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SYNTHESIS, CHARACTERIZATION OF COPPER NANOPARTICLES AND THEIR CATALYTIC APPLICATION

Niharika Nagar[1], Shikha Jain[2], Vijay Devra[3]

Department Of Chemistry, J.D.B. Govt. P.G. Girls College, Kota, Rajasthan, (India)

ABSTRACT

In this paper, we report on the synthesis of copper nanoparticles (Cunps) through a single route of chemical reduction method. The effect of different concentration of reducing agent on the morphology of Copper nanoparticles was investigated. The synthesized copper nanoparticles were characterized by UV-Visible spectrophotometer, Fourier Transform Infrared (FTIR) Spectrophotometer, Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM) analysis. The average size of copper nanoparticles was found to be 12 nm and spherical in shape at the optimal experimental conditions. The catalysis by colloidal copper nanoparticles was studied kinetically in the oxidation of L-Valine (Val) by peroxodisulphate (PDS) in acid aqueous medium. The copper nanoparticles catalyst exhibited very good catalytic activity.

Keywords: Ascorbic Acid, Copper Nanoparticles, Kinetics, L-Valine, Peroxodisulphate.

I. INTRODUCTION

The field of nanocatalysis has undergone an explosive growth during the past decades, both in homogeneous and heterogeneous catalysis [1, 2]. Since nanoparticles have a large surface to volume ratio compared to bulk materials, they are attractive to use as catalyst [3, 4]. Metal nanoparticles with high specific catalytic activity are ubiquitous in modern synthetic organic chemistry during the recent decades [5]. However how to reduce their dosage is one of the most exciting challenges due to the limiting reserves of noble metals. Some selective oxidation reactions are reported involving transition metal ions of Ag, Rh, Cr, Ru, Mn etc. are reported to act as catalyst for amino acids oxidations [6-10] with the emergence of metal nanoparticles possessing appreciable stability and high surface area per particle, their potential use as catalyst for organic biochemical relevant reactions [11-12]. Amongst them Copper nanoparticles are paid more attention due to their low cost and easy availability. Copper nanoparticles have also been considered [13-14] as an alternative for noble metals in many applications such as heat transfer and microelectronics [15]. In this study, highly stable colloidal dispersion of copper nanoparticles has been synthesized by chemical reduction method, using ascorbic acid as a reducing agent as well as capping agent. The particle size has been effectively controlled by the variation of reducing agent and temperature during the synthesis. The synthesized Cunps were characterized by UV-Visible Spectrum, SEM, TEM etc. techniques.

The kinetics of the oxidation of inorganic and organic substrates by peroxodisulphate under both catalyzed and uncatalyzed conditions have received considerable attention [16-17]. The peroxodisulphate ion is one of the strongest oxidizing agents known in aqueous solution. The standard oxidation reduction potential for the reaction is estimated to be -2.01V.

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

The reaction involve this ion are generally very slow in the absence of suitable catalysts [18].The transition metal ion catalysis oxidation of amino acid by peroxodisulphate was reported in aqueous acidic medium [19-21]. The oxidation of amino acids is of the utmost importance, both from a chemical point and in view of its bearing on the mechanism of amino acid metabolism. It has been observed that there is not enough information in the literature on the oxidation of amino acid by peroxodisulphate in presence of copper nanoparticles. The present investigation is a part of a broad programme for study of the catalytic effect of copper nanoparticles on the oxidation of Valine by peroxodisulphate in acid aqueous media.

II. EXPERIMENTAL

2.1 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%), L-Valine 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.

2.2 Synthesis Process

The one step synthesis scheme for copper nanoparticles initiates with dissolving copper chloride dihydrate (0.02 mol L^{-1}) in 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. 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 L-ascorbic acid and temperature to investigate the morphology of copper nanoparticles.

2.3 Instrumentation

UV-Visible spectroscopy from a double beam spectrophotometer (U.V. 3000^+ LABINDIA) was used for preliminary estimation of copper nanoparticles synthesis. 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.

2.4 Kinetic Study

The reaction was carried out in glass-stoppered Pyrex round bottom flask. Appropriate amount of the amino acid solution in acidic form, potassium sulphate, and water (to keep the total volume constant for all runs) were taken in the round bottom flask and thermostatted at 308 K for thermal equilibrium. A measured amount of peroxodisulphate was rapidly added to the mixture. The progress of the reaction was monitored by iodometric determination of unreacted peroxodisulphate in a measured aliquot of the reaction mixture at different intervals of time.

III. RESULTS AND DISCUSSION

3.1 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 [22]. Since surface Plasmon modes of metal nanoparticles like Au, Ag, Cu reside within the optical region of electromagnetic spectrum [23, 24], 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 “Fig. 1”.

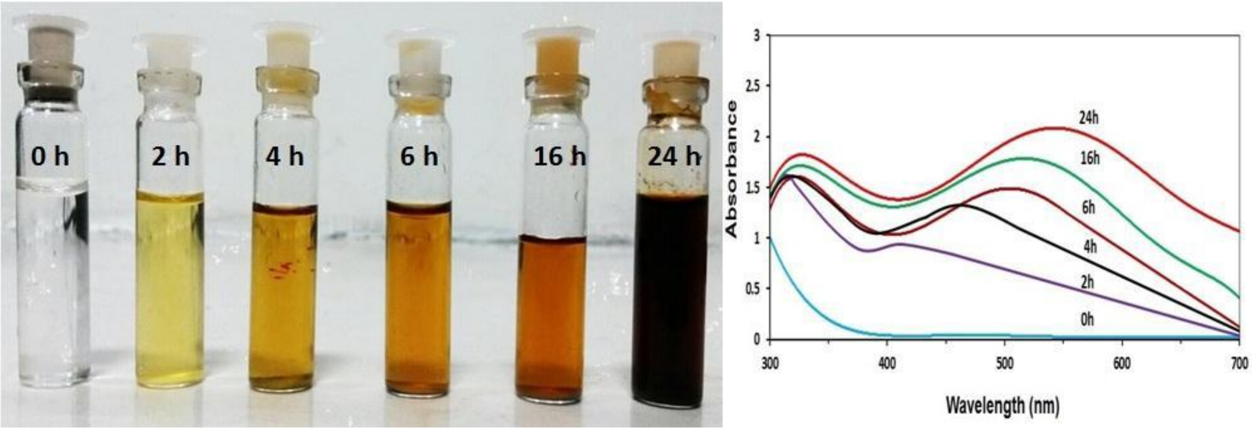


Fig. 1: The time evolution of the dispersion photographs and the UV-Visible spectra

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 [25]. 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 [26, 27]. 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 [28].

3.2 Effect of reducing agent concentration

To evaluate the effect of L-ascorbic acid concentration (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 "Fig. 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 (0.08, 0.09, 0.10 mol L^{-1}) of L-ascorbic acid are 28, 16, 12 nm respectively. The reason is that L-ascorbic acid molecules encapsulate Cu^{+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.

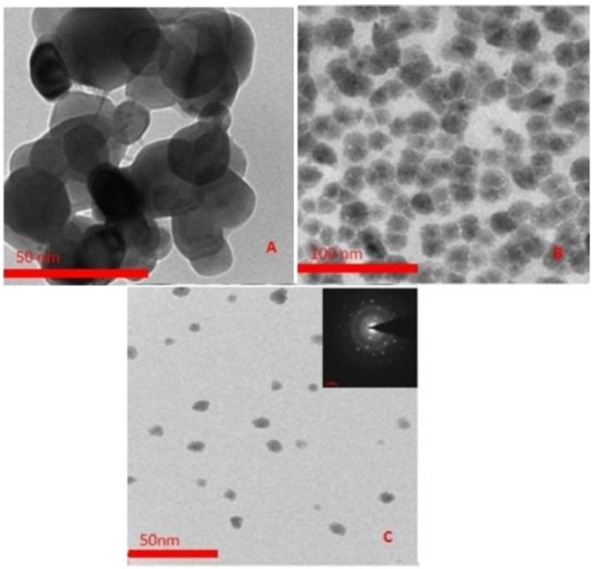


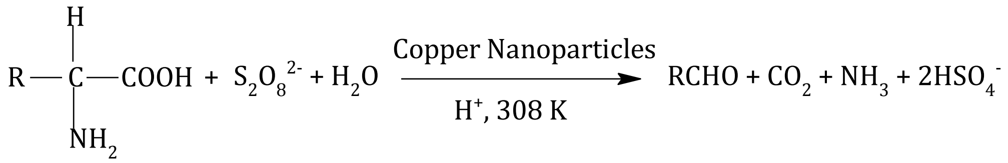
Fig. 2: TEM images of copper nanoparticles with variable concentration of L-ascorbic acid: (A) 0.08, (B) 0.09, (C) 0.1 mol L^{-1}

3.3 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[29], accompanying the donation of electrons to give semi-dehydroascorbate radical and dehydroascorbic acid hydration of 2-carbonyl is also reported [30] and finally converted into polyhydroxyl structure through hydrolysis[25]. 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.

3.4 Stoichiometry and Product analysis

Under the kinetic conditions, the reaction was carried out with excess of peroxodisulphate over Valine in presence of nanoparticles in a thermostat water bath at 308 K 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 [31]. From observations of different sets, the Stoichiometry of the reaction can therefore be presented by "equation 1".



$$R-\overset{\overset{\textstyle H}{|}}{\underset{\underset{\textstyle NH_2}{|}}{C}}-COOH + S_2O_8^{2-} + H_2O \xrightarrow[H^+,\ 308\ K]{\text{Copper Nanoparticles}} RCHO + CO_2 + NH_3 + 2HSO_4^- \quad —(1)$$

Where R represents $(CH_3)_2$-CH-

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.

3.5 Peroxodisul phate 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 [Val] = 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 "Fig. 3", indicating that the reaction is first order with respect to [PDS].

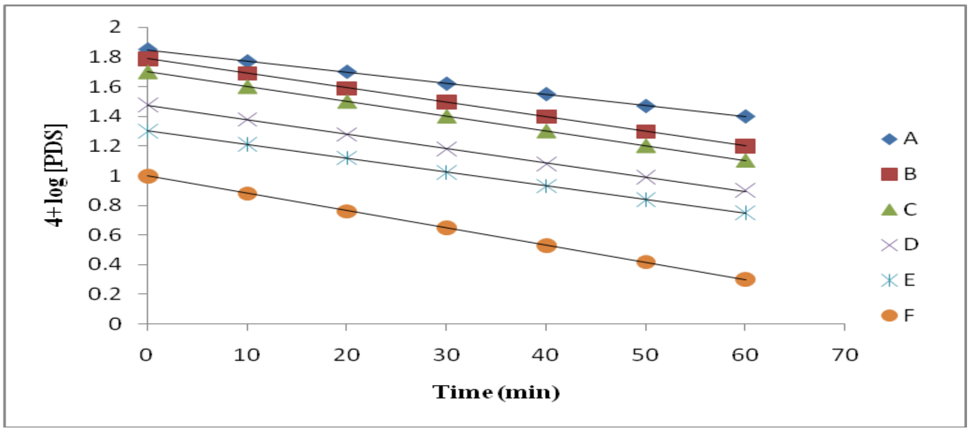


Fig. 3: First order plots of the variation of peroxodisulphate concentration at 308 K [Val]= 5.0×10^{-2}mol L^{-1}, [Cunps] = 1.0×10^{-5} mol L^{-1}, [PDS]$\times10^{-3}$ mol L^{-1} = (A) 1.0, (B) 2.0, (C) 3.0, (D) 4.0, (E) 5.0, (F) 6.0, (G) 7.5

3.6 Valine 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 Valine from1×10^{-2} – 7×10^{-2} mol L^{-1} at 308 K temperature. Plot of log k_{obs} versus log [Val] give straight line parallel to log [Val] axis indicating zero order dependence with respect to Valine “Fig. 4”.

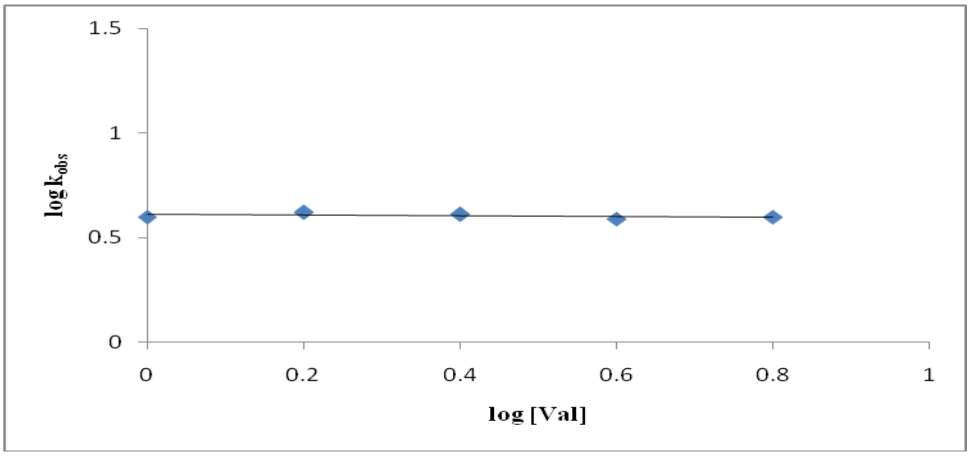


Fig. 4: First order plots of the variation of Valine concentration at 308 K [PDS]= 5.0×10^{-3} mol L^{-1}, [Cunps] = 1.0×10^{-5}mol L^{-1}, [Val]1.0×10^{-2} mol L^{-1} = (A) 1.0, (B) 3.0, (C) 4.0, (D) 6.0, (E) 7.0

3.7 Copper nanoparticles dependence

The effect of copper nanoparticles on the rate of oxidation of Valine has been studied at varying concentration of copper nanoparticles 1×10^{-6} - 1×10^{-5} mol L^{-1} at four different size of nanoparticles (28, 16 and 12 nm), synthesized at four concentration (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 0.08 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>28nm “Fig. 5”. 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.

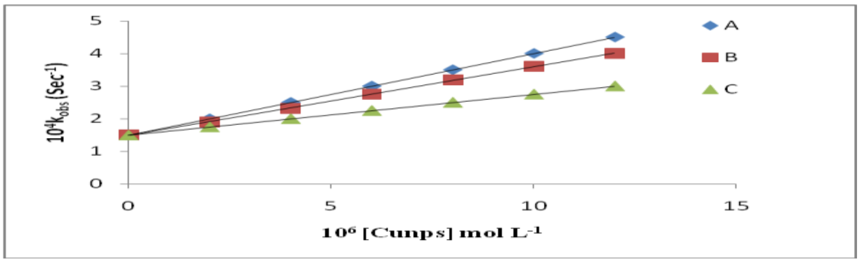


Fig. 5: The effect of [Cunps] at different size of Cunps in nm (A) 12, (B) 16, (C) 28 at fixed [PDS] = 5.0×10^{-3} mol L^{-1}, [Val] = 5.0×10^{-2} mol L^{-1} at 308K

3.8 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 was made against 1/T, yielded a straight line. The energy of activation (Ea),entropy of activation ($\Delta S\neq$), enthalpy of activation ($\Delta H\neq$), free energy of activation (ΔG) were obtained 24.69 KJ mol^{-1}, -237.32 JK^{-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.

3.9 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 Valine, oxidative deamination of Valine 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 Valine

IV. 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 – 28 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 Valine 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 Valine and peroxodisulphate in the presence of Cunps was first order.

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