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Rapid Communication

Investigation of synthesized nanosized copper by polyol technique with graphite powder

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ABSTRACT

Polyol method is a type of soft chemical method employed to prepare stable fine transition metals (TMs), without using any sophisticated instruments in a normal clean room environment. In the present work, pure nano-sized copper powder was prepared by reduction of copper (II) chloride dehydrate with sodium hydroxide in the glycerol environment at reaction temperature of 160 °C for 17 min. The Field Emission Scanning Electron Microscopy (FESEM) observation of synthesized copper powder showed the particle dimensions varying from 70 to 400 nm. The Energy Dispersive Spectroscopy (EDS) and X-ray Diffraction (XRD) analysis supported the 98.46% purity of synthesized copper powder. The Rietveld analysis confirmed the cubic structure for synthesized copper with cell parameter: $a = 3.63$ Å. Whereas the Ultraviolet–Visible Spectroscopy (UV–Vis) revealed damping of surface plasmon resonance due to inactive chloride monolayer at the particle surface. This copper powder heat-treated in carbon environment showed the presence of copper oxalate phase using XRD analysis, noted from the peaks at 36.2° and 46.4° for (120) and (200) planes, respectively; and Fourier Transform Infra Red (FTIR) Spectroscopy backed the presence of copper oxide (Cu_2O).

1. Introduction

Copper had been a well known TM[1] for the mankind, which had been repeatedly explored for its uniqueness and used by past and present researchers [1–4]. As most of TMs are easily oxidized, their multiple oxidation was controlled by vacuum drying [5,6] and using stabilizers like tri-sodium citrate ($C_6H_5O_7Na_3$) [7], reducing agents like sodium borohydride ($NaBH_4$) [8], chelating agents like PVP[2] [9], and ascorbic acid ($C_6H_8O_6$) as antioxidant [1]. The copper powder prepared from novel methods find applications in catalysis [2,8], MLCC[3] [2] and conductive ink due to its high electrical conductivity and high melting point [3]. There had been numerous reporting of aberrations pertaining to conductivity of copper with respect to gold and silver [5]. The polyol method was found as perfect process for pure copper powder synthesis, among various techniques available to prepare TMs [1–9]. This procedure is mainly employed for the metallic powder preparation in minimum time without any oxide or hydroxide bond formation. Further, this approach is considered as part of eco-green process, having high energy efficiency and low consumption, as it lacks any hazardous chemical usage in the form of reducing agent [10]. There is an interest toward studies on interaction of copper with graphite powder as it is a crystalline conductive form of carbon that can be used as inexpensive solid lubricant for the wear resistant applications [11]. The increase in the wear resistant properties due to addition of copper with graphite was also reported by Canakci et al. [12]. In the present research, nanosized pure copper powder synthesized using polyol method was mixed in varying proportions with graphite and was further annealed to understand the oxidation of copper using XRD[4] and FTIR[5].

Abbreviations: TM, transition metal; PVP, Polyvinylpyrrolidone; MLCC, Multi-Layer Ceramic Capacitors; XRD, X-Ray Diffraction; FTIR, Fourier Transform Infrared Spectroscopy; FESEM, Field Emission Scanning Electron Microscopy; EDS, Energy Dispersive Spectroscopy; UV–Vis, Ultraviolet–Visible Spectroscopy.

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[1] Transition Metal.
[2] Polyvinylpyrrolidone.
[3] Multi-Layer Ceramic Capacitors.
[4] X-ray Diffraction.
[5] Fourier Transform Infrared Spectroscopy.

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2. Experimental

2.1. Materials

All chemical substances were AR grade and utilized without further purification. Copper (II) chloride ($CuCl_2{\cdot}2H_2O$, Finar, 99% [MW = 170.48 g mol^{-1}]) was dissolved in the solution of sodium hydroxide (NaOH, Fisher Scientific, 99.5% [MW = 39.997 g mol^{-1}]) and glycerol ($C_3H_8O_3$, SRL, 99% [MW = 92.10 g mol^{-1}]). Here, graphite powder (Graphite, C, CDH, >99.5%, average particle size around 50 μm) was used as carbon source.

2.2. Method

The mixture of copper chloride (2.68 g), sodium hydroxide (1.90 g) and glycerol (57.74 ml) was stirred using magnetic stirrer at constant rate of 1000 rpm and constant temperature of 160 °C for about 17 min to obtain 1 g of pure copper powder. The visual appearance of the solution changed color from blue to reddish orange indicating completion of chemical redox reaction. After cooling of solution to 25 °C temperature, it was centrifuged at 6000 rpm. The samples were collected and washed with absolute ethanol several times till pure fine copper powder was obtained. The synthesized copper powder was subsequently mixed with 5, 7 and 10 wt% graphite powder by classical powder metallurgy route. The obtained mixtures were finely ground using conventional mortar and pestle, unidirectionally for 6 h, to reduce the particle size. Finally, the mixtures were heat-treated at 200 °C for 24 h using ordinary laboratory oven manufactured by Nisco, India.

3. Result and discussion

3.1. Chemical reaction process during copper preparation

The preparation of copper particles can be represented by the following chemical reactions:

$$CuCl_2 \cdot 2H_2O + 2NaOH \xrightarrow{\text{Room temperature}} Cu(OH)_2 + 2NaCl + 2H_2O \quad (1)$$

$$Cu(OH)_2 + C_3H_8O_3 \xrightarrow{160\ ^\circ C} C_3H_6O_3(Cu) + 2H_2O \quad (2)$$

Eq. (1) depicts the electrochemical reaction between ions of sodium and chloride leading to salt formation at room temperature. In this process, as mentioned earlier, the color of the solution becomes blue due to the presence of ($Cu(OH)_2$). Here, Cu^{2+} is slowly reduced to Cu; and the color of the solution completely changes to reddish orange after the formation of copper (II) hydroxide again from glyceraldehyde ($C_3H_6O_3$); and evaporation of water molecules at evaporation point. An extra mole of sodium hydroxide added helped in controlling particle size of copper due to the realization of desired pH of the solution, which was even reported previously [1,13].

3.2. Field Emission Scanning Electron Microscopy (FESEM) and Energy Dispersive X-ray Spectroscopy (EDS) analysis

FESEM[6] with EDS[7] from FEI Quanta 200F with Oxford – EDS system (IE 250X max 80) were used to understand the surface morphology of the synthesized copper powder. The FESEM image in Fig. 1 shows non uniform particle size distribution of copper particles at low magnification (20,000×), whereas Fig. 2 distinctly

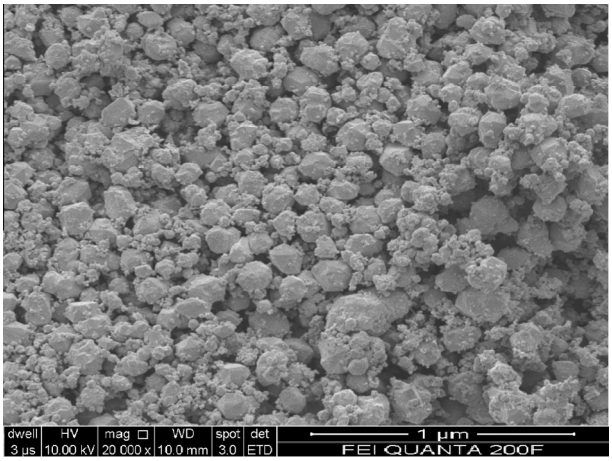

Fig. 1. Field Emission Scanning Electron Microscopy (FESEM) image at 20,000× magnification of copper. The picture depicts formation of clusters of nanosized copper powder.

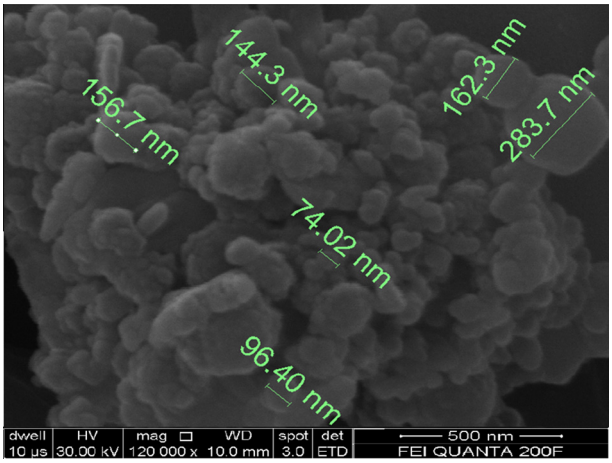

Fig. 2. Field Emission Scanning Electron Microscopy (FESEM) image at 120,000× magnification of copper. The picture depicts formation of nanosized copper powder of around 150 nm.

outlines the variation of particle size distribution from 70 nm to 300 nm at high magnification (120,000×). This size variation might be due to the sudden exposure of sodium hydroxide with the precursor during sample preparation [13]. However, clusters of nanosized copper powder particles are formed because of the weak coulombic forces of attraction. The chemical composition of the synthesized copper particles analyzed by EDS, as shown in Fig. 3, verified the 98.46% copper content. Thus, there is noticeable presence of oxygen and carbon, as seen in the EDS data given in Table 1, which can be attributed to the sample preparation consumables.

3.3. X-ray Diffraction (XRD) analysis

The XRD patterns of the sample were recorded using X-ray diffractometer XRD-6000 manufactured by Shimadzu analytical, Japan (wavelength: Cu Kα radiation $\lambda = 1.54$ Å). The scan shown in Fig. 4 was performed at room temperature with the scan rate of 0.5 deg/min. The XRD values were refined by Rietveld analysis to calculate the lattice parameters of the synthesized pure copper powder using FullProf suite program (version 2.05). The cell parameter obtained from this refinement was $a = 3.63$ Å and $\alpha = \beta = \gamma = 90°$, with direct cell volume calculated as 47.80 $Å^3$. Here,

[6] Field Emission Scanning Electron Microscopy.
[7] Energy Dispersive Spectroscopy.