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Synthesis and characterization of highly efficient copper nanoparticles and their catalytic application in oxidative kinetic study

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ABSTRACT

In the present work, we described the synthesis of copper nanoparticles (Cunps) through a single route of chemical reduction method.The effect of different concentration of reducing agent andtemperature on the morphology of Cunps was investigated. The synthesized copper nanoparticles were characterized by UV-Visible spectrophotometer, Fourier Transform Infrared (FTIR) Spectroscopy, Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM) analysis. The average sizes of copper nanoparticles were found to be 12, 16, 28, 55 nm at different concentration of L-ascorbic acid.The kinetics of copper nanoparticles catalyzed oxidation of glycine (Gly) by peroxodisulphate(PDS) in aqueous medium at 308 K has been studied. The copper nanoparticles catalyst exhibited very good catalytic activity.Interestingly, it was found that, the catalytic activity depends on the size of nanoparticlesand the kinetics of the reaction was found to be first order with respect to peroxodisulphate and independent of glycine concentration. Addition of neutral salts shows a retarding effect.

Keywords: Copper nanoparticles, glycine, L-ascorbic acid, peroxodisulphate, oxidation, kinetics.

INTRODUCTION

Amino acids are the precursors of essential bio-molecules such as proteins, hormones, enzymes, etc. Amino acids derived largely from protein in the diet or degradation of intracellular proteins one the final class of biomolecules which oxidation makes a significant contribution to the generation of metabolic energy. They are liable to lose their amino functional groups by two pathways: transamination or oxidative deamination [1, 2]. The kinetic investigation on the oxidation of amino acids is of great importance both from chemical point of view and its bearing on the mechanism of amino acids metabolism [3].Amino acids can undergo many kinds of reactions, depending upon whether a particular amino acid contains non-polar substituent. The specific metabolic role of amino acid includes the biosynthesis of polypeptides, proteins and synthesis of nucleotides [4].Glycine is an essential amino acid classified as non-polar and forms active sites of enzymes and helps in maintaining proper conformation by keeping them in proper ionic states.Several kinetic studies on the oxidation of amino acids both in acid and alkaline medium and also in presence of metal and non-metal ions catalysts have been reported [5-8]. Aqueous solutions of amino acids have been oxidized by Mn(II) [9],($[Fe(CN)_6]^{3-}$) [10], Chloramines T [11], Peroxomonosulphate [12],Peroxodisulphate[13] etc. in both acid and alkaline media. The peroxodisulphate ion is one of the strongest oxidizing agents known in aqueous solution. The standard oxidation reduction potential is estimated to be -2.01V.

$$2\ SO_4^{2-} \longrightarrow S_2O_8^{2-} + 2e^-$$

The reactions involving this ion are generally very slow in the absence of suitable catalyst [14]. The most thoroughly investigated catalyst is Ag(I) ion although reaction involving Cu(II) and Fe(III) ions also have been studied [15]. Kinetics and mechanism of decarboxylation of amino acids by peroxo oxidants is an area of intensive research because peroxo oxidants are environmentally benign oxidants and do not produce toxic compounds during their reduction.

The applications of transition metal nanoparticles as catalyst for organic transformations include hydrogenation [16], hydrosilation[17] and hydration reaction of unsaturated organic molecules [18] as well as redox [19] and other electron transfer process. Among the metal nanoparticles, Copper nanoparticles (Cunps) are very attractive due to their heat transfer properties such as high thermal conductivity. Copper nanoparticles also have high surface area to volume ratio, low production cost, antibacterial potency and catalytic activity, optical and magnetic properties as compared to precision metals such as gold, silver or palladium. The main difficulty lies in their preparation and preservation as they oxidized immediately when exposed in air. Scientists are using different inert media such as Argon, Nitrogen[20-22] to overcome this oxidation problem also using reducing, capping or protecting agents for the reduction of copper salt used. Some reducing and capping agents are very expensive and also have toxic effects. Physical and chemical methods are two basic techniques for the synthesis of Copper nanoparticle. Vacuum vapor deposition [23], pulsed laser ablation [24], pulsed wire discharge [25] and mechanical milling [26] are physical techniques while Chemical reduction [27], Micro emulsion techniques[28], sonochemical reduction [29], Electrochemical [30], Microwave assisted [31], and hydrothermal [32] are chemical approaches for the synthesis of nanoparticles. Biological or biosynthesis [33] techniques are also considered as chemical methods. Copper nanoparticles have high thermal conductivity [34] and also the production cost is very low as compare to noble metals. Copper nanoparticles production using chemical reduction method gives good results and it has simple control on the size and shape of particles under controlled parameters like concentration of reducing agent, temperature etc. but use of hazardous reducing and costly and protecting agent [35-41] makes the process toxic in some cases. To avoid the toxicity and to prepare Copper nanoparticles in green environment, we have used ascorbic acid in our chemical reduction process. Ascorbic acid works both as reducing and protecting agent, which makes the process economical, nontoxic and environment friendly [34]. Though studies on kinetics of oxidation of amino acid with peroxodisulphate have been widely carried out [42, 43], but in the present study, the universal nature of copper nanoparticles as catalysts was highlighted by employing highly efficient copper nanoparticles for the oxidation of glycine by peroxodisulphate in aqueous medium.

MATERIALS AND METHODS

Material

For the present work, we used analytical grade chemicals such as copper chloride dihydrate ($CuCl_2.2H_2O$-97%), L-ascorbic acid (vitamin C-98%), glycine and peroxodisulphate were obtained from E. Merck. A fresh solution of peroxodisulphate was prepared before starting the experiments. All chemicals were used as received without further purification. Double distilled water was employed throughout the study.

Synthesis of Copper Nanoparticles

The one step synthesis scheme for copper nanoparticles initiates with dissolving require amount of copper chloride dihydrate in 50 ml deionized water to obtain a blue solution. L-ascorbic acid (0.01 mol L^{-1}) drop wise added to the aqueous solution of copper salt while vigorously stirring at 353 K in oil bath. With the passage of time, the colour of dispersion gradually changed from white, yellow, orange, brown finally dark brown with a number of intermediate stages. The appearance of yellow colour followed by orange colour indicated the formation of fine nanoscale copper particles from L-ascorbic acid assisted reduction, finally changed into brown color the resulting dispersion was centrifuged for 15 minutes. The supernatant was placed under ambient conditions for 2 months. The studies were performed at different concentration of ascorbic acid to investigate the size and shapes of copper nanoparticles.

Characterization

UV-Visible spectroscopy from a double beam spectrophotometer (U.V. 3000^+ LABINDIA) was used for preliminary estimation of copper nanoparticles synthesis. FTIR (ALPHA-T –Bruker) provided information about oxidation product of the reaction. Morphological study of the copper nanoparticles was carried out with scanning electron microscope (SEM) (EVO 18 carlzeiss) and Transmission electron microscope (TEM) (FEI Techni G2S2 Twin). TEM and SEM images were recorded to confirm size distribution and shape homogeneity of synthesized copper nanoparticles.

Kinetic Measurements

All reactions were carried out in Erlenmeyer flasks painted black from the outside to check photochemical decomposition. Calculated volumes of copper nanoparticles and glycine were taken in a reaction vessel and were put in a thermostat maintained at 308K. To start the reaction the calculated quantities of potassium peroxodisulphate solution were added to the reaction flasks. The progress of the reaction was studied by estimating the remaining peroxodisulphate iodometrically at different interval of time. Since the concentration of amino acid is ten times more than that of the peroxodisulphate, a pseudo first order plots is drawn from which the values of k_{obs} is determined.

RESULTS AND DISCUSSION

Copper Nanoparticles Characterization Results

In recent years, several studies have shown that optical properties of metal nanoparticles depend upon the geometry and size, thus the optical response of metal nanoparticles can be control shape and size of metal nanoparticles [44].Since surface Plasmon modes of metal nanoparticles like Au, Ag, Cu reside within the optical region of electromagnetic spectrum [45, 46], optical spectroscopy can be used as primary tool for investigation of such nanoparticles. UV-visible spectral profile for copper nanoparticles was recorded with time. During the synthesis of copper nanoparticles in aqueous solution, the dispersion became colourless when L-ascorbic acid was added, and gradually turned to yellow, orange, brown and finally change into dark brown solution. The UV-Visible spectra of samples were recorded at different time intervals for every colour (Figure 1).

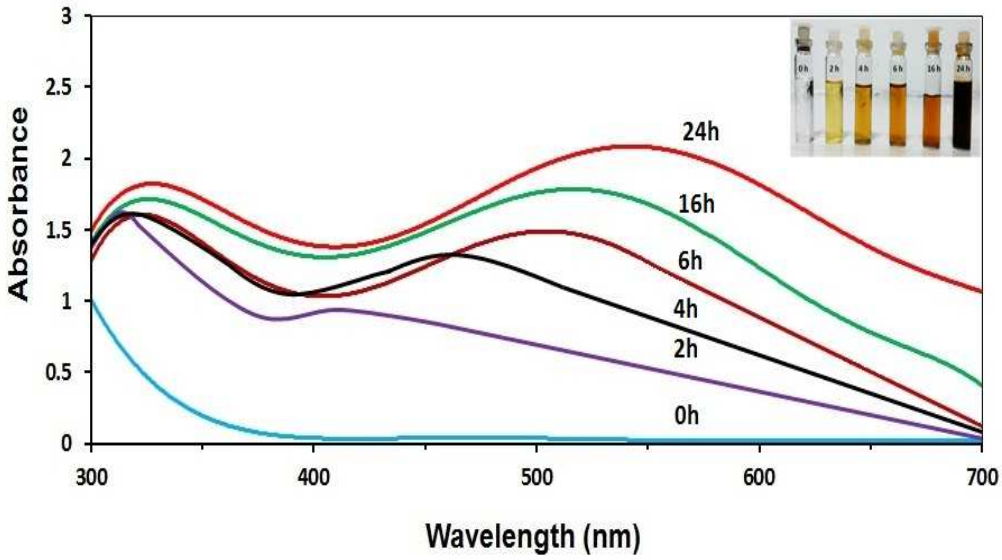


Figure 1:The time evolution of the dispersion photographs and the UV-Visible spectra

The spectacular colour change correlates with large shift of UV-Visible spectra. The first absorption peak of different curves is at 335 nm corresponding to oxidation product of L-ascorbic acid [47]. The second absorption peak is increasingly broadening with an increasing concentration of L-ascorbic acid. The absorption peak of copper nanoparticles has been reported at around 560 nm of UV-Visible wavelength which proves the formation of copper nanoparticles [48, 49].In this work, the resulting copper nanoparticles displayed a broadened peak at 550 nm wavelength, indicating the presence of small separated copper nanoparticles, it is well established fact that peak position and width are highly influenced by particle shape and size [50].

Effect of reducing agent concentration

To evaluate the effect of L-ascorbic acid concentration (0.07, 0.08, 0.09, and 0.10 mol L^{-1}) on the synthesis of copper nanoparticles were recorded on UV-Visible spectroscopy. The results indicate that a higher L-ascorbic acid concentration leads to a more effective capping capacity of L-ascorbic acid and then formed smaller Cu nanoparticles which can also be proved by the TEM images of copper nanoparticles (Figure 2).The TEM images show that the particles are spherical in shape and decrease in particle size with an increase in L-ascorbic acid concentration. The size of the copper nanoparticles with various concentration (0.07, 0.08, 0.09, 0.10 mol L^{-1}) of L-ascorbic acid are 55, 28, 16, 12 nm respectively. The reason is that L-ascorbic acid molecules encapsulateCu^{+2} and reduce Cu^{+2}into Cu(0), then oxidation products absorbs on the resulting copper nanoparticles surface preventing the particles from growing further as a result smaller copper nanoparticles obtained. Thus, the number of Cu^{+2}encapsulated in ascorbic acid molecules decreases with increasing concentration of L-ascorbic acid, leading to the formation of smaller copper nanoparticles.

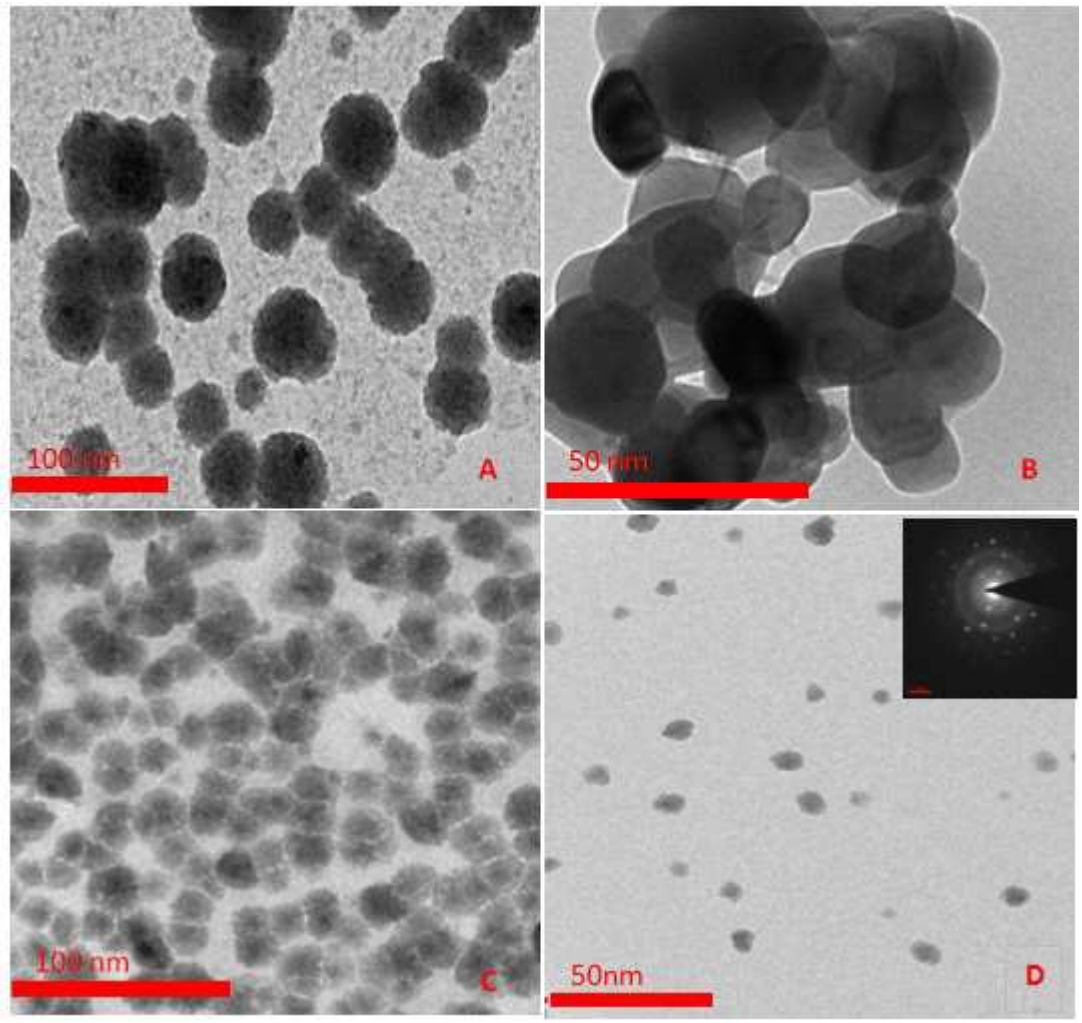


Figure 2:TEM images of copper nanoparticles with variable concentration of L-ascorbic acid: (A) 0.07, (B) 0.08, (C) 0.09, (D) 0.1 mol L^{-1}

Effect of reaction temperature

The present investigation reveals that nanoparticles did not synthesize below the temperature 333K in any conditions. This shows that reaction constant at this temperature is too low to progress the reaction. Therefore reaction temperature higher than 333K with appropriate concentration of the reactants should be inserted to the progress of the reaction for synthesis of copper nanoparticles. In Figure 3, SEM images A, B, C of copper nanoparticles synthesized at 343 K, 353 K, 363 K respectively, comparison of the images shows that the copper nanoparticles synthesized at 363 K have a wider range of size distribution. In addition, the nanoparticles were agglomerated in these conditions while copper nanoparticles synthesized at 353 K are well dispersed with an average size about 12 nm.

Basically, the reduction rate of Cu^{+2}ions was increases by increasing the reaction temperature. Therefore the synthesis rate is too high to control particle size at high temperature. When reducing agent adds to precursor solution at 363 K, rate of growth and agglomeration as well as nucleation of copper nanoparticles accelerated almost coincidently. These phenomena result in the formation of copper nanoparticles with high averaged size of the copper nanoparticles were precipitated. Thus moderate temperature (353 K) should be selected for synthesis of the copper nanoparticles with appropriate controlling on size.

Stability of nanoparticles

The stability of nanoparticles dispersion is key factor in their application. In this study L-ascorbic acid was used as both reducing and capping agent without any other special capping agent. The antioxidant properties of L-ascorbic acid came from its ability to scavenge free radicals and reactive oxygen molecules[51], accompanying the donation of electrons to give semi-dehydroascorbate radical and dehydroascorbic acid hydration of 2-carbonyl is also reported[52]and finally converted into polyhydroxyl structure through hydrolysis[47]. Therefore L-ascorbic acid

plays dual role as reducing agent and antioxidant of copper nanoparticles. As a result, the reaction can be done without any protective inert gas and the dispersion of copper nanoparticles is stable for 2 months after storage.

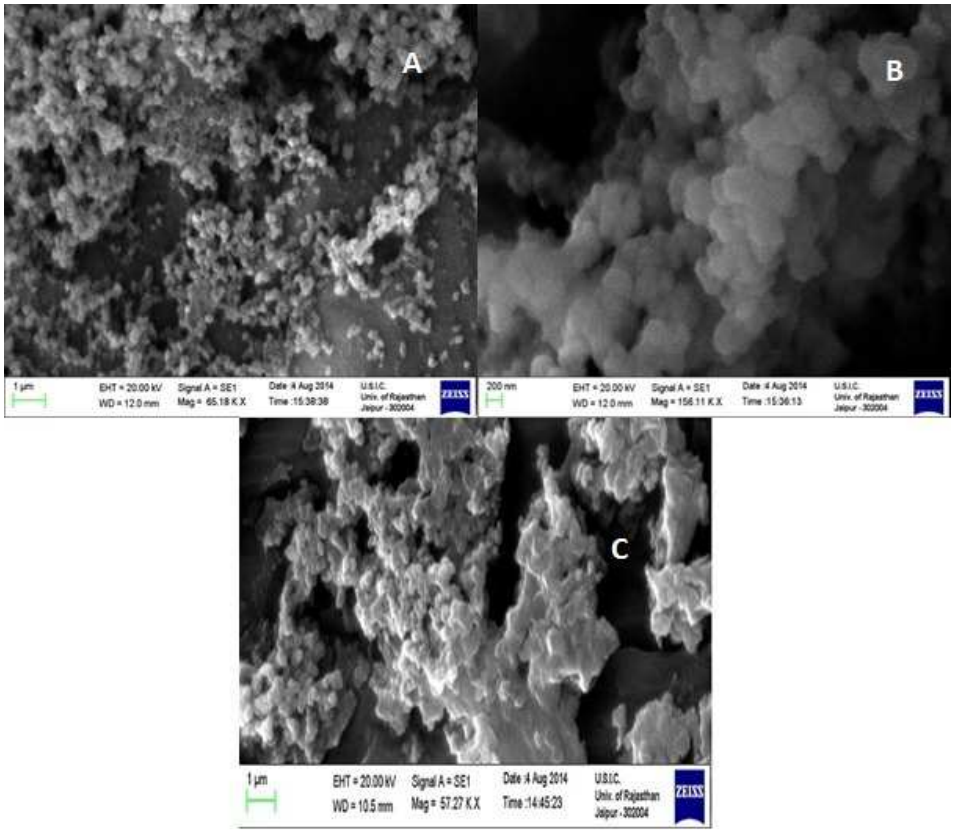
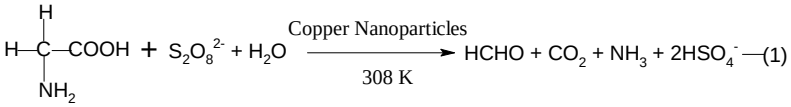


Figure 3: SEM images of synthesized copper nanoparticles with variation of temperature (A) 343 K, (B) 353 K, (C) 363 K

Stoichiometry and Product analysis

Under the kinetic conditions, the reaction was carried out with excess of peroxodisulphate over glycine in presence of nanoparticles in a thermostat water bath at 308K for 24 hours. The excess of peroxodisulphate was determined iodometrically. An addition of 2, 4-dinitrophenyl hydrazine in the reaction mixture yield brown precipitate of hydrazone derivative of aldehyde[13]. The product aldehyde was confirmed by its FTIR spectrum (Figure 4). The IR peaks at 3330 cm^{-1}, 2907 cm^{-1}, 1607 $cm^{-1}$are attributed to –NH, –CH, –C=N stretching respectively. From observations of different sets, the Stoichiometry of the reaction can therefore be presented by equation (1).



Ammonia identified by nessler′s reagent, brownish color was observed indicating deamination reaction, carbon dioxide was identified by freshly prepared lime water and the solution turned milky indicating decarboxylation reaction. The deamination of the glycine in presence of copper nanoparticles was shown in UV- Visible absorption spectrum (Figure 5).

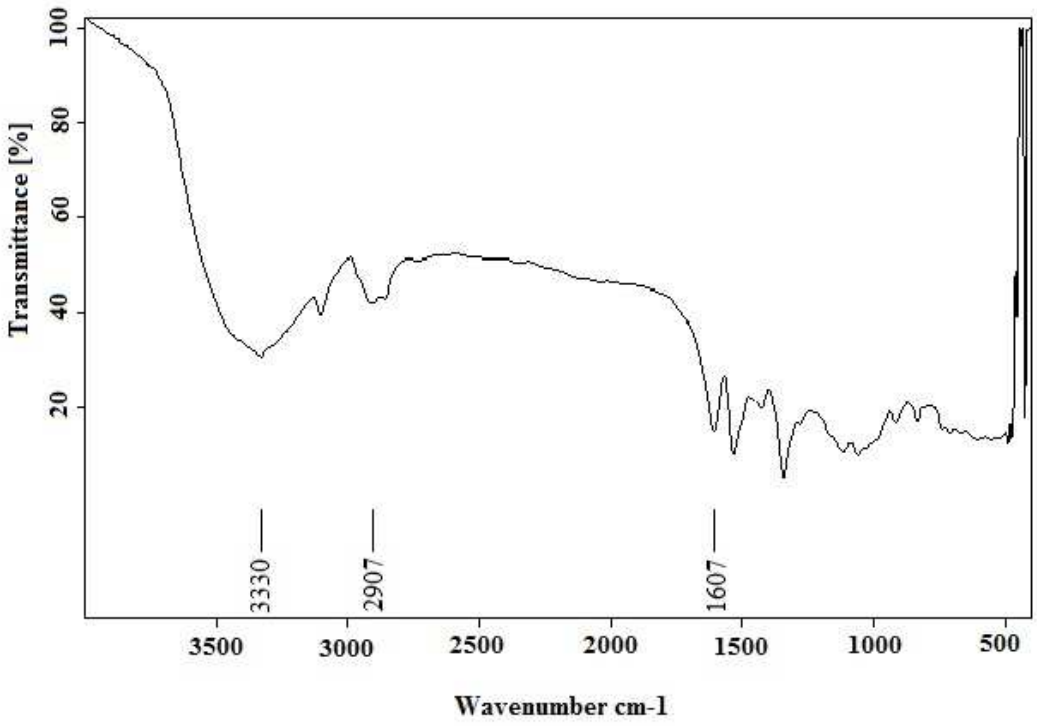


Figure 4: The FTIR Spectra of the oxidation product of glycine oxidation

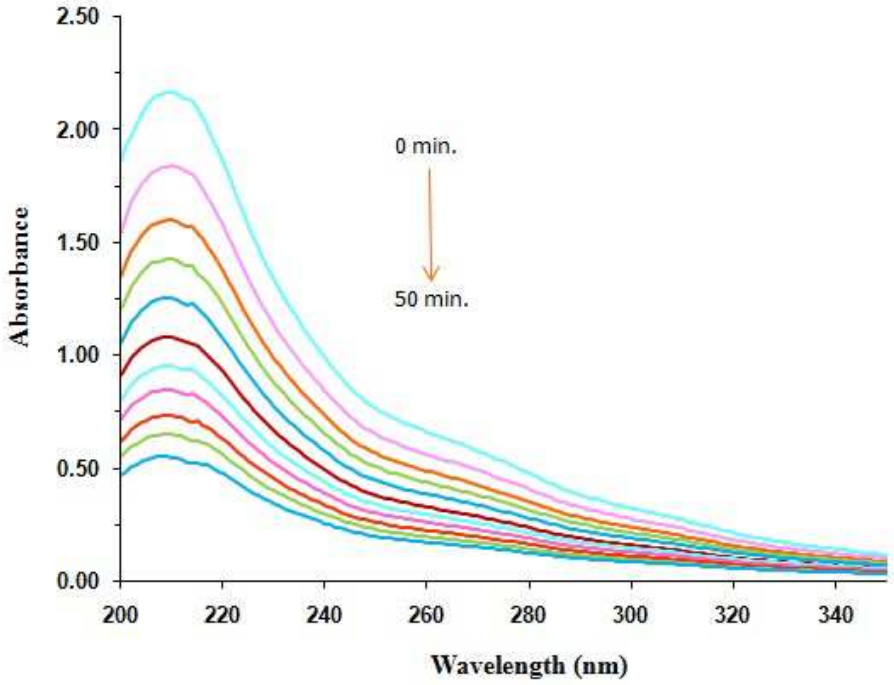


Figure5: UV spectra for the deamination of glycine (time 0-50 min.) in the presence of the copper nanoparticles at fixed [PDS] = 5×10^{-3} mol L^{-1}, [Cunps] = 1×10^{-5} mol L^{-1} at 308 K

Peroxodisulphate dependence

Kinetic runs were carried out by varying concentration of peroxodisulphate from 1×10^{-3}– 7.5×10^{-3} mol L^{-1}at fixed concentration of [Gly] = 5×10^{-2}mol L^{-1},[Cunps] = 1×10^{-5} mol L^{-1}at 308 K temperature. The plot of log [PDS] versus time was linear for each initial concentration of PDS (Figure 6), indicating that the reaction is first order with respect to [PDS].

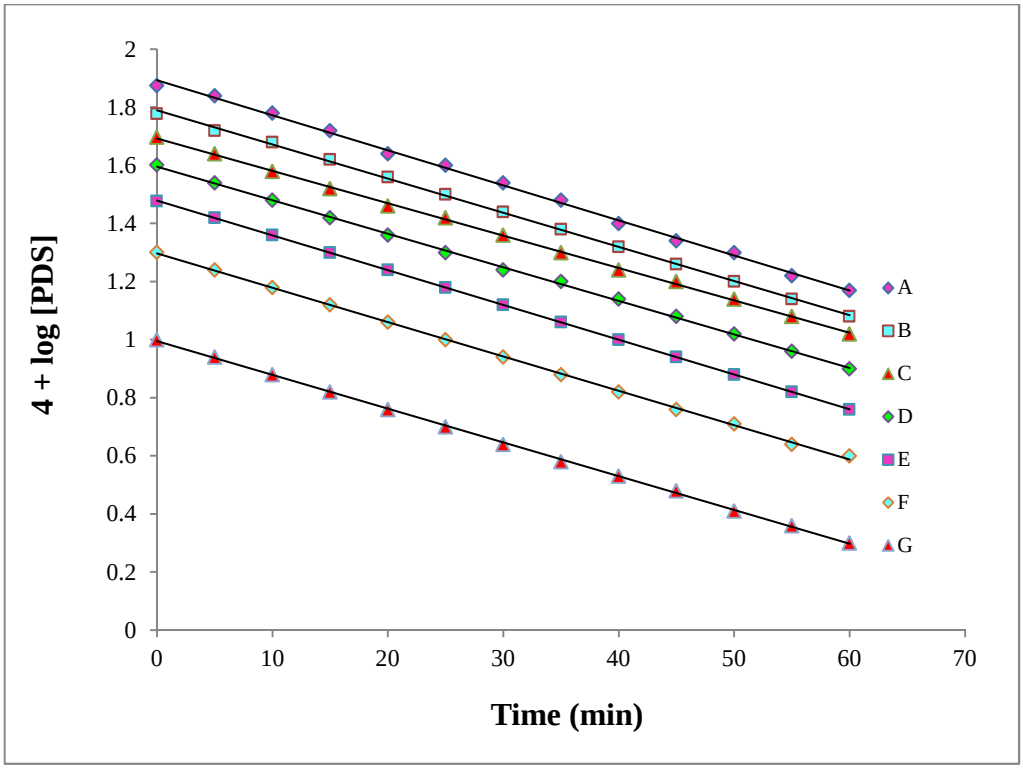


Figure 6: First order plots of the variation of peroxodisulphate concentration at 308 K
[Gly]= 5.0×10^{-2}mol L^{-1}, [Cunps] = 1.0×10^{-5} mol L^{-1}, [PDS]×10^{-3} mol L^{-1} = (A) 1.0, (B) 2.0, (C) 3.0, (D) 4.0, (E) 5.0, (F) 6.0, (G) 7.5

Glycine dependence

Reaction were carried out at constant concentration of all reactants [PDS] = 5×10^{-3} mol L^{-1}, [Cunps] = 1×10^{-5} mol L^{-1}and by varying initial concentration of glycine from1×10^{-2} – 7×10^{-2} mol L^{-1} at 308 K temperature. Plot of log k_{obs} versus log [Gly] give straight line parallel to log [Gly] axis indicating zero order dependence with respect to glycine(Figure 7).

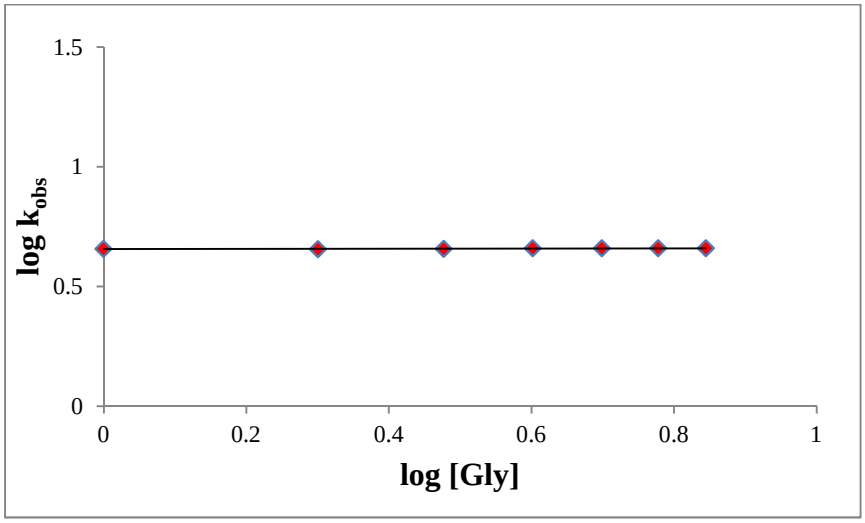


Figure 7: First order plots of the variation of glycine concentration at 308 K
[PDS]= 5.0×10^{-3}mol L^{-1}, [Cunps] = 1.0×10^{-5}mol L^{-1}, [Gly]×10^{-2}mol L^{-1} = (A) 1.0, (B) 2.0, (C) 3.0, (D) 4.0, (E) 5.0, (F) 6.0, (G) 7.0

Copper nanoparticles dependence

The effect of copper nanoparticles on the rate of oxidation of glycine has been studied at varying concentration of copper nanoparticles 1×10^{-6} - 1×10^{-5} mol L^{-1} at four different size of nanoparticles (55, 28, 16 and 12 nm), synthesized at four concentration (0.07, 0.08, 0.09, 0.10 mol L^{-1}) of ascorbic acid respectively, other reactant and reaction conditions were constant. The rate of reaction increases with increasing concentration of copper nanoparticles. The catalytic activity of copper nanoparticles seems different when concentration of reducing agent is

varied from 0.07 to 0.1mol L^{-1}.The difference in catalytic activity can be attributed to the size variation in the resulting copper nanoparticles. The trend in the calculated rate constant being 12>16>28>55nm (Figure 8). This effect can be attributed to the nanosize of the particles that as size decreases surface area increases and the active centre are also increases.

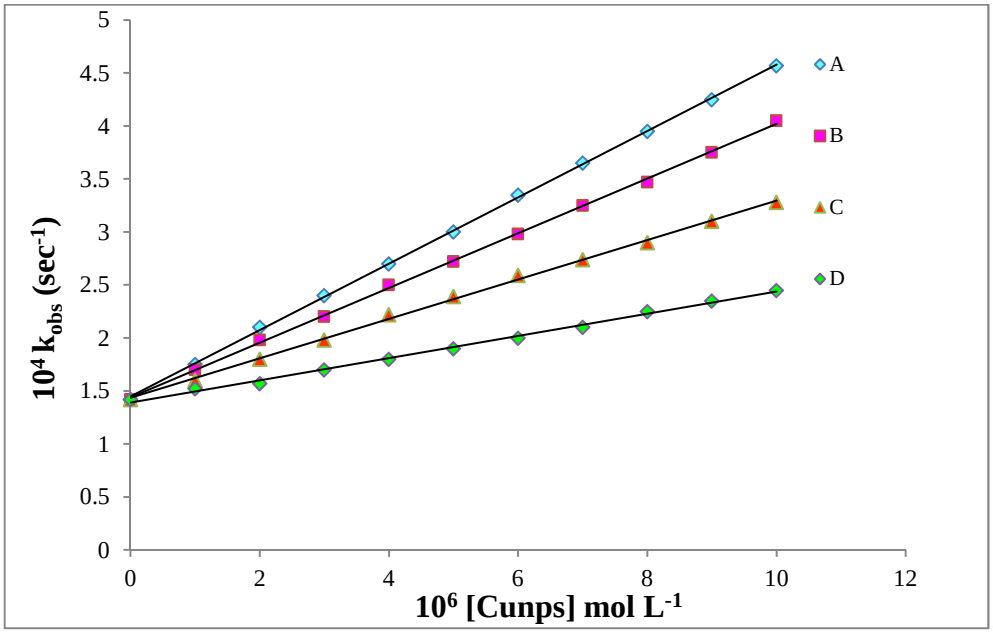


Figure 8: The effect of [Cunps] at different size of Cunps in nm (A) 12, (B)16, (C) 28, (D) 55 at fixed [PDS] = 5.0×10^{-3} mol L^{-1}, [Gly] = 5.0×10^{-2}mol L^{-1} at 308K

Temperature dependence

The effect of temperature on the rate of reaction was studied at three temperature 303 K, 308 K, 313 K respectively at constant concentration of other reaction ingredients. A plot of log k_{obs} was made against 1/T, yielded a straight line. The energy of activation (E_a),entropy of activation ($\Delta S^{\neq}$), enthalpy of activation ($\Delta H^{\neq}$), free energy of activation (ΔG) were obtained 24.69 KJ mol^{-1}, -237.32JK^{-1} mol^{-1}, 22.13 KJ mol^{-1}, 95.226 KJ mol^{-1} respectively.The high positive values of free energy of activation (ΔG) and enthalpy of activation (ΔH) indicated that the transition state was highly solvated while the negative values of entropy of activation (ΔS) was suggested the formation of rigid transition state with reduction in the degree of freedom of molecules.

Neutral Salts dependence

The effect of added neutral salt on the rate of reaction has been studied at varying concentration $1x10^{-3}$- $4x10^{-3}$of KCl, NH_4Cl and K_2SO_4 at fixed concentration of other reactant and constant conditions. The results shows (Table-1)the retarding effect of some ions on the rate of reaction of copper nanoparticles catalyzed oxidation of glycine by peroxodisulphate. The decrease in the rate constant is not strictly related to the increase in ionic strength and evidently there is a considerable specific effect of the ions. Similar observations have been obtained in earlier study [13].

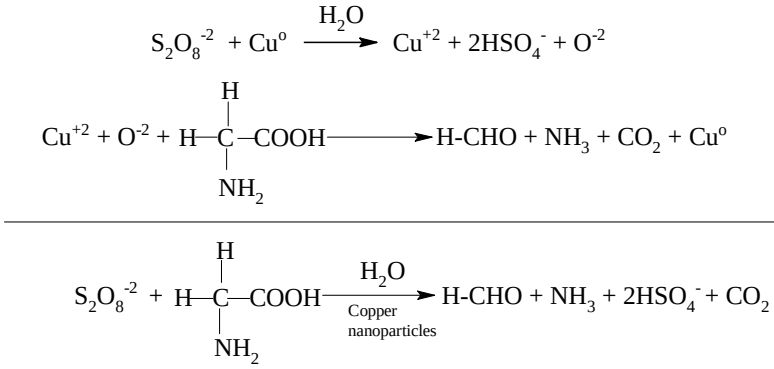
Table 1: [PDS] = 5×10^{-3}mol L^{-1}, [Cunps] = 1×10^{-5}mol L^{-1}, [Gly] = 5×10^{-2}mol L^{-1}, Temp. = 308 K

Neutral Salts	10^3 Concentration mol L^{-1}	Ionic Strength Contributed $10^3\times\mu$	Rate Constant 10^4 k_{obs} sec^{-1}
KCl	1.0	1.0	4.47
	2.0	2.0	4.38
	3.0	3.0	4.18
	4.0	4.0	4.08
NH_4Cl	1.0	1.0	4.41
	2.0	2.0	4.28
	3.0	3.0	4.05
	4.0	4.0	3.89
K_2SO_4	1.0	3.0	4.11
	2.0	6.0	3.93
	3.0	9.0	3.79
	4.0	12.0	3.51

Mechanism

The definite mechanism of the homogeneous metal nanoparticles catalyzed oxidation is not clear. Although identify the formation of transition species through certain physical measurements but it is very difficult to isolate and

characterize from homogeneous mixture. Since in the present study, the rate of reaction does not depend upon the concentration of glycine, oxidative deamination of glycine occurs in presence of peroxodisulphate only upon addition of copper nanoparticles while peroxodisulphate converted to hydrogen sulphate ion. The plausible mechanism in support of the observed kinetics is given in scheme-1.



Scheme 1: The plausible route of copper nanoparticles catalyzed oxidation of glycine

CONCLUSION

In the present work, highly stable dispersed copper nanoparticles were synthesized in aqueous medium without employing any protecting gas. By this green method, synthesis of monodispersed copper nanoparticles (ranging from 12 – 55 nm) employing by different concentration of reducing agent. L-ascorbic acid is used as both reducing and capping agent. The synthesized nanoparticles are highly stable and do not show sedimentation even after storage for 2 months. Moreover, it was clearly shown that reaction temperature has a remarkable effect on particle size and agglomeration of the synthesized copper nanoparticles. The catalytic activity of synthesized copper nanoparticles was investigated by the oxidation of glycine in aqueous medium. The size of copper nanoparticles decreases the catalytic activity of copper nanoparticles increases. The results of this study indicate that the reaction between glycine and peroxodisulphate in the presence of Cunps was first order.

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REFERENCES

[1] Laloo D,Mahanti MK,*JChem SocDalton Trans*, **1990**,1, 311.
[2] Alvarez-Macho MP, *Rev RoumChim*,**1993**, 38, 999.
[3] Devra V,*JIndChemSoc*, **2005**,82, 290.
[4] Barrett GC, Amino acids, peptides and proteins, Royal society of Chem., UK, **2006,** pp 219.
[5] Hiraemath RC, Mayanna SM, Venkatasubramanian N, *JChem Soc Perkin Trans II*,**1987,**2, 1569.
[6] Gupta D, Bhasin M, Devra V, Sharma I, Sharma PD, *Oxidation Communications*,**1996,**19, 242.
[7] Yadav MB, Devra V and Rani A,*Indian Journal of chemistry*,**2010,** 49A, 442.
[8] Chandraju S, Rangappa KS, Made Gowda NM,*Int J ChemKinet*,**1999,**31,525.
[9] Iloukhani H, Bahrami H,*IntJ ChemKinet*,**1999,**31,95.
[10] Jose TP, Nandibewoor ST, Tuwar SM, *J Solution Chem*,**2006,**35,51.
[11] Grover N, Kambo N, Upadhyay SK, *Indian JChem***,2002**, 41A**,**2482.
[12] Rayappan SM, Easwaramurthy D, Palanichamy M, Murugesan V, *Inorgani Chemistry Communications*, **2010,**13,131.
[13] Chandra G and Srivastava SN, *Bull Chem Soc*, **1971**, 44, 3000.
[14] Marshell H, *JChem Soc*,**1891,**59, 771.
[15] Woods R, Kolthoff IM and Meehan EJ, *InorgChem*,**1965,**4, 697.
[16] Nasirian A, *Int J Nano Dim*, **2012**, 2, 159.
[17] Lewis LN, Lewis N, *J Am Chem Soc*,**1986**, 108, 7228,Lewis LN, Uriarte R, *JOrganometallics*,**1990**, 9, 621.
[18] Hirai H, Komiyama H, *Bull Chem Soc Jpn*, **1986**, 59, 545.
[19] Spiro M, *Catal Today*, **1993**, 17, 517.
[20] Feldheim DL, Foss JR, *Metal Nanoparticles; Synthesis, Characterization, and Applications*, New York, USA, Marcel Dekker Incorporated, **2002,** pp 17.

[21] Siegel RW, Hu E, Roco MC, *Nanostructure Science and Technology: R & D Status and Trends in Nanoparticles, Nanostructured Materials, and Nano-devices*, 1 ed., In: WTEC Panel Report, Kluwer Academic Press, Dordrecht, Netherland, **1999**pp 1.
[22] Jana NR, Wang ZL, Sau TK, *Current Science*, **2000**, 79,1367.
[23] Yeh MS, Yang YS, Lee YP, *Journal of Physical Chemistry-B*, **1999**, 103, 6851.
[24] Liu Z, Bando Y,*Advanced Materials*,**2003**, 15, 303.
[25] Yatsui K, Grigoriu C, Kubo H, *Applied Physics Letters*, **1995**, 67, 1214.
[26] Oleszak D, Shingu PH, *Journal of Applied Physics*, **1996**, 79, 2975.
[27] Wang Y, Chen P, Liu M, *Nanotechnology*, **2006,**17, 6000.
[28] Pileni MP, *Journal of Physical Chemistry*, **1993**, 97, 6961.
[29] Kumar RV, Mastai Y, Diamant Y, *Journal of Materials Chemistry*, **2001**, 11, 1209.
[30] Molares M, Buschmann V, Dobrev D, *Advanced Materials*, **2001,** 13, 62.
[31] Takayama S, Link G, Sato M, *Microwave and Radio Frequency Applications, In: Proceedings of the Fourth World Congress on Microwave and Radio Frequency Applications*,, Austin, Texas, USA, **2004,**pp 311.
[32] Chu LY, Zhou Y, Dong L, *Advanced Functional Materials*, **2007**, 17, 933.
[33] Bali R, Razak N, Lumb A, *International Conferenceon Nanoscience and Nanotechnology*, **2006,** 0, 224.
[34] Umer A, Naveed S, Ramzan N, *NANO: Brief Reports and Reviews*, **2012**, 7, 1230005.
[35] Bonet F, Delmas V, Grugeon S, *Nano Structured Materials*, **1999**, 11, 1277.
[36] Murphy CJ, San TK, Gole AM, *Journal of Physical Chemistry B*, **2005**, 109, 13857.
[37] Pastoriza-Santos I,Liz-Marzan LM, *Langmuir*, **1999**, 15, 948.
[38] Tan YW, Dai XH, Li YF, *Journal of Materials Chemistry*, **2003**, 13, 1069.
[39] Chou KS, Ren CY, *Materials Chemistry and Physics*, **2000**, 64, 241.
[40] Lee Y, Choi JR, Lee KJ, *Nanotechnology*, **2008**, 19.
[41] Leopold N,Lendl B, *Journal of Physical Chemistry B*,**2003**, 107, 5723.
[42] Khalid MAA, *Arabian Journal for Science and Engineering*, **2008**, 33, 199.
[43] Khalid MA, Kheir AM, *Sudan Journal of Basic Sciences*, **2008**, 15, 69.
[44] Noguez C, *J Phys Chem C*,**2007**, 111, 3806.
[45] Chen F, Alemu N and Johnston RL, *AIP Advances*, **2011**, 1, 032134.
[46] Ghosh SK, Pal T,*Chem Rev*, **2007**, 107, 4797.
[47] Xiong J,Wang Y, Xue Q and Wu X, *Green Chemistry*, **2011**, 13, 900.
[48] Kapoor S, Joshi R, Mukherjee T, *Chemical Physics Letters*, **2002**, 354, 443.
[49] Zhang HX, Siegert U, Liu R and Cai WB, *Nanoscale Research Letter*, **2009**, 4, 705.
[50] Sharma V, Park K, Srinivasarao M, *Materials Science and Engineering R*,**2009,**65, 1.
[51] Wu CW, Mosher BP, Zeng TF, Yin ZL, *J Nanopart Res*, **2006**, 8, 965.
[52] Kerber RC, *J Chem Educ*, **2008**, 85, 1237.