Aerobic Oxidation of 5-Hydroxymethylfurfural (HMF) in Aqueous Medium over Fe-Doped-Poly(heptazine imide) Photocatalysts: Unveiling the Bad Role of Hydroxyl Radical Generation on the Catalytic Performance

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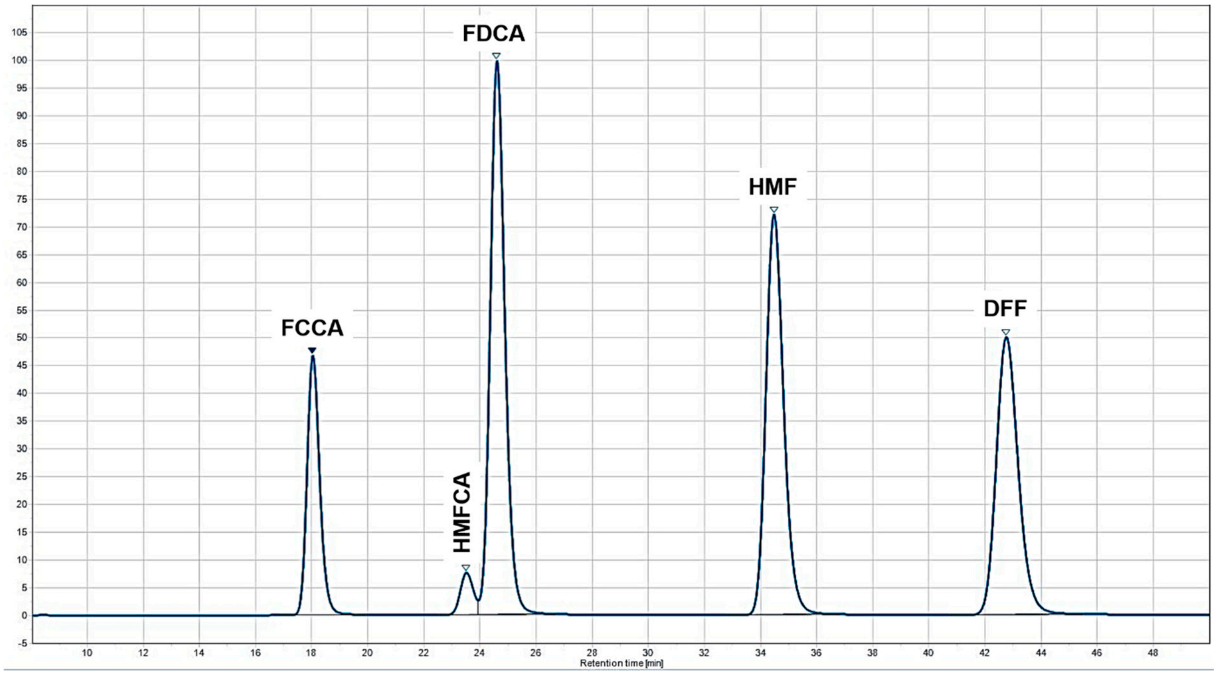

Figure S1. Chromatographic separation of HMF and its oxidation products using the method described in the experimental section.

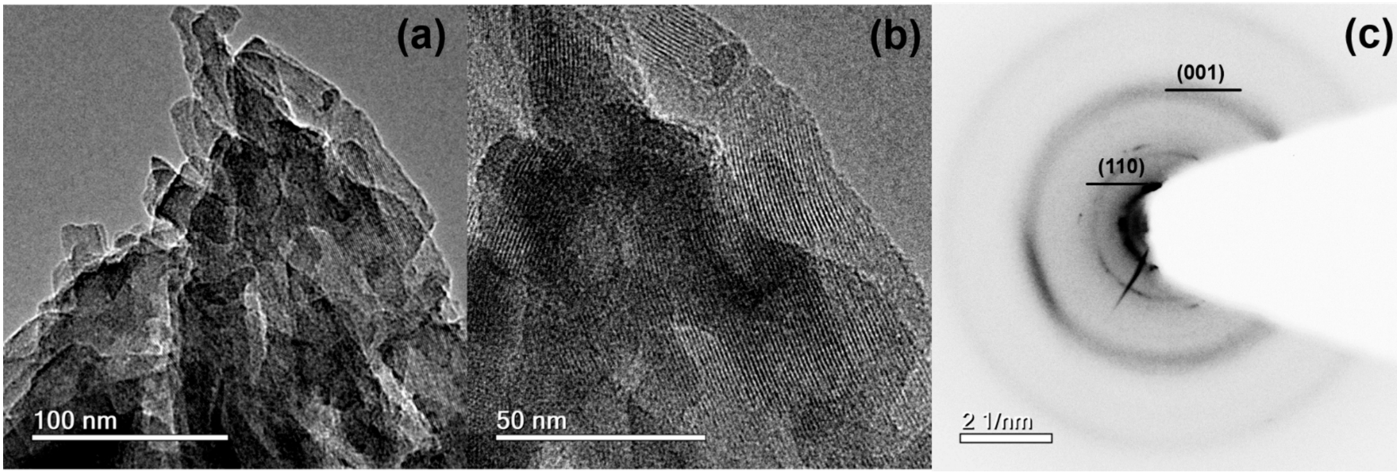

Figure S2. (a), (b) HR-TEM images of PHI(Na), (c) SAED of (b).

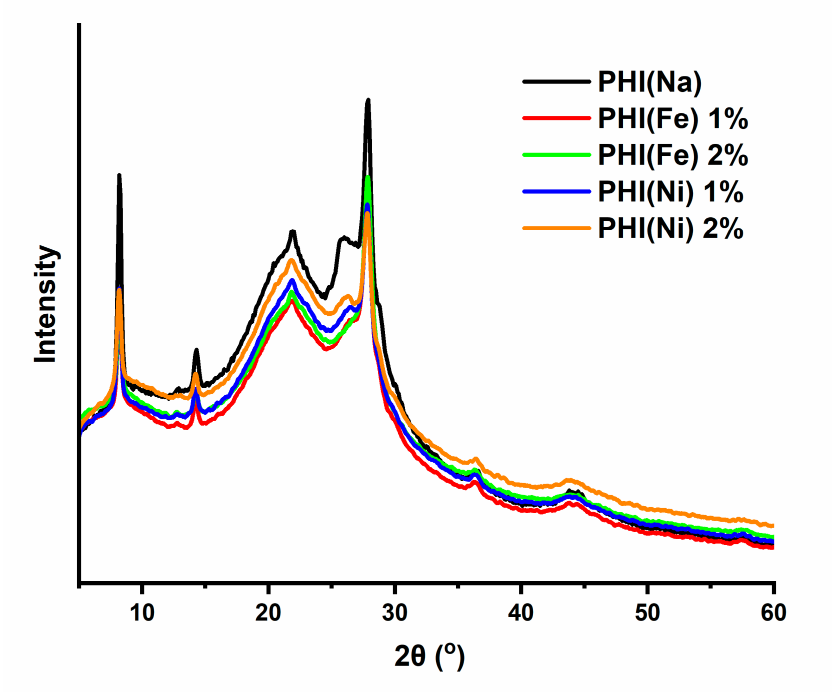

Figure S3. XRD powder pattern for PHI(Na), PHI(Fe) 1%, PHI(Fe) 2%, PHI(Ni) 1% and PHI(Ni) 2%.

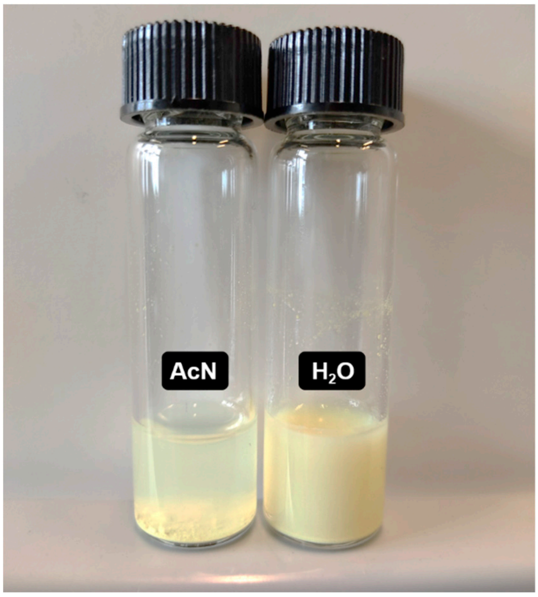

Figure S4. Difference between (Na)PHI suspension in water (H_2O) and acetonitrile (AcN).

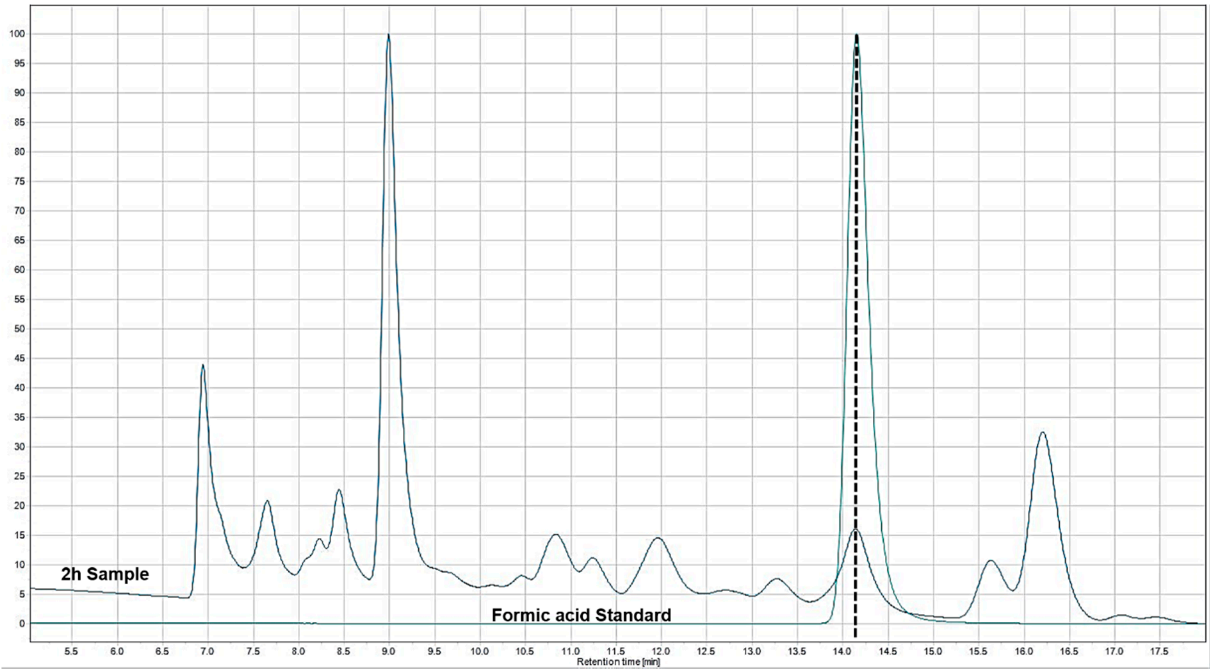

Figure S5. Chromatographic run of the sample collected after 2h of reaction overlapped with formic acid standard.

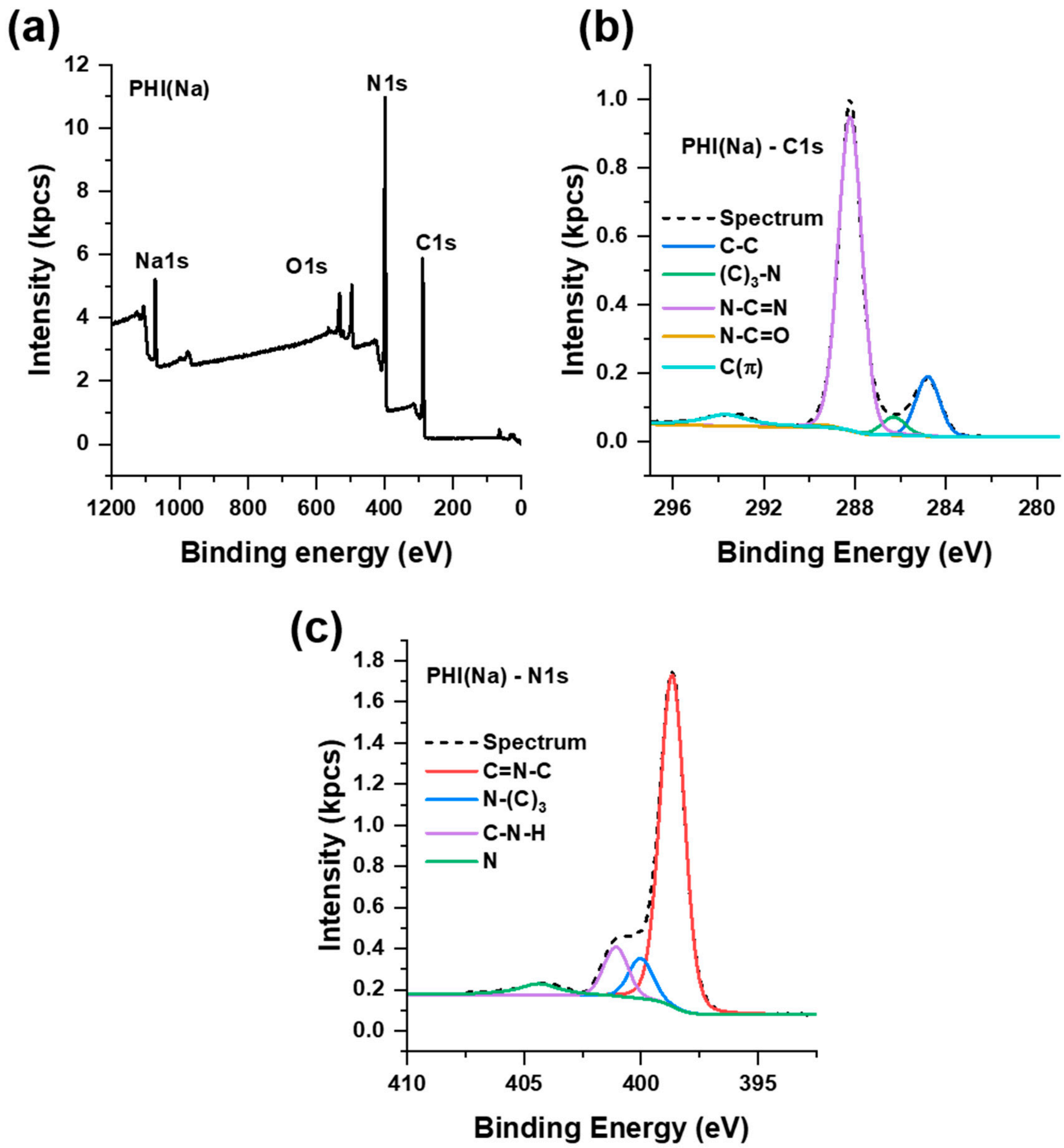

Figure S6. (a) Survey, high resolution spectra of (b) C 1s and (c) N 1s bind energy range for PHI(Na)

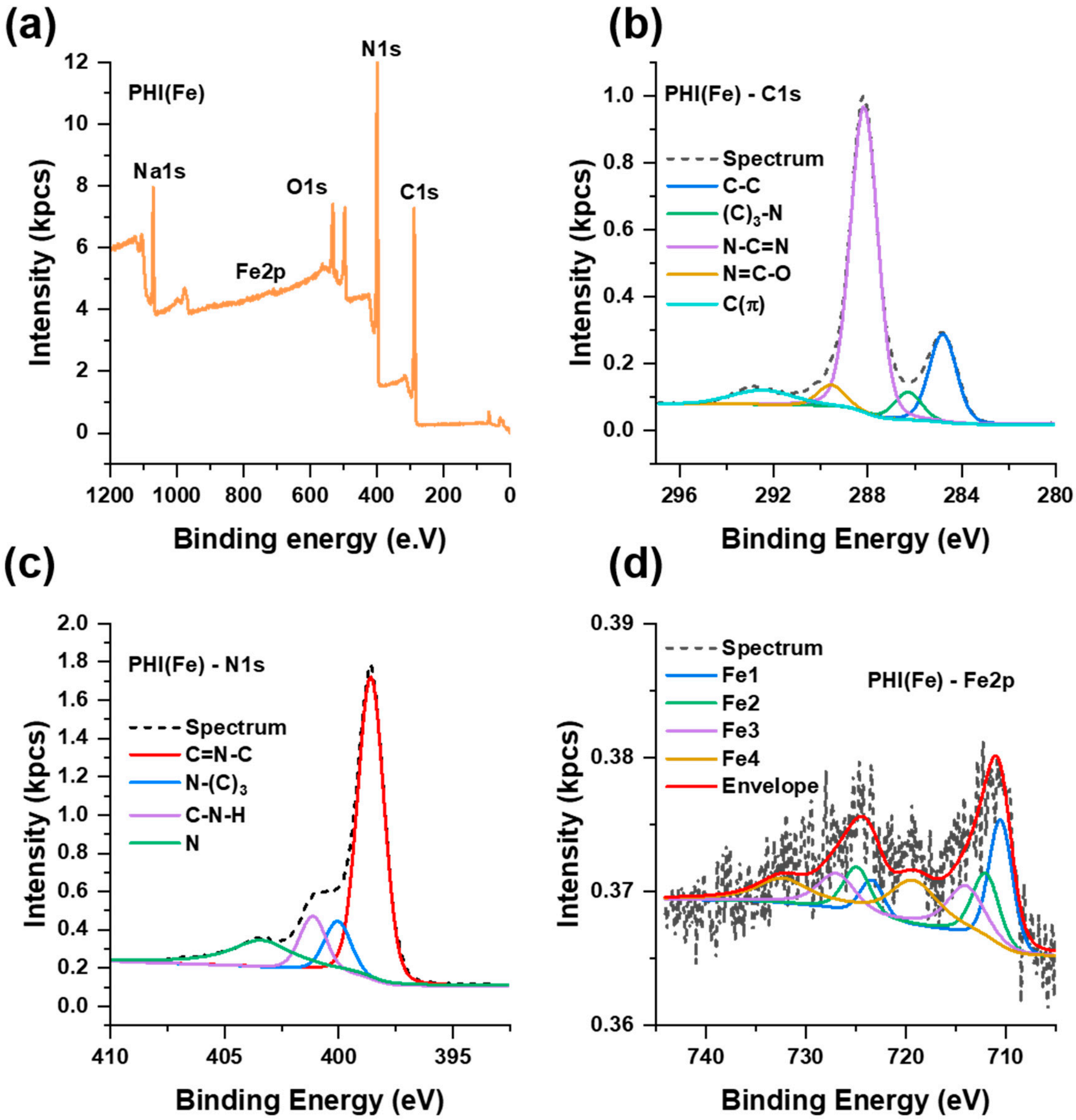

Figure S7. (a) Survey, high resolution spectra of (b) C 1s, (c) N 1s and (d) Fe 2p binding energy range for 0.1 wt% PHI(Fe).

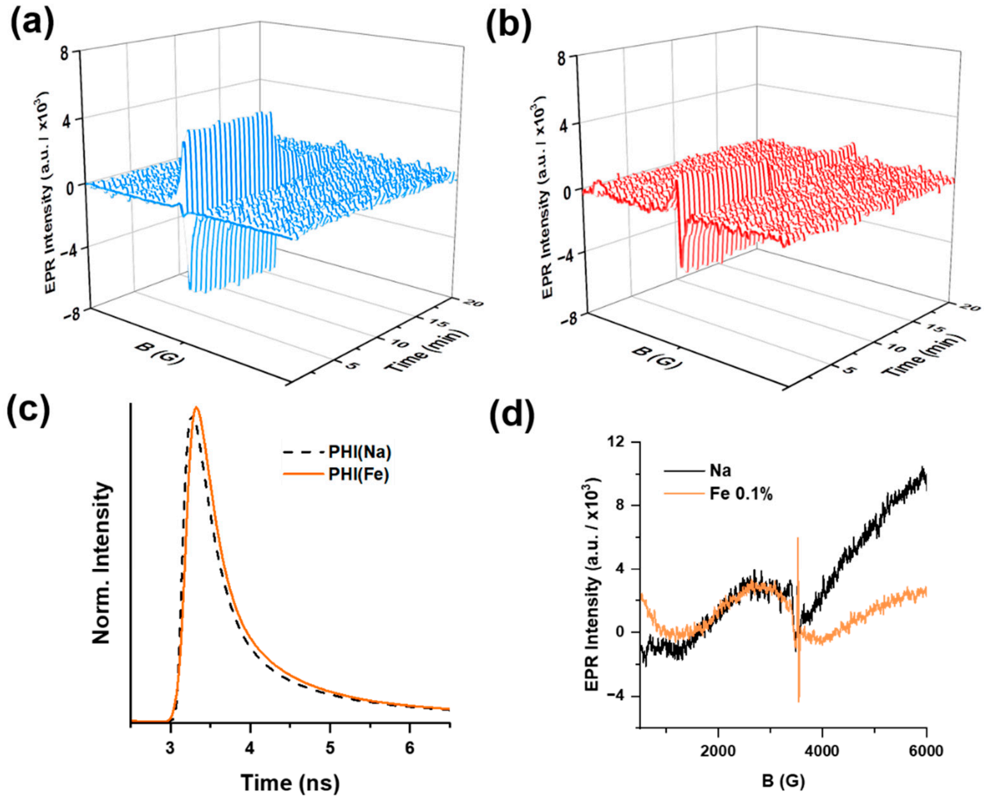

Figure S8. EPR spectra over time recorded in light ON for 10 min and then light OFF for 10 min obtained from (a) 1 wt% Fe PHI (b) 2 wt% Fe PHI, (c) TRPL for PHI(Na) and 0.1 wt% Fe PHI aqueous 5 mM HMF suspensions saturated with O_2 and (d) EPR spectra recorded for PHI(Na) and PHI(Fe) in dark showing the intrinsic signal of carbon nitride at g = 2.004.

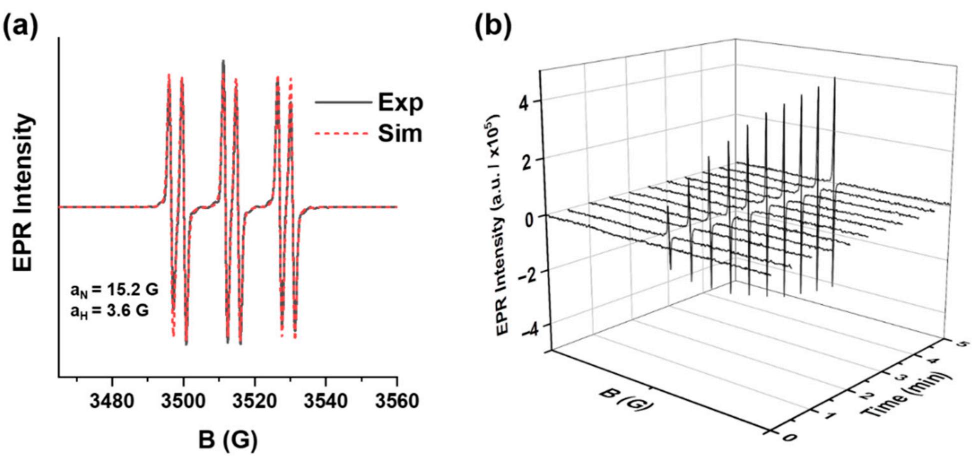

Figure S9. (a) Experimental and simulated spectra of α-hydroxy ethyl spin adduct of PBN obtained in 5mM HMF with 10% EtOH aqueous solution with 0.1 wt% Fe PHI, irradiated by a Xenon lamp with a >420 nm cut off filter; (b) 5mM HMF suspension of 0.1 wt% PHI(Fe) in Ar atmosphere irradiated over time.

Table S1. Theoretical amount of metal compared with experimental result of ICP-OES.

Photocatalyst	Metal (% m/m)	
	Theoretical	Experimental
PHI(Fe)	0.1	0.1
PHI(Co)	0.1	0.06
PHI(Cu)	0.1	0.3
PHI(Fe)	0.1	0.1
PHI(Fe) 1%	1.0	0.9
PHI(Fe) 2%	2.0	2.3
PHI(Ni) 1%	1.0	1.0
PHI(Ni) 2%	2.0	2.1

Table S2. DFF production rate comparing this work with literature results on HMF oxidation in aqueous medium in O_2 atmosphere.

Photocatalyst	DFF ($\mu mol.g^{-1}.h^{-1}$)	Ref.
PHI(Fe)	393.0	This work
Ti_3C_2Fx MXene/$CdIn_2S_4$	125.6	[1]
MoS2/CdIn2S4 (12.5%)	49.2	[2]
CTF Th@SBA-15	190.0	[3]
g-C_3N_4	26.7	[4]
1.5% Fe (III)/BMO	77.7	[5]
12% Bi2WO6/mpg–C3N4	0.2	[6]
Zn0.5Cd0.5S/1%MnO2	303.9	[7]

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