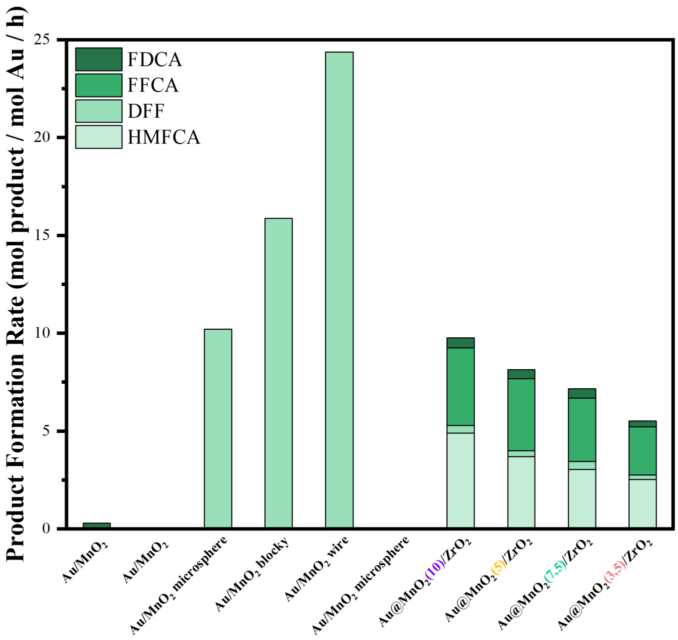


Fig. S11 Comparison of Au/MnO_2 and Au@MnO_2 systems for the oxidation of HMF under various reaction conditions. The results for Au@MnO_2 were obtained under irradiation at 365 nm UV light.

References

[1] Zeng, D., Wang, W., Cui, B., Jiang, B., Zhang, C., Zhang, L., Wang, W.: Base-free selective oxidation of 5-hydroxymethylfurfural to 2,5-furandicarboxylic acid over au/mno_2 catalyst. Fuel **381**, 133238 (2025) https://doi.org/10.1016/j.fuel.2024.133238

[2] Zhu, Y., Shen, M., Xia, Y., Lu, M.: Au/mno_2 nanostructured catalysts and their catalytic performance for the oxidation of 5-(hydroxymethyl)furfural. Catalysis Communications **64**, 37–43 (2015) https://doi.org/10.1016/j.catcom.2015.01.031

[3] Zhu, Y., Lu, M.: Plant-mediated synthesis of au–pd alloy nanoparticles supported on mno_2 nanostructures and their application toward oxidation of 5-(hydroxymethyl)furfural. RSC Advances **5**(104), 85579–85585 (2015) https://doi.org/10.1039/C5RA13157J