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Generation of Nano-copper Particles through Wire Explosion Method and its Characterization

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ABSTRACT

Nano-copper particles are produced in argon gas ambience by the controlled-current wire explosion process. Physico-chemical diagnostic studies, like Wide Angle X-ray Diffraction (WAXD), Thermo-Gravimetric Differential Thermal Analysis (TG-DTA) studies, Energy Dispersive Analysis by X-ray (EDAX) are carried out. The surfactants in the electrolyte served as both a templates and stabilizers during the synthesis procedure The Wide Angle X-ray Diffraction measurements have shown that nano-copper particles prepared by the process are mainly composed of (111), (200) and (220) orientation crystallites and also revealed all relevant Bragg's reflection for FCC crystal structure of copper metal. The particle size obtained through Scherrer's equation is about 36.34 nm. Fourier Transform Infra-Red (FTIR) test, HRTEM and Scanning Electron Microscope (SEM) studies confirmed the nano size of the particles in spherical shape with FCC structure of the copper particle. Also, the crystalline structures of the Cu nano particles were confirmed by the Wide Angle X-Ray Analysis results. The current density applied during the electro-deposition has an effect on the shape and yield of the copper nano-particles.

Key words: Nano particle, copper particle, plasma, wire explosion, WAXD, EDAX, HRTEM, TG–DTA, FTIR, SEM

INTRODUCTION

In recent years, a sizable research activity is witnessed the area of synthesis and fabrication of different size and shape of metal nano-particles. Nano-meter sized particles display many interesting optical, electronic, magnetic and chemical properties yielding applications in biological nano-sensors, optoelectronics, nano-devices, nano-electronics, information storage and catalysis (Feldheim and Foss, 2002). Like Au, Ag, Pd, Pt, the research is directed towards copper and copper-based compounds. The metallic Cu plays a significant role in modern electronics circuits. It has excellent electrical conductivity and low cost nano-particles (Schaper *et al*., 2004). Cu will gain increasing importance as is expected to be an essential component in the future nano-devices due to its excellent conductivity as well as good biocompatibility and its Surface Enhanced Raman Scattering (SERS) activity (Pergolese *et al*., 2006).

A substantial amount of research has been directed toward the synthesis of metal nano-particle in efforts to explore their special properties and potential applications (Ferrier *et al*., 1985; Yi and Fendler, 1995; Toshima and Yonezawa, 1998; Brust and Kiely, 2002). Fast and growing applications of metallic copper nano-particles, synthetic control over size, shape and composition of

the particles has led to many interesting investigations into their physical properties. Among various metal particles, copper nano-particle has attracted considerable attention because of their catalytic, optical and electrical conducting properties (Huang *et al*., 1997; Dhas *et al*., 1998; Vitulli *et al*., 2002; Liu and Bando, 2003). The melting point (Tm) of nano materials can be dramatically lowered by decreasing the size of the material relative to their bulk counterparts (Kim *et al*., 2006). This low temperature melting ability makes metal nano-particle potentially suitable materials for use in printed electronics. This can be easily annealed at lower temperatures to form conductive films of low resistance.

Currently, noble metals such as gold (Au) and silver (Ag) are being exploited for application despite of their costliness. In this regard, copper is a good alternative material as it is highly conductive and much more economical than Au and Ag. Several methods have been developed for the preparation of copper nano-particle, including thermal reduction (Huang *et al*., 1997), sono-chemical reduction (Huang *et al*., 1997; Kumar *et al*., 2001), metal vapor synthesis (Dhas *et al*., 1998), chemical reduction (Vitulli *et al*., 2002), vacuum vapor deposition (Liu and Bando, 2003), radiation methods (Casella *et al*., 1996), micro emulsion techniques (Lisiecki and Pileni, 1993; Qi *et al*., 1997; Pileni *et al*., 1999) and laser ablation (Yeh *et al*., 1999). Among these methods, the wire explosion method is found to be simple and most versatile for producing pure metal nano-particles.

In this study, the production of copper nano particles by wire explosion technique has been reported, which is a top down approach to produce nano-particle (Hahn and Averback, 1990; Ivanov *et al*., 1995; Jiang and Yatsui, 1998; Kwon *et al*., 2001; Rhee *et al*., 2002). Certain physicochemical diagnostic studies, like Wide Angle X-ray Diffraction (WAXD), Fourier Transform Infra-Red analysis (FTIR) and Energy Dispersive Angle X-ray Analysis (EDAX), have been carried out for characterization of the size and behaviour of the nano copper particles (Gracia-Pinilla *et al*., 2010). Also, the size and shape of the particles are analyzed by using Scanning Electron Microscope (SEM) and High Resolution Transmission Electron Microscopy (HRTEM) studies.

MATERIALS AND METHODS

The basic circuit used for exploding the copper wires to produce nano-particle is shown in Fig. 1. The capacitor is charged from the source and discharged through the wire as shown in Fig. 1. The explosion of wire is characterized by the energy introduced into the wire, which is higher than the evaporation energy of the material. The energy input time is shorter than the time required for any constraints to develop and larger than the required time for the current to spread

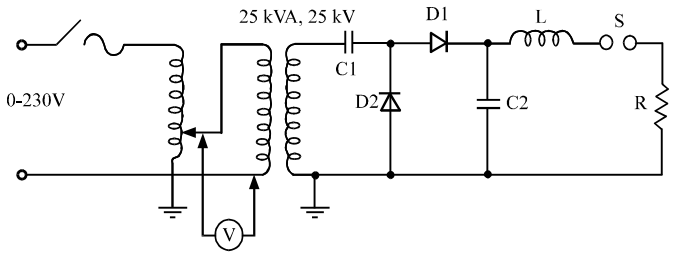

Fig. 1: Basic circuit of wire explosion method. The switch (S)-a high voltage trigatron gap, R-the exploding wire resistance and L-Contribution by the internal inductance of the capacitor and the lead inductance C1 and C2-capacitance, D1 and D2

Table 1: Details of experimental methods

Experimental details	Parameters
Capacitance	3 μF
Charging voltage	22 kV
Material	Copper
Wire diameter	0.5 mm
Length of the wire	90 mm
Ambience pressure	0.1 MPa
Ambience	Argon gas

over the wire radius. The details of circuit parameter, the respective value of the electronics item used and specification of the copper material used are shown in Table 1. A copper wire with 0.5 mm dia. and 90 mm long is used during production of nanocopper particles. The entire process is carried out at argon gas with ambiance pressure of 0.1 MPa. Special precaution was taken to keep the constancy of ambiance pressure, material dimension and electric power supply. More details of experimental methodology on formation of copper nanoparticles are explained.

FORMATION OF NANO-PARTICLES

Stage 1: Closing of switch S (Fig. 1), the voltage appeared across the wire and the current controlled by the RLC circuit increased, causing joule heating of the conductor, which eventually melted. The switch S is a high voltage trigatron gap, R is the exploding wire resistance and L is the contribution by the internal inductance of the capacitor and the lead inductance. The magnitude of current flow in the circuit depended on the resistance and the inductance in the circuit.

Stage 2: As per the Joule heating, the temperature of the conductor raised and discharged high current through the wire. The heating of liquid phase took place, followed by melting and eventually reaching of the boiling point and superheating before the liquid phase changes to gas phase.

Stage 3: After wire evaporation, the plasma expanded in the medium due to the enormous difference in the temperature and pressure between the plasma and the ambient gas. The expanded plasma particles were gradually cooled because of collision with ambient gas molecules. Finally, the plasma lost its expansive driving force. Hence, a low ambient pressure allowed a large expansion volume. This led to low number concentration of the substance during particle growth, resulting in small nano-particles.

CHARACTERIZATION METHODS

In the present study, WAXD measurements were carried out by X-ray diffractometer, a product of Philips. Using Cu Kα radiation wavelength (1.596 A°) and a scan rate of 2° min^{-1} at 2000 cycles, the copper nano material property was studied. A radial scan of Bragg angle (2Δ) vs. intensity was obtained with an accuracy of ±0.25 A° at the location of the peak. Powder morphology was observed with SEM (JEOL-Japan made and model JSM-840A) and the SEM is combined with Energy Dispersive Analysis through X-ray spectroscopy (EDAX). The Fourier Transform Infra-Red Spectroscopy equipment, the Perkin Elmer product, was used in the present study. A scan range in the wave number of 4000-400 cm^{-1} with a resolution of 2 cm^{-1} has been found to be adequate for spectroscopic analysis. The effective techniques like TG (Thermo-Gravimetric) and DTA

(Differential Thermal analysis) methods were used to study the chemical and physical phenomenon of formed nano copper particle as a function of temperature. The TG-DTA study was carried out with Netzch STA 409C equipment. The TG-DTA analysis of Cu nano-particle was carried out between 27-1300°C at the heating rate of 20 (k min^{-1}). Alumina was used a standard catalyst. The TEM studies were carried out on a Phillips transmission electron microscopy.

RESULT AND DISCUSSION

Several methods are used for the preparation of copper nanoparticles, including thermal reduction, sono-chemical reduction, metal vapour synthesis, chemical reduction, vacuum vapour deposition, radiation methods, micro emulsion techniques and laser ablation. Most of the aforementioned methods utilize an oxygen-free environment to synthesize copper as it readily oxidizes in air. Therefore, it is almost desire to characterize the formation of copper oxide during the processing of copper nanoparticles through copper wire explosion method.

The WAXD spectra of the nano-copper powder obtained using the wire explosion technique in argon gas ambience is shown in Fig. 2. It is found that XRD pattern still has the traces of oxide at 2θ (36.8°). But, due to metallic copper all Bragg's reflections are observed at 43.36°, 50.52° and 74.21° representing (111), (200) and (220) planes of FCC crystal structures of bulk copper. Peaks are very sharp due to the high nanocrystalline nature of copper. Particles size of copper nano powder prepared through wire explosion method was calculated from the Debye-Scherrer's equation, which is expressed as: Diameter of the particle, $d = \lambda K/\beta \cos\Delta$. An estimation of particle measurement by use of this equation revealed a crystallite size of about 36.34 nm. The scanning electron micrograph (Fig. 3) illustrated the morphology of the nano-copper particles prepared through wire explosion method in argon gas ambience. The SEM photograph has clearly indicated that the particles are sub-micron size ranges from 10 to 100 nm and a wide distribution of spherical particles are present in the produced nano-copper particles. This is confirmed further by doing TEM study.

The particles sizes of the nano crystalline copper powder were calculated by using the above equation. The sizes are tabulated in Table 2 for every diffraction peak and the values along with the average particle. The average particle size is about 36.34 nm.

The results of the EDAX indicated that 91.29 wt.% of copper and 8.71 wt.% of oxygen produced nano-Copper particles. Figure 4 is showing the FTIR spectra of copper powder material. It is

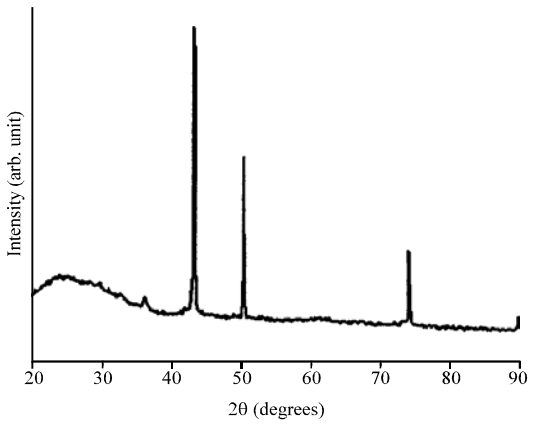

Fig. 2: WAXD spectra of the nano-copper particles

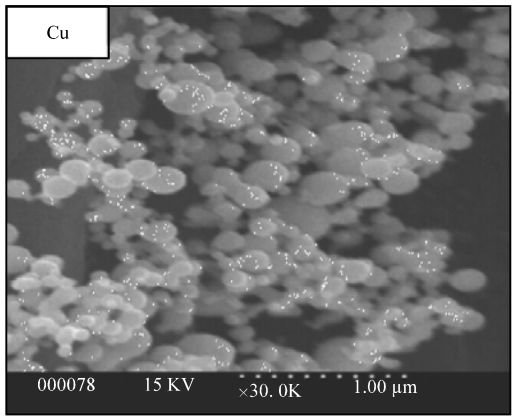

Fig. 3: SEM image of nano-copper particles

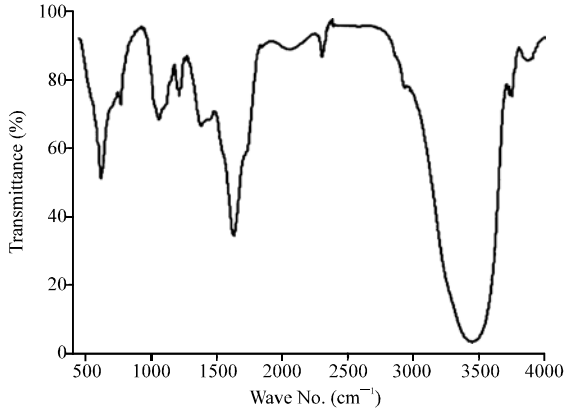

Fig. 4: FTIR spectra of nano-copper particles

Table 2: Particle size of the produced sample through Debye-Scherrer's Formula (λ = 1.54 A°, K = 0.89)

Diffraction angle (2θ) (degree)	Full width half maximum (β) (Radian)	Particle size (nm)
36.48	0.5191	16.11
43.36	0.1997	42.80
50.52	0.2022	43.42
74.21	0.2312	43.06

Average particle size 36.34 nm

realized that the presence of broad band at 3500 cm^{-1} is illustrated the stretching frequency of hydroxyl group present in the surface of the copper nano-particle. A small peak at 962 cm^{-1} indicates the formation of Cu-O-Cu bonding in copper Oxide. This gives additional evident in the WAXD results that copper oxide is present in the nano-particles. Figure 5a and b show the TG-DTA spectra of the copper nano particle formed by a wire explosion process. There is a slight increase in weight close to 100°C and at 200°C the weight increases in rapid manner. The total weight increase is about 23.85%, due to oxidation of copper nano particle to form copper oxides. The copper oxide is stable up to 1000°C and just above the temperature, there is a weight loss about 18%. It is described that the conversion of stoichiometric copper oxide into non stoichiometric one is associated

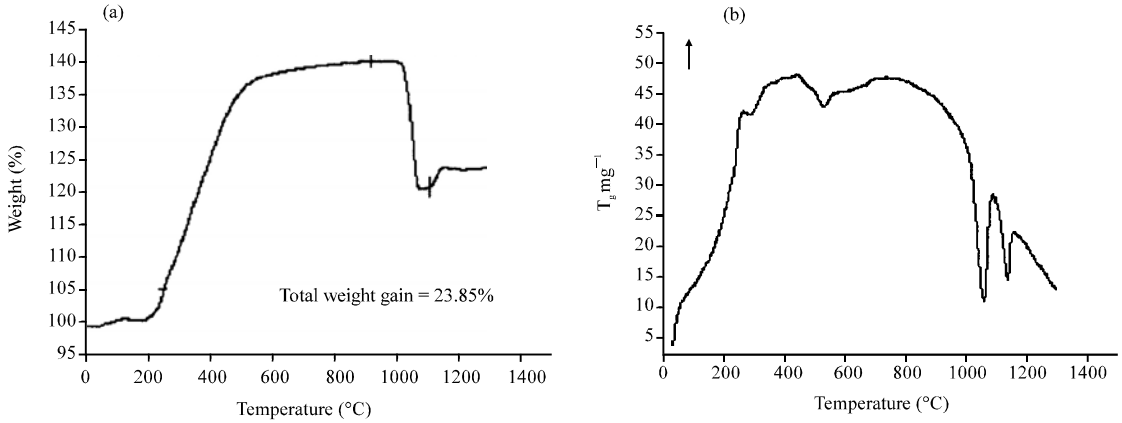

Fig. 5: TG-DTA spectra of the copper nano particle. (a) Copper TGA and (b) copper DTA

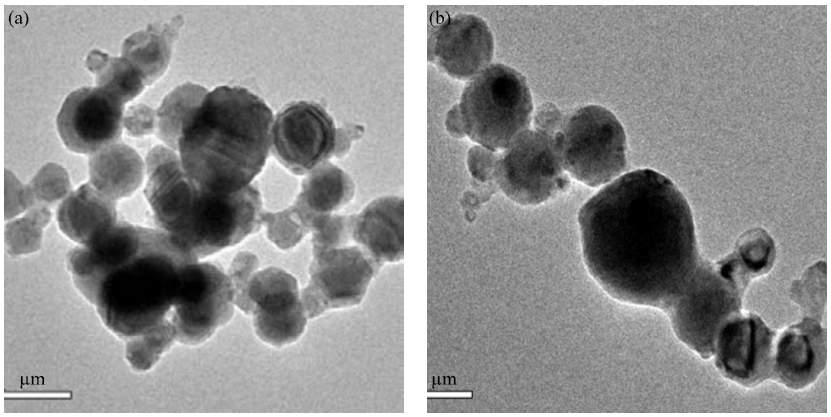

Fig. 6: (a, b) HRTEM Images of Nano Cu particles

with the release of oxygen, the resulting oxide is stable up to 1300°C. The DTG Trace clearly establishes the origin and end of such transformations. There is a broad exothermic peak between 200 to 400°C coincides with weight increase in Thermo Gravimetric Analysis. So, it is realized to be oxidation of copper nano-particles. There is an endothermic peak at 1058°C coincides with the high temperature weight loss in TGA.

No other endothermic peak is absorbed below the temperature. Hence the metal oxide may decompose without melting. There is an additional sharp endotherm with the maximum 1139°C, due to oxidation of the resulting non stoichiometric oxides of copper.

Typical micrographs of metallic copper nanoparticles (spherical, with size of 10-15 nm) formed by the wire explosion process at argon gas ambience are shown in Fig. 6a and b for different HRTEM resolutions. High resolution micrographs allow observing the crystal lattice of the particles obtained in the argon are in spherical shape with FCC structure of the copper particle as observed by HRTEM. The size of copper nanoparticles enters the range up to several tens of nanometers; however, the samples studied do not reveal a high monodispersity of the metal particles.

A study by HRTEM on samples determined the crystallographic and morphologic features as function of size and reported briefly. In Fig. 7, the particle size and particle lattice pattern is

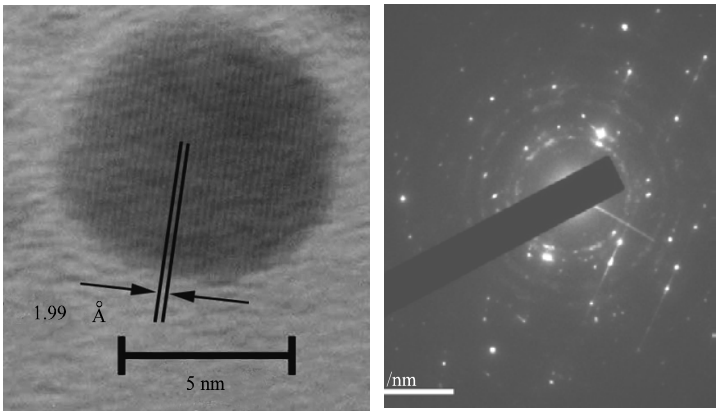

Fig. 7: The lattice pattern of Cu nano-particles

presented. The particle size lies in the range of a few nm to 100 nm. The lattice of Cu nano particle shows the lattice spacing in the HRTEM (high-resolution transmission electron microscopy) image of 1.99 A° is consistent with the distance for (111) lattice spacing in Cu. Similar results was reported by Gracia-Pinilla *et al*. (2010).

CONCLUSION

The present study illustrates simple, convenient and significant method for the synthesis of copper nano-particles through the electrical wire explosion of copper wire. The obtained copper particles through wire explosion method in argon gas ambience were confirmed to be phase-pure crystalline copper with Face Centered Cubic (FCC) structure (WAXD analysis). An estimation of particle measurement by use of Scherrer's equation revealed a particle size of about 36.34 nm. The SEM photograph clearly indicates that the particles are sub-micron size, which is confirmed further by doing HRTEM study.

The HRTEM results have shown that the particles obtained in the argon are in spherical shape with FCC structure of the copper particle. The particle size lies in the range of a few nm to 100 nm. This transmission electron microscope study also give the additional evidence to the Wide Angle X-Ray Analysis Results, which confirms that the particles prepared through the wire explosion method is of crystalline structure copper nano-particle and the average size of the particle is 36.34 nm. The TG-DTA spectra confirm the particle formed by a wire explosion process is copper powder. The FTIR provides the fingerprint identification of nano-copper particle formation in the wire explosion process. The EDAX results showed that the major composition of the powder consists of copper and very less amount of oxygen present in the prepared sample.

NOMENCLATURE

d = Diameter of the particle
λ = wave length in mm
K = constant for Cu K_{α}
β = Full width half maximum in radians
Δ = Bragg angle

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