Supplementary Information

$CuCo_2S_4$ nanoparticles synthesized via a thermal decomposition approach: evaluation of their potential as peroxidase mimics

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The key points and precautions to be taken care of during the synthesis of $CuCo_2S_4$ nanoparticles are as follows:

1. Reaction should be carried out using a silicon oil bath inside a fume hood.
2. Metal salts and thiourea should be taken in exact stoichiometric ratio and well dispersed via sonication for at least 3 minutes.
3. The reaction temperature should be maintained at 200 °C during the entire course of reaction.
4. Proper safety gloves and mask should be worn while performing the reaction.
5. All the organic waste solvent left after washing the precipitate (diphenyl ether, methanol) should be properly disposed or recycled.

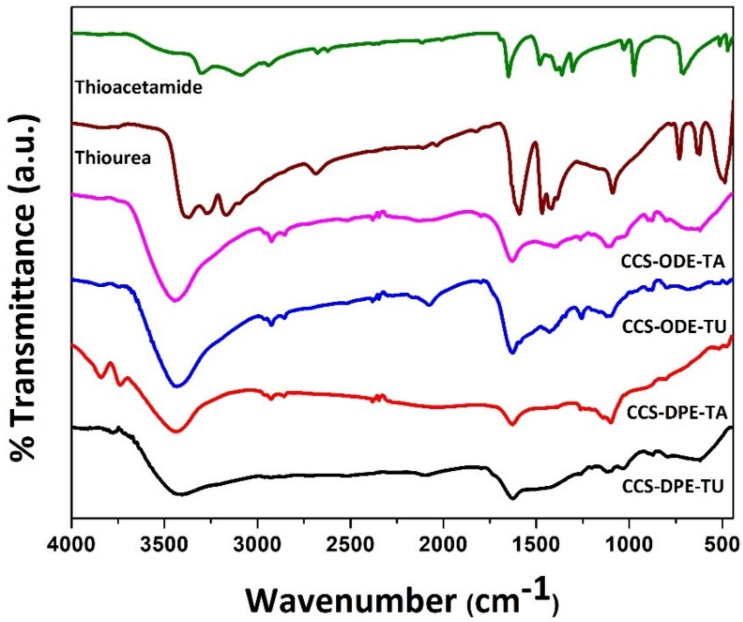

Fig. S1: FT-IR spectra of $CuCo_2S_4$ nanoparticles.

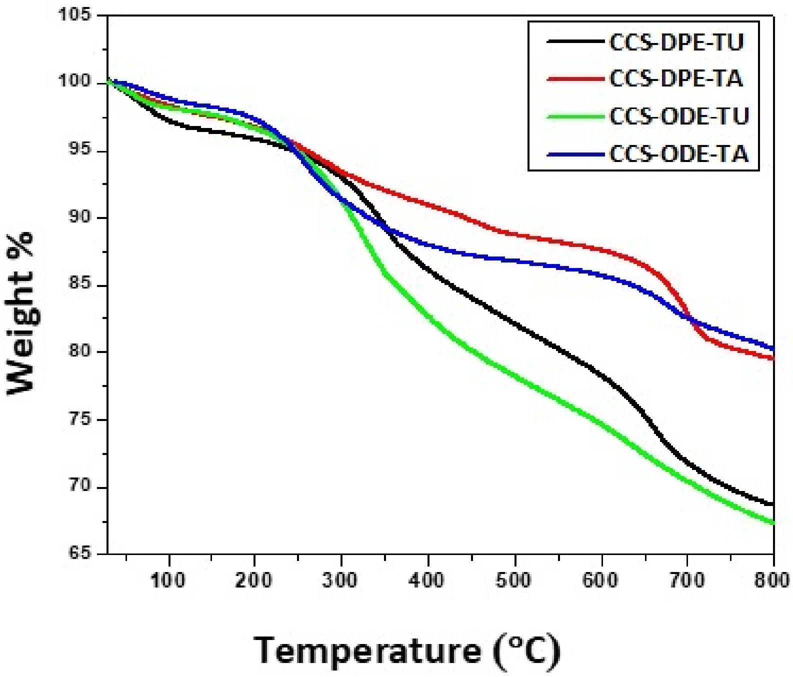

Fig. S2: TGA curves of $CuCo_2S_4$ nanoparticles.

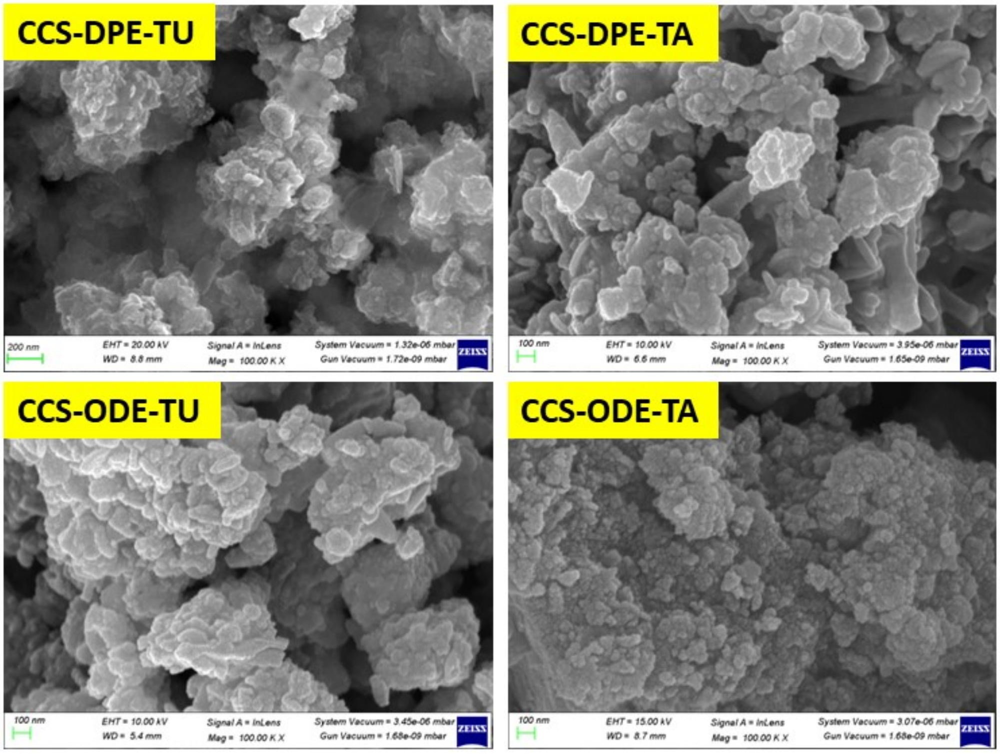

Fig. S3: FESEM images of $CuCo_2S_4$ nanoparticles.

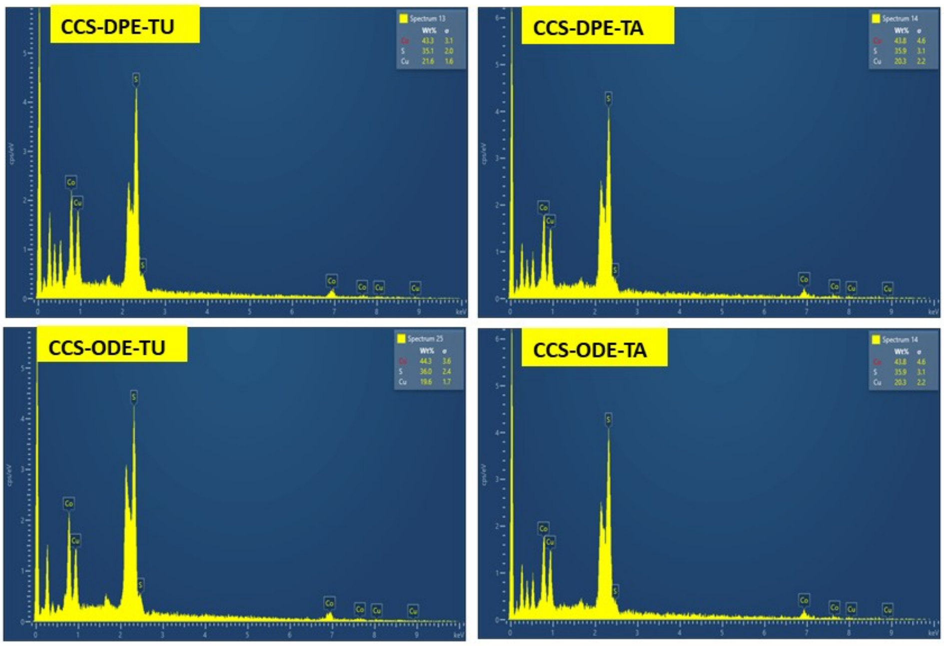

Fig. S4: EDS spectra of $CuCo_2S_4$ nanoparticles.

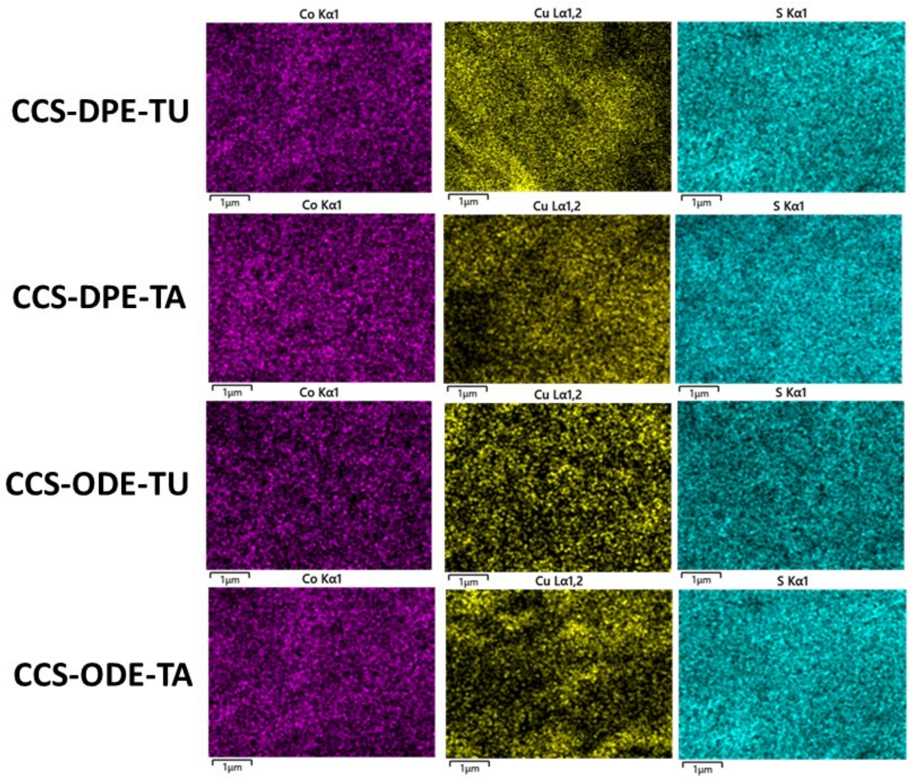

Fig. S5: Elemental mapping images of $CuCo_2S_4$ nanoparticles.

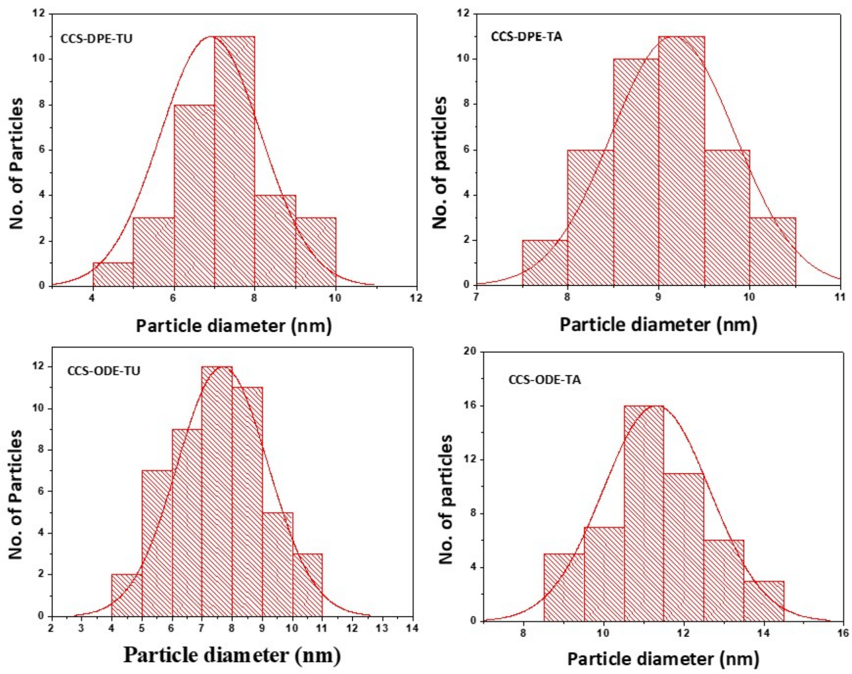

Fig. S6: Particle size histograms of $CuCo_2S_4$ nanoparticles.

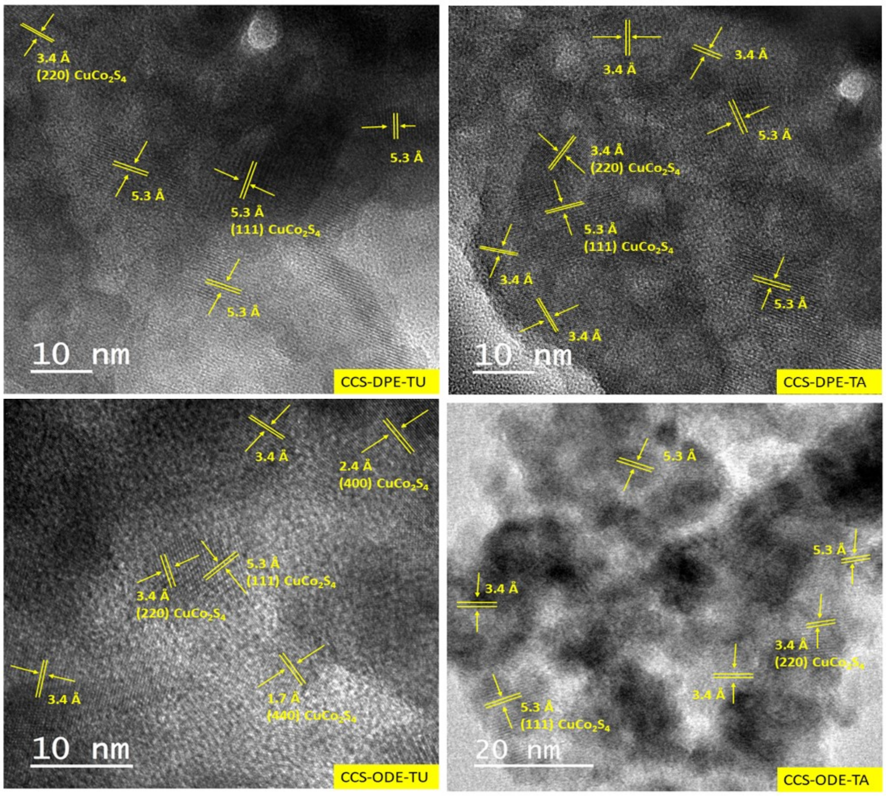

Fig. S7: HRTEM images of $CuCo_2S_4$ nanoparticles.

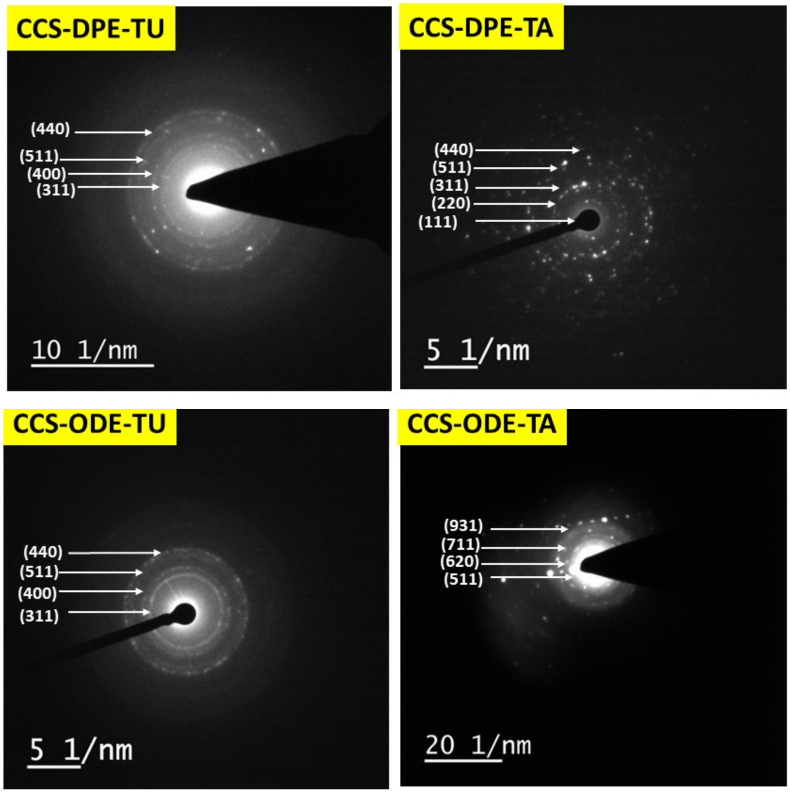

Fig. S8: SAED patterns of $CuCo_2S_4$ nanoparticles.

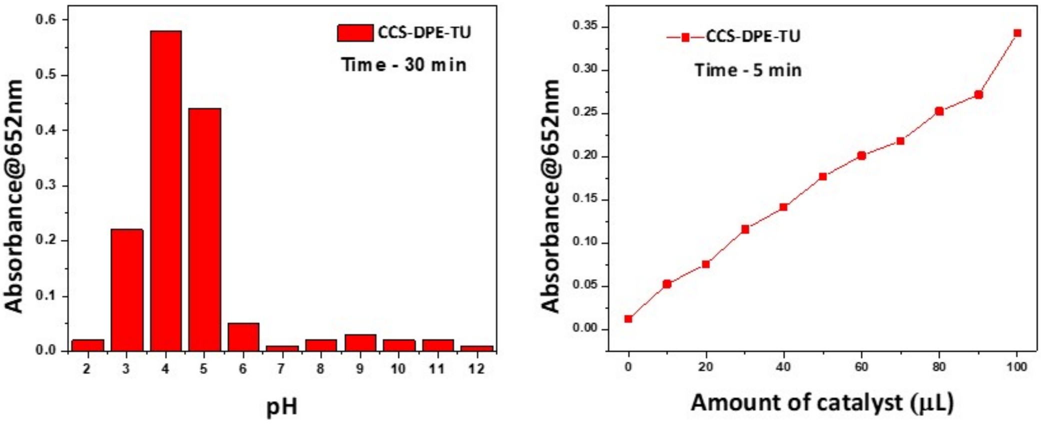

Fig. S9: Effect of experimental conditions on peroxidase-like activity of $CuCo_2S_4$ nanoparticles; (a) pH and (b) amount of catalyst.

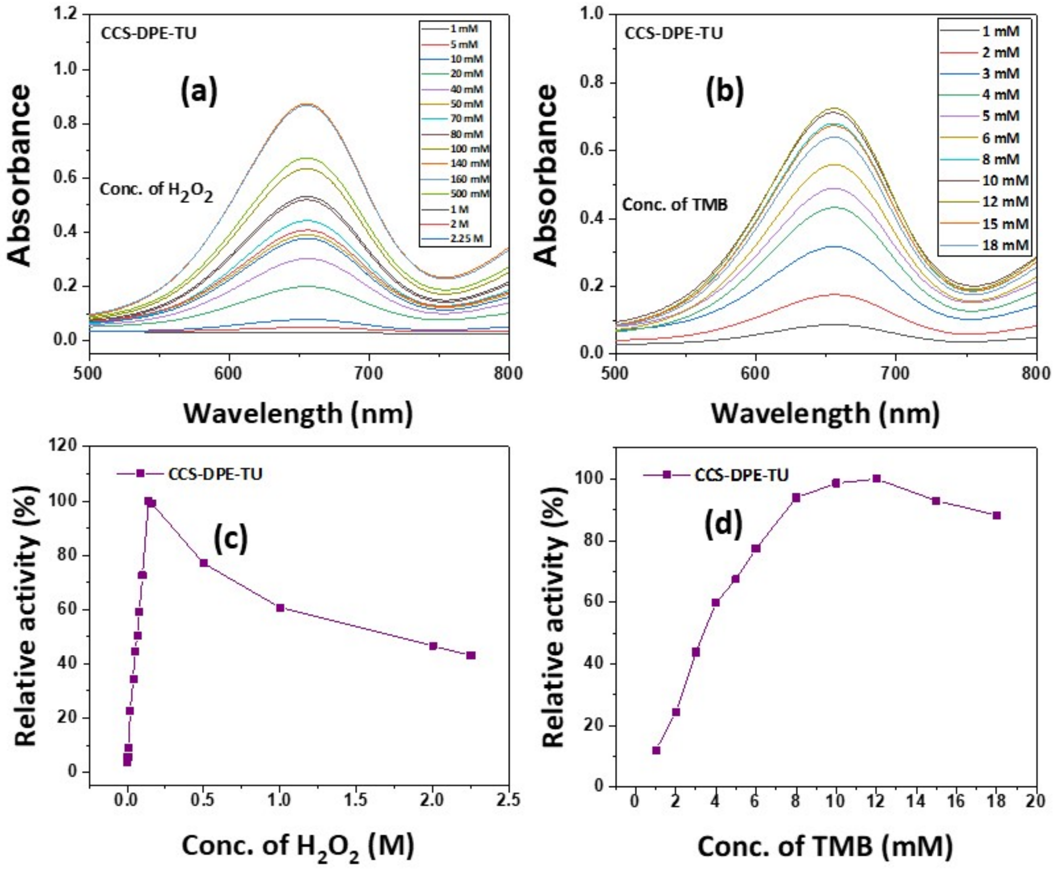

Fig. S10: Effect of concentration of H_2O_2 and TMB on peroxidase-like activity of $CuCo_2S_4$ nanoparticles (CCS-DPE-TU): (a,b) absorbance vs wavelength graphs for H_2O_2 and TMB, and (c,d) relative activity vs concentration graphs for H_2O_2 and TMB, respectively.

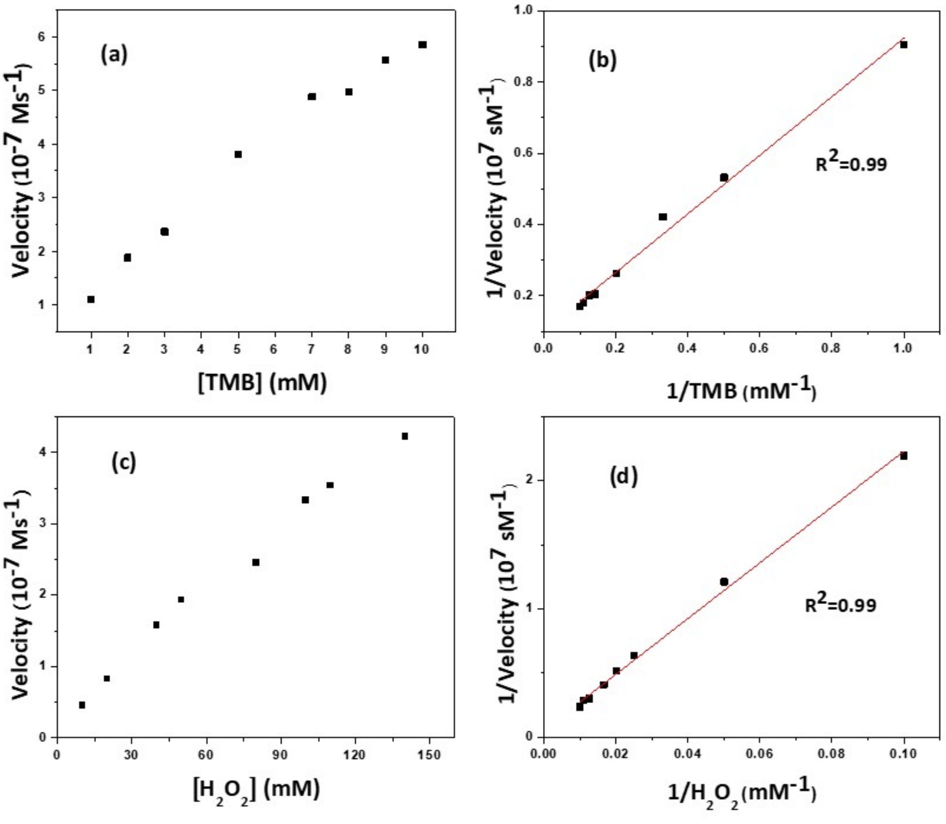

Fig. S11: Steady-state kinetics results of $CuCo_2S_4$ nanoparticles (CCS-DPE-TU): (a,c) Michaelis-menton curves using TMB and H_2O_2 as substrates, (b,d) corresponding Lineweaver-Burk double reciprocal plots.

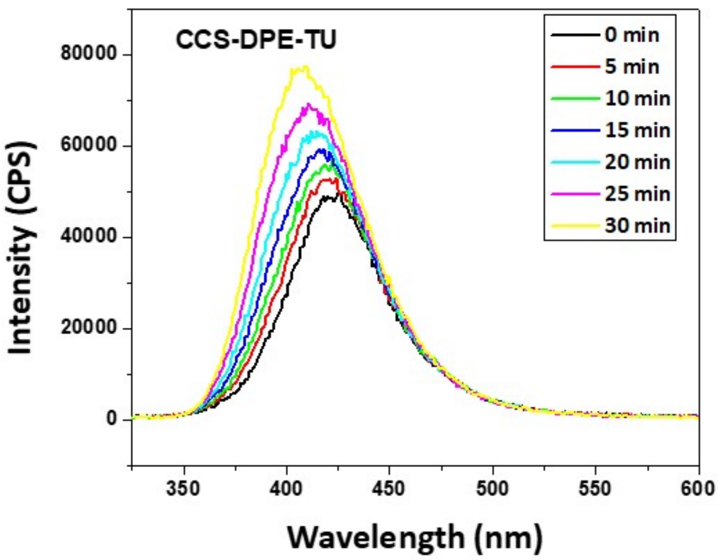

Fig. S12: Fluorescence spectra showing the formation of hydroxyl radicals during the oxidation of TMB by $CuCo_2S_4$ nanoparticles (CCS-DPE-TU) (λ_{exc} = 315 nm).

Table S1: FT-IR spectral results (cm^{-1}) of pure thiourea, thioacetamide and $CuCo_2S_4$ nanoparticles along with assignment.

Thiourea	Thioacetamide	CCS-DPE-TU	CCS-DPE-TA	CCS-ODE-TU	CCS-ODE-TA	Assignment
3369	3301	3432	3436	3434	3438	ν_{asym}(O-H)
3272	3093	–	–	–	–	ν_{asym}(N-H)
3168	–	–	–	–	–	ν_{sym}(N-H)
–	2941	2927	2924	2927	2923	ν_{asym} (C-H)
–	2782	2845	2849	2852	2849	ν_{sym}(C-H)
–	1649	–	–	–	–	δ(N-H)
1618	–	1630	1628	1624	1629	δ(O-H)
1428	1389	--	--	1412	1396	δ(C-H)
1329	1304	1261	1265	1259	1261	ν_{asym}(C=S)
–	–	1102	1098	1108	1107	ν_{asym}(Co-S)
1088	–	1037	–	1007	1015	ν_{asym}(C-N)
–	975	875	873	882	880	δ(C=S)
730	708	–	–	–	–	δ_{asym}(N-C-S)
633	–	–	–	–	–	δ_{asym}(N-C-N)
–	–	611	594	613	615	ν(Cu-S)
485	478	–	–	–	–	δ_{sym}(N-C-S)
–	–	458	461	470	468	ν_{sym}(Co-S)

Table S2: EDX analysis results of $CuCo_2S_4$ nanoparticles. The analysis was done at three different spots for each sample.

Sample code		Element			Stoichiometric formula
		Cu	Co	S	
CCS-DPE-TU	Wt. %	20.9	42.9	36.1	$CuCo_{2.4}S_{3.6}$
	At. %	15.0	33.3	51.6	
	Wt. %	21.2	43.8	34.9	
	At. %	15.2	34.6	50.2	
	Wt. %	21.4	43.9	34.7	
	At. %	15.4	34.8	50.1	
CCS-DPE-TA	Wt. %	19.6	44.3	36.0	$CuCo_{2.3}S_{3.7}$
	At. %	14.2	34.4	51.4	
	Wt. %	20.9	42.0	36.9	
	At. %	15.0	32.5	52.5	
	Wt. %	21.3	41.8	36.8	
	At. %	15.2	32.4	52.4	
CCS-ODE-TU	Wt. %	20.7	45.0	34.6	$CuCo_{2.5}S_{3.5}$
	At. %	14.7	35.6	49.6	
	Wt. %	19.9	46.7	33.4	
	At. %	14.6	36.9	48.5	
	Wt. %	19.5	46.0	34.6	
	At. %	14.2	36.0	49.8	
CCS-ODE-TA	Wt. %	20.6	44.7	34.7	$CuCo_{2.4}S_{3.6}$
	At. %	14.9	35.1	49.9	
	Wt. %	21.0	43.5	35.5	
	At. %	15.2	33.9	50.9	
	Wt. %	20.1	45.0	34.9	
	At. %	14.6	35.2	50.2	

Table S3: The surface area and particle size data for $CuCo_2S_4$ nanoparticles.

Sample code	Particle size (nm)	Surface area (m^2/g)
CCS-DPE-TU	6.9 ± 1.2	33
CCS-DPE-TA	9.1 ± 0.7	19
CCS-ODE-TU	7.6 ± 1.5	30
CCS-ODE-TA	11.3 ± 1.3	13

Table S4: Comparison of kinetic parameters for peroxidase-like activity of $CuCo_2S_4$ nanoparticles with those reported in literature for metal sulfide nanoparticles.

Catalyst	K_m (mM)		V_{max} (Ms^{-1})		Ref.
	TMB	H_2O_2	TMB	H_2O_2	
Co_3S_4 NPs	0.15	58.3	3.3×10^{-7}	3.3×10^{-7}	[30]
Co_9S_8 NPs	1.64	7.39	99×10^{-8}	35×10^{-8}	[31]
$CuCo_2S_4$ NPs	0.384	2.19	2.05×10^{-8}	3.77×10^{-8}	[43]
$NiCo_2S_4$ NPs	0.3	4.5	34.86×10^{-8}	4.32×10^{-8}	[68]
CuS NPs	0.0072	12	8.96×10^{-8}	2.09×10^{-7}	[71]
CuS NPs	0.064	1.753	76.4×10^{-8}	23.7×10^{-8}	[72]
CuS NPs	0.106	3.937	5.3×10^{-8}	2.139×10^{-8}	[73]
FeS_2 NPs	0.17	0.30	3.93×10^{-8}	5.67×10^{-8}	[74]
FeS NPs	0.008	7.67	1.07×10^{-8}	2.07×10^{-8}	[75]
CoS NPs	0.41	0.26	8.45×10^{-8}	0.61×10^{-8}	[76]
VS_2 NPs	0.28	3.49	41.6×10^{-8}	55.7×10^{-8}	[77]
MoS_2 NPs	0.54	2.81	3.88×10^{-8}	8.01×10^{-8}	[78]
MoS_2 NPs	2.53	0.135	58.9×10^{-8}	28.4×10^{-8}	[79]
WS_2 NPs	1.83	0.24	4.31×10^{-8}	4.52×10^{-8}	[80]
NiS NPs	0.241	0.347	5.09×10^{-8}	5.34×10^{-8}	[81]
CuS NPs	0.034	0.028	2.92×10^{-8}	19.87×10^{-7}	[82]
HRP	0.434	3.7	10×10^{-8}	8.71×10^{-8}	[83]
$CuCo_2S_4$ NPs	0.0008	0.0194	9.77×10^{-7}	9.24×10^{-7}	This work