



SYNTHESIS AND CHARACTERIZATION OF METALLIC COPPER AND ITS OXIDE NANOPARTICLES BY THERMAL DECOMPOSITION APPROACH USING COPPER(II) PRECURSOR

ARUNACHALAM DINESH KARTHIK¹ AND KANNAPPAN GEETHA^{2*}

¹P G Department of Chemistry, K. M. G. College of Arts and Science, Gudiyatham - 635 803 Vellore Dt. Tamil Nadu, India

²Department of Chemistry, P G and Research Department of Chemistry, Muthuramangam Govt. Arts College, Vellore - 632 002, Tamil Nadu, India.

*Corresponding Author: Email-dineshkarthik2008@gmail.com

Received: December 15, 2013; Revised: April 21, 2015; Accepted: October 29, 2015

Abstract-Nanoparticles have attracted extensive scientific and industrial interest due to their unique electronic, optical, and catalytic properties. Many techniques such as chemical reduction radiolysis reduction of copper ions with supercritical fluids and thermal decomposition methods are developed to synthesize copper nanoparticles. The primary application of copper nanoparticles is catalysis, just like the bulk copper metal. On the other hand, copper nanoparticles offer higher catalytic efficiency per gram than the bulk one due to their large surface-to volume ratios.

Copper and its oxide (Cu₂O and CuO) nanoparticles were synthesized by using Copper(II) oxalate precursor and oleylamine as capping agent. Copper and its oxide Nanoparticles so obtained were characterized by UV- Visible spectroscopy, Fourier Transform Infrared Spectroscopy, and X-Ray diffraction analysis. X-Ray diffraction analysis proves the formation of Copper and its oxide Nanoparticles. SEM and AFM analyses show the presence of nanoparticles.

Keywords- Metallic nanoparticles, Copper, Capping agent, thermal reduction and S E M.

Citation: Arunachalam Dinesh Karthik and Kannappan Geetha, (2015) Synthesis and Characterization of Metallic Copper and Its Oxide Nanoparticles By Thermal Decomposition Approach Using Copper(II) Precursor. International Journal of Chemical Research, ISSN: 0975-3699 & E-ISSN: 0975-9131, Volume 7, Issue 1, pp.-164-167.

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Introduction

Metal Copper nano powders with high purity are important as industrial materials in the fields of electronics and metallurgy. Among various metal particles, copper nanoparticles have attracted considerable attention because copper is one of the most important metals in modern technologies. Copper metal has great significance in all industries, particularly in the electrical sector due to low cost [1, 3]. For their application in electronics, the stability of the nanoparticles and their reactivity are important factors. In addition, they are also useful as an antibacterial agent.

Copper nanoparticles have been synthesized through different methods such as thermal decomposition [4-7], metal salt reduction, microwave heating, radiation methods, micro emulsion techniques, super critical techniques, laser ablation, polyol method, solvothermal method, DC arc discharge method and sonochemical reduction [8,17]. Among various techniques for synthesis of inorganic nanoparticles, thermal decomposition is one of the most common to produce stable monodisperse suspensions with the ability of self-assembly. Nucleation occurs when the metal precursor is added into a heated solution in the presence of surfactant, while the growth state take place at a higher reaction temperature [18,19]. We interested to synthesize metal nanoparticles via thermal decomposition [20,21]. A major interest at the moment is in the development of organometallic or inorganic compound for preparation of nanoparticles. Using novel compounds, a new way for preparing nanomaterial's by controlling the nanocrystal size, shape and distribution size. We synthesized copper nanoparticles by the thermal decomposition of the copper oxalate precursor in oleylamine. In this process, oleylamine was used as both the medium and the stabilizing reagent. We report the synthesis of metallic copper nanoparticles from a simple, low cost and reproducible process from copper oxalate as precursor. The aim of the present work is to prepare copper nanocrystals using the thermal decomposition method, and their physicochemical characterization [22,23].

Experimental

Materials

All the chemicals and reagents used were of analytical grade and were used as received without further purification, and a series of experiments were processed in order to synthesize by employing different method. CuSO₄·5H₂O and NaOH, Oleylamine, triphenylphosphine (TPP), toluene, hexane and ethanol were purchased from SD Fine and were used as received.

Characterization

Scanning electron microscopy (SEM) images were obtained on a Philips XL- 30E. Fourier transform infrared (FT-IR) spectra were recorded on a Shimadzu spectrophotometer using KBr pellets.

Synthesis of the Copper nanoparticles

Copper(II) Oxalate precursor was prepared by adding drop wise the solution of disodium oxalate to copper sulphate solution in the ratio of 2:1 under magnetic stirring for 15 minutes. The resulting blue precipitate was centrifuged and washed with ethanol several times. The product was dried. The Copper(II) oxalate (Cu₂(O₄C₂)₄·2H₂O) was characterized by UV and FT IR .

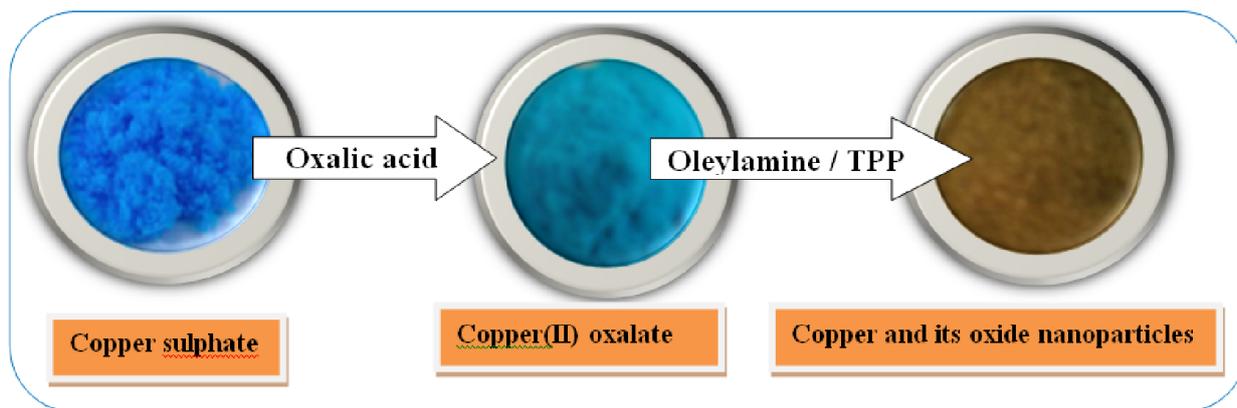
In this synthesis, Copper nanoparticles were prepared by the thermal reduction of the Copper(II) oxalate – oleylamine complex as a precursor. The Copper(II) oxalate – oleylamine complex was prepared by the reaction of 0.5 g of Copper(II) oxalate with 5 mL of oleylamine. The mixed solution was placed in a 40 mL three-neck distillation flask and heated up to 155 °C for 1 hr under a nitrogen atmosphere. The resulting metal-complex solution was injected into 5 g of triphenylphosphine (TPP) at 255°C. As the thermal decomposition proceeded, the azury solution turned to red, indicating the formation of metallic copper. The reddish brown solution was kept at 255 °C for 50 min, and was then cooled to room temperature. The reddish brown nanoparticles were precipitated by adding excess ethanol to the solution. The final product was washed with ethanol several

times to remove excessive surfactant.

Results and Discussion

[Fig-1] Shows on FT-IR spectroscopy is a useful tool to understand the functional group of any organic molecule a peak at 503 cm^{-1} confirmed the presence of Cu-O and Cu Nanoparticles. A twin peak at 623 cm^{-1} indicating the Cu - O Stretching vibration. The metal salt (Cu-O-C) Peak is appeared at 1109 cm^{-1} . The metal salt carbonyl group is appeared at 1645 cm^{-1} . The presence of the oleylamine group on the Copper nanoparticles [Fig- 2] is indicated by the N-H wagging mode from 651 to 854 cm^{-1} , NH_2 bending modes at 909 , 964 and 993 cm^{-1} , and NH_2 scissor mode at 1568 cm^{-1} [24, 25]. The spectrum, shown in [Fig-2], also reveals the characteristic peak of the C-N stretch at 1042 cm^{-1} which suggests that the C-N bonds in the amine groups, and therefore the oleylamine ligands, remain intact, capping the

Copper nanoparticles. The peak at 1450 cm^{-1} is associated with the C-H bending mode and the three peaks at 2920 , 2964 and 2955 cm^{-1} represent the C-H stretching modes of the oleylamine carbon chain. The presence of N-H peaks suggests that the amines are bound to the surface of the Copper nanoparticles. The following reaction mechanism (Scheme 1) is proposed. Upon injection of Copper(II) oxalate and oleylamine into hot TPP solution, the Cu-O bond is cleaved by the oleylamine group and Cu is subsequently reduced. The weak peak at 3444 cm^{-1} has been assigned to the -OH of ethanol used in the separation step. There was no evidence of the free precursor, because the stretch vibration of $\text{C}=\text{O}$ ($\nu_{\text{C=O}}$) and C-O ($\nu_{\text{C-O}}$) disappeared. So the oleylamine serves as the capping agent that controls growth.



[Scheme 1] : Schematic diagram of the formation of Copper and Copper oxide Nanoparticle

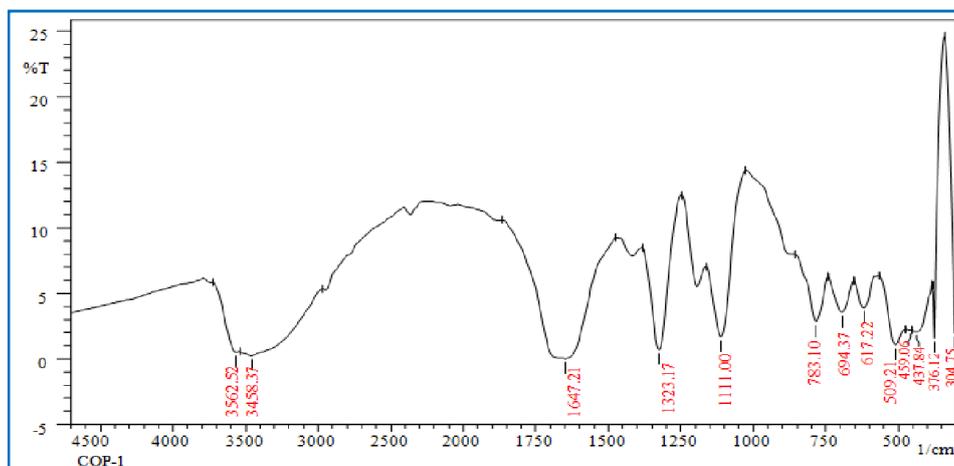


Fig-1 FT-IR spectra of Copper(II) oxalate Precursor

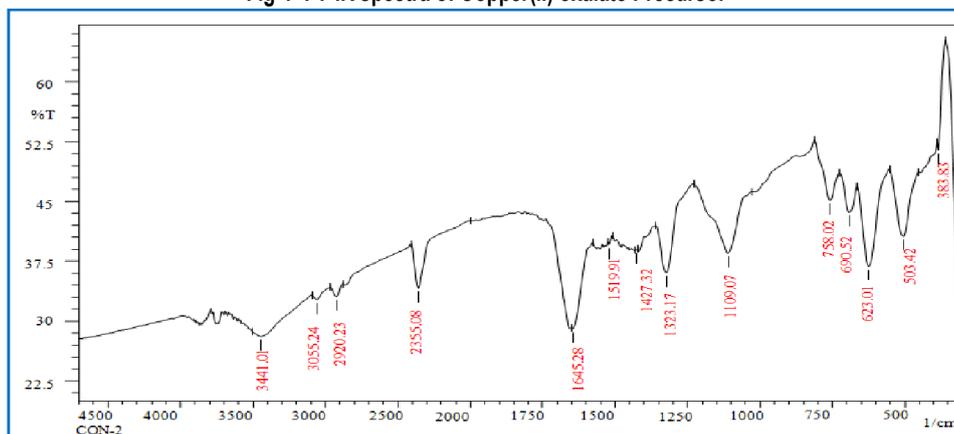


Fig-2 FT-IR spectra of Copper nanoparticles coated by Oleylamine

[Fig-3] shows on X-ray powder diffraction (XRD) pattern of Copper nanoparticles at room temperature. The XRD pattern is consistent with the spectrum of copper, and no peak is attributable to possible impurities. The peak positions are consistent with metallic copper. All possible peaks of copper are observed, which indicates the polycrystalline nature of the product. Bragg's reflections for Copper nanoparticles are observed in XRD pattern at 2θ value 23.79, 38.95, 43.54 and 45.00 representing [111], [200] and [220] planes of fcc structure of copper with the space group of $Fm\bar{3}m$ (JCPDS No. 4-0836). The size of the crystallites was estimated from Debye-Scherrer equation was about 35 nm. From the full width at half maxima (FWHM) of the [111] diffraction peak on the basis of the Scherrer formula: $D = 0.9 \lambda / \beta \cos \theta$, are about 75 nm for the nanoparticles synthesized.

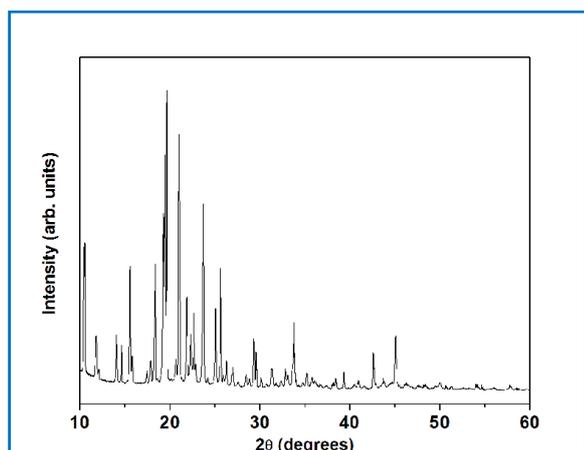


Fig-3 XRD pattern of the copper nanoparticles

The morphology of the product was examined by SEM. [Fig-4] depicts the SEM pictures of a sample of Copper nanoparticles. From the micrograph, it was observed that the nanoparticles were agglomerated. We may consider that when the reaction was carried out at 245°C, most organic molecules decomposed. Since only a few oleylamine molecules were adsorbed on the Copper nanoparticles, a loose solid flowerlike morphology was finally produced.

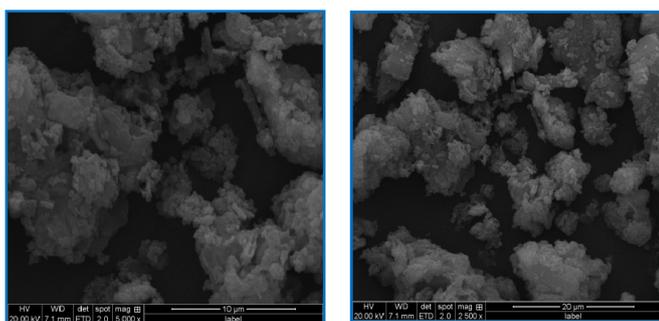


Fig-4 SEM images of the Copper nanoparticles

[Fig-5] Shows copper nanoparticles synthesized here show an absorption peak at around 598 nm. This peak can be assigned to the absorption of nanoparticles of copper. A modest blue shift (about 46 nm) of the absorption edge relative to that of bulk copper powder is observed. This observation alludes to the size effect to the Copper nanoparticles. This kind of stabilization of Copper nanoparticles is due to the capping of particles by oleylamine on thermal treatment. The arrangement of the capping agent, oleylamine, surrounding the nanoparticles is size dependent [26, 28].

[Fig-6] show the Cyclic Voltammogram (CV) of the copper nanoparticles was recorded in DMF with 0.1 M tetrabutylammonium perchlorate as supporting electrolyte in the potential range -2 to +0.1 V, with a conventional three electrode system composed of a platinum auxiliary, glassy carbon working

electrode and Calomel (Saturated KCl) as reference electrode. The reductive peaks correspond to Cu(II)/Cu(I) and Cu(I)/Cu(0) . i.e. $\text{CuO} \rightarrow \text{Cu}_2\text{O} \rightarrow \text{Cu}$. The redox peak currents increase linearly with increase in the scan rate from 20 to 100 MVs^{-1} [Fig-4] the oxidative peak corresponds to $\text{Cu} \rightarrow \text{Cu}_2\text{O} \rightarrow \text{CuO}$.

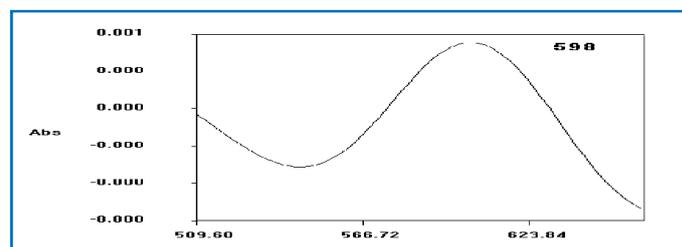


Fig-5 The UV-Vis absorption spectrum of the Cu nanocrystals.

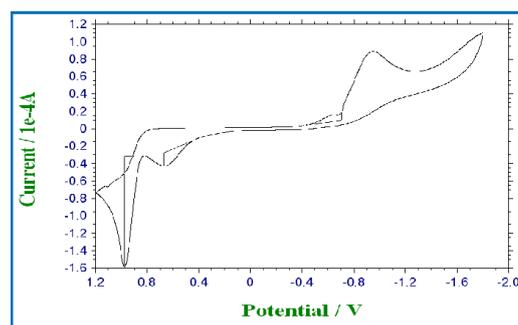


Fig-6 CV spectrum of the Copper oleylamine capped nanoparticles.

[Fig-7] shows the topography image (AFM) of oleylamine modified nanoparticles (transfer pressure is 20mN/m, mica substrate) acquired simultaneously at the same sample location. Results showed that the modified Copper and its oxide nanoparticles have typical core-shell structure. The oleylamine capped copper nanoparticles were composed of many nanoparticles arranged closely and orderly. The sizes of these nanoparticles in monolayer film are 50–100 nm.

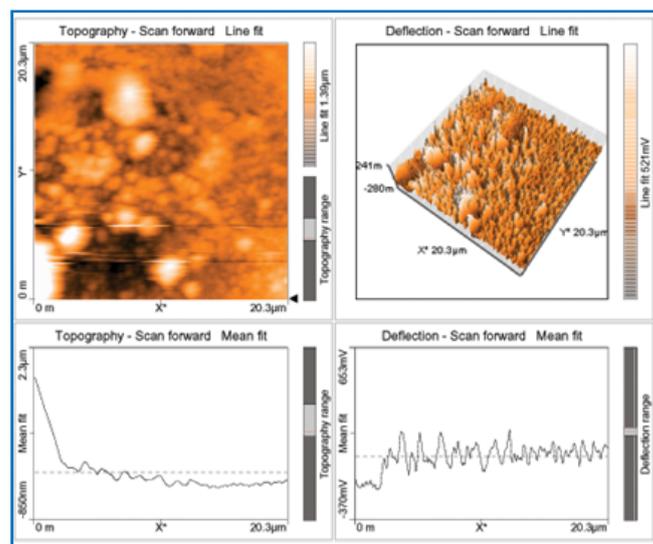
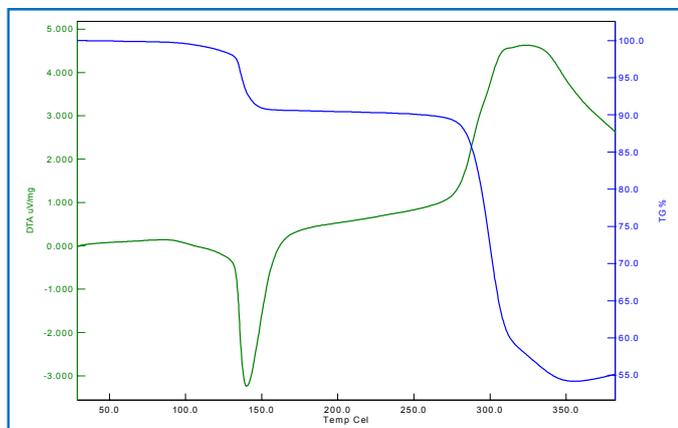


Fig-7 The AFM images of Oleylamine modified Copper nanoparticles

The TGA & DTA curve of the as prepared precursor is shown in [Fig-8]. To examine the thermal stability of the bulk powder compound Copper(II) oxalate, Thermal gravimetric (TG) and Differential thermal analysis (DTA) were carried out between 10 to 400°C under nitrogen flow. The compound was stable up to 240°C. Decomposition of compound occurred between 260°C to 290°C with the mass loss of 59%. The DTA curves displayed two endothermic peak effects at 180°C and 275°C.

Conclusion

Metallic Copper nanoparticles were synthesized by decomposition of copper(II) oxalate as precursor with the oleylamine that successfully resulted in oleylamine capped metallic nanoparticles. Copper and its oxide nanoparticles obtained find various potential applications in catalysis because of the high specific surface area. This synthetic method is simple and low cost.



[Fig-8 TGA and DTA of Copper(II) Oxalate.

Acknowledgment

Authors are grateful to the Principal, Muthurangam Govt Arts College and Vellore for providing facilities to undertake this work.

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