

Study of CuZnO-Carbon nanoparticles synthesized using arc-Discharge immersed in distilled water, a simple method

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Abstract

In this work, we present results on micro and nanoparticles of CuZnO-Carbon nanoparticles synthesized utilizing arc-Discharge method with the system immersed in distilled water, using a current from 200 A with constant voltage (27 V). These structures are characterized using scanning electron microscopy (SEM), X-ray diffraction, Raman spectroscopy and Uv-Vis spectroscopy. Our results demonstrate that such nanostructures can be prepared at low cost with high quality.

Keywords: CuZnO-Carbon Nanoparticles, arc-Discharge, distilled water.

1. Introduction

Interest in nanomaterials has increased in recent years due to their unique physical and chemical properties. Particles in size from 1 to 100 nm are characterized by vastly different properties from those of “bulk” materials with the same chemical composition. As the particles are reduced in size, the “bulk” properties of the particles disappear to be replaced by those of a “quantum dot”, following the rules of quantum mechanics. Due to the size reduction, the high specific surface/volume ratio leads to the expansion of the catalytic activity of the nanoparticle [1-2].

Alloy nanoparticles are another form of bimetallic nanoparticles [3-7], these consist of two or more metals with enormous potential to form compositionally ordered phases. Alloy nanoparticles generally show different properties than corresponding monometallic nanoparticles. Alloy nanoparticles are of interest because composition, crystalline phase, and morphology can be controlled to develop new nanophases with unique properties for many applications [8-9]. CuZn-based composites have been

synthesized by different techniques [10-11], as well as used for a wide variety of applications [1,12]. On the other hand, CuZnO have been proposed basically as a cathode for nitrate reduction and to determine the effect of the pH solution to activate sites on the surface of various elements [13], antimicrobial purposes for escherichia coli [14], glucose sensor [15], among other.

In recent decades, much attention has been paid to carbon-coated metal nanoparticles and as composites [16-18]. These are synthesized with different techniques and with many applications.

In this work, we present a study of the synthesis of CuZnO-Carbon nanoparticles using the arc-Discharge technique immersed in distilled water. The nanoparticles are characterized by scanning electron microscopy (SEM), X-ray, Raman spectroscopy, and Uv-Vis spectroscopy.

2. Experimental procedure

The arc-Discharge method is a technique with which it is possible to synthesize nanoparticles of alloys; it is fast, simple, clean and easily adaptable to the mass production of nanoparticles [19-25].

This system uses two electrodes, a 1 mm diameter commercial cylindrical CuZn bar and the other 6 mm of graphite, both with a length of 7.5 cm. First, the electrodes are cleaned with acetone, before being used; then these are placed in front of each other at approximately 1 mm. The technique uses a rectangular pyrex glass container, where the electrodes are immersed to a depth of 6 cm in distilled water. One of the electrodes is fixed and the other can be moved to conserve the plasma, for this, a current of 200 A is used, with a constant voltage of 27 V.

The next stage of the experiment is to collect the CuZnO-Carbon multi-composite nanoparticles using a pipette, placing them in a vial. Finally, this sample undergoes a sonication process for 60 min, this allows to improve the dispersion and selecting the nanoparticles.

3. Results and Discussion

To investigate the properties of the synthesized nanostructures, different techniques are used. A scanning electron microscope (JSM-5400LV, JEOL) has been used to explore morphology, combined with EDS, to perform elemental chemical analysis. An X-ray diffractometer (D8 Discover, Brucker) has been used to determine the crystallinity of the material. A Raman spectrometer (Lab Ram HR 800, Horiba Jovin Yvon) to determine its structural properties and a Uv-Vis spectrometer (Cary 50 Conc, Varian) to determine the optical absorbance of the particles and the gap energy.

3.1. Scanning electron microscopy

Figure 1 shows micrographs of the synthesis of the CuZnO-Carbon composite using the arc-Discharge technique immersed in distilled water. The observed sample was taken from the process explained above, due to the experience obtained in a previous work [26] where it was determined that the particle size is adequate, a result that we consider interesting to analyze. In the micrographs we can clearly observe the spherical particles on the surface and immersed in the synthesized compound using the aforementioned technique, this shape of the particles is a particular characteristic of the technique used.

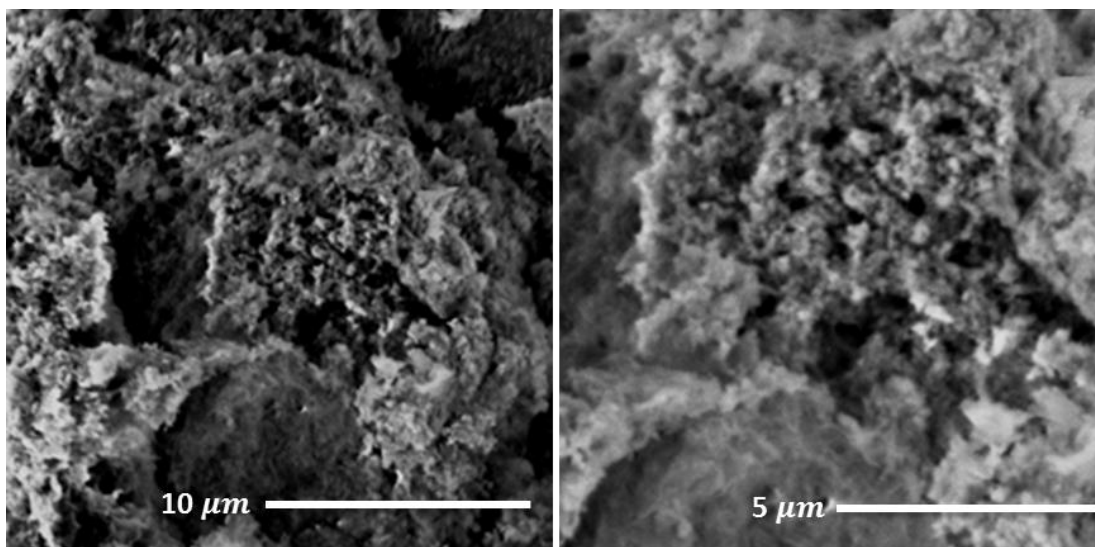


Figure 1. Micrographs of the CuZnO-Carbon nanoparticles synthesized using arc-Discharge technique immersed in distilled water. We can observe the spherical metallic nanoparticles on the surface and immersed in the carbon that performs the function of a matrix.

Figure 2 shows the results of a basic chemical analysis using EDS, where you can check the participation of the elements involved during the experiment. Quantitatively, it has been found that the percentages are: C: 9.25%, O: 25.96%, Cu: 13.01%, Zn: 51.55%. The share of silicon due to the substrate is: 0.23%.

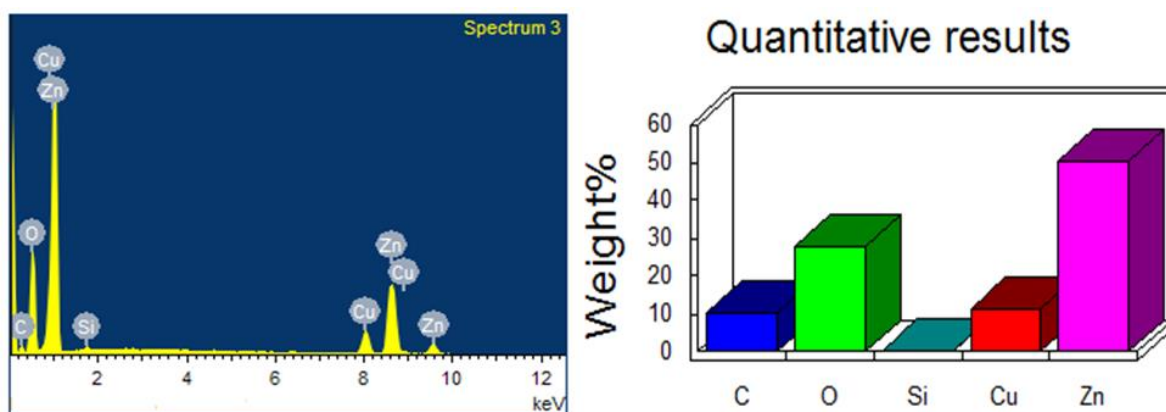


Figure 2. Basic chemical analysis obtained using EDS showing the elements involved in the synthesis carried out with the arc-Discharge technique immersed in distilled water.

In addition, a result that we consider relevant according to the results presented is that the carbon may be acting as a matrix or as a composite with respect to the bi-metallic oxide particles. These results allow us to say that they can have different applications.

3.2. X-Ray Diffraction

Figure 3 shows a typical X-ray diffractogram of CuZnO-Carbon nanoparticles prepared by arc-Discharge technique immersed in distilled water. These results reveal that there are two phases (CuO,

ZnO) and its compound (CuZnO). The peaks located for 2θ values at 31.81, 34.68, 36.23, 47.xx, 56.63, 62.96 and 68.33 are attributed to the CuZnO composite (Cu-0.1, Zn-0.9, O) according to the database PDF 04-019-3566, with a lattice parameter $a = 3.24595$ and a space group P63mc (186), with a compact hexagonal structure (HCP). The peaks positioned at $2\theta = 36.23, 38.94, 43.21$ are attributed to Zn according to PDF 00-004-0831 with an HCP structure, a lattice parameter $a = 2.66500$ and a space group P63/mmc. In position $2\theta = 43.21$ there is a contribution of CuZn (Cu0.85, Zn0.15) according to PDF 04-018-5556, with a cubic structure, a lattice parameter $a = 3.64900$ and a space group Fm-3m (225). Finally, there is a contribution at position $2\theta = 43.21$ attributed to Cu/Sn (Cu0.97, Sn0.03) according to PDF 04-003-7057 with a cubic structure, a lattice parameter $a = 3.63900$ and a space group Fm-3m (225). As has also been reported in [9,15,27-28].

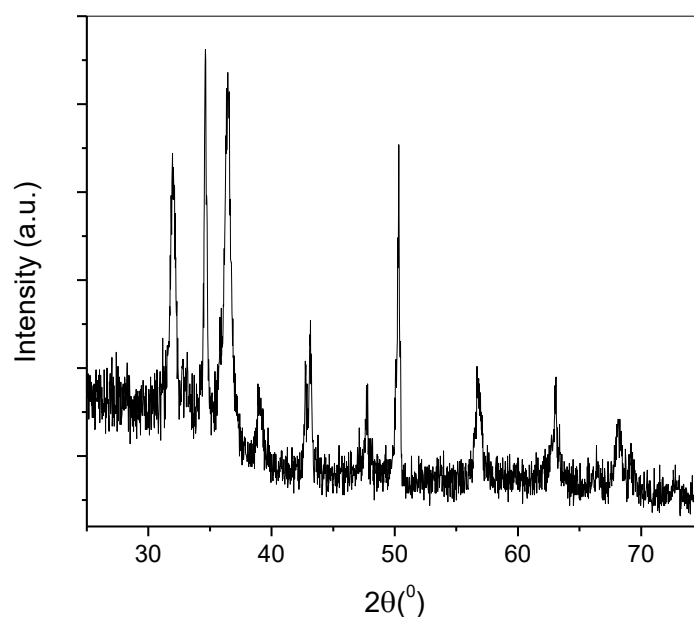


Figure 3. X-ray diffractogram of the CuZnO-Carbon nanoparticles synthesized using arc-Discharge technique immersed in distilled water.

3.3. Raman spectroscopy

Figure 4 shows Raman spectra of the CuZnO-Carbon nanoparticles synthesized using the arc-Discharge system immersed in distilled water. As we can observe, at 281 and 333 cm^{-1} there is a contribution attributed to CuO [29-30], around 500 cm^{-1} there is a contribution of Cu_2O [31]. On the other hand, in 438 and 608 cm^{-1} there is a contribution attributed to ZnO [32-34].

All carbons show characteristics in their Raman spectra in 800-2000 cm^{-1} : the D and G peaks, which are around 1360 and 1560 cm^{-1} , respectively, for visible excitation. Peaks D and G are due to sites sp^2 . The G peak is due to the bond tension vibration of all sp^2 atom pairs in rings and chains. Peak D is due to the breathing modes of sp^2 atoms in rings. So, if there are no rings there is no D peak. In the Ferrari-Robertson model [35] it is shown that as the G band moves towards a higher wavenumber, the material presents a greater structural order. In figure 4, the region described above is shown where peaks that represent the peaks described above are presented, this behavior has been reported as due to the vitreous

carbon species [31] in the synthetic CuZnO nanoparticles. This result complements the results presented with EDS, which shows the existence of carbon.

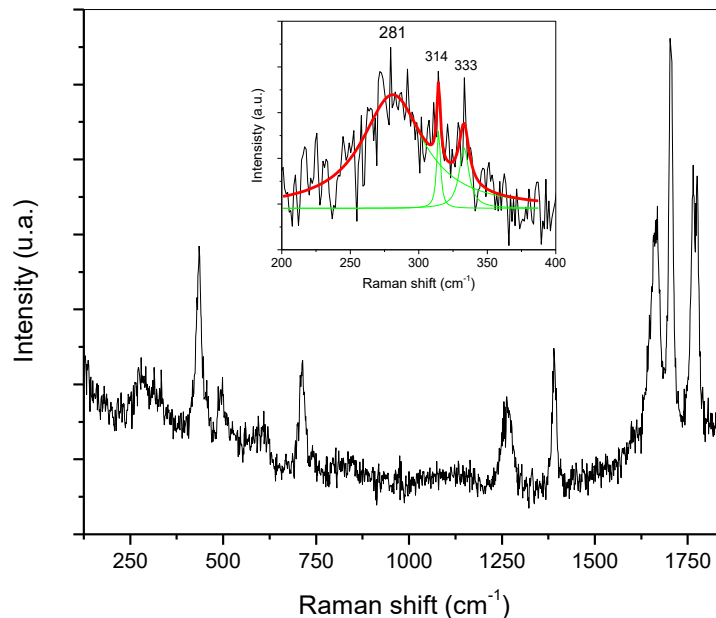


Figure 4. Raman spectrum of CuO-ZnO/Carbon nanoparticles synthesized using arc-Discharge technique immersed in distilled water.

3.4. *Uv-Vis spectroscopy*

Figure 5 shows the optical absorbance of the CuZnO-C nanoparticles synthesized at a current of 200 A, as a function of the wavelength in a range between 200-800 nm. We can notice an increase in the percentage of absorption, starting at 264 nm, as the wavelength increases, which indicates that the synthesized nanoparticles have good transparency. The spectrum in this work exhibits an absorption peak at 264 nm, a result that coincides with that reported in [34], on the other hand there is a lower intensity peak at 355 nm attributed to CuO [35].

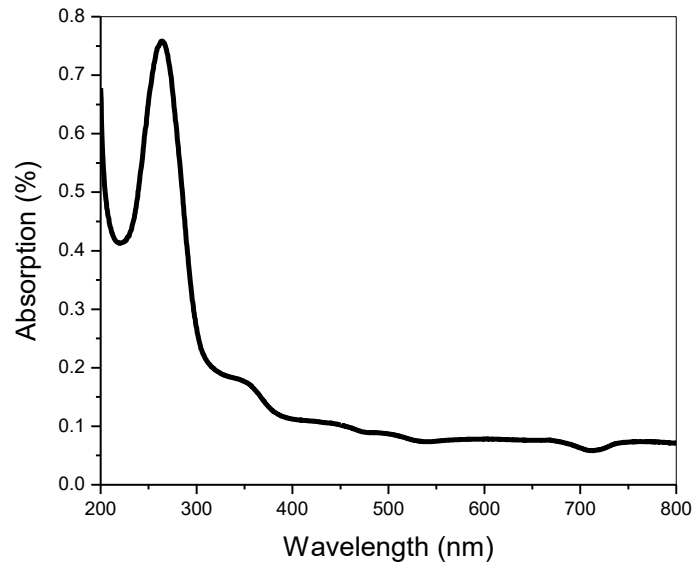


Figure 5. Optical absorbance spectrum of CuZnO-Carbon nanoparticles synthesized at 200 A by means of the arc-Discharge technique immersed in distilled water.

Figure 5 shows the optical absorbance of the CuZn-Carbon nanoparticles synthesized at a current of 200 A. With this information we can graph $(\alpha h\nu)^2$ as a function of $h\nu$ of the CuZnO-Carbon particles. Using the following expression:

$$\alpha = \frac{\alpha_0(h\nu - E_g)^n}{(h\nu)}$$

where E_g is the separation between the lower edge of the conduction band and the upper edge of the valence band, α is the absorption of the thin film, α_0 is the absorption coefficient, $h\nu$ is the photon energy and n is a constant. The values of n depend on the transition probability; this takes the values as $\frac{1}{2}$, $\frac{3}{2}$, 2, and 3 for a direct transition allowed, direct prohibited, indirect allowed and indirect prohibited, respectively. The usual method for determining E_g involves graphing $(\alpha h\nu)^{1/n}$ vs $h\nu$. Extrapolating the linear portion of $(\alpha h\nu)^{1/n}$ vs $h\nu$ to $\alpha = 0$, we can estimate the energy gap of the absorption peak. For this, a model is chosen:

$$\alpha = 2.303 \log \left(\frac{T}{d} \right)$$

where T is the optical transmittance and d is the thickness of the thin film, in our case we take it as the particle size. How do you know:

$$E = h\nu = \frac{1240}{\lambda(nm)} eV$$

with these data we can now graph: $(\alpha h\nu)^2$ vs $h\nu$. The results are presented in figure 6.

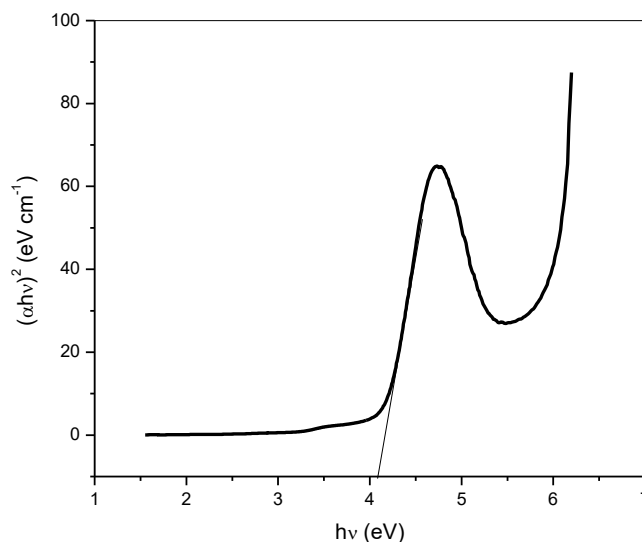


Figura 6. Graph of $(\alpha h\nu)^2$ vs $h\nu$ of CuZnO-Carbon nanoparticles synthesized using arc-Discharge technique immersed in distilled water for 200 A.

From the previous figure, the value of the energy gap can be quantitatively determined, which is equal to 4.1.

4. Conclusions

The arc-Discharge technique immersed in distilled water has been shown to be a potential technique for the growth of metallic and bimetallic nanoparticles of different sizes in controlled processes. In this work, nanoparticles of the materials involved, in this case CuZnO-Carbon have been synthesized at low cost and high quality. As far as we know there are no previous reports of the type of material synthesized in this work, this increases its relevance.

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References

1. M. Ghane, B. Sadeghi, A.R. Jafari, A.R. Paknehad. (2010). Synthesis and characterization of a Bi-Oxide nanoparticle ZnO/CuO by thermal decomposition of oxalate precursor method. *International journal of nano dimension*, 133-40. <https://dx.doi.org/10.7508/ijnd.2010.0x.003>.
2. T. Petrov, I. Markova-Deneva, O. Chauvet, R. Nikolov, I. Denev. (2012). SEM and FT-IR spectroscopy study of Cu, Sn, and Cu-Sn nanoparticles. *J. of the University of chemical technology and metallurgy*, 47197-206.

3. G. Schmid, H. West, J.-O. Malm, J.-O. Bovin, and C. Grenthe. (1996). Catalytic Properties of Layered Gold-Palladium Colloids. *Chem.—A Eur. J.* 2, 1099. <https://doi.org/10.1002/chem.19960020910>
4. L. M. Liz-Marzan and A. P. Philipse. (1995). Stable hydrosols of metallic and bimetallic nanoparticles immobilized on imogolite fibers. *J. Phys. Chem.* 99, 15120 <https://doi.org/10.1021/j100041a031>.
5. M. Michaelis, A. Henglein, and P. Mulvaney. (1994). Composite Pd-Ag Particles in Aqueous Solution. *J. Phys Chem.* 98, 6212
6. K. Torigoe, Y. Nakajima, and K. Esumi. (1993). Preparation and characterization of colloidal silver-platinum alloys. *J. Phys. Chem.* 97, 8304 <https://doi.org/10.1021/j100133a029>.
7. M. Cazayous, C. Langlois, T. Oikawa, C. Ricolleau, and A. Sacuto. (2006). Cu-Ag core-shell nanoparticles: A direct correlation between micro-Raman and electron microscopy. *Phys. Rev. B* 73, 113402 <https://doi.org/10.1103/PhysRevB.73.113402>.
8. A. Kamysny, J. Steinke, and S. Magdassi. (2011). Metal-based Inkjet Inks for Printed Electronics. *Open Appl. Phys. J.* 4, 19. <http://dx.doi.org/10.2174/1874183501104010019>.
9. M. Z. Kassae, E. Motamedi, M. Majdi, A. Cheshmehkani, S. Soleimani-Amiri, and F. Buazar. (2008). Media effects on nanobrass arc fabrications *J. Alloys Compd.* 453, 229. <https://doi.org/10.1016/j.jallcom.2007.06.002>.
10. N. Fan, Z. Li, L. Zhao, N. Wu, T. Zhou. (2013). Electrochemical denitrification and kinetics study using Ti/IrO₂-TiO₂-RuO₂ as the anode and Cu/Zn as the cathode *Chem. Eng. J.* 21483. <https://doi.org/10.1016/j.cej.2012.10.026>
11. M. Li., C. Feng, Z. Zhang, Z. Shen N. Sugiura. (2009). Electrochemical reduction of nitrate using various anodes and a Cu/Zn cathode *Electrochem. Commun.* 111853. <https://doi.org/10.1016/j.elecom.2009.08.001>
12. M. Ashfaq, N. Verma, S. Khan. (2016). Copper/zinc bimetal nanoparticles-dispersed carbón nanofibers: A novel potential antibiotic material. *Materials Science and Eng. C*, 59938-947. <https://doi.org/10.1016/j.msec.2015.10.079>
13. S. Yang, L. Wang, X. Jiao, P. Li. (2017). Electrochemical reduction of nitrate on different Cu-Zn oxide composite cathodes. *Int. J. Electrochem. Sci.*, 124370-4383. <https://doi.org/10.1016/j.ijelechem.2017.05.80>
14. M. Carbone, R. Briancesco, L. Bonadonna. (2017). Antimicrobial power of Cu/Zn mixed oxide nanoparticles to Escherichia coli. *Environmental nanotechnology, monitoring & management*, 797-102. <https://doi.org/10.1016/j.enmm.2017.01.005>
15. S. Ashok Kumar, H.W. Cheng, S.M. Chen, S.F. Wang. (2010). Preparation and characterization of copper nanoparticles/zinc oxide composite modified electrode and its application to glucose sensing. *Materials Science and Engineering C*, 3086-91. <https://doi.org/10.1016/j.msec.2009.09.001>
16. Y. Sun, C. Feng, X. Liu, S.W. Or, C. Jiu. (2014). Synthesis, characterization and microwave absorption of carbón-coated nanocapsules. *Materials research*, 17477-482. <http://dx.doi.org/10.1590/S1516-14392014005000005>
17. F. Jahanbakhsh, B. Ebrahimi. (2016). Modified activated carbon with zinc oxide nanoparticles produced from used tire for removal of acid Green 25 from aqueous solutions. *American Journal of Applied Chemistry*, 48-13. <http://doi.org/10.11648/j.ajac.20160401.12>

18. K.B. Rogushin, E. N. Sidorova, M.N. Efimov. (2017). Infra-red mediated synthesis of C-Cu-Zn nanocomposites using metal oxides and metal nitrates precursors. *IOP Conf. Series: J. of Physics: Conf. Series* 917092010. <http://doi.org/10.1088/1742-6596/917/9/092010>.
19. A.V. Nominé, Th. Gries, C. Noel, A. Nominé, V. Milichko, T. Belmonte. (2021). Synthesis of nanomaterials by electrode erosion using discharges in liquids. *J. Appl. Phys.*, 130, 151101 <https://doi.org/10.1063/5.0040587>
20. D. C. Tien, L. C. Chen, N. V. Thai, and S. Ashraf, (2010). Study of Ag and Au Nanoparticles Synthesized by Arc Discharge in Deionized Water. *Journal Nanomaterials*, 10, 110.
21. C.-H. Lo, T.-T. Tsung, and H.-M. Lin, J. (2007). Preparation of silver nanofluid by the submerged arc nanoparticle synthesis system (SANSS). *Journal of Alloys Compd.* 434–435, 659, <https://doi.org/10.1016/j.jallcom.2006.08.217>.
22. M. Z. Kassae, S. Soleimani-Amiri, and F. Buazar, J. Manuf. (2010). Diverse tungsten nanoparticles via arc discharge. *Journal of Manufacturing Processes*, 12, 85 <https://doi.org/10.1016/j.jmapro.2010.06.001>
23. S. Hosseynizadeh Khezri, A. Yazdani, and R. Khordad. (2012). Pure iron nanoparticles prepared by electric arc discharge method in ethylene glycol. *Eur. Phys. J. Appl. Phys*, 59, 30401. <https://doi.org/10.1051/epjap/2012110303>
24. K.-H. Tseng, J.-C. Huang, C.-Y. Liao, D.-C. Tien, and T.-T. Tsung (2009). Preparation of gold ethanol colloid by the arc discharge method. *J. Alloys Compd.* 472, 446. <https://doi.org/10.1016/j.jallcom.2008.04.084>
25. F. Buazar, A. Cheshmehkani, and M. Z. Kassae. (2012). *Journal of the Iranian Chemical Society*. 9, 151. <https://doi.org/10.1007/s13738-011-0038-3>
- B. Rebollo-Plata, M. P. Sampedro, G. Gallardo-Gómez, N. Ortega-Miranda, C. F. Bravo-Barrera, G. Daniel-Pérez, B. Zenteno-Mateo, D. Hernández-Cruz, and S. Jiménez-Sandoval. (2014). Growth of metal micro and/or nanoparticles utilizing arc-discharge immersed in liquid. *Revista Mexicana de Física*, 60227-232.
26. N. Panuthai, R. Savangla, P. Praserttham, S. Kheawhom. (2014). Characterization of copper–zinc nanoparticles synthesized via submerged arc discharge with successive reduction process. *Japanese Journal of Applied Physics*, 53, 05HA11. <https://doi.org/10.7567/JJAP.53.05HA11>
27. D. Grobmann, A. Dreier, C.W. Lehmann, W. Grunert. (2015). Encapsulation of copper and zinc oxide nanoparticles inside small diameter carbon nanotubes. *Microporus and Mesoporus Materials*. 202, 189. <https://doi.org/10.1016/j.micromeso.2014.09.057>
28. S. Qiu, H. Zhou, Z. Shen, I. Hao, H. Chen, X. Zhou. (2020). Synthesis, characterization, and comparison of antibacterial effects and elucidating the mechanism of ZnO, CuO and CuZnO nanoparticles supported on mesoporous silica SBA-3. *RSC Adv*, 102767. <http://doi.org/10.1039/C9RA09829A>
29. P.K. Giri, S. Bhattacharyya, R. Kesavamoorthy, B.K. Panigrahi, K.G.M. Nair. (2007). Correlation between microstructure and optical properties of ZnO nanoparticles synthesized by ball milling. *Journal of applied physics*, 102093515. <https://doi.org/10.1063/1.2804012>
30. I.A. Sukhov, G.A. Shafeev, V.V. Voronov, M. Sygletou, E. Stratakis, C. Fotakis. (2014). Generation of nanoparticles of bronze and brass by laser ablation in liquid. *Applied Surface Science*, 30279-82. <https://doi.org/10.1016/j.apsusc.2013.12.018>
31. M. Ram, G-S. Arya, K. Parmar, R.K. Kotnala, N.S. Negi. (2015). Structural, microstructural and raman study of co-doped zno nanocrystals synthesized by solution combustion method. *International*

journal of advances in engineering & technology 8329-336. <https://www.ijaet.org/media/9I27-IJAET0827753-v8-iss3-329-336.pdf>

32. E. Mosquera, C. Rojas-Michea, M. Morel, F. Gracia, V. Fuenzalida, R.A. Zárate. (2015). Zinc oxide nanoparticles with incorporated silver: Structural, morphological, optical and vibrational properties. *Applied surface science*. 347561-568. <https://doi.org/10.1016/j.apsusc.2015.04.148>
33. Po-Hsun Shih, Tai-Yue Li, Yu-Chen Yeh, Sheng Yun Wu. (2017). Phonon Confinement Induced Non-Concomitant Near-Infrared Emission along a Single ZnO Nanowire: Spatial Evolution Study of Phononic and Photonic Properties. *Nanomaterials*, 7353. <http://doi.org/10.3390/nano7110353>
34. A.C. Ferrari, J. Robertson. (2000). Interpretation of Raman spectra of disordered and amorphous carbon. *Physical review B*, 61, 14095. <https://doi.org/10.1103/PhysRevB.61.14095>
35. D. Demirci Gultekin, H. Nadaroglu, A. Alayli Gungor, N. Horasan Kishali. (2017). Biosynthesis and Characterization of Copper Oxide Nanoparticles using Cimin Grape (*Vitis vinifera* cv.) Extract. *Int. J. Metabolite*, 477-84. <http://doi.org/10.21448/ijsm.362672>