EFFECT OF THE WIRE THICKNESS ON THE MORPHOLOGY AND ANTIBACTERIAL PROPERTIES OF THE Cu-CuO AND CuO-SnO_2 NANOPARTICLES SYNTHESIZED VIA ELECTRICAL DISCHARGE METHOD

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In the present study, Copper Oxide and Copper-Tin Oxide nanoparticles have been synthesized via electrical discharge method in aqueous medium using thin wires as electrodes. By changing the experimental conditions, especially the wire thickness, various samples have been produced and prepared for characterization. The SEM results revealed that particles with mean particle size between 24 and 40 nm have been synthesized in different experimental conditions. The XRD data verify the presence of Copper, Copper Oxide and Tin Oxide phases in the synthesized particles. Also, the percentage of metallic phase have been changed between 46% and 80% and the fraction was increased with wire thickness. Finally, the results show that the antibacterial effect of the Copper-Tin Oxide particles have been increased with the decrement in mean particle size.

Keywords: Antibacterial effect, electrical discharge method, Copper Oxide, Tin Oxide

1. Introduction

Nowadays, nanostructures have been widely used in numerous medical and industrial applications due to their unique properties [1-5]. One important group of these applications is related to the antibacterial effects of metallic and metal Oxide nanoparticles. These nanoparticles kill bacteria through various mechanisms such as protein dysfunction, Reactive Oxygen Species (ROS), impair membrane function, genotoxicity mechanisms and interference with nutrient uptake [6-11]. The high specific surface area of these nanoparticles intensify the antibacterial effect due to the high bacteria-nanoparticle surface contact [6].
Antibacterial properties of Copper and Tin nanoparticles have been investigated in previous studies, also the antibacterial and anticancer effects of their oxides have

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been studied before [7-9]. The main proposed mechanism for the antibacterial effect of Cu and CuO nanoparticles is ROS in which the oxidative stress and interferation with the bacteria biofilm formation might damage and kill the bacteria [8].

Among numerous routes for nanostructures synthesis such as coprecipitation [12-14], ball milling [15], hydrothermal [16, 17], sol-gel [18], thermal decomposition [19] and electric discharge method, the later is recently used for synthesizing various metallic and non metallic nanoparticles. In this method, thin anodic wires are exploded in contact with a cathodic plate using a high power DC supply. The wire explosively vaporizes into gas atoms due to the high temperature of the electric arc generated from the power supply [20-22]. The gas atoms form initial solid embryos due to the rapid cooling process caused by the surrounding liquid or gas medium. Finally, the nuclei accumulation and growth leads to formation of the nanoparticles under controlled experimental conditions. Recently, various metallic and non metallic nanometric particles have been synthesized in different liquid media using the electric discharge method such as Pt, NiO, Ag, Cu, CuO, Au, WC, ZrO_2, ZnO and Al_2O_3 nanoparticles [20, 22, 23, 24]. The experimental conditions such as wire diameter, input power, current density and medium temperature and composition severely affect the size and morphology of the produced nanoparticles.

In the present work, Copper Oxide and Copper-Tin Oxide nanoparticles have been synthesized via electric discharge method through different experimental conditions. The effect of the experimental conditions have been investigated on the particles mean size and metallic phase percentage. The total contact area between bacteria and particles extremely increases with the particles size decrease. So, the antibacterial effect of nanoparticles strongly increases with the mean particle size decrease. The major aim of the present work was focused on investigating this effect and the antibacterial effect of the synthesized nanoparticles have been evaluated against E. Coli bacteria.

2. Experimental

2.1. Materials and methods

The initial materials for preparation of Cu-CuO and Cu-Sn Oxide nanoparticles were high purity copper wire (Copper concentration more that 99.9% in weight fraction) in five different diameters and high purity Tin. The Cu-CuO nanoparticles were synthesized using a DC power supply worked at 500, 250 and 100 A and 50 V and high purity copper wires as two electrodes. The electrodes were joined into the positive and negative poles of the power supply and the explosion, evaporation and further consolidation of the of the wire atoms due to their contact under high electric energy led to formation of the particles

(Fig. 1). The Cu-Sn Oxide nanoparticles were synthesized via similar approach, except that before the evaporation, a thin Tin layer was applied to the copper wires surface by dipping the wires in molten Tin. The obtained powders were collected, dried and prepared for characterization and bacterial tests.

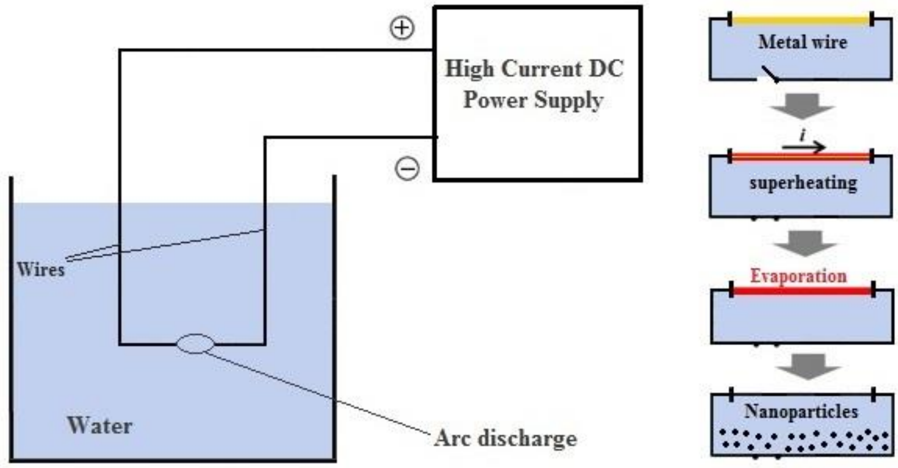


Fig. 1. The schematic image revealing the used electric discharge system.

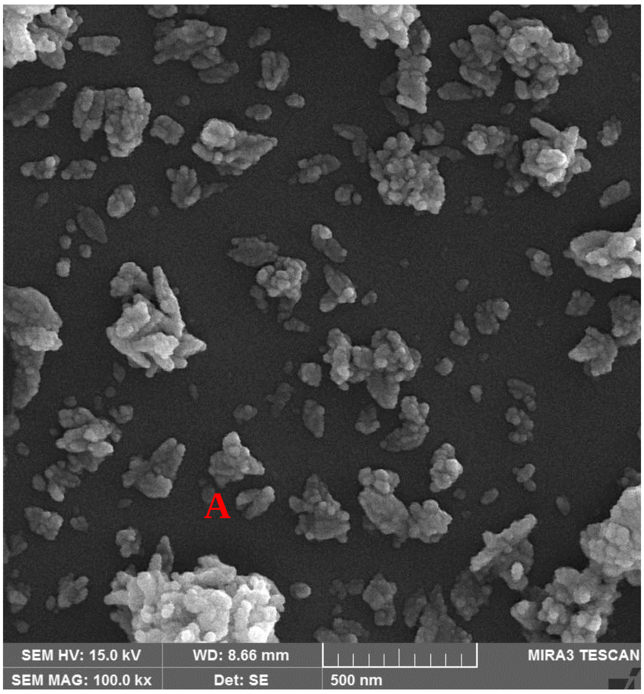
2.2. Characterization Methods

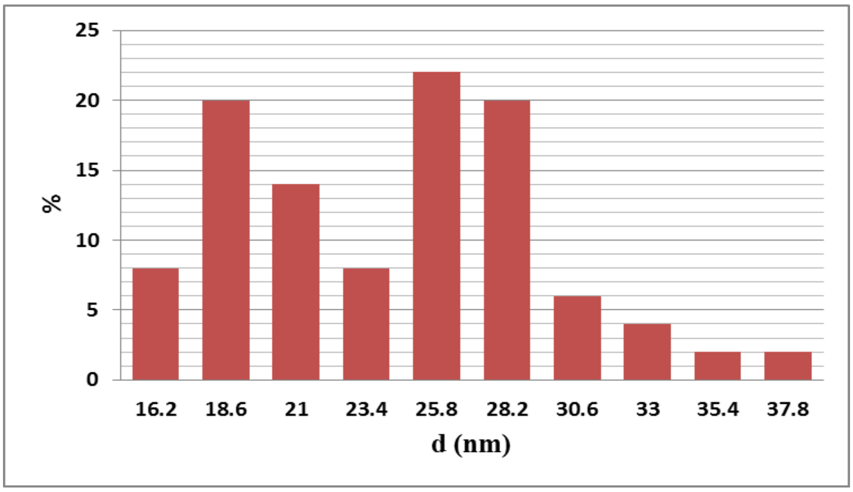
A JEOL SEM JSM-7401F was used on an accelerating voltage of 15kV for investigation of the size and morphology of the Copper Oxide particles. SEM imaging of the Cu-Sn Oxide samples was done using a Philips XL 30 instrument. The preparation of the SEM samples was performed accordingly: One trickle of the suspension containing particles was put on a small glass sheet. After the trickle drying, the glass was used and studied as the SEM specimen. A Siemens D5000X-ray diffractometer was employed for XRD analysis using Cu-Ka radiation.

Antibacterial effect of the nanoparticles was evaluated by investigating the optical density (OD) at 600 nm via Spectro UV- VIS (model UVD-3200) instrument. This method has been frequently used for evaluation of the bacterial growth by others [25-28]. Firstly, approximately 10^6*CFU* (OD600) of Escherichia coli (E. coli) bacteria were grown into 50*ml* of *Luria* Bertani (LB). Then, the nanoparticles were added separately into the bacteria medium with different dosages between 0 and 1000 ppm. The obtained cultures were put into a 37°C incubator for 8h and the OD was measured every 2h. Triplicates were performed for each time and particles concentration. The mean absorbent values of the three tests were reported. The results were compared with the control samples without nanoparticles. The lower OD means the lower alive bacteria and more antibacterial effect.

3. Results and Discussion

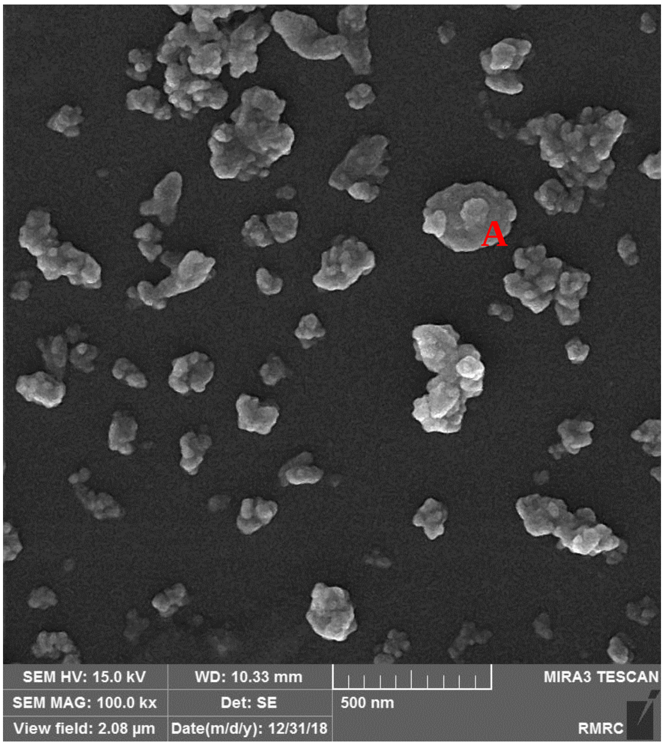
The SEM images and size histograms of samples A1, A2, A3 and A4 are presented in Figs. 2-a to 2-d.

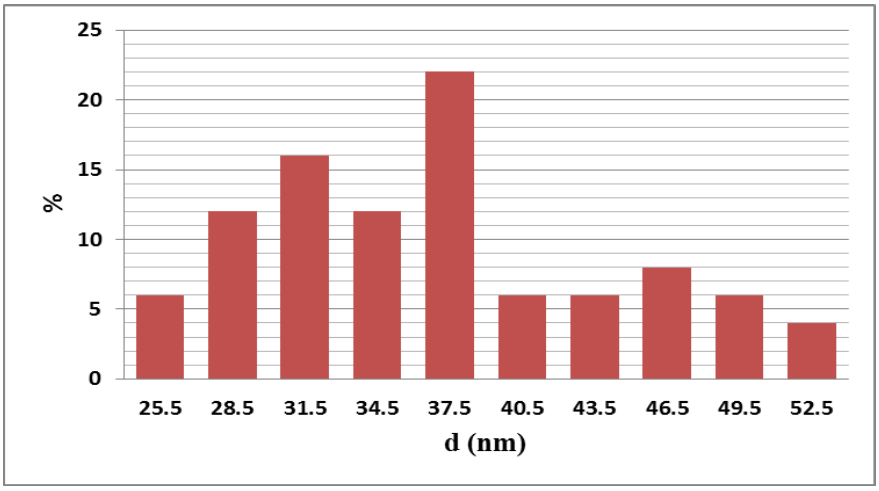




a)

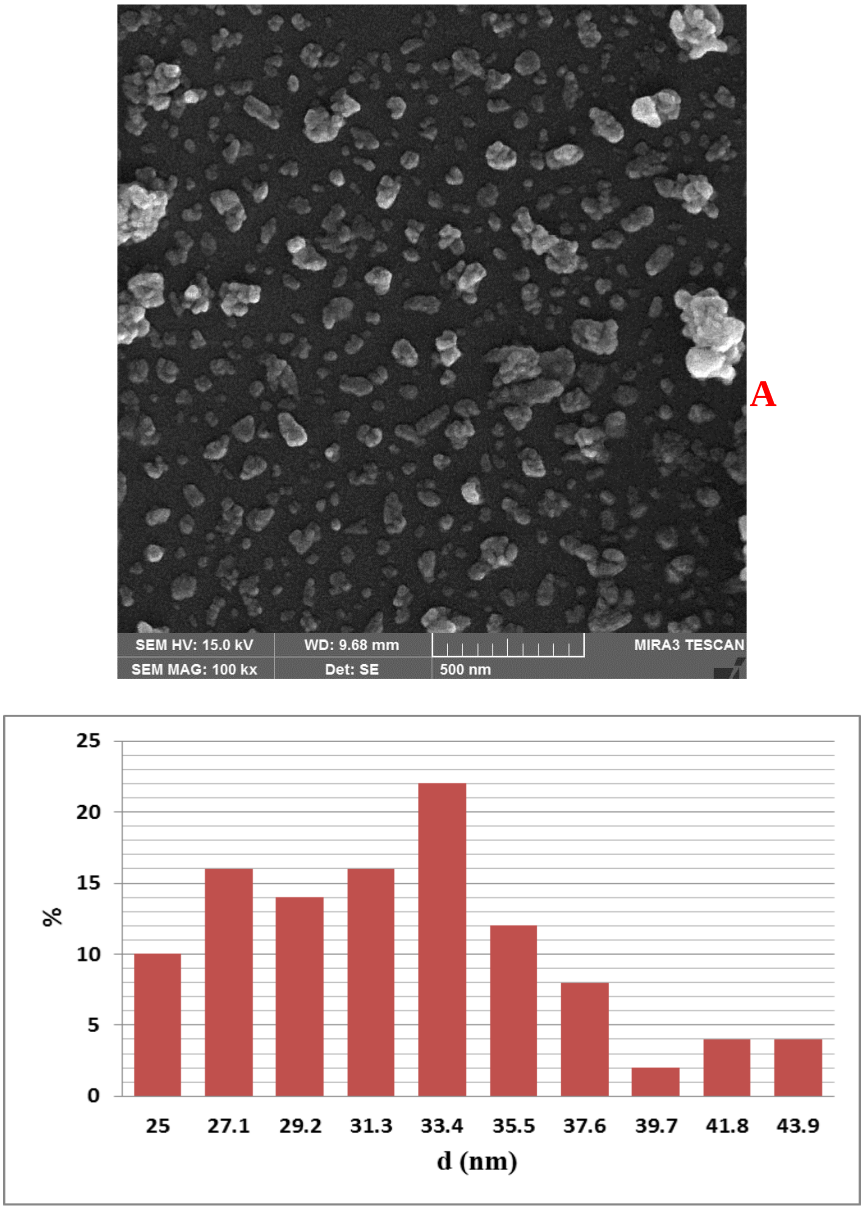
Fig. 2. SEM image and size histogram of sample: a) A1





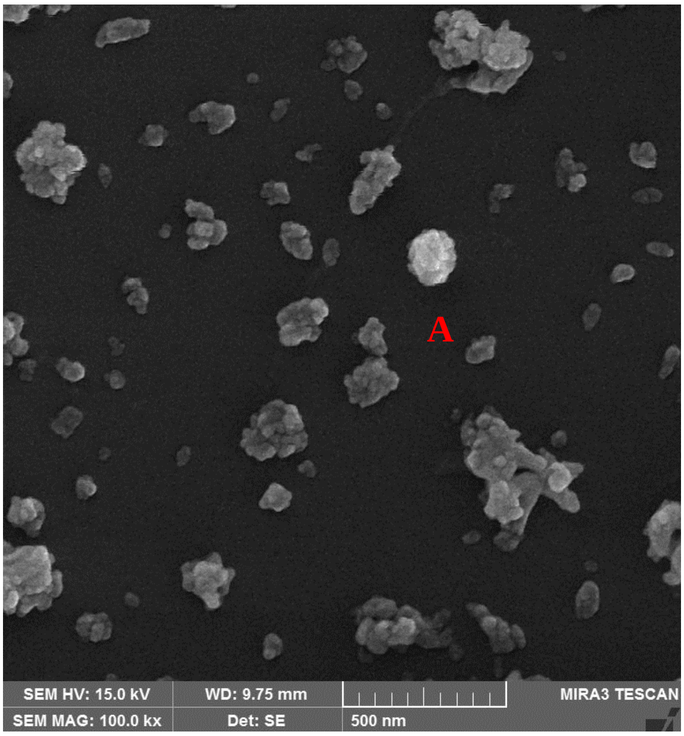
b)

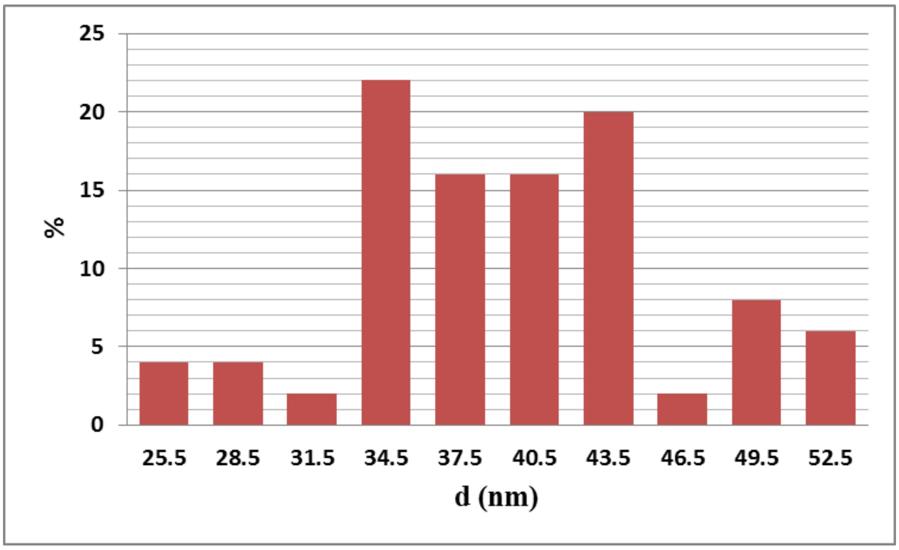
Fig. 2. SEM image and size histogram of sample: b) A2



c)

Fig. 2. SEM image and size histogram of sample: c) A3





d)

Fig. 2. SEM image and size histogram of sample: d) A4

The mean particle size of the prepared particles is varied from 24.5 to 39.7 nm by the wire thickness increase from 0.2 to 0.5 mm (table 1). The histograms and mean particle sizes have been obtained by considering at least 50 particles for

each sample. In the region of agglomerates, the individual particles have been considered (marked by red A). All of these samples were prepared in the current intensity of 500 A. The particles enlargement with the wire thickness increase is in good agreement with other reports [21-24]. The particles are spherical in shape due to the non preferred nature of the nucleation and growth in the synthesis approach. The initial gas atoms formed from the explosion are cooled rapidly by the surrounding liquid medium and form the initial embryos, then these initial embryos grow, join each other and lead to the formation of final particles. So no preferred growth direction exist and the particles will crystallize in the spherical and semi spherical shapes.
The XRD patterns of samples A1, A2, A3 and A4 are shown in Fig. 3.

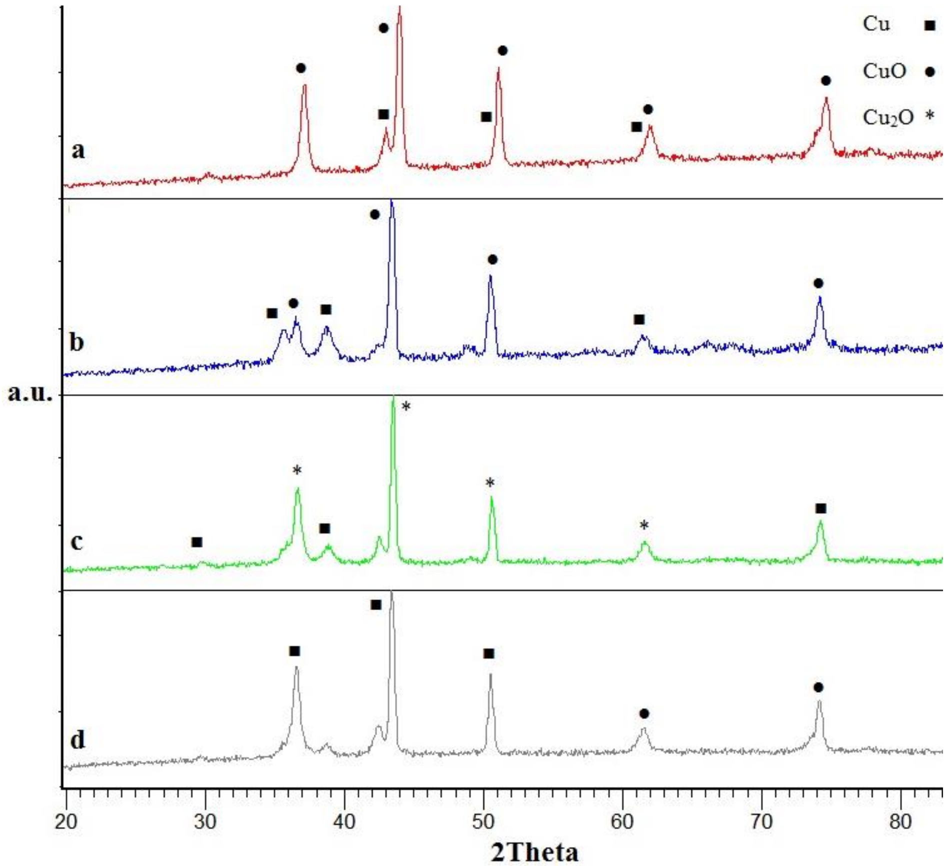


Fig. 3. XRD patterns of samples a) A1, b) A2, c) A3 and d) A4.

As seen in these patterns, the Cu, CuO and Cu_2O peaks are distinguished and verify the presence of the related phases in the synthesized powders. The weight percentage of the phases are estimated via rietveld method and reported too. The weight fraction of the metallic phase increases with wire thickness (table 1 and Fig. 4).

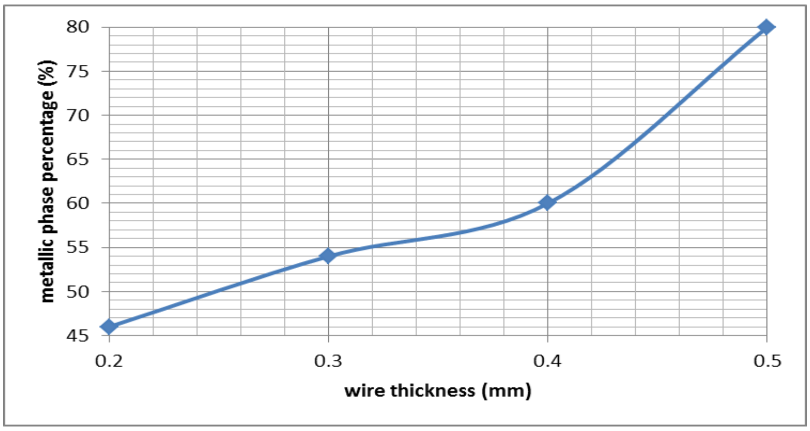


Fig. 4. The plot revealing the metallic phase percentage with the copper wire thickness.

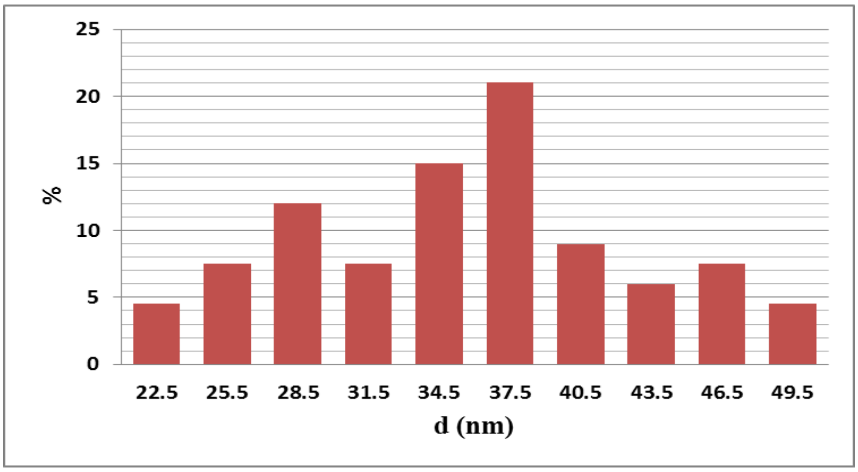
Table 1.

The experimental conditions for synthesizing A1 to A4

Sample	Wire Composition	Wire Thickness (mm)	Input current intensity (A)	Particles mean size (nm)	Fraction of the metallic phase
A1	Cu	0.2	500	24.5	46%
A2	Cu	0.3	500	28.8	54%
A3	Cu	0.4	500	32.2	60%
A4	Cu	0.5	500	39.7	80%

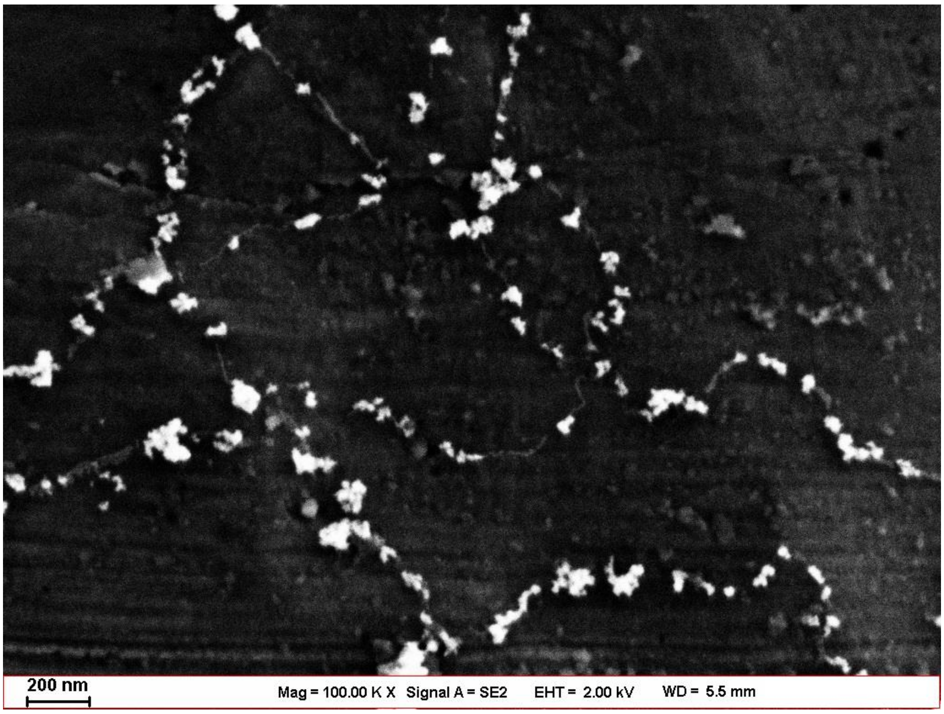
This regime can be explained by the fact that the ratio of the surface atoms to the whole atoms will decrease with the wire thickening. So, the fraction of the CuO and Cu_2O phases will decrease due to the lack of the available environmental Oxygen generated from the evaporation of aqueous medium. To the best of our knowledge, the effect of the wire thickness on the weight percentage of the Oxide phase has not been investigated in the electric discharge method before.

The SEM images and size histograms of samples A5, A6 and A7 synthesized in three different amperages are shown in Fig. 5. The mean particle size of the formed particles decreases with the current intensity increase (table 2). By the input electric energy increase, the final gas atoms temperature will rise and the cooling rate will increase too, so the atoms will form the smaller initial embryos and particles. Other researchers report a similar variation of particle size with the input electric energy [20]. The XRD plots of the samples A5, A6 and A7 are shown in Fig. 6 and verify the formation of Cu, CuO, Cu_2O and SnO_2 phases.



a)

Fig. 5. SEM image and size histogram of sample a) A5



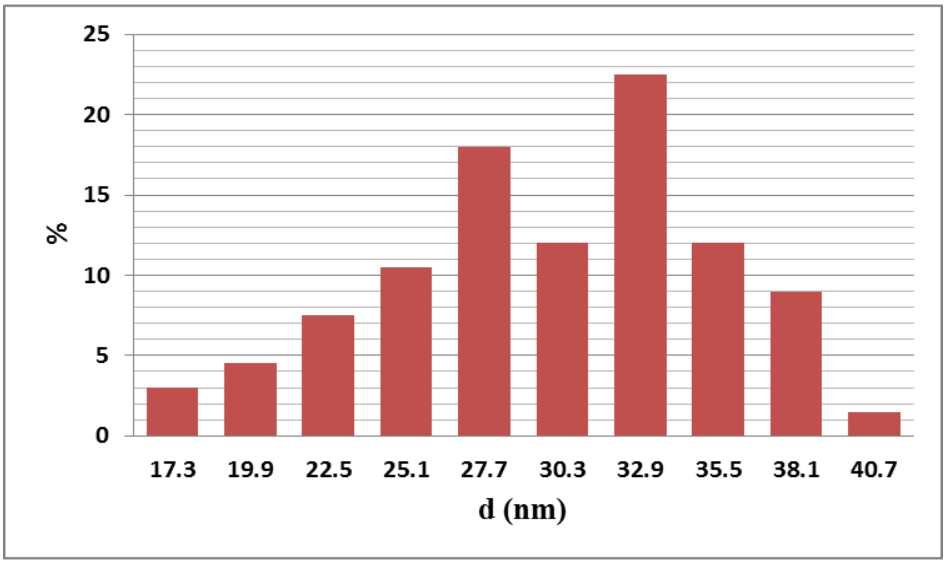


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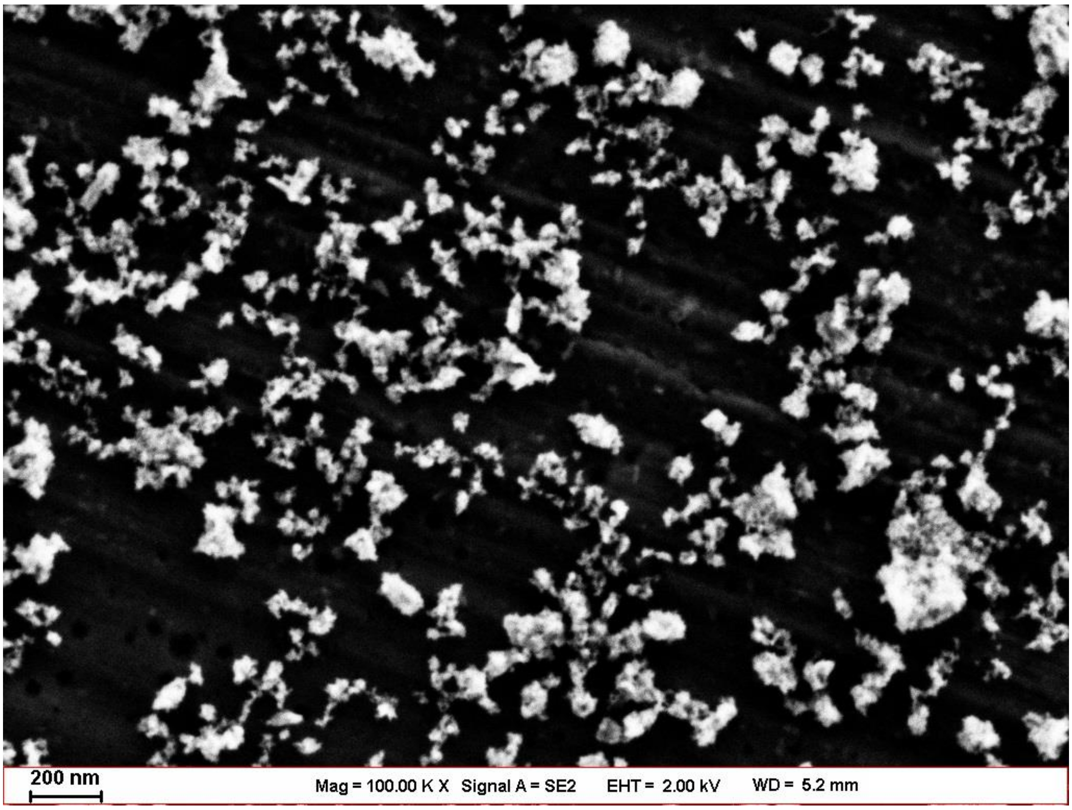
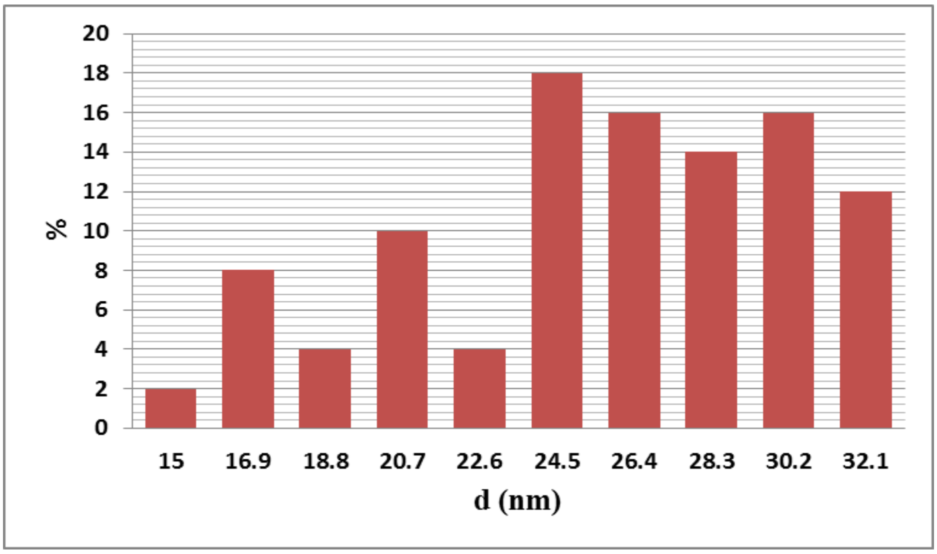
Fig. 5. SEM image and size histogram of sample b) A6





c)

Fig. 5. SEM image and size histogram of sample: c) A7

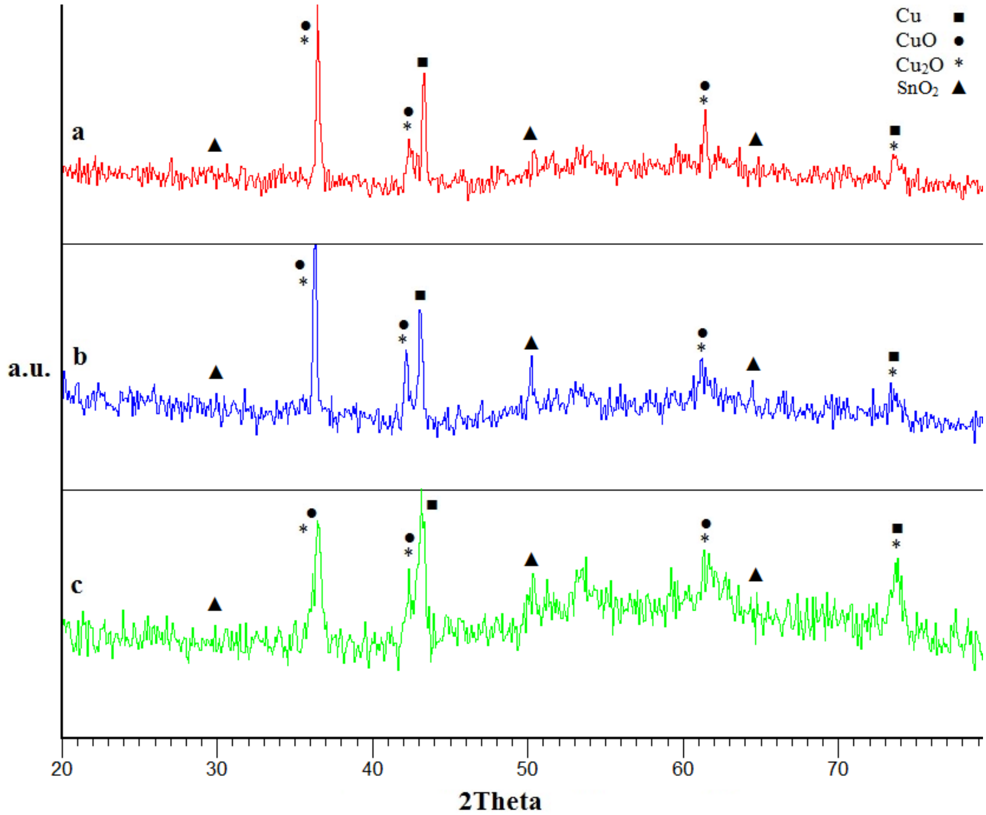


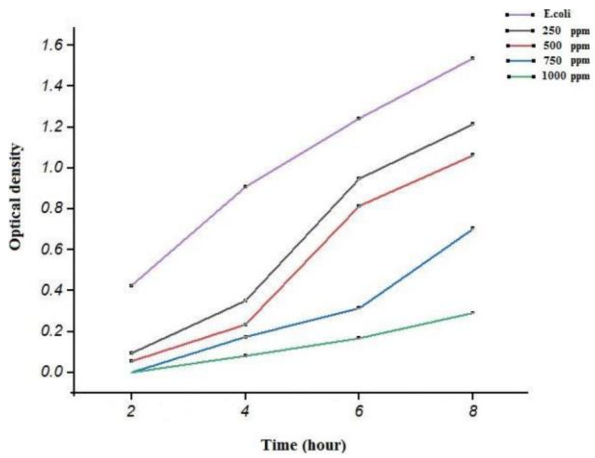
Fig. 6. XRD patterns of samples a) A5, b) A6 and c) A7.

Table 2.

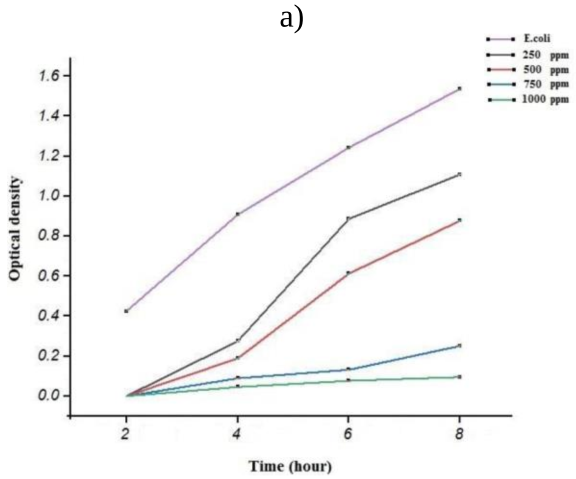
The experimental conditions for synthesizing A5, A6 and A7.

Sample	Wire Composition	Wire Thickness (mm)	Input current intensity (A)	Particles mean size (nm)
A5	Cu-Sn	0.22	100	35.7
A6	Cu-Sn	0.22	250	30.2
A7	Cu-Sn	0.22	500	25.6

The antibacterial activity of the Cu-Sn Oxide particles was evaluated via optical density method against the E. Coli bacteria and the results are presented in Figs. 7. As seen in Fig. 7, the antibacterial effect of the nanoparticles increases with the particles size decrement and concentration increment and this is in very good agreement with other numerous researches [8, 29-32]. This is due to the fact that the specific surface of particles increases with the particle size decrease, so the total contact area between particles and bacteria will increase too. As the ROS is known as the main mechanism of killing bacteria by the Oxide nanoparticles, the anti bacterial effect increases with the decrease in the mean particle size.



a)



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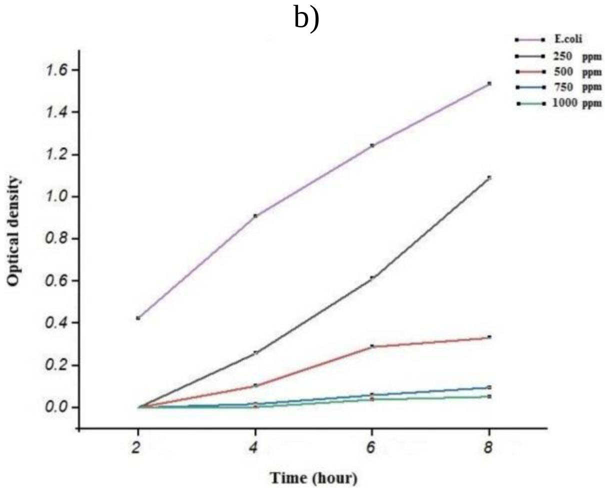

c)

Fig. 7- The OD diagrams of sample a) A5, b) A6 and c) A7 against the E. Coli bacteria revealing the samples antibacterial effect.

When the particles concentration is more than 500 ppm, the OD is negligible in the case of A6 and A7 samples and the bacteria growth is limited to very small amounts even in long incubation times.

3. Conclusion

In this work, the electrical discharge method have been effectively used for synthesizing nanometric Cu-CuO-Cu_2O and Cu-CuO-Cu_2O-SnO_2 particles. The fraction of the metallic phase as well as the mean particle size increases with the diameter of the used wires. The Cu-Sn Oxide nanoparticles reveal excellent antibacterial effect and this effect was more sever in the case of smaller particles with higher concentrations.

Acknowledgment

The authors would like to express their gratitude to Iran National Science Foundation (INSF) for supporting this research under grant number 96010336.

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