Electronic Supplementary Information

Zinc-triggered photocatalytic selective synthesis of benzyl acetate on inverse spinel CuFe₂O₄ 3D networks: a case of coupled redox photocatalytic reaction

Yihan Zhang^{a, †}, Jingqi Tian^{a, †}, Tengfei Jiang*^a, Huaiguo Xue^a

School of Chemistry and Chemical Engineering, Yangzhou University, 180 Siwangting Road, Yangzhou 225002, People's Republic of China. Email: jiangtengfei@yzu.edu.cn



Fig.S1. N_2 adsorption-desorption isotherms of $CuFe_2O_4$ (a) and $CuFe_2O_4$ -Zn^{0.5} (b).



Fig. S2. The SEM of samples CuFe₂O₄-Zn^{0.3} (a), CuFe₂O₄-Zn^{1.0} (b), CuFe₂O₄-Zn^{1.5} (c).





Table S1. Elemental analysis of samples CuFe₂O₄-Zn^{0.5}.

Element	Weight %	Atomic %	Uncert. %	Detector Correction	k-Factor
О(К)	30.81	62.22	0.44	0.49	2.008
Fe(K)	37.27	21.56	0.36	0.99	1.359
Cu(K)	30.92	15.72	0.36	0.99	1.601
Zn(K)	0.98	0.48	0.08	0.99	1.686



Fig. S4. Rietveld refinement of XRD pattern of CuFe₂O₄ sample.

Table S2. Rietveld refinement results of pure CuFe₂O₄.

Sample		Refinement data Lattice parameters						
	sig	sig R _b		R _{wp} R _{exp}		с	Density	
CuFe ₂ O ₄	1.04	4.53	5.68	4.96	5.94687	8.42621	5.383	

Table S3. The ratio of $Fe^{II}/(Fe^{II} + Fe^{III})$ and oxygen vacancy/total oxygen from XPS fitting.

Entry	Fe"/(Fe" + Fe"") (%)	Oxygen vacancy/Total oxygen (%)
CuFe ₂ O ₄	49.42	18.34
$CuFe_2O_4$ - $Zn^{0.3}$	58.75	20.70
CuFe ₂ O ₄ -Zn ^{0.5}	71.76	35.47
CuFe ₂ O ₄ -Zn ^{1.0}	65.58	32.31
CuFe ₂ O ₄ -Zn ^{1.5}	44.49	16.48



Fig. S5. High resolution XPS spectra of Cu 2p spectra in pure $CuFe_2O_4$ and $CuFe_2O_4$ -Zn^{0.5}.



Fig.S6. High resolution XPS spectra of Fe 2p spectra in pure $CuFe_2O_4$ and $CuFe_2O_4$ -Zn^{0.5}.



Fig. S7. The Raman spectra of CuFe₂O₄, CuFe₂O₄-Zn^{0.3}, CuFe₂O₄-Zn^{0.5}, CuFe₂O₄-Zn^{1.0} and CuFe₂O₄-Zn^{1.5}.



Fig. S8. Infrared spectra of CuFe₂O₄, CuFe₂O₄-Zn^{0.3}, CuFe₂O₄-Zn^{0.5}, CuFe₂O₄-Zn^{1.0} and CuFe₂O₄-Zn^{1.5}.



Fig. S9. LSV curves of CuFe₂O₄, CuFe₂O₄-Zn^{0.3}, CuFe₂O₄-Zn^{0.5}, CuFe₂O₄-Zn^{1.0} and CuFe₂O₄-Zn^{1.5}.



Fig. S10. The Z'--Z" plots of CuFe₂O₄, CuFe₂O₄-Zn^{0.3}, CuFe₂O₄-Zn^{0.5}, CuFe₂O₄-Zn^{1.0} and CuFe₂O₄-Zn^{1.5}.



Fig. S11. The Phase-Freq of CuFe₂O₄, CuFe₂O₄-Zn^{0.3}, CuFe₂O₄-Zn^{0.5}, CuFe₂O₄-Zn^{1.0} and CuFe₂O₄-Zn^{1.5}.



Fig. S12. GC-MS spectrum of samples CuFe₂O₄



Fig. S13. GC-MS spectrum of samples $CuFe_2O_4$ -Zn^{0.5}.

Compound number	Retention time (min)	Scan number	Area (AB * s)	Baseline height (AB)	Absolute height (AB)	Peak width 50% (min)	Start time (min)	End time (min)	Pea k type
1	4.368	256	884628589	72312175	114583606	0.02	4.325	4.379	М
2	5.161	329	1762227644	64916149	100268784	0.045	5.08	5.179	М
3	6.801	480	19093565	3624088	8368978	0.009	6.78	6.805	М
4	15.275	1260	55026384	4383054	7886679	0.021	15.253	15.296	М

Table S4. Analysis of GC-MS spectrum results of samples CuFe₂O_{4.}

Table S5. Analysis of GC-MS spectrum results of samples CuFe₂O₄-Zn^{0.5}

Compound number	Retention time (min)	Scan number	Area (AB * s)	Baseline height (AB)	Absolute height (AB)	Peak width 50% (min)	Start time (min)	End time (min)	Pea k type
1	4.346	254	175357377	21422287	29659414	0.014	4.325	4.359	М
2	5.128	326	541241349	31768248	42836648	0.028	5.076	5.138	М
3	6.421	445	2551266298	132680022	170465277	0.032	6.364	6.437	М
4	6.801	480	12187494	2151176	4519380	0.009	6.782	6.808	М
5	15.275	1260	306101651	9133878	21352626	0.056	15.06	15.29	М



Fig. S14. Open circuit potential decay curves of CuFe₂O₄, CuFe₂O₄-Zn^{0.3}, CuFe₂O₄-Zn^{0.5}, CuFe₂O₄-Zn^{1.0} and CuFe₂O₄-Zn^{1.5}.

Sample	τ (s)
CuFe ₂ O ₄	11.39
CuFe ₂ O ₄ -Zn ^{0.3}	21.67
CuFe ₂ O ₄ -Zn ^{0.5}	24.42
CuFe ₂ O ₄ -Zn ^{1.0}	16.84
CuFe ₂ O ₄ -Zn ^{1.5}	13.18

Table S6. The lifetime (τ) of the photoexcited electrons of CuFe₂O₄, CuFe₂O₄-Zn^{0.3}, CuFe₂O₄-Zn^{0.5}, CuFe₂O₄-Zn^{1.0} and CuFe₂O₄-Zn^{1.5}.



Fig. S15. Mott-Schottky plots of CuFe₂O₄ (a), CuFe₂O₄-Zn^{0.3} (b), CuFe₂O₄-Zn^{0.5} (c), CuFe₂O₄- $Zn^{1.0}$ (d) and CuFe₂O₄-Zn^{1.5} (e).

Table S7. Control experiments of selective synthesis of benzyl acetate by using $CuFe_2O_4$ -Zn^{0.5} sample.

Entry	Reactants	Scavenger	Light	Product	Selectivity (%)
1	Benzaldehyde + Acetic acid	Methanol	White	Benzyl acetate	70.55
2	Benzaldehyde + Acetone	Methanol	White	Benzyl acetate	0.24
3	Benzaldehyde + Isopropanol	-	Without	Benzyl acetate	0



Fig. S16. The photocatalytic selectivity for benzyl acetate synthesis as a function of the wavelength of the incident light.



Fig. S17. Recyclability of (a) $CuFe_2O_4$ and (b) $CuFe_2O_4$ - $Zn^{0.5}$ sample in photocatalytic selective synthesis of benzyl acetate.



Fig. S18. XPS survey (a), Fe 3p (b), O 1s (c), and Zn 2p (d) spectra of pure $CuFe_2O_4$ before and after recycling test.



Fig. S19. XPS survey (a), Fe 3p (b), O 1s (c), and Zn 2p (d) spectra of $CuFe_2O_4$ -Zn^{0.5} before and after recycling test.



Fig. S20. XRD patterns of $CuFe_2O_4$ (a) and $CuFe_2O_4$ -Zn^{0.5} (b) before and after recycling test.