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Synthesis and characterization of Copper and Copper Oxide nanoparticles by thermal decomposition method

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ABSTRACT

A simple method has been employed to synthesize Copper and Copper oxide nanoparticles from Copper (II) succinate precursor by thermal decomposition method using oleylamine as a capping agent. The particles synthesized with oleylamine and triphenylphosphine were well dispersed nanoparticles obtained from X-ray Diffraction (XRD). The Synthesized copper nanoparticles were characterized by UV-Visible, Fourier transfer Infrared Spectra, X-ray Diffraction, Atomic force microscope (AFM), Scanning electron microscope (SEM) and Cyclic Voltammetry (CV).

Keywords: *Metallic nanoparticles; Copper; Capping agent; Thermal reduction; Inorganic precursors.*

INTRODUCTION

Metal particles of nanometer dimensions have been extensively investigated in the recent years because of their present successful application sand of the perspectives of their use in various fields of science, technology and medicine. It is now well recognized that metal nanoparticles may serve as efficient catalysts in chemical and photographic processes [1, 2]. Copper is one of the most widely used materials in the world. It has great significance in all industries, particularly in the electrical sector due to low cost. Copper nanoparticles have been synthesized and characterized by different methods [3]. Stability and reactivity are the two important factors that impede the use and development of the metal cluster in a new generation of nanoelectronic device. These advantages are encountered in the following techniques thermal decomposition [4, 5], physical evaporation [6],laser ablation and thermal evaporation [7], laser assisted catalytic growth (LCG) [8], vapor liquid solid growth(VLS) [9], oxidation route [10], sol–gel methods [11].The technique of electro deposition is cheaper [12]. The synthesis and fabrication of Copper and Copper oxide nanomaterials with different morphologies have importance in both experimental and practical fields [13].

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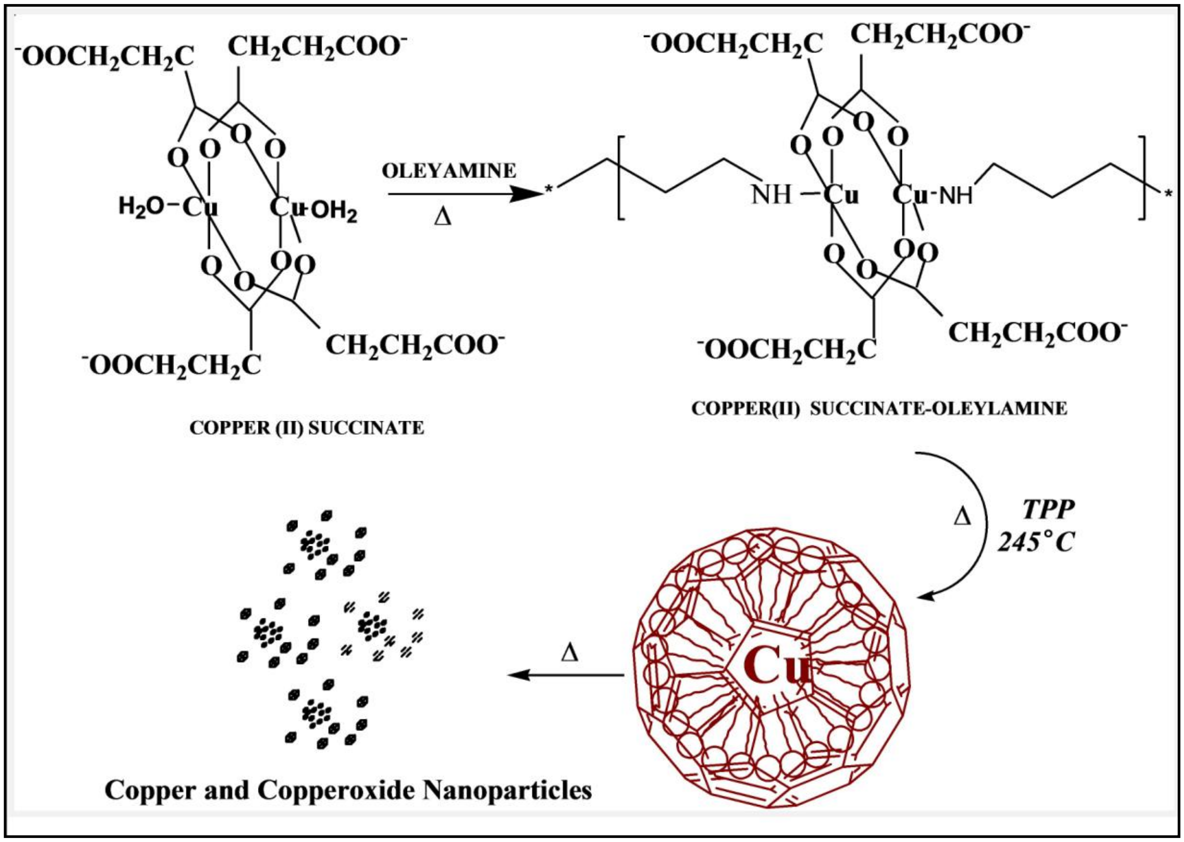
Till now, there have been many reports about the preparation of Copper and Copper oxide nanomaterials, as nanoparticles, nanoellipsoids, nanorods, nanowires, nanoribbons, nanoshuttles, and nanoleaves [14-16].

EXPERIMENTAL

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.

Copper (II) succinate precursor was prepared by adding drop wise the solution of disodium succinate 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) succinate was characterized by UV and FT IR.

In this synthesis, nanoparticles were prepared by the thermal reduction of the Copper (II) succinate – oleylamine complex as a precursor. The Copper (II) succinate –oleylamine complex was prepared by the reaction of 0.5 g of Copper(II) succinate with 5 mL of oleylamine. The mixed solution was placed in a 50 mL three-neck distillation flask and heated up to 145ºC for 1 hr under nitrogen atmosphere. The resulting metal complex solution was injected into 5 g of triphenylphosphine (TPP) at 245ºC. As the thermal decomposition proceeded, the azury solution turned to reddish brown, indicating the formation of metallic copper. The reddish brown solution was kept at 245ºC for 45 min, and was then cooled to room temperature [17].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. This product could easily be re-dispersed in nonpolar organic solvents, such as hexane or toluene [18] (Scheme 1).



Scheme 1. Schematic diagram of the formation of Copper and Copper Oxide Nanoparticle

RESULTS AND DISCUSSION

FT IR helped in ascertaining the functional group of Copper (II)succinate precursor and the formation of nanoparticles. Figure 1 Shows IR Spectrum of Copper nanoparticles with oleylamine as capping agent in the region of 4000cm^{-1} – 400cm^{-1}. The organic molecules are a part of the nanoparticles is clear from the spectra. As shown in Figure1, peaks corresponding to P–Ph stretching at 1761 cm^{-1}, rocking and bending mode of the methylene group **ω** (CH_2) at 1186cm^{-1}, bending mode of the phenyl group (**ω** CH) at 740 cm^{-1} and benzene ring at 686 cm^{-1} can be seen clearly.

The only difference among these characteristic peaks is either change in the peak intensity or a slight shift in the peak position. For example, the peak position of the longitudinal modes of free oleylamine and free TPP shifts to lower wave numbers after TPP and oleylamine are adsorbed on the surface of the nanoparticles. The FT-IR of the copper nanoparticles shows the intense adsorption peaks at 2918 and 2852 cm^{-1} attributed to the alkyl chains of oleylamine. The bands attributed to the antisymmetric and symmetric vibration modes of –N–H are observed at 3415cm^{-1}[19], Figure 1. Due to the coordination of the unpaired electron couple of the nitrogen atom, the vibration bands are observed in lower values than those expected for the free amine group, i.e., 3444cm^{-1}[20]. This indicates that oleylamine is bound on the surface through the unpaired electron couple of the amine group. From these results, a chemical bond can be formed between N and Cu atoms and a coordinate bond between P and Cu atoms on the surface of the nanoparticles Figure 1. Thus, the phenyl stretching mode (P–Ph) at 1473[18] and 1417cm^{-1} is still visible in Figure1. So the oleylamine and TPP serves as the capping ligand that controls growth. Triphenylphosphine (TPP) was widely used in the synthesis of phosphine-stabilized cobalt or other metal nanoparticles [21].

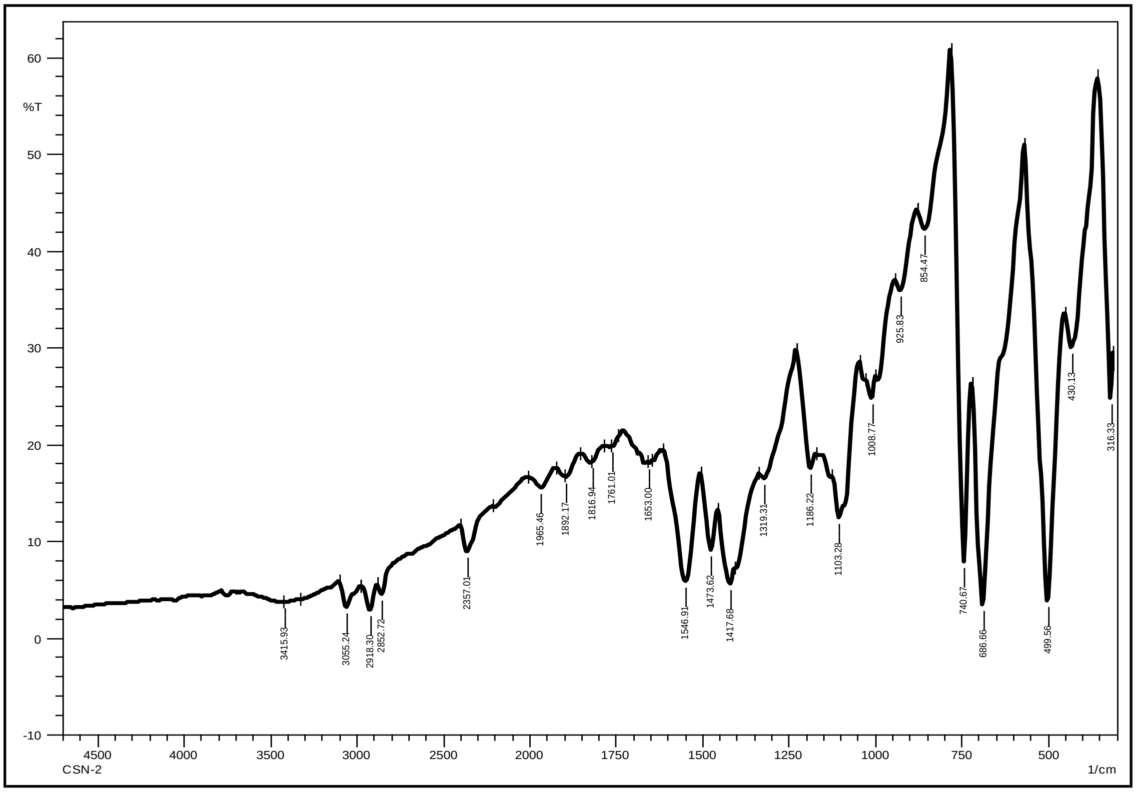


Fig. 1. F T IR spectra of Copper and its Oxide nanoparticles coated by oleylamine.

X-ray powder diffraction (XRD) pattern of nanoparticles at room temperature is shown in Figure 2. X – Ray diffraction is one of the most important and cases characterization tool used in nanomaterial's research field. The copper nanoparticles Synthesized got oxidized in due course. The XRD pattern is consistent with the Spectrum of Cu, Cu_2O and CuO nanoparticles. The XRD pattern is consistent with the spectrum of Cu, Cu_2O and CuO. Bragg's reflections for nanoparticles was observed in XRD pattern at 2θ value 38.95, 43.54, 49.00 and 75.45 representing Cu [110], [111], [200] and [220], Cu_2O and Cu [110], [211], [311] planes of FCC structure of copper with the space group of F_{m3m} (JCPDS No. 4–0836) [22]. Powder X-ray Analysis Data analysis shows the nanoparticles system is hexagonal lattice, Type P, the Lattice parameter was a= 4.9168 b= 4.9168 c= 5.408 and Alpha= 90 Beta= 90 Gama=120 Radiation, Cu Wavelength: 1.540598. The size of the nanoparticles estimated from Debye - Scherer equation is about average 50 nm. From the full width at half maxima (FWHM) of the [111] diffraction peak on the basis of the Scherer formula: $[D = 0.9\,\lambda/\,\beta\cos\theta]$.

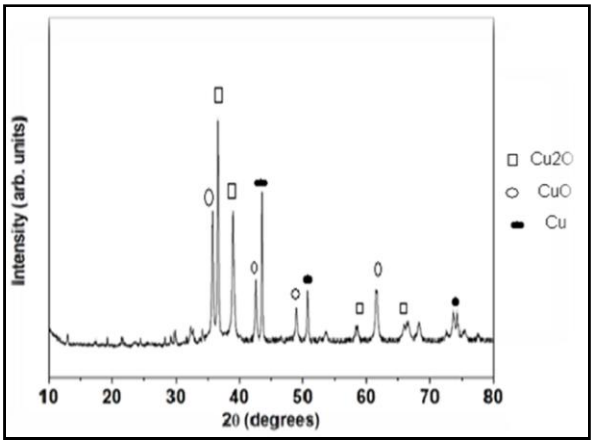


Fig. 2. XRD pattern of the Copper and its Oxide nanoparticles.

The morphology of the product was examined by SEM. Figure 3 depicts the SEM pictures of a sample of nanoparticles. From the micrograph, it was observed that the nanoparticles are agglomerated. When the reaction was carried out at 245°C, most organic molecules decomposed and since only a few oleylamine molecules were adsorbed on the nanoparticles, a loose solid rod-like morphology was finally produced. This observation alludes to the size effect of the nanoparticles. This kind of stabilization of 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 average 1.85µm.

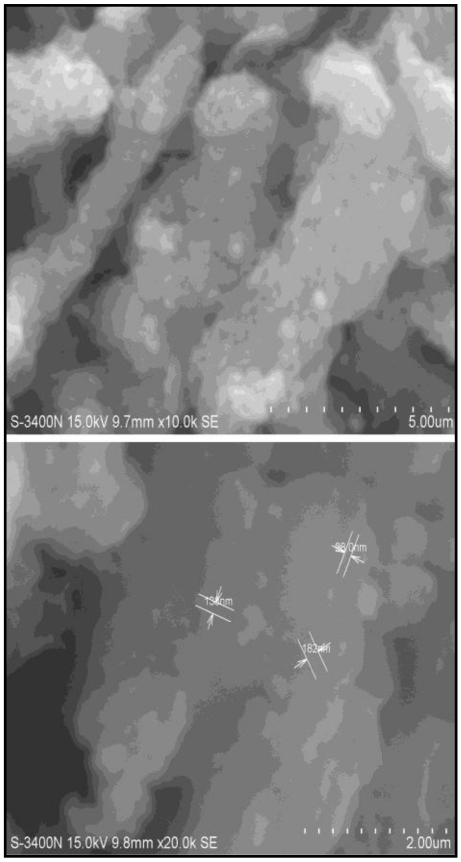
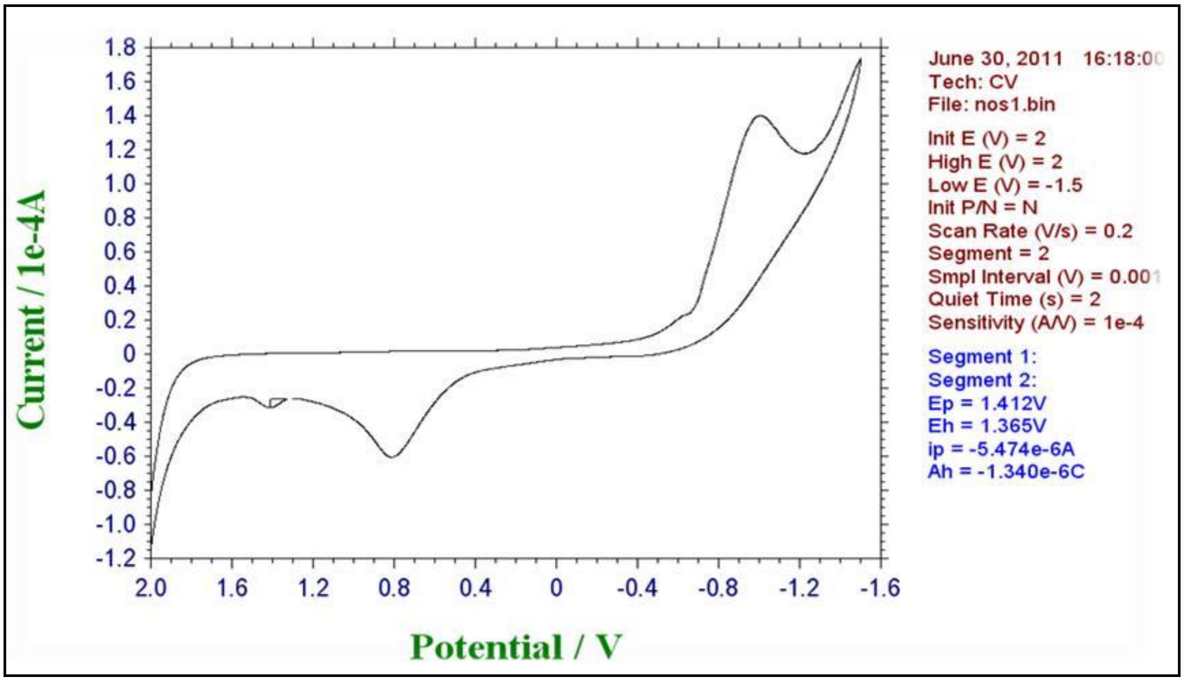


Fig. 3. SEM images of the agglomerated Copper and its Oxide nanoparticles.

Figure 4 show the Cyclic Voltammetry (CV) of the copper nanoparticles was recorded in DMF with 0.1 M tetrabutyl ammonium 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) reference electrode. The reductive peaks correspond to Cu (II)/Cu (I) and Cu (0). i.e $CuO \rightarrow Cu_2O \rightarrow Cu$. The redox peak currents increase linearly with increase in the scan rate from 20 to 100 Mvs^{-1}(Figure 4) the oxidative peak corresponds to $Cu \rightarrow Cu_2O \rightarrow CuO$.



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Segment 1:
Segment 2:
Ep = 1.412V
Eh = 1.365V
ip = -5.474e-6A
Ah = -1.340e-6C

Fig. 4. CV spectrum of the Copper and its Oxide oleylamine caped nanoparticles.

Figure 5 shows the Copper nanoparticles typically exhibit at around 500 nm [18] however the Copper nanoparticles synthesized here show an absorption peak at around 459 nm**.** This peak can be assigned to the absorption of nanoparticles of copper. Figure 6 shows the topography image of oleylamine modified nanoparticles (transfer pressure is 20 mN/m, mica substrate) acquired simultaneously at the same sample location. Results showed that the modified Copper and Copper oxide nanoparticle has typical core–shell structure. The oleylamine capped copper nanoparticle was composed of many nanoparticles arranged closely and orderly. The sizes of these nanoparticles in monolayer film are 50–100 nm.

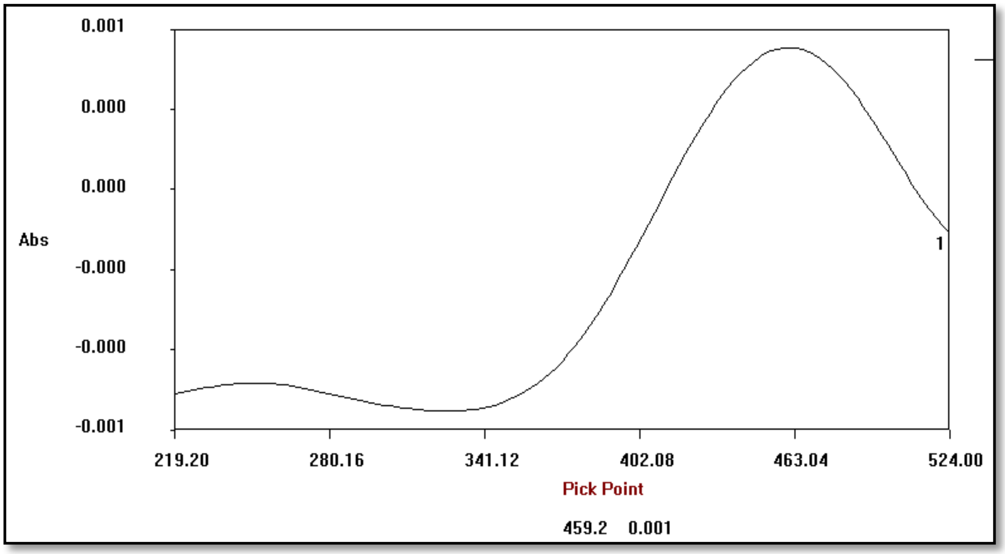

Fig. 5. The UV–Vis absorption spectrum of the Copper and its Oxide nanoparticles

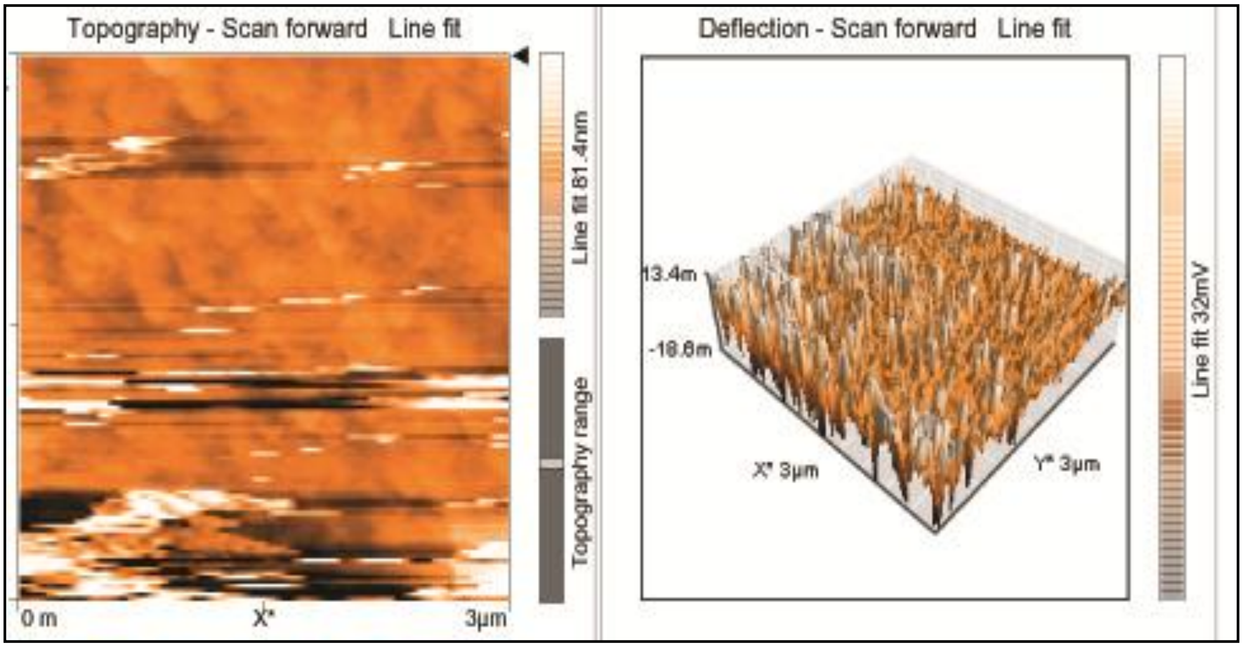

Fig. 6. The AFM images of Oleylamine modified Copper and its Oxide nanoparticles.

CONCLUSIONS

In summary, uniform flower-like Copper and Copper oxide nanoparticles of approximately the diameters of average 1.85µm size was successfully synthesized via a simple method using the copper (II) succinate as precursor. The refluxing time was found to have an influence on the morphology of the Copper nanoparticles. The obtained mesoporous Copper and Copper oxide nanoparticles obtained find various potential applications in catalysis, electrochemistry, and optics because of the high specific surface area.

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