Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Crystal Phase Induced Band Gap Energy Enhancing Photo-Catalytic Properties of Zn-Fe_2O_4/Au NPs: Experimental and Theoretical studies

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Supplementary supporting information

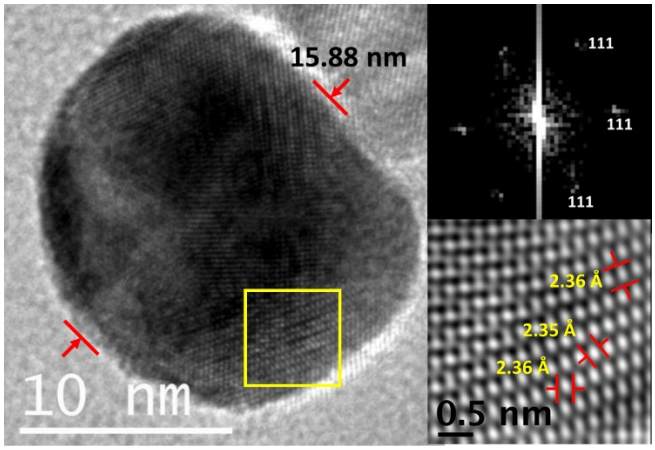


Figure S1. HRTEM micrography for indexation Au nanoparticles

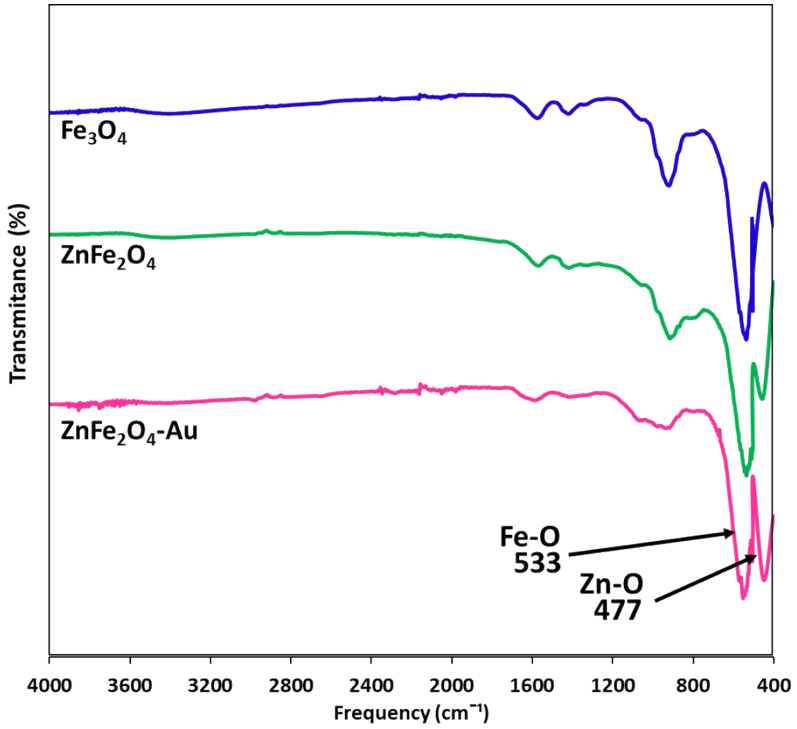


Figure S 1a. FTIR patterns of prepared iron oxide nanoparticles.

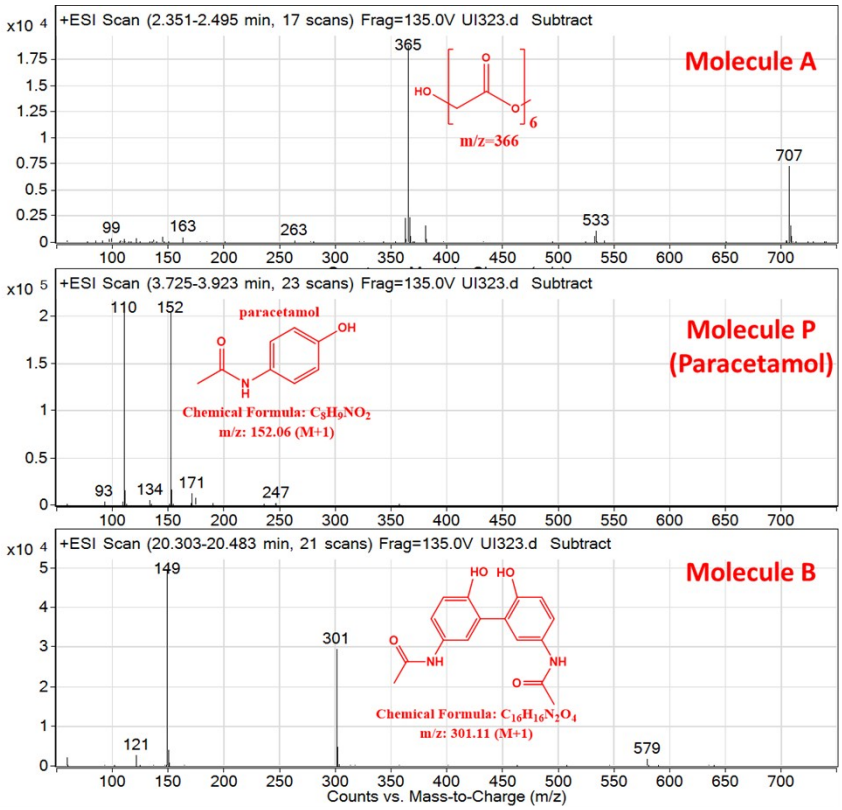


Figure S2. Mass spectrometry for HPLC separation peaks of commercial paracetamol tablets

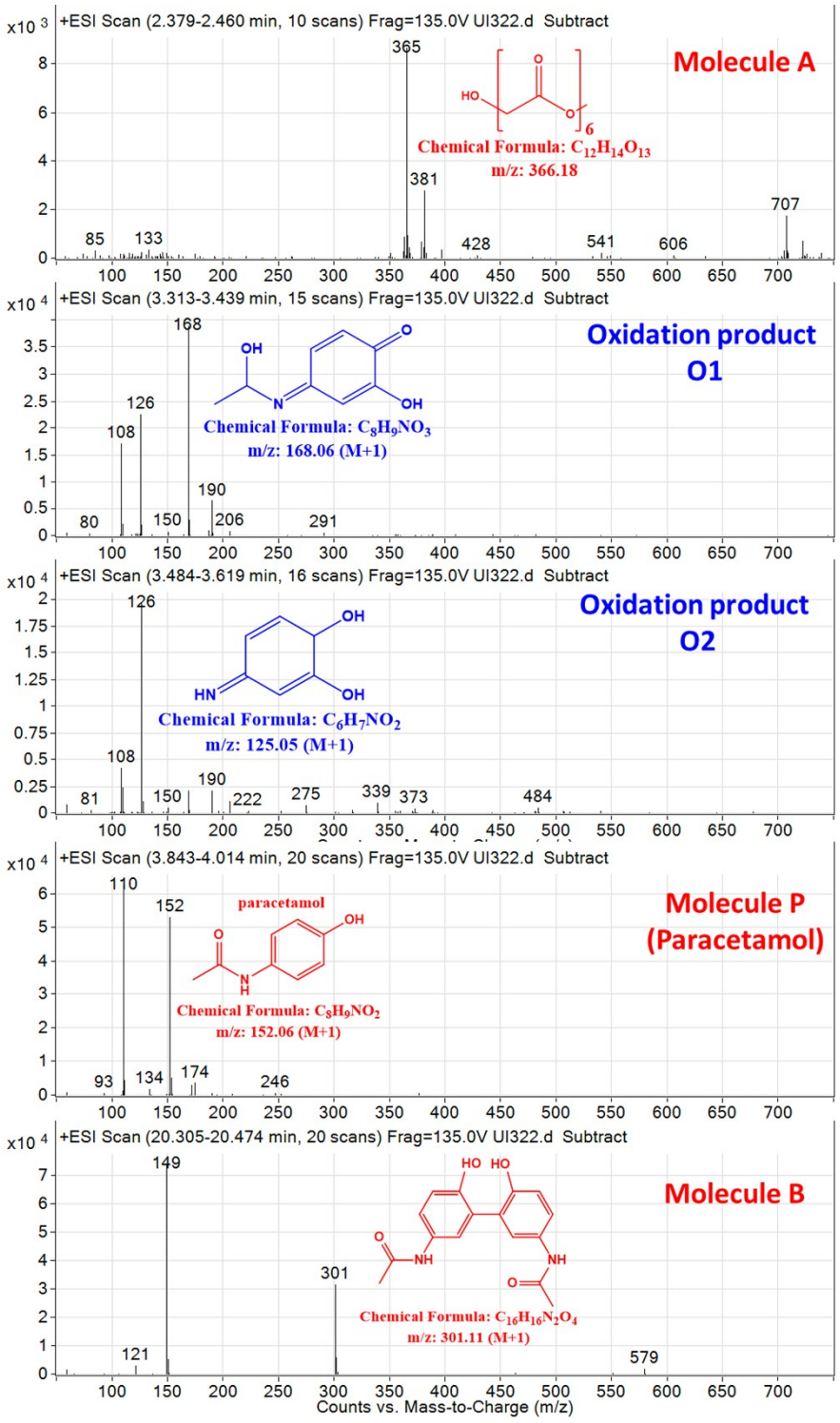


Figure S3. Mass spectrometry for HPLC separation peaks of oxidized paracetamol

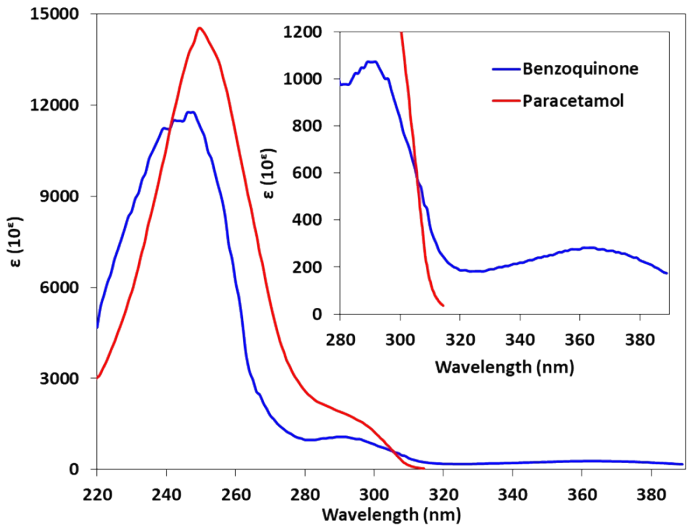
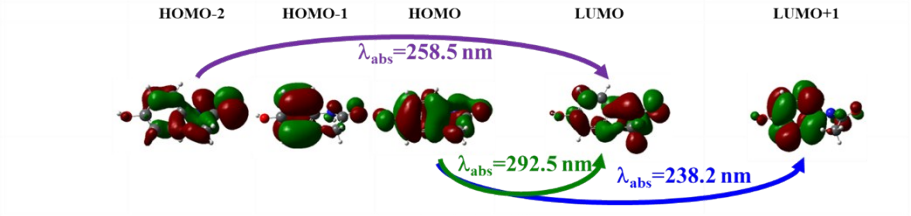


Figure S4. UV-Vis absorption profile of paracetamol and benzoquinone.

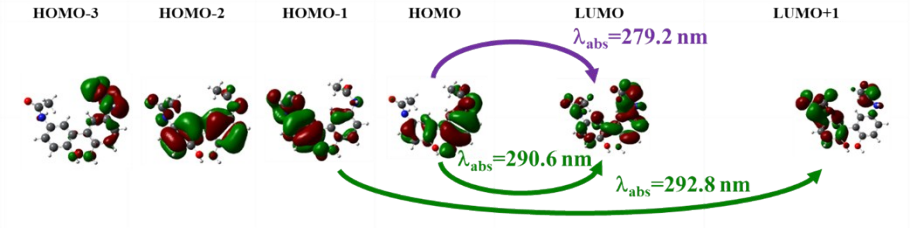
Paracetamol

Energy (cm^{-1})	Wavelength (nm)	Osc. Strength	Symmetry	Major contribs	Minor contribs
34189.03	292.49	0.0178	Singlet-A	H-2->LUMO (31%) HOMO->LUMO (56%)	H-3->LUMO (4%) H-2->L+2 (2%)
38685.57	258.49	0.0575	Singlet-A	H-2->LUMO (48%) HOMO->LUMO (37%)	H-1->LUMO (9%)
41985.19	238.17	0.0095	Singlet-A	H-1->LUMO (25%) HOMO->L+1 (49%)	H-3->LUMO (3%) H-1->L+2 (6%)



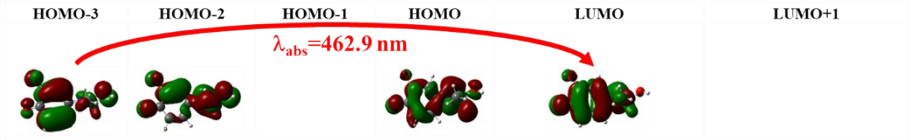
Paracetamol dimer (B)

Energy (cm^{-1})	Wavelength (nm)	Osc. Strength	Symmetry	Major contribs	Minor contribs
34156.77	292.76	0.0255	Singlet-A	H-4->L+1 (20%) H-1->L+1 (39%)	H-5->L+1 (5%) H-4->LUMO (4%
34411.64	290.59	0.0251	Singlet-A	H-3->LUMO (24%) HOMO->LUMO (36%)	H-3->L+1 (8%) HOMO->L+1 (8%)
35812.62	279.23	0.0484	Singlet-A	H-3->LUMO (30%) HOMO->LUMO (43%)	H-3->L+2 (5%) HOMO->L+1 (4%)



Product (O1)

Energy (cm-1)	Wavelength (nm)	Osc. Strength	Symmetry	Major contribs	Minor contribs
21602.75	462.90	0.0056	Singlet-A	H-3->LUMO (80%) H-2->LUMO (14%)	H-4->LUMO (4%)



Product (O2)

Energy (cm^{-1})	Wavelength (nm)	Osc. Strength	Symmetry	Major contribs	Minor contribs
24988.66	400.18	0.0017	Singlet-A	H-1->LUMO (13%) HOMO->LUMO (85%)	
31835.50	314.11	0.0168	Singlet-A	H-3->LUMO (72%) H-2->LUMO (24%)	

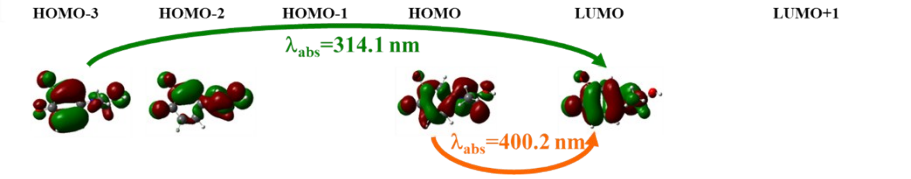


Figure S5. Theoretical parameters for UV-Vis spectra of HPLC identified products through (B3LYP/6-311G+)

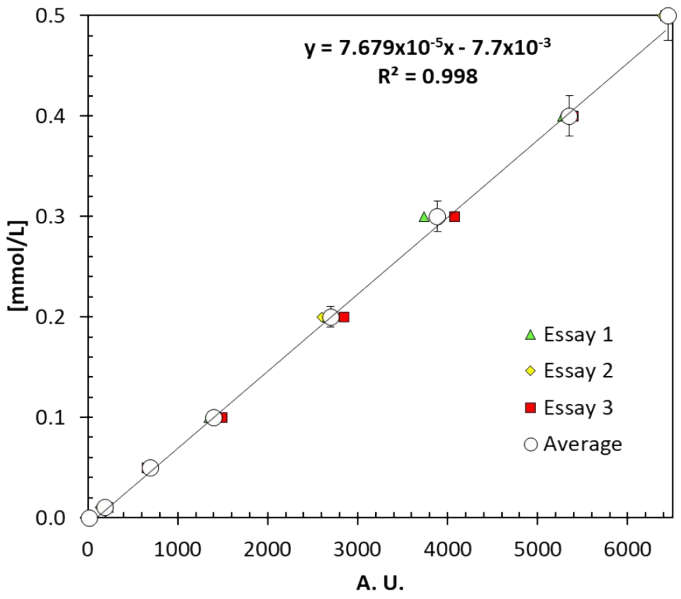


Figure S6. Calibration curve for identification of paracetamol by HPLC

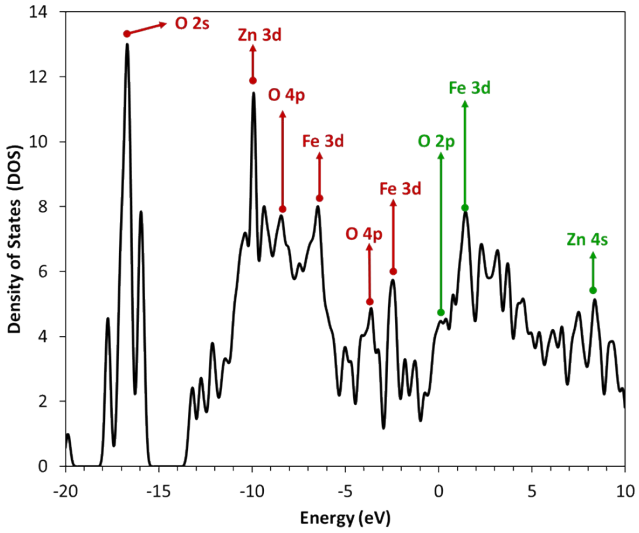


Figure S7. Total Density of States (DOS) for spinel $ZnFe_2O_4$.

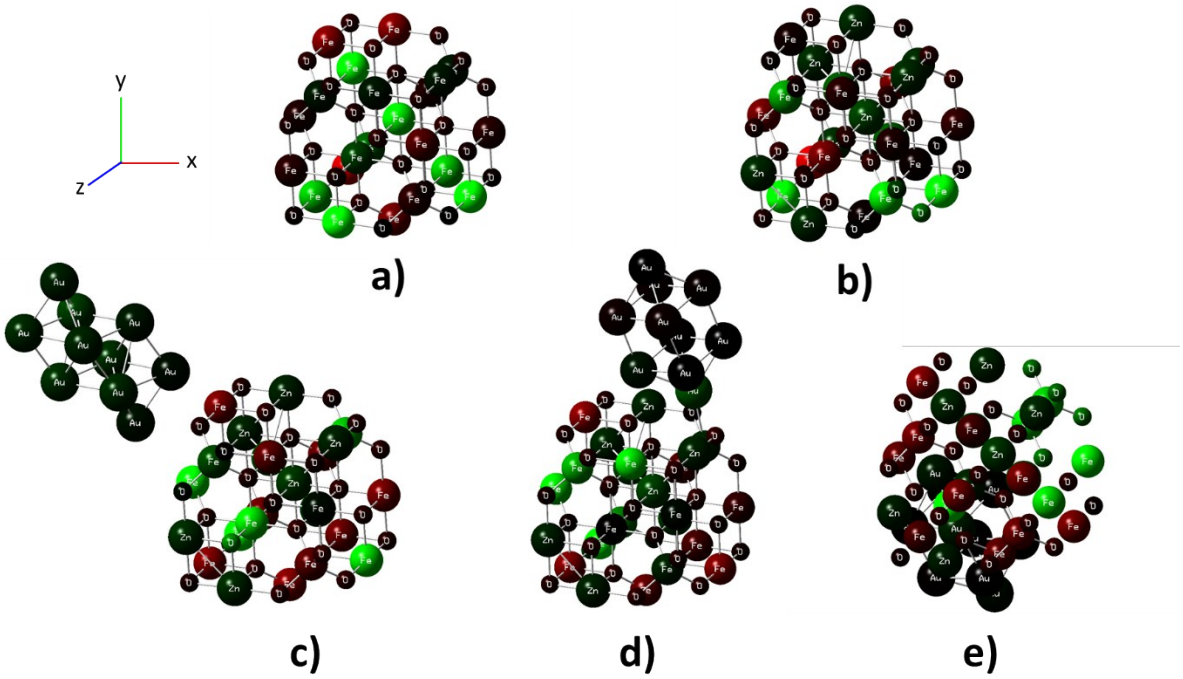


Figure S8. Mulliken charge for spinel ferrites with general formula MFe_2O_4 ($M=Fe^{2+}$, Zn^{2+}); a) Fe_3O_4, b) $ZnFe_2O_4$, c) $ZnFe_2O_4$[0T0]- Au_{10}, d) $ZnFe_2O_4$[001]-Au_{10}, e) $ZnFe_2O_4$[1T1]-Au_{10}.

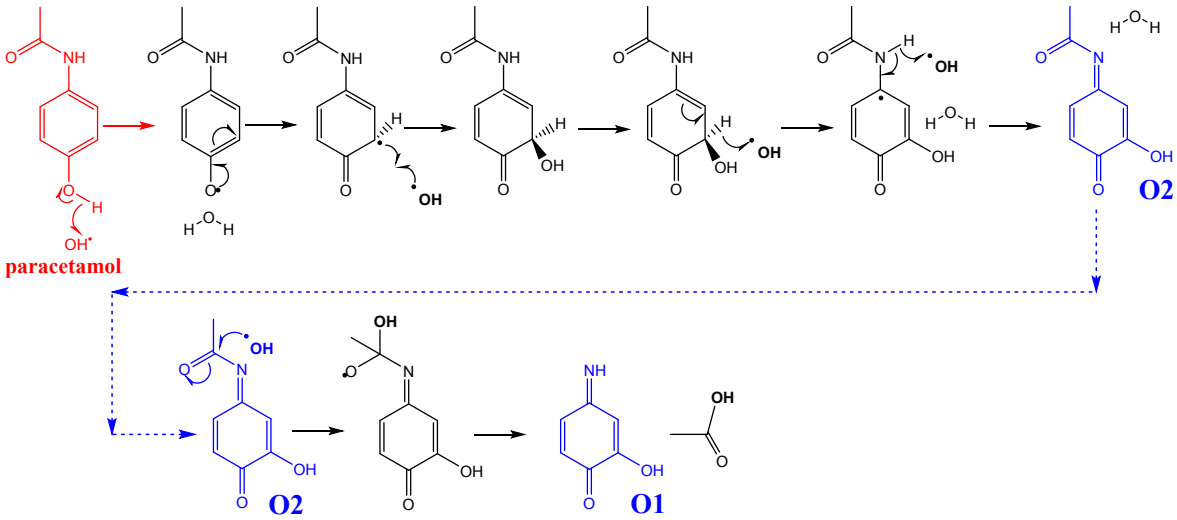


Figure S9. Detailed mechanism proposal for reaction pathway 1

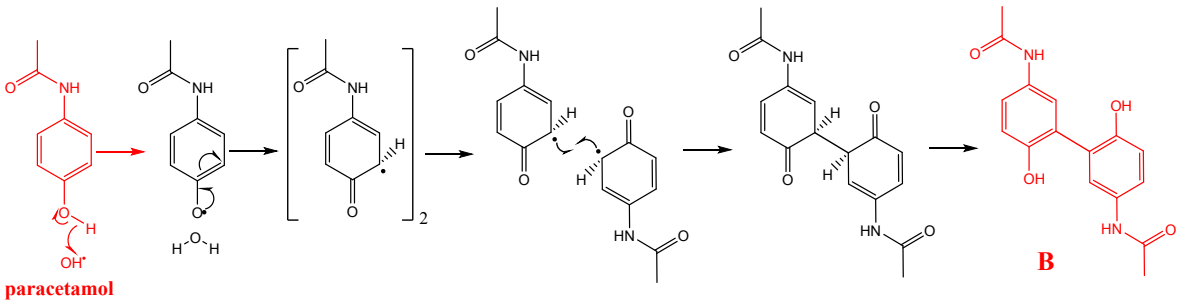


Figure S10. Detailed mechanism proposal for reaction pathway 2

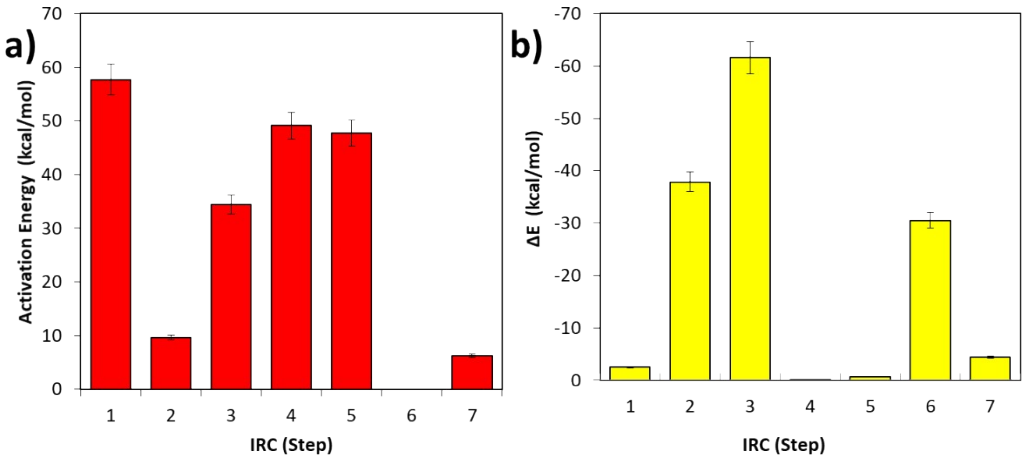


Figure 11. Thermodynamical features of reaction pathway 1 proposed for paracetamol oxidation by OH radicals; a) Activation Energy (E_A); b) Enthalpies of reaction (ΔH)

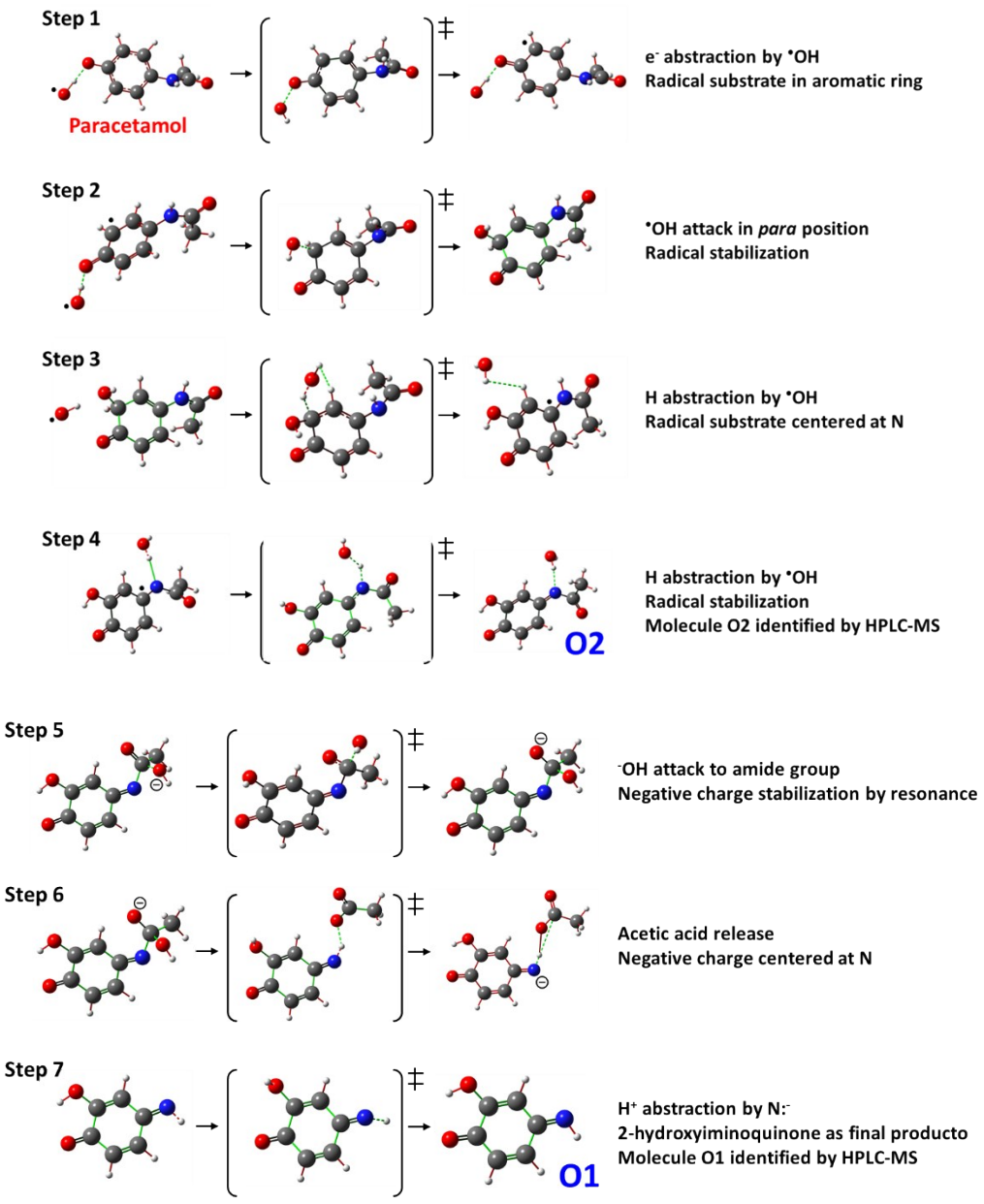


Figure S12. Reaction pathway summary

Table S1. Structure parameters calculated with HSEh1PBE functional compared with experimental values from spinel $ZnFe_2O_4$.

Parameter	*Fe_3O_4*	*$ZnFe_2O_4$*	*$ZnFe_2O_4$[0T0]- Au_{10}*	*$ZnFe_2O_4$[001]-Au_{10}*	*$ZnFe_2O_4$[1T1]-Au_{10}*	*$ZnFe_2O_4$ (exp.)*
Lattice parameter (Å)	7.97	7.98	7.98	7.99	7.99	8.27
Volume (Å^3)	506.26	508.16	508.59	510.08	510.12	565.60
Relative deviation (%)	3.76	3.63	3.63	3.52	3.52	-
$\Delta E_{HOMO-LUMO}$ (eV)	0.08	0.1	0.43	0.13	0.09	-
Bandgap (eV)	2.73	2.07	1.44	2.79	2.13	1.9
Relative deviation (%)	2.56	-8.21	31.94	-31.8	-10.79	-
Fe-O (Å)	2.08	2.08	2.09	2.09	2.09	2.04
Zn-O (Å)	-	2.02	2.02	2.03	2.02	1.99

Table S2. Thermodynamical parameters for spinel ferrites with general formula MFe_2O_4 (M=Fe^{2+}, Zn^{2+}); a) Fe_3O_4, b) $ZnFe_2O_4$, c) $ZnFe_2O_4$[0T0]-Au_{10}, d) $ZnFe_2O_4$[001]-Au_{10}, e) $ZnFe_2O_4$[1T1]-Au_{10}.

Parameter	*Fe_3O_4*	*$ZnFe_2O_4$*	*$ZnFe_2O_4$[0T0]- Au_{10}*	*$ZnFe_2O_4$[001]-Au_{10}*	*$ZnFe_2O_4$[1T1]-Au_{10}*
Total Energy (kJ/mol)	-13.8x10^6	-12.7x10^6	-16.1x10^6	-16.1x10^6	-15.9x10^6
Dipole moment (Dy)	299.7	380.5	749.2	364.7	951.7

Table S3. Atomic Mulliken charge analysis of studied ferrites

Atom	*Fe_3O_4*	*$ZnFe_2O_4$*	*$ZnFe_2O_4$[0T0]- Au_{10}*	*$ZnFe_2O_4$[001]-Au_{10}*	*$ZnFe_2O_4$[1T1]-Au_{10}*
			Mulliken charge		
Fe^{2+}	-0.69-(-2.98)	-0.21-(-2.61)	-2.86-(-3.56)	-0.06-(-3.55)	-1.88-(-3.24)
Zn^{2+}	-	0.94-1.43	0.90-1.20	0.88-1.74	0.81-1.48
Fe^{3+}	0.50-6.67	0.94-6.35	0.34-7.30	0.24-6.03	1.00-8.33
O^{2-}	-0.44-(-0.94)	-0.49-(-1.10)	-0.12-(-1.4)	-0.44-(-1.18)	-0.37-(-1.41)
Au^0	-	-	0.51-1.23	-0.40-2.27	0.34-0.91

Table S4. Thermodynamic values for calculated reaction pathway 1 in paracetamol degradation

IRC (Step)	**Total Charge**	**Spin**	**Activation Energy (EA)**	**Enthalpy (ΔE)**	**Total enthalpy (ΣΔE)**
			(kcal/mol)		
1	-1	doublet	57.724	-2.508	-2.508
2	-1	doublet	9.594	-37.893	-40.401
3	0	doublet	34.458	-61.575	-101.977
4	0	singlet	49.151	-0.010	-101.987
5	-1	singlet	47.759	-0.674	-102.662
6	-1	singlet	-14.478	-30.535	-133.198
7	0	Singlet	6.196	-4.439	-137.637