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SYNTHESIS AND CHARACTERIZATION OF METALLIC COPPER NANOPARTICLES VIA THERMAL DECOMPOSITION METHOD

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Abstract:

Copper (II) fumarate was used as a precursor to prepare metallic copper nanoparticles by thermal decomposition. Synthesis of inorganic nanoparticles by thermal decomposition is one of the methods to produce stable nanodisperse suspensions with the ability of self assembly. Copper (II) fumarate precursor was treated with oleylamine which is used as both the medium and the Stabilizing reagent. The precursor and copper nanoparticles were characterized by UV-Vis Spectroscopy, FT - IR, XRD, CV, AFM and SEM with EDAX. The metallic copper nanoparticles from a simple green synthesis, low cost and reproducible process from copper (II) fumarate as precursor.

1. Introduction:

In recent years, synthesis of transition metal nanoparticles is a growing research field in chemical science [1–3]. Nanoparticles which are ultra fine particles have the diameter from 1 to100nm and their properties are different form bulk materials. As the metal particles are reduced in size, the bulk properties of the particles disappear to be substituted to that of a ''quantum dot'', following quantum mechanical rules. It can thus be easily under- stood that metal nanoparticles' chemistry differs from that of the bulk materials [4]. Since with size reduction, the high surface area to volume ratio lead to enhanced catalytic activity [5]. Among various metal particles, copper nanoparticles have attracted considerable attention because copper is one of the most important metals in modern technologies [6]. Considerable interest has been focused on copper nanoparticles due to their optical, catalytic, mechanical and electrical properties [7–12]. Since late1980s, coppern an oparticles have attracted much attention of researchers because of their applications in catalysis [13]. The advantages of Cu nanoparticles are being cheap, high yields in mild reaction conditions and having short reaction times as compared to traditional catalysts [14, 15]. Cu nanoparticles have been synthesized through different methods such as thermal decomposition [16–19], metal salt reduction[20], microwave heating [21], radiation methods [22], micro emulsion techniques[23], supercritical techniques [24], laser ablation[25], polyol method [26], solvothermal method [27], DC arc discharge method [28], thermal and so no chemical reduction [29]. Among various techniques for synthesis of inorganic nanoparticles, thermal decomposition is one of the most common to produce stable mono disperse 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 takes place at a higher reaction temperature [30]. Recently Zhengand coworkers reported synthes is of nanosized CuO via thermal decomposition of copper oxalate [31], but up to now there has not been any report about synthes is of metallic copper nanoparticles with this precursor. Very recently, our group reported the synthesis of uniform sized nanoparticles of various transition metal oxides from thermal decomposition of metaloleate complexes which were prepared from there action of some organ metallic complexes. In the continuation of the development of simple synthesis of nano sized nanoparticles, we here in report on the synthesis of metallic copper nanoparticles froma simple, green, low-cost, and reproducible process from copperoxalate as precursor. In this process, oleylamine was used as both the medium and the stabilizing reagent.

2. Experimental:

All the chemicals and reagents used were of analytical grade and were used as received without further purificationand a series of experiments were processed in order to synthesize by employing different method. Copper (II) fumarate precursor was prepared by adding drop wise the solution of disodium fumarate 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 CopperII) fumarate was characterized by UV and FT IR.

2.1 Preparation of Copper and Its Oxide Nanoparticles from Copper (II) Fumarate: The Copper (II) fumarate – oleylamine complex was prepared by the reaction of 0.7 g of Copper (II) fumarate with 10 mL of oleylamine. The mixed solution was placed in a 50 mL three-neck distillation flask and heated up to 120ºC for 1 hr under nitrogen atmosphere. The resulting metal-complex solution was injected into 5 g of triphenylphosphine (TPP) at 260ºC. As the thermal decomposition proceeded, the azury solution turned to reddish brown, indicating the formation of metallic copper. The light brown solution was kept at 260ºC for 60 min, and was then cooled to

room temperature. The light brown nanoparticles were precipitated by adding excess ethanol to the solution. The final product was washed with ethanol several times to remove excessive surfactant. This product can be easily dispersed in nonpolar organic solvents, such as hexane or toluene.(**Scheme 1**).

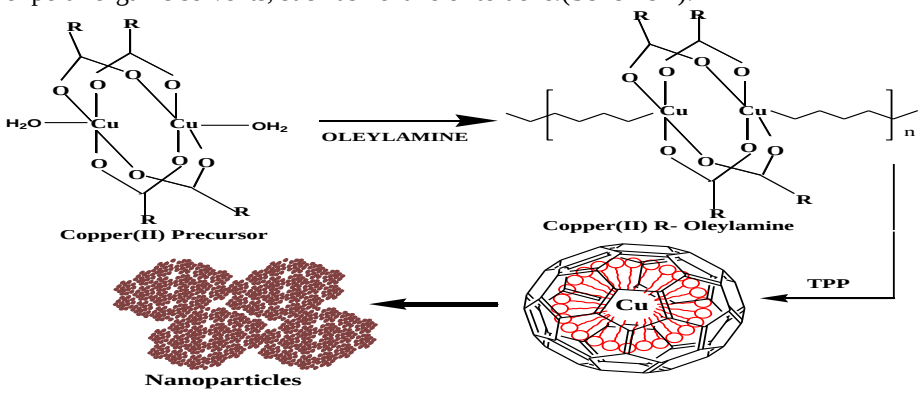

Figure 1: Schematic diagram of the formation of Copper and its oxide Nanoparticles (C1) by thermal decomposition method using oleylamine as capping agent

3. Results and Discussion:

3.1 Electronic Spectra: The UV– Visible spectra of Copper and its oxide nanoparticles are shown in (Figure 2 a & b**)** Copper and its oxide nanoparticles usually exhibits absorption bands in the range of 400-500 nmbecause of the surface plasmon resonance effect. There is only one strong surface plasmon resonance absorption peak at 400 - 450 nm in the UV–Visible spectrum of Copper and its oxide nanoparticles. This kind of stabilization of Copper and its oxide nanoparticles was due to the capping of particles by oleylamine in thermal process.

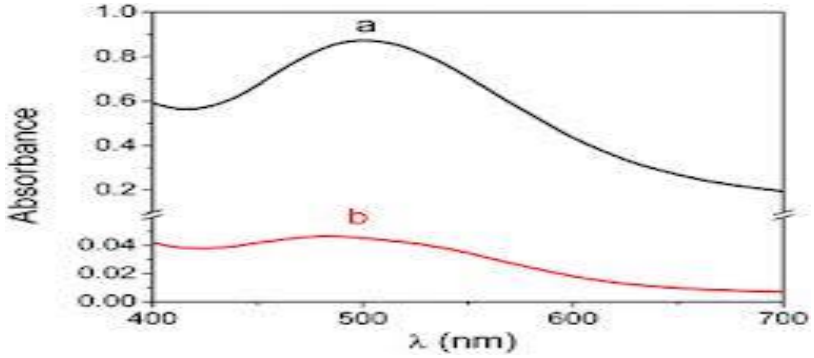

Figure 2(a & b): UV–Visible spectrum of Copper and its oxide nanoparticles (C 1) from Copper(II) fumarate precursor (P3)

3.2 FT-IR Spectroscopy:

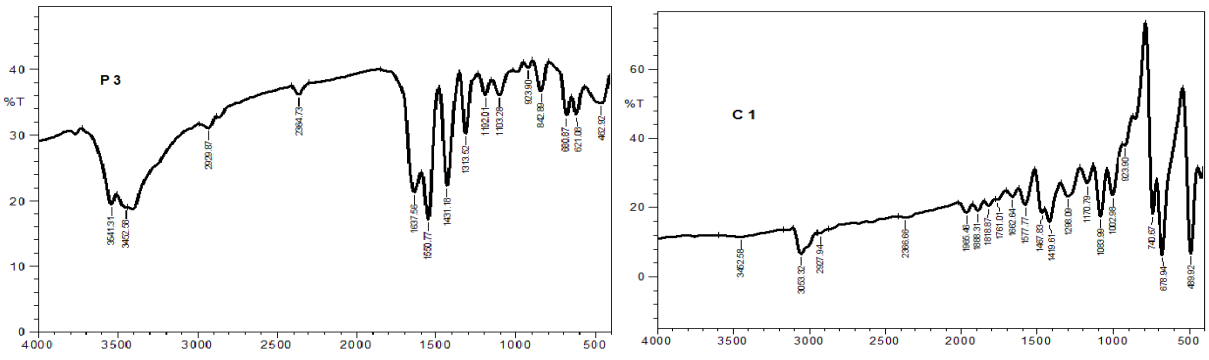

Figure 3: FT-IR spectrum of Precursor (P3) and Nanoparticles (C 1)

FT-IR spectroscopy is a useful tool to understand the functional group of any organic molecule. Figure 3 (P3) Shows Precursorand (C1) shows the Copper nanoparticles a peak at 680 cm^{-1} confirmed the presence Copper oxide nanoparticles. The metal salt (Cu-O-C) Peak is appeared around 1083-1109 cm^{-1}. The metal salt carbonyl group is appeared at 1645 cm^{-1}.The presence of the oleylamine group on the Copper nanoparticles is indicated by the N-H wagging mode from 651-860 cm^{-1}, NH_2 bending mode at 927 cm^{-1}, and NH_2 scissoring mode around 1580 cm^{-1}. The FT-IR spectra also reveals the characteristic peak of the C–N stretch around 1000 cm^{-1} which suggests that the C–N bonds are of the amine groups, and therefore the oleylamine ligands, remain intact, capping the Copper nanoparticles. The peak at 1467 cm^{-1} is associated with the C–H bending mode and the peak

at 2927 cm^{-1} represents the C–H stretching modes of the oleylamine carbon chain. Upon injection of Copper(II) precursors and oleylamine into hot TPP solution, the CuO bond is cleaved by the oleylamine group and copper is subsequently reduced. The weak peak around 3460 cm^{-1} has been assigned to the ethanol used in the separation step [31].

3.3 X-Ray Diffraction Studies: Powder X-ray Diffraction (XRD) is one of the primary techniques used by mineralogists and solid state chemists to examine the physicochemical make up of unknown materials. X-ray diffraction is one of the most important characterization tools used in solid state chemistry and materials science. XRD is an easy tool to determine the size and the shape of the unit cell for any compound. Powder Diffraction Methods is useful for Qualitative analysis (Phase Identification), Quantitative analysis (Lattice parameter determination & Phase fraction analysis) etc. Diffraction pattern gives information on translational symmetry - size and shape of the unit cell from Peak Positions and information on electron density inside the unit cell, namely where the atoms are located from Peak intensities. It also gives information on deviations from a perfect particle, Figure 4 Shows XRD pattern of C1if size is less than roughly 50–100nm, extended defects and micro strain from Peak Shapes & Widths.

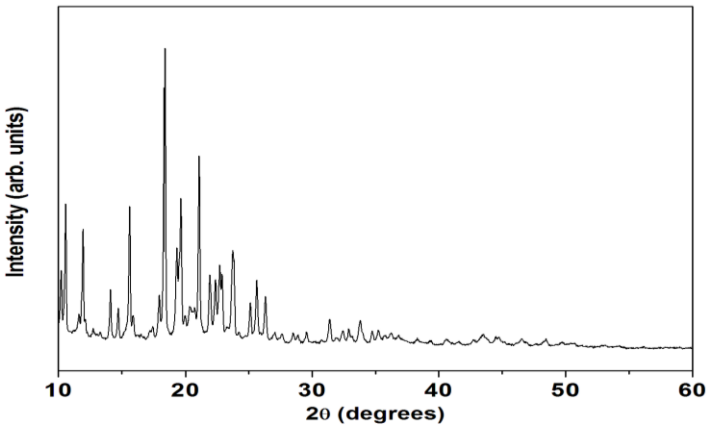

Figure 4: XRD pattern of C1

3.4 Peak Indexing: Indexing is the process of determining the unit cell dimensions from the peak positions. It is the first step in diffraction pattern analysis. To index a powder diffraction pattern it is necessary to assign Miller Indices (hkl) to each peak. Unfortunately it is not just the simple reverse of calculating peak positions from the unit cell dimensions and wavelength [32].

Table 1: Simple peak indexing

Peak Position (2θ)	1000xSin^2 θ	1000xSin^2 θ/46	Reflection	Remarks
43.84	138	3	(1 1 1)	$1^2+1^2+1^2= 3$
50.29	184	4	(2 0 0)	$2^2+0^2+0^2=4$
74.47	357	8	(2 2 0)	$2^2+2^2+0^2= 8$

Table 2: d Spacing values

2θ	D	1000/d^2	(1000/d^2) / 77	Theoretical value	hkl
43.84	2.07855	231.46	3.00	3	111
50.29	1.80094	308.31	4.00	4	200
74.47	1.27599	603.07	7.98	8	220

3.5 Particle Size Calculation: From this study, considering the peak at degrees, average particle size has been estimated by using Debye - Scherrer formula.

Average Crystalline Size;

$D = 0.9\lambda / \beta \cos\theta$, $\lambda = 1.5406 \times 10^{-10}$ m ,

β = Full width at half maximum (radian)

The average size of the nanoparticles, d spacing and microstrain values are shown in the Table 1 to 3.

Table 3: The particle size of Copper and its oxide nanoparticles

2θ of the intense peak (deg)	θ of the intensepeak (deg)	FWHM of Intense peak (β) radians	Size of the particle (D) nm	d spacing nm	Plane	Microstrain
43.77	21.89	0.1720	50.0	2.0667	(111)	0.107020
50.66	25.33	0.1720	51.3	1.8006	(200)	0.090844
75.95	37.96	0.5760	17.5	1.2877	(220)	0.184577

3.5 Cyclic Voltammetry: Cyclic voltammogram (CV) of the Copper nanoparticles was recorded in DMSO with 0.1 M tetrabutylammoniumperchlorate 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) reference electrode. The reductive peaks correspond to Cu (II)/Cu (I) and Cu (0). i.eCuO→ Cu_2O →Cu. The Cyclic voltammogram of Copper and its oxide nanoparticles is shown in the Figure 5. The redox potential values obtained from the Cyclicvoltammogram for the Copper and its oxide nanoparticles were quasi-reversible and the electron flow was sluggish.

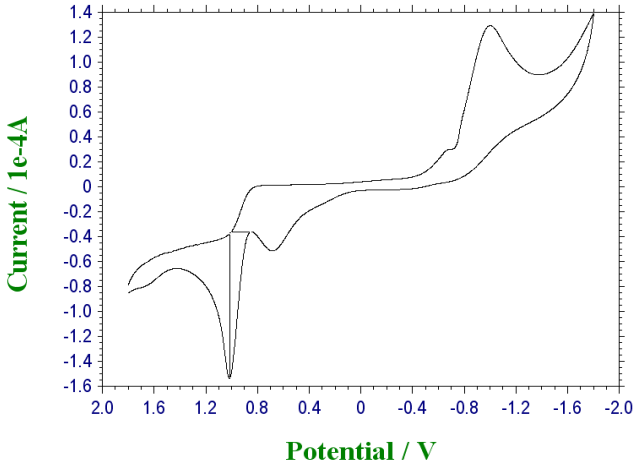

Figure 5: Cyclic voltammogram of C 1

3.6 Sem Analysis for Copper and Its Oxide Nanoparticles:

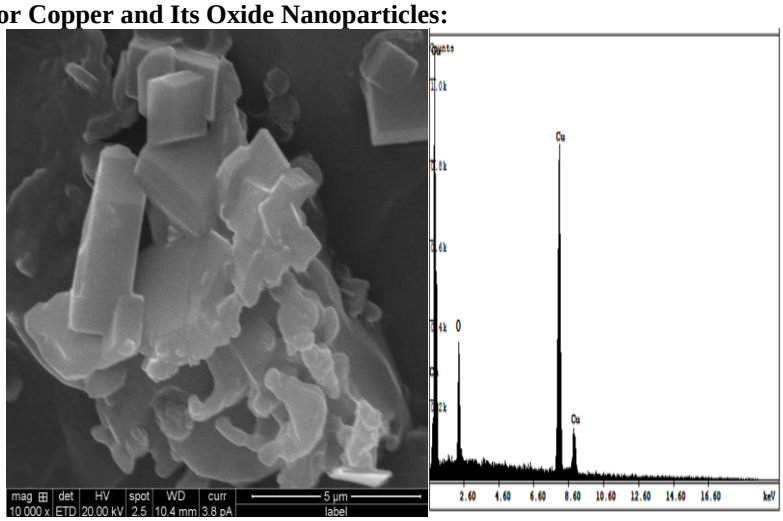

Figure 6: SEM with EDAX of C1 from P3

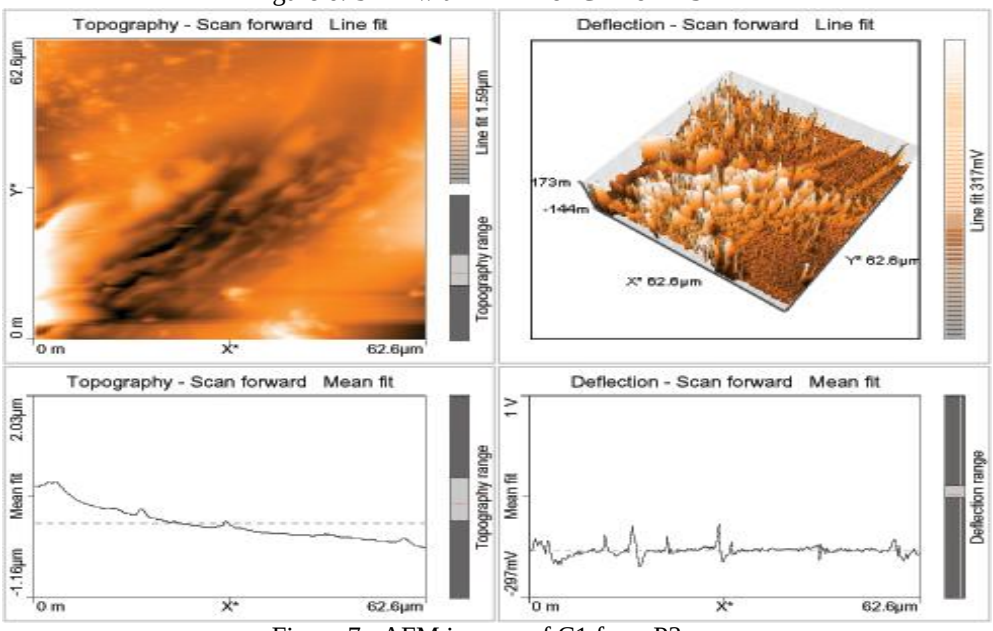

Figure 7: AFM images of C1 from P3

The morphology of the product was examined by Scanning Electron Microscope (SEM). Figure 6; depict the SEM pictures of a sample of Copper and its oxide nanoparticles. From the micrograph, it was observed that the nanoparticles are agglomerated. Since the reaction was carried out at 260°C, most of the organic molecule decomposes and only a few oleylamine molecules were adsorbed on the Copper and its oxide nanoparticles, a loose solid, rod and Cubic morphologies were finally produced. All the images show that the nanostructures are also made up of agglomerated Copper and its oxide nanoparticles. The Atomic force microscopic (AFM) photographs of the product are given in Figure7. On the ultramicroscopic scale of surface, atomic force microscopy (AFM) has been developed to obtain a three-dimensional image of a material surface on a molecular scale. Some loose spheres formed by aggregation of small particles can be observed in the AFM images. Surface measurement determines surface topography, which is essential for confirming a surface's suitability for a specific function. Surface measurement generally includes surface shape, surface finish and surface roughness.

4. Conclusion:

Copper and its oxide nanoparticles of size ranging 50 nm have been successfully synthesized via thermal decomposition of Copper (II) Fumarate- oleylamine complex. This method employs an inexpensive, reproducible process for the large-scale synthesis of Copper nanoparticles. FT-IR, XRD, CV, SEM and AFM results have concluded that Copper and its oxide nanoparticles were formed. The oleylamine method has an advantage in using TPP as reducing agent with required physiochemical properties that could support various biomedical applications.

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