Synthesis of Cu-CuO and Cu-Cu$_2$O Nanoparticles via Electro-Explosion of Wire Method

Reza Ahmadi$^{1,*}$, Ahmad Razzaghian$^{1}$, Zahra Eivazi$^{2}$ and Kobra Shahidi$^{1}$

$^{1}$Department of Metallurgy and Materials Engineering, Faculty of Engineering, Imam Khomeini International University (IKIU), P.O.Box 34148-96818, Qazvin, Iran.
$^{2}$Department of Materials Nano Materials, Faculty of Engineering, Tarbiat Modarres University, P.O.Box 14115-111, Tehran, Iran.

(*) Corresponding author: re.ahmadi@ENG.ikiu.ac.ir
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Abstract

We report an investigation on the synthesis of Copper Oxide nanostructures via the Electro-Explosion of Wire method. Cu-CuO and Cu-Cu$_2$O nanoparticles with mean particle size of 21.1 to 59.1 nm were synthesized by changing the applied current density and amount of used Tetra Methyl Ammonium Hydroxide as the surfactant. The X-ray diffraction analysis, field emission scanning electron microscopy and Fourier transform infrared spectroscopy techniques have been used for characterization of the prepared samples. The results confirmed the influence of surfactant application on the size, morphology and chemical composition of the synthesized nanoparticles, while the applied current density has only had a significant effect on the mean particle size.

Keywords: Electro-explosion of wire, Copper oxide, Nanoparticle, Tetra methyl ammonium hydroxide, Field emission microscopy.

1. INTRODUCTION

The synthesis, properties and application of Nanostructured materials have been studied vastly in recent years [1-5]. The unique mechanical, electric, magnetic, chemical and biological properties of these structures are mainly due to their large surface to volume ratio. These unique properties lead to different applications comparing to the traditional materials. Besides, various synthesis methods are employed for each application.

Among different techniques for synthesis of nanostructured materials such as coprecipitation [6-8], sol-gel [9-11], hydrothermal [12, 13], thermal decomposition [14] and Electro-Explosion of Wire (EEW), the latter is one of the most promising methods especially for synthesizing nanometric powders from metallic precursors. In this approach, very thin wires of ductile and conductive metals are exploded under electric discharge conditions originated from high power DC supplies. The high temperature of the electric arc vaporizes the wire into gas atoms [15-19]. Due to cooling effect of the surrounding media, the individual atoms form the initial nuclei through a desublimation process. Finally, the small nanoparticles are synthesized due to the nuclei accumulation. Recently, various metallic and ceramic nanoparticles have been produced via this technique including Cu, Ag, Au, WC, ZrO$_2$, Fe$_3$O$_4$, ZnO and Al$_2$O$_3$ nanoparticles [15, 16, 20]. Also, ZnS and CdS nanoparticles have been synthesized via explosion of pure Zinc and Cadmium wires in Na$_2$S medium, respectively [21-23].The size and morphology of the synthesized particles are strongly affected by experimental conditions such as input power, current density, medium temperature and wire diameter.
The effect of medium temperature on the mechanism of particles formation and also size and morphology of Copper Oxide nanoparticles has been studied recently. According to the published results, the mechanism of nucleation and growth of Cu-CuO particles changes from Ostwald Ripening (OR) to Oriented Attachment (OA) by increasing temperature and the mean particle size is maximum at low temperature regime of OR growth [15].

Cu and Cu-CuO nanoparticles have various electronic and optoelectronic applications due to their desired electronic properties. Some of these applications include field emission uses, electrode for Li ion batteries, solar cells and field effect transistors [15, 24]. Also, their implementation in antimicrobial applications [25], chemical sensors [26] and magnetic storage media [27] have been considered recently. The size, morphology and chemical composition of the Cu-CuO nanoparticles strongly affect their performance in the mentioned applications. Copper and Copper Oxide nanoparticles have been synthesized via EEW technique frequently. In one study, Cu/CuO/Cu$_2$O nanoparticles have been prepared by explosion of Copper wire in DI water and characterized via HRTEM, XRD, XPS, FT-IR, VSM and Raman Spectroscopy techniques. The XRD results showed only the presence of Cu and Cu$_2$O phases and the amount of the metallic phase was about twice of the others, but HRTEM, XPS, FT-IR and Raman Spectroscopy results verified the presence of trace amounts of CuO phase too [28]. The results of some other studies have revealed the presence of the Cu$_2$O phase in the structure of the nanoparticles synthesized via EEW method [29, 30]. Cu$_2$O might be oxidized to CuO due to the explosion conditions, but the very short time of the phenomenon can prevent the oxidation reaction and so the Cu$_2$O phase will be the stable phase in the final product [29]. In the present study, Cu-CuO nanoparticles have been synthesized via EEW method in various experimental conditions including different applied current densities and surfactant amounts. The synthesized nanoparticles, have been studied using Field Emission Scanning Electron Microscopy (FESEM), X-ray Diffraction (XRD) and Fourier Transform Infrared (FT-IR) techniques. The results show that the size, morphology and chemical composition of particles are affected by the surfactant to particles ratio, but the amount of current density only affects the mean size of the particles. The results revealed that Cu-CuO and Cu-Cu$_2$O nanoparticles with mean particle size between 21 and 59 nanometer have been produced via the EEW method.

2. MATERIALS AND METHODS
2.1. Sample Preparation
The experimental conditions for the synthesis of samples A1 to A7 are presented in table 1. All samples were synthesized via EEW method in various current densities between 3 and 16 kA/mm$^2$. Samples A1 to A4 were synthesized via explosion of 0.2 mm copper wires in DI water without surfactant and samples A5 to A7 were synthesized in the presence of various amounts of Tetra Methyl Ammonium Hydroxide (TMAH) as surfactant. The synthesized samples were prepared as suspension and solid specimens for FESEM, XRD and FT-IR characterizations.

2.2. Characterization Methods
A Siemens D5000X-ray diffractometer was employed for XRD analysis using Cu-Ka radiation. The IR spectra were recorded in the range of 400-4000 cm$^{-1}$ on a Nicolet Magna500 spectrometer. Samples were dried at 70 °C before fabrication of KBr pellet. A JEOLSEM JSM-7401F was employed on an accelerating voltage of 30kV for determination of morphology and particle size of the samples. The SEM samples were prepared as follows: One trickle of the suspension containing particles was put on a 1×1 cm$^2$ glass sheet. After the trickle drying, the glass sheet was studied as the SEM sample.
3. RESULTS AND DISCUSSION

FESEM images of samples A1-A4 are presented in Figure 1a-d, respectively. As seen from the size distribution diagrams, the mean particle size decreases from 59.1 to 32 nanometers by increasing the current density from 3 to 16 kA/mm². This is due to the fact that in high induced electric energies, small number of atoms form the initial embryo and reduces the final particle size. In other words, by increasing input electric power, the explosion temperature raises, so the cooling rate of initial Cu atoms increases and each Cu or CuO particle contains only a few number of Cu or O atoms. On the other hand, in the low levels of the applied energies and achieved temperatures, the total explosion and evaporation process could be prolonged and so the particle can grow to larger sizes. This result is in good coincidence with other reports [17, 31-33].

Figures 2a-c present the FESEM images of samples A5-A7, respectively. These samples were synthesized in the presence of TMAH. With increasing the molarity of the TMAH as surfactant, particle size decreases. TMAH molecules surrounded the initial embryos prevent from the fast growth of the particles.

The mean aspect ratios of the synthesized samples are listed in Table 1. This parameter is calculated by considering at least 50 particles for each sample. It seems that by increasing the amount of surfactant, the preferred growth planes are covered with TMAH molecules, so there is no significant difference between the growth rates of various crystallographic plans. In these conditions, spherical growth of particles is the dominate phenomenon and the mean aspect ratio decreases with the increasing of the surfactant amount. XRD patterns of samples A4 and A7 which synthesized with and without TMAH are shown in Figure 3.
It can be seen from marked peaks that Cu, CuO and Cu₂O phases formed. Using Rietveld method, the amount of Oxide phase in sample A7 is about twofold of sample A4 (66% respect to 32%). This is due to the fact that TMAH N(CH₃)₄OH decomposes in high temperature of wire explosion and copper oxide compounds form due to the formation of the free O atoms. This phenomenon is in contrast with the usual effect of surfactants in other synthesis methods in which the surfactant protects the surface from oxidation. Besides, the dominate Copper Oxide phases in A4 and A7 are Cu₂O and CuO, respectively. The O:Cu ratio in sample A7 is more than sample A4 due to the extra Oxygen from the decomposition of TMAH in A7.

As seen in Figure 3, the XRD peaks are sharper in the sample A4 comparing to the sample A7 and the mean crystallite sizes are 31.1 and 20.5 nm for samples A4 and A7, respectively. These results are in good agreement with the FESEM findings (Figures 2 and 3). The recent values have been calculated using Scherrer formula, the useful equation for calculating crystallite size that has been described elsewhere [34].

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The FT-IR spectra of samples A4 and A7 are shown in Figure 4. The characteristic bands of sample A7 appearing at 448.51 cm⁻¹, 1517 cm⁻¹, and 603.1 cm⁻¹ can be attributed to the Au and Bu modes of CuO along the [101] direction [35, 36]. The peaks observed at 998 cm⁻¹ and 1489.58 cm⁻¹ are
related to the asymmetric stretching vibration mode of the C-N band and the asymmetric methyl deformation mode from TMAH, respectively [37]. The broad peak at 3397.98 cm\(^{-1}\) is assigned to O-H band and the sharp peak at 1628.04 cm\(^{-1}\) is related to the absorbed water [38]. The peak at 2924.86 cm\(^{-1}\) is probably due to the ethanol contamination during to the FT-IR sample preparation [39]. The peak at 953.52 cm\(^{-1}\) could be assigned to the Cu-O-H bending mode. The peak at 2133.8 cm\(^{-1}\) probably is due to the NO\(_2^+\) species from the decomposition of N(CH\(_3\))\(_4\)OH [40].

The distinguishing peak seen at the FT-IR pattern of sample A4 is located at 618.48 cm\(^{-1}\) and is related to the C-O band of Cu\(_2\)O [41]. No peak from Cu-O band at CuO is seen in this spectrum. This is in good agreement with the XRD results and verifies the presence of CuO and Cu\(_2\)O phases in the samples A7 and A4, respectively. The peak at 1630.16 cm\(^{-1}\) is related to the absorbed water, similar to the sample A7.

**Figure 4.** FT-IR spectra of samples A4 and A7.

**4. CONCLUSION**

Cu-CuO and Cu-Cu\(_2\)O nanoparticles have been synthesized via EEW method with the mean particle size between 21.1 and 59.1 nm and aspect ratio between 1.03 and 1.35. The Oxygen content of the products was increased by increasing of TMAH due to the surfactant decomposition. XRD and FT-IR results verified the formation of Cu\(_2\)O and CuO phases with and without TMAH, respectively. According to the SEM findings, the particle size was decreased with increasing the amount of applied current density and TMAH (as the surfactant). The mean aspect ratio of particles was decreased with increasing TMAH which probably due to its effect on the growth of different crystallographic planes.

**REFERENCES**


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