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Synthesis and size control of copper nanoparticles and their catalytic application

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Abstract: The synthesis and catalytic properties of copper nanoparticles (Cunps) were reported using L-ascorbic acid as reducing and capping agent in aqueous medium. The effect of different concentrations of L-ascorbic acid on the particle size of Cunps was investigated. The synthesized Cunps were characterized by UV-Visible spectrophotometer, scanning electron microscopy (SEM), transmission electron microscopy (TEM) and Fourier transform infrared (FTIR) spectrophotometer. The result indicates that the size of copper nanoparticles decreases with the increase in concentration of L-ascorbic acid. L-Ascorbic acid plays an important role to protect the copper nanoparticles from oxidation and agglomeration which helps nanoparticles to get better stability for the application. The synthesized Cunps show excellent catalytic activity in the oxidation of serine (Ser) by peroxomonosulphate (PMS). The catalytic activity of Cunps increases with the decrease in size of Cunps. The Cunps are expected to be suitable alternative and play an imperative role in the fields of catalysis and environmental remediation.

Key words: copper nanoparticle; ascorbic acid; serine; peroxomonosulphate (PMS); oxidation; kinetics

1 Introduction

Major scientific interest targeting fabrication of metal nanoparticles of distinct shape and diminutive size has been developed in recent years because of their exclusive properties as compared to their bulk materials [1−3]. Metal nanoparticles with variety of shape and size allow exploring their fascination applications in fields like catalysis, electronics, sensor, and optical device [4−6]. Most of the unique properties of metal nanoparticles are a consequence of their nano-size scale regime. However, recently, MURPHY [7] has observed that properties of nano-materials are also influenced by their shape and size. Thus, special shaped nano-materials are the focus of the present scientific research. From the present literature perspective, development of suitable method for such nano-materials and their uses in various practical applications is an important task. Among all methods such as micro emulsions method [8], thermal decomposition method [9], laser ablation method [10] and aqueous chemical reduction method [11,12], aqueous reduction route is the most preferred for its simplicity, economical and ease of control over particle size and distribution with various experimental parameters [13−16]. The parameters such as temperature, reaction time, reducing agent, precursor type, concentration and even mixing, affect the nucleation, growth and agglomeration phenomena, consequently particle size distribution of nano-materials. Although UMER et al [17] reported that synthesis of copper nanoparticles has been carried via numerous routes, very less is known about the size dependent performance of copper nanoparticles as a suitable catalyst. The main question arises from stability of copper nanoparticles including the extreme sensitivity to oxygen and colloidal agglomeration. Therefore, there are several approaches related to the dispersion and oxidation resistance that needs to be solved before application. Some study reveals that to protect copper nanoparticles against oxidation, natural antioxidant ascorbic acid is utilized as reductant and antioxidant [18−20]. In the present investigation, the raw materials are same but synthesis routes have been changed, which result in the size variation of copper nanoparticles.

In this work, ascorbic acid (hydrogen potential of +0.08 V) can easily reduce metal ions with standard reduction potential higher than 0 V, such as Cu^{2+}, Ag^{+}, Au^{3+} and Pt^{4+} but cannot reduce these ions with potential less than 0 V such as Fe^{2+}, Co^{2+} and Ni^{2+}. Hydrogen free

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radicals released from ascorbic acid react rapidly with hydroxyl free radicals and oxygen, whose existence is usually related to the oxidation of the nanoparticles, so our experiment was performed without inert gas protection, and pure copper nanoparticles were obtained.

The catalytic activity of synthesized copper nanoparticles was evaluated in the oxidation of serine by peroxomonosulphate in aqueous medium. The transition metal nanoparticles are used as catalyst for many organic transformations [21−24]. Though studies on kinetics of oxidation of amino acid with peroxomonosulphate have been widely carried out [25,26], very few attempts have been made so far on the oxidative deamination of amino acid in the presence of metal nanoparticles [23]. So, we have attempted the synthesis of size controlled copper nanoparticles through a simple one phase aqueous route using ascorbic acid as reducing and capping agent and catalytic activities of these particles with different sizes have been tested on the oxidation of serine.

2 Experimental

2.1 Materials

Analytical grade chemicals such as copper chloride dihydrate ($CuCl_2·2H_2O$, purity of 97%) and L-ascorbic acid (vitamin C, purity of 98%) and serine obtained from E. Merck were used. Peroxomonosulphate (PMS) was obtained from Sigma-Aldrich under the trade name “Oxone”. A fresh solution of Oxone was prepared before starting the experiments. Remaining chemicals used were of analytical grade without any further treatment. Double distilled water was employed throughout the study.

2.2 Synthesis of copper nanoparticles

The one step synthesis scheme of copper nanoparticles initiates with dissolving copper chloride dihydrate (0.02 mol/L) in deionized water to obtain a blue solution. L-ascorbic acid (0.1 mol/L) was dropwise added to the aqueous solution of copper salt with vigorous stirring at 353 K in oil bath. With the passage of time, the color of dispersion gradually changed from white, yellow, orange, brown finally to dark brown with a number of intermediate stages. The appearance of yellow color followed by orange color indicated the formation of fine nanoscale copper particles from L-ascorbic acid assisted reduction. The resulting dispersion was centrifuged for 15 min. The supernatant was placed under ambient conditions for two months. The studies were performed at different concentrations of ascorbic acid to investigate the size and shapes of copper nanoparticles.

2.3 Characterization

UV-Visible spectroscopy from a double beam spectrophotometer (UV 3000^+ LABINDIA, path length 1.0 cm, spectral range from 200 nm to 800 nm) was used for preliminary estimation of copper nanoparticles synthesis. FTIR (ALPHA-T, Bruker) provided information about the binding interactions of L-ascorbic acid with zero valent copper particles. Morphological study of the copper nanoparticles was carried out with SEM (EVO 18, Carl Zeiss) image analysis. These dispersed nanoparticles were centrifuged and ultra-sonicated for 40 min. 30 μL aliquots were then extracted and deposited on stub for SEM analysis. Ultrasonicated dispersed suspension was mounted on carbon coated copper grid and TEM (FEI Techni G2S2 Twin) images were recorded to confirm size distribution and shape homogeneity of synthesized copper nanoparticles.

3 Results and discussion

3.1 Metal nanoparticles characterization results

UV-Visible absorbance spectroscopy has proved to be a very useful technique for studying metal nanoparticles because the peak position and shapes are sensitive to particle size. During the synthesis of copper nanoparticles in aqueous solution, the UV-Visible spectra of samples were recorded at different time intervals for every color change presented in Fig. 1.

The solution becomes colorless when L-ascorbic acid was added and turned to yellow, orange, brown and finally dark brown. Initially, there was no absorption peak, the absorption peak can be observed after two hours of reaction. There was an intensity increase with the reaction progressing, this was due to the growth

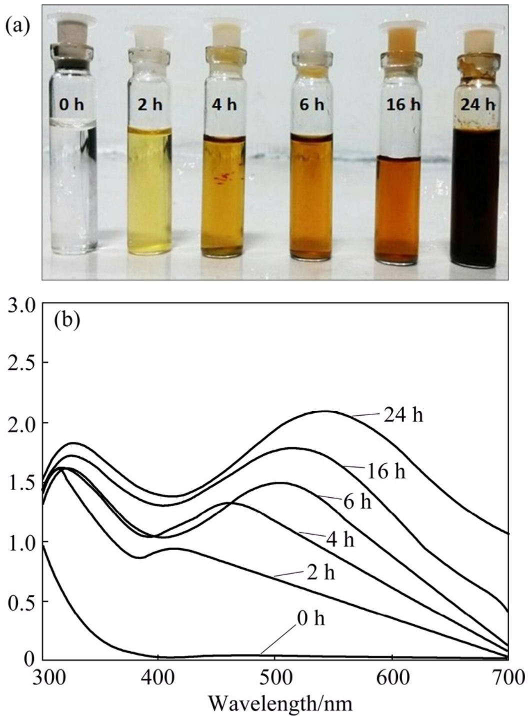


Fig. 1 Dispersion photographs (a) and UV-Visible spectra (b) of samples at different time intervals

of copper nanoparticles. The synthesis process was completed after 24 h.

The effect of L-ascorbic acid concentrations (0.08, 0.09 and 0.10 mol/L) on the UV-Visible absorbance spectroscopy of the synthesized copper nanoparticles is shown in Fig. 2. XIONG et al [27] observed that the first absorption peak of different curves was at 335 nm corresponding to oxidation product of L-ascorbic acid. The red shift of second absorption peak increases with an increasing concentration of L-ascorbic acid. The absorption peak of copper nanoparticles has been reported at around 560 nm which proves the formation of copper nanoparticles [28,29]. In this work, the resulting copper nanoparticles show a broadened peak at this wavelength indicating the presence of small separated copper nanoparticles.

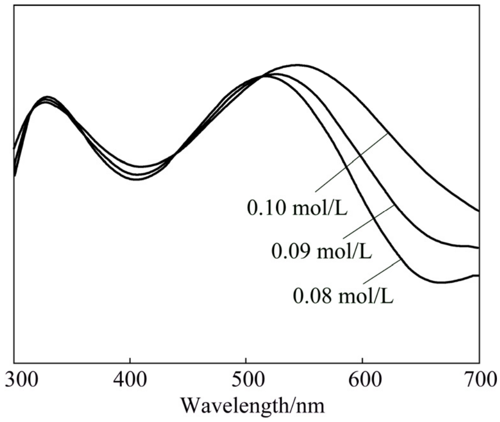


Fig. 2 UV-Visible absorption spectra of copper nanoparticles stabilized in L-ascorbic acid with various concentrations

The above result indicates that a higher L-ascorbic acid concentration leads to more effective capping capacity of L-ascorbic acid and then forms smaller Cu nanoparticles, which can also be proved by the TEM images with histograms of particle size distribution of synthesized copper nanoparticles presented in Fig. 3. The

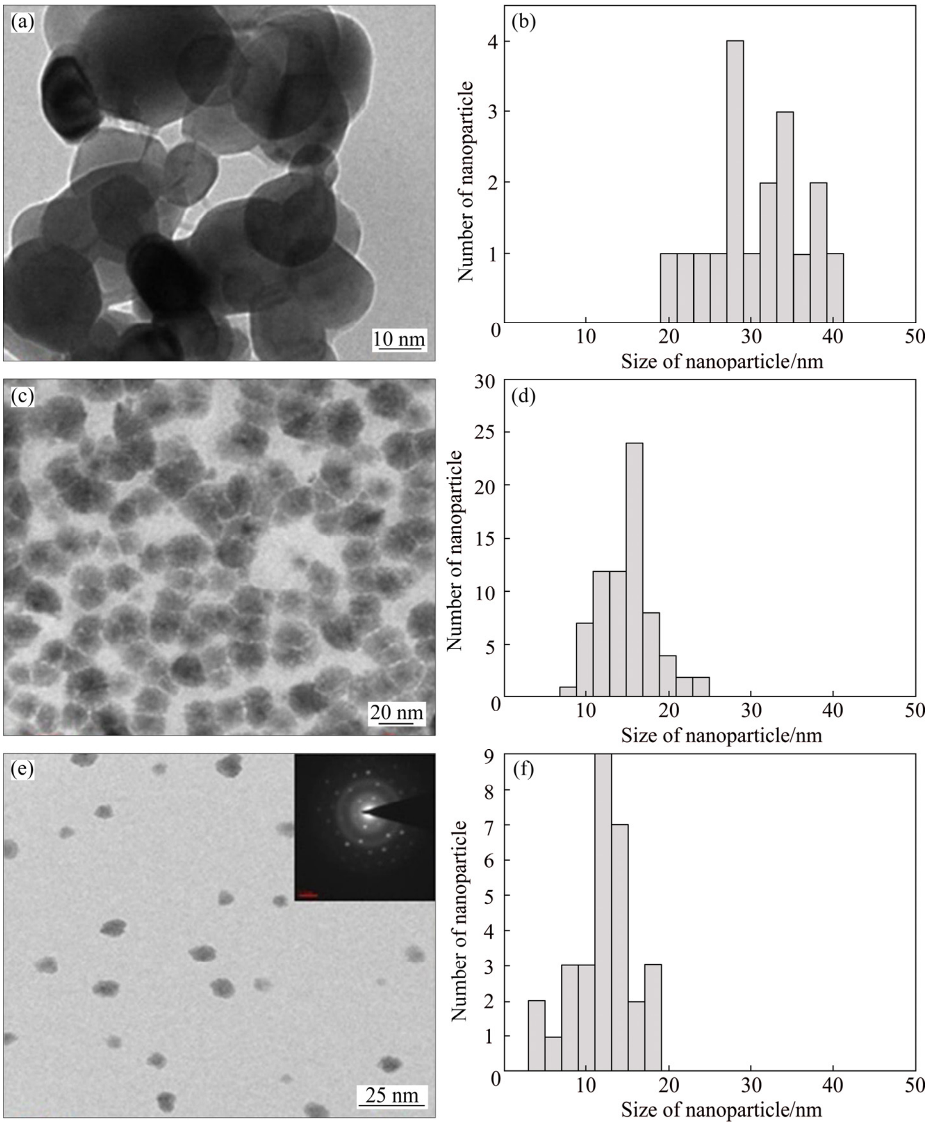


Fig. 3 TEM images with histogram of synthesized copper nanoparticles with various concentrations of L-ascorbic acid and average particle sizes: (a,b) 0.08 mol/L, d=28 nm; (c,d) 0.09 mol/L, d=16 nm; (e,f) 0.10 mol/L, d=12 nm

TEM images exhibit that the particles are spherical in shape. The histogram reveals that the size of copper nanoparticles decreases with increase in concentration of L-Ascorbic acid. The size of the copper nanoparticles at various concentrations (0.08, 0.09, 0.10 mol/L) of L-ascorbic acid are 28, 16, 12 nm respectively. The reason is that 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 which is also confirmed by the SEM image of copper nanoparticles shown in Fig. 4. SEM image confirms that the nanoparticles are grown with well defined morphology and are almost spherical in shape. So, the optimal conditions for the synthesis are 0.02 mol/L concentration of $CuCl_2·2H_2O$ and 0.10 mol/L concentration of L-ascorbic acid at 353 K.

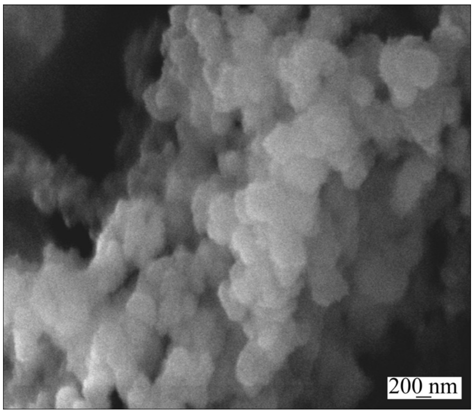
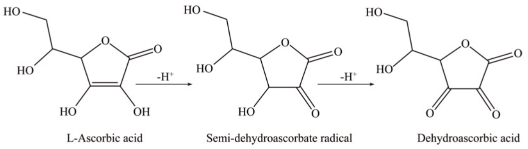


Fig. 4 SEM image of copper nanoparticles at optimal experimental conditions of $c(CuCl_2·2H_2O)=0.02$ mol/L, c(L-ascorbic acid)=0.10 mol/L and 353 K

3.2 Stability of copper nanoparticles

The stability of nanoparticles dispersion is the 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 photographs of dispersion before and after the storage (two months) are shown in Fig. 5.

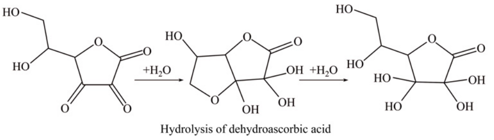
During the synthesis process, excessive L-ascorbic acid is essential to avoid the oxidation of copper nanoparticles. WU et al [15] reported that the antioxidant property of L-ascorbic acid comes from its ability to scavenge free radicals and reactive oxygen molecules, accompanying the donation of electrons to give semi-dehydroascorbate radical and dehydroascorbic acid (Eq. (1)).



(1)

Fig. 5 Photos of dispersion of synthesized copper nanoparticles before (a) and after (b) two months of storage

The dehydroascorbic acid has three carbonyl groups in its structure. The 1, 2, 3 tricarbonyl is too electrophilic to survive for few seconds in aqueous solution. Finally, the polyhydroxyl structure is obtained through hydrolysis (Eq. (2)) [27].



(2)

The extensive number of hydroxyl group can facilitate the complexation of copper nanoparticles to the molecular matrix by inter- and intra-molecular hydrogen bonding, and thus prevent the aggregation of copper nanoparticles. This result is consistent with that of FTIR analysis presented in Fig. 6.

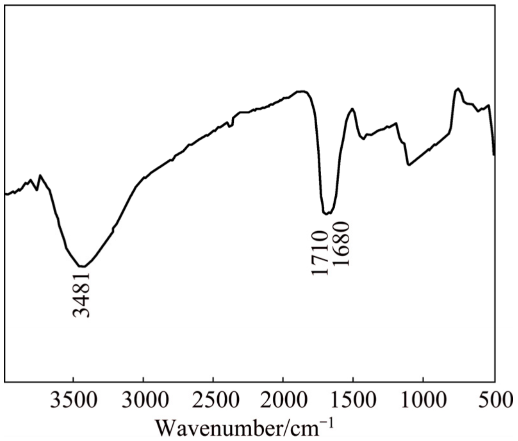


Fig. 6 FTIR spectrum of L-ascorbic acid stabilized copper nanoparticles

FTIR spectrum shows the peaks at 3481, 1710 and 1680 cm^{-1}. These peaks correspond to the hydroxyl, oxidated ester carbonyl groups and conjugated carbonyl groups, respectively. These results indicate the presence of polyhydroxyl structure on the surface of copper nanoparticles. The polyhydroxyl structure has an excellent dispersion effect on copper nanoparticles. Therefore, L-ascorbic acid plays dual role as reducing agent and antioxidant of copper nanoparticles. Thus, reaction can be completed without any protective inert gas.

3.3 Catalytic activity of copper nanoparticles

The catalytic activity of synthesized copper nanoparticles was evaluated in the oxidation of serine by peroxomonosulphate (PMS). The deamination of L-serine studied by the decrease in absorbance of serine at 206 nm at different intervals of time is shown in Fig. 7. The effect of copper nanoparticles on the rate of oxidation of serine has been studied at varying concentrations ($1\times10^{-6}-10\times10^{-6}$ mol/L) at three different nanoparticles, synthesized at three concentrations (0.08, 0.09 and 0.10 mol/L) of ascorbic acid with average sizes 28, 16 and 12 nm, respectively, at fixed c(PMS)=5×10^{-3} mol/L, c(Ser)=5×10^{-2} mol/L, $c(H^+)$=0.01 mol/L and 308 K. The rate of reaction increases with the increase in concentration of copper nanoparticles. The catalytic activity of copper nanoparticles seems different when concentration of reducing agent is varied from 0.08 to 0.10 mol/L. The difference in catalytic activity can be dependent on the size variation (28, 16, 12 nm) in the resulting copper nanoparticles, while keeping other reactant concentration and conditions constant, the catalytic activity depends on the size of copper nanoparticles. The trend of the rate constant (k_{obs}) with the size of nanoparticles is shown in Fig. 8. This effect can be attributed to the nanosize of the particles that surface area and the active center increase as particle size decreases.

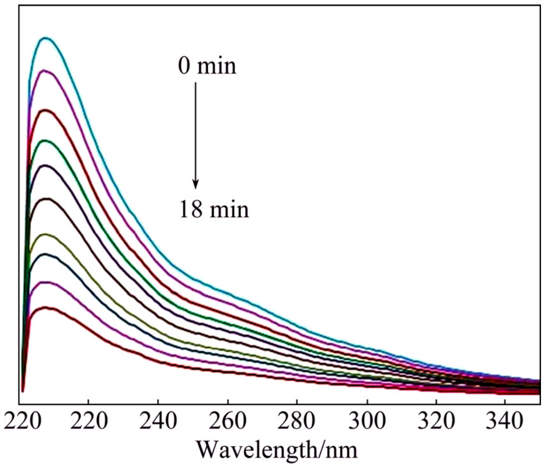


Fig. 7 UV spectra for deamination of L-serine at 206 nm in the presence of copper nanoparticles at fixed c(PMS)=5×10^{-3} mol/L, c(Cunps)=5×10^{-6} mol/L, $c(H^+)$=0.01 mol/L at 308 K

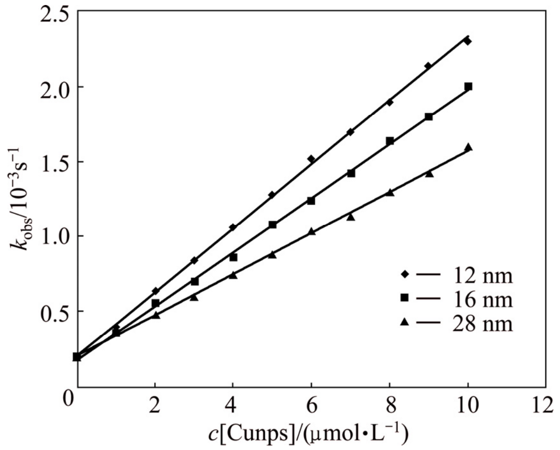


Fig. 8 Effect of c(Cunps) on oxidation of serine with different sizes of 12 nm (a), 16 nm (b), 28 nm (c) at fixed c(PMS)=5.0×10^{-3} mol/L, c(Ser)=5.0×10^{-2} mol/L, $c(H^+)$=0.01 mol/L and 308 K

4 Conclusions

1) Monodispersed copper nanoparticles (range 12−28 nm) employing different concentrations of L-ascorbic acid were synthesized by green method.

2) The characterization results indicate that a higher L-ascorbic acid concentration leads to more effective capping capacity and then forms smaller copper nanoparticles. FTIR spectra show the presence of polyhydroxyl structure on the surface of the copper nanoparticle that gives an excellent dispersion effect on copper nanoparticles.

3) The experimental investigation indicates that the optimal conditions for the synthesis are 0.02 mol/L concentration of $CuCl_2\cdot2H_2O$ and 0.10 mol/L concentration of L-ascorbic acid at 353 K.

4) The catalytic activity of synthesized copper nanoparticles was investigated in the oxidation of serine in aqueous acidic medium. The study reveals that the size of copper nanoparticles decreases as the catalytic activity of copper nanoparticles increases.

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铜纳米颗粒的制备、尺寸控制及催化应用

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摘　要：以维生素 C 为还原剂和覆盖剂，在水溶液中制备铜纳米颗粒，并研究其催化性能。研究不同维生素 C 浓度对铜纳米颗粒尺寸的影响。采用紫外−可见光分光光度计、扫描电子显微镜(SEM)、透射电子显微镜及傅里叶变换红外光谱计(FTIR)对所制备的铜纳米颗粒进行表征。结果表明，随着维生素 C 浓度的增加，铜纳米颗粒的尺寸减小。维生素 C 在防止纳米颗粒氧化和团聚过程中起重要作用，可帮助纳米颗粒在应用过程中保持较高的稳定性。所制备的铜纳米颗粒在 PMS 氧化丝氨酸过程中表现出优良的催化活性。铜纳米颗粒的催化活性随颗粒尺寸的减小而提高。铜纳米颗粒有望用于催化和环境修复领域并发挥重要作用。

关键词：铜纳米颗粒；维生素 C；丝氨酸；PMS；氧化；动力学

(Edited by Yun-bin HE)