Electronic Supplementary Material (ESI) for Dalton Transactions

Formation of self-inhibiting copper(II) nanoparticles in an autocatalytic Fenton-like reaction

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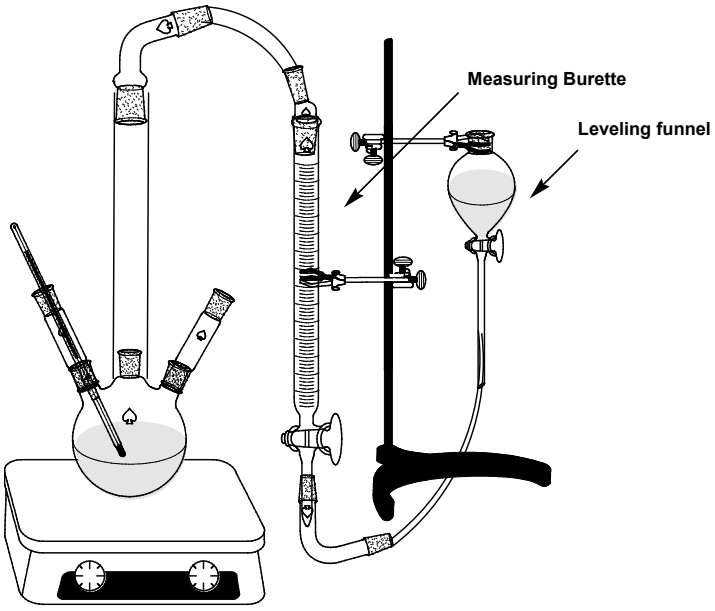
Contents

1.1 Experimental procedures

1.1.1 Monitoring decomposition of hydrogen peroxide

The decomposition of hydrogen peroxide was determined by measuring the volume of oxygen gas evolved. The reaction was carried out in a thermostated closed reactor at 20 ^{0}C. The experimental assembly was set up in which the reaction vessel was connected to a burette filled with water. The burette in turn was connected to a levelling funnel. The levelling funnel was adjusted accordingly to ensure that the pressure inside the burette was always constant (Atmospheric pressure). The decomposition of hydrogen peroxide generates oxygen gas which replaces water in the burette. The change in water level was recorded periodically as a measure of oxygen gas produced.

In a typical reaction, 4.5 μmol of copper (II) sulfate, 32.5 μmol of HEDP ligand were dissolved in 20 mM pH 10 ammonia/ammonium chloride buffer. Hydrogen peroxide (24.5 mmol) was injected in the closed reaction vessel and oxygen evolution was monitored over time. Total reaction mixture volume was 25 mL. The volume of oxygen gas was used to calculated hydrogen peroxide decomposition.



Reaction vessel at 20 ^{0}C

1.1.2 **Isolation & purification of nanoparticles**

A large scale experiment was carried out to isolate copper based nanoparticles. Copper sulfate (1.3 mmol) and HEDP ligand (1.3 mmol) were dissolved in 20 mM pH 10 ammonia/ammonium chloride buffer. Hydrogen peroxide (0.979 mol) was added to the reaction vessel (total reaction volume 1L). Addition of hydrogen peroxide immediate triggered the decomposition reaction. The reaction solution was stirred and temperature was maintained at 20 ^{o}C. After several minutes, yellow coloured solution was obtained and no further oxygen evolution was observed. A small amount of catalase (0.05 mL of aqueous suspension from Sigma, 20-50 mg/mL) was added to decompose remaining hydrogen peroxide and reaction solution was stirred for 30 minutes. Once all hydrogen peroxide was decomposed, reaction solution was concentrated under vacuum to obtain concentrated nanoparticle solution (200 mL). The solution at this stage was dark yellow-green in colour. The nanoparticles solution was purified through dialysis for 24 hours using Medicell International Ltd dialysis membrane [14.3 mm diameter, 30 kD molecular weight cut off (MWCO)].

After the dialysis, the solvent was evaporated under vacuum and a solid residue of nanoparticles was obtained for further experiments.

1.1.3 **Determination of copper and phosphorus**

Copper and phosphorus contents in nanoparticles residue were determined using atomic absorption spectroscopy (AAS) and inductively coupled plasma-atomic emission spectroscopy. ICP-AES analysis was carried out at analytical services, University of Manchester.

Nanoparticles (5 mg) were dissolved in 5 M nitric acid (100 mL). Copper content was first determined using AAS. A series of copper dilutions (5 – 50 ppm) were prepared in 5 M nitric acid using a standard copper solution from Sigma-Aldrich. A standard curve was obtained

and concentration of copper in nanoparticle solution was determined. The same sample was then submitted for the quantification of copper and phosphorus.

1.1.4 Determination of phosphate contents using molybdenum blue method

Phosphate content in reaction solution and isolated nanoparticles was determined by molybdenum blue colorimetric method.[1-4] All glassware was pre-rinsed with 2.5 M sulfuric acid to remove phosphate contamination. The colouring reagent was composed of

a) Sulfuric acid 2.5 M

b) Potassium antimonyl tartrate (0.27% solution)

c) Ammonium molybdate (4% solution)

d) Ascorbic acid (0.1 M)

The components B (5 mL), C (15 mL) and D (30 mL) were added to A (Sulfuric acid, 50 mL)) step by step to form coloring reagent. The solution was thoroughly mixed on each addition.

A standard 1000 ppm phosphate solution was purchased from Sigma-Aldrich. A series of phosphate dilutions (0.25, 0.5, 0.75 & 1.0 ppm concentration levels) were prepared using deionised water. To each standard solution, 8 mL of the colouring agent was added and volume was made up to 100 mL with deionised water. The solution was left for 10 minutes to develop colour. After 10 minutes, spectra were recorded against reagent blank using UV-Vis spectrophotometer and absorption value at 880 nm was used to develop a standard curve.

1.1.5 Analysing phosphate contents in the reaction solution

4.5 µmol of copper, 32.5 µmol of HEDP ligand were dissolved in 20 mM ammonia/ammonium chloride buffer pH 10. Hydrogen peroxide (24.5 mmol, total reaction volume 25 mL) was injected to start the decomposition reaction. The temperature of the

reaction solution was maintained at 20 ^{o}C. Sample aliquots (0.2 mL) were taken at regular time intervals and mixed with phosphate colouring reagent (8 mL). The volume of solution was made to 100 mL using deionised water. The solution was left for 10 minutes to develop colour. After 10 minutes, spectrum was recorded using UV-Vis spectrophotometer against reagent blank.

1.1.5.1 **Analysing phosphate in nanoparticles**

Solid residue of nanoparticles (1.9 mg) was directly dissolved in colouring reagent (8 mL). The mixture was stirred to make sure all the solid material was dissolved and subsequently volume was made up to 100 mL using deionised water. The spectrum was recorded against reagent blank. The % phosphate present in the sample was calculated using standard curve.

1.1.5.2 **Determination of carbonate content in nanoparticles**

Amount of carbonate in isolated nanoparticles was determined by IR spectroscopic method quantifying carbon dioxide evolution from nanoparticles. The experimental design involved mixing the nanoparticles with strong concentrated acid to generate carbon dioxide in a closed reaction vessel which was directly connected to gas IR cell of 10 cm path length.

For quantitative determination, a standard curve for carbon dioxide was obtained using a pre-dried anhydrous sodium carbonate. Sodium carbonate was mixed with phosphoric acid (85%). The absorption intensity for carbon dioxide at 2360 cm^{-1} from different levels of sodium carbonate employed was used to obtain a standard curve. Similarly, nanoparticles (15.7 mg) were dissolved in concentrated phosphoric acid (0.5 mL) and gas evolved was analysed.

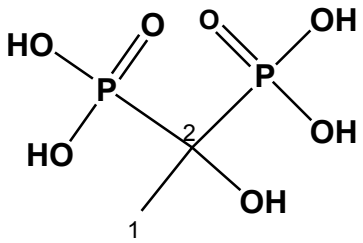
1.2 **Results**

1.2.1 **Elemental composition of isolated nanoparticles**

Element	*w/w %*
Carbon	1.535
Hydrogen	1.25
Nitrogen	-
Copper	53.5
Phosphorus	5.35 (13% phosphate by colorimetry)
Carbonate	7.7% (IR spectroscopy)

Figure S 1: Elemental composition of purified nanoparticles.

1.2.2 **NMR spectra of nanoparticles**



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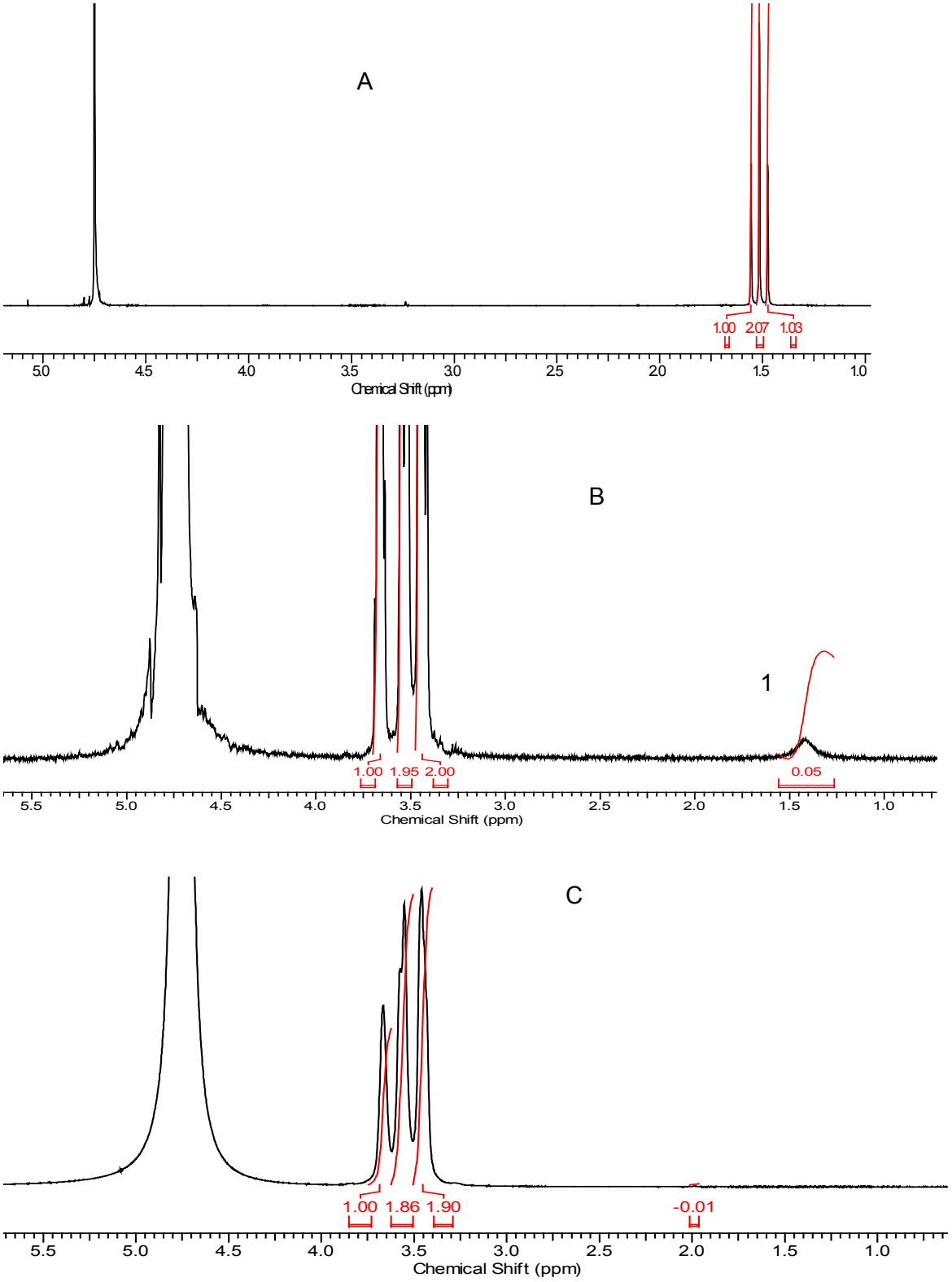
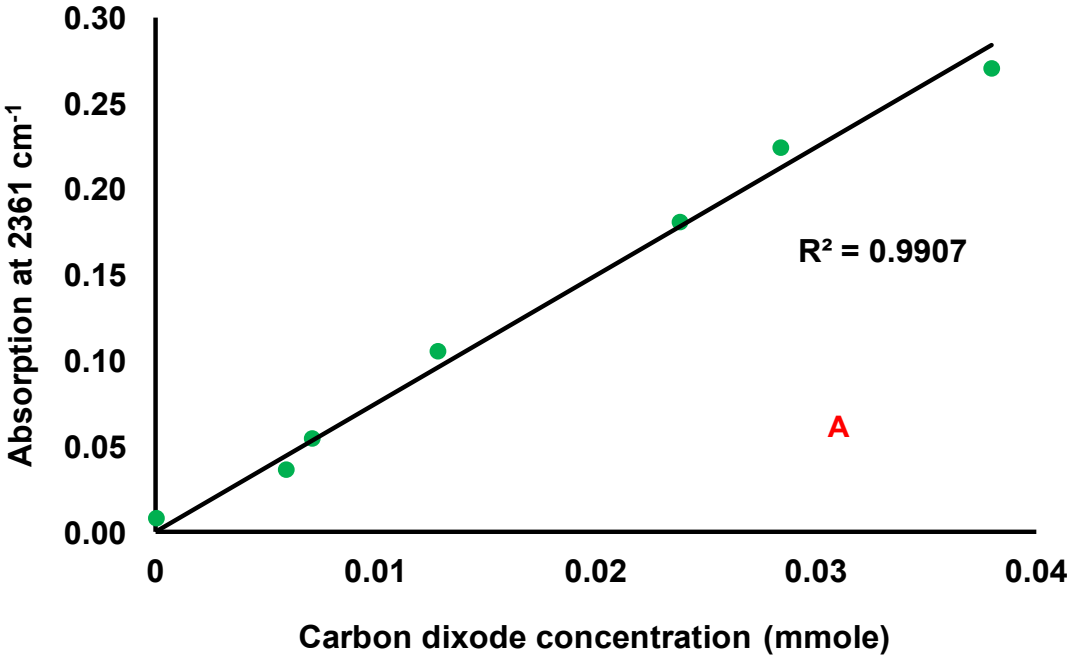


Figure S 2: Monitoring HEDP degradation: ^{1}H NMR of isolated nanoparticles. (A) HEDP ligand in D_2O (B) Cu/HEDP with glycerol (internal standard) in D_2O, 4.5 µmol of copper, 32.5 µmol of HEDP ligand dissolved in 20 mM pH 10 ammonia/ammonium chloride buffer (total reaction volume 25 mL). Solution was evaporated to remove buffer and solid residue was dissolved in D_2O with a few drops of concentrated nitric acid and glycerol. The proton NMR at 400 mHz showed a broadened (due to Cu^{2+}) peak for HEDP ligand (C) 5 mg nanoparticles

dissolved in 0.4 mL of concentrated nitric acid and subsequently dissolved in D_2O. Glycerol (0.1 g) was added and ^1H NMR was obtained at 400 mHz machine. The spectrum did not show signal for HEDP ligand.

1.2.3 Quantification of carbonate in nanoparticles using FT-IR spectroscopy



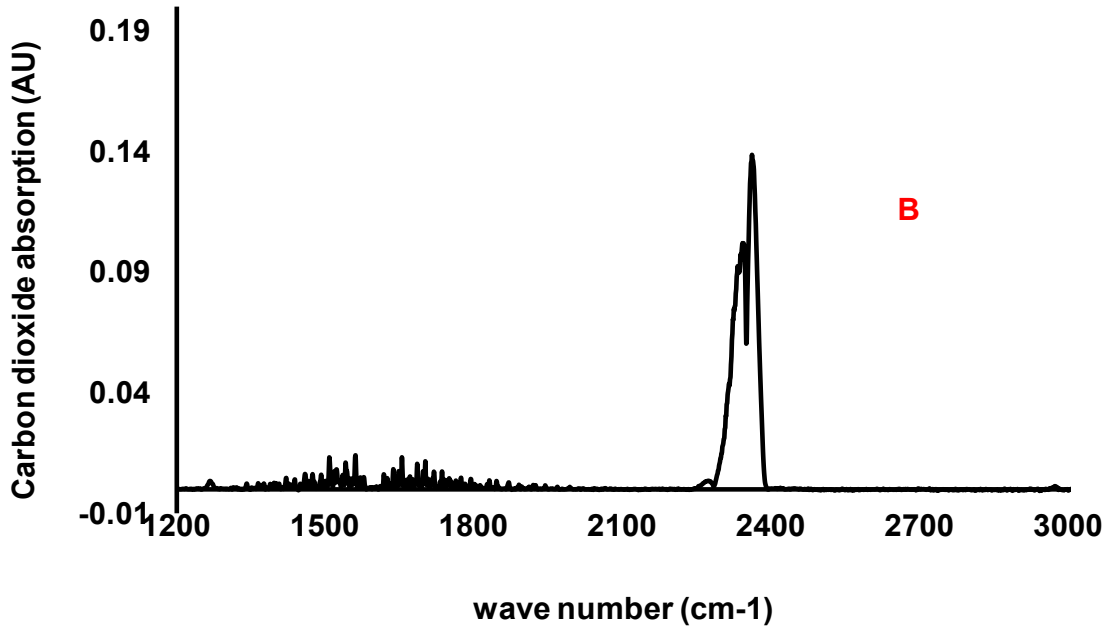
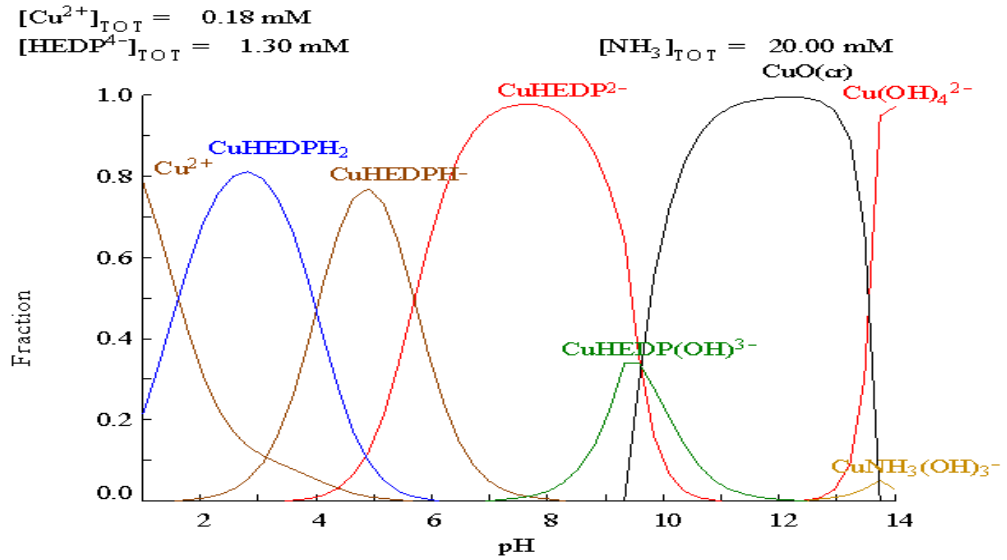
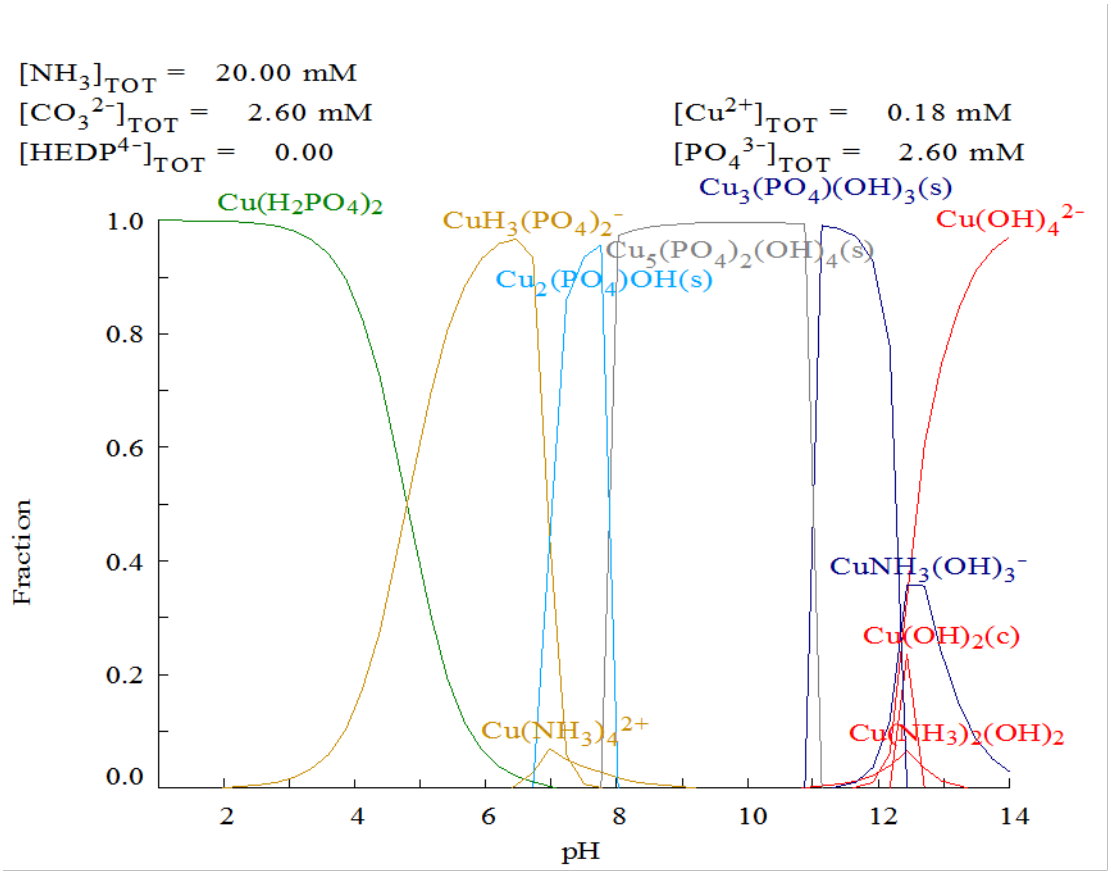


Figure S 3: (A) standard curve for quantification of carbon dioxide using FT-IR. (B) FT-IR spectrum of carbon dioxide from isolated nanoparticles. (See section 1.1.5.2)

1.2.4 Copper (II) speciation with different levels of copper (II) & HEDP ligand





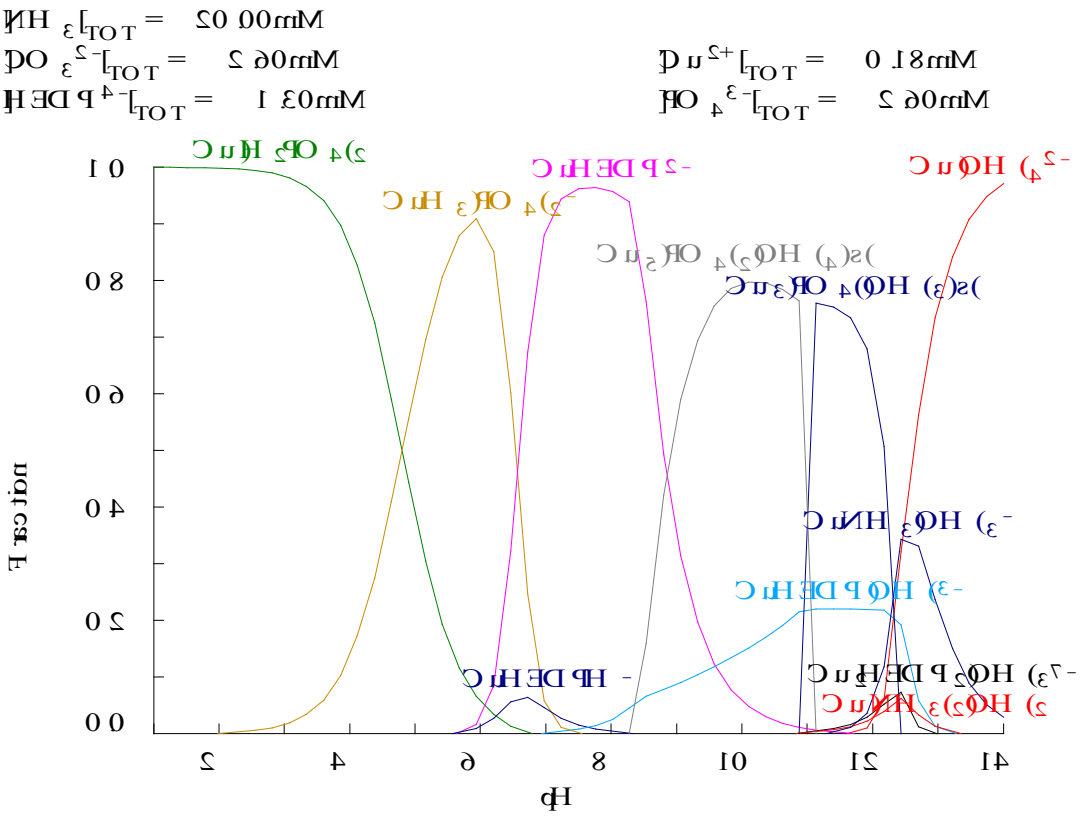


Figure S 4: Changes in copper speciation in 20 mM ammonia ammonia/ammonium chloride buffer and subsequent changes after complete degradation of HEDP ligand.

1.2.5 Copper speciation with HEDP ligand in 20 mM phosphate buffer system

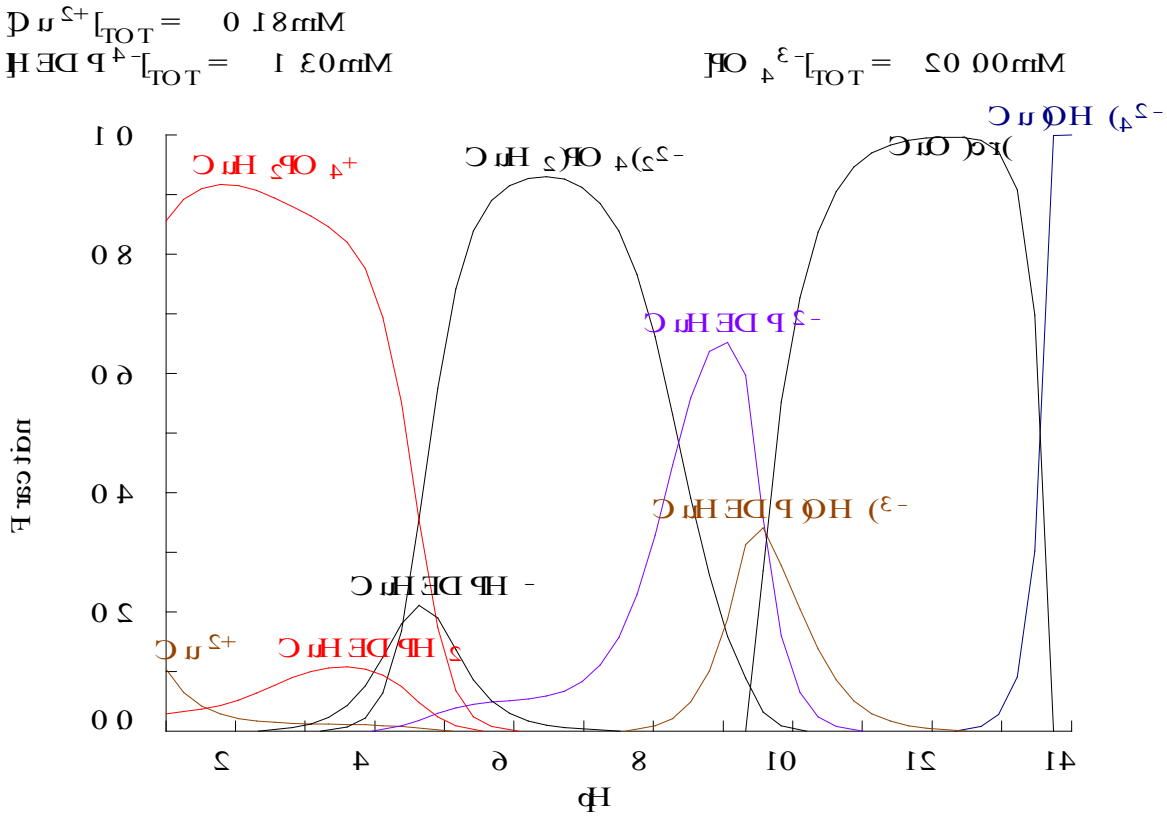


Figure S 5: Copper speciation with HEDP ligand in 20 mM phosphate buffer.

1.2.6 **Effect of adding phosphate and carbonate components in an ongoing hydrogen decomposition reaction**

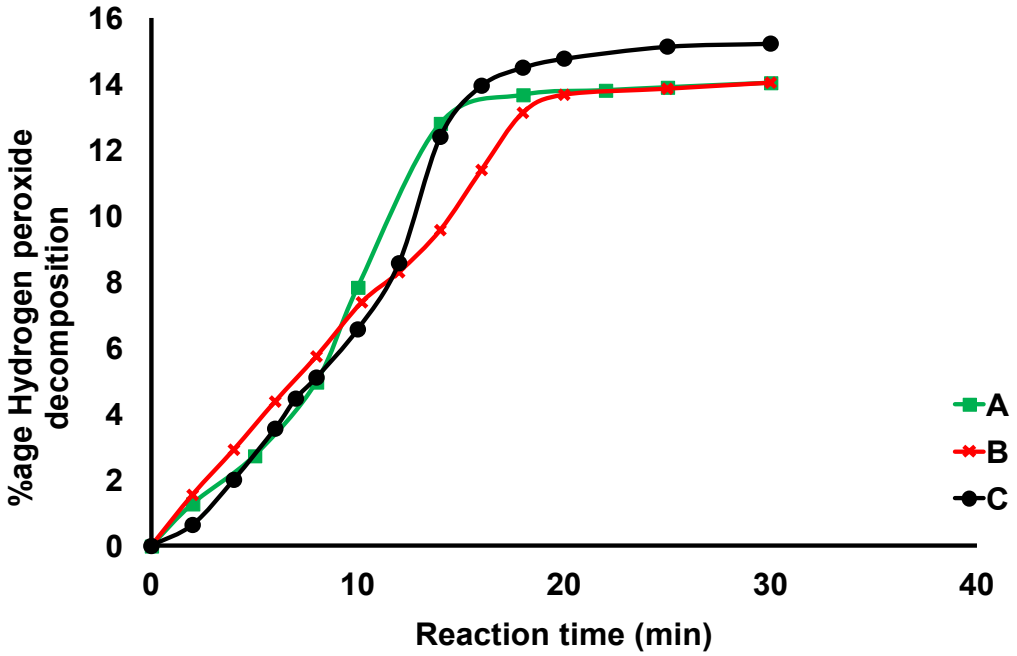


Figure S 6: Hydrogen peroxide decomposition in copper-HEDP system with phosphate and carbonates added at the 6th minute to an ongoing decomposition reaction. (A) 4.5 µmol of copper, 32.5 µmol of HEDP ligand dissolved in 20 mM pH 10 ammonia/ammonium chloride buffer with 24.5 mmol of hydrogen peroxide (total reaction volume 25 mL). Hydrogen peroxide decomposition was monitored over time. (B) To an ongoing reaction of A, 0.5 mL of 0.25 M phosphate buffer (disodium hydrogen phosphate-tri sodium phosphate) solution pH 10 was added at the 6th minute. (C) To another ongoing reaction A, 0.5 mL of 0.25 M ammonium carbonate was added at 6th minute using a syringe and hydrogen peroxide decomposition was monitored.

1.2.7 Copper-HEDP catalysed hydrogen peroxide decomposition using different buffer composition

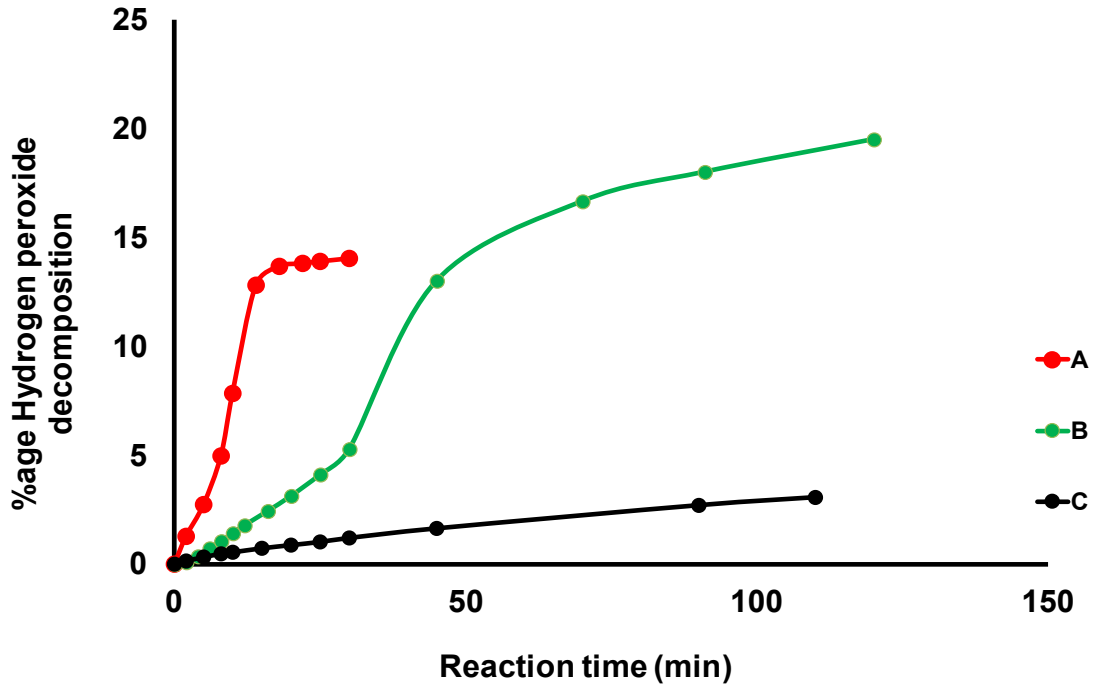


Figure S 7: Copper-HEDP catalysed hydrogen peroxide decomposition using different buffer composition. Total reaction volume in each case was 25 mL. (A) 4.5 µmol of copper (II) sulfate, 32.5 µmol of HEDP ligand dissolved in 20 mM pH 10 ammonia/ammonium chloride buffer with 24.5 mmol of hydrogen peroxide. Hydrogen peroxide decomposition was monitored over time. (B) 4.5 µmol of copper (II) sulfate, 32.5 µmol of HEDP ligand dissolved in 20 mM pH 10 phosphate buffer with 24.5 mmol of hydrogen peroxide. (C) 4.5 µmol of copper (II) sulfate in a ligand-free system dissolved in 20 mM pH 10 phosphate buffer with 24.5 mmol of hydrogen peroxide.

1.2.8 Copper-HEDP catalysed hydrogen peroxide decomposition at different ammonia levels

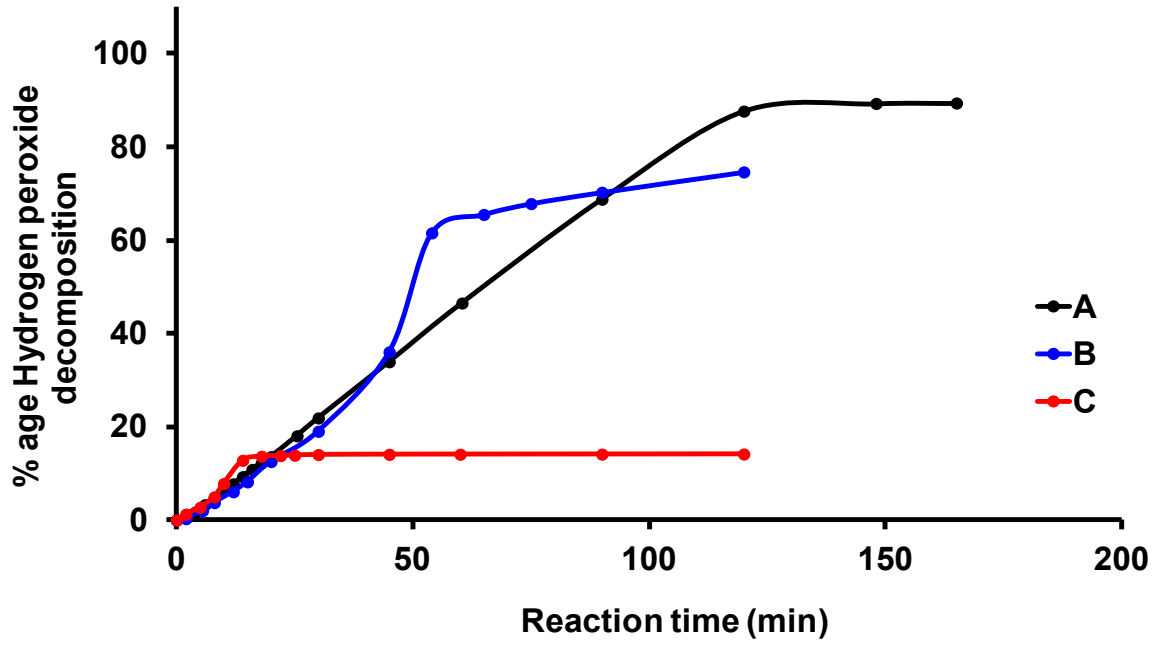
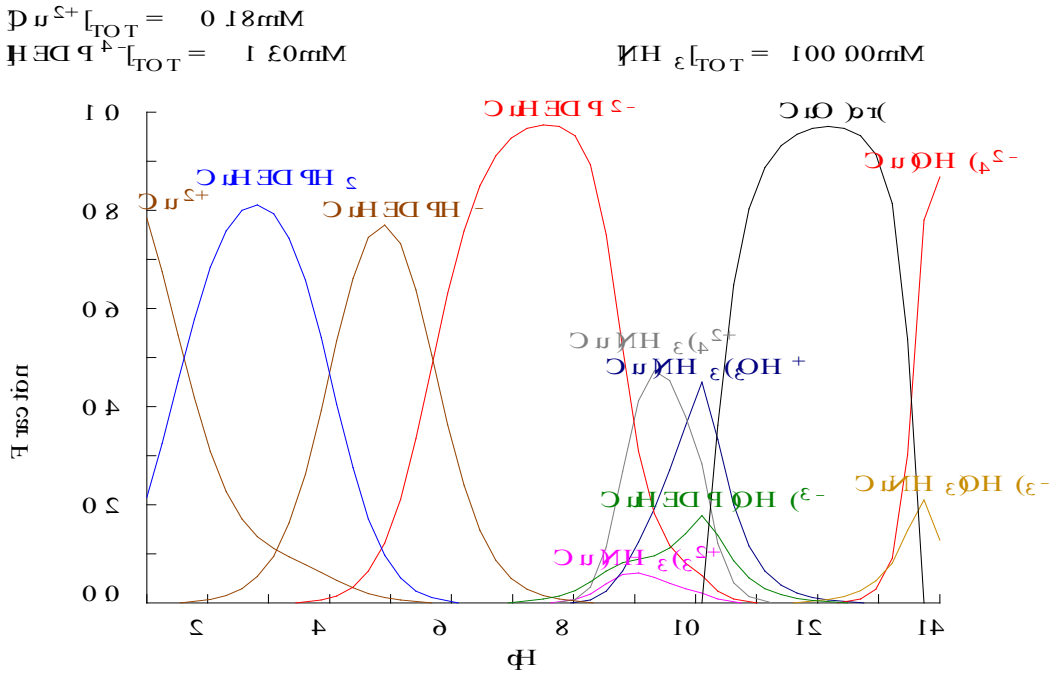


Figure S 8: Copper-HEDP catalysed decomposition of alkaline hydrogen peroxide at different ammonia level. Reaction solution contained 4.5 µmol of copper sulfate, 32.5 µmol of HEDP ligand dissolved in 20 mM pH 10 ammonia/ammonium chloride buffer with 24.5 mmol of hydrogen peroxide (total reaction volume 25 mL). Hydrogen peroxide decomposition was over time. (A) 400 mM ammonia/ammonium chloride buffer (B) 100 mM ammonium/ammonium chloride buffer (C) 20 mM ammonia/ammonium chloride buffer.

1.2.9 **Copper (II) speciation at higher ammonia levels**



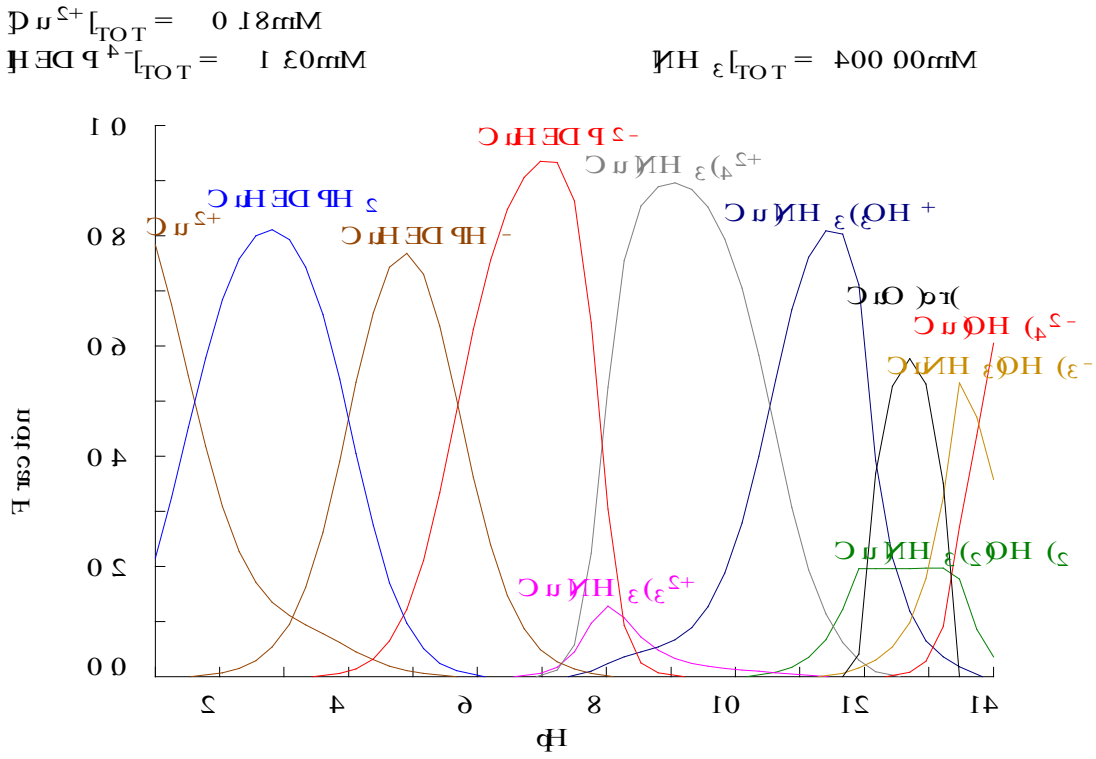


Figure S 9: Changes in copper speciation on increasing ammonia level in the reaction solution.

1.2.10 Copper-HEDP catalysed hydrogen peroxide decomposition at different hydrogen peroxide levels

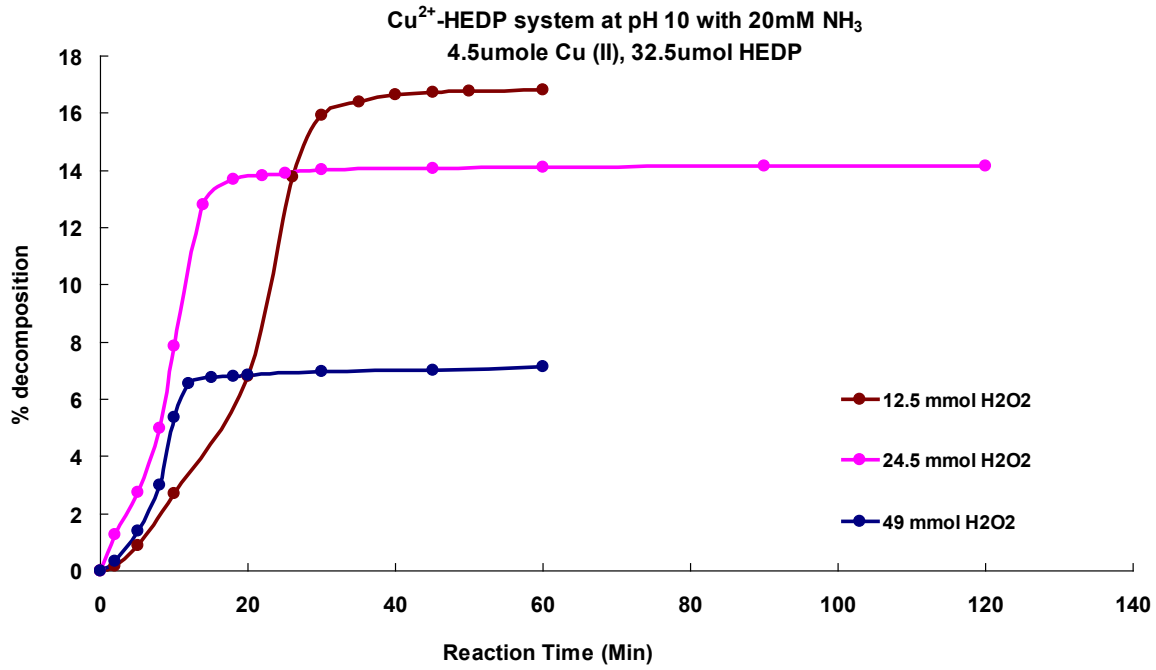


Figure S 10: Copper-HEDP catalysed decomposition of alkaline hydrogen peroxide at different hydrogen peroxide level. Reaction solution contained 4.5 µmol of copper sulfate, 32.5 µmol of HEDP ligand dissolved in 20 mM pH 10 ammonia/ammonium chloride buffer.

1.2.11 Copper-HEDP catalysed hydrogen peroxide decomposition: Oxidation of HEDP vs hydrogen peroxide decomposition

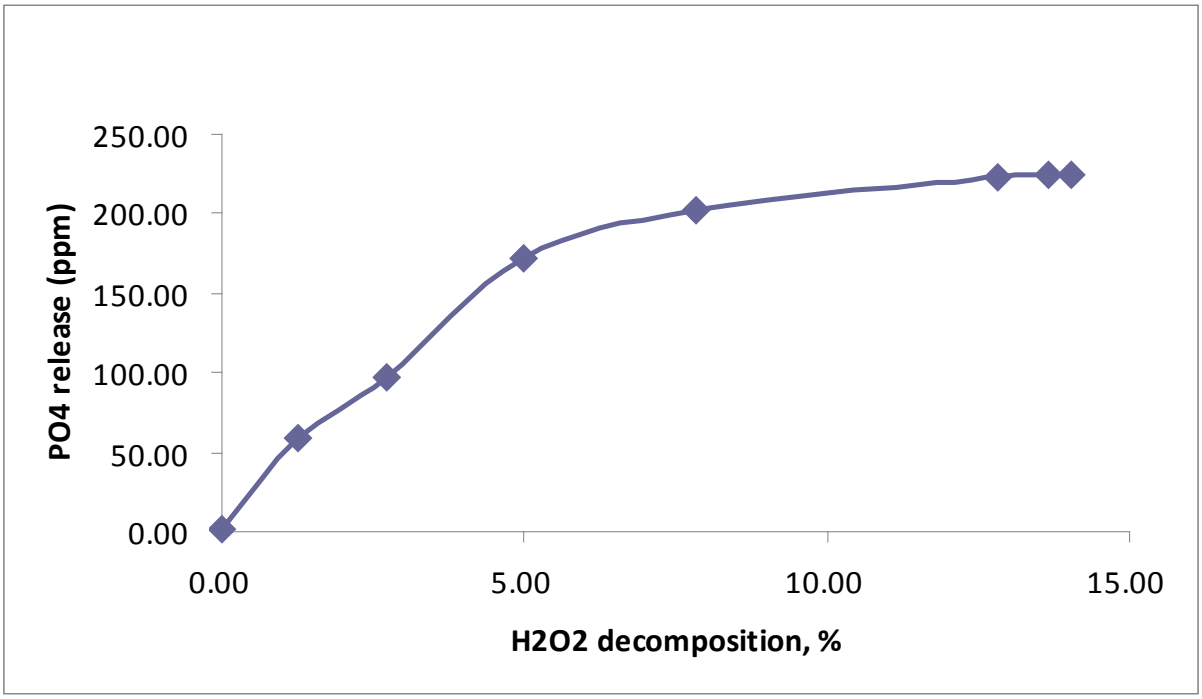


Figure S 11: Hydrogen peroxide decomposition as function of HEDP ligand degradation.

1.2.12 Effect of increasing copper (II) sulfate concentration in Cu-HEDP hydrogen peroxide decomposition reaction

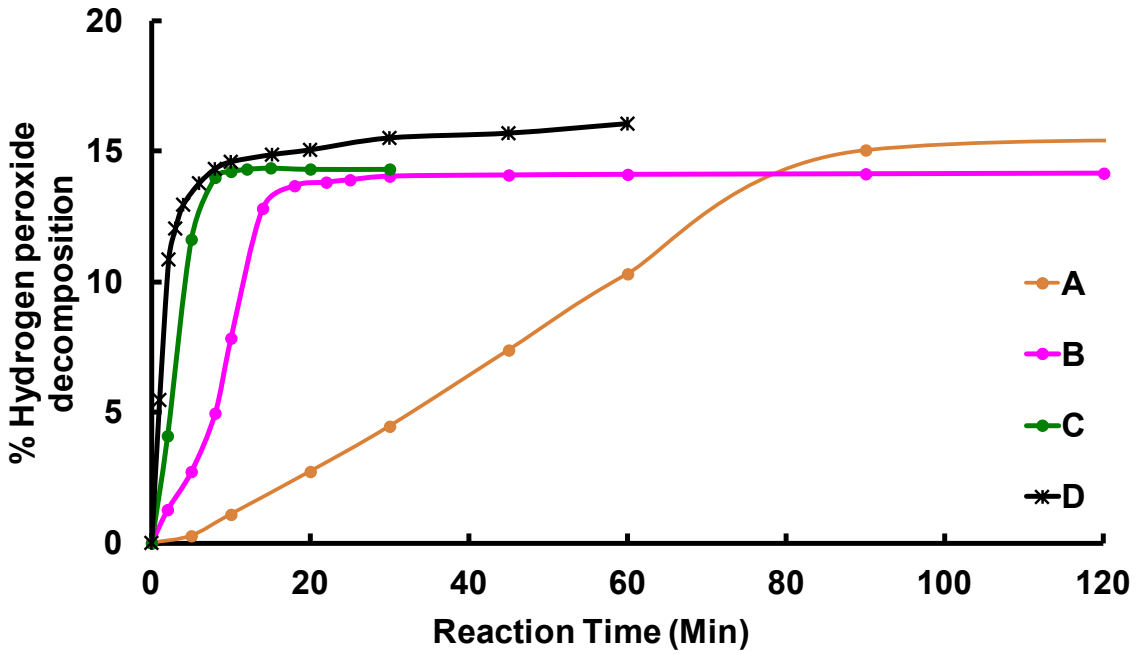


Figure S 12: Effect of increasing copper ion concentration in Cu-HEDP catalysed decomposition of alkaline hydrogen peroxide containing different levels of copper (II) sulfate, 32.5 µmol of HEDP ligand dissolved in 20 mM pH 10 ammonia/ammonium chloride buffer. 24.5 µmol of hydrogen peroxide was added to the reaction at zero time (total reaction volume was 25 mL). (A) 1.25 µmol of $CuSO_4$ (B) 4.5 µmol of $CuSO_4$ (C) 10 µmol of $CuSO_4$ (D) 20 µmol of $CuSO_4$.

1.2.13 Fabrication of copper based nanoparticles without using hydrogen peroxide

Experiment	Reaction volume	Cu (II) sulfate Conc.			Buffer used	Stirring	result
A	25 mL	125 µmol added slowly at 40 °C	250 µmol Na_2HPO_4	125 µmol $(NH_4)_2CO_3$	20 mM NH_3/NH_4Cl buffer pH 10	Stirred 2 hours	Cloudy blue PPT
B	25 mL	125 µmol added slowly at 40 °C	-	-	20 mM phosphate buffer pH 7	Stirred one hour	Cloudy blue
C	25 mL	4.5 µmol added slowly at 50 °C	-	-	20 mM phosphate buffer pH 7	Stirred overnight	No NPs
D	25 mL	4.5 µmol added slowly at 75 °C	-	-	20 mM phosphate buffer pH 9	Stirred overnight	No NPs, clear solution
E	**25 mL**	**12.5 µmol added slowly at 75 °C**	**-**	**50 µmol $(NH_4)_2CO_3$**	**20 mM phosphate buffer pH 9**	**Stirred overnight**	**NPs, UV & TEM**

Figure S 13: Fabricating nanoparticles without using hydrogen peroxide under different conditions of reactions. Reaction E showed formation of nanoparticles.

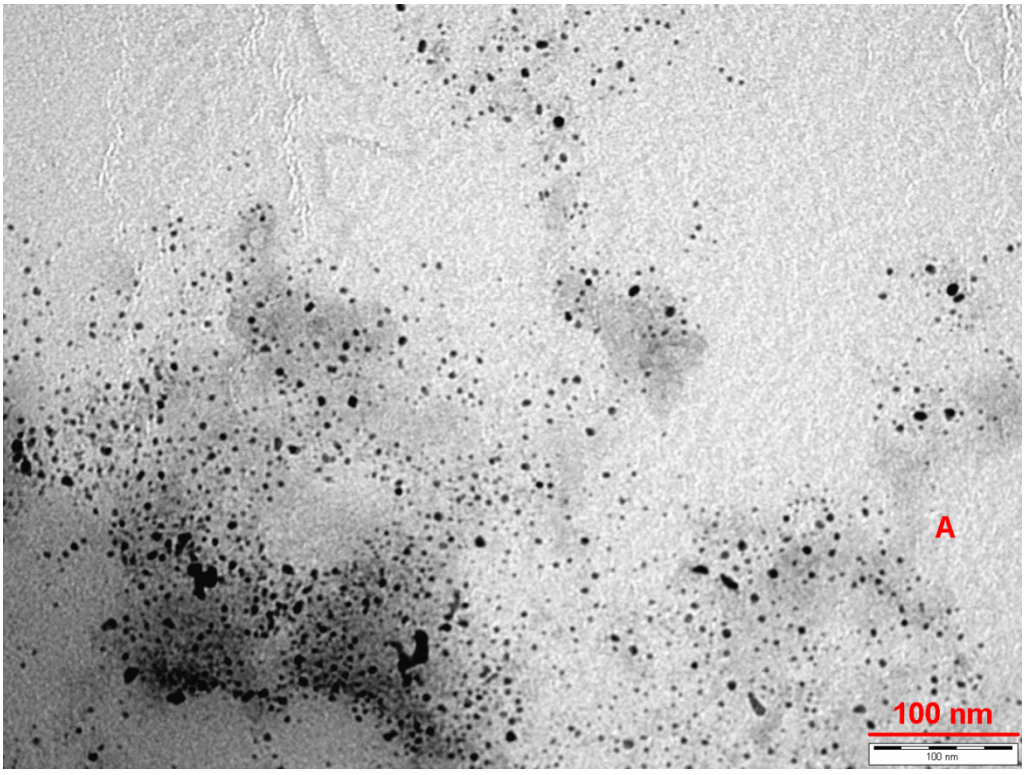


Figure S 14: TEM image of fabricated nanoparticles without using hydrogen peroxide.

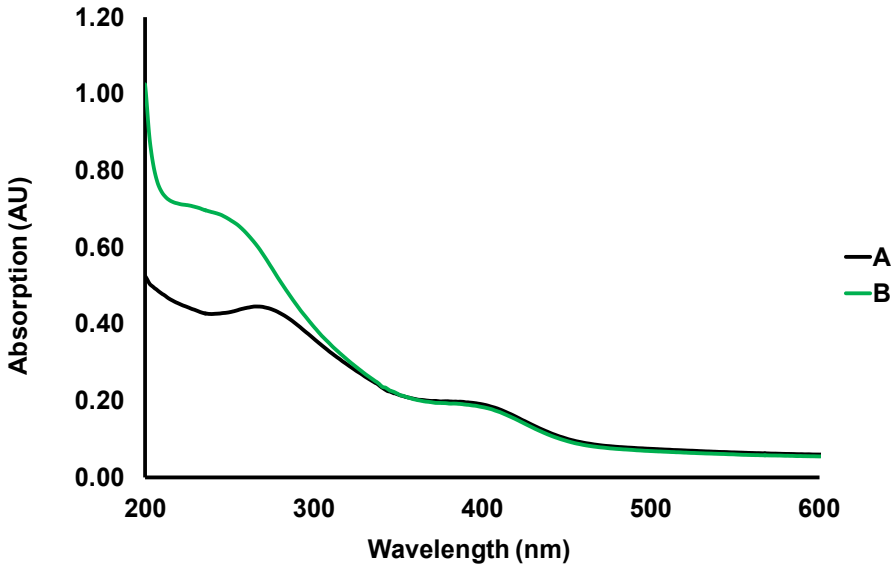


Figure S 15: UV-Vis spectra of fabricated nanoparticles without using hydrogen peroxide (A) 12.5 µmol of copper (II) sulfate with 50 µmol of $(NH_4)_2CO_3$ in 25 mL of 20 mM phosphate buffer pH 10. (B) Fabricated nanoparticles after 10 days kept at lab bench.

1.2.14 UV-visible study demonstrating changes in electronic spectra during the hydrogen peroxide decomposition reaction

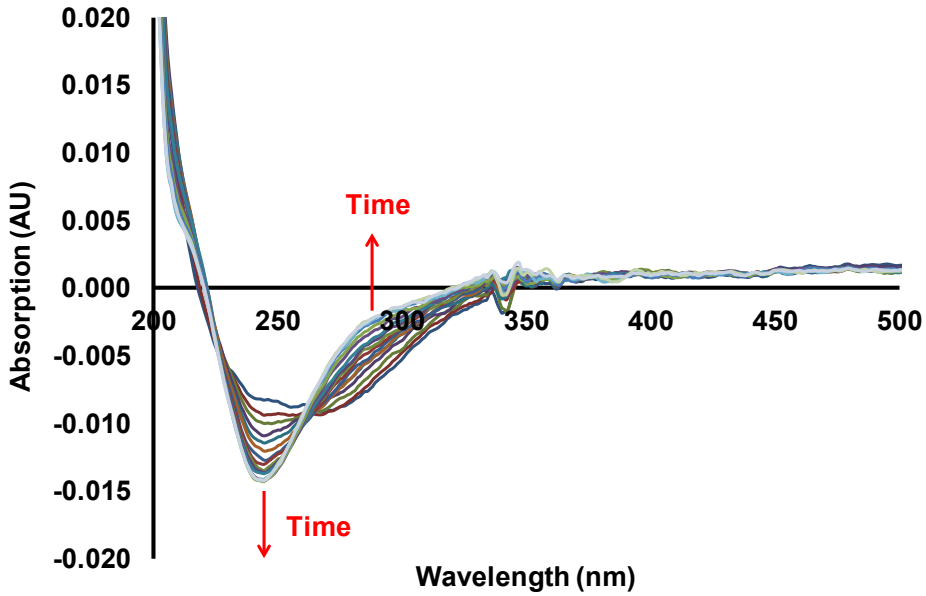
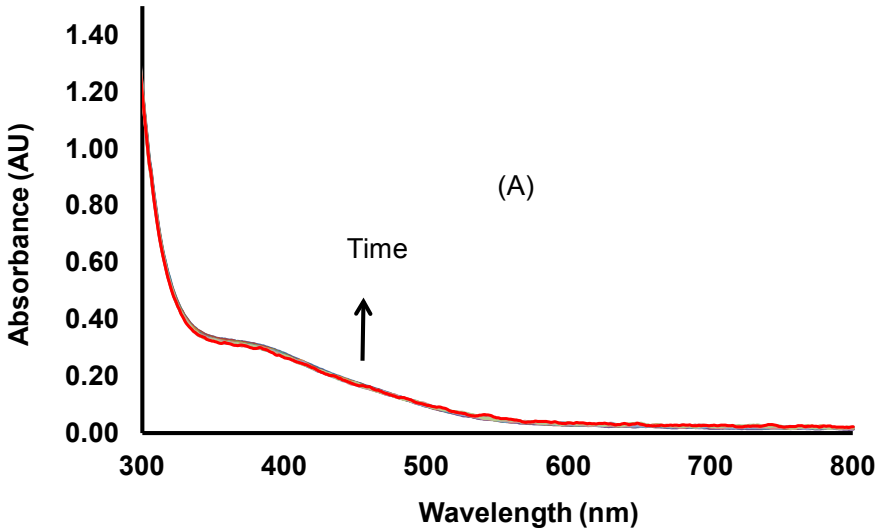


Figure S 16: UV-Vis spectra of Cu-HEDP reaction with hydrogen peroxide. Reaction solution contained 0.15 µmol of copper (II) sulfate, 0.15 µmol HEDP ligand in 20 mM pH 10

ammonia/ammonium chloride buffer pH 10. Hydrogen peroxide (0.3 µmol, total reaction volume 3 mL) was added and spectra were recorded immediately against reagent blank. Reaction was carried out in UV-vis cell. Spectra obtained every 2 minutes over 120 minutes show changes in the reaction solution.

1.2.15 Formation of nanoparticles in a ligand-free system in ammonia/ammonium chloride buffer



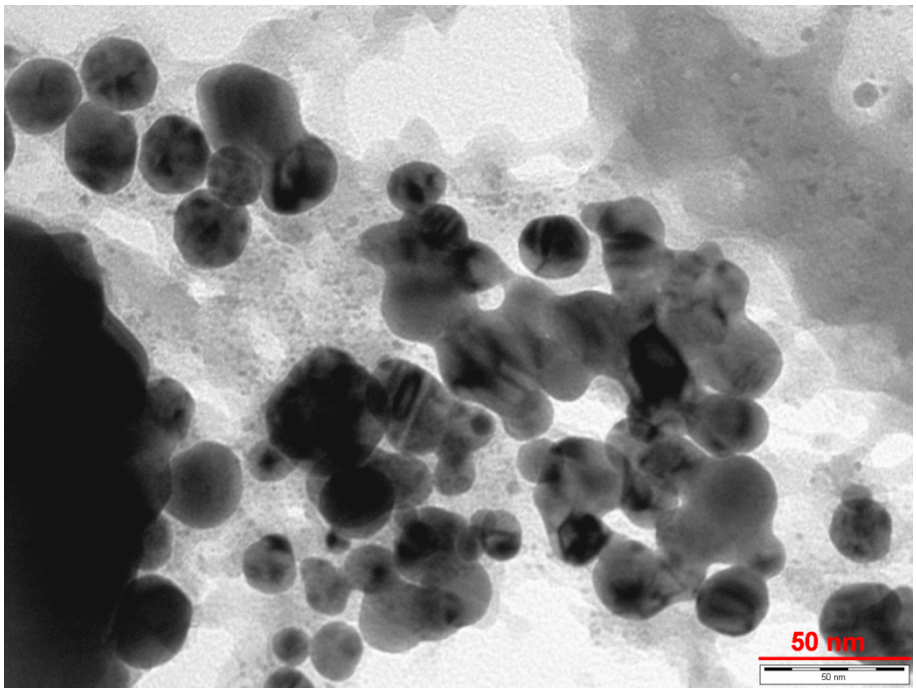
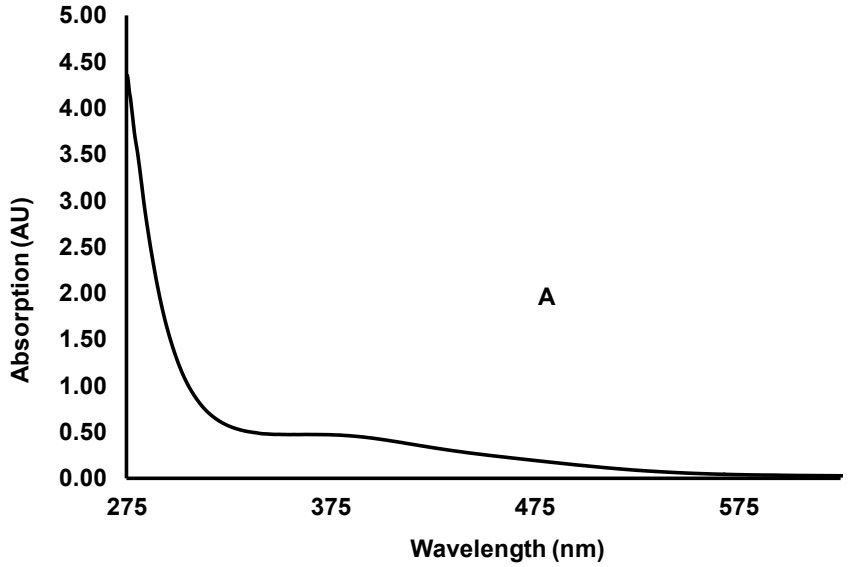


Figure S 17: Formation of nanoparticles in a ligand-free system. (A) Reaction was carried out in a UV-vis cell. The reaction solution contained 4.5 µmol of copper sulfate, 32.5 µmol of

HEDP ligand dissolved in 20 mM pH 10 ammonia/ammonium chloride buffer with 24.5 mmol of hydrogen peroxide (total reaction volume 25 mL). Spectra were obtained every 2 minutes after mixing with hydrogen peroxide against reagent blank. The yellow coloured solution was formed immediately on mixing with hydrogen peroxide. The UV-vis spectra showed formation of nanoparticles. (B) TEM images showed large aggregates of nanoparticles.

1.2.16 Formation of copper based nanoparticles in Cu (II) ligand-free system in a phosphate buffer



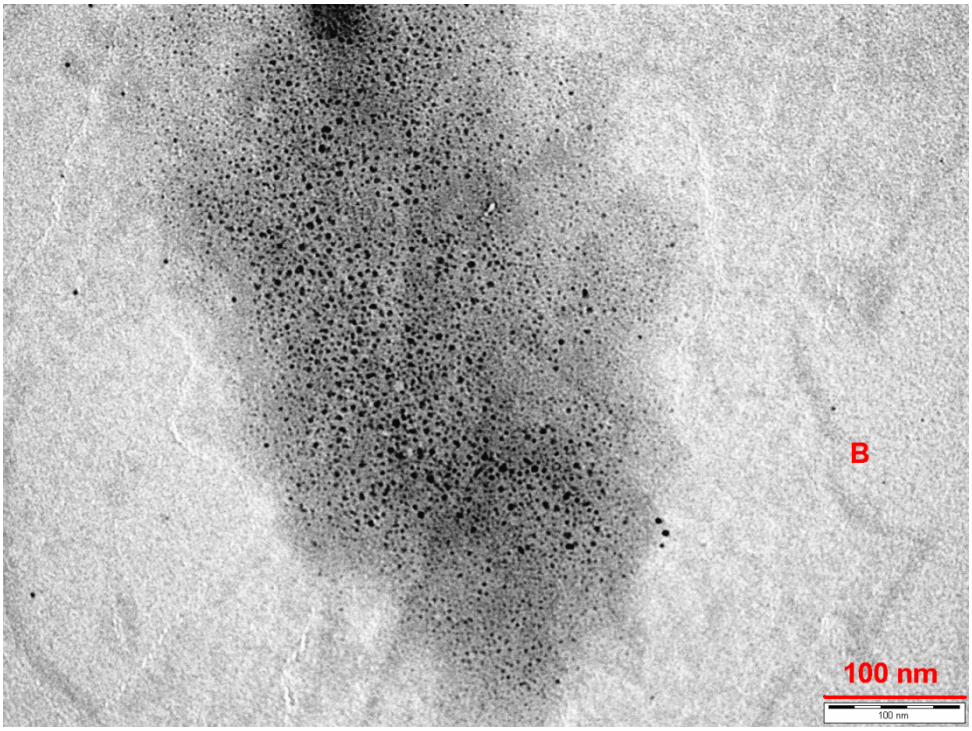


Figure S 18: (A) Formation of copper based nanoparticles in Cu (II) ligand-free system in a phosphate buffer. Reaction solution had 4.5 µmol of copper sulfate in 20 mM pH 10 phosphate buffer with 24.5 µmol of hydrogen peroxide (total reaction volume 25 mL). Yellow coloured solution was observed immediately on mixing with hydrogen peroxide. (B) TEM image of the reaction solution shows presence of nanoparticles.

1.3 References

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2. J. Murphy and J. P. Riley, *Anal. Chim. Acta*, 1962, **27**, 31-36.
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