X-Ray Study of Nanosized Copper Powder Produced by Sonoelectrodeposition Process

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ABSTRACT

Electrodeposition process coupled with ultrasonic vibration (sonoelectrodeposition) was used to deposit nanosized copper powder from acidic solution of copper sulphate. Thecathodic current density and the amplitude of vibration used are 37.5 mA/cm^2 and 35% from the maximum capacity of vibration respectively. Purity, morphology and size of the nanosized powder were studied. The XRD studies also reported.The copper powderhas a high purity with mean size of particles about 52 nanometer. XRD analysis confirms that the crystals, sizes are in nanosized range.

Keywords: Electrodeposition, Ultrasonic, Particle size, Morphology, SEM, EDS, XRD.

1. INTRODUCTION

Nanostructured materials (including metals) get an increasing importance in various branches oftechniques and science owing to their unique mechanical, magnetic, optical, thermoelectric and other properties [1,2]. Much attention has been paid to metalnanoparticles which exhibit novel chemical and physicalproperties due to their extremely small dimensionsand high specific surface area.Nanoparticles have properties different than those from bulk materials due todrastic reduction of particle size [3,4]. Nowadays researches on synthesis of metal nanoparticles arelargely studied their special properties; many methods have been developed for the fabrication of metal nanoparticles [5].

Among various metal particles, copper nanoparticleshave attracted considerable attention because of itsunique catalytic, optical and electrical conductingproperties [6-9].Several methods have beendeveloped for the preparation of coppernanoparticles, including wet chemical reduction [10,11], microwavereduction [12], metal vapor synthesis [13], radiationmethods [14], chemical reduction in organic template [15],Wire Explosion [16], andelectrodeposition technique [17-19]. Electrodeposition coupled with ultrasonic vibration was also used to synthesize copper nanostructures [20,21]. It requires careful selection of effective processingparameters.

Sonoelectrochemistry is the coupling of ultrasonic vibration to an electrochemical system. The term ‘sonoelectrochemistry’ appeared at 1990 [22]. Recently there is a growing interest of the application of

the sonoelectrochemistry in the preparation of nanopowders [23,24]. Sonoelectrochemistry method is a simple environmental friendly and cost effectiveness method used to produce metallic nanosized materials compared to most of other methods including radiation, thermal decomposition, vapor deposition, reduction in microemulsions and chemical reduction [25].

2. EXPERIMENTAL PROCEDURES

In this study, a nanosized copper powder was electrodeposited from acidic copper sulphate solution in electrodeposition cell under the effect of ultrasonic vibration (20 kHz) as shown in f**igure 1**. The vibrator horn was immersed inside solution between copper plates of cathode and anode. The amplitude of vibration was 35% from the maximum capacity of vibration. The catholic current density was37.5 mA/cm^2.After deposition, the copper was collected and washed several times with deionized water to remove impurities and then washed several times with ethanol to remove the water of washing.

An estimation of the impurity level was performed by X-ray energy dispersive spectroscopy (EDS) system (Energy Dispersive Si(Li) X-ray detector) connected with the scanning electron microscope. SATW window was used for chemical analysis of microscopic volumes for all elements with atomic number of more than Z = 4 (Be), Oxford Instruments Analytical Ltd England. The sample for test was dispersed in ethanol and dropped on aluminum foil placed on aluminum stump.

The surface morphology of copper particles was investigatedby scanning electron microscopy. Max. magnification ~ 50.000x. Five axis motorized high geared stage in extra-large chamber as standard. Accelerating voltage range 200V to 30000V, Model: 1450 VP LEO (Variable pressure operation), Leo electron microscopy Ltd, England.

To estimate the size of the particles, the product which is already agglomerated and settled in bottom of storing cans should be re-dispersed using ultrasonic bath. Alcohol containing well dispersed powder was entered to laser diffraction device (VASCO-Nano particle size analyzer, Cordouan Technologies, France)to examine the size of copper particles.

Samples of copper nano-powder were analyzed using XRD analysis by an X-Ray diffractometer. XRD analysis was used to test the existing phases and parameters of unit cell, through peak indexing process. Size of the crystalline phase was also determined using XRD data. Data was taken for the 2θ range of 20 to 90 degrees with a step of 0.018 degree.

3. RESULTS AND DISCUSSION

The qualitative EDS analysis **figure 2** shows that the product is a pure copper element. The peak of carbon is related to residual ethanol. The peak of aluminum is related to aluminum foil and to the aluminum stump.This analysis confirms the product is a pure copper element. The morphology of the powder is shown in **figure 3**. The morphologies of nanosized copper powder are Treelike through irregular, angular, and rounded.The size distribution of the copper particles is shown in **figure 4** and the mean size of the tested sample is about 52 nanometer. **Figure** 5 shows the present three peaks (from left to right): $peak_1$, $peak_2$, and $peak_3$, assigned to 2θ values of 43.379°, 50.399, and 74.321° respectively, using Bragg's law (1).

$$n\lambda = 2d \sin\theta \qquad (1)$$

To find the d-spacing of each peak.

Peak$_1$: 2θ = 43.379°, θ = 21.6895°, d-spacing (d_1) = 0.2085 nm.

Peak$_2$: 2θ = 50.399°, θ = 25.1995°, d-spacing (d_2) = 0.1809 nm.

Peak$_3$: 2θ = 74.321°, θ = 37.1605°, d-spacing (d_3) = 0.1275 nm.

These calculated values of d-spacing were used to find the corresponding miller indices (hkl) of diffraction plane of each peak (**table 1**). The dividing constant is equal to the difference between first two ($\frac{10}{d^2}$), and the results of ($\frac{\frac{10}{d^2}}{75.55}$) column need to be integer values.

These peaks and their corresponding plane are shown in **table 2** and they are almost identical in comparison to the standard diffraction peaks of copper (JCPDS, file No. 04-0836).

The calculated inter planar spacing d-spacing values were used to prove the element is copper, but anyway these values are not fully-identical to (JCPDS, file No. 04-0836) which is also not fully identical to ideal values of d-spacing. Ideal values can be calculated using formula (2).

$$\frac{1}{d^2}=\frac{h^2+k^2+l^2}{a^2} \qquad (2)$$

where *a* for copper = 0.3615 nm,

and using d-spacing value in Bragg's law (1) to calculate the ideal values of diffraction angles 2θ. **Table 3** lists the experimental and ideal values of inter planar spacing and diffraction angle 2θ of (111, 200 and 220) diffraction planes.

Average crystal size (D) of the tested particles can be estimated using Debye-Scherrer formula:

$$D = \frac{0.9\,\lambda}{\beta\, cos\theta} \qquad (3)$$

where:

λ: X-Ray wave length = 0.1541 nm.

β: full width at half maximum (FWHM) of the diffraction peak.

θ: diffraction angle of the peak.

For (111) plane, diffraction angle of the peak$_1$,θ = 21.6895° and β= 0.284° = $\frac{0.284*\pi}{180}$ = 0.00496 radians

Therefore,

$D = \frac{0.9 * 0.1541}{0.00496 * cos21.6895}$ = 30.1 nm

According to XRD results (**figure 5**), three peaks at 2θ values of 43.379°, 50.399°, and 74.321° respectively corresponding to (111), (200) and (220)planes of copper have been observed and

compared with the JCPDS, copper file No. 04–0836. The produced nanoparticles are a single phase of a pure copper element with FCC crystal structure. The crystal size was measured using the Debye-Scherrer formula for X-Ray crystal size determination and it was found to be 30 nanometer. This gives conformation that the sizes of particles are in nanosized range.

4. CONCLUSIONS

1- Electrodeposition process under the effect of ultrasonic vibration (sonoelectrodeposition) was successfully used to produce nanosized copper powder.

2- The purity of copper is approved.

3- The morphology of the powder is treelike through irregular, angular, barlike, and rounded.

4- The existing phase was FCC crystalline copper and the crystal size through nano range.\

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Table (1): peak indexing of tested sample.

Peak No.	2θ (degrees)	d-spacing (nm)	$\frac{10}{d^2}$	$\frac{\frac{10}{d^2}}{75.55}$	Remarks $h^2+k^2+l^2$	plane of diffraction
1	43.379	0.2085	230.03	3.05	$1^2+1^2+1^2=3$	111
2	50.399	0.1809	305.58	4.05	$2^2+0+0=4$	200
3	74.321	0.1275	615.15	8.14	$2^2+2^2+0=8$	220

Table (2): diffraction angles of tested sample and standard diffraction angles of copper.

Peak No.	Diffraction plane	Experimental diffraction angle 2θ (degrees)	Standard diffraction angle 2θ (degrees) of copper JCPDS, file No. 04-0836
1	111	43.379	43.297
2	200	50.399	50.433
3	220	74.321	74.130

Table (3): the experimental and ideal values of inter planar spacing and diffraction angle.

Diffraction plane	Ideal d-spacing, nm	Experimental d-spacing, nm	Ideal diffraction angle 2θ, degree	Experimental diffraction angle 2θ, degree
111	0.2087	0.2085	43.3314	43.379
200	.01808	0.1809	50.4484	50.399
220	0.1278	0.1275	74.1551	74.321

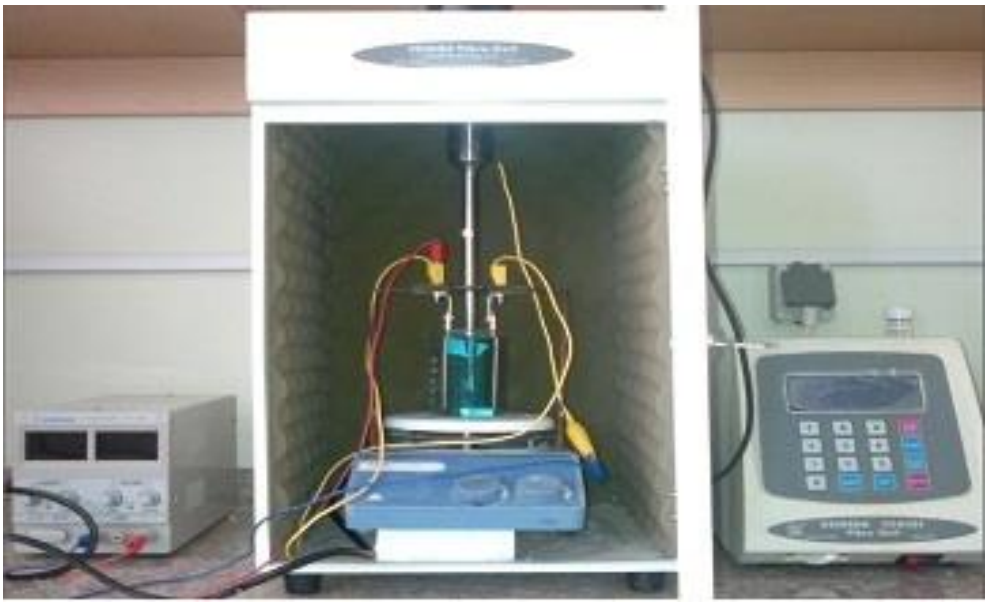

Figure (1): the electrodeposition cell setup.

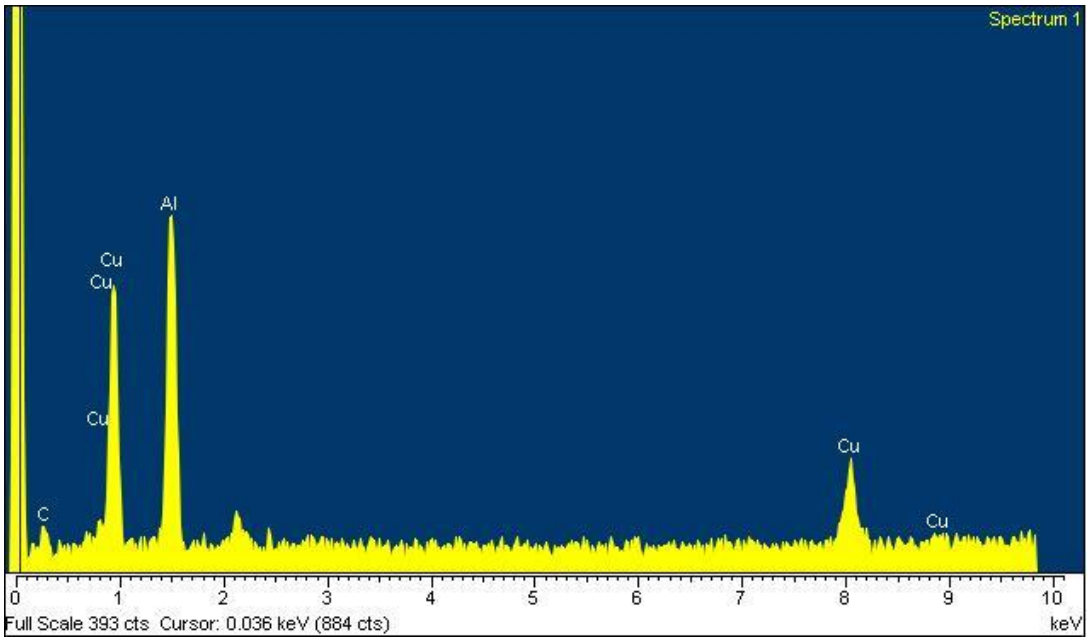

Figure (2): EDS analysis of nanosized copper powder.

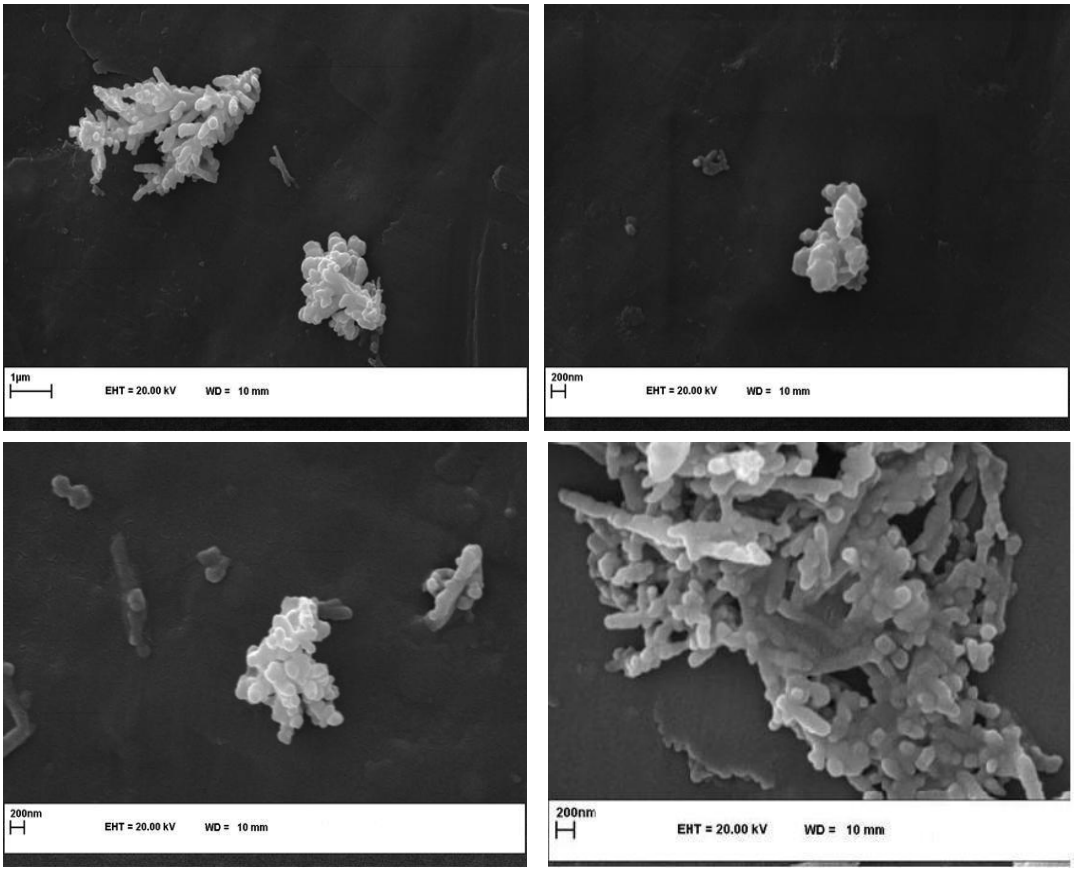

Figure (3): the morphology of the nanosized copper powder.

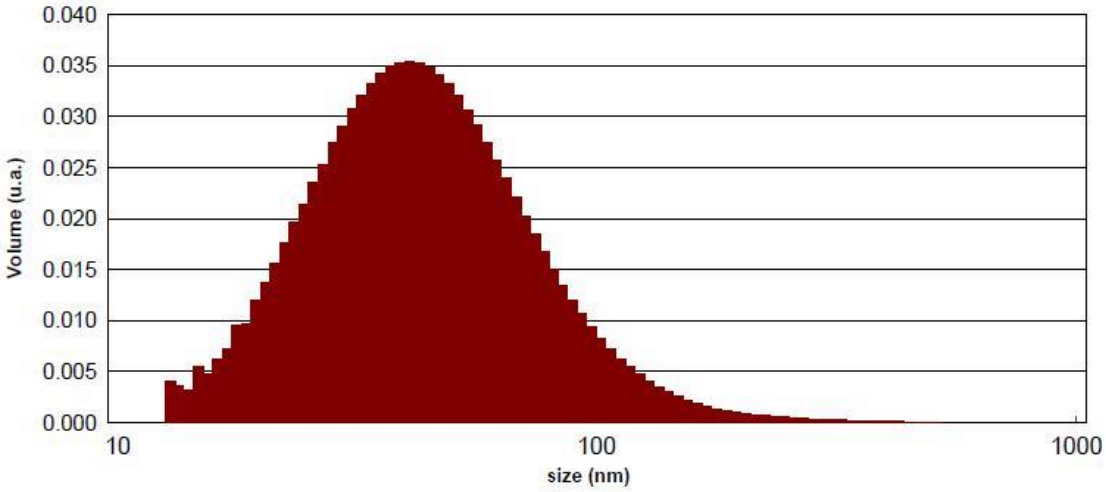

Figure (4): size distribution of nanosized copper powder.

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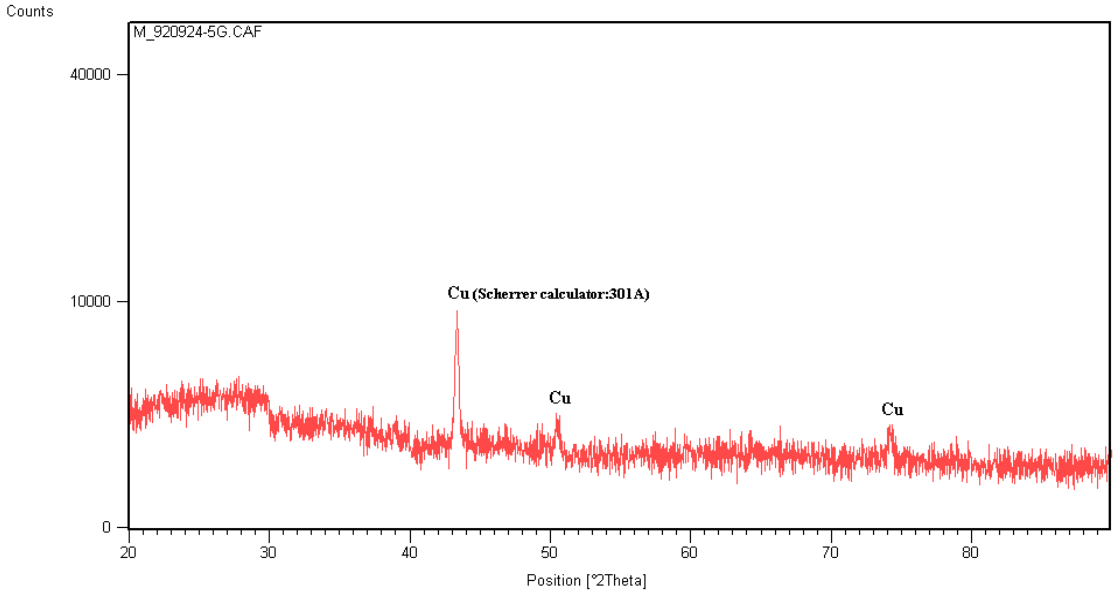

Figure (5): XRD of the sample.